NCHRP
REPORT 577

NATIONAL
COOPERATIVE
HIGHWAY
RESEARCH
PROGRAM

Guidelines for the Selection of Snow and Ice Control Materials to Mitigate Environmental Impacts

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LEVELTON CONSULTANTS LIMITED
Richmond, BC

Subject Areas
Energy and Environment • Maintenance

Research sponsored by the American Association of State Highway and Transportation Officials
in cooperation with the Federal Highway Administration

TRANSPORTATION RESEARCH BOARD

WASHINGTON, D.C.
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NATIONAL COOPERATIVE HIGHWAY RESEARCH PROGRAM

Systematic, well-designed research provides the most effective approach to the solution of many problems facing highway administrators and engineers. Often, highway problems are of local interest and can best be studied by highway departments individually or in cooperation with their state universities and others. However, the accelerating growth of highway transportation develops increasingly complex problems of wide interest to highway authorities. These problems are best studied through a coordinated program of cooperative research.

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The needs for highway research are many, and the National Cooperative Highway Research Program can make significant contributions to the solution of highway transportation problems of mutual concern to many responsible groups. The program, however, is intended to complement rather than to substitute for or duplicate other highway research programs.

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FOREWORD

By Christopher J. Hedges
Staff Officer
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This report presents guidelines for the selection of snow and ice control materials through an evaluation of their cost, performance, and impacts on the environment and infrastructure. The guidelines should be useful in helping maintenance managers develop a program that will minimize the environmental impacts of snow and ice control without compromising effective maintenance strategies. The Guidelines will help highway agencies fill their dual role of providing safe roadways for the driving public while serving as stewards to protect and enhance the natural environment.

Every year, considerable quantities of snow and ice control products are applied to highways, and environmental and regulatory agencies have questioned the environmental impact of these products. Transportation agencies are asked to use “environmentally friendly” or less toxic alternatives wherever possible, but there is no commonly accepted guidance for determining which products are acceptable. The traditional use of roadsalt has been prohibited in some locations, leaving highway agencies uncertain about how traffic safety can be maintained in bad weather. For example, Environment Canada has concluded that inorganic chloride roadsalts are harmful to the environment under the Canadian Environmental Protection Act, thus requiring development and implementation of improved management practices.

Studies of the most common chemical alternatives—sodium chloride (salt), magnesium chloride, calcium chloride, calcium magnesium acetate, potassium acetate, and urea—have focused on performance and cost under various weather conditions without evaluating their relative impacts on the environment. Several new chemical preparations, including some that are trademarked, have entered the market as snow and ice control chemicals for use by transportation agencies, but there is limited information about their environmental impacts. There is a need for rational decision-making guidelines to assist DOT maintenance managers in selecting the most appropriate snow and ice control materials for the conditions that exist in their jurisdictions.

Under NCHRP Project 06-16, a research team led by Levelton Consultants Ltd. conducted an extensive review of relevant technical information, then conducted a program of analytical laboratory testing on a wide range of products currently available in the North American market. The results were used to develop three products for the end user: a decision tool for the selection of the most appropriate snow and ice control materials to suit the specific needs of any given highway agency, a purchase specification that can be used by an agency once agency staff have selected materials for use, and a quality assurance monitoring program that includes procedures and standard test methods to characterize snow and ice control products before their purchase or use.

There are two major components to this report. Chapters 1 through 11 (a) summarize the review of technical information on the performance and environmental impacts of currently available snow and ice control materials, and (b) present the results of an analytical laboratory testing program designed to address gaps in the current literature and to develop a matrix of properties of 42 chemicals. The second component presents guidelines for the user with three products: a decision tool for the selection of materials, a purchase specification, and the quality assurance monitoring program. An electronic version of the decision tool and several appendixes to the final report can be downloaded from the TRB website at http://www.trb.org/TRBNet/ProjectDisplay.asp?ProjectID=883.

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SUMMARY

Guidelines for the Selection of Snow and Ice Control Materials to Mitigate Environmental Impacts

Every year, considerable quantities of snow and ice control products are applied to highways; environmental and regulatory agencies have questioned the environmental effects of these products. Transportation agencies are asked to use "environmentally friendly" or less toxic alternatives wherever possible, but there is no commonly accepted guidance for determining which products meet these criteria. The traditional use of road salt has been prohibited in some locations, leaving highway agencies uncertain about how traffic safety can be maintained in winter conditions.

Studies of the most common chemical alternatives—sodium chloride (salt, NaCl), magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$), calcium magnesium acetate (CMA), and potassium acetate (KA)—have focused on performance and cost under various weather conditions without evaluating their relative effects on the environment. Several new chemical preparations, including some that are proprietary formulations, have entered the market as snow and ice control chemicals for use by transportation agencies, but there is limited information about the environmental effects of these preparations.

Rational decision-making guidelines are needed to assist winter maintenance managers in selecting the most appropriate snow and ice control materials for the conditions that exist in their jurisdictions. A transportation agency must consider a range of factors when assessing snow and ice control materials for use, including performance, cost, potential for the material to impair the natural receiving environment, and potential for the material to impair infrastructure. Each agency will have unique objectives and conditions that influence the importance of each of these factors in the decision-making process. The overall objective of this project is to develop guidelines for selecting snow and ice control materials based on their properties and common site-specific conditions near roadways on which these products would be used.

This study was completed in two phases. Phase I involved collection, compilation, and quantification of relevant technical information related to snow and ice control materials. Phase II supplemented the information compiled in Phase I through analytical testing programs. The full body of knowledge was applied toward a snow and ice control material selection process that included a material decision tool, a purchase specification, and a quality assurance monitoring plan.

NCHRP Project 06-16 Phase I

Phase I of NCHRP Project 06-16 involved a comprehensive search to assemble information related to snow and ice control materials. The review included published information, current practices, research in progress, and a survey of highway maintenance professionals. The following topics were covered:

- Available materials, including typical costs, handling concerns, and application issues;
- Impacts to the environment and infrastructure related to common use, application, storage and disposal;
- Site-specific conditions that affect choices of materials;
- Product loading and fate/transport processes;
- Current and proposed specifications and regulations for material acceptance; and
- Parameters and test methods used as measures of performance and environmental properties.

The gathered information was categorized and quantified. Relevant product categories included NaCl, $CaCl_2$, $MgCl_2$, acetates (CMA and KA), organic matter from biomass (OMB), and abrasives. The most significant factors to be considered when selecting snow and ice control materials were determined to be cost, performance, effects on the environment, and effects on infrastructure.

How great an effect a snow and ice control material may have depends on such conditions as material type, application amounts, exposure pathways, chemical-specific impacts, and site-specific characteristics. A simple model was employed to determine that runoff from the roadway would be diluted 500 times at the point a snow and ice control material leaves the roadway.

Areas of greatest environmental concern included water quality and aquatic life, air quality, and vegetation impacts. Contamination of drinking water supplies could occur under some circumstances, especially for wells very close to areas of routine snow and ice control materials applications. Direct effects on soils are generally not a concern, but snow and ice control material can influence soil structure, and the presence of these materials in soil can further affect water systems and vegetation.

Atmospheric corrosion processes on exposed metals are extremely complex. Most information depends on specific conditions, and study conclusions can be wide ranging and, in some cases, contradict one another. Corrosion related to a given snow and ice control material may show various responses between product concentrations, metal types, and even between alloys within the same metal group. Despite the weakness in specific information, some general assessments exist:

- Chloride-based snow and ice control chemicals are the most corrosive to metals with the hygroscopic chlorides of magnesium and calcium being the most aggressive because of the longer time of wetness;
- Acetate-based and organic snow and ice control materials tend to cause less corrosion than chloride-based chemicals, but can still accelerate corrosion by increasing the conductivity of the moisture;
- Additives used to inhibit corrosion that are tested in the laboratory can show reductions in corrosion rate of the metals being tested, but they may show little or no inhibiting effect on other metals (even those in the same metal group) and may accelerate corrosion of other metals.

Snow and ice control chemicals can have detrimental effects on concrete infrastructure. These can be separated into three general categories:

- The enabling and/or acceleration of corrosion of concrete reinforcing (rebar) resulting from chloride ion penetration. This effect is primarily related to bridges, but there is a possibility of a secondary risk in concrete pavements with doweled joints or continuous reinforcement.
- Reactions of snow and ice control materials with the cement paste, resulting in deterioration of the cement matrix. This effect is primarily a risk for concrete pavements and the

amount of deterioration is directly related to the quality of concrete. Current evidence suggests that magnesium chemically reacts with the cement paste in a process that reduces concrete strength.
- All snow and ice control chemicals by definition of their action increase the number of freezing and thawing cycles on the concrete in service. This can result in deterioration in the form of freezing and thawing and/or scaling.

It was expected that the findings of the information assessment conducted through Phase I of this study would identify gaps in information. In general

- Technologies and products employed for snow and ice control are continually evolving, and current information is not always available.
- For many of the laboratory studies conducted, limited field correlations are available.
- Many materials have had a relatively short history of use (less than 10 to 15 years) and it is unclear what the potential for long-term adverse effects are over decade time scales.

NCHRP Project 06-16 Phase II

Phase II of this study began with an analytical testing program. The information gathered through this program was combined with the information developed through Phase I to develop a practical snow and ice control material selection process that included a material decision tool, an environmental purchase specification, and a quality assurance monitoring program.

Analytical Program

The analytical program was designed to help address gaps in information and to help establish a matrix of significant properties for common snow and ice control chemicals in the areas of environmental chemistry, aquatic toxicity, concrete corrosion, and atmospheric corrosion.

Forty-two products were obtained that represented the 2004 U.S. and Canadian market in terms of product type (NaCl, $MgCl_2$, $CaCl_2$, CMA, and KA), manufacturers, regional sources, and additives. Abrasives were not included in the test program, given that material sources are too numerous and varied. All products received full chemical analysis. Fifteen materials representing each material type and common additive combination were selected for aquatic toxicity, concrete corrosion, and atmospheric corrosion assessments.

The benefit of conducting a large-scale analytical assessment on a wide range of snow and ice control materials using the same test methods is that it provides data that can be directly compared for trends so that significant material attributes can be identified.

Chemical Analysis

From the chemical analysis program, the following general conclusions can be made:

- High organic matter concentrations, which can lead to biochemical oxygen demand (BOD) concerns in aquatic systems, are associated with acetate materials and with materials containing organic matter from biomass (OMB). For the latter, levels depended on the proportion of OMB in the blend. Solids with OMB generally had much lower organic matter levels than liquid counterparts.
- Nutrient (nitrogen and phosphorus) levels found in many of the materials tested can be considered a potential environmental concern. Nutrient levels had a strong relationship

to the presence of OMB materials in the product blend. Higher nutrient levels were also present in other material types.
- Cyanide could be a potential environmental concern for materials, such as solid NaCl, that routinely contain iron-cyanide anti-caking agents. More research and information is necessary to assess the bio-availability of iron-cyanide materials under field conditions conclusively.
- Overall, metals levels were below levels considered to be a significant environmental concern, although the literature indicates that higher metals levels have routinely been observed in snow and ice control materials.
- The variability in the data between products, and the general lack of strong trends, outside of those already listed, suggests that it is important to continue to monitor chemical attributes of snow and ice control materials through a quality assurance monitoring plan.

Aquatic Toxicity

Aquatic toxicity testing was conducted on fifteen snow and ice control products following U.S. EPA standard test methods for chronic exposure to various levels of aquatic biota, including vertebrates, invertebrates, and algae:

- Fathead Minnow 7-day Survival and Growth Test, which also included acute toxicity data for Fathead Minnow 96-hour Survival Test;
- *Ceriodaphnia dubia* 3-brood Survival and Reproduction Test; and
- *Selenastrum capricornutum* 96-hour Growth Test

The tolerance thresholds determined from the testing were compared with the expected dosage that organisms would receive in the field based on dilution at the margin of a roadway of 500:1—this would be close to the amount of dilution for many applications.

Although it is likely that the most sensitive organisms would be affected in some way at dilutions that could be expected at the margin of a roadway for many snow and ice control materials, it is also true that dilutions greater than 500:1 can be expected within a relatively short distance beyond the roadway. Therefore, the toxicity data imply that there could be an impact zone relatively close to the roadway, bounded by dilutions that offset acute or chronic toxicities close to the roadway.

Atmospheric Corrosion

Linear Polarization Resistance (LPR), a mature, rapid, and sensitive corrosion rate measurement technique, was used to assess atmospheric corrosion rates. Of particular benefit was the potential suitability of LPR for evaluating the corrosiveness of inhibited snow and ice control materials and the effect of roadside dilution.

Fifteen snow and ice control materials with and without inhibitors were tested on five commonly available alloys representative of materials used in highway infrastructure and vehicles. These included structural steel alloy (A36), magnesium alloy (AZ91C-T6), wrought aluminum alloy (AA6061-T6), cast aluminum alloy (AA356.2), and brass alloy (CDA 360). To represent material concentrations expected in the field, LPR assessments were conducted on liquid snow and ice control materials at 100 percent (v/v–percent volume per volume) (as received), 10 percent (v/v) and 1 percent (v/v) concentrations for each alloy. The following conclusions were obtained through this study:

- Overall, the structural steel alloy (A36) demonstrated the lowest corrosion rate values while the magnesium alloy (AZ91C-T6) demonstrated the highest corrosion rate values.

Wrought aluminum alloy (AA6061-T6), cast aluminum alloy (AA356.2), and brass alloy (CDA 360) demonstrated intermediate corrosion rate values.

- With the exception of structural steel (A36) and brass (CDA 360), corrosion rates increased with increasing snow and ice control material concentration. Structural steel corrosion rates were sufficiently low that identification of trends may have been obscured by measurement variability at these levels. Brass corrosion rates were highest when snow and ice control materials were at the 10-percent concentration level.
- Overall, chloride-based snow and ice control materials (NaCl, $CaCl_2$, $MgCl_2$, and blended chlorides) displayed similar corrosion rates for each metal type tested at each concentration level. This suggests little difference in corrosion rates between chloride-based snow and ice control materials. Field conditions along with other snow and ice control material properties (such as hygroscopicity) may contribute more to the relative corrosiveness of these materials in the service environment. Other corrosion mechanisms not emulated by aqueous testing may be significant.
- Acetate materials (CMA and KA) demonstrated a range of LPR corrosion rates for the alloys assessed:
  - The lowest corrosion rates were for structural steel (A36). Observed values bordered on the minimum practical detection ability of test instrumentation for all acetate types.
  - Acetates were equally or slightly less corrosive than chlorides to magnesium (AZ91C-T6).
  - Acetates were equally or slightly more corrosive than chlorides to brass (CDA 360).
  - For aluminum alloys (AA356.2 and AA6061-T6), acetates containing potassium (KA) demonstrated corrosion rates equal to chloride-based snow and ice control materials. CMA demonstrated a much lower corrosion rate for these alloys.
- The effectiveness of corrosion inhibitors was varied and poorly quantified. In some cases, these materials provided no detectable corrosion improvement; in other cases, corrosion improvement appeared to depend on the concentration level of the test solution. This suggests that although some benefit may be realized from the use of these materials, the overall effectiveness under field conditions (including dilution) and after exposure to numerous potential alloy types is questionable.

Concrete Corrosion

The concrete corrosion analytical testing program was initiated in June, 2004, and was based on the following standard tests:

1. ASTM G 109 with the objective of relatively assessing fifteen snow and ice control materials for their potential to initiate corrosion on embedded reinforcing;
2. ASTM C 1556 with the objective of providing a relative assessment of chloride ion diffusion rates for $MgCl_2$, $CaCl_2$, and NaCl.

In designing this program, it was recognized that similar studies conducted in the past used poor quality concrete, mortars, and pastes in order to reduce the test duration. These materials do not represent concrete used in real-world structures and it was important that the current project use a more realistic concrete mix design (higher quality, $w/c < 0.40$, air content 5–8%).

Initial estimates, extrapolated from past studies, were that corrosion initiation would occur 1 to 2 years after test commencement. Regrettably, after 2 years, test samples have not yet produced detectable changes in corrosion potential. Acknowledging the time and budget constraints of NCHRP Project 06-16, it was decided to complete the project without the contribution from the concrete corrosion testing component.

Decision Tool

When selecting a snow and ice control material, the factors affecting the decision processes can be numerous and complex. The framework provided here is relatively straightforward and addresses the most common and significant items. Decision categories include cost, performance, potential to impair the natural environment, and potential to impair infrastructure. These balance economic value related to cost and performance with potential consequences of use related to environmental and corrosion impacts. User input is a key element to the tool to ensure that maintenance area conditions are represented. The end product is a practical tool that generates a numerical evaluation that can be used to compare snow and ice control materials.

Each agency will have unique objectives and priorities that will affect their selections for the decision categories and these will be expressed through percentage weighting of importance. Decision subcategories that support the natural environment and infrastructure decision categories are relatively straightforward and represent the most significant components contributing to the higher level decision category.

To quantify risks of impairment for environmental and infrastructure subcategories resulting from each snow and ice control material type, numerical rankings were developed. These were based on a material's potential to elicit an effect on a receptor, as developed from a comprehensive information review and analytical test results. These values were applied where sensitive receptors existed in the maintenance area as identified through user-completed receptor inventory worksheets for each decision subcategory.

When assessing relative cost and performance of snow and ice control materials, many factors are influential and considerable research continues to be done here. The Decision Tool uses the following approaches:

- Cost is based on the purchase price of the dry active ingredient. Active ingredients include the five primary snow and ice control chemicals: $NaCl$, $MgCl_2$, $CaCl_2$, CMA, and KA.
- Performance is based on melting potential derived from phase curve information and expected winter temperature in the maintenance region. Melting potential represents the chemical's ability to melt ice at a specified temperature.

These approaches may not be ideal; however, they provide a standardized and practical method that reasonably represents the dominant component for each decision category.

For each decision category, a weighted score is generated. These are summed for each material to produce a numerical product score that is used to compare snow and ice control material types objectively. Once a material type has been selected, various sources may exist. Considerable variation in certain attributes can exist among similar material types from different sources or between batches from the same source. A Purchase Specification containing concentration-based guidelines for key attributes will allow transportation agencies to screen out unsuitable products. The Purchase Specification is supported by a Quality Assurance Monitoring Program to assess received materials and by standard test methods to measure these attributes.

Product selection occurs after a review of the Purchase Specification and supplemental considerations that may include but are not limited to product availability (delivery times and quantities), quality testing results, and equipment availability.

Purchase Specification

This Purchase Specification was developed to assist transportation agencies with mitigating effects to the natural environment by allowing the user to qualify and compare snow and ice control materials based on key environmental attributes. The Purchase Specification is to be applied after the agency has completed the Decision Tool and a snow and ice control material type has been selected for use.

Aquatic systems are the primary environmental concern associated with snow and ice control materials. The Purchase Specification focuses on snow and ice control material chemical attributes that could impair aquatic systems under normal use but are not addressed through the Decision Tool. Numerical criteria specific to snow and ice control materials have been established based on

- U.S. EPA numerical water quality criteria for the protection of aquatic life and drinking water (based on U.S. EPA National Recommended Water Quality Criteria: 2002, EPA-822-R-02-047, November 2002).
- Site-specific factors, specifically receiving water type, size, and current nutrient levels.
- The default value for expected roadway runoff dilution is estimated to be 500 times at the point the materials leave the roadway. This may be adjusted up or down to reflect any other assumed or measured dilution factor.

The Guidelines for Maximum Concentrations (GMCs) of constituents in snow and ice control materials are shown in Table 3-2. These concentrations were derived assuming that the concentrations of the applied materials are diluted 500 times at the point these materials leave the roadway. Three general categories exist according to type of snow and ice control material:

1. The first category includes chemical products with a calcium or magnesium base, which are the two components of hardness for water. Concentration limits (i.e., aquatic life criteria) for certain metals (e.g., Cd, Cu, Pb, Ni, Ag, Zn) depend on hardness, which can reduce their relative toxicity. Therefore, the maximum allowable concentrations for these metals are highest when calcium and magnesium are major components of ice and snow control materials.
2. A second category applies to snow and ice control chemicals that contain neither calcium nor magnesium as major constituents (NaCl, KA, agriculturally derived organic materials). Such products lack any hardness-inducing component in large quantities, which requires more restrictive limits for metals whose toxicity is affected by hardness.
3. The third category of snow and ice control materials is abrasives. These materials are not soluble, but may contain contaminants that are soluble. Abrasives obtained from industrial processes (such as metallurgical slag, mining waste, and furnace slag) can contain high toxicant levels. GMC values are based on the assumption that abrasives to be tested will be leached in pH-adjusted (acidic) water according to U.S. EPA Method 1311, Toxicity Characteristic Leaching Procedure (Revision 0, July 1992), which incorporates a liquid-to-solid ratio of 20:1(50 grams abrasive plus 1 L extraction fluid).

Quality Assurance Monitoring Program

The Quality Assurance (QA) Monitoring Program takes the form of a suite of qualifying tests and submittals for the agency to characterize snow and ice control products before purchase or use. This section includes procedures for collecting and testing received snow and ice control chemicals. Standard test methods used to quantify material characteristics are also referenced.

To ensure suitability of the products with agency purchase specifications, it is suggested that QA procedures be included in contract documentation.

CHAPTER 1

Introduction

1.1 Problem Statement and Research Approach

Every year, considerable quantities of snow and ice control products are applied to highways, and environmental and regulatory agencies have questioned the environmental effects of these products. Transportation agencies are asked to use "environmentally friendly" or less toxic alternatives wherever possible, but there is no commonly accepted guidance for determining which products meet these criteria. The traditional use of roadsalt has been prohibited in some locations, leaving highway agencies uncertain about how traffic safety can be maintained in bad weather. For example, Environment Canada has concluded that inorganic chloride roadsalts are harmful to the environment under the Canadian Environmental Protection Act (CEPA), thus requiring development and implementation of improved management practices.

Studies of the most common chemical alternatives—sodium chloride (salt), magnesium chloride, calcium chloride, calcium magnesium acetate, potassium acetate, and urea—have focused on performance and cost under various weather conditions without evaluating their relative effects on the environment. Several new chemical preparations, including some that are proprietary formulations, have entered the market as snow and ice control chemicals for use by transportation agencies, but there is limited information about their environmental impacts. There is a need for rational decision-making guidelines to assist DOT maintenance managers in selecting the most appropriate snow and ice control materials for the conditions that exist in their jurisdictions.

The overall objective of this project was to develop guidelines for selection of snow and ice control chemicals and abrasives, based on their composition, performance, potential environmental effects, and cost of the product together with common site-specific conditions near roadways on which these products would be used. For this study, environmental impacts were defined to include effects on human health; aquatic life; vegetation, animals, and aquatic environments; air quality; vehicles; and physical infrastructure including bridges, concrete roadways and structures, railway electronic traffic signaling systems, and power distribution lines.

1.2 Scope of Study

Phase I of NCHRP Project 06-16 involved collection, compilation, and quantification of relevant technical information about snow and ice control materials. This information was to be used in preparing a draft report to include a framework for a proposed material selection guideline, an assessment of applicable analytical test methods, identification of areas where insufficient information is currently available, and a revised work plan. Phase I covered Tasks 1 through 6 of the NCHRP Project 06-16 research plan. These tasks were as follows:

1. **Task 1 (Information Search).** This task involved a comprehensive search to assemble information about snow and ice control materials. The review included published information, current practices, and research in progress and covered the following topics:
    - Available materials, including typical costs, handling concerns, and application issues;
    - Environmental impacts related to common use, application, storage, and disposal;
    - Site-specific conditions that affect the choices of materials;
    - Product loading and fate/transport processes;
    - Current and proposed specifications and regulations for material acceptance; and
    - Parameters and test methods used as measures of performance and environmental properties.

    One component of this task involved developing a survey questionnaire that was distributed to state TRB research advisory panel members, provincial highway agencies, other roadway maintenance agencies, and vendors and distributors of snow and ice control products.

The survey sought information on the current status of use for snow and ice control materials, effects on the natural receiving environment, effects on infrastructure, product selection processes, and products commercially available for use. The research team sought follow-up information from survey respondents via telephone as required. The findings are provided in Chapters 2 through 4.

2. **Task 2 (Assessment of Information).** This task summarized the information gathered from Task 1 and categorized and quantified the most significant factors that should be considered in the selection of snow and ice control materials. A summary of findings is included at the end of each area reviewed, and a general assessment is provided in Chapter 6.
3. **Task 3 (Draft Framework for Product Selection).** This task applied the most significant factors identified in Task 2 in a draft framework for the selection of snow and ice control materials. The objective of this task was to provide the user with a practical process and the necessary information to make a decision given a user-defined set of goals—it was not the intent to be completely prescriptive.

   Product rankings were developed by assessing user-identified site-specific factors and product attributes known to affect these factors. Product attributes were further developed through Phase II of this study. For example, a material attribute known to adversely affect aquatic environments might receive a less favorable ranking if such areas were present. Product rankings were further processed through user-weighted product selection categories. Final product scores were developed and used to compare the merits of individual products. The draft framework for materials selection is provided in Section 6.2. The draft framework for product selection was used in Phase II of the study to create a decision tool for selecting products for use in common situations.
4. **Task 4 (Review of Analytical Test Methods).** This task identified and justified the test methods that were most effective for measuring the properties and constituents that determine the environmental impacts of the current range of snow and ice control materials. The potential for environmental impacts resulting from snow and ice control products can be assessed through analytical measurement of product properties and constituents and comparing these measurements to known specifications and criteria. Currently numerous test procedures are being used to measure performance and environmental impacts of snow and ice control materials, and it is not uncommon for laboratories to provide technically valid, yet conflicting test results. In order to assess the potential for risk of a product and to ensure comparability of test results among products, test facilities, and jurisdictions, the parameters of concern and the methods for measurement must be well defined. Review of the analytical test methods is provided in Chapter 5.
5. **Task 5 (Identification of Gaps in Information).** This task identified data gaps and needs, from Tasks 1 through 4, that exist because snow and ice control strategies are continually evolving, new products are being developed, and research efforts are providing new information. Information gaps are summarized in Section 6.3.
6. **Task 6 (Interim Report).** After completing Tasks 1 through 5, the research team prepared an interim (Phase I) report that summarized the information obtained and assessed, provided a draft framework for snow and ice control material selection, reviewed the analytical test method used to assess these materials, and identified gaps in information.

CHAPTER 2

Operational and Performance Considerations

2.1 Products Used and Properties

Snow and ice control materials include various chemical product types as well as abrasives. These have been classified as shown in Table 2-1.

Chloride salts include sodium chloride (NaCl), calcium chloride ($CaCl_2$), and magnesium chloride ($MgCl_2$). Organic products include acetates (e.g., calcium magnesium acetate [CMA] and potassium acetate [KA]) and other organic materials that mostly include agricultural by-products. Manufactured organic materials (e.g., glycols, methanol, and nitrogen products) are most commonly used for airport applications and see limited roadway applications.

Some hybrid mixtures containing chloride salts and organic products are often available in both solid and liquid form. These typically involve the addition of an agriculturally derived organic product to a chloride salt with the intent of reducing corrosion. Additionally, snow and ice control materials (i.e., NaCl) are often purchased by an agency in solid form and made into brine using onsite equipment.

Snow and ice control materials can be characterized by their primary components, the form in which they are used, and the optimum eutectic temperature. Table 2-2 lists the general properties for chloride-based snow and ice control chemicals. The optimum eutectic temperature for a given product is the lowest temperature at which a product will freeze when at the optimum ratio of chemical to water (*1*). This can also be stated as the lowest freeze-point achievable by a given chemical through an optimum ratio of chemical to water. The prices shown in Table 2-2 are from contracts published in 2003 available on the Internet. These prices should be considered as representative values only and may vary, primarily because of shipping costs. For example, Salt Lake City, Utah, salt prices were $13.80 in U.S. dollars (USD) per U.S. ton and in Yellow Knife, Northwest Territories, the prices were $85.37 (USD) per ton. Annual totals for quantities used are not available, except for roadsalt. The lack of data on the product sales volumes is believed to result from there being no trade association for the suppliers of the numerous proprietary blenders and resellers.

2.1.1 Chloride Salts

Chloride-based snow and ice control materials are generally produced from the mining of surface or underground deposits, extracting and fractionating well brines, industrial by-products, or through solarizing saltwater. Natural well brines are usually, but not always, associated with petroleum and natural gas production and are found in locations throughout the United States and Canada, including Alberta and Texas. Generally, these brines are composed of several chemicals and usually are processed to extract various commercial products, including snow and ice control materials. Solarization is the ponding of natural salt brines from seawater or salt lakes (e.g., Salt Lake in Utah and the Dead Sea in Israel) and allowing solar energy to evaporate the water. The various products crystallize at different concentrations (depending on solubility), allowing the manufacturer to separate the various chemicals from the original brine.

2.1.1.1 NaCl Solid (Roadsalt) and Liquid (Brine)

Roadsalt or sodium chloride is the most commonly used snow and ice control chemical. Most of the roadsalt used in the United States and Canada comes from underground mining, solution mines, and solarization.

Solution mining is a process of injecting hot water into a subsurface deposit of salt or other chlorides through a well. The hot water forms a solution that is pumped to the surface and evaporated to recover the various chemicals. Salt is mined in Alberta, New Brunswick, Nova Scotia, New York, Kansas, Louisiana, and other areas of the United States and Canada. Solarization is used to produce salt in San Francisco, Salt Lake City, Louisiana, Mexico, and Chile.

Table 2-1. Snow and ice control materials.

Material Type	Snow and Ice Control Material	Primary Components
Chloride Salts	Sodium Chloride (NaCl)	Na, Cl
	Calcium Chloride ($CaCl_2$)	Ca, Cl
	Magnesium Chloride ($MgCl_2$)	Mg, Cl
Organic Products	Calcium Magnesium Acetate (CMA)	Ca, Mg, $C_2H_3O_2$
	Potassium Acetate (KA)	K, $C_2H_3O_2$
	Agricultural By-Products	Complex sugars
	Manufactured Organic Materials	Varies with product (i.e. glycol, methanol)
Nitrogen Products	Urea	Urea, Ammonia
Abrasive	Abrasives	Varies with the source of the material

2.1.1.2 Calcium Chloride ($CaCl_2$)

Calcium chloride ($CaCl_2$) is primarily produced from natural well brines and as a by-product of the Solvay process. The Solvay process involves combining sodium chloride and calcium carbonate ($CaCO_3$) to produce sodium carbonate (Na_2CO_3) and $CaCl_2$.

2.1.1.3 Magnesium Chloride ($MgCl_2$)

Magnesium chloride ($MgCl_2$) is most commonly obtained through solarizing natural salt brines. Magnesium chloride brine, along with magnesium sulfate ($MgSO_4$) is the most soluble of the components in the natural brines. The most common sources of magnesium chloride in the United States and Canada are the Great Salt Lake in Utah and the extensive salt works in San Francisco Bay. Some magnesium chloride is produced as a by-product from metallurgical processes, but these sources may contain sufficient trace metal contaminants (e.g., arsenic) to be of concern and should be analyzed carefully before being accepted for use.

2.1.1.4 Blended Chlorides

There are two types of blended chlorides: those that occur naturally and those that are custom-blended. The natural-blended chlorides come from complex well brines and natural deposits of mixed chlorides such as the salt flats in Utah. The natural sources are usually not highly processed and thus their chemical constituents can be variable. Custom-blended chlorides usually consist of two to three chemicals. NaCl is typically the major component, with other chlorides added to improve low-temperature performance and/or the hygroscopic properties of the blend. Many of these custom-blended products also include a corrosion inhibitor.

2.1.2 Organic Products

Organic snow and ice control products are, for the most part, manufactured products. Some are wholly synthesized (e.g., CMA and KA); others are refined from agricultural sources (e.g., by-products from grain processing, brewing, winemaking, and similar sources). Table 2-3 lists the general properties for organic snow and ice control products. The optimum eutectic temperature for a given product is the lowest temperature at which a product will freeze when at the optimum ratio of chemical to water (*1*). This can also be

Table 2-2. Chloride salts, general properties.

Material	Chemical Formula	Forms Used	Optimum Eutectic Temperature °C (°F) @ % Concentration [1]	Common Sources	Approximate Annual usage Tonnes (Tons) North America	Median Cost (USD) per Ton (survey of Internet contracts) [2]
Sodium Chloride	NaCl	Primarily solid, but increasing use of liquid	-21 (-5.8) @ 23.3%	Mined from natural deposits, solarization of natural brines	21,080,000 (22,291,000) (Salt Institute)	$ 36
Calcium Chloride	$CaCl_2$	Mostly liquid brine, some solid flake	-51 (-60) @ 29.8%	Natural well brines, by-product of the Solvay process	Not Available	$120
Magnesium Chloride	$MgCl_2$	Mostly liquid brine, some solid flake	-33 (-28) @ 21.6%	Solarization of natural brines, natural well brines, by-product of metallurgical process	Not Available	$ 95
Blended Chlorides	Varies with product	Solid and liquid	Varies with product	Natural well brines, solarization of natural brines, mined from natural deposits	Not Available	$142

[1] Source: (*2*)

[2] as of October 2003

Table 2-3. Organic products, general properties.

Material	Chemical Formula	Forms used	Optimum Eutectic Temperature °C (°F) @ % Concentration [1]	Common Source(s)	Approximate Annual usage Tonnes (Tons) North America	Median Cost (USD) per Ton (survey of Internet contracts)[2]
Calcium Magnesium Acetate	CaMgAc	Mostly liquid with some solid	-27.5 (-17.5) @ 32.5%	Reaction of Highly Concentrated Acetic Acid with Dolomite Limestone	Not Available	$1280
Potassium Acetate	KAc	Liquid only	-60 (-76) @ 49%	Reaction of Highly Concentrated Acetic Acid with caustic potash (KOH). This reaction produces potassium acetate and water.	Not Available	Not Available
Agricultural By-Products	NA	Liquid only	Usually blended with chloride-based products	Refined from Agricultural base materials	Not Available	Blends $ 108
Other Organic Materials	Glycols Methanol	Liquid only	Varies with product	Varies	Not Available	Not Available

[1] Source: (*2*)

[2] As of October 2003

stated as the lowest freeze-point achievable by a given chemical through an optimum ratio of chemical to water. The prices shown in Table 2-2 are from contracts published in 2003 available on the Internet. These prices should be considered as representative values only and may vary, primarily because of shipping costs.

2.1.2.1 Calcium Magnesium Acetate (CMA)

CMA was the result of an FHWA effort to find a low-corrosion biodegradable substitute for roadsalt. Although CMA meets the project objectives, it is relatively costly to produce. CMA is produced by reacting high-grade acetic acid with dolomite limestone. Acetic acid (the acid in vinegar) is the product of fermentation of agricultural (usually corn) products. Under normal conditions, the fermentation process can produce a 4- to 5-percent solution of acetic acid. The production of CMA requires a 25-percent solution of acetic acid to be viable. Subsequently, much of the cost of CMA is the result of producing high-concentration acetic acid.

Acetic acid can be made in various ways. For example, fermentation of corn or other organic products yields a solution of approximately 4 percent. Other methods, such as air oxidation of butane, produce a much higher yield of acetic acid. The acid is then distilled from the other ingredients to obtain glacial acetic acid. CMA is now made from the direct reaction of acetic acid and dolomitic lime.

2.1.2.2 Potassium Acetate (KA)

Potassium acetate is a commercially available chemical used in numerous chemical and pharmaceutical processes. It is a non-chloride, high-performance product originally designed for use as a runway deicer. Potassium acetate is commercially manufactured using the same high-grade acetic acid as CMA; therefore, cost is an issue when considering roadway snow and ice control.

2.1.2.3 Agricultural By-products (Organic Biomass)

Agricultural additives for snow and ice control are refined from various agricultural feedstock, including corn, wheat, and rice. Currently, these are all proprietary products and, thus, little is known of the actual manufacturing/refining process. However, in most cases, these products are reduced organic biomass. These products are usually used in conjunction with chloride-based products, although stand-alone products have been marketed. These products have demonstrated significant corrosion-inhibiting characteristics under certain conditions, as well as claims of increased overall product performance.

2.1.2.4 Other Organic Materials

Other organic compounds are used for snow and ice control. One group of compounds is alcohols (e.g., methanol or ethanol). These are usually distilled from organic feedstock, although some can be synthesized from petroleum sources. Alcohols are volatile and flammable and present some storage and handling concerns. Glycols are another common group of organic chemicals used for snow and ice control. The most common glycol-related compounds encountered are ethylene and propylene glycol. These are found in commercial automobile antifreeze products. These compounds are used as aircraft deicers and have seen limited roadway application.

2.1.3 Sand or Abrasives

Sanding materials or abrasives are used in most areas of Canada and the United States, commonly as the primary method to enhance traction on ice-covered roadways. Abrasives provide no ice-melting capabilities. The chemistry of sanding materials depends on the original source. Sanding materials or abrasives are produced by crushing natural deposits of stone, screened or crushed from natural deposits or from scoreaceous volcanic deposits (sometimes called cinders in the western areas of the United States and Canada). Other sources of sanding materials are metallurgical slag (often referred to as cinders in the eastern areas of the United States and Canada), "clinker" ash from coal-fired boilers, and natural river sands. The approximate annual use is unknown because of the large number of commercial and non-commercial sources.

2.2 Storage

Material storage is an important operational and cost consideration and may also be of concern because of releases of stored materials into the natural receiving environment. Unwanted releases of snow and ice control materials from storage facilities have contributed to roadsalts being placed on the Priority Substances List under the Canadian Environmental Protection Act (CEPA) (*3*).

2.2.1 Solid Snow and Ice Control Materials

Proper storage of solid snow and ice control material entails having appropriate receiving and loading equipment, adequate access to the stockpile, and proper protection against escape of chemicals or leachate (*4*). Solid snow and ice control chemicals should always be stored inside to prevent runoff of salts dissolved by precipitation. Storage structures should be constructed on an impermeable pad of asphalt, concrete, or other suitable material graded away from the center of the storage area for drainage. The pad should extend around the exterior of the structure and be graded away from the building, so runoff does not enter the structure. Storage structures should also allow for gathering any stormwater or runoff that may occur. This can be accomplished by providing a runoff control system for proper discharge or collection of materials for reuse. Permanent storage structures should be constructed to withstand the pressure from the material and the stress of loaders pushing materials against the inside walls. Alternatively, temporary barriers can be used to protect the storage structure walls when the original walls alone may not have adequate strength (*4*).

2.2.2 Liquid Snow and Ice Control Materials

Liquid storage details include adequate tank capacity, proper-sized pumps and hoses for quick loading, and recirculation capability to maintain product consistency should settling occur. Liquid chemical storage should include containment barriers sufficient to contain and recapture spills or the volume released from a tank rupture.

2.2.3 Sand or Abrasives

The storage of sanding materials entails having appropriate loading equipment and adequate access to the stockpile. In many cases, abrasive piles are treated with liquid snow and ice control chemicals to prevent freezing. In such cases, proper runoff protection is required.

2.3 Handling and Application Methods

In general, the exposure effects of snow and ice control chemicals are relatively mild and key concerns are stated on Material Safety Data Sheets (MSDS). Most products can produce dust in their dry form and may irritate the respiratory system. Eye and skin irritation is a common concern when handling snow and ice control chemicals in liquid form. Eye, skin, and respiration protection is recommended under certain conditions.

Appropriate equipment is needed for handling and applying snow and ice control chemicals. Application equipment can vary greatly from new equipment to equipment built to customized versions of existing equipment. Calibration and regular re-calibration of equipment is of the utmost importance to achieve control of the rate of application.

2.4 Agency Survey—Current and Future Status of Use in the United States and Canada

A survey was distributed to assist in defining snow and ice control material use in North America. The questionnaire was distributed to U.S. DOTs (through the members of the TRB Research Advisory Council); Canadian provincial transportation agencies; and various other agencies involved in using and distributing snow and ice control materials. The survey (included as Appendix A, which is available for download from the TRB website) was designed to gather the following information:

- Product use and methods of application,
- Environmental concerns,
- Corrosion concerns, and
- Product selection process.

Twenty-eight organizations (i.e., 22 states, 3 provinces, and 3 cities) responded. Detailed summaries of responses are provided in Appendix B, which is available for download from the TRB website. With a few exceptions, the survey respondents included the primary U.S. and Canadian agencies involved in snow and ice control and constituted a good geographical cross section from east to west.

2.4.1 Product Use and Methods of Application

Respondents were asked what snow and ice control materials were used and what their preferences (rankings) were among materials. Table 2-4 summarizes the results. Some respondents listed more than one material as their primary or secondary preference. As an example, three respondents listed both NaCl solid and NaCl brine as their primary choice. This could indicate that the users might be developing storm-specific strategies for each of the chemicals.

2.4.1.1 Chloride-Based Snow and Ice Control Materials

As expected, solid NaCl was the most commonly used snow and ice control chemical and was considered a first preference for 57 percent of the respondents. The total quantity of salt used (4.7 million tons) when compared with other products further supports this finding. NaCl brine, in most cases produced on site by the agency, was a first or second choice for 43 percent of the respondents. Several respondents had both salt and salt brine as their first preference.

Magnesium chloride, used as a liquid, was the next preferred chemical with 14 of the respondents rating it as either their first, second, or third preference (50 percent). Calcium chloride, primarily used as a liquid, was the next most popu-

Table 2-4. Snow and ice control material preference.

Material	1st Choice	2nd Choice	3rd Choice	4th Choice	5th Choice	6th Choice
NaCl solid	57% (16)	18% (5)	4% (1)	0	0	0
NaCl brine	11% (3)	32% (9)	7% (2)	0	4% (1)	0
Salt-based solid products plus other ingredients	4% (1)	4% (1)	0	0	0	0
Chloride-based brines plus organic additive	0	4% (1)	0	4% (1)	7% (2)	0
$CaCl_2$	7% (2)	18% (5)	18% (5)	14% (4)	0	0
$MgCl_2$	14% (4)	7% (2)	29% (8)	0	14% (4)	0
CMA	0	4% (1)	0	7% (2)	0	0
KA	4% (1)	7% (2)	0	0	0	4% (1)
Abrasives	21% (6)	18% (5)	7% (2)	11% (3)	7% (2)	4% (1)
Abrasive/NaCl mixture	4% (1)	0	0	0	0	0
Sand mixed with salt solids plus inhibitor	0	4% (1)	0	0	0	0

Source: Agency survey (based on current practices) lar, with 12 of the respondents rating it as either their first, second, or third preference (43 percent).

For the most part, respondents reported $MgCl_2$ and $CaCl_2$ to be used as blended products containing organic materials used as corrosion inhibitors. A natural product containing a combination of sodium, magnesium, and potassium chlorides had some high preferences from western states. This product was used as a stand-alone product and blended with an organic-based corrosion inhibitor.

2.4.1.2 Organic Deicers

The purely organic snow and control chemicals include calcium magnesium acetate (CMA), potassium acetate (KA), and some proprietary organic products. These materials are not as popular as chloride-based products, but are used as either stand-alone liquids, blended with inorganic liquids, or as stockpile treatments. In general, they are not the most preferred products; they tend to be used for special cases (e.g., for low-corrosion applications such as bridge decks).

2.4.1.3 Hybrid Deicers

Use of hybrid organic/inorganic deicers is limited. This class of chemicals, which uses a blend of significant amounts of both organic and inorganic deicing chemicals, is usually designed for low-corrosion applications.

2.4.2 Natural Environment Concerns

The survey covered some issues pertaining to the environment, including areas of environmental concerns, material storage practices, and applicable environmental regulations for use of snow and ice control materials.

2.4.2.1 Areas of Environmental Concern

The survey asked respondents to prioritize their environmental concerns by allocating percentage weighting to each concern. They were also asked if they had modified their operations to address these problems. Weighted averages were used because not all of the respondents completed this section. Survey results are provided in Table 2-5. Water quality appears to be the greatest environmental concern, followed by air quality, vegetation, and endangered species. Air quality issues are more important in western regions, whereas water quality is important in eastern regions. A few agencies separated subsurface (wells) from surface contamination as a concern, but for this study, they were combined as aquatic impacts. Survey results indicate that some agencies modified operations to address environmental concerns; however, no specific information was given as to how this was accomplished.

2.4.2.2 Materials Storage

Respondents were asked to describe current storage procedures for abrasives, solid chemicals, and liquid chemicals (see Table 2-6). The data reflect the total number of respondents. Some agencies listed multiple methods of storage for each category, whereas some did not respond. Responses indicate that, although most abrasives are stored outdoors and uncovered, significant amounts are stored indoors. Most solid chemicals are stored indoors on impermeable

Table 2-5. Environmental concerns.

Environmental Concern	Priority Ranking	Modified Operations
Aquatic Impacts (Surface and Subsurface)	40 %	46% (13)
Air Quality	27 %	36% (10)
Vegetation	20 %	25% (7)
Endangered Species	13 %	18% (5)
Other – Public Input	1 %	4% (1)

Table 2-6. Materials storage.

Materials	Outside Uncovered	Outside Covered	Indoor Storage	Impermeable Pad	Runoff Control
Abrasives	68% (19)	32% (9)	29% (8)	25% (7)	29% (7)
Solid Chemicals	11% (3)	36% (10)	79% (22)	54% (15)	50% (14)
Liquid Chemicals	NA	NA	NA	50% (14)	22% (11)

pads with some form of runoff control. However, some respondents reported storing solid chemicals outdoors with and without cover. Some store solid chemicals indoors without impermeable pads and/or runoff control. To a limited extent, liquid chemicals are stored in areas with runoff control.

2.4.2.3 Environmental Regulations

The survey asked the respondents if environmental regulations governed their operations (see Table 2-7). Many respondents (38 percent) indicated that environmental regulations were not a concern, despite national policies in both the United States and Canada. It is unclear whether the survey question was well understood or whether a general lack of understanding exists regarding specific environmental regulations.

Table 2-7. Environmental regulations governing snow and ice control practices.

Regulating Agency	Responses
Federal	10 (36%)
State/Provincial	7 (25%)
Other	3 (11%)

2.4.3 Corrosion Concerns

The survey addressed issues pertaining to corrosion impacts, including prioritizing corrosion concerns, along with the less common side effects on railway traffic control signaling and electrical power lines.

2.4.3.1 Areas of Corrosion Concerns

The respondents were asked to rank their corrosion concerns by allocating percentage weightings to each concern (see Table 2-8). They were also asked if they had modified their operations to address these problems and if they are conducting or had conducted related research. Weighted averages were used because not all of the respondents completed this section.

Corrosion to concrete reinforcing steel was found to be the primary concern, followed by corrosion of vehicles, general concrete damage, structural steel, and roadside structures. The survey results also indicate that some agencies modified operations to address corrosion concerns; however, such modifications were not explained.

Table 2-8. Corrosion concerns.

Concerns	Priority Ranking	Modified Operations
Concrete Reinforcing	30 %	22% (6)
Vehicles	22 %	26% (7)
Concrete Damage	20 %	22% (6)
Structural Steel	16 %	26% (7)
Roadside Structures, Utilities, and Equipment	12 %	11% (3)
Other	(no response)	(no response)

2.4.3.2 Railway Traffic Control Signaling

Four respondents (i.e., Colorado, Missouri, Montana, and Ontario) indicated incidences where snow and ice control materials have affected the operation of railway traffic control signaling. Follow-up efforts were unable to substantiate a relationship beyond anecdotal accounts.

2.4.3.3 Power Distribution Lines

Only one agency (South Dakota) reported incidences where snow and ice control materials have affected power lines. Based on media reports, such problems have been observed in several areas.

2.4.4 Purchasing Issues

The respondents were asked to provide information on selection processes for snow and ice control materials, including information on applicable specifications and details of quality assurance protocols.

2.4.4.1 Purchase Selection Criteria

The respondents were asked to rank present purchasing criteria for snow and ice control materials by assigning percentages to each criterion (see Table 2-9). They were also asked to do the same for future purchases. Weighted averages were used because not all of the respondents completed this section.

Table 2-9. Product selection process.

Criterion	Present Priority Average	Future Priority Average
Environmental	7.3 %	9.6 %
Corrosion	8.5 %	9.8 %
Human Exposure	3.5 %	3.8 %
Purchase Price	38.7 %	35.2 %
Cost of Use (i.e., Capital and Operational)	6.7 %	6.8 %
Storage and Handling	7.7 %	7.8 %
General Performance and Ease of Use	14.6 %	14.0 %
Climatic Requirements	10.5 %	11.1 %
Tradition	2.1 %	1.5 %
Others (e.g., friction, odor, wildlife attraction)	0.4 %	0.4 %

Purchase price was the most important criterion for the respondents and probably will remain so. Seven of the respondents cited “tradition” as a current purchase criterion and four respondents indicated they would continue to use tradition as a purchase criterion in the near future.

Environmental issues were most important in western regions, while corrosion issues were more important in the Midwest and eastern regions. Some movement toward increasing future attention paid to corrosion and the environment concerns was evident; however, the changes were small.

2.4.4.2 Purchasing Specifications and Quality Assurance

Respondents were asked to describe applicable purchase specifications for snow and ice control materials. Purchase specifications are used by agencies to identify minimum qualification before considering a particular product for purchase. Table 2-10 provides details.

Ninety-three percent of respondents indicated that some levels of product specifications were in place. The specifications for purchasing abrasives were mostly agency specifications and tend to involve measurement of simple physical attributes (e.g., particle size distribution), but attributes such as fracture and durability are also common. Purchases of solid chemicals were primarily based on state specifications usually derived from AASHTO or ASTM specifications. These specifications tend to involve physical attributes (e.g., size distribution and moisture content). Purchases of liquid chemicals were primarily based on PNS or state specifications. In many cases, non-PNS members have used the PNS specifications as a model for agency specifications. Further descriptions of test protocols associated with AASHTO, ASTM, and PNS specifications are provided in Chapter 5.

Survey responses detailing agency quality assurance testing are shown in Table 2-11. Most respondents (93 percent) indicated that some form of QA testing is being conducted. Fifty-seven percent of the respondents reported the level of effort (i.e., number of loads tested). QA test frequency ranged from 1 to 100 percent of loads, with the median being 10 percent. The wide variation in the level of quality control and quality assurance may result from one or more of the following factors:

- The prevalent and long-term use of solid NaCl, which tends to be a relatively uniform product with fairly simple specifications as compared with liquid chemical products with more complex specifications;

Table 2-10. Purchasing specifications for snow and ice control materials used by agencies.

	AASHTO	ASTM	PNS	Agency	Other
Abrasives	(Not Available)	3 (11 %)	(Not Available)	16 (57 %)	4 (15 %)
Solid Chemicals	4 (15 %)	6 (22 %)	6 (22 %)	12 (43 %)	3 (11 %)
Liquid Chemicals	(Not Available)	2 (7%)	10 (37 %)	11 (39 %)	2 (7%)

AASHTO – American Association of State Highways and Transportation Officials
ASTM – American Society for Testing and Materials
PNS – Pacific Northwest Snowfighters

Table 2-11. Quality testing.

Agencies Conducting Quality Testing	Level of Effort	PNS Protocols	SHRP Protocols	Agency Protocols	Others
26 (93 %)	10 %	7 (25 %)	2 (7 %)	12 (43 %)	3 (11 %)

- The cost of testing, particularly when extensive laboratory testing is needed (This is particularly true when using the PNS specifications that are far more extensive in scope);
- The use of AASHTO and ASTM specifications, which have been a standard for solid NaCl for a number of years (these specifications primarily address gradation and moisture content, which are not normally tested in the field); and
- The use of agency specifications that tend to involve testing during the production of the materials and enforcement on initial delivery. (Little or no follow-up testing is common.)

2.5 Application Strategies

Various strategies are available for applying snow and ice control materials to roadways. Depending on weather conditions, site-specific factors, and level-of-service goals, an agency's options include materials selection as well as the timing, rate, and frequency of application. Just as no one tool is suitable for every job, no one application strategy is suitable for all weather conditions. Application strategies should, therefore, be viewed as tools that can be selected and used as necessary. For this study, snow and ice control application strategies are classified as anti-icing, deicing, and abrasive use (see Table 2-12).

2.5.1 Anti-Icing

Anti-icing is a proactive strategy in which snow and ice control materials are applied before a snow, ice, or frost event. This strategy prevents precipitation from bonding (i.e., freezing) with the pavement surface, or, at the very least, weakens bonds that may be formed, for easier removal than with deicing. Anti-icing applications are not limited to liquid chemicals. Properly timed applications of either dry or prewetted chemicals can prevent bond formation if these materials can be held in place and not removed by traffic action. As such, anti-icing with solids can be very effective on sidewalks and other areas not subject to vehicle action.

Application rates in most of the research literature are expressed in either dry weight per lane mile or per lane kilometer. However, in actual practice, the rates are usually expressed in terms of liters or kilograms per lane kilometer or gallons or pounds per lane mile, depending on whether liquids or solids are being applied. Table 2-13 shows typical application rates used for anti-icing, based on the actual mass

Table 2-12. Application rates for various snow and ice control strategies.

Strategy/ Method	Materials	Pavement Temperature Ranges[1]	Application Rates[2]
Anti-Icing	Liquid Chemicals, Solid Chemicals, Pre-wet Solid Chemicals	0° C to -12° C (32° F to 10° F)	18-110 Kg /Lane /Km (65 – 400 Lbs / Lane/ Mile)
Deicing	Pre-wet Solid Chemicals, Dry Solid Chemicals	0° C to -18° C (32° F to 0° F)	113 – 400 Kg /Lane /Km (200-700 Lbs / Lane/ Mile)
Abrasives	Pre-wet Abrasives, Dry Abrasives	No limits	225 – 2,700 Kg /Lane /Km (500-6,000 Lbs / Lane/ Mile)
	Abrasive/Salt Mixes	0° C to -18° C (32° F to 0° F)	225 – 2,700 Kg /Lane /Km (500-6,000 Lbs / Lane/ Mile)

[1] Source: (*6*)
[2] Source: (*6, 7*)

Table 2-13. Typical chemical application rates for anti-icing activities at –10°C to –0°C (15°F to 32°F).

Reference	Dry chemical spread rate, kg/lane-km (lb/lane-mi)			
	Light icing	Light snow	Heavy snow	Freezing rain
"Manual of Practice for an Effective Anti-Icing Program" FHWA/CRREL (*2*)	7-36 (25-130)	28 - 55 (100 - 200)	28 - 55 (100 – 200)	21 - 110 (75 – 400)
"Manual of Practice for Anti-Icing of Local Roads" New Hampshire T2 (*8*)	18-36 (65-130)	28 - 55 (100 - 200)	28 - 55 (100 – 200)	21 - 110 (75 – 400)

of solids applied for 0°C to –10°C. Within this temperature range, most snow and ice control products have similar levels of performance.

A properly managed anti-icing program could reduce these application rates through analysis of actual experience. When anti-icing programs began in Washington State and Oregon, application rates were 65 L (18.2-kg dry chemical using a 28-percent solution) per lane-km (30 gal per lane-mile) for morning frost. As crews gained experience and evaluated operations, rates as low as 18 L (6.5-kg dry chemical using a 28-percent solution) per lane-km (8.5 gal per lane-mile) could be used while maintaining an equivalent level of performance (*1*). These low application rates were then used in cases where rain was predicted to immediately follow the frost event. This strategy reduced the amount of chemical applied and consequently released to the environment with storm runoff (*1*).

2.5.2 Deicing

Deicing is a reactive snow and ice control strategy that involves the application of a chemical on top of a layer of snow, ice, or frost that is already bonded to the surface of the pavement (*1*). Typical application rates for dry chemicals range from 25 kg per lane kilometer (100 lbs. per lane mile) to as much as 130 kg per lane kilometer (500 lbs. per lane mile); however, sometimes more are used, depending on conditions.

Deicing typically involves the application of solid NaCl and, as with any dry application, traffic action can result in a significant (up to 80 percent or more) loss of material to the roadside environment. A Montana study (*5*) found that deicing typically requires 5 times the amount of chemical product that anti-icing requires.

2.5.3 Pre-wetting

Pre-wetting is injecting or spraying a liquid chemical on solid chemicals or abrasives to enhance their effectiveness and reduce material loss and other forms of waste. It is a viable and desirable alternative to dry application of solid materials (*1*).

If the solid material is a chemical, such as NaCl, the wetting agent initiates the formation of brine faster than would occur without pre-wetting. Once brine is formed, it is more likely to stay on the roadway surface than be displaced by traffic action. A Danish study (*9*) assessed the retention of NaCl applied as a 20-percent brine versus pre-wet NaCl. Statistical analysis of 1,800 test results indicated that about 90 percent of the salt from brine remained on the roadway compared with 60 to 65 percent for pre-wetted NaCl. Much lower retention is expected after application of dry chemicals. Roadway retention for both application methods was also found to decrease at similar rates as traffic levels increased. Solid chemicals, most commonly salt, can be pre-wet with any of the available liquid chemicals, including salt brine. In present practice, dry salt is pre-wet with 35 to 45 L of liquid per metric tonne (8 to 10 gal per U.S. ton). These rates will and should vary with experience and temperature. Some application rates for the total pre-wet product from Ontario (*10*) are shown in Table 2-14.

When pre-wetting abrasives, the wetting agent adds weight as well as cushions the impact as the particle hits the roadway. There is also evidence that the liquid may help the material "stick" to the roadway. If the roadway surface has a layer of compacted snow or ice, the pre-wet liquid will partially melt the ice and allow the abrasive particle to become embedded in the ice layer. The net effect is that the abrasive particle becomes far more resistant to displacement from traffic action, further reducing material loss from the roadway. A Montana study (*5*) reported that pre-wetting of abrasives before application can reduce the amounts applied by 50 percent in cold temperatures. Abrasives can be pre-wet with any of the available liquid chemicals. As with solid chemicals, dry abrasive is pre-wet with 35 to 45 L of liquid per metric tonne (8 to 10 gal per U.S. ton). These rates will and should vary with experience, temperature, and storm conditions.

Table 2-14. Variable salt application rates with on-board pre-wetting.

Precipitation Type	Road Surface Temperature Range °C (°F)		
	Warmer than -5° (23°) Kg/lane-km (Lbs/lane-mile)	-5° (23°) to -10° (14°) Kg/lane-km (Lbs/lane-mile)	Less than -10° (14°) to -18° (-1°) Kg/lane-km (Lbs/lane-mile)
Frost	25 (97)	35 (136)	35 (136)
Light snow	35 (136)	50 (195)	65 (253)
Heavy snow	65 (253)	65 (253)	85 (331)
Freezing rain	65 (253)	85 (331)	85 (331)

Source: (*10*)

2.5.4 Dry Abrasive/Chemical Mixes

Application of abrasive/salt mixes, a popular strategy, typically involves approximately 1:1 mixtures of abrasive and salt. This strategy is not as cost-efficient as using chemicals only and is less effective at reducing accidents. Kuemmel and Bari (*11*) concluded that accident reductions for two-lane highways using the salt/abrasive mixtures were less than with salt only. Accident frequency on freeways was higher when salt/abrasive mixtures were used than when only salt was used. Cost/benefit calculations showed the application of salt/abrasive mixtures did not recover winter maintenance costs on two-lane highways during the 11-hour analysis period and freeways operations recovered costs in 6 hours, substantially slower than with salt only.

2.5.5 Abrasive Use

Sanding has long been a strategy of choice by many agencies, because it is a very visible low-cost approach to managing pavement friction. However, it has been shown that when abrasives are placed "dry" on the road surface (without significant pre-wetting) they provide at best, a very short term increase in road surface friction (*12*). As roadway traffic levels increase, and vehicle speeds are greater than 30 mph (48 kph), any benefit from abrasive use diminishes. Table 2-15 presents the practices for use of dry abrasives recommended by the Iowa Highway Research Board (*12*).

Table 2-15. Abrasive use.

Road Type	Use of Dry Abrasives
Freeways	Inappropriate
Rural roads, paved	Inappropriate
Rural roads, gravel	Only on low speed sections (perhaps hills and curves)
Rural intersections	Only on low speed approach length of gravel roads
High speed urban roads	Inappropriate
Low speed urban roads	Only in certain locations and when snowpack will persist
Urban intersections	Only when snowpack will persist

Source: (*12*)

Abrasive gradation (particle size) can also affect roadway retention. In one study, researchers (*8*) measured the retention of sand particles resulting from traffic and wind under various snow and ice conditions. They found retention ranged from 10 percent for natural fine sand to 50 percent for manufactured coarse sand. Typical gradations for abrasive material are shown in Table 2-16.

In addition to performance-related issues, other costs of abrasive use can include increased insurance claims and environmental impact. A Colorado study (*13*) concluded that "the major benefits of increasing use of liquid chemical deicers include the reduction of the insurance cost because of reduced chance of windshield damage and cleaner air." Since the implementation of the findings from the research on "Environmentally Sensitive Sanding and Deicing Practices," in 1994, the Denver metropolitan region has not violated the U.S. EPA PM-10 Standard.

2.5.6 Stockpile Treatment

Stockpile treatment involves treating stockpiles of abrasive materials or solid chemicals with an appropriate chemical to ensure that under cold-weather conditions these materials do not freeze into clumps that make the materials difficult to handle and apply (*1*). Typically chloride mixtures (liquid or solid) are added at 5 percent (by weight) chemical to a stockpile for "frost proofing."

A stockpile of abrasive materials can be frost-proofed by mixing a small amount of chemical into it as the stockpile is being made. This is the first step in reducing the incidence of frozen lumps. When frost-proofing sanding material, it is advisable to use only enough chemical to keep the material workable. Both liquids and solids chemicals can be used to treat stockpiles of abrasive materials.

Solid chemicals can and often do attract moisture, causing the stockpile to freeze into lumps that present a workability problem. Stockpiles of solid chemicals can be "frost-proofed" by adding a small amount of liquid chemical with a lower ultimate eutectic temperature than the stored solid.

Table 2-16. Typical abrasive gradations

Sieve Size	British Columbia Ministry of Transportation and Highways			Oregon Department of Transportation
	Designated 12.5 mm % passing	Designated 16 mm % passing	Designated 19 mm % passing	Designated 6.75 mm (.25 in) % passing
19.000 mm (3/4")	–	–	100	–
16.000 mm (5/8")	–	100		–
12.500 mm (1/2")	100	–		–
9.500 mm (3/8")	–	80–100	80–100	100
6.750 mm (1/4")	–	–	–	80–100
4.750 mm (#4)	50–95	50–95	50–95	–
2.360 mm (#8)	30–80	30–80	30–80	–
1.500 mm (#10)	–	–	–	8–22
0.600 mm (#25)	10–50	10–50	10–50	–
0.375 mm (#40)	–	–	–	0–10
0.300 mm (#50)	0–25	0–25	0–25	–
0.075 mm (#200)	0–6	0–6	0–6	0–2

Source: (*1*)
"–" indicates data not available

2.5.7 Application Strategy Studies

Numerous accounts illustrate the value of using more proactive snow and ice control strategies (i.e., anti-icing and pre-wetting) and using liquid snow and ice control materials. Three different studies outlined below illustrate the value of using all of the available application strategies appropriately. In each case, multiple strategies were used to achieve the desired results in a cost-effective and environmentally sensitive manner. These three studies are typical of results obtained elsewhere in the United States and Canada when traditional methods are replaced with more cost-effective strategies. The result is more cost-effective and efficient use of chemicals and sand.

2.5.7.1 Cypress Bowl

A case study (*14*) conducted for the Cypress Bowl ski area near Vancouver, BC, illustrates how an agency can vary application strategies to address changing storm conditions and meet desired levels of service goals. Traditional strategies involving dry abrasives, dry salt, and abrasive/salt mixes were replaced by techniques that involved using various combinations of chemicals and application methods (i.e., anti-icing and pre-wetting of salt and/or abrasives) to address each specific storm event. This change yielded a 39-percent reduction in material costs and a 28-percent reduction in operation costs. Volumes of applied materials were also reduced, further reducing the potential for effect on the natural receiving environment. Abrasive use decreased by 64 percent and chlorides use decreased by 73 percent.

The reduction in chlorides was calculated by inventorying the roadsalt used in the *before* and *after* periods and adding the magnesium chloride used in the *after* period. The chloride quantities were calculated using the molecular weights shown in Table 2-19, adjusting for moisture content in the solid salt and other non-chloride ingredients in the magnesium chloride solution.

The Cypress Bowl study, which benefited from highly detailed weather data, was able to use a weather index developed by the Washington DOT to determine weather differences. The weather index used in this study was derived from the original SHRP weather index. This index produced a result in the range of −50 (severe) to 50 (mild).

At Cypress Bowl, the months of March 2000 and March 2001 yielded weather index numbers of −12.30 and −11.36, respectively. Because the winter index values are not linear, one cannot infer anything except that the 2 months were relatively equal in weather severity. Given the small difference in indexes and the range of possible index results, the comparisons made were much more accurate than other studies.

2.5.7.2 Idaho DOT

An Idaho DOT study (*15*) found significant benefits when traditional methods (i.e., deicing using NaCl and abrasive use) were replaced with liquid chemical anti-icing. The area studied was on US 12 near Orofino in the winding Clearwater River canyon. The results of 3 year's operations (1997 to 2000) are shown in Table 2-17 and demonstrate significant reductions in labor, abrasive use, and accidents. The Idaho study used a 5-year average for setting the baseline of comparison. Although this is a workable approach and yields a reasonable comparison, it is still not as accurate as truly one-to-one weather comparisons.

Table 2-17. Idaho results.

	Average Annual Labor Hours	Average Annual Abrasives Used	Average Annual Accidents
Before 1997	650	1475 cu. M	16.2
1997-2000 Period	248	247 cu. M	2.7
Percent Reduction	*62%*	*83%*	*83%*

Source: (*15*)

Table 2-18. Colorado DOT materials use from 1992 to 2000.

Year	Sand (tons/mile)	Salt (NaCl) (tons/mile)	Liquid Deicer (gallons/mile)
1992	0.25	1.1	<0.5
1993	0.20	0.9	<0.5
1994	0.17	1.3	<0.5
1995	0.29	0	<0.5
1996	0.19	0	1
1997	0.23	0	3
1998	0.17	0	5
1999	0.09	0	8
2000	0.04	0	11

Source: (*13*)

2.5.7.3 Colorado Department of Transportation (CDOT)

A CDOT study (*13*) investigating the effects of abrasive use on air quality cited a general improvement in air quality as evidenced by the fact that Colorado has not exceeded a U.S. EPA PM-10 standard for seven winters. This improvement correlated with a shift in winter maintenance activities, away from abrasive and salt (NaCl) and toward snow and liquid snow ice control chemicals. This study concluded that the "optimal maintenance strategy involves an optimum mix use of liquid deicers and sand without the total elimination of the latter." Because of the study's statewide scope, it did not attempt to compensate for different weather conditions among regions; however, the author noted where weather could have been a factor in differences in results. Table 2-18 provides further detail.

2.6 Materials Loading

In winter maintenance operations, the amount of material applied for roadway affects the product loading to the natural receiving environment significantly. Environmental impact of materials used in winter maintenance is related to the type of product used and the amount applied. Any measure to reduce volumes of materials applied can reduce the magnitude of environmental effects.

2.6.1 Product Selection

The product used determines the "constituent speciation" (what is in the product) and "constituent concentration" (how much of each constituent is present). As an example, Table 2-19 shows the amounts of component elements and ions in the most commonly used chloride-based snow and ice control chemicals. The selection of a particular product can affect the amount of a constituent chemical released to the environment. Regardless of loading, a certain level of service must be maintained. Depending on the weather conditions, certain materials may be more effective than others. It is possible to gauge performance by assessing eutectic or phase curve information and calculating differences in dilution factors between products at a given temperature. Dilution of a chemical takes place as it melts water and subsequently reduces the concentration of the solution until it will freeze.

The performance index (PI) is a comparison tool that determines how much melting takes place before the solution will freeze at a given temperature. A higher PI indicates more melting can occur before freezing and thus better performance. The formula for a PI is

$$PI = (BC/EC) - 1$$

Where

BC = the concentration of chemical as applied to the roadway surface.

EC = the concentration (read from the phase curve) at which the brine will freeze after dilution at the stated surface temperature.

Example: NaCl (23.3 percent) and KA (50 percent) compared at −6° C (21°F).

For NaCl (23.3%), the beginning concentration (BC) is 23.3% and the ending concentration (EC) is 9%. This provides a PI of 1.59.

For KA (50%) the BC is 50 percent and the EC is 13 percent. This provides a PI of 2.85.

Table 2-19. Molecular weight calculations for chloride-based chemicals.

Cation	Atomic Weight	Compound	Molecular Weight	% Chloride	% Cation
Sodium	22.98977	Roadsalt (NaCl)	58.442	60.66 %	39.34% (Na)
Magnesium	24.3050	Magnesium Chloride ($MgCl_2$)	95.210	74.47 %	25.53% (Mg)
Calcium	40.078	Calcium Chloride ($CaCl_2$)	110.983	63.89%	36.11% (Ca)

Using the above comparison, one could reasonably conclude that a smaller application of KA would yield the same results in terms of ice removal at this temperature. PI is used to estimate relative performance of products, but can be affected by changes in temperatures, so care should be taken in its use.

2.6.2 Application Amounts

The amount of snow and ice control materials entering the environment is directly related to the application rate combined with the number of applications being made. A key factor in application rate and frequency of application is weather condition, which will dictate either the application rate or the number of applications, or both. Thus, weather conditions will, in most cases, dictate the total amount of a particular snow and ice control material applied. The effect of weather is illustrated by the weather- and temperature-dependent application rates shown in Tables 2-13 and 2-14. Hygroscopic properties, pavement type, pavement texture, and traffic volumes can also affect application rates and frequencies, but are relatively minor in effect.

Application rates are determined to suit specific site and weather conditions and, as a result, are highly variable. Chemical application is not a "do it by the formula" process and, if correctly done, should be variable with the goal of adjusting to conditions. The most important of these conditions is weather, which is also the least predictable. However, in the context of this study, which was to compare the environmental effects of materials, the effect of climate could be somewhat normalized because materials were compared with one another under the same climate and weather conditions (*1*).

2.6.3 Strategy Selection

Selection of a strategy, or sequence of strategies, can affect the total loading of a snow and ice control material. There is significant anecdotal evidence that the use of anti-icing and pre-wetting strategies singly, or in concert, can reduce the total environmental loading of materials significantly (*14–16*). The Cypress Bowl Case Study (*14*) illustrates the reduction in environmental loading that can be achieved by proper strategy selection. The study's validity results from the fact that the weather conditions for both study periods were nearly identical, allowing a one-to-one comparison of the before and after strategies. No other published studies were found with identical weather conditions between compared periods. Anti-icing and pre-wetting of solid materials can reduce the total environmental loading significantly. Table 2-20 shows that reduction in the application rates cited for the various strategies can affect the total loading for the materials of choice. These estimates are based on data presented in Tables 2-13 and 2-14. Liquid application data have been converted to equivalent solid mass of chemical. Figure 2-1 illustrates the data in Table 2-20 and shows how selection of snow and ice control strategies can affect the overall environmental loading of ice and snow control materials.

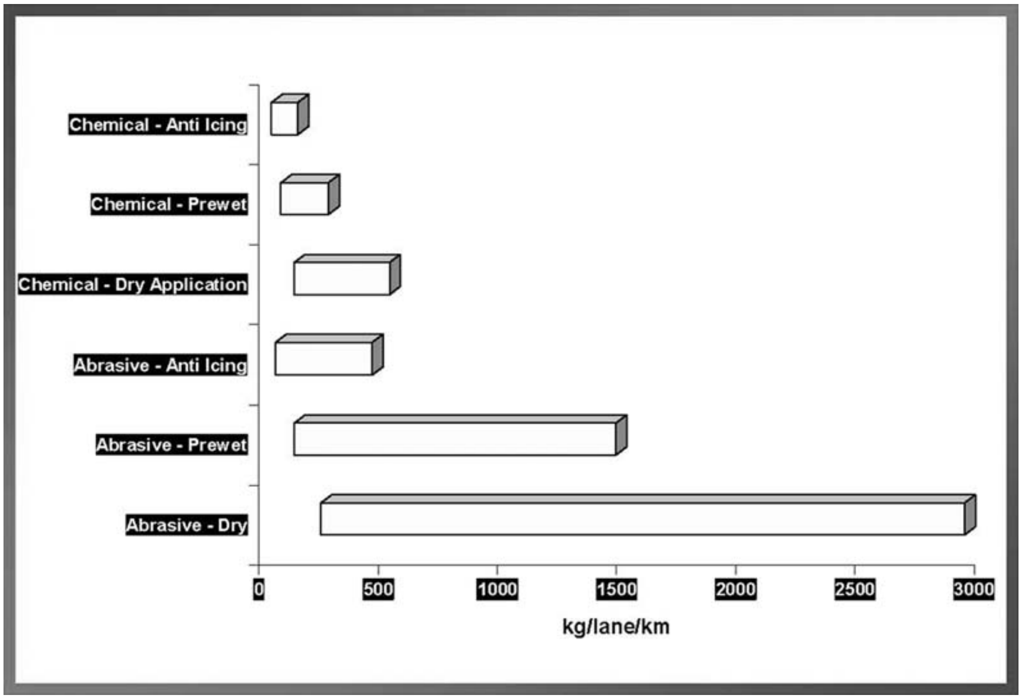


Figure 2-1. Comparative application rates for select snow and ice control strategies.

Table 2-20. Reduction in material application loading from changes in strategies.

	Original Loading[1]				Pre-wetting Solids Loading[2]				Anti-Icing Loading[3]			
Original Strategy	Low		High		Low		High		Low		High	
	Kg	(Lb)	Kg	(Lb)	Kg	(Lb)	Kg	(Lb)	Kg	(Lb)	Kg	(Lb)
Dry Abrasives	225	(500)	2700	(6000)	113[5]	(250)	1350[5]	(3000)	34[4]	(75)	405[4]	(2100)
Dry Solid Chemicals	113	(200)	400	(700)	57[5]	(100)	200[5]	(350)	18[1]	(65)	110[1]	(400)

[1] From Tables 2-12 and 2-13.

[2] Assumes pre-wetting of abrasives or solid chemicals as indicated by original strategy.

[3] Assumes liquid or solid chemical is used. Abrasives may have been used under certain circumstances.

[4] Source: Average from Idaho (*15*) and Cypress Bowl (*14*) studies

[5] Source: Montana (*5*)

CHAPTER 3

Impacts to the Natural Environment

3.1 Environmental Pathways

All snow and ice control materials can affect the natural receiving environment. The magnitude of the effect depends on conditions such as the types of materials, quantities being applied, transport pathways, exposure pathways, exposure duration, chemical-specific impacts, and other site-specific environmental characteristics. The distribution of snow and ice control materials into the environment involves complex and interrelated processes that can be simplified into a conceptual model showing primary transport mechanism and pathways and areas of effect (see Figure 3-1).

Initial discharge of snow and ice control materials into the receiving environment can occur during transport, storage, or application on roadways. Roadway application is the primary source of discharge based on the volumes of materials applied; however, spills and discharges from storage or transport can cause significant localized effects. Transport to the environment begins when the snow and ice control material is applied to the roadway. Materials will either leave the roadway as (1) a liquid, through splashing, spraying, or gravity drainage; or (2) as a dried residue mobilized or re-suspended by traffic action and wind. Product leaving the roadway as runoff may directly discharge to receiving surface water bodies or percolate into soils. Product released into soils will either accumulate (in soil solutions or through soil adsorption) or permeate the soil and combine with groundwater. Where soil solution or groundwater comes in contact with the root zone of vegetation, uptake through the roots can occur. Chemical carried as runoff, that has percolated through the soil, or that has reached the groundwater will often be transported to surface water bodies. Products forced into the air by vehicle motion, wind, or plowing will be deposited on vehicles, the road surface, the roadside (e.g., roadside cover and ditches), adjacent soils, vegetation, the snow layer, surface waters in the surrounding vicinity, or combinations thereof. Secondary transport processes will cause solid deposits to migrate to soils, surface waters, and groundwater as described above.

3.1.1 Soil Transport

Snow and ice materials are deposited on roadside soils from splashing, spraying, gravity drainage, or plowing. The magnitude and the spatial extent of effect depend on local features and conditions, such as the slope of the roadside, direction of drainage, type of highway drainage system, soil type, vegetative cover, presence of snow and ice, and precipitation (*18*). In addition to accumulating in the snowpack, some solids percolate vertically into the soil or are transported horizontally through runoff. Sites with steep slopes in addition to compacted soils (i.e., clays) are characterized by high runoff and low infiltration rates and promote the horizontal movement of runoff (and soluble ions) in preference to vertical movement (*19*). On the other hand, sites with low slopes and drainage, low runoff volumes, and permeable soils all contribute to the downward movement of solubilized ions into the soil. Jones et al. (*19*) determined that compacted soils could result in 75-percent runoff and 25-percent infiltration, while permeable soils could result in 35-percent runoff and 65-percent infiltration.

Movements of salts through frozen ground have shown near-normal infiltration up to 10.2 cm in heavy-textured soils (*19*). Light-textured soils (i.e., typical farming and pasture) have shown almost no infiltration. These are extremely complex processes. Methods of predicting salt infiltration in frozen soil are not available, and the movement of moisture through soil is not yet fully understood.

Novotny et al. (*20*) determined that most solids (i.e., total solids and dissolved solids) accumulation occurs within 1 meter from the edge of the roadway in snow piles formed by plowing operations and traffic. The concentration of solids during winter increases linearly until the snow pile melts in the spring. Enrichment and “first flush” effects describe the

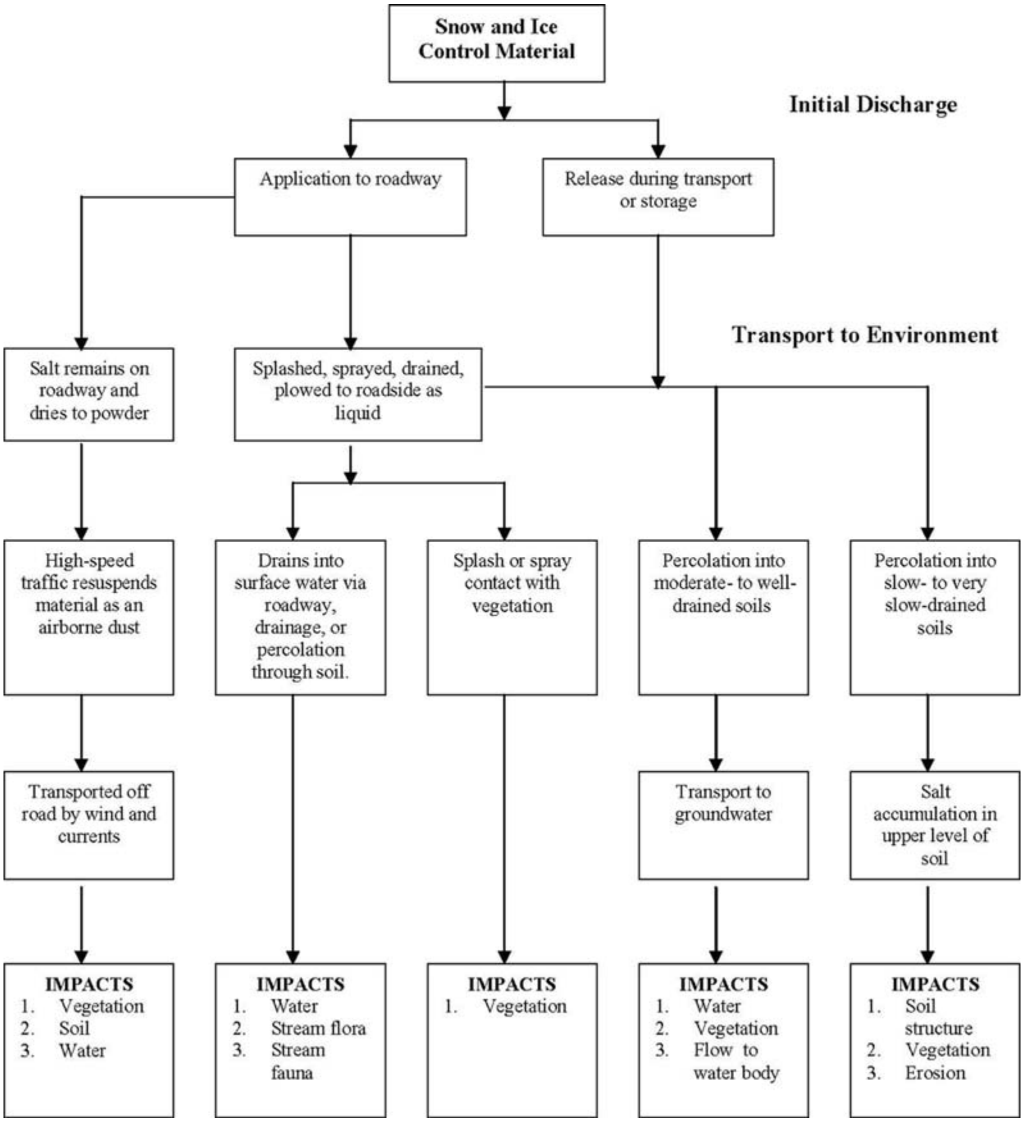


Figure 3-1. Environmental pathway model modified from TRB (17).

physical and chemical process occurring in the roadside snowpack. Ions are rejected from the crystalline lattice of snow during repeated freezing and melting and become available for washoff during the first stage of snowmelt. This can result in high runoff concentrations during early spring washoff.

A Canadian study (*21*) mapped salt concentrations throughout the Canadian landscape and found concentrations to be highest in areas near salt depots and along roadsides. On a regional level, salt accumulations tended to vary with climate. The highest salt accumulations in soil occurred in the Prairie provinces, whereas in areas with considerable rainfall, such as British Columbia or Atlantic Canada, effects of roadsalt applications were either negligible or are not cumulative over the course of the snow-free season. Effects are cumulative in areas where dilution resulting from surface runoff and soil percolation is severely limited by low precipitation rates or restricted access to percolating water. The greatest effects are, therefore, associated with areas with the highest loads, with the lowest soil percolation rates. Effects are calculated to be greatest on soils with the highest levels of sodium saturation when subjected to low EC water (*21*).

Studies of sodium and chloride levels in soil generally indicate that the greatest concentrations are found within 2 to 3 meters of the pavement edge (*22*). However, depending on local conditions, impact areas can be more extensive. For instance, one study (*23*) reported higher-than-background concentrations of sodium and chloride as far as 10 meters from the roadway. High concentrations of sodium and chloride are not usually found at depths below 1 meter (*22, 24*).

McBean and Al-Nassri (*25, 26*) also investigated the distance that salt applied to roads can travel from the road and contaminate the surrounding soil or receiving water. They determined that a 10-m setback is sufficient to protect most vegetation from the effect of snow and ice control material applications; beyond 10 meters, concentrations of snow and ice control chemicals dropped to background levels. If the soil is well drained, the extent of impact may be as little as 5 meters from the road for deep gravelly, stony soil (*27*).

Earlier studies concluded that, although salt levels in roadside soils may be high in spring, salt is readily leached from the top meter of soil and disappears in the summer, whereas other studies document a steady buildup of salts in the soil (*20*).

Cain et al. (*28*) summarized 10 studies, including studies referenced above, that provided measurements of substrate (i.e., soil, soil water, or solutions) of chloride, sodium, or NaCl following application at specific distances from the roadway. The assessment found, for the most part, that elevated levels of sodium (over 500 ppm) tended to occur within 10 meters of the roadway. Elevated chloride levels (over 500 ppm) were also found to occur within the same distance.

Based on an assessment of these studies of snow and ice control materials over roadside soil (from splash, spray, and runoff), the effects on soil are concluded to typically drop quickly beyond the first 10- to 20-m-wide strip of land bordering the roadway or along paths of overland flow.

3.1.2 Air Transport

Snow and ice control materials can be transported through the air and deposited as a splash or spray. Aerosols and resuspended dried materials can be transported by vehicle turbulence or winds and can be carried further by winds blowing across the highway. Airborne materials can affect soil and water concentrations; however, deposition of materials on vegetation tends to be a primary concern with this transport mechanism. Traffic and weather patterns play a key role in determining the distance that materials are transported from the roadway. Kelsey and Hootman (*29*) found that dispersion of aerosols from a highway is related to traffic volume and speed. The findings suggest that NaCl aerosol dispersion is extensive and could be at least 15-m high within 67 meters of a highway. Kelsey and Hootman also found that the higher the plume formed by traffic, the farther it is likely to be carried by winds. A study conducted by the Connecticut DOT found airborne salt to travel as far as 300 feet laterally from the roadway under heavy traffic conditions. Chung (*30*) found that salt spray could also be transported for distances greater than 500 feet under high wind conditions. A European report determined that more than 90-percent of spray or splash next to a primary motorway was deposited along a corridor about 15-m wide and that the amount deposited decreased exponentially with increasing distance (*31*). This study also found vertical distribution to be distributed more or less exponentially with height from the roadway, with most deposition occurring up to 3 meters in height.

Topography can also contribute to the extent of aerial transport. A TRB study (*32*) found that wooded areas downhill within 40 to 60 feet of heavily traveled salt-treated highways are primary candidates for salt-related damage as compared with similar uphill areas.

3.1.3 Water Transport

Whereas the extent of deposition of snow and ice control materials through soil or through the air pathways is somewhat predictable, transportation of these materials into groundwater and surface waters is more involved and depends on site-specific conditions. Materials may reach surface water bodies through direct runoff, groundwater percolation, and, to a lesser degree, airborne deposition. Studies have been done to monitor highway runoff. Results indicate that in highway drainage systems, the lack of base flow, uncertainty in dates and times of expected precipitation, the short time scale of runoff, and the first-flush phenomenon may prevent meaningful data from being obtained using a manual sampling program (*33*). Many studies have attempted to model the concentrations of direct runoff (*34–36*); however, findings have been highly variable and dependent on site-specific factors such as precipitation amounts, first-flush effects, soil infiltration, hydraulic conductivity, and dilution effects. In general it can be conservatively estimated that snow and ice control materials will be diluted 500-fold as they leave the roadway and can be diluted substantially more as the distance from the roadway increases, but site-specific studies are critical for support of state or regional programs. Further discussion of runoff and dilution effects is provided in Section 3.4.3.1.

3.2 Framework for Protection of Environmental Systems

3.2.1 U.S. Regulations

The United States has general environmental protection legislation that prohibits contamination of air, land, and water; however, few of these address roadsalt specifically.

3.2.1.1 National Pollutant Discharge Elimination System (NPDES)

Since 1987, the U.S. Environmental Protection Agency (U.S. EPA) has been required by Congress to control stormwater runoff. NPDES requires permitting of stormwater discharges from industrial and construction activities and separate municipal storm sewer systems (MS4s). In

November 1990, the U.S. EPA adopted Phase I regulations pertaining to stormwater discharges from MS4s serving more than 100,000 people, construction activities disturbing greater than 5 acres, and industrial runoff into surface waters. The program was expanded when the Phase II final rules were passed in December 1999, through permitting requirements for construction activities disturbing 1 to 5 acres and small MS4s in urbanized areas. Some states have classified road maintenance stockpiles and operational sites as industrial sites requiring separate permitting and pollution control plans. Road maintenance, including snow and ice control activities, is controlled as part of stormwater permitting. Regulation outside stormwater regulation zones is much weaker, but may involve best management practices to minimize polluted runoff.

3.2.1.2 Endangered Species Act

The U.S. Congress passed the Endangered Species Act (ESA) in 1973 to establish federal legal authority for preventing extinction of species within the United States and for contributing to the prevention of extinction globally by prohibiting personal or commercial traffic in endangered species or their by-products from other parts of the world. The ESA is administered by the U.S. Fish and Wildlife Service for non-marine species and by the National Marine Fisheries Service for species that have marine affinities. These two agencies decide, based on legal and regulatory criteria, which species should be listed. Listing is initiated through information gathered by the agencies or information provided by other parties, which may be governmental or private. Species are classified as "endangered" if they are in imminent peril of extinction and as "threatened" if they are progressing notably toward the status of endangerment. Many states have laws that reinforce or enhance the scope of the ESA.

The ESA and its state counterparts restrict human interactions with listed species. The act prohibits "take," which for the purposes of the ESA is defined as harvesting or causing unintended mortality or stress as a by-product of any activity within the range of the species. The act also requires that "critical habitat" (defined by the listing agencies) not be destroyed and requires the agencies to prepare "recovery plans" that set guidelines for an extension of abundance or range of the listed species. Thus, both private and governmental activities may be restricted within the range of a listed species.

Although federal water-quality regulations within the United States are not applied to road application materials, with the exception of urban areas where stormwater permits are required, the ESA is directly applicable to such materials, just as it would be to any other major activity that could have environmental effects. Therefore, the presence of endangered species near roads where snow and ice control materials are applied would require that the applicators (i.e., states or local governments in most cases) specifically evaluate the potential threat to the species. The listing agency might require consultation on ESA issues, or an evaluation could be undertaken voluntarily (e.g., Lewis, 1999 (*52*)) as a means of ensuring that the activity would not be later found in conflict with the ESA or similar state legislation.

3.2.1.3 Clean Air Act

Protecting public health, the environment, and quality of life from the detrimental effects of air pollution has been a strong national priority since 1970, when Congress passed the Clean Air Act. Under this authority, the U.S. EPA has established air quality standards—known as National Ambient Air Quality Standards (NAAQS)—for six pollutants. Recently, the U.S. EPA completed its review of the current air quality standards for ground-level ozone (commonly known as smog) and particulate matter (or PM). Of particular interest to users of sanding materials or abrasives are the PM-10 regulations. Annual and 24-hour NAAQS for PM were first set in 1971. Total suspended particulate (TSP) was the first indicator used to represent suspended particles in the ambient air. Since July 1, 1987, however, the U.S. EPA has used the indicator PM-10, which includes only those particles with an aerodynamic diameter smaller than 10 micrometers. These smaller particles probably are responsible for most of the adverse health effects of PM because of the ability of the particles to reach the thoracic or lower regions of the respiratory tract.

3.2.1.4 Other Programs

The U.S. EPA has, to date, not developed methods to address toxicity to soils (*37*). The U.S. EPA is considering adding sodium to the Contaminant Candidate List (CCL); however, the primary stressor for this initiative is the protection of drinking water and aquatic environments (*38*).

3.2.2 Canadian Regulations

Environment Canada investigated Canadian programs, initiatives, and guidelines related to roadsalts (*39*) and found relatively few statutes or regulations directed at reducing the adverse environmental impacts of snow and ice control materials. Although most jurisdictions have general environmental protection legislation that prohibits contamination of air, land, and water, few of these address roadsalt specifically. Regulations for use and release of snow and ice control materials into terrestrial environments tend to be less of a concern from a regulatory standpoint when compared with effects on aquatic environments. Some jurisdictions have implemented specific groundwater protection strategies that could affect the location of salt storage facilities. Even fewer regulations are in place directly addressing effects on soils and terrestrial biota from snow and ice control materials.

Roadsalts were put on the Priority Substances List under the Canadian Environmental Protection Act (CEPA) in 1995 because of concerns about large quantities of chlorides affecting the environment. After a thorough scientific assessment (*3*), it was determined that roadsalts pose an environmental risk and that management plans should be developed to reduce the effects of roadsalts on the environment. Environment Canada's "Risk Management Strategies for Road Salts" (*40*) suggests that the environmental objective for protection of soil is to protect soil integrity. This ensures that application of roadsalts does not result in deleterious effects on physical and chemical parameters (e.g., soil structural stability, soil dispersion, soil permeability, soil swelling and crusting, soil electrical conductivity, and soil osmotic potential). It is further assumed that an environmental objective developed for vegetation will be protective enough for soils.

In Canada, most published guidelines for salt contamination in soil are based on measures of electrical conductivity and the sodium adsorption ratio (*41*). Notable exceptions include a recent guideline put forward by the Alberta Energy and Utilities Board limiting chloride concentrations in sand used for roadbed construction to 3,000 mg Cl/kg of sand. British Columbia has draft criteria for sodium and chloride in soil based on site-specific factors (i.e., hydraulic conductivity and species-specific impacts) and land use (i.e., agricultural, urban park, residential, commercial, and industrial). These were developed through analysis of toxicity data for soil invertebrates and plants.

The Canadian Council of Ministers of Environment (CCME) provides Environmental Quality Guidelines based on toxicological data for potential receptors (e.g., plants, invertebrates, wildlife and microorganisms) and land use categories (*37*). Soil criteria for sodium, magnesium, calcium, and chloride have not been developed (*42*).

3.2.3 Others

The Pacific Northwest Snowfighters (PNS) is a consortium of states and provinces (i.e., Idaho, Montana, Oregon, Washington, and British Columbia) that has developed a list of physical, environmental (primarily based on aquatic standards), and corrosion-related specifications for qualification of snow and ice control materials (*43*). Products found to meet minimum specifications are included on a qualified products list (QPL). Participating highway agencies, when issuing tenders, may request that vendors be included on the QPL before consideration. Many jurisdictions and agencies not directly involved in the PNS consortium have, to some degree, also adopted the PNS specifications for product selection.

3.3 Components of Concern

This report evaluates a range of snow and ice control products that can be classified by their primary components (see Table 3-1). In general, the primary components dictate the type and magnitude of effect that may result when introduced to the natural receiving environment. Secondary attributes are material properties typically associated with the product as an additive or contaminant and that influence the type and magnitude of effect (*44*). Table 3-1 lists the most commonly encountered secondary attributes associated with each material, but it is not an exhaustive list.

Table 3-1. Primary components and secondary attributes of selected snow and ice control materials.

Material Type	Snow and Ice Control Material	Primary Components	Secondary Attributes
Chloride-Based Salts	Sodium Chloride (NaCl)	Na, Cl	Heavy metals, CN, P
	Calcium Chloride ($CaCl_2$)	Ca, Cl	Heavy metals, P
	Magnesium Chloride ($MgCl_2$)	Mg, Cl	Heavy metals, P
Acetates	Calcium Magnesium Acetate (CMA)	Ca, Mg, $C_2H_3O_2$	BOD
	Potassium Acetate (KA)	K, $C_2H_3O_2$	BOD
Organic Products	Agricultural By-products (Organic Biomass)	Organic Matter (complex sugars)	BOD, Heavy metals, Phosphorus, Nitrogen
	Manufactured Organic Materials	Organic Matter – varies with product (i.e., glycol, methanol)	BOD
Nitrogen Products	Urea	Urea, Ammonia (i.e., Nitrogen)	Not Available
Abrasive	Abrasives	Air Quality - PM10, PM2.5 Water Quality - Sedimentation	Heavy metals, P

Chloride-based salts are the most common chemical products used for snow and ice control, followed by acetates (see Section 2.4.1). Many commercially available chloride-based products are blended with corrosion inhibitors. Most corrosion inhibitors are proprietary, although they typically consist of reduced sugar by-products or co-products from agriculture and food industries. Urea products and manufactured organic materials (e.g., glycols) are typically associated with airport deicing. These products are more costly than chloride products and are not commonly used for roadway application. Abrasives used for snow and ice control are typically derived from regional sources. Concerns include poorer air quality (PM-10, PM-2.5), stream sedimentation, and potential to contribute heavy metals.

Primary components and secondary attributes listed in Table 3-1 can be combined into common groupings. The six primary components of environmental concern are chloride (Cl), sodium (Na), calcium (Ca), magnesium (Mg), potassium (K), and acetate ($C_2H_3O_2$). Secondary attributes associated with these products include heavy metals, ferrocyanide yielding the cyanide anion (CN), phosphorus (P), nitrogen (N), and organic matter quantified as biochemical oxygen demand (BOD).

3.3.1 Ferrocyanides

If roadsalt becomes exposed to air with fluctuating humidity while in storage, it can cake, making it difficult to handle and apply to roadways. When atmospheric humidity is high (i.e., exceeding 70 percent) a brine solution forms on the surface of the salt crystals. When relative humidity drops, water evaporates, and the brine solution recrystallizes between the salt crystals, causing aggregation of the salt crystals. Ferrocyanide can be added to decrease the solubility of sodium chloride in the absorbed moisture, which reduces the amount of recrystallization. These compounds include

- Sodium ferrocyanide, $Na_4Fe(CN)_6 \cdot 10H_2O$, commonly known as yellow prussiate of soda;
- Sodium ferrocyanide, $Na_3Fe(CN)_6 \cdot H_2O$;
- Potassium ferrocyanide, $K_4Fe(CN)_6 \cdot 10H_2O$, commonly known as yellow prussiate of potash; and
- Ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$, commonly known as Prussian Blue.

Effective concentrations of these products are typically less than 0.01 percent by weight.

The fate of ferrocyanide ions in the environment is unclear. Negatively charged ions tend to be rejected by soils and move readily with percolation and groundwater; however, a study conducted by Olson and Ohno (*98*) speculated that, because the relative proportion of cyanide with respect to salt was low, the ferrocyanide may be adsorbed onto soil particles. Ferrocyanide ions can decompose to cyanide ions when exposed to ultraviolet light in a process termed "photodecomposition." The degree to which this occurs is unclear, as is the extent of volatilization of HCN ions after photodecomposition. It is unlikely that photodecomposition will occur once ferrocyanide ions are in soils or groundwater. Laboratory experiments have shown that decomposition of ferrocyanide complexes in soils (in the dark) is slow. The half life for ferrocyanide in soil ranged from 1 year at a low pH of soil water to 1,000 years at levels greater than pH 7 (*20*).

3.3.2 Radioactivity

Radioactivity is expressed as a concern with some brines obtained through groundwater wells—specifically for those associated with oil and gas drilling operations. The U.S. EPA estimates that 30 percent of oil and gas operations in the United States have naturally occurring radioactive matter (NORM) in brine and brine solids to be of sufficient concern (*45*). Radiation levels for petroleum (i.e., oil and gas) produced water range between 0.1 and 9,000 pCi/g (*46*). Regions of concern include, but are not limited to, the U.S. Gulf States, the U.S. Midwest (e.g., Illinois, Michigan, Kansas, and Oklahoma) and the Appalachian states. In most cases, NORM-containing brines produced through oil and gas drilling operation are re-introduced into the subsurface. In some cases, however, these materials are reused for snow and ice control.

A New York State study (*47*) found NORM in wastes produced from oil and gas drilling operations. Of these wastes, the highest concentrations of radium were found in brines, which are traditionally "disposed of" for reuse as roadway snow and ice control materials. The study concluded, however, that, even if it is assumed that all brines contain the highest detected level of radioactivity, the resulting dose would be less than 30 percent of the 10 millirem per year standard presented in the New York State Department of Environmental Concern (NYSDEC) Technical Administrative Guidance Memorandum (TAGM) 4003. Brines can have significant levels of radioactivity and their reuse on roadways could be hazardous to human health and the environment. Limited information is available detailing more specific regions of concern for NORM materials or what percentages of produced brines used for snow and ice control contain NORM. Individual states have jurisdiction over the production and subsequent use of NORM materials.

3.4 Aquatic Environments

3.4.1 Protection of Aquatic Resources

In Canada and in Europe, the general pattern for protecting aquatic resources is legislation and regulation directed at specific activities or specific classes of pollutants. A good example under the CEPA of 1999 is the development of management plans that deal specifically with roadsalts (*3*). In the United States, the approach has been somewhat different in that aquatic resources are protected by broad federal legislation, which is then applied incrementally to specific activities until the overall goals are achieved. Both systems are effective if rigorously implemented.

The most relevant federal legislation in the United States for the protection of aquatic resources is the Federal Water Pollution Control Act (1948) and its amendments. The act originally was focused primarily on public health through protection of domestic water supplies, but was drastically broadened in 1972 and again in 1977, at which time the Act and its amendments became known as the Clean Water Act (*48*). An amendment of the Clean Water Act in 1987 added permitting requirements for certain stormwater drainages. The goal of the Clean Water Act, as given in 33 USC Section 101, is to "maintain and restore the chemical, physical, and biological integrity of the nation's waters" and, ultimately, to eliminate pollution from the waters of the United States. Progress toward the achievement of this goal will be incremental.

The U.S. Clean Water Act places a set of requirements on states for protection of water quality, aquatic life, and aquatic environments, as summarized below (see http://www.epa.gov/region5/water/cwa.htm). To a large extent, implementation and enforcement of the regulations occur at the state level. State laws and state regulatory bodies typically implement the requirements of the Clean Water Act, but there is some flexibility, allowed through oversight procedures exercised by the U.S. EPA, for differences in the application of Clean Water Act requirements from one state to another, according to regional circumstances. In some states, the U.S. EPA maintains direct application of the Clean Water Act, either because the state has opted not to seek authorization to implement the act or because the U.S. EPA considers state efforts to do so inadequate.

States are required to divide their waters into segments (e.g., portions of drainage basins or clusters of water bodies that have similar characteristics) and to classify the waters thus subdivided according to use. Uses vary from state to state and may be elaborately subdivided in some cases. Uses recognized by most states include domestic water supply, agricultural water supply, support of aquatic life, and recreation.

The Clean Water Act requires that each state have basic standards for the protection of all uses in all waters of the state. These standards, which are reviewable by the U.S. EPA and must be reviewed periodically by the state itself along with the classification system, set technically based thresholds for impairment of use. For example, a coldwater fish fauna that is part of the aquatic life classification for a particular stream segment may invoke strict standards for heavy metals, which are harmful in very small amounts to coldwater fishes. Thus, the classification system leads to a matrix of requirements, most of which are of a chemical nature, for support of the use, which in turn sets the stage for regulation of sources of impairment. The Clean Water Act regulates "point sources" of pollution—those that originate from a specific discharge point (i.e., typically a pipe and typically excluding such unengineered sources as snow piles). Point sources of discharge are required to hold a valid NPDES permit (see preceding section), which prescribes the maximum amounts of regulated substances in or attributes of a discharge. These limits are established by application of the standards (i.e., by calculating the amount of a particular substance that could be assimilated into a receiving water without causing a violation of the standard). States or local governments can enhance federal regulations in some cases. The same is true in Canada for provinces. For example, the province of Quebec has detailed regulations dealing explicitly with snow dumps and snow removal.

The U.S. Clean Water Act also allows for some segments not to be classified according to use. In such cases, the states must follow antidegradation regulations in issuing permits for discharge. Antidegradation limits, which substitute for standards derived from specific uses, vary by state, but may require that the amount of any regulated substance cannot be changed by more than a specific percent (e.g., for Colorado, it is 15 percent of the available assimilative capacity available at the time the regulation was adopted) from the ambient value. Some categories of nonpoint source pollution are not yet regulated through the Clean Water Act. Agriculture, for example, is an acknowledged diffuse source of pollution, but it is not explicitly regulated by the Clean Water Act, although the federal government has begun to invest money in incentives to reduce agriculturally derived nonpoint source pollution.

Use of road application materials for snow and ice control is not explicitly regulated by the U.S. Clean Water Act, but could be regulated indirectly in urban areas through stormwater permitting. Even so, individual states could use the Clean Water Act as a template for state legislation that would control application of materials to roads. Even in the absence of regulations, the framework of the Clean Water Act is useful as a basis for assessing the potential for impairment and the thresholds for impairment at specific locations. For example, application of snow and ice control materials by a state agency could be assessed on the basis of the rate of application, the rate of transport from the roadway to waters of the state, and the resulting concentrations of regulated substances in relation to the established standards for those substances as used by the state in its point source regulations. This approach has been taken by the state of Colorado and other states and is used here as the main basis for evaluating the effects of road application materials to aquatic resources (see Figure 3-2).

3.4.2 Potential Types of Impairment of Aquatic Resources by Snow and Ice Control Materials

From the view of potential impairment of aquatic resources, it is useful to think of snow and ice control materials as consisting of three groups of constituents (see Table 3-2). The major constituents, aside from water in the case of solutions, are those that account for the bulk of the dissolved or solid materials. Examples in the case of chemical solutions could include magnesium, calcium, sodium, chloride, and dissolved organic matter, as well as other less common possibilities.

A second category of constituents can be designated as additives (reviewed by Cappelow et al. 1993 (*49*)). These substances, which often are proprietary and thus not described specifically by vendors except under unusual circumstances, typically are intended to reduce corrosion or, in the case of solids, caking of the main ingredients. They are additives in that they are introduced intentionally at concentrations of 1 percent to a few percent of the major ingredients. Examples vary widely, but anti-corrosion agents can include heavy metals such as zinc, inorganic ions such as phosphate, and organic substances such as citrate; anti-caking agents include salt (NaCl) to prevent caking of sand and ferrocyanide to prevent caking of bulk sodium chloride.

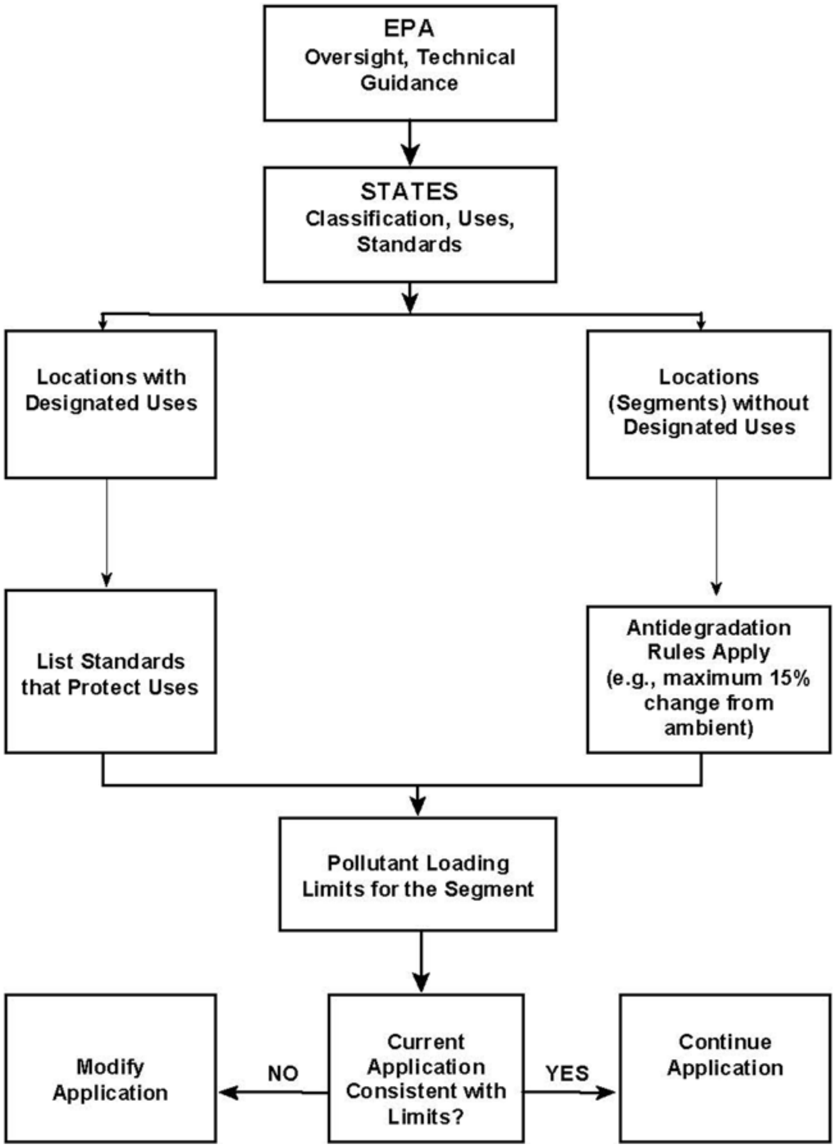


Figure 3-2. Flowchart showing concepts derived from the U.S. clean water act for evaluation of snow and ice control materials.

Table 3-2. Three groups of constituents for consideration in assessing impairment of aquatic resources.

Constituent Group	Examples
Major Constituents	Sand, chloride, acetate, magnesium, organic matter
Additives	Phosphate corrosion inhibitor, ferrocyanide
Contaminants	Heavy metals, phosphorus, nitrogen

A third category of constituents can be called contaminants. Substances belonging to this category are not introduced intentionally; they are a by-product of the source material and its processing. For example, heavy metals are found in natural sources of salts used in many control materials. Similarly, sand and other abrasives carry soluble or fine particulate components that will appear on the roadway when these materials are applied.

The major ingredients of snow and ice control chemicals typically are chosen in such a way as to ensure that they are benign in small to moderate amounts. For example, sand as an abrasive or calcium and magnesium as components of chemical mixtures would not commonly be suspected of causing environmental damage through toxicity or other direct mechanisms. When characteristically benign substances are used in very large amounts, however, potential environmental damage should be considered. Additives, although used in relatively small amounts compared with the main ingredients of deicers, can be harmful in smaller amounts. This is the case for heavy metals, which are toxic to aquatic life above specific thresholds that often are quite low, and phosphate, which is a potential source of nutrient enrichment that can cause eutrophication (see below). Contaminants present perhaps the greatest problem for evaluation because they often are not quantified fully by vendors and encompass a wide range of compounds, some of which (e.g., mercury and cadmium) can be a matter for concern at very low concentrations.

The following text discusses potential environmental impairment associated with each of the three main groups of constituents shown in Table 3-2. Toxicity is perhaps the first type of impairment to come to mind and needs to be considered for all constituents. Furthermore, judgments on toxicity need to reflect the current sophistication of knowledge about toxicity in relation to concentration. It is not appropriate to designate specific substances as toxic and others as nontoxic, given that toxicity is a matter of concentration. For example, the metal zinc is an essential nutrient for aquatic plants and animals, but is also toxic to aquatic life at relatively low concentrations (*50*). Thus, it does not make sense to classify zinc as a toxic substance, but rather to think in terms of the amounts and forms of zinc that can be present in a given environment without impairment of aquatic life or other uses of water. The maximum amounts of any substance that can be present without environmental impairment for a specific situation are best determined by an approach similar to that outlined in Figure 3-2.

Toxicity is not the only mechanism of environmental impairment. Impairment can be physical, as in the case of excessive sand added to flowing waters, or it can be biogeochemical, as in the case of eutrophication through addition of nutrients or through stimulation of microbial respiration by the addition of organic matter. Impairment may even consist of complex multistep processes such as those resulting from the displacement of one ionic substance by another within a soil, thus causing a change in the chemistry of surface waters. Some mechanisms of impairment are well documented; others are not.

Along with mechanisms, gradients of concentration must be considered as an aspect of environmental impairment. For example, a heavy metal included as an additive or contaminant in a deicing compound could reach toxicity thresholds in undiluted deicer but still not cause receiving waters in the environment to rise above the toxicity threshold because of dilution processes occurring on or near the roadway. Dilution is further discussed in Section 3.4.3.1.

3.4.2.1 Major Constituents

Major constituents that are most common in snow and ice control materials include particulate abrasives, alkali or alkali-earth cations (i.e., calcium, magnesium, sodium, potassium), the anion chloride, and organic substances that may either be synthesized (e.g., acetate) or derived from biomass (e.g., corn by-products).

Particulate Abrasives. Particulate abrasives include sand, crushed rock, cinder, and potentially any other particulate substance available in quantity at a specific location. Such materials present two general types of potential impairment: chemical and physical. Evaluations of potential for chemical impairment could involve toxicity tests (see Section 3.4.3.2) and tests for chemical composition (see Table 3-3). The first priority among these is toxicity testing. A general toxicity test should involve not only the raw application materials with appropriate amounts of dilution, but also pulverized material to represent the actual condition of the abrasive on the roadway under traffic. Any indication of general toxicity would lead to more specific testing to determine specific constituents responsible for the general toxicity. Consideration of organic and nutrient content is separate from consideration

Table 3-3. Chemical composition of three sources of sand (with salt added) used by CDOT during winter, 1997–1998.

	µg/g Dry Mass Salt with Sand		
	Source 1	Source 2	Source 3
Major Ions			
Ca	197	146	101
Mg	138	<5	<5
Na	52,000	18,000	9,000
Cl	79,000	27,000	14,000
Nutrients			
P Soluble Reactive	0.27	1.01	0.34
P Total Soluble	0.31	1.20	0.38
P Particulate	1.60	2.03	2.09
P Total	1.91	3.23	2.47
Other Inorganics			
Cu soluble	0.15	0.15	0.25
total	0.30	2.5	4.3
As soluble	<0.5	<0.5	<0.5
total	<0.5	<0.5	<0.5
Cd soluble	<0.00	<0.00	0.01
total	0.06	0.06	<0.02
Cr soluble	<1	<1	<1
total	<1	<1	<1
Hg soluble	<0.01	<0.01	<0.01
total	<0.01	<0.01	<0.01
Ni soluble	<1	<1	<1
total	1	<1	<1
Pb soluble	<0.5	<0.5	<0.5
total	0.6	<1.7	<4.2
Se soluble	0.15	<0.1	0.1
total	<0.1	<0.1	<0.1
Zn soluble	<1	<1	<1
total	1.0	5.5	8.6

Source: (*52*)

Large variation in Na and Cl corresponds to varied additions of NaCl, which prevents caking

of toxicity. Organic content for abrasives typically would be low and thus usually not important. Nutrient content is easily determined and, although unlikely to raise impairment issues in most cases, deserves consideration.

Physical impairment caused by abrasives can be attributed either to particulate bed load or to suspended solids. Most particles that fall within the size category of sand (0.0625 to 2.0000 mm) typically move through a stream as bed load, except under the highest flow conditions. Bed load consisting of sand can block interstitial spaces between particles of larger size, such as gravel or cobbles. Under these conditions, substantial impairment of invertebrate and fish communities may occur because the interstitial spaces are important either as habitat or, in the case of fish, for spawning (*51*). Interception of sand before it enters the stream is possible through retention of storm flow because particles of this size settle relatively rapidly, but interception of sand typically is expensive and requires maintenance involving the removal of accumulated particles from retention basins.

Abrasives typically contain fines (here used to mean particles smaller than sand), but also show an increase in percentage of fines through reduction in average particle size on the roadway under traffic. Fines typically reach surface waters in suspended form and remain in suspension until they reach an area with low water velocity, particularly lakes and wetlands, where they are removed by gravity. Fines may contribute to blockage of interstitial spaces in stream beds, particularly if the spaces are already partially blocked by sand (*51*).

Suspended solids (often measured as turbidity) are regulated for the protection of aquatic life and sometimes also for aesthetic reasons (*Federal Register*, 10 December 1998, Vol. 63, Number 237). Thus, it is possible to use dilution testing in combination with site-specific water-quality standards for suspended solids in evaluating the suitability of a particular abrasive.

Chloride. Chloride is the third most common anion in inland waters (*53*). Its natural concentrations range from approximately 1 mg/L at large distances from marine sources in areas that lack sedimentary rocks up to concentrations that equal or exceed those of seawater under arid conditions where concentration by evaporation occurs. Most commonly, background chloride concentrations fall within the range of 1 to 10 mg/L (*54*). Because chloride is consistently present in inland waters, the tolerance of aquatic life for chloride, which is a component of protoplasmic fluids, is quite high (*31, 49*).

The freshwater aquatic life criteria for chloride as determined by the U.S. EPA (*Federal Register*, 10 December 1998, Vol. 63, Number 237) are 860 mg/L for acute exposure (one hour) and 230 mg/L for chronic exposure (96 hours or more); standard application of the criteria allows one exceedance every 3 years. Chloride is highly mobile in soils (*55*). Thus, a large portion of the chloride leaving a road (40 to 70 percent) can be expected to be flushed from the adjacent watershed in the same year (*19, 52*).

The U.S. EPA's aquatic life criteria or associated state standards can be used in evaluating whether or not a snow and ice control product leaving the roadway under the influence of precipitation will impair aquatic life and, if so, the distance beyond the roadway that would be encompassed by any zone of exceedance. Because some freshwater organisms (e.g., adult rainbow trout) are much more tolerant than others of chloride, concentrations of chloride exceeding the criteria are more likely to change the composition of aquatic communities than to impair all species (*19, 56*); even so, such changes could be of major ecological concern. At even higher concentrations, chloride could be harmful to the potability of water, as can be the case of drinking water wells near a road where chloride is added (*21*).

Where chloride is applied as a main ingredient of snow and ice control materials, substantial augmentation of chloride concentrations in receiving waters is likely. Figure 3-3 shows an example for two Colorado streams. Background concentrations of chloride in these streams are very low (ca. 1 mg/L), and the addition of snow and ice control materials raises the concentrations by a factor of as much as 100. Peak concentrations occur during the application season, when the supply of chloride is high and the amount of dilution (stream flow) is low. Concentrations are suppressed by spring runoff. Even during the summer after runoff, chloride concentrations are notably above background. Despite the large change in chloride concentrations in a relative sense, however, chloride concentrations in this case did not exceed the aquatic life chronic standard, even though the stream is relatively small and the rate of application for the road, which is at the Continental Divide, was very high.

Numerous cases have been recorded in which surface waters receiving road runoff have concentrations of chloride far exceeding the aquatic life standards (summarized by Environment Canada (*3, 99*)). These examples involve situations for which relative dilution is especially low. As explained in Section 3.4.3.1, relative dilution is under the combined influence of rate of application, road surface per unit of drainage area, climate, and related factors.

Pollutants that accumulate in terrestrial or aquatic environments can be especially troublesome if pollution continues over long intervals. Among dissolved solids found readily in surface waters, chloride is among the least likely to accumulate. As stated by Drever, chloride is not removed or supplied significantly by interaction with rocks and is not precipitated as a salt until very high salinities are reached. Thus, the annual addition of chloride will raise the mean and maximum concentrations of chloride in the waters of a particular watershed by adding a concentrated source, but will not lead to significant accumulation of chloride in soils or waters on an annual basis, except where there is not enough water to produce runoff, or where the deep waters of lakes or ponds become stabilized and insulated by excess density derived from salt (see below). Seasonal variations in chloride may occur, of course, in response to seasonality of application of chloride or the immobilization of runoff by very cold weather.

Chloride may liberate mercury bound to wet sediments (*57*). This phenomenon has been little studied, however, and

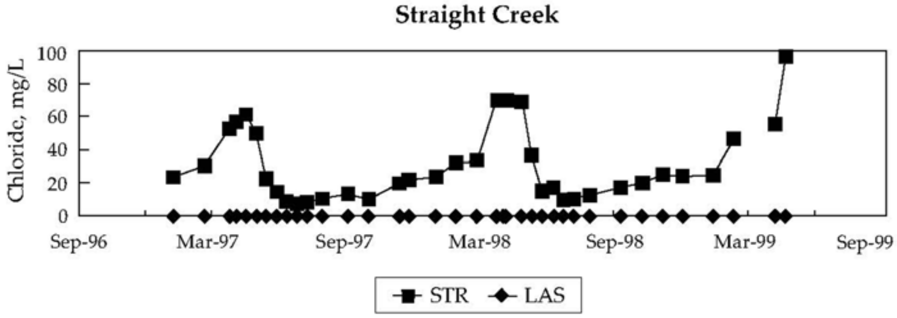


Figure 3-3. Comparison of chloride concentrations (mg/L) in (1) Straight Creek, Colorado, which receives runoff from I-70 affected by sand and salt and magnesium chloride solutions, and (2) Laskey Gulch, a tributary of Straight Creek that does not receive road drainage (Source: (52)).

unusual mercury concentrations in water have not yet been reported for streams receiving road drainage containing chloride.

Alkali and Alkaline-Earth Cations. The cation forms of calcium, magnesium, sodium, and potassium are common ingredients, either singly or in mixtures, of liquid snow and ice control solutions. These are also the four major cations by concentration in unpolluted inland waters (*53*). Consequently, tolerances of aquatic life and of human beings for these ions are quite high, and, because all four of the ions are constituents of protoplasm (e.g., Cowan (*58*)), they can be listed as essential nutrients for all animals and plants.

Calcium and magnesium are held moderately well by soils, where they may be bound firmly to phosphate or carbonate or to organic complexes or minerals (*59*). Soils also release calcium and magnesium to some degree. This release sustains concentrations of calcium and magnesium in inland waters that range from a few mg/L in waters derived from granitic lithology to much higher concentrations where rocks are sedimentary or where concentration occurs by evaporation (*55*). Calcium and magnesium are among the first ions to precipitate from water as salts are concentrated (*60*) and thus tend to be depleted in highly saline waters.

There are no aquatic life standards or other general use protective upper limits for calcium and magnesium in water, except as related to hardness associated with very high concentrations of Ca and Mg in relation to domestic water supply for maintenance of cleaning performance. Thus, it is unlikely that addition of calcium or magnesium to water would be seen as an environmental threat or a threat to the domestic use of water. As in the case of chloride, addition of calcium and magnesium to soils could change either the physical features of the soil or cause ion exchange reactions to occur that would result in the liberation of other substances that would not otherwise be released (*59*). However, no published literature indicates that the calcium and magnesium derived from snow and ice control materials would be sufficient to induce large changes involving these mechanisms.

Sodium and potassium are weakly held by soils under most circumstances (*59*). They are present in inland waters at concentrations that range from about 1 mg/L up to very high concentrations in saline waters (*55*). Sodium and potassium are less likely to precipitate chemically than calcium and magnesium and so may be concentrated by evaporation to a high degree.

There are no general aquatic life standards for sodium or potassium. Because high daily intake of sodium is contraindicated for individuals who have high blood pressure, there are reasons to consider potential for contamination of groundwaters with sodium at thresholds that might meaningfully affect daily intake of sodium by humans (*61*). To be regulated through the U.S. Safe Drinking Water Act, a substance must be known to have adverse effects on human health, be likely to occur in public water systems at levels of public health concern, and be reducible by regulation by an amount corresponding to a meaningful reduction in health risk for persons served by public water systems. The U.S. Safe Drinking Water Act amendments of 1996 required the U.S. EPA to publish a list of unregulated contaminants designated “Contaminant Candidate List,” or CCL. The contaminants on this list are different from contaminants included in actual or proposed national primary drinking water regulations. Thus, the list is essentially a means of keeping track of contaminants not regulated but could be regulated in the future. The 1998 CCL, which followed from the 1996 regulation, listed sodium among 50 chemical constituents.

No health advisory has ever been issued by the U.S. EPA for sodium. A drinking water guidance is 20 mg/L, which is nonenforceable and based on a recommendation of the American Heart Association; the U.S. EPA believes that the guidance is excessively restrictive, but has not made official changes in it as yet. The U.S. EPA also has used the National Research Council’s dietary guidance of 120 mg/L, which corresponds to 10 percent of average total sodium intake at a drinking water intake of 2 liters per day, for evaluating sodium concentrations in drinking water. In a national survey of 59,000 groundwater-based systems, approximately 13 percent showed concentrations in excess of 120 grams per milliliter. Causes for exceedances were not diagnosed for this study, however.

In its most recent drinking water advisory, the U.S. EPA notes that about 3 percent of the U.S. population is on sodium-restrictive diets, which range in stringency between 250 and 2000 mgd. Drinking water concentrations of sodium would be mandatory for inclusion in calculations of the daily sodium intake in these cases. Typical dietary intake of sodium in the United States is 4000–6000 mgd. At concentrations of about 500 mg/L, the palatability of water is notably reduced, which would likely cause a search for an alternate drinking water supply. Thus, except for highly restrictive diets, drinking water intake is likely to be a minor proportion of the total. The U.S. EPA concludes that regulation may not present a meaningful opportunity for reduction of health risk, but continues to believe that the drinking water advisory is useful where water is contaminated with sodium for roadsalts; specific sodium contamination of surface water supplies that would impair raw water for treatment and distribution is much less likely than contamination of individual wells near roadways. If contamination of a central supply did occur, evidence of it would be known from mandatory testing of centralized water supplies as conducted in the United States. Exceedance of guidelines is most likely for individual shallow wells very near roadways where sodium-containing deicers are used in quantity. In such instances, it is advisable that well water be tested annually during winter or spring for sodium contamination.

The effect of applying any of the four major cations as a major ingredient of snow and ice control materials is to increase the supply of these substances to receiving waters. Where the background concentrations of the major cations are low to moderate, the result typically will be a notable increase in concentration. For example, Lewis (*52*) documented changes in annual maximum magnesium concentration ranging from 50 percent to almost tenfold in Colorado streams receiving magnesium as a component of a magnesium chloride solution and increases in sodium concentrations by a factor of as much as 25 when sand containing salt was applied to roads in the same watersheds. Although these changes in concentration represent a substantial chemical perturbation of the receiving waters, there is no evidence at present that they cause any biotic responses, given the benign nature of the four major cations within the lower ranges of concentration.

Saline Mixtures. Liquid snow and ice control mixtures typically are saline; their ionic content usually includes one or more of the four major cations mentioned above as well as chloride or a small organic anion. Total salinity of water is subject to regulation for human potability (500 mg/L, secondary drinking water standard). Salinity may affect the welfare of aquatic life, and in part is controlled for this purpose by chloride standards (see the discussion of chloride above).

An indirect effect of salinity that occurs through its influence on water density has been documented and should be considered a potential type of environmental impairment associated with runoff containing salinities well above those of the ambient waters. At a given temperature, saline waters are denser than waters containing only small amounts of salts (*53*). Waters containing moderate to high amounts of salt, therefore, may form a distinct bottom layer in a small water body such as a pond or wetland pool or in some cases even a lake (*63–65*). The formation of such layers is likely only where current velocities are low (i.e., it is unlikely in streams or other waters flowing at velocities exceeding a few centimeters per second). If such a layer does form, however, it can be residual in that mixing caused by wind may be insufficient to disrupt the layering. If so, the bottom layer, being deprived of contact with the surface, could become anoxic (without oxygen). The development of anoxic conditions over sediment not normally anoxic can be harmful to aquatic life, at least on a temporary basis until the layering breaks down. Under extreme conditions (long winters with high use of sodium chloride), the isolation of the saline bottom layer may be essentially permanent, and the accompanying bottom conditions would not support aquatic life except for microbes. A lake's permanent failure to mix fully is designated meromixis (*53*), which can be maintained by recurrent runoff of saline water. Although there is no easy modeling or other well-established approach to predict the development of salinity-induced layering caused by snow and ice control materials, the condition is relatively easily diagnosed in the field with commonly available instruments (e.g., dissolved oxygen meter, conductance meter).

Organic Matter. Organic matter may be synthesized industrially as small molecules to make up a bulk anionic component of a chemical snow and ice control material (e.g., acetate for CMA). Alternatively, unrefined organic matter from agriculturally derived biomass (particularly corn) may be used as a nonionic additive to a saline mixture such as a magnesium chloride solution. In either case, the primary type of impairment to be explored is an increase in biochemical oxygen demand (BOD) in the receiving waters, which could produce hypoxic (low oxygen) or anoxic conditions in these waters. Biochemical oxygen demand is caused by the use of organic substrates by microbes, which oxidize the organic matter using oxygen obtained from the water, thus creating a strong oxygen demand. If the microbial demand is not offset by reaeration processes or by photosynthesis, hypoxia or complete loss of oxygen can be the result. These kinds of adverse effects involving BOD are most likely in waters that move slowly because such waters have minimal physical exchange of oxygen with the atmosphere (i.e., low reaeration rates). Temperature also affects the rate of oxygen consumption, but relative influence of water management is likely to be predominant, given that temperature varies little for liquid water during winter. Environments most likely to be affected would include pools, wetlands, and small lakes.

The amount of organic matter in a liquid mixture can be determined by carbon analysis (typically through combustion followed by infrared spectrophotometry: APHA 1998 Method 5310 B (*67*)). The potential oxygen demand of a specific amount of carbon can be obtained from the stoichiometry of respiration (slightly over one mole of O_2 per mole of C). Thus, the total oxygen demand can be calculated for a given mass or volume of material applied to a roadway. Organic matter also can be measured indirectly with a standard BOD test (*67*). The difficulty in using information from either test is that adverse effects of organic matter on oxygen are determined in large part by the speed with which the organic material is decomposed by microbes in the natural environment and the likelihood that standing waters or slowly flowing waters will intercept the organic matter as it passes through the drainage network. This issue is discussed further in Section 3.4.3.3.

Natural concentrations of total organic carbon in surface water range generally between 2 and 15 mg/L, although occasionally they may be higher (*66*). The corresponding BOD would be approximately 3 to 20 mg/L (*67*). Snow and ice control materials not containing organic matter as a major ingredient may have organic carbon content as high as a few thousand mg/L (e.g., Lewis 2000 for magnesium chloride (*68*)), which corresponds to BODs that could be as high as 5000 to 10,000 mg/L. In the context of expected dilution on or near the roadway, however, the total augmentation of oxygen demand from this source would be noticeable only over a very small area or perhaps not noticeable at all, depending on the speed of water movement.

The presence of organic matter as a major ingredient is associated with total organic carbon concentrations within the range of 20,000 to 70,000 mg/L (e.g., Lewis 2000 (*68*)), which corresponds to BOD exceeding 100,000 mg/L (see also data tabulated by Fischel 2001 (*69*)). In this case, organic matter subsequent to dilution on or near the roadway could exceed the amount of organic matter in water by a factor of 10 or more and thus could affect a substantial volume of receiving water, especially if the water happened to be standing or moving slowly. Thus, inclusion of organic matter as a major ingredient in deicers raises the issue of oxygen depletion as a potential impairment. Even though this potential obviously exists, it is not always manifest. For example, if runoff immediately joins a large, rapidly flowing water body that offers a very high amount of dilution, the effects of even these amounts of organic matter may not be detectable.

3.4.2.2 Additives

Although additives may include any substances that vendors find capable of enhancing performance, the most likely prospects are selected heavy metals, inorganic anions, and small organic molecules.

Heavy Metals. Heavy metals may be used with liquid snow and ice control formulations as a means of reducing corrosion. Zinc is an example of a metal used in this way (Table 3-4). Potential risks associated with zinc or other heavy metals are discussed below in connection with contaminants. Use of heavy metals at unacceptable concentrations in the context of designated uses, especially aquatic life uses, which are particularly restrictive for heavy metals, can be achieved by determining thresholds for heavy metals through dilution calculations in conjunction with numeric standards for specific metals on specific stream segments (Figure 3-2).

Table 3-4. Comparison of two brands of $MgCl_2$ deicer, one of which probably contains zinc and phosphate as additives.

Constituent	$MgCl_2$ Type 1	$MgCl_2$ Type 2	Environmental Standard
Zn, mg/L	1	39	0.07
Total P, mg/L	12	82	0.015*

Source: (*52*)
*no state standard; typical stream concentration is shown

Other Inorganic Substances. Phosphorus, in the form of phosphate, may be used as an additive for corrosion control. Snow and ice control materials and additives derived from agricultural matter are also associated with high phosphorus concentrations. A complete discussion of environmental problems associated with phosphorus is given below in connection with contaminants. Phosphorus is present in only small amounts in unpolluted waters (typically 10 to 100 μg/L). Therefore, an additive that contains phosphate, even if constituting less than 1 percent of total ingredient mass (e.g., Table 3-3), can increase phosphorus concentrations in the receiving waters to an amount that might be undesirable from the viewpoint of eutrophication. As in the case of heavy metals, the best approach is to use stream standards or other guidelines (e.g., antidegradation principles) to set a cap on the amount of phosphorus that can be added and advising vendors of this maximum amount.

Ferrocyanide salts (e.g., Na_4FeCN_6) are added as anticaking agents to bulk salts (primarily NaCl) in solid form. The free cyanide ion (mostly joined to hydrogen as HCN) is highly toxic, but it has a high affinity for metals and, therefore, often is present in bound form, in which case it is much less toxic (*50*). Ferrocyanide itself has relatively low toxicity, but in the presence of solar irradiance or low pH, it may dissociate and thus liberate the cyanide ion (*3*). Therefore, ferrocyanide is an additive of concern and is listed by the U.S. EPA as a toxicity concern. There is insufficient evidence to date as to whether liberation of free cyanide from ferrocyanide in connection with roadsalts is a serious problem (*3*, *20*, *70*).

Organic Matter. Small organic molecules such as citrate or triethanolamine (TEA) may be used to inhibit corrosion. When added at 1 percent to a few percent, small organic substances such as this, although easily biodegraded and thus potentially a source of BOD in surface waters (*35*), may be acceptable because dilution reduces their concentrations rapidly to such a degree that negative effects on oxygen concentrations are unlikely to cause impairment. Impairment is least likely where receiving waters have high energy and where the added organic matter, after dilution on or near the roadway, is near the natural inventory of organic matter in the water (usually 2 to 15 mg/L (*53*)), and most problematic where runoff enters small bodies of still water and where the added concentrations greatly exceed the natural inventory of dissolved organic matter.

3.4.2.3 Contaminants

Contaminants can be divided for convenience into key nutrients, inorganic substances other than key nutrients, and organic substances. Although any of the 20 or more elements required by organisms for the synthesis of biomass can be classified as nutrients, the nutrients of greatest importance in aquatic systems are nitrogen and phosphorus. These nutrients often are called "key nutrients" or "limiting nutrients" because they are in lowest supply relative to biotic demand (*71*). Addition of key nutrients to surface waters often causes a biotic response in the form of increased plant growth. Where this increased plant growth markedly increases the amount of plant biomass, the result is generally considered undesirable and is termed "eutrophication."

Phosphorus. Phosphorus (P) is often considered the element most likely to limit plant growth in inland waters. Phosphorus has a strong multiplier effect on plant biomass because it constitutes only about 1 percent of the dry mass of plant matter (*72*). Therefore, a plant community (consisting of rooted aquatic plants or of algae) that has exhausted its phosphorus supplies, which is often the case under natural circumstances, will respond to the addition of a pound of phosphorus by the creation of about 100 pounds of new dry biomass, or approximately 500 pounds of wet biomass. Because of this multiplier effect, relatively small amounts of phosphorus can change aquatic ecosystems drastically. Undesirable side effects include excessive organic matter leading to deoxygenation of poorly circulated waters, aesthetic nuisance, harmful algal blooms, and change in the community composition of organisms, including fishes (*73*).

It is traditional for environmental purposes to divide total phosphorus in surface waters into three categories: dissolved inorganic, dissolved organic, and particulate (*67*). The sum of these categories is total phosphorus. Dissolved inorganic phosphorus is present in water primarily in the form of ionized phosphoric acid (*60*). It is often referred to as "soluble reactive phosphorus" (SRP) because the test by which it is determined leads to the detection not only of dissolved inorganic phosphorus, but also an indeterminate fraction of small phosphorus-bearing organic molecules (*74*).

Dissolved organic phosphorus (DOP) typically is determined through digestion of a filtered sample. The digestion procedure reduces all organic dissolved phosphorus to inorganic form. Subsequent application of the SRP test gives the combination of the original SRP plus the dissolved organic phosphorus that was unreactive prior to digestion, thus producing an estimate of total dissolved phosphorus (TDP). Subtraction of SRP from total dissolved phosphorus produces an estimate of DOP. Both SRP and DOP often are quite scarce in unpolluted natural waters (e.g., < 10 µg/L for each of these fractions (*72*)). Constant uptake of phosphorus in these forms, which are available for uptake by plants, suppresses the ambient concentrations, even though soluble phosphorus is also being generated by the decomposition process.

Particulate phosphorus may be structurally bound to organic material or it may be bound (mostly externally) to particles; clays are particularly good carriers of phosphorus in adsorbed form (*59*). Total phosphorus typically is analyzed by a digestion procedure that liberates the phosphorus as soluble reactive P, followed by application of the SRP test (*67*).

The dissolved fractions of phosphorus are more readily available for uptake by plants than the particulate fractions. Vendors whose products contain a substantial amount of phosphorus may explain that a substantial portion of the phosphorus is in the particulate fraction or a stable component to the organic fraction and therefore should not be counted as a potential agent of impairment for the environment. This is incorrect in that these forms of phosphorus often can be mobilized through biogeochemical processes (*53*). It is customary in estimating the critical phosphorus loading of lakes, for example, to make evaluations of impairment based on total phosphorus load (*75*). Therefore, the environmental characteristics of snow and ice control materials should be evaluated primarily in terms of total phosphorus, rather than specific phosphorus fractions.

Phosphorus can be expected as a contaminant in all materials derived from natural sources, including salt deposits and biomass. Abrasive mixtures (e.g., sand) and salt deposits used in preparing liquid snow and ice control mixtures typically contain relatively small amounts of P contamination (Table 3-5), although each new material for proposed use should be evaluated for phosphorus content. In contrast, when biomass is a bulk component (main ingredient) of control materials, the materials often show very high phosphorus content (Table 3-5).

The vulnerability of natural aquatic environments to perturbation by phosphorus loading varies according to the natural phosphorus supply to the environment. Waters that receive small amounts of phosphorus from natural sources are termed "oligotrophic" and can be sensitive to small additions of phosphorus (*72*). Water bodies that lie within watersheds with naturally rich phosphorus supplies can tolerate more anthropogenic phosphorus without showing significant change. Therefore, the thresholds for phosphorus

Table 3-5. Concentrations of nutrients in three classes of snow and ice control materials.

	Sand with Salt, µg/g		$MgCl_2$, mg/L		$MgCl_2$ + Organic, mg/L	
	Brand 1	Brand 2	Brand 1	Brand 2	Brand 1	Brand 2
Soluble Reactive P	0.27	1.01	0.4	4.3	28	40
Total Dissolved P	0.31	1.2	0.7	11.7	67	116
Particulate P	1.6	2.0	0.3	2.7	3	18
Total P	1.9	3.2	1.0	14.4	70	134
Ammonia	-	-	4	-	31	43

Source: (*52, 68*)
“ - ” indicates data not available

addition can be expected to vary significantly from one location to another.

Because phosphorus is not a toxicant, many states in the U.S. have no standards for phosphorus except perhaps on a site-specific basis for especially sensitive areas. There is a general conclusion among aquatic scientists, however, that controls are needed on nutrients in the U.S., and particularly phosphorus (*71*). The U.S. EPA has been directed to develop and circulate nutrient criteria that it proposes as the basis for control of nutrients (phosphorus and nitrogen) in surface waters (*76*). The U.S. EPA likely will insist that states include limits on nutrients in their basic standards. When this occurs, there will be numeric standards for phosphorus and nitrogen in all states. Until then, advisory information on nutrient concentrations can be obtained from the U.S. EPA criteria or from the application of an antidegradation concept.

Nitrogen. Like phosphorus, nitrogen can be divided for environmental purposes into dissolved inorganic, dissolved organic, and particulate forms. The composite of these is total nitrogen. Dissolved inorganic nitrogen in inland waters consists almost entirely of ammonia and nitrate. Dissolved organic forms are partially labile (easily used by microbes and readily recycled in the environment) and partly refractory (*77*). Particulate nitrogen typically is a component of living or nonliving biomass.

Ammonia is easily assimilated by plants, for which it is an ideal nitrogen source. Ammonia is also a toxicant, however, and can cause impairment or death of aquatic life above specific threshold concentrations (*78*). Thus, concentrations of ammonia are regulated for protection of aquatic life. Natural concentrations of ammonia in toxic waters are very low (<50 µg/L; Lewis (*79*)) because of the high plant demand for ammonia and the tendency of microbes to convert ammonia, in the presence of oxygen, to nitrate by the process of nitrification. Enrichment of the low concentrations of ammonia in natural waters may stimulate plant growth where nitrogen is a limiting nutrient, and in this way ammonia could be considered a potential source of impairment related to eutrophication (*71*). At even higher concentrations (usually >1 mg/L, but variable), the toxicity of ammonia to aquatic life (particularly fishes and invertebrates) introduces an additional potential for impairment (*78*).

The thresholds for impairment of aquatic life by ammonia have been thoroughly studied, but they must be evaluated on a site-specific basis. Cold water fauna, for example, are much more vulnerable than warm water fauna. Furthermore, the toxicity of ammonia in water varies with pH and temperature. In 1999, the U.S. EPA prepared new criteria for ammonia (*80*) to replace the older criteria (1985 (*78*)) that had been used throughout the United States for almost twenty years. The new criteria are being adopted by states through requirements of the U.S. EPA. Based on either the new criteria or the older criteria that still govern many state standards, the appropriate maximum ammonia concentration for a given site can be evaluated numerically.

Nitrate also is readily assimilated by plants in water and can serve as a primary source of nitrogen to support protein synthesis when ammonia is scarce, as is commonly the case. Nitrate typically is more abundant in inland waters than ammonia, although unpolluted waters typically show concentrations below 200 µg/L (*79*). Nitrate, in contrast to ammonia, is not toxic to aquatic life at any concentration likely to occur even in wastewaters, although at very high concentrations (10 mg/L) there is a human-health threshold for nitrate content in drinking water supplies (http://www.epa.gov/safewater/mcl.html).

Dissolved organic nitrogen in natural systems consists of a mixture of tissue degradation byproducts and excreted organic compounds that come from organisms. Examples of substances that would be included under this heading are amino acids and nucleotides. In addition, more complex organic materials containing nitrogen are derived from soils and mostly fall under the heading of humic and fulvic acids. These compounds are resistant to degradation (*53*). Typically organic nitrogen is similar in concentration to inorganic nitrogen in inland waters, although dissolved organic nitrogen may become the primary dissolved form if the demand on the inorganic pool is strong. Natural concentrations typically are below 400 µg/L (*79*).

Particulate nitrogen usually is the smallest component of total nitrogen in natural waters (*79*). Because it comes from biomass, it is typically associated with various natural organic compounds that compose organisms.

As in the case of phosphorus, total nitrogen should be the main index by which nitrogen content is evaluated. A separate evaluation of ammonia and nitrate content is warranted because ammonia is potentially toxic to aquatic life at high concentrations and nitrate is limited for drinking water supplies.

Ammonia is unlikely to be a significant component of snow and ice control mixtures that are primarily inorganic. For example, salt and sand mixtures or liquid control materials derived from natural salts typically do not contain large amounts of ammonia (Table 3-5). Biomass, when present as a bulk constituent of deicers, may contain large amounts of ammonia, however, which requires evaluation from the viewpoint of toxicity and potential stimulation of plant growth (Table 3-5).

Nitrate is an unlikely major contaminant of snow and ice control materials, although analysis for nitrate is warranted whenever a new type of material is considered for use. Similarly, dissolved organic nitrogen and particulate nitrogen are likely to be present only in small amounts in inorganic snow and ice control materials, but many be more problematic for materials containing bulk organic matter from biomass; little is known of these components.

Inorganics Other Than Key Nutrients. Although the list of inorganic substances that can be found in the environment runs to many thousands of compounds, environmental impairment typically can be evaluated from the perspective of a relatively short list of elements that have the highest possibility to cause impairment through toxicity either in elemental form or as a constituent of an inorganic compound. The elements of low atomic mass do not appear on the list because they are either rare or are known not likely to cause impairment through toxicity. Many heavy elements also do not appear because of their scarcity. As a result, the list consists of heavy elements recognized as most likely to cause impairment. This list of elements commonly is referred to as "heavy metals." Strictly speaking, however, some of the elements on the list are not metals (Table 3-6).

The substances listed in Table 3-6 can impair waters either for support of aquatic life or for human consumption. For most substances, thresholds of impairment for aquatic life are lower than the thresholds for impairment of domestic water supply (e.g., see U.S. EPA criteria cited above). The substances differ substantially in thresholds of concentration considered to be toxic. For example, thresholds for mercury typically are in the range of 10 parts per trillion because mercury is multiplied in concentration as it is transferred from one level in the food web to another. Cadmium and silver have somewhat higher but still very low thresholds, whereas most of the other substances have thresholds considerably higher, but still low on an absolute scale. The actual toxicity of the substances shown in Table 3-6 typically is conditional on the environmental matrix. For example, hardness (i.e., calcium and magnesium content) affects the toxicity of copper and zinc (see U.S. EPA criteria cited above). Also, inorganic dissolved forms generally are far more toxic than bound forms to aquatic life (*60*).

Those elements from the list in Table 3-6 most likely to create problems by way of contamination in snow and ice control materials include zinc, copper, lead, and cadmium (*3, 52, 69*). All four of these elements tend to become concentrated, probably by evaporation mechanisms, in salt deposits used as sources of magnesium chloride for liquid snow and ice control materials. Other elements on the list may create problems under specific circumstances. Variation in the contaminant concentrations for elements in Table 3-7 from one vendor to another or even from one batch to another should be anticipated.

Table 3-6. Heavy metals and other inorganic substances most likely to contaminate snow and ice control mixtures.

Element	Atomic Mass	Representative Regulatory Threshold in Water ***, µg/L
Arsenic*	75	150
Cadmium	112	1
Chromium	52	65
Copper	64	11
Iron	56	1000
Lead	207	3
Manganese	55	1300
Mercury	201	0.01
Nickel	59	29
Selenium*	79	5
Silver	108	0.02
Zinc	65	111
Cyanide**	-	5

*These elements are metalloids, not metals.

**CN^-, not an element but often included in this group for convenience.

***For chronic protection of aquatic life (except mercury, which is for protection of humans in relation to fish consumption); exact limits may vary substantially on a site-specific basis. For more information on concentrations, see criteria documents for specific substances prepared by the USEPA.

Table 3-7. Chemical composition of two sources of liquid $MgCl_2$ used by CDOT during winter, 1997–1998.

		Milligrams per Liter $MgCl_2$ Solution	
		Brand 1	Brand 2
Cu	sol	0.2	0.6
	tot	0.7^+	0.6^+
As	sol	2.4	6.4
	tot	2.2*	(Not Applicable)
Cd	sol	<0.01	0.01
	tot	0.11*	<0.05*
Cr	sol	<2	<2
	tot	<2	<2
Hg	sol	<0.02	<0.02
	tot	<0.02	<0.02
Ni	sol	<2	<2
	tot	6	<2
Pb	sol	<1	<1
	tot	<1*	<1*
Se	sol	0.2	0.02
	tot	<0.2	<0.02
Zn	sol	<2	<2
	tot	<2	4*

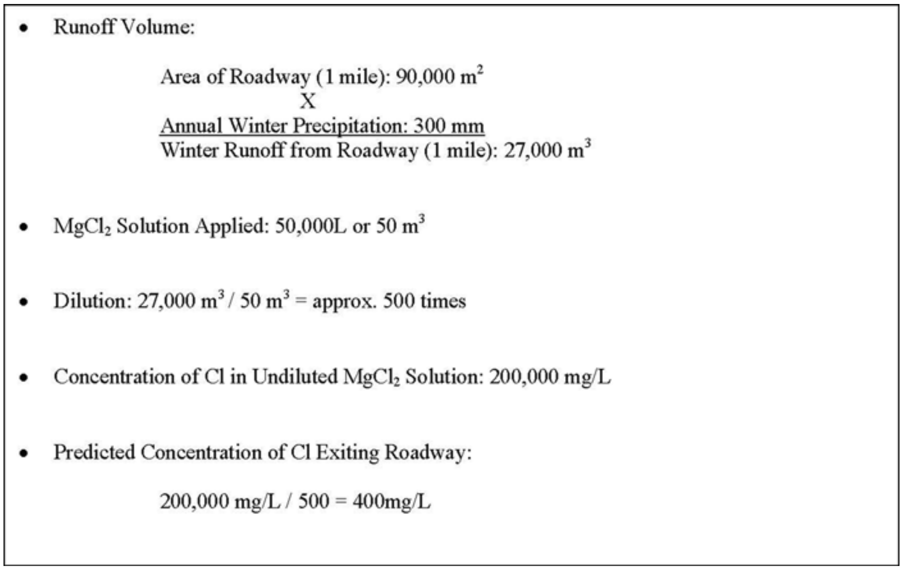
Source: (*52*)
sol = soluble; tot = total recoverable
*Lower than the same brand in 1996-1997
$^+$Higher than the same brand in 1996-1997

3.4.3 Evaluation of Specific Snow and Ice Control Materials

Evaluation of specific deicers involves the use of screening protocols with sufficiently broad coverage to consider all potential types of impairment and to take site-specific considerations into account. There are four steps in the evaluation of a specific type of snow and ice control material: (1) dilution analysis, (2) toxicity screening, (3) screening for potential to cause eutrophication or oxygen depletion, and (4) field monitoring.

3.4.3.1 Dilution Analysis

Because the harm that can be caused by a given substance that might enter an aquatic environment from a road depends strongly on concentration of the substance in the environment, the amount of dilution that will occur between the road and the receiving waters (e.g., streams, lakes, and wetlands) is estimated as a first step in evaluating potential impairment (*52*, *68*). The simplest approach is to use historical information for application rates in relation to the total amount of winter precipitation. Such an examination of historical data leads to calculation of a characteristic ratio of annual application rate to annual winter precipitation. For simplicity, it can be assumed that most or all winter precipitation falling on the road becomes runoff and that it carries away all of the application materials. These generalizations are not entirely correct but, when used in conjunction with a margin of safety to offset estimation errors, they provide a basis for screening. More detailed types of quantification can be conducted if screening shows that the likelihood of impairment is not clear from simple approximations. In most cases, however, either there is clear potential for impairment or there is no reason to suspect impairment from a simple dilution analysis. Figure 3-4 illustrates the steps taken for determination of expected dilution for snow and ice control materials. The substance for which the calculations are being made in this case is chloride. The area available for dilution prior to exit of chloride to the environment is here assumed to equal the area of the road as well as shoulders and



- Runoff Volume:

  Area of Roadway (1 mile): 90,000 m^2
  X
  Annual Winter Precipitation: 300 mm
  Winter Runoff from Roadway (1 mile): 27,000 m^3

- $MgCl_2$ Solution Applied: 50,000L or 50 m^3
- Dilution: 27,000 m^3 / 50 m^3 = approx. 500 times
- Concentration of Cl in Undiluted $MgCl_2$ Solution: 200,000 mg/L
- Predicted Concentration of Cl Exiting Roadway:

  200,000 mg/L / 500 = 400mg/L

Figure 3-4. Steps for determining predicted concentration of a component of $MgCl_2$ solution as it leaves the roadway (based on: (52)).

embankments. Characteristic winter precipitation is used to compute runoff per mile for an entire winter. The total amount of $MgCl_2$ solution characteristically applied in a winter of characteristic precipitation is obtained from application records, which then allows a dilution ratio to be computed. In this case the ratio was 500:1.

Given the initial concentration of chloride in the solution, plus the dilution ratio, the predicted mean concentration can be estimated at the exit point (i.e., margin of the roadway). In this case, the estimate indicated 400 mg/L, which is above the chronic standard (i.e., 290 mg/L, long-term exposure) but below the acute standard for chloride for protection of aquatic life (i.e., 840 mg/L, short-term exposure). Use of the chronic standard for judging possible impairment allows a considerable margin of safety over use of the acute standard, which might be more applicable to most actual occurrences of runoff. Although the runoff is anticipated to exceed the target concentration (290 mg/L in this case), additional dilution of considerable magnitude is anticipated over short distances beyond the exit point. As shown by Figure 3-5 for this particular application, the dilution factor rises rapidly to 1:10,000 within less than 1meter from the exit point. Dilution might not rise so rapidly under some conditions, such as those involving the presence of a hydrologically isolated wetland, pond, or small lake near the roadway. Thus, evaluation of the significance of a computed concentration at the exit point involves knowledge of the site, particularly as regards the expected dilution immediately beyond the roadway.

Table 3-8 summarizes the main factors that influence the concentrations of snow and ice control materials in receiving waters beyond the roadway. The amount of road surface per unit of watershed area is a critical factor that is most evident in the contrast between urban and rural conditions. Concentrations of snow and ice control materials reach their maximum under urban conditions or at other locations where the amount of road structure is very high in relation to the amount of watershed area (e.g., bridges and interchanges). Under such conditions, concentrations of chloride and other soluble constituents, or the augmentation of bedload in the case of abrasives, can far exceed any limits that might be set for the protection of aquatic life (examples given by Environment Canada (*3*)).

A more subtle influence on concentrations of snow and ice control materials is the amount of runoff from the roadway in relation to the rate of application. Because some materials may be applied to prevent the formation of ice (e.g., $MgCl_2$), they may, under some climatic conditions, be applied when the amount of runoff that ultimately results from an anticipated icing event is minimal. In such cases, the dilution of the snow and ice control material will be less than would be the case for conditions that typically produce large amounts of precipitation.

The characteristics of receiving waters also affect the final concentrations of snow and ice control materials that appear in surface waters. The most adverse conditions involve waters that flush slowly, are of low volume, and are close to the road-

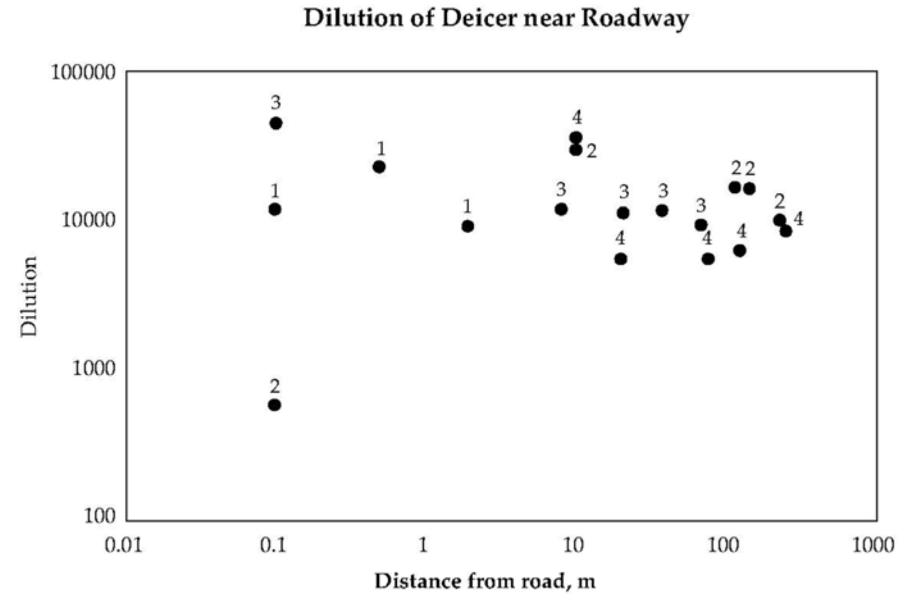


Figure 3-5. Dilution of deicer as related to distance along four transects (numbered 1–4) from side of a paved surface (I-70, near the Continental Divide, Colorado). Dilutions above 10,000 are likely to be underestimated. Source: (52).

Table 3-8. Factors that influence concentrations of snow and ice control materials in receiving waters (streams, lakes, wetlands).

Factor	Effect on Snow and Ice Control Materials in Receiving Waters
Higher road surface per unit watershed	Increases concentrations
Higher roadway runoff	Decreases concentrations
Higher rate of application	Increases concentrations
Greater distance to receiving water	Decreases concentrations
Greater volume of receiving water	Decreases concentrations
Greater flushing of receiving water	Decreases concentrations

way. At the other end of the spectrum are water bodies of high volume at considerable distance from the roadway that show a high rate of water renewal. For example, a large stream with a high winter flow located several thousand feet from a road would be much less responsive to the application of snow and ice control materials than a shallow wetland or pond adjacent to a roadway and not connected to a permanent stream.

Although the factors in Table 3-8 could be quantified, it would be difficult to produce an algorithm that would be sufficiently flexible to allow reliable predictions in most situations. More feasible is a qualitative inventory of the kinds of aquatic environments near a specific segment of road in conjunction with field monitoring that involves indicators of dilution (see below).

3.4.3.2 Toxicity Screening

In principle, screening for toxicity could be conducted on the basis of a comprehensive chemical analysis, which would be evaluated in the context of the expected dilution and the known toxicity thresholds, often given as numeric standards for particular substances. In practice, this approach has several drawbacks. First, the toxicity of mixtures is not always the same as might be expected from the list of concentrations for individual components, because of interaction of components. Second, a strictly analytical approach may omit analysis of an unusual toxicant, thus failing to detect toxicity. In view of similar problems for effluents, which are mixtures of uncertain composition, the U.S. EPA introduced whole effluent testing (WET) as a screening tool. Although WET testing does not entirely displace analysis of known toxicants, it adds a degree of certainty to the conclusion that a particular mixture is not likely to cause impairment beyond a specific amount of dilution.

Protocols for testing of mixtures are well established. They are based on bioassay tests applied to specific organisms now widely available for use in testing such as *Ceriodaphnia*, a water flea; the fathead minnow, a small fish; rainbow trout; and *Selenastrum capricornutum*, a common type of suspended algae (see Lewis 1999 (*52*) for examples of these tests). Species of special concern ((i.e., threatened, endangered) should be tested as well (e.g., Lewis 1999 (*52*)). Further discussion of aquatic toxicity protocols is provided in Section 5.3.8. Testing of *Ceriodaphnia* is perhaps most common because it is less complicated than the testing of fish and gives a good representation of the response of some of the most sensitive kinds of organisms in aquatic environments. Although U.S. EPA documents can be referenced for the detailed protocols, the basic concept is application of the material being tested on the test organisms over a sequence of concentrations to the test organisms under controlled conditions for specific time intervals followed by tabulation of mortality or sub-lethal effects. The exact conditions of such tests are tightly proscribed so that the results are easy to evaluate on a standardized basis. In the case of a snow and ice control material, the range of appropriate dilutions would begin at concentrations higher than those expected under actual circumstances and extend to concentrations lower than expected under actual circumstances, thus bracketing the expected concentrations.

If bioassay testing indicates toxicity of the mixture at dilutions near those expected beyond the roadway, the materials can simply be rejected for use or, if reasonable alternative formulations are not available, further analysis can be conducted to isolate the cause of toxicity, thus providing guidance to a vendor about required changes in the formulation. Analysis for suspected toxicants would first include the most likely causes of toxicity. If these tests did not indicate that any of the analytes were likely causes of toxicity, more unlikely causes of toxicity would be analyzed.

The analytical protocols for individual constituents should be taken from analytical methods approved by the U.S. EPA, by *Standard Methods for the Examination of Water and Wastewater* (*67*), or by other widely used, government-approved authorities. Because these methods change from time to time, the list of approved methods should be reconsulted periodically. Further discussion of environmental analytical test protocols is provided in Section 5.3.

There is one especially important limitation to the use of approved analytical methods. The approved method in question must be capable of providing a quantitative estimate of the concentration of a substance of interest within the range of environmental concern. In other words, it is wrong to apply a method approved but actually intended for application to concentrations far above the thresholds of interest. In such cases, the results may indicate no detection when the substance is present above concentrations that are environmentally significant. Detection limits should always be given with the results of individual tests.

If a bioassay test shows no indication of toxicity, it is still advisable to conduct analyses for substances most likely to be present at concentrations that could cause toxicity. This is a check on the bioassay test and also indicates substances that may be approaching concentrations of concern. Such information can be passed to a vendor for pre-emptive action.

3.4.3.3 Testing for Nutrients and Oxygen Depletion Potential

Because impairment is not limited to toxicity, testing must extend beyond toxicity. The concentrations of total phosphorus and phosphorus fractions, as well as total nitrogen and nitrogen fractions, should be obtained for snow and ice control materials. Through dilution analysis, the amounts of these plant nutrients passed from the roadway can be calculated. Where numeric standards are available, the likelihood of causing the receiving waters to exceed a standard also can be estimated. Where no standards are available, the U.S. EPA nutrient criteria can be used, or an approach based on antidegradation can be used as an index of potential impairment.

Organic matter, when present as a bulk constituent, poses the possibility of oxygen depletion in receiving waters. The total oxygen demand associated with water leaving the road should be estimated. The estimate can be conducted through analysis of total carbon (*67*), through a standard 5-day BOD test (*67*), or through a specialized BOD test (*68*).

As mentioned in Section 3.4.2.1, the analysis of total carbon can be used to estimate maximum potential oxygen demand based on the stoichiometry of respiration. Standardized BOD tests, which are routine for wastewater effluents, have a similar intent and, in some senses, are more realistic in that they account for the fact that some of the organic matter in the mixture may be resistant to use by bacteria and therefore not a significant short-term contribution to oxygen demand. The deficiency of the standard 5-day BOD test is that it is conducted under conditions that deviate strongly from ambient conditions for unpolluted streams because it involves the addition of nutrients and maintenance of a high, constant temperature. Therefore, its application to a relatively unpolluted water for purposes of estimating oxygen drawdown is problematic. In addition, the standard BOD test does not provide information on the time course of oxygen depletion.

An alternative to the standard BOD test has been introduced by Lewis (*68*) specifically for evaluating snow and ice control compounds. As in the case of the standard BOD tests, water samples are held in closed containers that do not admit the passage of oxygen from the atmosphere. Unlike the standard BOD tests, however, the test is based on incubation at a characteristic temperature (e.g., relatively low temperature for a coldwater environment), and the incubation medium is water drawn from the receiving water (e.g., stream, lake, or wetland). The snow and ice control material is added within the range of expected dilution or somewhat above that range, and the progressive loss of oxygen is monitored over a 24-hour or longer interval to produce a time course of oxygen depletion. The results of such tests typically show a lag in the response of bacteria to the presence of bulk organic matter, probably because the microbes most able to use specific kinds of organic matter are present initially in small quantities and build up exponentially as they exploit the organic matter. Thus, oxygen demand may be relatively low for as long as several days and then become extremely high. Knowledge of this time lag may be important for evaluating the location where effects may be noticed in the receiving waters. For example, if dissolved oxygen depletion is observed only after a period of 2 or 3 days, downstream environments that hold waters temporarily separated from the sources by 2 or 3 days would be expected to show the maximum response.

3.4.3.4 Field Monitoring

Some types of environmental impairment are difficult to forecast from chemical analyses or toxicity testing. Therefore, field monitoring is an important adjunct to laboratory studies. Field monitoring can be limited to relatively simple methods, but must include broad spatial coverage of the areas receiving substantial amounts of runoff from the roads and ideally would include continuous monitoring of selected sites. Most important is sampling of slowly flowing waters by use of meters that can detect specific conductance, which indicates the presence of salts and dissolved oxygen. Indicators of potential effects of snow and ice control materials would include substantial depression of dissolved oxygen below saturation or selective accumulation of saline water, especially near the bottom of standing waters or slowly flowing waters. Low oxygen would suggest the possibility of excessive organic matter emanating from the road, and saline layers would indicate excessive salt reaching slowly flowing waters.

Where wells are present, well sampling done in a comparative manner involving other wells not affected by road runoff or more distant from the runoff source can be used in testing the groundwater intrusion of runoff waters influenced by snow and ice control materials. The simplest index would be specific conductance, which would increase in response to any significant intrusion of roadway runoff influenced by snow and ice control materials. Initial evidence of intrusion could be followed by more detailed analysis of constituents of concern from the viewpoint of drinking water.

3.4.4 Overview of Specific Snow and Ice Control Materials

Likelihood of specific kinds of environmental impairment varies greatly among snow and ice control materials. Anticipation of the most likely problems may save time and effort in evaluating specific materials. Table 3-9 summarizes the foregoing text.

3.4.5 Conclusions

The suitability of a particular snow and ice control material for a specific location depends on its general type, its formulation, its application rate, and the characteristics of the receiving environment. These four considerations can be brought together according to the approaches outlined above. The following general conclusions can be made:

- Small water bodies offer less dilution than large water bodies. Consequently, acceptability of any given material with a potentially adverse environmental effect tends to increase as the size of the receiving water increases.
- Abrasives block interstitial spaces within coarse substrates, thus damaging habitat. This particular category of damage is not an issue for aquatic bodies with fine substrates.
- Organic matter and nutrients cause oxygen depletion or eutrophication where potential dilution is low, but are much less likely to be harmful where dilution is high. Higher nutrient levels tend to be associated with OMB materials. Nutrient-poor water bodies have a lower tolerance than nutrient-rich water bodies to additional nutrient loadings.
- Nutrient-poor streams typically contain organisms not tolerant of oxygen depletion. Nutrient-rich streams are more likely to experience oxygen depletion and, therefore, typically contain organisms more tolerant of oxygen depletion. Therefore, the tolerance of nutrient-poor streams for oxygen demanding substances, such as acetate and OMB, is rated lower for nutrient-poor streams than for nutrient-rich streams, particularly if the streams are small.
- The probability that the chloride standard for aquatic life will be exceeded is highest for standing waters of small volume and lowest for flowing waters of large volume.

When considering drinking water obtained from groundwater, the following conclusions exist:

- Magnesium, calcium, and chloride are not associated with impairment of human health.
- Sodium in groundwater is a potential threat to persons with cardiovascular impairment, although the threshold concentration for health effects is relatively high.
- Addition of organic carbon compounds (e.g., acetate or mixed organic matter from biomass) may cause deoxygenation of groundwater, which in turn could cause release of potentially harmful substances such as heavy metals into the groundwater and could be a cause of taste and odor problems.

In some instances, a clear likelihood of impairment will be identified. Whether such impairment falls outside regulatory limits or not depends on law (i.e., state law within the United States). For governmental agencies, however, it is advisable to consider water-quality standards as a strong guideline for the application of snow and ice control materials even when the

Table 3-9. Generalized potential for impairment and its most likely causes for broad categories of snow and ice control materials.

Name	Potential for Impairment	Most Likely Cause of Impairment
$CaCl_2$	Moderate	Excessive chloride loading; additives containing metals or phosphorus; contamination with copper, zinc, lead, or cadmium.
$MgCl_2$	Moderate	Excessive chloride loading; additives containing metals or phosphorus; contamination with copper, zinc, lead, or cadmium.
NaCl	Moderate	Excessive chloride loading, metal contaminants; ferrocyanide additives.
Chloride-based salt plus bulk organics	High	Excessive chloride loading; additives containing metals or phosphorus; contamination with copper, zinc, lead, or cadmium. Organic matter leading to oxygen demand; nutrient enrichment by phosphorus and nitrogen.
CMA	Moderate	Organic content leading to oxygen demand.
KA	Moderate	Organic content leading to oxygen demand.
Sand or sand with salt	High	Turbidity; increased bedload.

regulations have not been directly applied to such materials. In most instances, effective control materials that minimize risk of impairment can be found.

3.5 Soils

The primary reason to consider the effects of snow and ice control material on soil is that the presence and movement of these materials through the soil can further affect vegetation, groundwater, and surface water. Soil conditions such as permeability, erosion, and soil stability can also be influenced.

The effects of snow and ice control materials on soil structure and chemistry have been well documented. Although many studies have directly assessed the effects of snow and ice control materials on roadside soils, a great deal of information is also available by adapting information from studies that had very different purposes—most commonly agriculture-related studies investigating the effects of salinity from intensive irrigation, saltwater intrusion, or inorganic fertilizer applications. Two general mechanisms for impact to soil exist:

- Modification to soil chemistry, including accumulation of ionic species, cation exchange processes, and mobilization of metals from soil; and
- Modification of physical soil characteristics.

After roadway application, some snow and ice control materials will be deposited on roadside soils. Depending on the specific products applied, increased levels of primary components will occur (refer to Table 3-1). For example, application of NaCl will elevate sodium and chloride concentrations, whereas CMA will increase calcium, magnesium, and acetate concentrations. Associated increases will also be realized for secondary attributes such as BOD, heavy metals, cyanide, and phosphorus, where applicable. The degree to which a certain material accumulates in the soil depends on product properties, soil permeability, adsorption, water percolation, vegetative uptake, and biodegradation.

Soils are known to contain negatively charged binding sites on the surfaces of soil particles. Positively charged cations (e.g., sodium, calcium, magnesium, potassium, heavy metals) introduced into soil water will adsorb onto the negative binding sites. Cation Exchange Capacity (CEC) is the ability of a cation to replace on a soil particle another cation of weaker affinity or smaller concentration. The relative adsorption affinity of select cations is as follows (*81*):

High Adsorption Affinity $H^+ > Ca^{2+} > Mg^{2+} > K^+ > Na^+$ Low Adsorption Affinity

Hydrogen ions have a greater affinity for soil binding than calcium and so forth, although the process is also affected by concentration. For example, excessive loading of sodium onto a soil can displace calcium ions, even though calcium has a higher adsorption affinity than sodium. The process can be reversed through introduction of additional calcium, which has a greater adsorption potential to CEC sites and will easily displace the sodium.

Anionic species such as chlorides have a negative charge and do not bind well to like-charged soil particles. Anions are typically transported through soil with soil water percolation or with groundwater movement.

CEC has been shown to be a function of soil type. A compilation of CEC data for different soil types from across the United States has been prepared by RCI (*81*). In general, sand and sandy loam soils tended to have very low CEC (i.e., 2.0 to 17.1 meq/100g dry soil), silt loams had intermediate values (i.e., 9.4 to 26.3 meq/100g dry soils), and clay and clay loam soils had the highest values (i.e., 4 to 57.5 meq/100g dry soil). It was further demonstrated that clay soils could adsorb up to 5 times more sodium chloride than sand.

Application of snow and ice control chemicals, specifically sodium, to soils can influence the physical properties of the soil. Sodium exchange is a measure of a soil's capacity to bind sodium ions. High levels of sodium exchange are particularly detrimental to soil structure in that soil particle sizes are reduced, which can lead to increased soil compactness. Increased compactness further reduces soil permeability and can result in increased surface runoff conditions and erosion of soils.

In certain cases, cationic species (Na, Ca, Mg, and K) may displace heavy metals already bound to soil particles in a process commonly referred to as metals mobilization. Increased mobility implies an increased dissolution of metals to soil pore water, where they may either resorb onto other soil sites, interact with soil organic material, form metal acetate pairs, bioaccumulate, or move with the hydraulic gradient in groundwater with eventual discharge to surface water (*82*). Mobilized metals are more biologically available than soil-bound metals and pose a greater risk to vegetation, terrestrial organisms, and aquatic life.

The potential for metals mobilization is highest where the soil already contains high levels of heavy metals and where concentrations of applied cations (from snow and ice control chemicals) are greatest. These conditions are characterized by the roadway environment, where soils tend to already have higher-than-background levels of cationic heavy metals from vehicle and pavement attrition (*82, 83*). Metals commonly found in roadside environments are listed in Table 3-10. The risk of heavy metal mobilization in roadside soils is therefore likely if sufficient quantities of cations from snow and ice control materials are available.

Novotny et al. (*20*) found the partitioning coefficient for metals is inversely proportional to the salt concentration of the snowmelt. This means that during winter, salt-laden

Table 3-10. Heavy metals released by vehicles.

Heavy Metal	Traffic Source
Lead	Tire wear, lubricating oils and grease, bearing wear
Zinc	Tire wear, motor oil, grease
Iron	Vehicle rust, highway structures, engine parts
Copper	Metal plating, brake lining, bearing wear
Cadmium	Diesel oil, tire wear
Chromium	Metal plating, brake lining wear

Source: (*84*)

snowmelt or soil pore water may have a higher proportion of dissolved metals. Dissolved trace metals are more toxic to biota, whereas the adsorbed or particulate fraction is considered less biologically available.

Temporal effects also influence the degree of metal mobilization resulting from high cation concentrations. Field studies have observed "extreme differences [higher levels]" in cadmium and zinc soil concentrations between winter/spring and summer/fall (*20*). This difference was attributed to leaching of metals from the soil caused by high levels of NaCl from deicing salts in the winter/spring period.

3.5.1 Chloride

Chloride is the primary anionic component of NaCl, $CaCl_2$, and $MgCl_2$. Chloride does not easily precipitate, is not biodegradable, is not readily involved in biological process, and does not adsorb significantly to mineral/soil surfaces. Chloride is therefore extremely mobile and tends to move with soil water percolation and groundwater flow. Chloride is often used as a tracer to delineate the extent of salt movement through the subsurface because of its ability to move without significant impedance.

The literature does not directly associate chloride with any negative impacts to soil properties; however, chloride, in conjunction with an associated cation (i.e., Na, Ca, Mg), can increase soil conductivity, which can further lead to increases in soil osmotic pressure.

There is some evidence from laboratory experiments that chloride passing through soil contributes to mobilization (to groundwater) of some heavy metals, such as cadmium, zinc, and lead (*83*). The premise is that chloride can form complexes with metals in soils, potentially releasing them into the environment (*83, 84*). Doner (*85*) found that higher chloride concentrations in soils increased the rate of mobility of nickel, copper, and cadmium through soil through the formation of chloro-complexes. It is however extremely difficult to separate the influence of chloride ions from the cationic species initiating metals mobilization. At best, the chloro-complexes reduce the affinity of the mobilized metal to resorb on to other soil CEC sites. However, supporting field evidence is limited. A field study in southern Ontario found that concentrations of heavy metals in groundwater beneath roadside soils were similar to those in non-highway locations (*86*), suggesting that the effect is not significant. Another field study conducted in British Columbia failed to detect any trends in soil metals concentrations after winter applications of $MgCl_2$ and NaCl (*34*).

3.5.2 Sodium

Effects of sodium on soil structure and chemistry have been well documented. Elevated concentrations of sodium in soil have long been an agricultural concern, and many studies have investigated salinity effects related to intensive irrigation, saltwater intrusion, and inorganic fertilizer applications. NaCl use for snow and ice control has further increased interest in sodium-related impacts to soil.

Of the primary cations associated with snow and ice control materials ((e.g., Na, Ca, Mg, K), sodium is most commonly used and also has the greatest potential to negatively affect soil properties. Accumulation of sodium in soil can bring about undesirable properties such as increased osmotic pressure, reduced permeability, and the potential for cationic exchange processes (including nutrient imbalances and metals mobility).

The most significant effect sodium has on soil is its ability to adversely affect soil structure. Excessive amounts of sodium will exchange with calcium and magnesium already bound to soil particles. Calcium and magnesium ions tend to aggregate (bind) organic and inorganic particles within the soil, whereas sodium causes them to break apart. When soil is broken up, the particles wash through the soil; pores become sealed and permeability is reduced. Clay soil structure is also affected because sodium adsorption causes clay particles to swell—this also reduces soil permeability.

The effect of sodium on a particular soil type can be classified by the soil's ability to bind sodium on its negatively charged soil sites. The term Exchangeable Sodium Percentage (ESP) is the amount of cation exchange capacity taken up by sodium (Na_{exch}) on a particular soil type and can be demonstrated by the following equation (*87*):

$$ESP = Na_{exch}/CEC \times 100$$

Soils with high ESP will disperse and also plug up easily, whereas low ESP soils do not disperse readily and will maintain soil permeability (*21*). In general ESP values of 13 or higher are considered potentially hazardous to soil quality (*29*). Morin et al. (*21*) further classified soils based on perceived potential impacts from sodium (Table 3-11).

Over time as sodium is applied to roads, sodium will accumulate in roadside soils, cumulatively. Higher-than-normal salt concentrations can be further exacerbated by

Table 3-11. Soil types classified based on potential impact from sodium.

Level of Impact	Soil Type
Low	Highly permeable, coarse textured. Sands, loamy sands, sandy loams, silts
Medium to Low	Low permeable. Compacted clays, clay loams, loams, sandy clay loams, silt loams
Medium	Highly permeable. Organically enriched clay, clay loams, loams, sandy clay loams, silt loams
High	Medium permeability, medium texture. Non-compacted loams, sandy clay loams, silt loams
Highest	Soils enriched with swelling clay

Adapted from: (*21*)

low precipitation conditions. As reductions in permeability related to sodium take effect, there will be lower water movement through the soil, further increasing the potential for sodium accumulation and further still decreasing permeability. The net result of decreased soil permeability means that more water can flow over land and cause erosion (*22, 88*). This can be of particular concern when considering structural stability for roads.

Excessive levels of sodium can also affect soil pH. When the exchange capacity of a soil becomes greatly saturated by sodium and depleted of calcium and magnesium, the soil is considered to be an alkali soil, and the pH of the soil may increase (*19*). Other studies have demonstrated reversed results, indicating that pH change depends on other factors as well.

Sodium can also cause metals mobilization; however the extent depends on specific soil conditions. Areas with the highest impact will be where there is a high percentage of clay content with a high exchangeable sodium ratio and low precipitation (*21*), as well as areas already containing high levels of available metals such as roadside environments are of concern.

3.5.3 Calcium

The effect of calcium on soil has been adequately documented in the literature, including studies of $CaCl_2$ and CMA use for snow and ice control, $CaCl_2$ used as a dust suppressant, and $CaCl_2$ used as a soil stabilizer for agricultural applications.

Calcium is generally thought to have beneficial effects on soil physical properties when compared with sodium. A high concentration of calcium causes fine clay particles to clump together and aggregate. The presence of soil aggregates creates macropores in the soil that permit better water drainage and improved aeration (*89*). A University of Washington study (*36*) found that Ca associated with CMA did not significantly affect the physical properties of soil (e.g., permeability, plasticity, and strength). Brandt (*90*) further suggested that $CaCl_2$ and NaCl mixtures used for snow and ice control could prevent the need for adding materials like gypsum to periodically decrease the sodium contamination of roadside soils.

Several studies have investigated the potential for calcium to mobilize metals in soil. Many of these studies involve assessments of CMA, which includes calcium as well as magnesium. A California laboratory study (*91*) found that a CMA solution that leached through soils tended to exchange calcium and magnesium with other metals already present in the soils. Results indicated that CMA could extract iron, aluminum, sodium, and potassium from roadside soils. Laboratory and field tests conducted by Horner (*36*) also indicated potential for CMA to mobilize and release trace metals from soils. Laboratory experiments conducted by Elliot and Linn (*82*) using CMA also found preferential adsorption of Ca and Mg at soil exchange sites and displaced heavy metal ions in soil solution. Of particular interest were increased desorbed H^+ ions, which will reduce pH and further promote the dissolution of metals adsorbed to soil particles. More recent studies by Amrhein et al. (*92*) have compared the mobilization of trace metals in soils treated with solutions of NaCl and CMA. The results of these investigations indicated that CMA probably has less effect than NaCl on trace metal movement in soil. Tests also showed that calcium and magnesium ions were advantageous for the permeability and structure of soil. Sodium, on the other hand, tended to destroy soil structure by dispersion of soil aggregates.

3.5.4 Magnesium

There is limited information directly discussing the effects of magnesium on soils. Most information is available though investigations conducted for CMA, which involve the combined effects of calcium and magnesium ions. As discussed for calcium (Section 3.5.3), magnesium is also thought to be beneficial to soil permeability and soil structure and can reduce dispersion of organic matter and clay (*20*). Magnesium also can exchange on soil particles in a process that may mobilize heavy metals. Magnesium is however not as strongly adsorbed as calcium to soil particles (*81, 89*).

3.5.5 Potassium

Few published reports detail the effects of potassium applications on soil. Potassium is an important plant nutrient commonly applied in fertilizer blends. It can be tolerated at high concentrations by most plants; however, at high application rates it can increase osmotic pressure of the soil (*93*). Like the other cations typically associated with snow and ice control materials (i.e., Na, Ca, and Mg), excessive levels of potassium should have the potential to influence cation exchange processes and increase the mobility of heavy metals.

3.5.6 Acetates

Information regarding the effects of acetates on soil properties has been drawn from studies conducted on CMA and, to a lesser extent, KA. The acetate ion (CH_3COO^-) is organic and can be used by many species of micro-organisms as a nutrient. Generally, all acetates will degrade by microbial action to carbon dioxide and water. A University of Washington study (*36*) revealed that, at temperatures above 10°C, a high level of CMA-acetate decomposition was achieved within 2 weeks, while at 2°C, 4 weeks were required for full decomposition. Therefore, the direct effects from acetates are relatively short lived and confined to an area around the roadway—the extent of transport of acetates through the soil subsurface does not typically exceed 10 meters (*36*).

CMA has been shown to influence the mobilization of heavy metals from soil. This process is predominantly related to the cationic exchange processes related to calcium and magnesium, but acetate is thought to have some influence on the process. Ammonium acetate is commonly used to leach metals from soils for analytical testing purposes. Ammonium initiates the ion exchanges with the bound metal after which the acetate complexes (binds) the metal, helping to maintain it in solution. There have therefore been concerns that acetates introduced as snow and ice control materials can increase the solubility of metals in soil water, preventing potential readsorption to soil. Laboratory studies conducted by Amrhein and Strong (*83*) found that, after metals are mobilized from cation exchange processes, acetate forms stronger metal pairings than chloride, potentially increasing the trace metal concentration in solution. However, this process is deemed unlikely to persist under field conditions because of biochemical processes involved with acetate degradation (*83*).

Laboratory tests comparing the effect of CMA and NaCl on trace metals mobility found mobility associated with CMA did occur but was less than for NaCl (*83, 94*). The addition of CMA to soil initially may increase the mobility of metals and their leaching from contaminated soil—both calcium and magnesium have higher soil adsorption affinities than sodium. There is also concern that rapid, microbial decomposition of CMA could lead to low redox (oxygen deficient) conditions in roadside soils and to the leaching of acetate to groundwater. Low redox conditions resulting from CMA decomposition could have a strong influence [increase] on trace metal solubility as well.

Conversely, an important effect of acetate degradation is that it creates neutralization conditions when bicarbonate is produced. This will increase soil pH and assist in immobilizing solubilized metals and results in a net decrease of leaching from soil (*82, 83*). Acetate itself has also been found to provide similar buffering capacity (*82*).

Elliot and Linn (*82*) also found with CMA that preferential adsorption of Ca and Mg at exchange sites displaced bound metal ions into solution and desorbed H+, which promoted dissolution of adsorbed metals. This was counteracted by the pH neutralizing effect of acetate ions, so that within 10-pore volume displacements, the presence of CMA resulted in a net suppression of leachate metal ions. Soils with higher acidity may resist this neutralization.

Many of the study conclusions cited above are based on laboratory testing, and limited information is available that replicates these findings when subjected to the highly variable conditions experienced in the field.

3.5.7 Organic Products

Organic products used for snow and ice control include a range of manufactured materials such as glycol and agricultural by-products—typically agriculturally derived organic biomass products blended with chloride-based salts as a corrosion inhibitor. There is limited specific information detailing the effects of organic products on soil properties, but, based on their organic constitution, it is expected that they would be subject to degradation by soil micro-organisms. Degradation could lead to anaerobic conditions in the soil, which can decrease soil pH and increase the solubility of adsorbed metals.

Klecka et al. (*95*) investigated biodegradation of five different glycol-based aircraft deicing fluids in soil. Glycol biodegradation was observed in soil at concentrations ranging from 392 to 5278 mg/kg, suggesting that high levels of the deicing fluids are unlikely to be inhibitory to soil micro-organisms. Regardless of the type of glycol present (e.g., ethylene glycol, propylene glycol, diethylene glycol), biodegradation rates were very similar. Average rates were 66.3 to 93.3 mg/kg soil per day at 25°C, 19.7 to 27.0 mg/kg soil per day at 8°C, and 2.3 to 4.5 mg/kg soil per day at −2°C. Although biodegradation rates decrease as temperature decreases, it was expected that biodegradation would play a major role in removing residual levels of glycols from soils. Use of glycols for roadway snow and ice control is not practical because of cost, and they are rarely used for this purpose.

3.5.8 Urea

Few studies have been conducted detailing the effects of urea-based snow and ice control materials on soil properties. Urea is a common component of commercial fertilizers and, when placed in the soil, is quickly hydrolyzed (usually within

2 to 10 days depending on soil temperature) to ammonium. When soil micro-organisms convert urea to ammonium, there can be a short-term increase in pH in the area immediately around the fertilizer granule. This effect is more pronounced at low soil moisture levels, at high temperatures, and in light sandy soils. At pH values greater than 7.5, ammonia gas also can be generated. This ammonia gas will usually dissolve in the available soil water or adsorb to soil particles and not pose any problems. If conditions are dry, however, free ammonia gas can persist in the soil pore space, and this can damage plant roots when fertilizer has been banded near the root system (*96*).

3.5.9 Abrasives

Abrasives have few direct effects on soil because they do not chemically react and tend to remain on the surface of the soil. However, concerns have been raised about the trace constituents associated with the abrasive materials. Some materials have shown high levels of available trace materials (e.g., metals that may leach into the environment). Oberts (*97*) noted that sand obtained for the Minneapolis metropolitan area contained high levels of phosphate related to the calcium phosphate mineral, apatite, which was present in the source material.

3.5.10 Ferrocyanide Products

Ferrocyanide complexes are commonly associated with NaCl, and have limited direct effect on soil properties. Ionic effects are negligible when compared with NaCl, because approximate concentrations are typically less than 0.01 percent by weight of NaCl. The fate of ferrocyanide ions in soil is unclear. Negatively charged ions tend to be rejected by soils and move readily with percolation and groundwater; however, a study conducted by Olson and Ohno (*98*) speculated that, because the relative proportion of cyanide with respect to salt is low, the ferrocyanide may be adsorbed onto the soil particle. The photodecomposition process requires ultraviolet light to occur, and it is unlikely this process will occur once ferrocyanides are in soils or groundwater. Laboratory experiments have shown that decomposition of ferrocyanide complexes in soils (in the dark) is slow. The half life for ferrocyanide in soil ranged from 1 year at a low pH of soil water to 1,000 years at levels greater than pH 7 (*20*).

3.5.11 Conclusion

Snow and ice control materials can affect soils both chemically (i.e., by affecting concentrations of available ionic components in the soil) and physically (i.e., by affecting soil structure). Chemical effects to soils are not a significant concern when considering soils as the sole impact receptors. Increases of concentrations of snow and ice control materials in soil tend to have a far greater effect on terrestrial vegetation and to a lesser extent aquatic quality.

Physical effects are more of a concern, specifically when considering sodium accumulation, which is known to break down soil structure. Breakdown of the soil structure can reduce water and air permeability and can lead to erosion conditions. However, magnitude of impact depends on the types of soil present (Table 3-11). Documented cases of NaCl applications adversely affecting the stability of roadside soils were not found.

Snow and ice control materials containing calcium or magnesium tend to improve soil structure and permeability by increasing aggregation of fine soil particles. Products containing organic components are partially or fully biodegradable in the soil and have little known effect. Mobilization of heavy metals is a concern when excessive levels of cationic components are introduced to roadside soils; however, limited field evidence has been obtained to support this.

3.6 Soil Biotic

Much of the information relating the effects of snow and ice control materials to soil microbial species has been summarized in a literature review conducted by Butler for the Environment Canada CEPA Priority Substances List Roadsalt Assessment (*99*). This study specifically sought information for NaCl, KCl, and $CaCl_2$; however, limited literature was found directly assessing exposures and effects of these snow and ice control materials to soil microbial communities. Study findings were thus developed by adapting information from studies that had different purposes, most commonly the effects of high salinity from intensive irrigation or inorganic fertilizer applications. Therefore, the lack of published information on the effects of snow and ice control materials on soil invertebrates was clearly identified as a data gap in the Environment Canada CEPA Priority Substances List Roadsalt Assessment.

3.6.1 Chloride-Based Salts

High concentrations of salts in the soil can affect soil microbial activity via osmotic stress as well as apparently ion-specific stresses, though the magnitude of effect is very difficult to gauge. Organisms tend to be highly adaptable and soil characteristics (e.g., pH, ion exchange capacity, ammonium level and fertilization state, and matric water potential) can influence the magnitude of effect. The organisms most likely to be at risk are those in intimate contact with the dissolved solids in the soil water (e.g., protozoa, nematodes, earthworms, and arthropods) (*99*).

Affected soil strips along roadsides are typically narrow and, even if total sterilization occurs as a result of snow and ice material application, rehabilitation probably will occur after conditions return to normal (*99*). A European study cited by Butler and Addison (*99*) found that some changes to the soil faunal community should be expected as a result of roadsalts; however, even in the absence of salt impingement, the strips of soil next to the roadway must already be considered disturbed environments. Organisms inhabiting the roadside community probably are drawn from a pool of species adapted to disturbed environments and are not necessarily indicative of the "natural" population through which the road passes.

Few studies have assessed the potential process for effect to soil microbial species. Gunter and Wilke (*100*) determined that enzyme activity of soil bacteria decreased during the period of sodium chloride runoff. The decease resulted from a general decrease in microbial activity (i.e., metabolism) and not from enzyme shutdown or death. The effects were temporary. Activities returned to normal levels after the ions had leached from the roadside soils. It was not determined whether the effect was caused by the sodium or chloride ion, or both, but it does represent an effect on the balance of soil microbial chemistry.

Bright and Addison (*41*) developed British Columbia matrix numerical soil standards for NaCl by constructing species sensitivity distributions based on mortality (LC_{20}) and EC_{50} (Median Effects Concentration) for a range of soils and moisture contents in British Columbia (Table 3-12). Using soil concentrations based on the 25th percentile of ranked study concentration data for various species, the authors developed toxicity thresholds that found lethal effects for NaCl to occur at 4,700 mg/kg whereas non-lethal effects would occur at 1,200 mg/kg. The authors also conducted laboratory tests that compared the toxicity of commercial roadsalt (99 percent NaCl, containing approximately 15 ppm ferrocyanide) with analytical grade NaCl for two soil invertebrates (*F. candida* and *O. folsomi*). They found no discernible difference between responses for both organisms, suggesting that reagent grade NaCl was a valid surrogate for commercial salt products and, perhaps more important, suggesting that ferrocyanide as used in commercial NaCl preparations produces no measurable effect on the species tested. This study also found no discernible differences in toxicity between KCl and NaCl for selected soil invertebrates.

Table 3-12. Relationship between percent of soil invertebrate species potentially affected and soil NaCl concentrations.

Percent of Species Sensitivity Distribution	Predicted Soil Concentration of NaCl (mg/kg, dry weight basis) Corresponding to Effect Type and Level	
	LC_{20}	EC_{50}
5	3200	660
10	3500	770
15	3900	890
20	4300	1000
25	4700	1200
30	5200	1400
35	5700	1600
40	6300	1900
45	6900	2200
50	7600	2500
55	8300	2900
60	9200	3400
65	10000	4000
70	11000	4600
75	12000	5300
80	13000	6100
85	15000	7200
90	16000	8300

Source: (*41*)

3.6.2 Urea and Potassium Acetate

Transport Canada (*101*) assessed the effects of urea and potassium acetate used as runway deicers on soil microbial communities at Halifax International Airport. They found no discernible differences between the sites tested with respect to

- The in situ concentrations of total heterotrophic bacteria, whether these bacteria were either anaerobic or aerobic or psychrophilic (low-temperature) or mesophilic (moderate temperature) bacteria;
- The in situ concentrations of fungi, whether these fungi were either psychrophilic (low-temperature) or mesophilic (moderate temperature) mold; and
- Soil respiration characteristics of the rate of carbon dioxide evolved, the proportion of organic carbon metabolized, or the temperature coefficient.

One of the less-studied aspects of soils with respect to snow and ice control materials is the role of soil bacteria and fungi in nutrient cycling and transfer (*101*). Bacteria in soils are responsible for the decomposition of organic matter to forms that can be used by plants. Fungi, specifically microrhizae, are associated with the roots of many species of plants and enable the transfer of essential nutrients (e.g., zinc, manganese, and copper) from soils to the roots. The interference with the metabolism of bacteria or microrhizae may adversely affect vegetation and warrants further investigation.

3.6.3 Ferrocyanides

Ferrocyanide compounds have limited bioavailability and are not considered toxic (*20*). However, they can decompose to a more toxic free-cyanide form. Fast breakdown of complex ferrocyanide is caused by photodecomposition by ultraviolet light and results in the formation of HCN gas, which is volatile. If the rate of formation of the gas is less than the rate of volatilization, an increase in the aqueous concentration for available cyanide will occur. This may be transported to soils next to the roadways.

Photodecomposition requires ultraviolet light in order to occur, and it is unlikely this process will occur once ferrocyanides are in soils or groundwater. Laboratory experiments have shown that decomposition of ferrocyanide complexes in soils (in the dark) is slow. The half life for ferrocyanide in soil ranged from 1 year at a low pH of soil water to 1,000 years at levels greater than pH7 (*20*).

3.6.4 Conclusion

Cain et al. (*28*) summarized various field studies that measured NaCl concentration in roadside soils. At distances less than 10 meters from the roadway, cases were cited where NaCl concentrations were greater than the toxicity thresholds developed by Bright and Addison (*41*). However, it was found that NaCl concentrations at distances greater than 10 meters from roadways were generally greatly reduced. The roadside soil environment is affected by a wide range of stressors not related to snow and ice control. It is also likely that the organisms inhabiting the roadside community are drawn from a pool of species adapted to disturbed environments and are not necessarily indicative of the "natural" population through which the road passes. It is suggested that routine snow and ice control practices do not pose a significant risk to roadside microbial populations outside what would already be considered "disturbed environment."

3.7 Vegetation

The adverse effects of snow and ice control materials on roadside vegetation have been known for some time. Unlike effects on soil and surface water, damage to roadside vegetation is highly visible and well publicized, especially in forests and parklands next to highways. Numerous reports and reviews have been written during the past three decades documenting the effect of these materials on the environment. The following is a historical summary based on *TRB Special Report 235* (*17*):

> *Incidents of vegetation injury were first reported in Minnesota during the 1950's, when trees along city boulevards started to show signs of salt-related decline (102). New Hampshire also reported the death and removal of nearly 14,000 trees along 3700 miles of salt-treated highways (103). Investigations of salt's impact on vegetation were conducted during the 1960's and 1970's in New Hampshire, Minnesota, Michigan, and several other snowbelt states, usually in response to concerns about damage to roadside trees (103–106). More recently, damage to trees and other roadside vegetation has been investigated in the Adirondack region in New York, the Lake Tahoe basin of California and Nevada (107, 108) and Europe (109, 110).*

Studies have found significant effects on plants because of intake of salt ions from contaminated soil and/or water through the roots and damage from aerial deposition on leaves and stems. Often, damage may result from both soil uptake and aerial deposition and, in many cases, may not be noticeable until a buildup of salt ions in the plant tissue reaches toxic levels over the course of several years. Effects can occur through various modes (e.g., biochemical, physiological, physical, and chemical processes). The literature clearly indicates that effects can be significant, but depend on a wide range of factors unique to each site. Most research on the effects of snow and ice control materials on roadside vegetation generally finds that damage is limited to areas both (1) exposed to high levels of chemical splash/spray or runoff and (2) containing salt-sensitive species.

The effects snow and ice control compounds have on terrestrial vegetation, as identified in the literature, can be classified into three groups:

1. Aerial deposition;
2. Ion uptake and accumulation from soil; and
3. Osmotic stress.

3.7.1 Aerial Deposition

When salt is deposited on foliage, it may either stay on the exterior plant parts (e.g., needles, leaves, and stem) or be transported to the interior of the plants either through young shoots, buds, or over-wintering needles (i.e., conifer leaves). Direct injury from deposition on mature bark has not been observed, even in salt-sensitive species (*28*). Moran et al. (*62*) (*29*) found salt spray to be responsible for a condition called "leaf burn," a process where leaf tissue is damaged through contact with highly ionized salts. Salt spray was also found to cause desiccation of plant tissues, a process where cell water diffuses from the cell to the area of greater ion concentration. In addition to drought or desiccation, Cain et al. (*28*) also found injury related to penetration of phytotoxic ions of NaCl through the stem, bud, and leaf tissues. General symptoms of injury related to aerial deposition of salts on vegetation include (*28*)

- Death of stems and buds on young shoots;
- Delayed resumption of spring growth;
- Reduced new growth compared with uninjured plants;
- Reduced vigor and growth of trees (because of repeated injury over time); and
- Premature leaf drop for conifers, further reducing photosynthetic capacity.

Hanes et al. (*111*) determined that susceptibility of plants to absorption of roadsalt spray and splash depends on the growth stage. Salt deposited on foliage is more readily transported into an actively growing plant than a dormant one. Snow and ice control chemicals are applied in winter when plants are dormant, and therefore effects to dormant deciduous trees and grasses should be low because of this mechanism. Salt ions that accumulate on plant surfaces can be washed off by precipitation, reducing the effect from this mechanism; however, the author further stated that salt ions will be deposited on surrounding soils and can still continue to be taken up through their roots during the winter.

Susceptibility of plants to aerial deposition can also be related to plant vigor (i.e., young or aging trees may be affected more than healthy mature trees). Also, the age and size of a plant may influence the magnitude of effect. For example, young trees may be more sensitive to salt spray than mature trees because, on mature plants, the crown, the foliage, and the new shoots may be above the zone of spray (*28*).

3.7.2 Ion Uptake and Accumulation from Soil

Commonly used snow and ice control chemicals (e.g., sodium chloride, magnesium chloride, calcium chloride, potassium chloride, CMA, and KA) introduce the potential for high levels of constituent ions (e.g., sodium, magnesium, calcium, potassium, and chloride) in the soil environment. These ions will accumulate or migrate though the soil based on precipitation, soil permeability, cation exchange capacity, and hydraulic conductivity. When these ions reach the root zone, they are taken up by the root system at a rate equal to the transpiration rate from leaves where they will accumulate in plant tissues (*22, 88, 111*). General symptoms in response to elevated soil levels of Na, Ca, and Cl include general plant decline, reduction in leaf size and plant growth, leaf chlorosis, leaf burn, and tissue death (*28*). Seed germination can also be reduced or delayed.

Studies attribute specific damages to vegetation to excessive chloride levels, not sodium levels. Hanes et al. (*111*) examined the effect of salt on silver maples and found that, although the amount of sodium absorbed by the plant was proportionally higher than chloride, it appeared that less sodium was accumulated over time. Although the accumulation from high levels of sodium can be detrimental to the plant, the study results indicated that there is more danger to the plants from chloride accumulation. Another study concluded more chloride than sodium is absorbed by plants because sodium is more readily adsorbed onto soil particles; however, sodium may contribute to plant injury by increasing osmotic stress (*84*).

Any effects that may occur depend on plant sensitivities to the specific ion. Calcium, magnesium, and potassium are all essential elements for plant growth. Because of this, most plants can tolerate relatively high levels. Westing (*88*) did, however, demonstrate that excessive calcium in soils may decrease both sodium and potassium uptake.

Sodium and chloride, on the other hand, have been shown to induce toxic effects at levels above 0.3 percent dry weight in leaves for sodium (*88*) and above 0.5 percent dry weight for chloride (*22, 88*). Extreme sodium levels in soils can interfere with potassium uptake by plants and cause calcium deficiency (*22, 88*).

3.7.3 Osmotic Stress

In general, an increase in ion concentration in soils will increase soil salinity and cause osmotic stress to plants. This is a situation where a high concentration of salts causes an osmotic potential between the soil water and the plant. Osmotic stress can inhibit the plant's ability to absorb water and can cause nutritional imbalances by disrupting the uptake of nutrients (*22, 28, 107*). Not only will osmotic stress reduce the root's ability to uptake water from the soil, it can lead to dehydration and collapse of plant root tissues. Osmotic stress can also cause cellular damage, which can lead to reduced shoot growth and drought-like symptoms (*22, 28, 107*).

Water availability can affect osmotic stress conditions. Species that have a marginal tolerance to salt stress may become salt intolerant under drought conditions. In addition, drought stress has been shown to aggravate vegetation with pre-existing salt damage and may lead to increased severity of symptoms (*112*) (*108*).

Excessive ionic concentrations in soil will also disrupt nutrient balances. Crop yield has been shown to decrease with increasing levels of soil conductivity, regardless of the level of sensitivities (*21*). The ionic dynamics in soils are complex, and specific mechanisms remain poorly understood; however, in general, any excessive concentration of ions can disrupt natural balances.

Experiments have shown that plasmatic resistance to salts is lowest during the growth season and highest in the winter when the plants are dormant. Lab experiments have also shown that repeated prolonged above-ground contact causes far more damage than repeated short-lived contacts (*31*).

Where excessive soil concentrations of sodium exist, not only is osmotic stress a concern, the soil structure can deteriorate—soil pores become clogged, permeability decreases, and soils can crust (refer to Section 3.5.2). Clogged soil pores reduce the space available for penetration and permeation of air and water through the soil. Reduced water supply can induce drought-like conditions, further exacerbating the effects associated with an osmotic stress condition. Reduced soil air supply will affect root growth. Soil crusting reduces shoot emergence of subsurface seeds and root penetration of both surface and subsurface seeds, resulting in reduced plant establishment (*28*).

3.7.4 Species Sensitivities

The effect of snow and ice control materials on roadside vegetation varies by species, and several investigators have compiled lists of relative tolerances of native and horticultural species. NaCl "sensitivity lists" have been prepared by Hanes et al. (*111*) and Sucoff (*103*). Agencies have used this information to assist in selecting tolerant species for areas with high-expected levels of roadsalt application. A literature review conducted by Cain et al. (*28*) found that vegetation most sensitive to the effects of chlorides include native grasses; wetland species, such as sphagnum moss and sedges; and maple, pine, Douglas Fir, dogwood, peach, and plum trees. In Canada, 53 percent of principal forest trees species have been rated as sensitive to roadsalt and 73 percent of principal genera of forest trees contain species that have been rated as sensitive to roadsalt (*28*).

In general, grassy vegetation is more salt tolerant than are trees and woody plants (*88*). Hanes et al. (*111*) found the following general salt sensitivities:

- Most grasses are fairly adaptable to high concentrations of Na and Cl;
- Woody trees are fairly tolerant;
- Conifers are least tolerant; and
- Younger plants are more susceptible than aged plants.

Species that have a marginal tolerance to salt stress may become salt intolerant under drought conditions. In addition, drought stress has been shown to aggravate vegetation with pre-existing salt damage and may lead to increased severity of symptoms *(108, 112).*

3.7.5 Other Factors Affecting Impacts to Vegetation

The magnitude of effect that snow and ice control materials may elicit on roadside vegetation depends on a wide range of conditions. First, effect is directly related to the exposure concentration, which depends on application amounts and specific transport mechanisms. General details on the mechanisms and extent of soil, water, and aerial transport were discussed in Section 3.1. Secondary factors include distance from roadway, season, duration of exposure, age and health of plant species, and soil conditions. The effects of snow and ice control chemicals to vegetation can also be affected by a complex set of site-specific factors and conditions. The Transportation Research Board (*32*) developed the following list identifying factors that affect the degree of vegetation damage resulting from salts:

- Temperature: The effects of salts are compounded by higher temperatures that cause increased dehydration through foliage, faster movement of salt to the plant, and increased salt absorption through the roots.
- Light: Exposure to direct sunlight increases the rate of dehydration.
- Humidity: High humidity lowers the rate of dehydration and, therefore, helps alleviate water stress.
- Wind: Exposure to wind may increase the rate of dehydration.
- Soil water: As salinity increases, the soil water available to plants decreases.
- Soil texture and drainage: The ability of soil to retain salt is partially determined by soil texture and drainage characteristics. For example coarse-textured soils are quickly leached of salt, and steep slopes may not absorb salt because of rapid runoff.
- Precipitation: Rainfall and other precipitation can flush salt deposits from foliage and dilute salt solutions in soil water. On the other hand, precipitation can transport salts via surface runoff to roadside soils.

Effects on vegetation can be subject to temporal effects. Laboratory experiments have shown that plasmatic resistance to salts is lowest during the growth season and highest in the winter when plants are dormant (*31*). Most plants have completed their active growing cycles before the arrival of winter. Therefore, the primary exposure is uptake of salt via the soil once growth resumes in the spring, which generally occurs within the first 10 meters of the roadway, or where salt levels are elevated because of runoff, drainage patterns, or soil water movement (*28*). Elevated levels of snow and ice control materials in soil have generally been found to decrease over the growing season as a result of rainfall and runoff (*23, 24*).

Backman and Folkeson (*109*) found vegetation damage "to a remarkable and previously unknown extent" that occurred in spring 1994 alongside Swedish roadways. Effects were attributed to three interacting factors. First, roadsalt consumption was higher than usual during the preceding two winter seasons. Second, applications occurred relatively late in the season—the last application was in early April. Third, subsequent months reported near drought conditions with unusually high temperatures and low precipitation. Salts were not sufficiently washed away from foliage or the soil before spring growth (bud unfolding). This combined with unfavorable weather conditions caused a high degree of impact. Though the study concluded that salt contributed to the damage, it was also indicated that roadside vegetation is exposed to severe conditions as a result of several interacting stress factors. In many cases, this may lead to generally weakened conditions, predisposing the vegetation to damage from other factors that include exhaust emissions, high wind velocity, higher soil and air temperatures, and longer periods of sunlight.

In a study assessing roadside tree injury and decline at 17 sites in interior British Columbia (*113*), common stressors potentially involved in roadside decline were investigated, including (1) highway winter and summer maintenance; (2) climate; (3) herbicide use; (4) vehicle metal emissions; (5) point source pollution; (6) insects and diseases; and (7) animal discharges. Roadsalt was found to be a major inciting stressor; however, other factors such as climate (i.e., summer drought) and vehicle trace metal emissions were significant independently or in combination with other factors.

Blomqvist (*114*) found symptoms of salt damage in coniferous trees to not only impact the biota itself (e.g. browning needles and needle loss), but also participate in other causal relationships such as lower photosynthetic capacity, increased amount of salt in the soil water, osmotic stress, inhibition of water uptake, stress avoidance of the plant, and energy expenditure. Most of these effects will, in the end, diminish the growth and can predispose the tree to damage from fungi or insects.

Eppard et al. (*115*) assessed overstory vegetation in the environmentally sensitive Lake Tahoe basin and found approximately 45 percent of the study trees were affected by one or more factors such as insect infestation, fungus, ozone, or salt. The two main types of damage were attributed to insects (17.46 percent) and salt (15.05 percent).

Separating the different stress factors can be difficult given that one factor may have predisposed the tree to damage, another factor may have triggered the damage, and a third may have contributed to the actual killing of the tree. Effects also may not be realized for many years until accumulation of ions is sufficient to elicit toxic effects to the vegetation. Because of the wide range of circumstances and conditions, it is difficult to develop a general model to predict salt damage to vegetation. However, the literature indicates that certain conditions are most likely to result in problems. The following injury patterns are based on those developed by Cain et al. (*28*):

- Injury occurs in a linear pattern along roads or in areas where runoff from roads collects;
- Injury is more severe on the side of the plant facing the road;
- Injury is more severe on the downhill side of the road;
- Injury decreases with the distance from the road;
- Injury is worse on the downwind side of the road;
- Parts of woody plants covered by snow or sheltered from spray lack injury symptoms;
- Parts of trees above the salt spray zone are not injured or are injured less;
- Salt spray injury only extends a short distance into dense plants;
- Injury in coniferous plants becomes evident in late winter and continues into the growing season; and
- Injury in deciduous trees becomes evident in spring when growth resumes and continues into the growing season.

3.7.6 Specific Effects Associated with Select Snow and Ice Control Materials

3.7.6.1 Sodium Chloride

Sodium chloride toxicity to plants has been widely studied, and evidence reveals that the damage to plants is more from high chloride concentrations than from high cation concentrations. Hanes et al. (*111*) conducted a study examining NaCl damage on silver maples and found that salt-damaged plant tissues contained sodium concentrations between 0.03 percent and 0.08 percent, whereas chloride concentrations were between 0.67 percent and 1.18 percent. Whereas 0.08 percent sodium is not considered a toxic level, chloride levels greater than 0.20 percent will result in damage to leaves and stems and 0.50 percent chloride will ultimately result in plant death. Study conclusions indicated that, although accumulation of sodium is detrimental to plants, there is more danger to plant life from accumulation of chloride ions.

Although sodium is not an essential element, it is commonly found in plants and has improved the quality of certain vegetable crops (*28*). Chloride is a micronutrient required in small amounts for plant growth (adequate plant tissue concentration is around 100 ppm). Excessive levels of chloride in plant tissues may lead to necrosis, burning of leaf tips and margins, and eventual death. Some plants, however, can screen out chloride through their root membranes. Most annual crops and short-lived perennials are moderately to highly tolerant of chlorides. Trees, vines, and woody ornamental plants are often sensitive to chlorides (*116*). Similar effects and concerns can therefore be anticipated from other chloride-containing snow and ice control materials, namely $CaCl_2$, $MgCl_2$, and KCl.

Cain et al. (*28*) developed threshold soil concentration values from estimates of effects concentrations providing 25-percent effects level, No Observed Effects Level (NOEL) and Low Observed Effects Level (LOEL) values and critical toxicity values estimated from experimental evaluations or field sampling applications of NaCl. Threshold values for root exposure to Na ranged from 215 to 300 ppm, and for Cl was 300 ppm. Threshold values for tissue exposure to Na ranged from 200 to 650 ppm, and for Cl, values ranged from 800 to 1650 ppm.

Bright and Addison (*41*), during the development of British Columbia matrix numerical soil standards for NaCl, constructed species sensitivity distributions based on lethal impacts (LC_{20}) and non-lethal impacts (25th percentile of species sensitivities distribution based on EC_{50}) for a range of plant species. Lethal effects for NaCl in soil were developed to be 840 mg/kg (275 mg/kg Na, 425 mg/kg Cl) whereas non-lethal effects were realized at 700 mg/kg (220 mg/kg Na, 440 mg/kg Cl).

3.7.6.2 Calcium Chloride

Calcium chloride has been used as a snow and ice control chemical and as a road dust suppressant. A literature review revealed that there have been far fewer studies of the environmental impact of calcium chloride than sodium chloride. Many of the studies have evaluated the effects of calcium chloride as a dust suppressant. Although the rates and timing of application and transport mechanisms differ when comparing snow and ice control and dust suppressant use, the resulting ion-specific environmental impacts should be comparable.

Because of its widespread occurrence in rocks and soils and its ready solubility, calcium is present in nearly all waters and is more abundant than any of the other alkaline-earth metals (e.g., sodium, potassium, and magnesium). The addition of calcium from snow and ice control activities would typically be low when compared with the amount already present in the environment. In contrast, although chloride is present in all natural waters, the concentration is quite low in most areas. The primary cause of damage to roadside plants is the accumulation of chloride in plant tissues to toxic levels and, therefore, $CaCl_2$ poses a negative risk to vegetation (*62*).

Calcium is considered one of the major plant nutrients, given that it is a structural component of cell walls (*117*). Most plants have between 1 percent and 2 percent by weight of dry matter of calcium in their leaves. Calcium is a macronutrient required in larger concentrations for plant growth, and adequate plant tissue concentration is 5000 ppm (0.5 percent) (*28*). For calcium chloride to adversely affect vegetation, the calcium chloride must migrate into the soil water or groundwater or significantly increase the salinity of the soil. Elevated concentrations of $CaCl_2$ in soil cause osmotic stresses. Direct contact with the vegetation by salt spray and runoff can also cause injuries, including a general inhibition of growth, specific branch and vegetation die-off, or, in the extreme case, the death of the tree or plant. An Environment Canada study (*118*) found that most of the observed calcium chloride-induced vegetation damage has been attributed to direct contact—the absorption of salt splashed on the foliage.

A Belgian study (*119*) investigated the effect of $CaCl_2$ on four common roadside tree species. The study monitored timing of bud-break, development and spread of foliar necrosis, and changes in leaf and soil chloride content for each species. Effects varied among species, but were typically found to be a result of chloride ion concentrations.

In a study investigating $CaCl_2$ used as a dust suppressant in the Yukon, the authors reported that there had been no observed or reported instances of roadside vegetation injury or die-off related to areas where calcium chloride had been applied (*120*). $CaCl_2$ applied as a dust suppressant is not transported as splash and spray to the same degree as when it is applied for snow and ice control and any effect observed would be related to soil transport.

A European study (*121*), comparing the uptake of sodium, calcium, and magnesium chloride by spruce seedlings, concluded that the presence of calcium ions had beneficial effects on ion regulation. A reduction of accumulation of sodium in needles and young shoots occurred when calcium chloride was added to the sodium chloride. There was also a trend for reduced uptake of chloride in the presence of calcium ions compared with sodium, magnesium, or potassium.

3.7.6.3 Magnesium Chloride

Magnesium chloride has also been used in recent years both for snow and ice control and for roadway dust suppression. Few published reports directly relating to either the vegetation impacts of magnesium chloride or its environmental impact exist. Many inferences can, nevertheless, be made based on the constituent components, namely Mg and Cl. The environmental impact of magnesium chloride should be similar to that of $CaCl_2$, given that both are chloride salts, with a cation with little known specific ion adverse effects.

Magnesium is an important plant nutrient because it is an essential component of chlorophyll and is not considered toxic even at high concentrations (*35, 61, 89*). The content of magnesium in plant leaves typically ranges from 0.1 percent to 0.4 percent of dry matter (*117*).

A discussion of the potential toxicity to plants resulting from the application of liquid $MgCl_2$ as a dust suppressant is given in a report by McLaren Environmental Engineering (*122*). The author states that the potential toxicity to plants from the use of magnesium chloride is based on the type of plant and on the amount of exposure to the salt solution. Exposure to plants could occur through direct contact of magnesium chloride to plant leaves and stems or by indirect contact via increasing the concentration of soluble salts—osmotic stress impacts—within the plant root zone away from the area of application.

Direct contact of plant leaves with $MgCl_2$ would adversely affect plants by creating an osmotic imbalance and subsequent dehydration, resulting ultimately in defoliation of the plant. The primary effect of increased concentrations of soluble salt in the plant root zone, which could occur from magnesium chloride application, is also osmotic, because high salt concentrations make it difficult for the plant to obtain water for growth. Excessive magnesium levels can also cause nutritional imbalances in plants. For example, excessive levels of magnesium in soil may produce calcium deficiencies in plants (*89*).

In summary, the few published articles dealing with $MgCl_2$ applications suggest that there is a low potential for damage to vegetation. However, there have been no laboratory or field studies reported in the literature to confirm this hypothesis. Given the similarities of $MgCl_2$'s components and physical properties to those of $CaCl_2$, it is suggested that the impacts associated with $MgCl_2$ use will be very similar to $CaCl_2$ use.

3.7.6.4 Acetate Products (CMA and KA)

Acetate-based snow and ice control materials include CMA and KA. CMA was developed in the early 1980s as an alternative to chloride-based snow and ice control chemicals, whereas KA has seen use for airport deicing. Both these products partially consist of an acetate anion component and associated cations: Mg, Ca, and K. Any effects directly associated with these cations as components of $CaCl_2$ or $MgCl_2$ can be related to CMA use. Potential effects include osmotic stress and some ion-specific impacts.

Extensive studies have been conducted to evaluate the effects of CMA on terrestrial vegetation (*36, 91*) and preliminary laboratory tests and literature reviews indicated that CMA is harmless to plants. Winters et al. (*91*) conducted (1) tests using foliar spray applications to potted plants and (2) soil-leaching experiments. The results demonstrated that CMA was less harmful to plants than NaCl. Of the 18 tree species tested, only 1, the Russian olive, was damaged more by CMA than NaCl. Horner (*36*) conducted a laboratory study consisting of various applications of CMA to vegetation by spraying and flooding and found CMA did not affect the yield, cover, vigor, or rooting of various herbaceous and woody plants. All species tested withstood root zone applications of up to 2500 mg/L, which is a much higher concentration than expected from routine deicing treatments. Concentrations of 5,000 and 10,000 mg/L reduced yield or killed the plants tested. Horner further concluded that CMA at concentrations used for snow and ice control does not harm terrestrial vegetation, except when concentrations in the root zone are high enough to cause osmotic stress in the root zone.

Transport Canada (*123*) conducted field tests to compare the environmental impact of KA with other deicers at Halifax airport from 1990 through 1994. A limited number of tests were done to evaluate the effects of KA on vegetation. Greenhouse growth studies indicated little or no inhibition of surface vegetative growth when KA was added at concentrations likely to be encountered during normal operating conditions (i.e., below 500 mg solids/L). However, at concentrations approximately double this (1000 mg/L), there was almost a 50-percent inhibition of growth.

3.7.6.5 Organic Products

Few assessments have looked at the effects of organic-based snow and ice control materials on vegetation. This is perhaps a result of the number and variability of available proprietary products. Many of these products are biodegradable, and it is generally assumed that they pose minimal concern for vegetation when compared with other types of snow and ice control materials. Many of the organic corrosion inhibitors contain appreciable concentrations of phosphorus, a plant nutrient that can stimulate growth in small quantities. These products have also been shown to contain high levels of ammonia, which also can serve as a plant nutrient to stimulate plant growth.

3.7.6.6 Other Materials (Urea, Potassium Carbonate)

Monitoring of urea used at airports has shown no negative effect to vegetation because chemically, urea breaks down as urea molecules, as opposed to chlorides (*29*). The drawback of urea is the excessive fertilization it causes at the roadside (*31*). Excessive nitrogen levels can also result in increased thatch build-up and the possible incidence of more insects and disease. As well, at pH values greater than 7.5, ammonia gas can be generated. This ammonia gas will usually dissolve in the available soil water or adsorb to soil particles and not pose any problems. If conditions are dry, however, free ammonia gas can persist in the soil pore space, and this can damage plant roots when fertilizer has been banded near the root system.

An Austrian study found the application of up to $100\ gm^{-2}yr^{-1}$ K_2CO_3 exerted a fertilizing effect on a test plot, with slightly higher biomass yields than the untreated control (*93*). When application was increased to $200\ gm^{-2}yr^{-1}$ K_2CO_3, the fertilizing effect disappeared. When annual doses of 200 to 400 $gm^{-2}yr^{-1}$ K_2CO_3 were applied, biomass dropped by 23 percent. In comparison, annual doses of 200 to 400 $gm^{-2}yr^{-1}$ NaCl reduced biomass yield by up to 41 percent. This study also found that, over time, accumulation of K_2CO_3 led to osmotic stress in the plants that led to cellular adjustments made at the expense of growth.

Snow and ice control materials may render certain metals more available for uptake by plant roots, possibly resulting in plant toxicity, depending on the type and amount of metals present in the soil (*28*). Limited information is available on the effects of heavy metals associated with snow and ice control materials on roadside vegetation.

3.7.6.7 Abrasives

Use of abrasives for snow and ice control can stress and smother roadside vegetation. Small particles can adhere to the stomates and affect the regulation of oxygen, carbon dioxide, and water vapor between the plant and the atmosphere. Fischel (*69*) cited information from Audesirk and Audesirk (*124*) indicating that blocked stomates can also reduce or inhibit photosynthesis and can prevent the plant from adsorbing nutrients from the soil.

3.7.7 Conclusion

An assessment of the gathered information suggests that most impacts associated with roadside vegetation impairment can be linked to (1) extremely high levels of ions contacting foliage and/or the root zone and (2) ion-specific damage related to chloride ions. As a result, most highway agencies are faced with either accepting some degree of salt-related vegetation damage or modifying operations to reduce the amounts of detrimental materials reaching vegetation.

Cain et al. (*28*) summarized the zone of impact as linear along highways with the effect from aerial dispersion of NaCl extending up to about 40 to 100 meters from the road edge, although this depends on local conditions such as salt load, traffic volume and velocity, local topography, and prevailing winds. Effects on woody communities have been noted up to 100 meters, and severe effects have been noted up to 40 meters. Elevated soil levels of roadsalts normally occur up to the first 10 to 20 meters of the highway or along paths of overland drainage and this is where most effect occurs.

Effects associated with roadside vegetation impairment from snow and ice control materials are linked to extremely high levels of ions contacting foliage and roots and damage related to elevated chloride levels. Vegetation damage is of greatest concern within the primary material deposition zone 10 meters from the roadway. Although certain types of vegetation are more tolerant to these stresses than others, a conservative approach ensures the greatest level of environmental protection.

Chloride materials have the greatest potential to impair vegetation. Sodium can degrade soil structure, which can impede water uptake and root growth. Evidence suggests that acetate materials can also affect vegetation through osmotic stress damage, although this does not occur to the same degree as for chlorides. It is generally agreed that OMB materials pose minimal concern to vegetation when compared with inorganic salts. Abrasives are not completely innocuous—they can cause smothering concerns in some instances.

It is suggested that a wide range of stressors not related to snow and ice control already affects the roadside environment and, in certain cases, the species present are not necessarily indicative of the "natural" population through which the road passes. Therefore, some damage may be manageable. That being said, it is better that the snow and ice control practices used reduce the amounts of detrimental products being transported to the vegetation.

3.8 Air Quality

With conventional snow and ice control products such as abrasive/salt mixtures, airborne fine particulate from the entrainment of dried abrasives and salt left on roadways can contribute to local air quality deterioration and may even affect the health of some members of the population. Fine particulate can penetrate deep inside the lungs, resulting in respiratory damage. Airborne particulate may also cause visibility deterioration in an area. The U.S. EPA standard for PM-10 is 50 $\mu g/m^3$ annually, and 150 $\mu g/m^2$ (in a 24-hour period) with three allowable exceedances over a 3-year period (*69*). Mountain regions typically contain localized air sheds that have limited recharge and are of particular concern for air quality issues. The survey conducted for this report (see Section 2.4.2.1) returned similar findings: transportation agencies in the mountainous western United States listed air quality as a primary environmental concern related to snow and ice control materials.

The City of Boulder, Colorado, found that vehicles contributed to 87 percent of particulate matter less than 10 (m in diameter (PM-10) and that most of this (90 percent) consists of road dust and sand thrown in the air by passing vehicles (*125*). The percentage of total PM-10 emissions from road dust has been shown to increase between 50 percent to 90 percent during the 24-hour period following road sanding (*69*).

Denver has poor air dispersion during the winter months and was designated to be in non-attainment for the PM-10 standard with the passage of the Clean Air Act Amendments of 1990 (*126*). Testing of filter samples in the Denver area showed that a large fraction of the particulate problem resulted from re-entrained road dust. Denver historically relied on abrasives for winter maintenance, but improved air quality by using a harder sanding material (less prone to crushing from vehicle action) and incorporating liquid snow and ice control materials in some areas.

An Idaho DOT study (*15*) found abrasive use to be reduced by 86 percent after traditional methods (deicing using NaCl and abrasives) were replaced with liquid chemical anti-icing. Similarly, a Colorado study (*13*) investigating the effects of abrasive use on air quality cited a general improvement in air quality as shown by the fact that Colorado has not exceeded a U.S. EPA PM-10 standard for seven winters. This improvement correlated with a shift in winter maintenance activities, away from abrasive use, toward snow and ice control chemicals.

There is limited information assessing the effect of both dry and liquid snow and ice control chemicals on air quality. It is generally thought that use of these materials has a net benefit on air quality. Newer application methods (e.g., anti-icing and pre-wetting) can also lead to significant reductions in abrasive use. It is possible that liquid products can dry and be re-suspended or be released as an aerosol, potentially causing localized air quality concerns. This is likely more of a concern for NaCl than for $MgCl_2$ and $CaCl_2$, both of which are hygroscopic and will tend to retain water, potentially preventing re-entrainment.

Accounts of lung, skin, and eye irritation have been linked to aerosols and spray produced by roadsalts. Data shown in Table 3-13 indicates that snow and ice control materials can cause some level of inhalation irritation. The extent or magnitude of impact of these pathways has not been well developed.

In general, use of abrasives can result in air quality degradation because of increases in airborne fine particulate. This is particularly true in areas with limited recharge or existing air quality issues. Therefore, reduced use of abrasives will result in reduced airborne fine particulate and improved air quality. Application strategies such as anti-icing and pre-wetting, and use of liquid snow and ice control chemicals may significantly reduce abrasive application quantities.

Table 3-13. Rat toxicity data (LD_{50}) for selected liquid deicers.

Chemical	LD_{50} [mg/kg] (rats)
Magnesium Chloride	8100
CMA	3150
Calcium Chloride	4000
Sodium Chloride	3750
Potassium Acetate	3250

Adapted from (*81, 131*)

3.9 Animals

Impairments to animal populations from roadsalts have included traffic hazards caused by salt-hungry animals as they seek roadside salt accumulation (*19*). It is also speculated through repeated observations of apparent behavioral toxicity as well as new information on the toxicology of oral salt ingestion in birds that salt toxicity per se is contributing to the vulnerability of birds to road traffic (*127*).

3.9.1 Wildlife

Sodium is an indispensable component of physiological processes in all vertebrates, but is toxic when taken in excess. Animal tolerance to salt is usually quite high, although increased concentrations of salt can cause concerns in smaller animals. Some wildlife species actively seek out sources of salt to ingest, most notably large ungulates such as moose, deer, elk, and bighorn sheep. Roadways with applied salt are an obvious source for these animals.

The predominant hazard that roadsalt poses to animals has been expressed to be vehicle injury when these animals are attracted to salt residuals on the roadside. Roadsalt attraction has been identified as a contributor to vehicular kills of bighorn sheep and elk in Jasper National Park (*127*) and to moose-vehicle accidents in northern Ontario and Quebec (*19*).

The peak volume for moose sightings near roadways and for moose-vehicle accidents occurs in the spring, which is when roadway salt is abundant in roadside puddles—researchers believe that moose are attracted to these accumulations because of the increased dietary need for salt owing to horn growth in males and lactation in females (*128*). Fraser (*129*) found that 70 percent of moose-vehicle accidents in northern Ontario occurred between May and June. It has been expressed that when moose are drinking salty water, they tend to lose their fear of humans and vehicles (*19*). Deer have also been reported to exhibit similar behavior.

The Wisconsin DOT has monitored motor vehicle-deer accidents beginning in 1979 (*130*) and its findings contradict those of Fraser (*129*). Findings indicate that deer crashes peak during October–November (38.1 percent of annual crashes) with a secondary peak in May–June (16.2 percent of annual crashes). The high incidence of crashes during the October–November period does not coincide with normal roadway snow and ice control activities and is suggested to be related to behavioral changes associated with mating.

It is not known what the effect on other small mammals may be. The only documented study found was in a review by Jones et al. (*19*) that observed salt toxicosis in cottontail rabbits in Wisconsin. Laboratory experiments testing for salt tolerance showed behavioral symptoms characterized by depression and thirst, followed by excitement, tremors, torticillis, opisthotonus, retropulsion, complete incoordination, coma, and eventually death. Examination of the specimens also found similar physiological impairments.

Jones et al. (*19*) also cited studies that assessed the effects of salts in domestic animals. Sheep were able to tolerate saltwater concentrations up to 13,000 mg/L of NaCl, much higher than would be expected to result from roadsalt application. With turkeys and chickens, very high levels of NaCl were required to cause death—levels up to 4,500 mg/L and 5,000 mg/L in food respectively. Swine, cattle, and horses have also been shown to be quite tolerant to high levels of salt. The reports of salt toxicosis in free-ranging vertebrate wildlife have been the result of exposure to roadsalt, drought, ice, hypersaline lakes, and discharge ponds for various industries. In most cases, it was found that drinking more water could compensate for salt overdoses.

3.9.2 Birds

An extensive literature review assessing the effects of roadsalts on birds was conducted for Environment Canada by Brownlee et al. (*127*). In the literature, 12 published reports were found associating bird kills with salted roads. Two incidents were formally diagnosed as salt poisoning and observations of potentially aberrant behavior suggestive of toxicosis were made in several other cases. Brownlee et al. (*127*) found several authors made observations that birds exhibited behavioral deficits—most commonly unusual fearlessness and could be approached easily—related to salt ingestion. These severe behavioral impairments were observed as well as the finding of elevated brain sodium levels. The most common observation of unusual fearlessness documented in both birds and mammals could be an early symptom of intoxication or it could be the manifestation of animals under extreme salt hunger modifying their usual behavior toward potential danger (*127*).

It is often assumed that salt is ingested in order to fulfill a physiological need associated with a largely vegetarian diet. However, the taking of salt crystals as grit (in order to aid in grinding food and to provide supplementary minerals in birds with low-calcium diets) cannot be ruled out (*127*). Birds select grit on the basis of size, color, and shape, and crushed salt particles are irregular in shape and translucent to white in appearance, characteristics that have been observed to be features of choice in tests carried out with House sparrows. Particle sizes of normally applied NaCl roadsalt (between 1 to 10 mm) overlap broadly with the preferred grit size for the birds.

Finches tend to be the most susceptible to salt ingestion. Brownlee et al. (*127*) determined that as few as 3 cubic or 5 spherical 2.4-mm salt particles could provide a lethal dose to a Cardueline Finch. Birds can be sub-lethally impaired following ingestion of a single salt particle and could be killed by as few as two particles. Birds are at a higher risk of salt toxicosis when water availability is reduced during severe winters (*19*). Melted snow on the roadway may be the most obtainable source of water, which depending on the concentration of salt may compound the problem.

Conclusions from the review conducted by Brownlee et al. (*127*) suggest that the contribution of roadsalt to wildlife kills has long been underestimated by wildlife managers and transportation officials.

3.9.3 Toxic Effects

The acute oral toxicity level of a chemical is an indicator of its toxicity and can be expressed as a LD_{50} value. This value is the dosage which is fatal to half of the test animal population. The higher the LD_{50} value the less toxic the chemical. The acute oral toxicity in rats for several chemicals present in snow and ice control formulations is listed in Table 3-14.

Using rats as test subjects Hiatt (*131*) compared acute toxicities for CMA and NaCl in Table 3-13. CMA exhibited similar toxicity to NaCl for acute oral toxicity, as well as skin and eye irritation potential. No inhalation or dermal toxicity was available for NaCl at the time of study; CMA exhibited low toxicity by both of these routes of exposure. For the subchronic oral toxicity test, CMA produces no toxicity at a “limit” testing dose, thus indicating low toxicity upon repeated exposure.

LD_{50} values (rats) in the range of 500 to 5,000 mg/kg are considered slightly toxic, whereas values within the 5,000 to 15,000 mg/kg range are practically non-toxic (*131*). Although the table shows that chloride deicers are slightly toxic to rats, tolerance in animals is related to body size. Animals have a relatively high tolerance for elevated chloride levels and, if adequate drinking water is available, ingestion of excessive chlorides should not adversely affect wildlife and birds (*120*).

3.9.4 Bioaccumulation of Heavy Metals

As discussed in Section 3.5, heavy metal ions can be displaced by specific ions such as calcium and magnesium. These metal ions may bioaccumulate in the food chain (*81*); however, information is lacking in public literature relating this potential effect to snow and ice control materials.

Table 3-14. Comparative acute toxicity of select snow and ice control materials.

Toxic Effect	NaCl	CMA	$CaCl_2$	$MgCl_2$	Description
Acute Oral Toxicity LD_{50}	3,150 mg/kg Slightly toxic	3,750 mg/kg Slightly toxic	1000-2000 mg/kg Slightly toxic	4000-8,100 mg/kg	Test relevant to occasional human over-exposure.
Acute Inhalation Toxicity LD_{50}	N/A	> 5000 mg/m^3	Corrosive	Non-irritating	Toxicity test with exposure from breathing.
Eye Irritation	Mild to moderate irritant	Moderate irritant	Corrosive	Slight irritant	Measures irritation or damage from direct eye contact.
Skin Irritation	Non-irritating	Mildly irritating	N/A	N/A	Tests ability to irritate or damage skin on contact.
Acute Dermal Toxicity LD_{50}	N/A	> 5000 mg/kg	Corrosive	Minor irritation	Tests whether absorption of enough compound across the skin can lead to systemic toxicity.
Dermal Sensitization	None found in literature	No reaction	N/A	N/A	Predicts ability to elicit allergic skin reactions.

Adapted from (*131*), (*81*)

3.9.5 Conclusions

Snow and ice control materials have been linked to reports of salt toxicosis from ingestion and to reports of increases in vehicle-animal collisions. Some information suggests salt toxicosis from ingestion is a concern for small animals such as birds, although most terrestrial animals have high salt tolerances, especially when adequate drinking water is available. It is unclear whether snow and ice control materials increase vehicle-animal collision rates. Some research supports this, but most current information suggests other conditions contribute much more significantly to vehicle-animal collisions.

3.10 Human Health and Exposure

Snow and ice control materials can affect human health through three main routes: ingestion, inhalation, and dermal contact. The degree of potential harmful impact is further influenced by factors such as the chemical concentration (dose), duration of exposure, frequency of exposure, and individual variability (*16*).

Indoor air quality associated with snow and ice control material storage, and processing also affects workers' health and exposure. If the product is shipped to the user in powder/solid form, dust may be generated during the preparation of the liquid formulation. Manufacturers and suppliers typically recommend ventilated storage and processing areas on MSDS sheets. Although most liquid snow and ice control formulations are generally considered non-toxic and are only mildly irritating, recommended handling practices by suppliers should be followed to minimize workers' exposure. Indoor air quality data is generally lacking in published literature because effects tend to be site-specific.

Toxicity is the measure of the capability of a chemical to cause injury. Toxicity parameters including acute oral toxicity, acute inhalation toxicity, acute dermal toxicity, eye irritation, skin irritation, and sub-chronic oral toxicity have been reported for several chemicals used in deicer formulations and are provided in Table 3-13. For oral toxicity, the LD_{50} value given in Table 3-13 represents the chemical dosage predicted to be fatal to one-half of the animals tested. Chemicals with lower LD_{50} values are more toxic.

Caution should be exercised in extrapolating or comparing toxicological data presented in Table 3-13 and 3-14 given that some of the data was based on tests on commercial deicing formulations while other results were generated using the solid/pure form of the deicing chemical. In addition, the toxicities of other additives or impurities present in deicing formulations have not been investigated. Hence, a more in-depth examination of the published toxicity data is warranted. Human health concerns associated with handling of snow and ice control materials are associated with very high doses and any real concerns can easily be mitigated by using proper safety measures (e.g., protective clothing and ventilation).

CHAPTER 4

Impacts to Infrastructure and Vehicles

4.1 Concrete and Concrete Infrastructure

Snow and ice control chemicals are known to affect concrete structures—either through deterioration of the concrete paste or corrosion of the reinforcing steel. Corrosion of reinforcing steel has typically been the primary deterioration mechanism and has been linked to use of chloride-based snow and ice control chemicals such as NaCl, $CaCl_2$, and $MgCl_2$. NaCl has been the most widely used salt, although $CaCl_2$ and $MgCl_2$ use has increased in recent years. There have been claims regarding the relative corrosion of these products; however, there is some disagreement in the literature.

Regardless of the chloride-based salt used, corrosion of reinforcing steel is inevitable, although the time to corrosion initiation or rate may vary by product. To address these effects, alternative non-chloride snow and ice control chemicals have been introduced. Various research has been conducted on these chemicals—significant efforts have been conducted on calcium-magnesium-acetate (CMA). Urea, potassium acetate, and glycols have been widely used for airports; however, their associated costs have limited their use on roadways. The level of research investigating the effects on concrete is limited, but considering that these chemicals are used because they are non-corrosive to aircraft parts, their effect on reinforced concrete is probably not detrimental.

NaCl has been used for more than 50 years and associated long-term effects to reinforced concrete are fairly well understood. Although there has been extensive research into the use of alternative materials (e.g., $MgCl_2$, $CaCl_2$, and CMA), there is limited data about their long-term effects. This literature review emphasizes the effects of corrosion on reinforcing steel. The effects on concrete are addressed to a lesser extent.

Concrete is a composite material consisting of stone and sand held together in a matrix of hydrated cement paste. The cement paste is porous and, under normal ambient conditions, the pores are filled with a highly concentrated solution of ions that dissolve from the cement. The two major components of the hydrated cement paste are calcium-silicate-hydrate (C-S-H) and calcium hydroxide [$Ca(OH)_2$]. The C-S-H phase provides the bond strength of concrete. The $Ca(OH)_2$ does not contribute significantly to the strength, but buffers the pH of the pore solution to about 12.5. At this pH level, a protective oxide film forms at the steel surface (passive layer), reducing corrosion rates to negligible levels in the absence of chlorides.

Winter conditions (i.e., freezing and thawing cycles and application of chloride-based snow and ice control chemicals) can affect the durability of reinforced concrete in several ways:

- Physical deterioration of the concrete surface through scaling,
- Chemical reactions between the salt and the cement paste or aggregates causing degradation of the cement paste, and
- Diffusion of chloride ions resulting in corrosion of the reinforcing steel.

Chloride-containing snow and ice control materials are the predominant materials used for snow and ice control, and chloride ion concentration in concrete is a widely used measure of assessing corrosion-related problems. Chloride-containing materials will be discussed with respect to chloride diffusion properties, corrosion problems, and effects on the concrete matrix. Effects of non-chloride snow and ice control materials will be discussed with respect to reinforcing steel corrosion and concrete degradation. Limited information is available for many of these materials and their ability to corrode reinforcing steel—probably because of their limited use when compared with chloride products and because they contain no measurable common corrosion indicator, such as chloride.

4.1.1 Corrosion of Concrete-Embedded Reinforcing Steel

Reinforcing steel embedded in concrete is protected against corrosion by the high alkalinity (pH > 12.5) of the concrete pore solution, consisting of saturated $Ca(OH)_2$, sodium ions, and potassium ions. The high pH induces a "passive" layer (i.e., chemical coating) on the surface of the reinforcing steel, reducing the rate of corrosion to negligible levels—the concrete acts as a chemical as well as a physical barrier. The breakdown of the passive layer initiates active corrosion on the reinforcing steel and can be caused by the following (*132*):

1. Chloride-induced corrosion;
2. Neutralization (pH reduction) of the concrete paste following exchange between Ca^{2+} and Mg^{2+} ions; and
3. Carbonation-induced corrosion, which is a reaction of the cement paste with atmospheric carbon dioxide.

When discussing snow and ice control materials, only chloride-induced corrosion and neutralization are of concern. Carbonation, although possible in addition to the other mechanisms, is not normally a problem with the quality of concrete used in bridge decks and will not be considered further here.

4.1.1.1 Chloride-Induced Corrosion

Chloride-induced corrosion of reinforcing steel is the most widely occurring cause of concrete deterioration and is well documented in the literature. Chloride-induced corrosion poses the highest risk to structural integrity because it causes a very localized attack of the steel, referred to as "pitting corrosion" (*132*). Chloride-induced corrosion is also considered the major cause of corrosion of reinforcing steel in concrete resulting in high cost for maintenance and repairs (*133*). When considering corrosion to concrete reinforcing steel, chloride ions can be introduced from two general sources:

1. Contaminants in the concrete mix, unintentionally from mix water or aggregates, or intentionally such as for an accelerator (e.g., $CaCl_2$); and
2. Exposure of hardened concrete to environmental conditions (e.g., sea water or snow and ice control salts), allowing ingress of chlorides into the pore structure of the concrete.

Chloride-induced corrosion is extremely complex and not fully understood. It is assumed that chloride ions destroy the passive layer that forms on reinforced steel (depassivation) by replacing some of the oxides in the passive film, which further causes an increase in ion solubility and conductivity in the concrete cover (*132, 134*). Without the passive layer, corrosion can occur if sufficient water and oxygen are available. Chloride-induced corrosion mainly causes pitting corrosion with local anodic and cathodic areas along the rebar (see Figure 4-1).

The localized small anodic areas will dissolve at a low potential, whereas the larger passive area of the steel acts as a cathode where oxygen reduction takes place at a comparatively higher potential, creating a galvanic cell on a very small scale. This localization is promoted by the typically uneven distribution of chlorides in the concrete. The rate at which the dissolution of iron will progress depends on the cathode-to-anode ratio, the electrical resistivity of the concrete, chloride concentration, and availability of oxygen. This localized attack is particularly dangerous because typical signs of corrosion are not readily visible—general expansion resulting in cracking of the concrete cover may not occur.

If occurring over a longer section of bar, cracking of the concrete cover occurs as a result of the volume of the corrosion products (i.e., various forms of iron oxide) that is several times greater than that of iron. The tensile forces exerted on the concrete are large enough to cause cracking of the

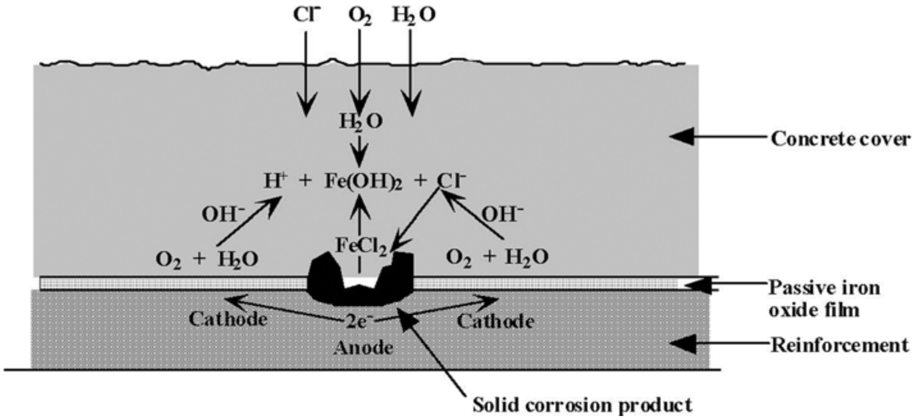


Figure 4-1. Localized chloride-induced pitting corrosion of steel in concrete.

concrete cover, delaminations, and, ultimately, spalling of the concrete.

The typical threshold value (concentration) for chloride in concrete to initiate rebar corrosion of black steel is 0.4 percent by weight of cement; however, values as low as 0.15 percent may be considered dangerous. The threshold value by weight of cement may be hard to determine for real structures, because the cement content of the concrete may be unknown. Typically, threshold values for chloride-induced corrosion range from 0.025 to 0.040 percent by mass of concrete.

The chloride threshold value also depends somewhat on the pH of the concrete pore solution at the reinforcing steel level. Both $MgCl_2$ and $CaCl_2$ cause a drop in concrete paste pH, whereas NaCl raises the pH (*135*). This suggests that the chloride threshold for NaCl may be somewhat higher than for $MgCl_2$ and $CaCl_2$. However, this argument requires that the cation diffuses through the concrete at a rate similar to that of chloride. If the diffusion rate of the cation is lower than for chloride, the pH effects will not necessarily influence the corrosion initiation threshold value.

Considering that chloride-induced corrosion is independent of the associated cation, there is no reason to consider any relative differences in corrosivity between various chloride salts—the steel does not differentiate between the source of chloride. The amount of chlorides that will penetrate the concrete and their rate of penetration do, however, affect corrosion. This process depends on the amounts of materials applied as well as the type of application (i.e., liquid versus solid). When applying chlorides in solid form, a large amount may be blown off the roadway by wind or passing cars, whereas spray-applied brine will adhere to the roadway for extended periods. Surface concentration of materials can be further affected by washoff from precipitation. It is, therefore, difficult to estimate the chloride loading accurately when using different types of applications.

4.1.1.2 Chloride Diffusion Properties

The initiation of reinforcing steel corrosion depends on the ingress of detrimental chemicals, such as chlorides, through the concrete cover. Thus, the rate at which these chemicals penetrate the concrete determines the time at which the steel will start to corrode. In some cases, the initiation time is considered the end of the service life of a structure, regardless of the rate at which the steel is corroding.

Chloride is a relatively small, negatively charged anion that can diffuse through concrete as a result of concentration gradients—chloride ions will tend to move away from areas of high concentration. The pore structure and micro-cracks that are always present in concrete can influence chloride penetration significantly. However, chloride diffusion through concrete has been shown to not only depend on the quality of the concrete but also on the type of salt used. Chloride penetration thorough larger (macro) cracks is typically much greater because such cracks allow passage for water and salts. These cracks can be a result of shrinkage, loading, and corrosion.

Two experimental laboratory studies have determined diffusion coefficients to be greatest for $MgCl_2$, less so for $CaCl_2$, and lowest for NaCl (*136, 137*). For ordinary Portland cement (OPC) mortar samples, the effective diffusion coefficient of $MgCl_2$ was about 3 times greater than that of NaCl, and $CaCl_2$ was about 2.5 times greater that that of NaCl (Table 4-1). When using slag-blended cement, the effective diffusion coefficient is significantly smaller for all three salts used, although the same ranking of the salts exists (Table 4-1). The lower diffusion rates when using slag-blended cement can be attributed to the much denser pore structure that occurs—an average pore radius of 16 nm for slag-blended cement versus 31 nm, at the same overall concrete porosity (*136*). Other supplementary materials (e.g., fly ash and silica fume) will have similar effects on the permeability of concrete.

The ranking of diffusion coefficients between the two studies also appears to be independent of the salt concentrations used. While Deja and Loj (*136*) used saturated solution concentrations (36 percent NaCl, 34 percent $CaCl_2$, and 29 percent $MgCl_2$), Kondo et al. (*137*) used 0.5 M solutions (2.6 percent NaCl, 5.5 percent $CaCl_2$, and 4.8 percent $MgCl_2$)—almost 10 times more dilute. In a laboratory study conducted by Callahan (*140*), it was also determined that $CaCl_2$ penetrated concrete faster than NaCl when using the ASTM G 109 ponding test.

The water-to-cement (w/c) ratio of the mortar mixes used in Deja and Loj's (*136*) research was 0.5, whereas the w/c ratio of the pastes used by Kondo et al. was not stated. As mentioned, when using slag-blended cement, the variation between the different salts is much smaller. This suggests that the quality and type of concrete mix should be considered

Table 4-1. Chloride diffusion coefficients for different salts.

Salt Type	Diffusion Coefficient (m^2/s) x 10^{-12}		
	OPC Mortar (*138*)	Slag Blended Cement Mortar (*138*)	OPC Paste (*139*)
NaCl	9.1	1.4	6.6
$CaCl_2$	22.9	1.5	9.9
$MgCl_2$	29.0	1.8	20.8

when selecting snow and ice control chemicals. It is likely that a high-quality concrete mix with a w/c ratio of less than 0.40 will result in lower diffusion coefficients.

Diffusion of chloride in porous materials (i.e., concrete) has also been linked to moisture content. Experimental diffusion coefficients can vary between 2.7×10^{-12} and 12.9×10^{-12} m^2/s, where increased saturation is associated with higher diffusion rates (*141*). This suggests that chloride ions can penetrate faster when the concrete remains moist.

A field study by the Montana DOT Engineering Division showed chloride diffusion rates in concrete to be more than twice as high in areas where both $MgCl_2$ and NaCl were used than in areas where only NaCl was applied (*142*). Diffusion coefficients were calculated based on chloride sampling at various depths of bridge decks for twenty bridges along a 100-km-long stretch of Interstate 90 in western Montana. Fifty kilometers (ten bridges) of the highway were exposed to NaCl only and fifty kilometers (ten bridges) were exposed to $MgCl_2$ and NaCl since about 1989. Diffusion coefficients for $MgCl_2$ were calculated to be 120 percent greater than for NaCl (1.81×10^{-12} compared with 0.82×10^{-12} m^2/s). There was some variation in the results of this study, depending on the sampling location—higher diffusion coefficient values were determined for wheel paths than for other locations of the roadway. These results are comparable in magnitude to the laboratory results of the blended cements, suggesting that realistic mix design properties are required in laboratory studies to allow extrapolation to "real" structures. There is also a good correlation of the relative ratios between salt types and the field and the laboratory studies, further indicating that $MgCl_2$ has a diffusion coefficient between 2 and 3 times greater than that for NaCl.

Several problems have been suggested regarding the validity of the conclusions of the Montana study (*143*). The section of the highway exposed to $MgCl_2$ is subject to more severe weather conditions—about twice as much precipitation—and is at higher elevations than the section exposed to NaCl only. It is difficult to comment on the rebuttal by Williams without being able to verify either application rates or possible sampling variations. However, application rates will affect surface chloride concentration, unless they were at saturation levels. Larger amounts of snow and associated flushing by meltwater or more rainfall during the summer were presented as plausible explanations. Considering the results of the study in the context of laboratory studies, the findings are not unrealistic. Higher chloride diffusion rate test results attributed to $MgCl_2$ are supported by the fact that $MgCl_2$ opens up the concrete pore structure (*144*). In addition, possible deterioration of the microstructure, including micro-cracking as a result of mineral growth, can increase concrete permeability and cause a higher rate of chloride diffusion (*145*).

Similar observations were made by Arya et al. (*146*) when submerging concrete samples in salt solutions. Although no diffusion coefficients were determined, chloride contents in the samples varied considerably with the different salt types (Table 4-2). Furthermore, the percentage of bound chlorides was higher for $MgCl_2$ than for $CaCl_2$ and for NaCl—probably because of the more readily occurring chemical reactions of the Mg^{2+} with the cement paste phases. The age of the samples at the time of exposure was only 2 days and 6-mm-thick cement paste discs of 49 mm diameter were used. These very immature and thin specimens were used to achieve rapid saturation as well as to minimize damage to the pore structure. Other experiments in the same study showed that curing time and w/c ratios had little influence on chloride binding.

The Montana DOT field study (*142*) supports the laboratory test results, suggesting that real conditions are very similar to observations made in the laboratory; however, there are several problems in making reliable predictions for possible service life (e.g., high w/c ratios, sample size, sample age, and the use of mortar or cement paste instead of concrete). Although it is not possible to determine an exact time to corrosion initiation reliably, a relative comparison is possible based on the findings of these studies. Rather than using the diffusion coefficients derived in the laboratory and in the field study as absolute values, they should be considered in relative terms—the ratio of D_{Mg}/D_{Na}.

The following limitations should be considered when translating the laboratory results to practical applications:

- Cement paste and mortar was used instead of concrete;
- Sample sizes were typically small;

Table 4-2. Effect of cation binding in OPC paste.

	Chloride content (% by weight of cement)		
	NaCl	$CaCl_2$	$MgCl_2$
Free chlorides	0.831	0.765	1.480
Bound chlorides	0.804	1.408	2.347
Total chlorides	1.635	2.173	3.827
Bound/total (%)	50	65	61

Source: (*146*)
w/c = 0.5, samples immersed in 20g Cl^-/L solution

- Experimental w/c ratios were greater than for typical mix designs;
- Chloride concentrations were not necessarily representative of application concentrations; and
- Exposure conditions (e.g., temperature, precipitation) were not representative of natural conditions.

The above-referenced laboratory studies and field study suggest that chlorides associated with $MgCl_2$ diffuse through concrete at the greatest rate, followed by chloride associated with $CaCl_2$, then NaCl. Such differences in relative chloride diffusion rates can result in a reduction in the time to corrosion of reinforcing steel. Despite the stated limitations, the findings in these studies remain valid for practical applications, at least on a relative basis, although adjustments, particularly with respect to time, are required.

4.1.1.3 Calcium Magnesium Acetate (CMA)

There has been a significant amount of research applied to the use of CMA as a snow and ice control material. The researchers generally agree that CMA is less corrosive than chloride-based materials and may even act as a corrosion inhibitor (*147–152*). Many of the corrosion studies involving CMA were carried out on reinforcing steel bars or steel coupons directly exposed to CMA solutions, rather than embedded in concrete. These conditions are more representative of atmospheric corrosion and thus more applicable to structural steel, light standards, or automotive components and not necessarily representative of steel embedded in concrete. In these studies, CMA was found to be less corrosive than chloride salts. This led to studies where CMA was blended with NaCl to evaluate its corrosion-inhibiting qualities. Ihs and Gustafson (*149*) found that a 20/80 NaCl/CMA mixture (w/w) reduced corrosion rates by 45 percent when compared with pure NaCl when in solution. Conversely, other studies found limited corrosion inhibition in NaCl/CMA mixtures. Ushirode et al. (*153*) found CMA not to be effective as an inhibitor for NaCl concentration over 0.1 M, even at relatively high concentrations of CMA of 1.0 M.

Although steel exposed to CMA solutions corrodes at significantly lower rates than steel exposed to chlorides, it has been suggested that steel embedded in concrete may react differently. A study by Locke et al. (*151*) concluded that active corrosion rates for steel exposed to CMA solutions are about 2 to 4 times less than for steel exposed to NaCl solutions. However, possible changes in the pore solution chemistry of the cement paste may result in macrocell corrosion because of potential differences between different layers of steel. Potential shifts of more than 600 mV were observed for steel in mortar samples exposed to 10-percent CMA solutions with all potentials being in the active range, typically between –600 and –700 mV_{CSE} (*151*). These potential shifts were measured after several months of exposure. Once active corrosion of steel embedded in concrete is initiated, the corrosion rates may not differ between concrete exposed to NaCl and CMA.

These effects of macrocell corrosion have been contradicted by Chollar and Virmani (*154*), who did not measure any significant potential shifts or corrosion of reinforcing steel embedded in concrete slabs and ponded with CMA solution. Comparable slabs exposed to NaCl exhibited potential shifts of up to 500 mV over the 4-year test period. The ponding solutions used were 3-percent NaCl, 3-percent CMA, and 5-percent CMA. The slabs contained only one mat of rebar and thus macrocell effects between different layers of rebar could not be evaluated, considering the relatively small change in potential for CMA.

No studies were found in the literature measuring the diffusion rates of CMA into concrete.

Callahan (*150*) investigated the corrosion-inhibiting properties of CMA on NaCl for concrete-embedded reinforcing steel. When using the ASTM G 109 ponding test, Callahan found CMA to be ineffective as a corrosion inhibitor when using two parts of NaCl and one part of CMA (*150*).

Special Report 235 by the Transportation Research Board summarized many of the findings from previous U.S. studies and it was concluded that CMA was significantly less corrosive than chloride-based materials (*155*). Concrete deterioration was limited to salt scaling for both materials, although deterioration was somewhat more severe when using rock salt. Neither materials reportedly had any effects on the strength or hardness of the concrete (*155, 156*).

4.1.1.4 Urea

Urea is typically used as a runway deicer by airports. Its chemical composition, $CO(NH_2)_2$, suggests urea is unlikely to have any corrosive effects on steel reinforcement. There is limited literature available discussing the effect of urea on reinforced concrete, although its use as a corrosion inhibitor has been suggested. The electrochemical behavior of urea indicates that it provides protection of the steel from depassivation (*153*). However, that study showed that urea only acted as a corrosion inhibitor to NaCl concentrations of less than 0.1M. Thus the general use of chlorides mixed with urea is considered not to be effective at inhibiting corrosion.

4.1.1.5 Proprietary Products

Various proprietary salts for snow and ice control have been introduced to the market. These typically include blends of various chloride salts and may or may not include corrosion inhibitors. However, considering that the constituents of these salts are not published, research data is of limited scientific value. In many cases, the proprietary salts are closely related to the chloride salts mentioned above. Often corrosion inhibitors are added to improve corrosivity tests on metal coupon samples. However, these test procedures are not applicable to steel in concrete.

4.1.1.6 *Corrosion Inhibitors*

No literature was found that evaluated the effectiveness of corrosion inhibitors when used with snow and ice control materials at reducing corrosion of steel embedded in concrete. Inhibitor tests are typically carried out on steel coupon samples and represent atmospheric corrosion conditions. Many of the corrosion inhibitors commonly used for snow and ice control are derived from agricultural by-products—these materials tend to be highly biodegradable. As the migration properties of these and other inhibitor products are not known, their usefulness for inhibiting corrosion of steel embedded in concrete is questionable. Migrating corrosion inhibitors have been developed for application to concrete; however, these are designed to penetrate concrete through application of relatively high dosages and allowance of sufficient time to impregnate the concrete.

4.1.2 Effects of Snow and Ice Control Materials on Cement Paste

In addition to chloride-induced corrosion of steel reinforcing, snow and ice control chemicals can affect the durability of the concrete paste physically (i.e., by increasing the freezing and thawing cycles within the concrete) and chemically (i.e., by reaction of the salt with the concrete matrix) (*157, 158*).

Without salt application, scaling of concrete can occur as a result of the expansive forces of freezing pore water near the concrete surface. As the number of freeze-thaw cycles increases, so does the potential for scaling. When salts are applied to the concrete surface, they increase the frequency of freezing and thawing cycles over what would be experienced under ambient conditions. This effect occurs when the applied salt reduces the freezing point at the concrete surface, then the salt is diluted as a result of precipitation or meltwater, after which the surface water is allowed to re-freeze because of its lower salt content.

Physical effects on concrete durability appear to be independent of the type of salt used and are more a function of concrete quality (e.g., adequate air entrainment) and weather conditions (e.g., the number of freezing and thawing cycles). Although physical processes contribute to scaling, the salt-related deterioration that occurs in conjunction with this process is of primary concern. This process, termed “salt scaling” has been recognized as the main frost-related concrete deterioration problem in several countries (*157*).

Research by Lee et al. (*159*) has shown that different chloride-based snow and ice control chemicals (i.e., NaCl, $MgCl_2$, and $CaCl_2$) can cause varying degrees of damage to concrete. This is however, mainly a result of specific chemical reactions between the associated cations (i.e., Mg^{2+}, Na^+, Ca^{2+}) with various phases of the cement paste. Additionally, if reactive aggregates (e.g., dolomitic limestone) are present, deterioration from chemical reactions between the cation and the aggregate has also been observed (*159*).

4.1.2.1 *Magnesium Chloride*

Several researchers agree that $MgCl_2$ causes more severe deterioration to concrete than do NaCl or $CaCl_2$, because of the reaction of Mg^{2+} with components of the cement paste (*138, 145, 159–163*). The $MgCl_2$ reacts with the cementitious C-S-H in the cement paste to produce non-cementitious magnesium-silicate hydrate (M-S-H) and $CaCl_2$:

$$MgCl_2 + \text{C-S-H} \rightarrow \text{M-S-H} + CaCl_2$$

Additionally, $MgCl_2$ reacts with $Ca(OH)_2$ in the cement paste to produce magnesium hydroxide ($Mg(OH)_2$), also known as brucite, and $CaCl_2$:

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$$

Both of these reactions are favored because M-S-H and $Mg(OH)_2$ are thermodynamically more stable than C-S-H and $Ca(OH)_2$. The formation of M-S-H is particularly detrimental to the concrete because its lack of binding capacity weakens the cement paste, resulting in loss of strength as it replaces the C-S-H. This, combined with the expansive forces generated through $Mg(OH)_2$ formation, can accelerate concrete deterioration. Such processes eventually will lead to physical crumbling of the concrete (*145, 159, 160*). In many of the exposure tests, complete loss of concrete strength was observed (*138*).

The replacement of $Ca(OH)_2$ with $Mg(OH)_2$ will also reduce the pH of the pore solution [pH =12.6 for saturated $Ca(OH)_2$ and pH = 9.0 for saturated $Mg(OH)_2$] which, if occurring at the rebar level, will result in the loss of passivation of the steel and allow the onset of active corrosion, even in the absence of chloride ions (*164*). This effect, combined with the presence of chloride ions, will further accelerate the corrosion of the rebar. It is not known at what rate $Mg(OH)_2$ will replace $Ca(OH)_2$, specifically at the rebar level.

Although most research studying the effects of salts on concrete has used laboratory-prepared concrete specimens, the samples used by Cody et al. (*145*) were cores removed from “actual” structures in Iowa that were between 8 and 40+ years old. These cores were exposed in the laboratory to various salts and subjected to repeated freezing and thawing cycles. Deterioration from $MgCl_2$ appeared to be independent of the concrete quality, which was described as "durable" and "non-durable" service life concrete. "Durable" concrete has had a service record of more than 40 years, whereas "non-durable" concrete has had a service record of less than 15 years. The "non-durable" concrete contained relatively porous, fine-grained reactive dolomite coarse aggregate, which contains significant amounts of magnesium. All concrete types contained dolomitic limestone aggregates, because it is common throughout the State of Iowa. The Iowa study concluded that $MgCl_2$ and $CaCl_2$ caused deterioration of the concrete by (1) promoting expansion of the concrete through $Mg(OH)_2$ formation and other mineral growth and (2) chemical reactions with the cement paste, whereas NaCl proved to be less detrimental (*145*).

Experiments assessing the effects of magnesium products on concrete durability have shown that $MgCl_2$ acts differently than magnesium sulfate ($MgSO_4$) in that $MgCl_2$ causes the cement pore structure to open whereas $MgSO_4$ causes a densification (*144*). The densification caused by $MgSO_4$ results from sulfate expansion, which results in the pores being filled, before eventually causing disintegration of the cement paste. The opening of the pore structure is attributed to the leaching of $Ca(OH)_2$ during the exchange from Ca^{2+} to Mg^{2+} to form $Mg(OH)_2$, as discussed above. This was confirmed by examination using a scanning electron microscope. Similar observations were made by Wakeley et al. (*163*), although the greater porosity was only observed in the first millimeter near the surface. Magnesium hydroxychloride formed near the surface and the loss in strength was attributed to the formation of M-S-H. The researchers could not identify $Mg(OH)_2$ near the surface of the mortar specimens using energy dispersive X-ray analysis. The absence of $Mg(OH)_2$ was attributed to the $Mg(OH)_2$ phase being more transient than expected and that M-S-H formed more readily.

Helmy et al. (*165*) also determined $MgCl_2$ to be more detrimental to concrete than NaCl, even when using blended cement. The formation of $Mg(OH)_2$ and loss of strength were observed in samples exposed to $MgCl_2$ after 12 months of exposure. The samples were immersed in 4-percent solutions that were renewed every month. Specimens exposed to NaCl had higher compressive strength values than those exposed to $MgCl_2$, even higher than those exposed to freshwater after 12 months of exposure.

Conversely, Rechenberg and Sylla (*166*) found that formation of $Mg(OH)_2$ at the concrete surface acts as a protective layer, preventing the ingress of aggressive species. They observed the formation of $Mg(OH)_2$ exclusively near the surface and found no deterioration of concrete specimens (w/c ratios of 0.50 and 0.70) even after 10 years of exposure to 2,500 mg Mg^{2+}/L $MgCl_2$ solution.

Although there is some disagreement about deterioration of the cement paste, there is consensus that magnesium readily reacts with the various cement phases. Some research has found deterioration of cement paste within the concrete matrix; others observed deterioration to be limited to the surface. There also appears to be consensus that $Mg(OH)_2$ and M-S-H are the most predominant reaction products.

To date, there have not been any observed effects to "real" structures that can attribute concrete deterioration to $MgCl_2$ use. However, the relatively short experience with any $MgCl_2$ use as a snow and ice control material (approximately less than 15 years) does not allow long-term predictions to be made.

4.1.2.2 Sodium Chloride

Concrete exposed to NaCl typically showed very little surface distress from salt scaling (*138*) (*145*). Surface distress of concrete subject to freezing and thawing more likely may be caused by physical rather than chemical mechanisms if NaCl is used. This conclusion by the authors reflects the observation that 0.75 M NaCl solution caused more extensive deterioration to the concrete surface than 3.0 M NaCl did. Generally, salt scaling appears to be limited to the concrete surface when NaCl is used.

Long-term use of NaCl has not shown any deterioration or loss of strength of the cement matrix in concrete structures. Samples immersed in 4-percent NaCl solution actually had higher strength than samples exposed to freshwater after 12 months of exposure (*165*). Therefore, the primary detrimental effect of NaCl on the concrete appears to be through corrosion of the reinforcing steel.

4.1.2.3 Calcium Chloride

$CaCl_2$ has been widely used as a snow and ice control material for many years. Detrimental effects on concrete structures as a result of $CaCl_2$ use do not appear to be more significant than those of NaCl, although laboratory studies suggest that the extent of deterioration caused by $CaCl_2$ falls between the levels produced by NaCl and $MgCl_2$. Concrete samples exposed to $CaCl_2$ deteriorated in similar ways to samples exposed to $MgCl_2$, although the deterioration was slower and less severe for $CaCl_2$ (*138*) (*145*). Calcium chloride primarily affected concretes containing reactive dolomite aggregates because $CaCl_2$ enhanced the dedolomitization reactions, releasing magnesium to form $Mg(OH)_2$ and M-S-H (*159*). Considering that dolomitic limestone is not used in all jurisdictions, there is less concern over this type of deterioration.

Cody et al. (*145*) concluded that $MgCl_2$ and $CaCl_2$ most likely will cause long-term deterioration in the concrete when compared with NaCl; however, a relationship between "real" applications and laboratory data could not be established. There is no evidence of more pronounced deterioration on concrete structures in areas where $CaCl_2$ has been applied for several years.

4.1.2.4 Calcium Magnesium Acetate (CMA)

Although most of the earlier studies involving CMA have focused on its effects on steel corrosion, there is limited information about its effect on the concrete itself. There is disagreement about its effects on the durability of the concrete, especially when considering potentially detrimental effects of magnesium on the cement paste matrix (see Section 4.1.2.1) (*149, 167, 168*).

Ihs and Gustafson (*149*) found that, compared with NaCl, surface scaling of concrete was reduced when using CMA. A similar observation was made for CMA by Peterson (*167*), who found that a layer of $Mg(OH)_2$ formed at the concrete surface exposed to CMA. Similar to all magnesium salts, it was found that CMA causes a dissolution of hardened cement paste, although the dissolution depended on temperature—the dissolution was very slow at 5°C and rapid at 20°C.

A laboratory study by the Ministry of Transportation of Ontario (*169*) concluded that good-quality concrete resisted scaling by both NaCl and CMA. Less scaling was observed when using CMA (compared with NaCl) on lower quality concrete mixes that tended to scale. A further field study by the Ministry of Transportation of Ontario did not identify any detrimental effects of CMA on concrete surfaces or corrosion, although the study period was limited to the winter of 1986–87 (*170*).

In contrast with the previous studies, Santagata and Collepardi (*168*) found the cement matrix of concrete can be severely attacked by CMA and exposures of air-entrained concrete with a w/c ratio of 0.45 percent to a 25-percent CMA solution resulted in significant degradation of the concrete. This led to compressive strength losses of up to 50 percent. When using slag-blended cement (i.e., 40-percent slag) these effects were somewhat mitigated, suggesting that the aggression is probably associated with leaching of $Ca(OH)_2$ from the limestone Portland cement. This agrees with other studies and can be attributed to the exchange of $Ca(OH)_2$ with $Mg(OH)_2$, which does not possess any strength characteristics (see Section 4.1.2.1).

4.1.3 Concrete-Embedded Reinforcing Steel and Concrete Paste Conclusions

Snow and ice control chemicals can be detrimental to concrete infrastructure in the following three ways:

- The enabling and/or acceleration of corrosion of concrete reinforcing (rebar) resulting from chloride ion penetration. This effect is primarily related to bridges; however, there is a possibility of a secondary risk in concrete pavements with doweled joints or continuous reinforcement.
- Reactions of snow and ice control materials with the cement paste, resulting in deterioration of the cement matrix. This effect is primarily a risk for pavements and the extent of deterioration is directly related to the quality of concrete. Evidence suggests that magnesium readily reacts with the cement paste in a process that reduces the concrete strength.
- All snow and ice control chemicals, by definition of their action, increase the number of freezing and thawing cycles on the concrete in service. This can result in deterioration in the form of freezing and thawing and/or scaling.

Considerable research is being done on the effects of snow and ice control materials on concrete paste. To date, there have been conflicting findings as to how the various materials affect the durability of the concrete. Traditional snow and ice control materials (e.g., NaCl and $CaCl_2$) are known to have some detrimental effects on concrete, causing primarily scaling of the concrete surface, although no problems with the bulk properties of the concrete are known. With good-quality concrete, scaling problems can be avoided. Some laboratory studies have shown deterioration of the cement paste and bulk properties of the concrete by $CaCl_2$; however, the material is widely used, and these findings do not appear to be substantiated in field applications.

Laboratory studies with magnesium-based materials (e.g., $MgCl_2$ and CMA) have found chemical degradation of the concrete matrix as a result of magnesium reacting with the calcium-silica-hydrate (C-S-H) by replacing the calcium with magnesium and, in time, resulting in strength loss of the concrete. There have been some reports of $MgCl_2$ causing deterioration of the concrete in the field; however, there does not appear to be a widespread problem. However, $MgCl_2$ is used to a somewhat lesser extent. Considering the reactivity of magnesium, long-term effects are possible and, given the findings of past studies, future work will be required. Close monitoring of structures where $MgCl_2$ is used is also recommended.

Chlorides enable and/or accelerate corrosion of concrete reinforcing. Current evidence suggests that chloride associated with magnesium may have higher chloride diffusion coefficients than NaCl or $CaCl_2$. Considerable research is ongoing and, for practical purposes, all chloride materials have been ranked equally high in causing corrosion of the reinforcing steel.

This study includes an analytical research program investigating the relative chloride diffusion coefficients of chloride-based snow and ice control materials. After 1.5 years of exposure testing, corrosion has not been initiated for any of the materials. The rankings will remain based on the comprehensive literature assessment, because this time of exposure can be considered short when viewed in terms of concrete durability where current service life requirements in the order of 30 to 100 years are commonly specified. Acetate-based materials, OMBs, and abrasives are not considered corrosive to concrete reinforcing.

4.1.4 Atmospheric Corrosion Costs

Atmospheric corrosion is one of the most important degradation processes that limits the life of motor vehicles and roadside infrastructure where snow and ice control materials are used for winter road maintenance. Corrosion damage results in extensive loss of capital. A study in 1976 (*171*) concluded that the damage caused by snow and ice control chemicals on water supplies, health, vegetation, highway structures, vehicles, and underground utilities exceeded $3 billion per year or approximately 15 times the amount of money spent on purchasing and applying snow and ice control chemicals. Later studies have estimated the cost of corrosion from these chemicals for motor vehicles and highway infrastructures to have increased.

Menzies (*172*) estimated the annual cost of corrosion from snow and ice control chemicals for cars, light trucks, vans, recreation vehicles, heavy trucks, and buses to be approximately $900 million for corrosion prevention on 1.4 million new vehicles, and approximately $1.4 billion for the depreciation cost of the 86 million vehicles in operation. These costs total approximately $2.3 billion annually.

A report commissioned by the FHWA in 1999 on the corrosion costs and prevention strategies in the United States (*173*) summarized the annual corrosion-related costs to motor vehicles to be approximately $23.4 billion per year. This cost was divided into three components: (1) increased manufacturing cost because of corrosion engineering and the use of corrosion-resistant materials ($2.56 billion per year); (2) repairs and maintenance necessitated by corrosion ($6.45 billion per year); and (3) corrosion-related depreciation of vehicles ($14.46 billion per year). The same study estimated the annual dollar impact of corrosion on steel highway bridge components to be $2 billion for maintenance and the cost of capital for bridge substructures and superstructures, and approximately $500 million for the maintenance painting cost for steel bridges. Although all the costs associated with vehicle and infrastructure impairments in the 1999 study (*173*) are not due to snow and ice control materials, they are thought to be the primary contributing factor.

4.1.5 Forms of Corrosion

Numerous authors and studies have discussed the various forms of corrosion that can occur on motor vehicles, roadside infrastructures, and steel bridges (*172–181*). Forms of corrosion include uniform or general corrosion, crevice corrosion, poultice corrosion, pitting, galvanic corrosion of dissimilar metals, and filiform corrosion of aluminum and magnesium alloys. All the above forms of corrosion require water and an ionic species such as chloride or another electrolyte for accelerated corrosion.

Crevice corrosion, poultice corrosion, and pitting are all forms of oxygen concentration cell corrosion. These forms of corrosion all occur because of a difference in the concentration of dissolved oxygen at one point as compared with another point on the metal surface. The direction of the corrosion reaction is always toward equilibrium, which occurs by reducing the concentration of oxygen where it is highest. The surfaces in contact with the solution containing the higher concentration of dissolved oxygen will become cathodic. The surfaces in contact with the solution containing the lower concentration of dissolved oxygen will become anodic. The anodic surfaces will suffer accelerated corrosion.

The various forms of corrosion that typically occur on motor vehicles, steel bridge components, and roadside infrastructure are summarized in the following sections.

4.1.5.1 Uniform or General Corrosion

Uniform or general corrosion is defined as (1) a type of corrosion attack (deterioration) uniformly distributed over a metal surface or (2) corrosion that proceeds at approximately the same rate over a metal surface (*182*). Uniform or general corrosion is usually not a significant problem except on brake components, structural members (e.g., frames and underbodies of motor vehicles) where thinning can result in a loss of strength, or electrical components where corrosion can cause failures. Most other components are relatively massive or are protected by coatings.

4.1.5.2 Crevice Corrosion

Crevice corrosion is defined as localized corrosion of a metal surface at or immediately next to an area shielded from full exposure to the environment because of proximity between the metal and the surface of another material (*182*). Crevice corrosion occurs in cracks or crevices formed between mating surfaces of assemblies. The surfaces may be the same or dissimilar metals or one surface may be a nonmetal (e.g., scale, surface deposits, washers, or gaskets). Crevice corrosion is a form of localized attack from oxygen concentration cells where rapid perforation to failure can occur on film-protected metals (e.g., aluminum, magnesium, and stainless steel). Crevice corrosion can also cause corrosion product wedging failures of fasteners because of axial tensile overload.

4.1.5.3 Poultice Corrosion

Poultice corrosion is also called deposit corrosion or attack and is a term used in the automotive industry to describe the corrosion of vehicle body parts as a result of the collection of roadsalts and debris on ledges and in pockets kept moist by weather and washing (*182*). Poultice corrosion is another form of localized attack from oxygen concentration cells (*183*). Deposits that have accumulated can soak up corrosive (ionic) substances (e.g., snow and ice control chemicals) and act as a sponge to trap moisture.

Little or no corrosion occurs while the entire assembly is dry or wet. During the drying period, adjacent wet and dry areas develop and differential aeration cells develop at the edge of the wet zone. This can lead to rapid corrosion.

4.1.5.4 Pitting Corrosion

Pitting is a form of localized corrosion that results from local cell action that produces cavities starting at the surface. The cavities may or may not become filled with corrosion products, and corrosion products may form nodules over the pit cavities (*184*). Pitting occurs when a film-protected metal (e.g., aluminum, magnesium, or stainless steel) is almost, but not completely, resistant to corrosion. Only a small amount of metal is corroded, but perforations can lead to costly repair of expensive equipment such as motor vehicles. Pitting is a form of localized attack that primarily occurs on aluminum, magnesium, and stainless steels, especially if chlorides are present. Once pitting has initiated, the mechanism is similar to crevice or poultice corrosion with the pit acting as the crevice.

4.1.5.5 Galvanic Corrosion

Galvanic corrosion is defined as accelerated corrosion of a metal because of an electrical contact with a more noble metal or non-metallic conductor in a corrosive electrolyte (*182*). The more active metal becomes the anode and may suffer rapid corrosion in the vicinity of the contact. Snow and ice control materials significantly increase galvanic corrosion by increasing the conductivity of the electrolyte. The most prevalent problem in motor vehicles is contact of aluminum components with steel.

4.1.5.6 Filiform Corrosion

Filiform corrosion is another form of crevice corrosion that can occur on aluminum and magnesium alloy surfaces under an organic coating. It appears as a random distribution of threadlike filaments on the metal surface under organic coatings (*182*). Corrosion typically initiates at holidays (i.e., voids and thin spots in the coating) and mechanical damage on the organic coating surface.

4.1.6 Atmospheric Corrosion of Motor Vehicles, Roadside Infrastructure, and Metal Bridges

Corrosion is an electrochemical reaction in which the metal is oxidized in the presence of moisture and atmospheric oxygen. The addition of an electrolyte (e.g., salt or other snow and ice control chemicals) facilitates electron transfer and greatly accelerates the corrosion.

Atmospheric corrosion of metals occurs when the surfaces become wet. The rate of atmospheric corrosion on the wet surface is accelerated by the presence of ionic substances such as chlorides. The total time of wetness is important because this affects the total corrosion, especially if chlorides are present. The availability of oxygen is also important because oxygen concentration cells develop under deposits and in crevices and pits. The processes involved in atmospheric corrosion are complex and involve numerous interacting and constantly varying factors (e.g., weather conditions, air pollutants, material conditions, and temperature).

4.1.6.1 Atmospheric Corrosion of Motor Vehicles

Motor vehicle corrosion can be classified into two major categories: structural corrosion and cosmetic corrosion (*185*). Structural corrosion is corrosion degradation that causes a loss of integrity such as perforation of body panels, corrosion of brake components, and deterioration of frame, underbody or bumper support systems. Cosmetic corrosion only affects the aesthetic appearance of the motor vehicle such as rust staining and blistering of painted body panels and discoloration and pitting of trim. A general differentiation between perforation corrosion and cosmetic corrosion is that perforation corrosion occurs from the inside of the body panels, while cosmetic corrosion occurs on the outside of the body panels, trim, and wheels (*175*).

Localized corrosion from oxygen concentration cells (e.g. crevice, poultice, pitting, and filiform corrosion) and galvanic corrosion are probably the most significant causes of corrosion failures in motor vehicle service. All forms of localized corrosion can be defined as selective removal of metal by corrosion at small special areas or zones on a metal surface in contact with a liquid or moist environment. It usually occurs under conditions where most of the metal surface is either not attacked or is attacked to a much lesser degree than the localized sites.

The motor vehicle environment is a dynamic condition because of road splash that carries snow and ice control chemicals and other ionic materials to the metal surface, as opposed to roadside components such as signage, guard rails, bridges, and buried structures that are basically static. Motor vehicle design has resulted in complex shapes, joints, and configurations that result in areas where deposits can build up. These deposits retain moisture and ionic species, producing oxygen concentration cells where poultice and crevice corrosion can occur.

Crevice corrosion and poultice corrosion typically occur where dirt and moisture are trapped—between adjacent pieces of metal, under gaskets and at fasteners, or on the surface of motor vehicle components. This is compounded by ingress of snow and ice control chemicals and other ionic materials (e.g., acid rain) that increase the conductivity of the trapped moisture. Aluminum alloys are more prone to crevice corrosion and galvanic corrosion when coupled to steel.

The motor vehicle exhaust system has become a critical component because of government legislation requiring zero-leak performance with suggested design lives approaching 240,000 km (150,000 miles) in the future (*186*). Stainless steels have performed well, but with higher operating temperatures from efforts to increase gasoline mileage and reduce emission levels, much more corrosion-resistant materials will be required. Snow and ice control chemicals splashed on hot exhaust system components can cause severe corrosion from hot (molten) salt corrosion and, as such, these chemicals will become a much more important aspect as a source of failure in the future.

4.1.6.2 Atmospheric Corrosion of Roadside Infrastructure and Metal Bridges

General corrosion and crevice corrosion are the principal forms of corrosion observed on roadside infrastructures and metal bridges. Roadside infrastructure and steel bridges suffer uniform corrosion, especially at coating failures, severe crevice corrosion at riveted and bolted joints, and localized corrosion under deposits (i.e., poultice corrosion). Severe corrosion at riveted and bolted joints can cause tensile failures of fasteners because of corrosion product wedging (i.e., rust jacking).

In the United States, approximately 15 percent of all bridges are structurally deficient because of corrosion (*173*). The primary cause of bridge steel structural corrosion is chloride-induced corrosion with the chlorides resulting from snow and ice control chemicals and marine exposure. General corrosion damage also occurs on roadside metal guardrails, signage, and so forth.

Corrosion can also be accelerated on numerous metallic components alongside roads and highways because of snow and ice control chemicals. Such components include drainage systems; fixtures such as sign posts, light standards, traffic signal wiring, guardrails, wire fencing and metal retaining walls, and noise barriers; underground utility lines, pipelines, and storage tanks; and objects such as bronze statues and monuments and metallic building siding and roofing (*185*).

Probably, there is damage to railroad-owned property at and near railroad crossings because of snow and ice control chemicals. Such damage would include corrosion of rails and switching sections, wiring, and so forth. The railroad systems apparently do not consider this type of corrosion to be a major expense and do not track this data (*173*). Further information detailing issues related to railway traffic control signaling is provided in Section 4.2.1.

4.1.7 Motor Vehicle, Roadside Infrastructure, and Bridge Materials

Motor vehicles, roadside infrastructure, and metal bridges used a very wide range of metals, non-metals, and combinations of materials in intimate contact for their fabrication and construction (*175*, *186*, *187*). Materials are described in the following sections.

4.1.7.1 Steel and Cast Irons

Steel components include a very wide range of carbon, alloy, high-strength, low-alloy, and weathering steels. They can be hot-rolled or cold-rolled sheet, plate, bar, pipe and tubing; hot-rolled sections; forgings; or castings. The steel components can be bare, metallic-coated (e.g., zinc- or chromium-plated) or organic-coated (e.g., painted).

Motor vehicles typically use hot-rolled steel sections for frames, bumpers, and other structural parts, which may or may not be coated; steel tubing for brake lines; cold-rolled coated steel sheet for body panels and fuel tanks; and steel castings or forgings for fittings, steering components, and so forth. Stainless steel sheet is used for motor vehicle trim, fuel tanks and exhaust systems. Stainless steel is also used for tubing applications.

Roadside infrastructure and steel bridges use many grades of structural steel that can be galvanized and/or painted.

Cast irons and ductile irons are used for motor vehicle engines and drive train components, brake drums and disks, and miscellaneous fittings. Roadside infrastructure and bridges use cast iron and ductile iron cable eyes, fittings, column bases, and so forth.

4.1.7.2 Aluminum Alloys

Numerous aluminum alloys and forms of aluminum are used and can be bare, metallic-coated (e.g., chromium-plated) or have organic coatings (e.g., painted). Motor vehicles use various coated and uncoated sheet aluminum alloys for body panels, fuel tanks, trim, radiators, and so forth. Aluminum alloy castings and/or forgings are used for wheels, engine and drive train components, and miscellaneous fittings. Aluminum tubing is also used. Aluminum alloy tubing, piping, extrusions, castings, and forgings are used for guardrails, handrails, light standards, and so forth, while sheet and plate aluminum alloys are used for building cladding, signage, and so forth.

4.1.7.3 Magnesium Alloys

Magnesium alloy die or permanent mold castings and forgings are used for motor vehicle wheels, transmission housings, and other miscellaneous brackets and supports.

4.1.7.4 Copper and Copper Alloys

The principal use of copper is for electrical wiring in motor vehicles, roadside infrastructure, and bridges. Some copper tubing is also used for various applications. Copper alloys (e.g., brass) are also used for electrical contacts, motor vehicle radiators, and brake line fittings. Brasses and bronzes are used for roadside heritage statues, markers, and so forth.

4.1.8 Snow and Ice Control Chemicals

There are extensive references in the literature discussing atmospheric corrosion of various types of snow and ice control chemicals on motor vehicles and roadside infrastructure as well as comparisons of corrosion rates from field and in accelerated laboratory tests (*185, 188-199*).

Snow and ice control chemicals are typically ionic or nonionic chemicals or mixtures of chemicals with or without corrosion inhibitors. They typically have high solubility in water at low temperature; relatively low molecular weight; and eutectic temperatures lower than the expected ambient temperature (*189*). Numerous chemical substances could be used for snow and ice control, but the number actually used is relatively small because of cost, availability, environmental constraints, and so forth.

In discussing atmospheric corrosion processes, snow and ice control chemicals can generally be grouped as follows: chloride-based salts (e.g., sodium chloride, potassium chloride, magnesium chloride, calcium chloride, and mixtures of chlorides or salt brines); acetate-based products (e.g., calcium magnesium acetate and potassium acetate); and miscellaneous organic compounds (e.g., glycols, alcohols, and proprietary agricultural by-products—primarily sugar-based organic biomass). Many commercially available products also consist of proprietary blends of snow and ice control chemicals with and without corrosion inhibitors.

4.1.8.1 Chloride-Based Snow and Ice Control Chemicals

Chloride-based salts are all highly corrosive to motor vehicle components and roadside infrastructure but vary in degree, with the most corrosive being the hydroscopic chlorides (e.g., magnesium chloride and calcium chloride). The hydroscopic chlorides are more corrosive because deposits remain moist and allow corrosion to occur for a much longer period. It has been demonstrated that when acid rain is present, there is a synergistic effect (increase in corrosion rate) with chloride salts (*200*).

4.1.8.2 Acetate and Organic Snow and Ice Control Chemicals

The acetate-based and miscellaneous organic deicer chemicals tend to result in significantly lower corrosion rates than the chloride-based deicer chemicals (*185, 200*). Generally, even the most innocuous snow and ice control chemical can still cause significant corrosion of metals if the chemical increases the conductivity of the moisture in contact with the metal surface and/or increases the time of surface wetness.

4.1.9 Corrosion Inhibitors

Any substance added in small amounts to a corrosive environment that effectively reduces the corrosion rate of a metal or alloy can be called a corrosion inhibitor. Corrosion inhibitors are chemical substances or combination of substances that, when present, prevent or reduce corrosion without significant reaction with the components of the environment. Many commercially available snow and ice control materials contain inhibitors. Agricultural by-products, proprietary in nature, are very popular additives to chloride-based chemicals. Other materials such as triethanolamine (TEA) and phosphates, carbonates, and silicates are not as popular, but have also been used to reduce corrosion effects.

There are basically three types of inhibitors (*174, 184, 201–203*):

- Anodic, which limit the anodic half-cell of the corrosion reaction;
- Cathodic, which impede the cathodic half-cell of the corrosion reaction; and
- Absorption or Passivating, which form a physical barrier on the metal surfaces.

Liquid phase or moist condition inhibitors are classified as anodic, cathodic, or mixed inhibitors, depending on whether they inhibit the anodic, cathodic, or both electrochemical reactions.

Corrosion inhibitors tend to be metal and environment specific. No inhibitors retard corrosion significantly for all metals and alloys and all snow and ice control chemicals.

4.1.9.1 *Anodic Inhibitors*

Anodic inhibitors typically are used in near-neutral solutions where insoluble products (e.g., oxides, hydroxides, or other salts) are formed. Anodic inhibitors form or cause the formation of passivating films that inhibit the anodic metal dissolution reaction. When the concentration of an anodic inhibitor is insufficient, corrosion can be enhanced rather than inhibited.

Typical anodic inhibitors are often called passivating inhibitors and include chromates, nitrites, molybdates, phosphates, carbonates, and silicates. In practice, only phosphates, carbonates, and silicates tend to be suitable for snow and ice control chemicals and they are used primarily to prevent corrosion of iron-based alloys.

They are the most efficient inhibitors because they can almost completely prevent corrosion, but they are also dangerous inhibitors because they can accelerate corrosion (i.e., cause severe localized attack) at low concentrations. Extensive studies of inhibitors have shown the accelerated corrosion effect of low anodic inhibitor concentrations, but apparently no studies have been carried out to evaluate the corrosive effect of snow and ice control chemicals when they are diluted and the anodic inhibitor concentration is less than optimal.

The passive oxide film is cathodic to steel, and, when the passive film is penetrated by mechanical damage or by dissolution or there is insufficient inhibitor for the entire metal surface, the exposed metal becomes a small anodic area in the middle of a large cathodic area of passive film. Rapid localized corrosion can then occur in the anodic area. Steel can be easily passivated in any aqueous solution except those that contain easily oxidized substances in solution or high concentrations of chloride ions.

Snow and ice control chemicals with anodic inhibitors can show low corrosion rates in laboratory corrosion tests where the anodic inhibitor is at the proper concentration, but deicing chemicals applied to roadways become diluted, which can result in severe localized corrosion of motor vehicles and roadside infrastructure.

4.1.9.2 *Cathodic Inhibitors*

Generally, cathodic inhibitors are less effective than anodic inhibitors (*174*). Cathodic inhibitors reduce corrosion primarily by interfering with or preventing the oxygen reduction reaction. Cathodic inhibitors are considered to be safe inhibitors because they decrease general corrosion but do not stimulate pitting or localized attack. Precipitating inhibitors are cathodic inhibitors. They cause insoluble films to form on the cathode surfaces under localized conditions of high pH, thus effectively isolating the cathode from the solution. Typical precipitating inhibitors or cathodic inhibitors are calcium bicarbonate, zinc ions, polyphosphates, and phosphonates. They are all suitable for inhibiting snow and ice control chemicals.

4.1.9.3 *Mixed Inhibitors*

Most commercial inhibitors are organic compounds that cannot be designated as either anodic or cathodic and are known as mixed inhibitors. The effectiveness of organic inhibitors is related to the extent to which they reabsorb and cover the metal surface. Absorption of the organic inhibitor depends on the structure of the inhibitor, on the surface charge of the metal, and on the type of electrolyte. Mixed inhibitors protect the metal in three ways—physical absorption, chemisorption, and film formation (*203*).

Organic compounds constitute a broad class of corrosion inhibitors that cannot be designated specifically as cathodic or anodic. Cathodic inhibitors (e.g., amines) or anodic inhibitors (e.g., sulphamates) will be absorbed preferentially depending on whether the metal is charged negatively or positively respective to the solution.

Numerous organic-based corrosion inhibitors are being widely used in conjunction with chloride-based snow and ice control materials. These are typically by-products from a wide range of processes, most typically processing of agricultural biomass. As such, these materials may contain a wide range of constituents, including amines, phosphates, hetrocyclic nitrogen compounds, sulfur compounds and numerous natural compounds such as proteins, plant extracts, phytic acid (inositol hexaphosphoric acid), rice bran, soybean cake, and grapeseed oil (*195*).

4.1.9.4 *Phosphorous-Based Inhibitors*

Numerous inhibited proprietary deicing chemicals contain relatively high levels of phosphorous. In most cases, it is unknown whether the phosphorous is present as a phosphate, polyphosphate, or phosphonate. The form of phosphorous is extremely important because phosphates are anodic or dangerous inhibitors while polyphosphates and phosphonates are cathodic or safe inhibitors (*174, 190, 201*).

4.1.10 Discussion of Atmospheric Corrosion of Snow and Ice Control Chemicals

The results of snow and ice control chemical corrosion tests depend heavily on the corrosion test methods used and the metals tested. In addition, no corrosion inhibitors are suitable for all metals and all snow and ice control chemicals.

These facts have led to numerous conflicting ranking results for snow and ice control chemicals. For example

1. There is general agreement that calcium magnesium acetate (CMA) is less corrosive to steel components than sodium chloride (*185, 194, 196, 199, 204–208*) but there is some disagreement that it is less corrosive to aluminum components (*185*, *199*).
2. Some work has shown magnesium chloride to be less corrosive than sodium chloride (*191, 205, 206*), while other work has shown it to be more corrosive (*187*). The variation in ranking probably is strictly because of test procedures given that roadside infrastructure and vehicles will stay wet longer when magnesium chloride is used.
3. Calcium chloride and inhibited calcium chloride have been shown to be less corrosive than magnesium chloride and sodium chloride (*197, 205, 210*), have similar corrosion (*195, 206, 211*), or much more severe corrosion (*198*).
4. Inhibited calcium chloride is more corrosive than non-inhibited calcium chloride (*210*).

Overall, chloride-based snow and ice control materials are corrosive to metal components. Numerous studies have attempted to rank these materials relatively for corrosion but complex contributing factors limited the development of definitive conclusions. From the standpoint of developing practical rankings, these materials have been ranked equally high for their potential to cause corrosion. Information suggests that acetate-based materials are less corrosive to steel than chlorides, but may lead to corrosion concerns for other alloys. While OMB materials are accepted as being non-corrosive to metals, limited evidence suggests that these materials, used as corrosion inhibition additives, significantly reduce corrosion rates under field conditions.

4.1.10.1 Motor Vehicles

The most detrimental forms of corrosion for motor vehicles are localized corrosion (i.e., e.g., crevice, poultice, and pitting) and galvanic corrosion—not uniform or general corrosion.

4.1.10.2 Roadside Infrastructure

Cosmetic corrosion is the most prevalent form of roadside infrastructure corrosion. General or uniform corrosion also occurs very frequently but usually is not a problem because of the massive metal sections involved.

4.1.10.3 Metal Bridge Components

Metal bridges and their components and similar structures can suffer general or uniform corrosion, but the most detrimental forms of corrosion are localized (i.e., poultice and crevice) corrosion. Poultice corrosion occurs under deposits and can be significant, but the most serious and detrimental is crevice corrosion of structural steel riveted and bolted joints. Crevice corrosion in riveted and bolted joints causes corrosion product wedging or rust jacking which can cause the rivets and bolts to “pop” (fail catastrophically because of axial tensile overload). Once crevice corrosion has initiated in a structural steel joint, it is almost impossible to prevent the corrosion from continuing, even if the structure is recoated.

4.1.10.4 Snow and Ice Control Chemicals

The chloride-based snow and ice control chemicals are the most corrosive with the hydroscopic chlorides of magnesium and calcium being the most aggressive because of the longer time of wetness. The acetate-based (e.g., calcium magnesium acetate) and miscellaneous organic chemicals all tend to cause significantly less corrosion than the chloride-based snow and ice control chemicals, but they can still accelerate corrosion because they increase the conductivity of the moisture.

4.1.10.5 Inhibitors

Snow and ice control chemical corrosion inhibitors that are tested in the laboratory can show significant reductions in corrosion rates of the metals being tested, but they may show little or no inhibiting effect on other metals (even those in the same metal group) and may in effect accelerate corrosion of some metals. To develop any meaningful general corrosion rate data for deicing chemical corrosion inhibitors, tests must be run over a wide range of concentrations for both the corrosion inhibitor and the deicing chemicals, and also under a number of ambient conditions to simulate field conditions.

4.2 Other Impacts to Infrastructure

4.2.1 Railway Traffic Control Signaling

Concerns have been raised about the effect of snow and ice control materials on the operation of railway traffic control signaling. Anecdotal information is available, but formal studies addressing the frequency, mechanism, and magnitude of occurrence are not. Various groups involved with railroad issues were contacted, including the Federal Highway Administration (FHWA), the Federal Railroad Administration (FRA), and the Association of American Railroads (AAR). Limited information beyond anecdotal accounts was obtained, and inquiries were further referred to the American Railway Engineering and Maintenance-of-Way Association (AREMA). AREMA Technical Committee 36, Highway Rail

Grade Crossing Warning Systems, has the purpose of developing concepts, providing information, and recommending practices for the design, installation, operation, and maintenance of highway railroad grade crossing warning equipment and systems. This group is aware of occurrences of snow and ice control chemicals affecting railway traffic control devices, but incidences are typically addressed on a case-by-case basis.

Modern railway traffic control devices involve electric circuit-based train detection to initiate traffic warning signals and gates. Three general train detection systems are used (*212*):

1. **DC, AC-DC, or AFO Grade Crossing Island and Approach Circuits.** These train detection systems use a battery or transmitter at one end of track section and a relay, receiver, or diode at the other end. A train on the section of affected track will shunt the circuit and de-energize the relay, further triggering operation of the signal mechanisms. This type of system will continue until the train leaves the circuit.
2. **Motion-Sensitive Devices (MS).** This train detection system detects the presence of train movement within a given electronic track circuit. This type of system will continue until the train stops or leaves the circuit.
3. **Constant Warning Time (CWT) Systems.** This train detection system detects the speed and distance of a train entering the circuit and activates traffic control devices to provide a desired warning time.

Each of these train detection systems relies on the transmittance of electrical current through the rails for proper operation. These circuits are designed to be "fail-safe," and any break in continuity will trigger the most conservative event—a traffic-signaling event.

High ionic salt solutions have low electrical resistivity (i.e., they can transmit electrical current through solution) and can affect track circuit electrical continuity, which can trigger signal operation without the presence of a train in the circuit. Salt solutions can also cause early initiation of traffic signaling for CWT train detection systems. To counter these conditions, some signal maintenance engineers may increase the output of the train detection systems. However, when conditions return to normal, this can lead to over-energized circuits that, in theory, can fail to detect oncoming train traffic at the proper time.

Reasonable and consistent traffic warning times re-enforce the railway traffic control system credibility. A major factor affecting the credibility of these systems is an unusually high number of false activations at active crossings (*213*). Unreasonable or inconsistent warning times have been linked to undesirable driver behavior. Research has shown that when warning times exceed 40 to 50 seconds, drivers will accept shorter clearance times at flashing lights, and a significant number will attempt to drive around the gates. It has been identified that every effort should be made to minimize false activations (*213*).

Observed cases of snow and ice control materials affecting railway traffic control signaling typically involve the use of extremely high levels of chloride-based products. Other site-specific conditions can also influence the process. For illustration, one example involves railroad tracks crossing a roadway at the foot of a hill. Heavy applications of roadsalts applied to maintain roadway mobility produced high volumes of salt brine that ran downhill and pooled across the tracks. The presence of the electrically conductive solution between the tracks shunted the track circuit and resulted in false signal activation.

The Idaho and Missouri DOTs have conducted field trials to trigger railway signaling with $MgCl_2$ and NaCl applications, but were unable to measure any changes in signal levels after application. It is unknown whether various snow and ice control materials have higher or lower incidences or magnitudes of impact. However, given that false activations have been reported and the presumed mechanism of impact is highly conductive ionic solutions affecting track circuitry, occurrences are likely linked to chloride-based products. It can also be inferred that any measures taken to reduce applications near rail crossings and pooling across the tracks can minimize effects. However, measures to limit the use of ionic (electrically conductive) snow and ice control materials at railway crossings are outweighed by safety concerns requiring adequate traffic mobility across the tracks.

4.2.2 Power Distribution Lines

As with railway traffic control signaling, concerns have been raised about the effect of snow and ice control materials on the operation of power distribution lines. Anecdotal information is available; however, formal studies addressing the frequency, mechanism, and magnitude of occurrence are not.

Electrical power is most commonly distributed by wires suspended on poles or towers. Insulators, made of a fast-drying non-conducting material such as glass, porcelain, or composite materials, are used to hold the wires and to minimize current loss and grounding. Insulator failure because of "natural/ambient" conditions has been a concern and has resulted in loss of current, line shorting, and pole fires. A basis description of the mechanism is as follows (*214*):

1. Hot and dry weather conditions allow accumulation of pollutants on the insulators and can dry wooden poles.
2. Damp conditions bring moisture, allowing the pollutants on the insulators to become slightly conductive.
3. Current leaks across the insulator and can cause line current losses, shorting, or heating and potential fire of wooden poles.

High ionic salt solutions can exacerbate the process. These solutions have low electrical resistivity (i.e., they can readily conduct electrical current through solution) and, when they coat insulators, can allow transfer of current around the insulator to a greater degree than without salts. Incidents related to snow and ice control materials have included loss of current, shorting of transmission lines, and wooden pole fires resulting from the leak of current across the insulator.

All accounts of effects related to snow and ice control materials involve chloride-based materials. Salts that have been deposited on an insulator and have dried pose little immediate concern. However, these materials can become conductive when moisture is present, such as during damp or foggy conditions. For this reason, it is suggested that $CaCl_2$ and $MgCl_2$ pose the greatest potential concern because they are hygroscopic—these materials can combine with water and maintain a moist conductive coating on the insulator, even during dry conditions.

The degree of aerial deposition plays a defining role in whether or not effects occur. Major multi-lane and high-speed highway traffic can aerially disperse salt aerosols quite extensively. Kelsey and Hootman (*29*) estimated NaCl aerosols at least 15 meters high within 67 meters of a roadway. Vertical distribution was also found to be distributed more or less exponentially with height from the roadway, with most deposition occurring up to 3 meters (*31*). Power lines subjected to high levels of aerial dispersion and locations where power lines are exceptionally close to the roadway are of particular concern. Extreme cases include power lines directly next to elevated roadways such as alongside an overpass or bridge.

CHAPTER 5

Analytical Methods Used to Measure Attributes of Snow and Ice Control Materials

A snow and ice control material's performance and potential for adverse effect can typically be defined by some measurable attributes of the material. Much effort has been put into developing and conducting tests to measure these attributes. In many cases, however, test results have not been reproducible under field conditions. In other instances, two technically relevant test methods provide conflicting conclusions. This causes confusion in the industry by preventing direct product comparisons, which further affects product selection processes and quality assurance efforts.

Section 2.4.4 indicates many jurisdictions have purchase specifications detailing required product attributes and that some level of quality testing is being conducted to ensure conformance with these specifications. The level of effort varies from simple to detailed by jurisdiction. For example, many agencies qualify product shipments through simple hydrometer measurements, whereas other groups conduct full chemical assessments for environmental attributes of concern. Whatever the level of effort, it is desirable that these tests be done quickly, with minimal cost, and using standard available test equipment.

The focus of this study is the assessment of environmental, not performance-related, attributes. However, there is some overlap of the two categories, and some benefit from the standpoint of product selection processes to discuss some performance-related characteristics. The general areas of snow and ice control material testing are categorized to include the following attributes:

- Physical—includes specific gravity, freeze point, eutectic temperature, gradation, and settleability;
- Chemical and Environmental—includes heavy metals, chemical species, and toxicity; and
- Corrosion—atmospheric, concrete, and concrete reinforcing.

5.1 Specification Sources

Many jurisdictions have developed internal specifications and test procedures; however, these often have involved adapted existing standards. The following organizations are recognized as providing standard test methods developed directly for testing snow and ice control materials:

- Pacific Northwest Snowfighters,
- Strategic Highway Research Program,
- ASTM, and
- AASHTO.

5.1.1 Pacific Northwest Snowfighters (PNS)

The PNS is a consortium of states and provinces (i.e., Idaho, Montana, Oregon, Washington, and British Columbia) that have developed a list of physical, environmental, and corrosion-related specifications for snow and ice control materials (*43*). Test methods have been defined to measure physical, chemical, toxicological, and corrosion attributes and, in many cases, use or adapt existing standard test methods. Many other jurisdictions and agencies have adopted the PNS specifications in the development of their own product specifications and quality testing processes.

5.1.2 Strategic Highway Research Program (SHRP)

SHRP, a unit of the National Research Council, was active between 1988 and 1993 in evaluating and implementing new technologies for the nation's transportation agencies. A "Handbook of Test Methods for Evaluating Chemical Deicers" was prepared that contained a selection of specific test methods for the complete characterization of chemical deicers (*215*). Test methods include assessment of physiochemical properties, deicing performance, effect on metals and concrete, and ecological impacts.

5.1.3 American Society for Testing and Materials (ASTM)

ASTM International is a standards development organization that provides a forum for the development and publication of voluntary consensus standards for materials, products, systems, and services. ASTM provides specifications and standard test methods for snow and ice control materials; however, these tend to be limited in scope, focusing on measurement of physical characteristics and corrosion-related test methods.

5.1.4 American Association of State Highway and Transportation Officials (AASHTO)

AASHTO specifications for snow and ice control materials typically reference or modify ASTM procedures.

5.2 Physical Attributes

5.2.1 Specific Gravity

Specific gravity is a material's density (mass/volume) compared with water. Many agencies use specific gravity to monitor the percentage of the active ingredient in purchased liquid snow and ice control products. ASTM D 1429 details various methods for specific gravity measurement for waters and brines:

- Test Method A—Pycnometer: involves weighing a pycnometer (a fixed volume vessel) containing the product at 20°C ± 1°C.
- Test Method B—Balance: involves the use of a plummet to determine liquid weight by displacement.
- Test Method D—Hydrometer: involves a float-type device consisting of a weighted barrel and calibrated specific gravity gradations. A hydrometer will float higher in a denser liquid (i.e., one containing high solids) than a less dense liquid.

SHRP references ASTM D-1122-90a, which is a method developed for engine coolants, but is very similar to ASTM D 1429, Test Method D-Hydrometer (*215*).

Agencies traditionally have compared specific gravity measurements to standard reference tables to determine the percentage of active ingredient (i.e., $CaCl_2$, $MgCl_2$) in a purchased liquid product. For example, standard reference tables state that a 30-percent $CaCl_2$ solution has a specific gravity of 1.284 (*216*). Standard reference tables should be used with caution because they apply to pure products, and many available liquid products contain secondary constituents or consist of more than one base product (i.e., liquid salt plus a corrosion inhibitor). In such cases, it is desirable that the vendor provides a product specific gravity versus concentration curve for that product.

Although specific gravity is a quick and simple method for providing a general idea of product concentration, direct chemical analysis methods are more defensible.

5.2.2 Freezing Point and Eutectic Temperature

ASTM D1177 describes a method (to determine the freezing point of engine coolants) that can be applied to liquid snow and ice control materials. Solutions are cooled with stirring while time and temperature are recorded. The freezing point is taken as the temperature at the point of intersection of temperature versus time and after the onset of freezing (*215*). Eutectic temperature is the lowest freeze point temperature achievable for a given product in solution (*1*). Eutectic temperature, by definition, applies to pure products and in practice (e.g., for commercially available blends) a phase curve can be developed for a range of active ingredient concentrations. This involves measurement of the freezing characteristics of a solution with a previously identified concentration.

5.2.3 Gradation

Methods for determining particle size distribution of solid products typically are based on methods similar to ASTM C 136, Sieve Analysis of Fine and Coarse Aggregates. The following test methods apply to snow and ice control products:

- ASTM D 632, Standard Specification for Sodium Chloride and
- ASTM D 98 and ASTM D 345, Standard Specifications for Calcium Chloride.

5.2.4 Particle Degradation

In the case of abrasives, hardness indicates resistance to mechanical degradation (i.e., e.g., abrasion). Harder materials are less prone to crushing from vehicular action, which can reduce potential air quality concerns. Particle degradation testing is commonly referred to as "Los Angeles Abrasion" testing and standard test methods include

- ASTM C 131, Standard Test Method for Resistance to Degradation Aggregate by Abrasion and Impact in the Los Angeles Machine and
- AASHTO T 96-02.

5.2.5 Settleability

The PNS has developed a method to determine percent Total Settleable Solids and percent Solids Passing a No. 10 Sieve after a liquid chemical is stored at a specified cold temperature (-17.8 ± 1°C for $MgCl_2$ and -29 ± 1°C for $CaCl_2$) without agitation for 168 hours (1 week) (*43*). The test procedure is designed to determine the potential for solids formation under extreme field storage temperatures. Solids formation in liquid products severely affects the operation and performance of application equipment.

5.3 Chemical and Environmental Attributes

Many test methods applied to snow and ice control materials to determine chemical and environmental attributes have been adapted from tests used for other purposes such as for water and wastewater. PNS has taken leadership in addressing environmental concerns attributed to snow and ice control materials, and many other jurisdictions have incorporated their programs.

Certain considerations are necessary when adapting water and wastewater methodologies to snow and ice control products. These include high specific gravity, extreme analyte concentrations, and the potential for chemical interferences. Standard test methods used for water and wastewater samples are conducted on volumetrically measured sample aliquots. Liquid products used for snow and ice control commonly have densities approximately 15 to 35 percent greater than water, and procedures must be modified to ensure representative gravimetric aliquots are analyzed. Alternatively, volumetrically derived sample results (i.e., mg/L) must be converted to a gravimetric basis after analysis.

Units of measurement commonly included in specifications and reported with test results have resulted in some confusion. Ambiguous units such as parts per million (ppm) or percent (%) should be clarified to reflect the basis of measurement—milligrams per liter (mg/L), milligrams per kilogram (mg/kg), percent volume per volume (% v/v), percent mass per volume (% w/v) or percent mass per mass (% w/w).

Chemical analysis of solid products typically requires dissolution of the product before analysis. The approach described by PNS requires a 25-percent (w/w) preparation with distilled or deionized water (*43*). Care is required to ensure material solubility is not exceeded when preparing these solutions.

The following assessments of standard chemical analysis methods are not intended to be proscriptive. In many cases, more than one approach could provide acceptable test data. Trends in analytical chemistry are moving toward performance-based methodologies (PBMs). A PBM specifies the data quality objectives (DQOs) that are to be achieved but leaves the laboratory and its customer to determine the chemical and instrumental procedures by which the DQOs are to be met. The goal of a PBM is to provide reasonable flexibility in the choice of analytical method and instrument used. The intent of the PBM is to allow for technical advances in measurement science to be implemented in the future and permits the analyst to modify methods to deal with the realities of the sample such as matrix effects, interferences, and limitations in sample size. It also allows for continuous improvement in the quality of laboratory operations. That being said, certain benefits are realized by specifying standard test methods, especially from the standpoint of maintaining a standardized program that involves product qualification and quality testing.

5.3.1 Active Ingredient

Active ingredient refers to the primary component of the material. For example, when purchasing commercial liquid calcium chloride, the chemical constituent, $CaCl_2$, would be considered the active ingredient. An accurate assessment of the active ingredient is important to ensure “purchased” and “received” product concentrations are equivalent for contract purposes. Many agencies also use active ingredient concentration to select application rates for a desired snow and ice control performance.

Active ingredient concentrations may be estimated using specific gravity charts or be directly determined through various analytical techniques, including titrations and instrumental analysis. Measurable active ingredients include $CaCl_2$, $MgCl_2$, NaCl, CMA, and KA, and can be estimated by direct measurement of primary components, most typically the cationic species. For example, Ca would be measured for $CaCl_2$, and Ca and Mg are measured for CMA.

Specific gravity measurements can be used to estimate product concentrations using standard reference tables when near-pure products are being used. Alternatively, product suppliers may provide specific gravity versus concentration tables specific to a product.

Titration procedures are available for calcium and magnesium determination. ASTM E 449 involves an EDTA titration for $CaCl_2$, and ASTM C 245 provides a titration procedure for $MgCl_2$. These simple wet chemistry test procedures can be quite effective at measuring percent level concentrations as is common for snow and ice control products.

Instrumental analysis procedures are more complex, but provide a higher level of certainty in the measurement. Ca, Mg, Na, and K are metals that can be detected by various instrumental procedures including atomic absorption spectroscopy, atomic emission spectroscopy, and mass spectroscopy (refer to Section 5.3.2). PNS suggests atomic absorption (AA) spectroscopy (using lanthanum chloride ionization suppression) or inductively coupled plasma (ICP) spectroscopy when determining active ingredient concentrations, but further states that product compliance or price adjustments will use the AA techniques (*43*). Detailed knowledge of interferences should be known, and special considerations should be taken to address extremely high solids concentration (i.e., sample dilutions).

5.3.2 Metals

Many snow and ice control products are obtained from natural sources such as deposits or wells or are agriculturally derived. In addition to primary constituents, other impurities including heavy metals are often present. The term heavy metals typically refers to any metallic chemical element that has a relatively high density and is toxic, highly toxic, or poisonous at low concentrations. Heavy metals are defined by PNS (and generally accepted) to include arsenic, barium, cadmium, chromium, copper, lead, mercury, selenium, and zinc (*43*).

Analysis requires minimum levels of detection in the range of parts per million (mg/L or mg/kg) and thus requires more sophisticated instrumental analysis. The assessment of low analytical levels poses certain challenges, specifically when these elements are incorporated in a matrix containing percent levels of an active ingredient. Instrumental techniques include AA spectroscopy, ICP-atomic emission spectroscopy (ICP-AES), and ICP mass spectroscopy (ICP-MS).

5.3.2.1 AA Spectroscopy (FAA and GFAA)

AA spectroscopy occurs when a ground state atom absorbs energy in the form of a specific wavelength and is elevated to an excited state. The amount of light absorbed at this wavelength is proportional to the concentration of atoms of the selected element. Either a flame (Flame Atomic Absorption (FAA)) or electrothermal vaporization using a graphite furnace (Graphite Furnace Atomic Absorption (GFAA)) may be employed to elevate the atom to an excited state.

FAA is relatively simple to use and extensive applications including those for snow and ice control products are available. Excellent precision makes it a preferred technique for the determination of major constituents (i.e., Ca, Mg, Na, and K) and higher concentration analytes. GFAA techniques are well documented, although not as completely as FAA techniques. GFAA has exceptional detection limit capabilities, but a limited analytical working range.

Some metal ions in samples are present as strong complexes—they are not easily decomposed to atoms in the flame—thereby providing a low result. This is particularly true for Ca or Mg determinations when phosphates are present. This is overcome by adding an ionization suppressant such as lanthanum chloride ($LaCl_3$) to samples, which binds the phosphate, releasing the Ca or Mg for detection. The PNS method for the determination of Ca and Mg by FAA references the use of lanthanum chloride when determining Ca and Mg by atomic absorption (*43*).

5.3.2.2 ICP-AES

AES is the process in which the light emitted by excited atoms or ions is measured. The emission occurs when sufficient thermal or electrical energy is available to exit a free atom or ion to an unstable energy state. The energy is created through an ICP (applying an RF field to argon gas) that can reach temperatures up to 10,000 °K. Light is emitted when the atom or ion returns to the more stable configuration in the ground state. The emitted wavelengths are specific to a particular element and their intensity is proportional to the concentration.

ICP-AES is a well-documented technique with multi-element analytical capabilities and a suitable working range and levels of detection—parts per billion detection is possible for some elements (*217*). Operator skill levels are intermediate between FAA and GFAA.

5.3.2.3 ICP-MS

ICP-MS is the synergistic combination of an ICP ion generation and a quadrupole mass spectrometer. Ions are quantified based on their mass/charge ratio. Ions of the selected mass/charge ratio are directed at a detector that quantifies the number of ions, further providing a sample concentration.

Applications are well documented and continue to grow rapidly. ICP-MS requires operator skill levels similar to those for ICP and GFAA.

ICP-MS combines multi-element detection capabilities with exceptionally low detection limits—parts per trillion (ppt) levels are possible for some elements (*217*). An important limitation is that samples with higher solids levels (i.e., 0.2 percent) cannot be tolerated. However, given the extremely low levels of detection, samples may be diluted and still provide results well below regulatory limits.

5.3.2.4 Method Selection

Each of the techniques listed above for metals determinations is technically suitable for the measurement of metals (and active ingredients) in snow and ice control products. A skilled operator with knowledge of potential analytical interferences and methods of compensation is essential in ensuring that performance-based objectives are met. The main selection criteria include

- Detection limits required,
- Equipment availability, and
- Ability to meet desired quality objectives.

5.3.3 Total Phosphorus

Phosphorus can exist in various forms including orthophosphate, which is readily soluble, and total phosphorus, which includes bound/combined phosphorus and requires more aggressive analytical techniques such as hydrolysis using heat and acid before determination. Orthophosphates are thought to be more environmentally available, although total phosphorus can degrade to orthophosphates.

It is important when determining phosphate concentrations that a total determination be conducted. PNS (*43*) references APHA *Standard Methods for the Examination of Water and Wastewater* (*67*), which includes hydrolysis methods employing perchloric acid, sulfuric/nitric acids, or persulfate.

PNS methodologies include a dilution step before analysis involving preparation of a 1-percent (v/v) test solution (10 mL of liquid sample is acidified and diluted to 1,000 mL with ASTM D 1193 Type II water) before phosphorus determination (*43*). Analytical results are reported as mg/L of phosphorus on the 1-percent solution. Unless a thorough understanding of the dilution procedure and the sample specific gravity is known, it is difficult to relate the determined result to phosphorus concentration in the snow and ice control product.

Section 3.4.2.3 discusses how the environmental characteristics of snow and ice control materials should be evaluated primarily in terms of total phosphorus, rather than specific phosphorus fractions.

5.3.4 Nitrogen

Forms of nitrogen present in snow and ice control products include

- Nitrite (NO_2^-),
- Nitrate (NO_3^-),
- Ammonia (NH_3),
- Organic Nitrogen (TON),
- Total Kjeldahl nitrogen (TKN), and
- Total Nitrogen (TN).

Nitrite and nitrate are commonly determined together and are referred to as "nitrate and nitrite." Ammonia and organic nitrogen are commonly determined together and are referred to as total Kjeldahl nitrogen (TKN). Nitrogen compounds are commonly reported as the nitrogen equivalent.

Test methods for determination of nitrogen compounds can be referenced in APHA Standard Methods (*67*), and various options are available for each nitrogen compound. It is the laboratory's responsibility to ensure that the selected methods meet accepted performance criteria for application to snow and ice control materials.

As discussed in Section 3.4.2.3, total nitrogen should be the main index by which nitrogen content is evaluated. A separate evaluation of ammonia and nitrate content is warranted because ammonia is potentially toxic to aquatic life at high concentrations, and nitrate is limited for drinking water supplies.

5.3.5 Organic Matter (BOD and COD)

Biochemical oxygen demand (BOD) is an empirical test used to determine the relative oxygen requirements of a sample and provides indication of biodegradable organic matter. The standard 5-Day BOD test has fixed incubation conditions of 20 ± 2°C for 5 days (*67*). It may be desirable in some cases to conduct the BOD test over longer periods of time and at various temperatures to reflect biodegradability under alternate (i.e., field) conditions. The 5-day BOD test procedure referenced in APHA Standard Methods (*67*) has widespread acceptance and is commonly conducted at most environmental laboratories. PNS references this method as well (*43*).

Chemical oxygen demand (COD) is used to measure the oxygen equivalent of the organic matter content of a sample that is susceptible to a strong chemical oxidant (*67*). COD can be conducted relatively quickly and can be empirically related to BOD. COD values should always be equal to or greater than BOD. The COD test procedures referenced in APHA Standard Methods (*67*) have widespread acceptance and are commonly conducted at most environmental laboratories. PNS references these methods as well (*43*).

5.3.6 pH

pH is the negative log of the hydrogen ion concentration in solution and represents the intensity of the acidic (low pH) or basic (high pH) character of a solution. Standard test methods involve the use of a calibrated electronic pH meter. These devices determine hydrogen ion activity by potentiometric measurement using a standard hydrogen ion electrode and a reference electrode. pH measurement is relatively free from interferences from color, turbidity, colloidal matter, oxidants, reductants, or high salinity, except for sodium error at $pH > 10$ (*67*). Most standard methods for pH measurements of liquids are relatively similar. Two examples include ASTM D 1293 and those listed in APHA Standard Methods.

PNS (*43*) references ASTM D 1293 for the measurement of pH, but requires a sample dilution of one part chemical and four parts distilled water before measurement.

5.3.7 Cyanide

Cyanide (CN) compounds exist as simple cyanides, where the CN^- ion is soluble and biologically available, or as complexed cyanide compounds, where the CN^- ion is sparingly or almost insoluble and not biologically available. Methods of analysis typically involve a digestion process (using acids, reducing agents, and/or ultraviolet light) to convert cyanide compounds into cyanide gas, which is distilled and adsorbed into a basic (NaOH) solution, from which a CN^- determination can be made.

Test methods to determine cyanide can be referenced in APHA Standard Methods (*67*). The chemistry of cyanide analysis is complex and subject to numerous interferences. It is the laboratory's responsibility to ensure that the selected methods meet accepted performance criteria for application to snow and ice control materials.

5.3.8 Aquatic Toxicity

The literature provides generalized protocols for conducting ecological toxicity tests of various chemicals and materials. Methods specific to snow and ice control materials do not exist. Both Environment Canada and the U.S. EPA detail methods for assessing toxicity to aquatic organisms (see Table 5-1). These procedures involve exposure of a test organism to various material concentrations under controlled conditions for a specified period. Based on the observed effects, a toxicity test endpoint value can be derived as follows:

- LC_{50}, or the median lethal concentration, is an estimate of the sample concentration that causes 50-percent mortality of the test organism during the specified period.
- The IC_{25} or IC_{50}, or the inhibition concentration, is an estimate of the sample concentration that causes a 25-percent or 50-percent reduction in growth or reproduction during a specified period.

Test duration designates whether the measured endpoint applies to acute or chronic toxicological effects. The U.S. EPA and Environment Canada recognize the 7-day fathead minnow test as a chronic bioassay for freshwater fish whereas the 96-hour test is recognized as an acute test. It has been judged that the 7-day test is sufficient in length to evaluate chronic toxicity. In addition, this test assesses the life stage of the representative fish considered most sensitive to adverse effects from chemicals and provides endpoints for growth and survival. By conducting a 7-day test, one can determine the 96-hr LC_{50} and 7-day LC_{50} as well as a 7-day EC_{50} on growth, in addition to other endpoints, including LC_{25}, EC_{25}, lowest observable effect concentration (LOEC) and no observable effect concentration (NOEC).

The assays shown in Table 5-1 provide chronic toxicity endpoints for fish, invertebrates, and algae. These tests are recognized as chronic tests by both Environment Canada and the U.S. EPA and are commonly used to examine sub-lethal effects to aquatic organisms in programs such as Environment Canada's Environmental Effects Monitoring, and the U.S. EPA's NPDES.

The fathead minnow chronic test is an early life stage test that measures sub-lethal effects at the life stage of the organism considered most sensitive to adverse effects from chemicals. The *Ceriodaphnia dubia* test represents a lifecycle test where

Table 5-1. Freshwater toxicity test methods.

Test Method	Standard Reference Method
Fathead Minnow (or Rainbow Trout) 96-hour Survival Test	US Environmental Protection Agency, 1993, Methods for Measuring the Acute Toxicity of Effluents and Receiving Water to Freshwater and Marine Organisms, 4th Edition, EPA/600/4-90/027F
Fathead Minnow 7-day Survival and Growth Test	US Environmental Protection Agency, 1994, Short-Tern Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to Freshwater Organisms, 3rd Edition, EPA/600/4-91/002
Ceriodaphnia dubia 3-brood Survival and Reproduction Test	US Environmental Protection Agency, 1994, Short-Tern Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to Freshwater Organisms, 3rd Edition, EPA/600/4-91/002
Selenastrum capricornutum 72-hour (Environment Canada) Growth Test	Environment Canada 1992/1997 amendments. Biological Test Method: Growth Inhibition Test Using the Freshwater Alga *Selenastrum capricornutum* Report EPS1/RM/25.
or	
Selenastrum capricornutum 96-hour (US EPA) Growth Test	US Environmental Protection Agency, 1994, Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to Freshwater Organisms, 3rd Edition, EPA/600/4-91/002

three reproductive cycles are represented. This test measures effects on survival and reproduction to aquatic invertebrates. The algae test is a chronic test that measures effects on growth and survival to aquatic plants over several life cycles.

The tests proposed involve representative organisms from three trophic levels in the aquatic environment—vertebrates, invertebrates, and plants. These three tests should be sufficient to examine the potential for adverse effects to a range of organisms in aqueous environments.

5.4 Evaluation of Concrete-Related Test Methods

Several standard test procedures have been developed to evaluate the performance of reinforced concrete exposed to snow and ice control materials. The test methods applicable to concrete and reinforcing steel are outlined in SHRP-H-332, *Handbook of Test Methods for Evaluating Chemical Deicers,* as follows:

- SHRP H-205.8, Test Method for Rapid Evaluation of Effects of Deicing Chemicals on Concrete;
- SHRP H-205.9, Test Method for Evaluation of Scaling Effects of Deicing Chemicals on Concrete Surfaces; and
- SHRP H-205.12, Test Method for Evaluation of Corrosive Effects of Deicing Chemicals on Steel Reinforcement in Concrete

These test methods are typically based on ASTM standards. The individual test procedures are discussed below.

5.4.1 SHRP H-205.8, Test Method for Rapid Evaluation of Effects of Deicing Chemicals on Concrete

The objective of this test method is the evaluation of the effects of snow and ice control materials and freezing and thawing cycling on the structural integrity of concrete. This test method uses small cylindrical concrete samples—1.5 inches in diameter and 1.875 inches in length.

The test specifies the concrete mix proportioning, casting, and curing of the samples. No air entrainment is used in the concrete. The samples are placed on sponges in a sealed container exposed to the specified snow and ice control test solution. The samples are subjected to ten freezing and thawing cycles by placing them in a freezer at –17.8 °C for 16 to 18 hours followed by thawing for 6 to 8 hours. The temperature and time parameters are as in ASTM C 672-98, *Standard Test Method for Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals.* The condition of each sample is evaluated by drying and weighing the largest intact part of each specimen after deteriorated concrete has been removed. The test method used deionized water and NaCl solutions as control conditions.

Although this test provides a fairly quick assessment of the freezing and thawing resistance of the concrete specimen, it is of limited value in evaluating snow and ice control materials. Several issues have to be considered when evaluating these materials that are not addressed in this test method.

The concrete mix does not contain any air entrainment, making it naturally susceptible to freezing and thawing damage. Thus, most damage is most likely caused by the freezing and thawing action. The damage caused by the deicing material is more likely a function of how well it can protect the sample from freezing, rather than a result of the aggressiveness of the material. This may explain why some materials perform better than others. Regardless of the deicing material used, the small samples probably will freeze completely during the long exposure at −17.8°C.

The concrete mix proportions use an unrealistically high w/c ratio of 0.51, resulting in a relatively poor-quality concrete compared with that in highway structures. For concrete exposed to freezing and thawing as well as snow and ice control materials, a much lower w/c ratio is typically used or even required by applicable standards.

Considering the long freeze cycles with the short thaw cycles, it is very unlikely that any chemical attack of the concrete matrix would be significant. Therefore, the relatively low number of cycles cannot be used to estimate the long-term effects of a snow and ice control material. Chemical attacks will take much longer to cause damage. In addition, these reactions will continue during the warmer temperature times of the year after the snow and ice control material has permeated the concrete.

Overall, this test method is a test for freezing and thawing resistance of the concrete. To obtain realistic results for the effects of snow and ice control materials, more representative conditions should be considered. The use of air-entrained concrete is now the standard for concrete exposed to freeze/thaw conditions. The number of cycles should be increased, and the thaw periods extended. Considering that freeze/thaw resistance is not the property that is to be evaluated, the use of higher freezing temperatures and shorter freeze cycles may also be considered.

5.4.2 SHRP H-205.9, Test Method for Evaluation of Scaling Effects of Deicing Chemicals on Concrete Surfaces

This test method is used to evaluate scaling effects on horizontal concrete surfaces exposed to freezing and thawing cycles in the presence of deicing chemicals. The effects are evaluated qualitatively by visual examination and quantitatively by weight loss. Concrete samples used in this test are 152 mm × 305 mm × 76 mm in size and are contained in a well holding the test solution. Similar to SHRP H-205.8, the mix proportions, casting, and curing are specified. The concrete does not contain air entrainment. It is recommended that deionized water and NaCl solution be used as control samples. The same concerns for air entrainment and w/c ratio arise as for SHRP H-205.8.

After the samples have been cured, they are ponded with deicer solution and exposed to the same conditions as in SHRP H-205.8. The samples are exposed to five freezing and thawing cycles and evaluated. Scaled material is washed and scraped from the sample surface, filtered, dried, and weighed. The surface is visually examined and rated in accordance with ASTM C 672-98, *Standard Test Method for Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals* as follows:

Rating	**Condition of surface**
0	No scaling
1	Very slight scaling (3.2 mm) depth,
2	Slight to moderate scaling
3	Moderate scaling (some aggregate visible)
4	Moderate to severe scaling
5	Severe scaling (coarse aggregate visible over entire surface)

After evaluation, the samples can be subjected to subsequent cycles, with evaluations being carried out after each set of five freeze/thaw cycles.

With the exception of using non-air-entrained concrete, this test is more realistic in evaluating various snow and ice control materials. Considering that ASTM C 672-98 allows for the use of air-entrained concrete, it would be more realistic for comparison with real structures. Also, the use of air-entrainment would eliminate additional deterioration as a result of freeze/thaw action.

To obtain meaningful results, the test should be carried for as many freeze/thaw cycles as possible. Some deterioration may require several years to establish. Longer thaw cycles should be considered because chemical reactions and ion diffusion are favored by higher temperature levels.

Another problem with ponding tests is the exclusion of oxygen from the concrete surface. Most real structures are subjected not only to freezing and thawing but also to wetting and drying.

5.4.3 SHRP H-205.12, Test Method for Evaluation of Corrosive Effects of Deicing Chemicals on Steel Reinforcement in Concrete

This test method is based on ASTM G 109-99, *Standard Test Method for Determining the Effects of Chemical Admixtures on the Corrosion of Embedded Steel Reinforcement in Concrete Exposed to Chloride Environments*, and involves the ponding of mortar or concrete prisms (280 mm × 152 mm × 114 mm) with a deicing solution.

One deformed #4 bar (12.7-mm diameter) is embedded 19 mm from the top surface and two bars are embedded 25 mm from the bottom of the prism. The top and bottom bars are connected with a resistor to form a macrocell, across which the potential difference can be measured. The macrocell current between the top and bottom bars can be calculated using Ohm's law. The samples are ponded with solution 3.8 mm in depth, and the voltage is measured at monthly intervals. As chlorides penetrate the sample and reach the top bar, it will begin to corrode, acting as an anode whereas the bottom bars then act as cathodes. The magnitude of the macrocell current provides information about the corrosion rate of the top bar.

This test measures two properties: the permeability of the concrete to chloride ions, and corrosion rate. Using the same concrete properties, one can evaluate the diffusion properties and corrosiveness of different snow and ice control materials.

Depending on the quality of the concrete, time to corrosion initiation may be fairly long. However, long-term tests typically provide the most meaningful results. Installation of bars at various depths may provide additional information about the diffusion of chloride ions. The relative long-term exposure also allows the evaluation of the effects of snow and ice control materials on the concrete matrix—possible chemical reactions between the chemical and the cement and/or aggregates.

As discussed for SHRP H-205.9, ponding tests are limited in their applicability to real structures. Spray application of the solution may be a more realistic test procedure than ponding.

5.4.4 Summary of Concrete-Related Test Methods

5.4.4.1 General

As for most laboratory test procedures, there are limitations in these test standards when making predictions for field applications. It is difficult to make service life predictions for 20, 30, 50, or even 100 years on the basis of several days or months of laboratory testing. It is well known that chlorides penetrate concrete, but it is more difficult to predict the rate at which this occurs. Changes in concrete technology and snow and ice control systems will influence the service life of structures.

It may take several years to make conclusive statements about the effects of a particular snow and ice control material from field use. To allow extrapolation from laboratory data to long-term field performance, one has to attempt to develop tests that resemble real application and climate conditions. Simply ponding samples is not sufficient. Accelerated tests can be considered if exposure conditions are realistic and only when the number of cycles is increased to represent real-world conditions. Any long-term study should be complemented by full-scale field studies if at all possible.

Considering the advancement in concrete technology, the SHRP and other related test methods need to be modified to incorporate mix designs developed for the intended ice control chemical exposure. Air entrainment and SCMs are commonly used, and test methods must accommodate those. Ideally, test samples should be prepared using the concrete actually being used in a particular region rather than the lower quality concrete now designated in some of the test procedures. For example, the effects of SCMs in improving concrete durability generally and reduction in ion diffusion specifically here are well-documented (*138*).

The study team believes that SHRP H-205.8 is of limited value for the purposes of this study. It measures freezing and thawing scaling resistance only. SHRP H-205-12 is the most relevant test for the effect of snow and ice control chemicals on concrete itself and, more important, concrete rebar corrosion. It has the disadvantages of long test times and incomplete representation of field exposure.

5.4.4.2 Test Methods Under Development

The study team is aware that substantial relevant research work is under way. Much of that work relates to the transport phenomena of ions into concrete. One problem with this work, when considering ions other than chlorides, is that there are no standard test methods for profiling the diffusion of such ions with depth of penetration into concrete.

Following are some ASTM test methods in advanced stages of development or recently introduced:

- *C 1556, Standard Test Method for Determining the Apparent Chloride Coefficient of Cementitious Mixtures by Bulk Diffusion.* This method provides the diffusion coefficient needed for modeling and will be used in Phase II to provide relative diffusion values for the various ice control chemicals.
- *Standard Method for Indication of Concrete's Ionic Conductivity.* This test uses the RCP equipment to determine conductivity, which is a fundamental part of corrosion. Such corrosion current flow is greatly influenced by the presence of diffused compounds and is again relevant to the detrimental action of ice control chemicals.
- *Field Rate of Absorption.* This test is similar to the ISAT test used in Europe. It may find value here given its ability to quickly determine, in situ and non-destructively, the susceptibility of an existing concrete to ion penetration.
- *Rate of Sorptivity*. Sorptivity is the rate of absorption of liquids.

There is also parallel research into test procedures being sponsored by AASHTO:

- TP64-2003, *Provisional Standard Test Method for Predicting Chloride Penetration of Hydraulic Cement Concrete by the Rapid Migration Procedure* and
- TP26-94, *Method for the Relative Permeability of Concrete by Surface Air Flow.*

A few highway departments are already using some of these tests. They will be contacted in Phase II about their experience.

5.5 Evaluation of Atmospheric Corrosion Testing

Laboratory corrosion tests typically are used to attempt to predict the corrosion behaviors of metals versus various corrodants when service history is lacking or unavailable and time, budget, or suitable field test site constraints do not allow field or test track testing. Experience has shown that all metals and alloys do not respond alike to the many factors that control corrosion and that "accelerated" corrosion tests give indicative results only or may even be entirely misleading (*218, 219*).

Laboratory corrosion tests are particularly useful for comparing materials and environments. They allow the application of quality control measures and can provide insight into corrosion mechanisms. Corrosion under natural conditions can take long periods to materialize; thus, most laboratory corrosion tests are designed to accelerate the corrosion processes. Test results must therefore be used with some caution because they may bear little or no relationship to field use (*196, 208, 215, 218, 220*). Corrosion test results typically depend on both the test method used and the subject metals tested. Results can vary dramatically from test to test and thus are not comparable (*175, 196, 202, 206, 208*). Standardized laboratory corrosion tests are useful techniques to compare various chemical compounds such as inhibitors or snow and ice control chemicals, but typically they do not predict performance in real-world conditions (*191, 218, 220*). Laboratory corrosion tests can basically be broken down into five general classes: immersion testing, poultice testing, salt-spray testing, electrochemical testing, and test track testing.

5.5.1 Immersion Testing

Immersion testing, probably the most common corrosion test method used, involves immersion of the sample within a liquid. There can be numerous variations in the test conditions such as temperature, agitation rate, and atmosphere. Immersion tests can entail the following (*174, 187, 188, 195–198, 206, 208, 215, 218, 221-229*):

- Total immersion (specimen completely immersed in the solution);
- Alternate immersion (specimen immersed in the solution for a period and then removed from the solution and allowed to dry);
- Partial immersion (lower portion of the specimen is immersed in the solution with the upper half in air or vapor); and
- Numerous variations.

All immersion testing can normally be carried out with oxygen contact or with inert gas to exclude oxygen contact.

Immersion of test specimens in a corrosive medium appears to be a simple test, but, to ensure reproducibility of test results, numerous test conditions must be controlled (e.g., temperature, humidity, chemical concentration and volume, time, surface area, flow rates, and number of samples).

Immersion corrosion tests basically all follow or are modifications of ASTM G 31, "Standard Practice for Laboratory Immersion Corrosion Testing of Metals" (*218*), or NACE Standard TM-01-69, "Laboratory Corrosion Testing of Metals for the Process Industries" (*219*). These standard practices describe accepted procedures for and factors that influence laboratory immersion corrosion tests, particularly mass loss tests. The factors include specimen preparation, apparatus, test conditions, methods of cleaning specimens, evaluation of results, and calculation and reporting of corrosion rates. These practices also emphasize the importance of recording all pertinent data and provide a checklist for reporting test data. ASTM G 31 is based on the NACE standard with modifications to relate more directly to practices. Specific corrosion testing protocols are described in the following sections.

5.5.1.1 PNS (NACE Standard TM-01-69 as Modified by the Pacific Northwest States)

This procedure is an intermittent immersion test used to evaluate snow and ice control chemicals for qualification (*43*). The PNS test uses 1/2-inch flat steel washers for each deicer test solution. In each test, a single washer is exposed to the 3-percent snow and ice control chemical solution, 3-percent sodium chloride solution, and distilled water. The test consists of 72 cycles of intermittent exposure with 10 minutes in the liquid and 50 minutes air drying per cycle. For PNS acceptance, the chemical must have a corrosion weight loss of at least 70 percent less than the sodium chloride standard solution. The PNS test has shown significant variability—probably because of the lack of control of test conditions such as temperature and humidity. It is unlikely that the PNS test shows any direct correlation with field exposure, given that the test is conducted at a single inhibitor concentration and is an immersion test. The PNS test is not suitable for evaluating the effect of chemicals on metals (e.g., aluminum, magnesium, or stainless steel) (*187*) or galvanic corrosion.

5.5.1.2 SAE J2334 – Cosmetic Corrosion Lab Test

This corrosion test method was developed for determining cosmetic corrosion performance of coating systems, substrate, process, or design (*187, 230, 231*). It can be used as a validation tool as well as a development tool. The test uses ten standard steel sheet materials painted with a full automotive paint system consistent with standard practices used in the automotive industry. The test can be performed either manually or automatically, depending on the equipment available. Testing for 80 cycles by either method reproduces results obtained in the field after 5 years of vehicle exposure in the Snow Belt area of the United States and Canada.

The test procedure consists of an application of a salt solution (0.5 percent NaCl, 0.1 percent $CaCl_2$, and 0.075 percent $NaHCO_3$) by dip, fog, or spray for 15 minutes at ambient conditions; a drying period of 17 hours and 45 minutes at 60°C and 50-percent relative humidity; and then a 6-hour exposure at 50°C with a 100-percent relative humidity. For automatic operation, this is repeated daily for 80 cycles; for manual operation, the samples are allowed to dry at 60°C and 50-percent relative humidity on weekends and holidays. This test method could be classed as either an intermittent immersion test or an intermittent salt-spray or fog test, depending on the method of salt application (i.e., dip, fog, or spray).

The tests are monitored with weight loss bare steel coupons, and the coated samples are evaluated by scribe creep back values or corrosion rate (weight loss) measurements. This test procedure is a field-correlated test for motor vehicle coating systems on steel substructures. It has an excellent correlation with results obtained in 5-year tests on road-driven cars in the Snow Belt area of the United States and Canada. If corrosion mechanisms other than cosmetic or general corrosion are to be examined using this test, field correlation must be established.

5.5.1.3 SHRP H-205.7 "Test Method for Evaluation of Corrosive Effects of Deicing Chemicals on Metals"

This SHRP test method was developed to evaluate the corrosive effects of deicing chemicals on metal substrates (*215, 232*). This test method was also intended to evaluate the effectiveness of corrosion-inhibiting additives to snow and ice control chemicals and the effects of other aqueous, near-neutral pH solutions. The test method is a weight loss immersion corrosion test with air aspiration into the solution for deicing chemicals and inhibitors using deionized water and 3-percent sodium chloride master solutions as a comparison of the relative effectiveness. It is specified as a matrix test with duplicate exposures ranging from 1 to 8 weeks and inhibitor concentration, less than optimum, optimum, and greater than optimum. It gives no guidelines as to the acceptable corrosion behavior for the tested materials.

5.5.2 Poultice Corrosion Testing

This poultice corrosion test was devised to simulate poultice and crevice corrosion on automobiles and the results are reported in "*Development of Poultice Corrosion Tests for Automobiles*" (*198*). The poultice corrosion testing procedure consists of two types of test methods: (1) partially inserting rectangular sheet metal samples into washed sand doped with various deicing chemical solutions; or (2) forming U-shaped channels with sealed ends from metal sheets and then filling the channels with washed sand doped with various deicing chemical solutions. The test samples are exposed to a cyclic testing procedure that consists of a 22-hour exposure in a humidity chamber at 95-percent relative humidity and 40°C followed by a 2-hour exposure at ambient conditions. The test samples are evaluated for corrosion after various exposure times (up to 16 weeks), by weight loss measurements and measured thickness loss. Given that the corrosion tends to be highly localized at the air-sand interface, the measured thickness loss is indicative of localized corrosion rates such as would occur from poultice corrosion or crevice corrosion.

5.5.3 Salt-Spray Testing

Salt-spray testing has been used for approximately 100 years as an accelerated corrosion test to determine the comparative corrosion resistance of various metals and alloys and the corrosion protection of organic and inorganic coatings on metallic substrates. There are numerous variations (*174, 181, 186, 187, 207, 221, 222, 224–226, 233–235*). The principal objective of salt-spray (fog) testing is to provide a rapid procedure for comparing the performance of materials and coatings. Salt-spray testing is an acceptable tool for evaluating the uniformity of thickness and degree of porosity of metallic (e.g., zinc) and nonmetallic protective coatings. In most, if not all cases, there is little correlation with service performance.

Many government agencies and automotive companies have developed their own standards and procedures. Many of these have been revised to conform with most of the details of the ASTM specifications, but they still incorporate several statements relating to practices that experience has shown to be desirable or beneficial for achieving reliable, reproducible results and maximum correlation among laboratories (*174*). The following are typical salt-spray (fog) corrosion test procedures. Most are similar, but have different operating parameters.

5.5.3.1 ASTM B 117 "Standard Method of Salt-Spray (Fog) Testing" (224)

This is the most commonly used salt-spray (fog) testing for inorganic and organic coatings. It is not suitable for testing metallic (e.g., zinc) coatings (*235, 236*) or localized corrosion (e.g., crevice and poultice corrosion). The test conditions are as follows:

- Exposure time—8 to 3,000 hours, depending on product or type of coating;
- Test media—5-percent sodium chloride solution with a pH of 6.5 to 7.2; and
- Test temperature—35°C (95°F) in the exposure zone of the closed cabinet.

5.5.3.2 ASTM G 85 "Standard Practice for Modified Salt-Spray (Fog) Testing Annex 1 – Acetic Acid – Salt-Spray (Fog) Testing" (226)

This test is also used for testing inorganic and organic coatings, but is particularly applicable to the study or testing of decorative chromium plate and cadmium plate on steel or zinc die castings and for the evaluation of the quality of a product. Typical test conditions are as follows:

- Exposure time—can be as brief as 16 hours, but is typically 144 to 240 hours or longer;
- Test media—5-percent sodium chloride with pH adjusted to 3.1 to 3.3 by adding acetic acid; and
- Test temperature—35°C (95°F) in the exposure zone of the closed cabinet.

5.5.3.3 ASTM B 368 "Standard Practice for Copper-Accelerated Acetic Acid – Salt-Spray (Fog) Testing (CASS Test)" (225)

This test is primarily used for the rapid testing of decorative plating on steel and zinc die castings, but is also useful in the testing of anodized, chromated, or phosphated aluminum. The test conditions are as follows:

- Exposure time—ranges from 6 to 720 hours;
- Test media—5-percent sodium chloride with addition of 0.26 gram per liter $CuCl_2 \cdot 2H_2O$ and pH adjusted to 3.1 to 3.3 with acetic acid; and
- Test temperature—49°C (120°F) in the exposure zone of the closed cabinet.

5.5.4 Electrochemical Testing

Corrosion is an electrochemical process and thus electrochemical techniques can be used as rapid procedures to evaluate and study most, if not all, forms of corrosion. Corrosion requires an anode and a cathode in electrical contact with an ionic conduction path through an electrolyte. Typical electrochemical procedures and tests are described in references (*174, 190, 221, 227–229, 237*).

Linear polarization resistance (LPR) is a common electrochemical technique that measures instantaneous corrosion rates. It has been shown to correlate well in near-neutral solutions with weight-loss measurements for a wide variety of metals and corrosive media. Unfortunately, most corrosion of motor vehicles occurs in moist or humid environments with only a thin film of moisture present. Thus, LPR is not suitable and/or measurements do not typically correlate with service conditions and are thus unreliable.

LPR measurements could be used as a rapid test method to compare the corrosivity of various chemical deicers and inhibitors under different concentrations, temperatures, inhibitor concentrations, or length of exposure time. LPR would also be suitable for evaluating the effect on inhibitors with roadside dilution. Many types of inhibitors can accelerate localized corrosion if they are not present at sufficient levels to protect all of the metal surfaces. Protected surfaces become cathodic to unprotected surfaces and if the cathodic-to-anodic ratio is large, very rapid corrosion can occur on the anodic areas.

LPR testing is referenced in:

- ASTM G 3, "Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing";
- ASTM G 96, "Standard Guide for On-Line Monitoring of Corrosion in Plant Equipment (Electrical and Electrochemical Methods)"; and
- ASTM G 102, "Standard Practice for Calculating of Corrosion Rates and Related Information from Electrochemical Measurements."

5.5.5 Test Track Testing

Test track testing is basically a form of accelerated field tests. Test tracks are designed to simulate field corrosion conditions, but in an accelerated time frame. They typically subject the motor vehicles to controlled humidity, soaking and drying (corrosion booth), salt mist or spray, salt splash troughs, mud and gravel roads, grit and gravel troughs and mileage accumulation (*234*, *238*). The corrosion test results from test track tests have generally shown good correlation with customer motor vehicles inspection and field corrosion measurements using coupons mounted on motor vehicles (*234*).

5.5.6 General Comments Regarding Laboratory Corrosion Tests

Laboratory corrosion tests are accelerated corrosion tests and, therefore, may have little or no correlation with field experience (*191, 215, 220–222, 234–236, 239*). Most of the accelerated corrosion test procedures commonly accepted by the automotive industry are designed for cosmetic corrosion of steel and coated steel (*237*). Cosmetic corrosion is typically exterior corrosion that occurs as a result of the breakdown or damage to a coating system. This type of corrosion does not normally affect function or structural strength, but does compromise appearance.

Laboratory corrosion tests may be applicable to some degree to all metals, but they may not give valid comparisons even within the same metal systems (*223*). In addition, rankings of snow and ice control chemicals will vary with the corrosion test procedures used and the metals and coatings tested (*187*). The tests typically are designed to determine the comparative corrosiveness of snow and ice control chemicals relative to a particular sodium chloride concentration under controlled and reproducible conditions that are not typical of field conditions (*215*).

Caution should be exercised for accelerated laboratory corrosion tests because these tests are based on numerous assumptions and arbitrary testing conditions. Corrosion data developed using bulk solutions do not necessarily correlate with corrosion in humid or moist environments such as occur on motor vehicles exposed to snow and ice control chemicals.

Weight-loss measurements are widely used for evaluating corrosion resistance. Weight-loss is a suitable method for general corrosion, but it is not suitable for the most detrimental forms of motor vehicle corrosion (e.g., localized corrosion such as pitting, crevice corrosion and under-deposit attack (poultice corrosion), and galvanic corrosion).

Immersion corrosion tests such as the PNS test are rapid and provide an acceptance ranking for snow and ice control chemicals based on a single sample (typically steel) and single concentrations of chemical and inhibitor. Therefore, test results do not necessarily bear any relationship to field conditions. In addition, the PNS tests appear to have inter-laboratory and intra-laboratory variations and are not suitable for metals other than steel. The validity of the PNS test to predict uniform or general corrosion field conditions could be improved by running duplicate samples, controlling temperature and humidity, and running the test at a number of dilution ratios to try and simulate field conditions. These changes to the PNS test procedure will still not provide correlation with field conditions because of localized corrosion, galvanic corrosion, or corrosion of metals other than steel.

Salt-spray (fog) tests are primarily for the evaluation of organic coatings on steel. They might be adapted to evaluate forms of localized corrosion by using the deicing chemicals and inhibitors for the test media, instead of the normal salt solutions in environmental chambers with programmed drying periods.

Electrochemical corrosion tests can be used to evaluate general corrosion of snow and ice control chemicals and corrosion inhibitors over various concentrations; it is much more difficult, but not impossible, to devise a test program to evaluate localized corrosion and galvanic corrosion.

CHAPTER 6

General Assessment of Information

6.1 General Conclusion

All snow and ice control materials have some potential for affecting the receiving environment and/or infrastructure. The magnitude of the effect depends on a wide range of conditions, including types of materials, quantities being applied, transport pathways, exposure pathways, exposure duration, chemical-specific impacts, and other site-specific characteristics. Assessment of the information gathered through this study has indicated where potential areas of impairment related to snow and ice control materials are most likely. Relevant product categories include NaCl, $CaCl_2$, $MgCl_2$, acetates, organic biomass products, and abrasives. These material types represent the typical cross section of the present market. Potential impairments associated with these materials can also be applied to many of the available blended materials.

6.1.1 Natural Receiving Environment

Table 6-1 summarizes the potential environmental impairment, including the estimated magnitude of effect and a description of the contributing factors. The estimated magnitude of effect has been based on the assessment and conclusions developed in the referenced sections.

The most significant areas of potential impairment include water quality/aquatic life, air quality, vegetation, soils, and animals. They also are the general areas of environmental concern indicated in the survey of agency comments (refer to Table 2-5). The exception is soil impacts, which have been included based on assessment of technical information. Direct effects on soils are generally not a concern, but snow and ice control material can influence soil structure, and the presence of these materials in soil can further affect water systems and vegetation.

Environmental areas reviewed in this study and found not to be of significant concern include effects to soil biota and effects to human health. Routine snow and ice control practices do not pose a significant risk to roadside microbial populations outside what would already normally be considered a disturbed environment. Human health concerns associated with handling of snow and ice control materials are associated with very high doses and any real concerns are mitigated through application of proper safety measures (e.g., protective clothing and ventilation) that should already be in place.

In addition, contamination of drinking water supplies to a degree considered an impairment for a raw water supply could occur under some circumstances, especially in the case of individual wells very close to a point of routine application for deicing materials.

6.1.2 Infrastructure Corrosion

6.1.2.1 Atmospheric Corrosion

Atmospheric corrosion processes related to snow and ice control chemicals are complex and it is difficult to provide generalized evaluations. Much of the literature reviewed provides information that depends on specific conditions; and study conclusions tend to be wide-ranging and, in some cases, contradict one another. Discrepancies are related to the specific conditions under which the assessment was carried out, including type of snow and ice control material; presence, type and concentration of corrosion inhibitor; alloy materials being assessed; corrosion type being monitored; and specific test method/conditions used. Despite the weakness in specific information, some broad assessments can be developed:

- Chloride-based snow and ice control chemicals are the most corrosive to metals with the hygroscopic chlorides of magnesium and calcium being the most aggressive because of the longer time of wetness.
- Acetate-based and organic snow and ice control materials tend to cause significantly less corrosion than chloride-

Table 6-1. Generalized potential environmental impairment related to common snow and ice control chemicals.

Environmental Impact	Road Salt (NaCl)	Calcium Chloride ($CaCl_2$)	Magnesium Chloride ($MgCl_2$)	Acetates (CMA and KA)	Organic Biomass Products	Abrasives
Water Quality/ Aquatic Life (Section 3.4)	Moderate: Excessive chloride loading, metal contaminants; ferrocyanide additives.	Moderate: Excessive chloride loading; heavy metal contamination.	Moderate: Excessive chloride loading; heavy metal contamination.	High: Organic content leading to oxygen demand.	High: Organic matter leading to oxygen demand; nutrient enrichment by phosphorus and nitrogen; heavy metals.	High: Turbidity; increased sedimentation.
Air Quality (Section 3.8)	Low: Leads to reduced abrasive use.	Low: Leads to reduced abrasive use.	Low: Leads to reduced abrasive use.	Low: Leads to reduced abrasive use.	Low: Leads to reduced abrasive use.	High: Fine particulate degrades air quality.
Soils (Section 3.5)	Moderate/High: Sodium accumulation breaks down soil structure and decreases permeability and soil stability; potential for metals mobilization.	Low/Moderate: Improves soil structure; increases permeability; potential for metals mobilization.	Low/Moderate: Improves soil structure; increases permeability; potential for metals mobilization.	Low/Moderate: Improves soil structure; increases permeability; potential for metals mobilization.	Low: Probably little or no effect; limited information available.	Low: Probably little or no effect.
Vegetation (Section 3.7)	High: Spray causes foliage damage; osmotic stress harms roots; chloride toxicosis.	High: Spray causes foliage damage; osmotic stress harms roots; chloride toxicosis.	High: Spray causes foliage damage; osmotic stress harms roots; chloride toxicosis.	Low: Little or no adverse effect; osmotic stress at high levels.	Low: Probably little or no effect.	Low: Probably little or no effect.
Animals (Section 3.9)	Low: Sodium linked to salt toxicosis and vehicle kills; magnitude unclear.	Low: Probably little or no effect.	Low: Probably little or no effect.	Low: Probably little or no effect.	Low: Probably little or no effect; limited toxicity information available.	Low: Probably little or no effect.

Conclusions based on the assessment of information reviewed in this study.

based chemicals, but can still accelerate corrosion by increasing the conductivity of the moisture.

- Corrosion related to a given snow and ice control material may show various responses between product concentrations, metal types, and even between alloys within the same metal group.
- Snow and ice control chemical corrosion inhibitors tested in the laboratory can show significant reductions in the corrosion rate of the metals being tested, but they may show little or no inhibiting effect on other metals (even those in the same metal group) and may, in effect, accelerate corrosion of some metals.
- To develop any meaningful general corrosion rate data for snow and ice control chemicals and corrosion inhibitors, tests must be run over a wide range of concentrations and also under a number of ambient conditions to simulate field conditions.

6.1.2.2 Concrete Corrosion

Snow and ice control chemicals can have detrimental effects on concrete infrastructure. These can be separated into three general categories:

- The enabling and/or acceleration of corrosion of concrete reinforcing (rebar) resulting from chloride ion penetration. This effect is primarily related to bridges; however, there is a possibility of a secondary risk in concrete pavements with doweled joints or continuous reinforcement.
- Reactions of snow and ice control materials with the cement paste, resulting in deterioration of the cement matrix. This effect is primarily a risk for concrete pavements and the amount of deterioration is directly related to the quality of concrete. Evidence suggests that magnesium reacts chemically with the cement paste in a process that reduces the concrete strength.
- All snow and ice control chemicals by definition of their action increase the number of freezing and thawing cycles on the concrete in service. This can result in deterioration in the form of freezing and thawing and/or scaling.

6.1.3 Other Infrastructure

Chloride-based snow and ice control products can affect the operation of railway traffic control signaling and power distribution lines. This is related to their ability to become conductive, and in general, effects are related to extreme conditions. In the case of railway traffic control signaling, this may involve pooling of brines across tracks; for power distribution lines, it may involve power lines close to elevated bridges and overpasses. However, the information is weak regarding the frequency and magnitude of effect.

6.2 Draft Material Selection Framework

6.2.1 Approach and Assumptions

A process for selecting preferred snow and ice control materials for generic application situations was developed considering responses from the agency survey (see Section 2.3) and information on product characteristics, environmental effects, and material effects, as discussed in Chapters 2 through 4. When selecting a snow and ice control material, a series of steps and factors is considered. Figure 6-1 illustrates the selection process. The general process is straightforward; however, certain components (e.g., the "decision tool") are more involved. This complexity makes it difficult to develop a model that incorporates "all" possible cases. The framework proposed here addresses the most common and most significant factors involved in selecting snow and ice control products.

Before selecting a snow and ice control material, application methods must be selected by the agency. Application methods have considerable influence on level of service, and significant research has been applied toward developing guidelines for selecting snow and ice control application methods (*6*). A challenge in developing a material selection process is to maintain independence from the application method selection processes, while realizing that significant interrelations exist. For example, application methods influence volumes of materials released to the environment and, therefore, influence the potential for environmental impact. When general application methods are selected before materials, the influence the application method can have on material selection can be carried through the material selection process.

Once application methods are agreed on, an agency will choose a list of candidate snow and ice control products. A matrix of significant properties will exist or, in the case of newer products, be developed, and then preliminary qualification will be applied through comparison with a specification. Materials meeting specification requirements will be "qualified" for further assessment using the decision tool.

The decision tool is the most complex component of the material section process and combines product rankings that reflect the material's potential for impairment with agency objectives weighted by importance. A guidance tool for agencies was developed in Phase II of this study and includes a list of potential operational issues and areas of impairment, along with general recommendations to assist agencies in assigning weights to decision categories.

Table 6-2 lists the four decision categories that form the framework for the decision tool: cost, performance, natural environment, and corrosion. These categories balance operational concerns ("value" related to cost and performance) with potential consequences of use ("costs" related to environmental and corrosion impacts). Also indicated is the average weighting given to categories as indicated from the survey of agency comments (see Section 2.4.4.1). Environmental and corrosion concerns currently are given much lower agency importance than cost and performance. Although these priorities may not be ideal, it is nonetheless the current reality.

Table 6-2 also lists subcategories that contribute to the development of natural environment and corrosion decision categories. These were selected based on agency survey results and study team experience. The divisions are relatively straightforward and provide a reasonably thorough representation of the higher level decision category.

Development of similar subcategories for cost and performance offers the following challenges:

- The cost of snow and ice control involves direct costs (i.e., purchase price) and indirect costs (i.e., operational costs and capital costs). Direct and indirect costs can be influenced by factors outside the scope of information gathered in this study. Additionally, indirect costs are related more to application strategy/policies than material selection. For this study, cost will represent purchase price per kilogram of solid material as provided by each agency.
- Performance is a broad term that may have numerous measures depending on conditions being assessed. For this study, general performance will be represented by temperature performance assessed through application of eutectic temperatures using the Performance Index description in Section 2.6.1.

The result of the decision tool is a numerical product score that can be used to compare selected products objectively. Product selection occurs after a review of other agency considerations that may include, but not be limited to, concerns with product availability (e.g., delivery times and quantities), quality testing results, and equipment availability.

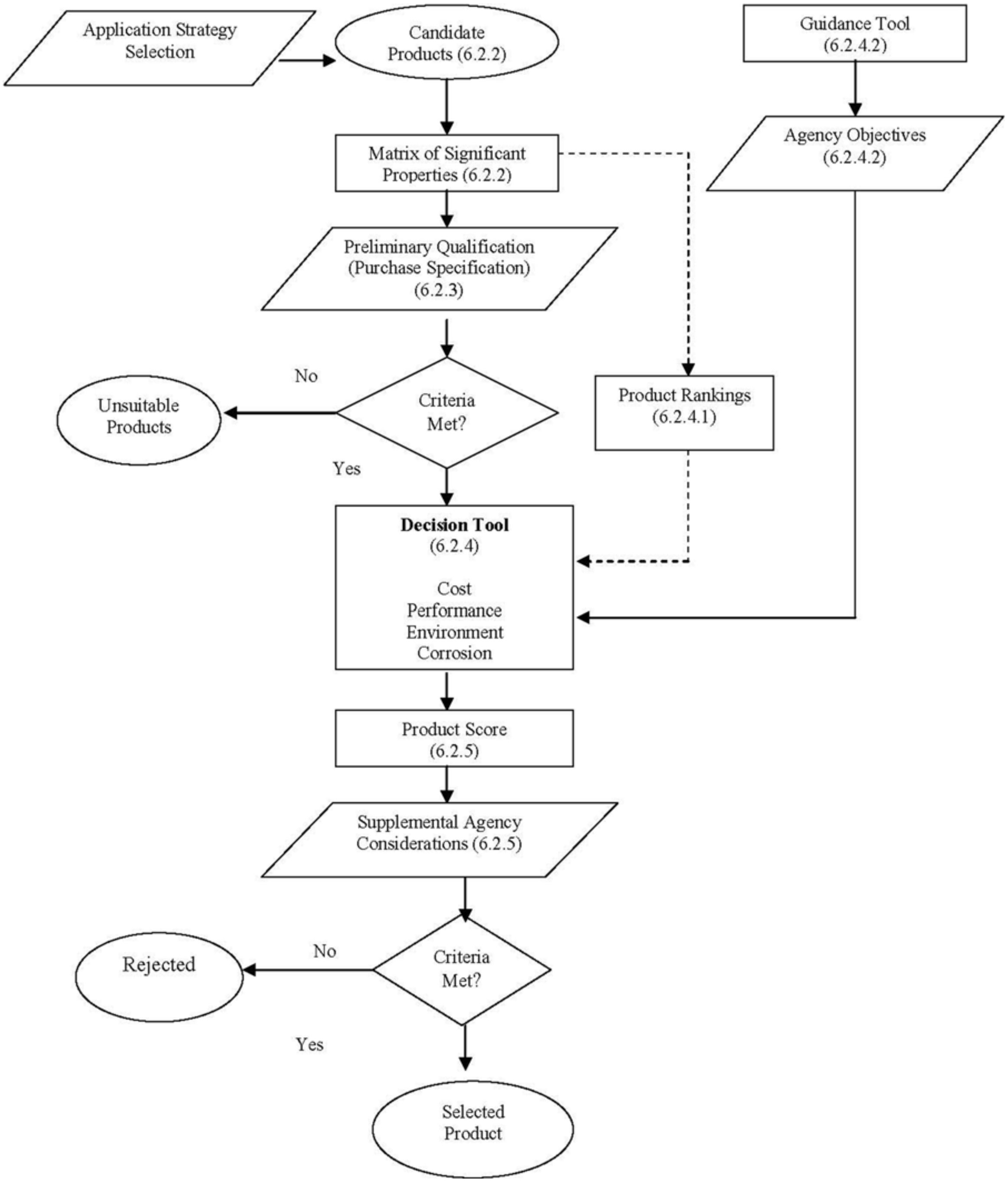


Figure 6-1. Flowchart for materials selection process.

The following sections describe the material selection processes in greater detail.

6.2.2 Candidate Product Selection and Matrix of Significant Properties

As an initial step in product selection, an agency will select a list of candidate snow and ice control products. For each product, an associated matrix of significant properties will exist or be developed. This will consist of a series of tables that cross-references a material with a measured parameter. In cases where non-tested attributes are a concern, a descriptive rating will be applied in place of a numerical test result. Application methods will be given consideration here, because they have significant bearing on the volumes of materials released to the environment.

The approach here is to characterize each material on the basis of components that affect cost, performance, the natu-

Table 6-2. Decision tool framework.

Decision Category	Weighting[1]	Decision Subcategory
Cost	45	Agency Input Required
Performance	33	
Natural Environment	12	Aquatic
		Air
		Vegetation
		Soil
		Animals
Corrosion	10	Vehicles
		Infrastructure
		Concrete
		Concrete Reinforcing

[1] Agency Survey, Section 2.3.4.1

ral receiving environment, and corrosion. A matrix of significant properties was developed during Phase II of this study. The information included in the "matrix of significant properties" will also be used in the decision tool to develop product rankings (see Section 6.2.4.1).

6.2.3 Preliminary Qualification

Agencies may choose minimum qualifications that singularly affect the selection of a product. An example is a purchase specification addressing product cost, toxicity, corrosion, or other policies important to the agency. This process allows agencies to reject unsuitable products and generate a "short list" of products for detailed assessment quickly. Phase II of this study involved developing a purchase specification for agencies to use in this step.

6.2.4 Decision Tool

The decision tool combines the product rankings developed in this study and agency objectives for several decision categories and subcategories (see Table 6-2). The product is a numerical score for a material/application selection that can be compared among materials. The decision tool consists of a relatively simple software application.

6.2.4.1 Product Rankings

The study team developed product rankings based on the technological appraisal of information gathered and assessed in this study and based on agency input. This takes the form of a matrix embedded in the decision tool that provides a numerical product ranking for each product/subcategory combination. Five levels of numerical ranking (1 = poor; 2 = poor/moderate; 3 = moderate; 4 = moderate/good; 5 = good) provide sufficient numerical range to separate "poor" and "good" product performance effectively during subsequent modeling (decision tool), without being overly complex.

In the case of natural environment and corrosion, the study team developed product rankings at the "subcategory" level that were based on a material's potential for impairment. These were similar to the evaluations prepared in Section 6.1 (Tables 6-1 and 6-3), but were supplemented by the informa-

Table 6-3. Generalized potential corrosion impairment related to common snow and ice control chemicals.

Environmental Impact	Road Salt ($NaCl$)	Calcium Chloride ($CaCl_2$)	Magnesium Chloride ($MgCl_2$)	Acetates (CMA and KA)	Organic Biomass Products	Abrasives
Atmospheric Corrosion to Metals (General)	High: Will initiate and accelerate corrosion.	High: Will initiate and accelerate corrosion; higher potential for corrosion related to hygroscopic properties	High: Will initiate and accelerate corrosion; higher potential for corrosion related to hygroscopic properties	Low/moderate: Potential to initiate and accelerate corrosion due to elevated conductivity.	Low: Potential to initiate and accelerate corrosion due to elevated conductivity claims of mitigation of corrosion require further evaluation.	Low: Probably little or no effect
Concrete Matrix (Section 4.1)	Low/moderate: Will exacerbate scaling; low risk of paste attack.	Low/moderate: Will exacerbate scaling; low risk of paste attack.	Moderate/high: Will exacerbate scaling; risk of paste deterioration from magnesium reactions.	Moderate/high: Will exacerbate scaling; risk of paste deterioration from magnesium reactions	Low: Probably little or no effect.	Low: Probably little or no effect
Concrete Reinforcing (Section 4.1)	High: Will initiate corrosion of rebar.	High: Will initiate corrosion of rebar.	High: Will initiate corrosion of rebar, evidence suggests $MgCl_2$ has highest potential for corrosion of chloride products	Low: Probably little or no effect.	Low: Probably little or no effect; claims of mitigation of corrosion require further evaluation	Low: No Effect

Conclusions based on the assessment of information reviewed in this study.

tion from the testing program and matrix of significant properties developed in Phase II of this study. For example, one material may pose a significant corrosion risk to concrete reinforcing and be assigned a score of "1 = poor." Alternatively, a second material posing lower risk may be assigned a score of "4 = moderate/good."

Cost and performance rankings are applied at the "category" level and are developed based on user input. For example, an agency will provide purchase cost information, because these costs can be significantly affected by transportation costs, and are not similar for all agencies. To assess performance requirements, agencies will provide information on the pavement temperatures (i.e., lowest 85th percentile) expected for the region. Many agencies do not routinely experience extreme cold temperatures and, therefore, would receive limited additional performance benefit from low-temperature-performance snow and ice control materials.

To illustrate the approach, Table 6-4 provides an example of preliminary product rankings for two potential product/application strategies: (1) Abrasive/NaCl deicing; and (2) $MgCl_2$ anti-icing. These illustrate the categories and subcategories used and the aspects of the product considered to formulate a product ranking. These do not reflect the actual rankings developed during Phase II of this study, but they are reasonable approximations based on the current knowledge.

6.2.4.2 Agency Objectives

Each agency will have a unique set of concerns specific to their conditions. For example, in certain regions, legislation may require protection of a particular aquatic environment; in other regions, corrosion of infrastructure may be a concern. It must also be recognized that there is a high degree of reluctance to depart from traditional materials and methods because of political, personal, or other reasons. The goal here is to have the agency express policies, objectives, operations, and other conditions though numerical weighting of the categories and subcategories listed in Table 6-2. Agencies will apply their criteria on two levels:

1. Agencies will assign weights to decision "categories"—cost, performance, natural environment, and corrosion. This level of weighting reflects general policy concerns.
2. Agencies will assign weights to "subcategories." This represents objectives and concerns at the operational level. A guidance tool was developed in Phase II of this study and includes a list of potential operational issues and areas of impairment, along with general recommendations.

Table 6-5 provides current thinking on the general areas an agency will need to consider. To ensure this process is practical at the operational level, the requested informa-

Table 6-4. Proposed product rankings for abrasive/NaCl deicing vs. $MgCl_2$ anti-icing.

Category	**Subcategory**	**Description**	**Product Ranking[1] (1=poor; 5= excellent)**	
			Abrasive/ NaCl Deicing	**$MgCl_2$ Anti-icing**
Cost	-	User input (example): cost of $MgCl_2$ > Abrasive/NaCl	5	3
Performance	-	User input (example): general operational low temperature -4°C; $MgCl_2$ marginally better than Abrasive/NaCl	4	5
Environment	Aquatic	Abrasives have high potential to impact aquatic environments; $MgCl_2$ is a moderate concern	1	3
	Air	Abrasives have high potential to impact air quality	1	5
	Vegetation	Both NaCl and $MgCl_2$ can impact vegetation; risk for anti-icing is lower due to lower volumes of chemical release	5	4
	Soil	NaCl can impact soil structure, both NaCl and $MgCl_2$ can potentially mobilize metals	4	2
	Animals	Both NaCl have low (unclear) potential to impact species, potential roadkills related to NaCl attraction	4	5
Corrosion	Vehicles	Both NaCl and $MgCl_2$ increase corrosion; $MgCl_2$ may be more aggressive due to its hygroscopic properties	2	1
	Metal Infrastructure	Both NaCl and $MgCl_2$ increase corrosion; $MgCl_2$ may be more aggressive due to its hygroscopic properties	2	1
	Concrete Matrix	Evidence suggests $MgCl_2$ may impact the concrete matrix	4	2
	Concrete Reinforcing	Both NaCl and $MgCl_2$ increase corrosion; evidence suggests $MgCl_2$ may initiate corrosion sooner	2	1

[1] Rankings based on Tables 6-1 and 6-3, except for Cost and Performance, which illustrate "examples" of agency input.
" – " indicates not applicable

Table 6-5. Operational objectives and concerns.

Decision Subcategories	Agency Inputs and Areas of Potential Impairment
Purchase Cost	1. Agency to input cost for candidate products
Temperature Performance	2. Agency to input mean winter temperature
Aquatic	3. Site-specific; regional stream standards; or antidegradation criteria 4. Road density per unit watershed area 5. Presence of standing or slowly moving waters near application area 6. Locations of unusual sensitivity (endangered or threatened species, spawning habit) 7. Shallow drinking water wells (downstream) overlain by permeable soils
Air	8. Poor air dispersion
Vegetation	9. Protected habitats within 30m of roadway 10. Aesthetic objectives
Soil	11. Potential for changes in soil structure (ESP >13) 12. Protected habitats within 30 m of the roadway
Animals	13. Protected habitats within 30 m of the roadway
Vehicles	14. Assumed constant for all agencies
Steel Infrastructure	15. Structural steel infrastructure 16. Pipelines along roadway, on bridge structure
Concrete	17. Aged/poor quality concrete
Concrete Reinforcing	18. Reinforced concrete decking 19. Aged/poor quality concrete

tion must not be overly detailed, yet adequately address the most significant areas of concern. If an agency has a concern not explicitly considered in the decision tool, agency staff will be able to address this through adjustment of assigned weights, as appropriate. Using the proposed methods as a guideline, an agency will be able to develop weightings specific to the circumstances.

The agency will also define other critical information at this step, such as the road sections of particular concern. It is anticipated that the decision tool can be applied to road areas ranging from small specific sites, such as bridges, to an entire maintenance region.

6.2.4.3 Decision Tool Model

The decision tool mathematically combines product rankings and agency objectives for general categories and provides a product score that can be compared with other products. The process is best illustrated using a case example:

Example:

An agency has traditionally conducted abrasive/NaCl deicing and is considering switching to $MgCl_2$ anti-icing. The agency has provided input to generate product rankings; policy objectives ("category" level weightings); and operational objectives ("subcategory" level weightings), as follows:

1. Product rankings are as shown in Table 6-4.
2. Current agency weightings for the decision "categories" are as shown in Table 6-2 (i.e., cost = 45 percent; performance = 33 percent; natural environment = 12 percent; and corrosion = 10 percent).
3. Current agency weighting for natural environment and corrosion decision "subcategories" are represented in Table 6-6.

Table 6-7 shows the mathematical steps involved in combining product rankings, policy objectives (categories), and operational objectives (subcategories). The final result is a product score. With the information illustrated in this example, the final product score for Abrasive/NaCl deicing is 68, which is higher than the $MgCl_2$ anti-icing score of 64. Although the resulting scores are similar, based on the information in this example, Abrasive/NaCl deicing best meets agency objectives.

6.2.5 Product Selection

The decision tool provides a numerical product score for snow and ice control materials assessed; however, it is not

Table 6-6. Example: Agency objectives for decision subcategories.

Decision Category	Subcategory	Agency Objectives	Subcategory Weighting (%) Max. = 100% per Decision Category
Natural Environment	Aquatic	Primary concern; low recharge, protected water bodies adjacent to large portions of maintenance area	50
	Air	Minor concern	10
	Vegetation	Aesthetic concern	20
	Soil	Not a concern	10
	Animals	Not a concern	10
Corrosion	Vehicles	Concerns from public and trucking industry	40
	Infrastructure	Minimal concern	10
	Concrete Matrix	Minimal concern	10
	Concrete Reinforcing	Aged bridge inventory	40

necessary that an agency selects the highest ranked product. The decision tool modeling process is not ideal, and final product scores are best estimates based on the input information. As illustrated in the example (Section 6.2.4.3), it is expected that scores will be similar among products. In such cases, agencies may allow other considerations to influence their product selection. These may include, but not be limited to, concerns with product availability (e.g., delivery times and quantities), quality testing results, and equipment availability.

6.3 Information Gaps

It was expected that the findings of the information assessment conducted through this study would identify gaps in information. Technologies and products employed for snow and ice control are continually evolving. As well, many of the effects surrounding snow and ice control are highly complex and variable, making development of any definitive conclusions difficult. General information gaps are included in this section and those gaps specific to the natural environment and infrastructure are included in Sections 6.3.1 and 6.3.2 respectively.

The factors that affect the transport of snow and ice control materials and their ability to affect the receiving environment are extremely complex. In general, the magnitude of impact is related to product-specific properties and dose at the environmental or infrastructure receptor. Prediction of dose at the receptor is complex and can be affected by numerous contributing factors. These may include types of materials, quantities being applied, transport pathways, exposure pathways, exposure duration, receptor sensitivity, and other site-specific environmental characteristics. It is, therefore, not possible to account for all conditions when developing a product selection tool. At best, generalized assessments based on the most common and most significant factors can be made.

Many of the studies reviewed made conclusions based on information provided through laboratory studies or adapted from studies conducted for purposes other than snow and ice control, and limited field correlations were available. Additionally, many materials have had a relatively short history of use (less than 10 to 15 years), and it is unclear what the potential for long-term adverse effects are over decade time scales. Addressing this will require much more information based on field studies than currently is available. Although the main types of impairment seem to have been identified, the actual documentation and modeling of these types of impairment under specific field conditions are not available.

6.3.1 Information Gaps—Natural Environment

The scientific and technical literature supporting an evaluation of snow and ice control materials as related to natural environments is relatively weak in certain areas, given the scope and magnitude of road applications. Exam-

Table 6-7. Decision process example – Abrasive/NaCl deicing vs. MgCl$_2$ anti-icing.

Material: Abrasive & NaCl Application Strategy: Deicing

Product Ranking (1=poor; 5= excellent)	Decision Subcategory Level			Decision Category Level		
	Subcategory	User Weight %[1]	Score (1-5)	Category	User Weight %[2]	Score (Maximum = 100)
▨	▨	▨	5.00	Cost	45	68
▨	▨	▨				
▨	▨	▨				
▨	▨	▨	2.00	Performance	33	
▨	▨	▨				
▨	▨	▨				
1	Aquatic	50	2.40	Natural Environment	12	
1	Air	10				
5	Vegetation	20				
4	Soil	10				
4	Animals	10				
2	Vehicles	40	2.20	Corrosion	10	
2	Infrastructure	10				
4	Concrete	10				
2	Concrete Reinforcing	40				

Material: MgCl2 **Application Strategy: Anti Icing**

Product Ranking (1=poor; 5= excellent)	Decision Subcategory Level			Decision Category Level		
	Subcategory	User Weight %[1]	Score (1-5)	Category	User Weight %[2]	Score (Maximum = 100)
▨	▨	▨	3.00	Cost	45	64
▨	▨	▨				
▨	▨	▨				
▨	▨	▨	4.00	Performance	33	
▨	▨	▨				
▨	▨	▨				
3	Aquatic	50	3.50	Natural Environment	12	
5	Air	10				
4	Vegetation	20				
2	Soil	10				
5	Animals	10				
1	Vehicles	40	1.10	Corrosion	10	
1	Infrastructure	10				
2	Concrete	10				
1	Concrete Reinforcing	40				

[1] Maximum = 100 per category (i.e. natural environment or corrosion); [2] Maximum = 100 (i.e. sum of cost, performance, natural environment, and corrosion)

ples of information gaps related to receptors in the natural environment include

- When considering aquatic toxicity, only a handful of bioassay studies are available for snow and ice control materials.
- It is difficult to judge the degree of variability between lots for such materials with respect to toxicity or other environmental effects such as nutrient content, or to produce statistically robust information on the toxicity or other environmentally relevant characteristics of snow and ice control materials in various categories. Thus, much more extensive chemical and bioassay testing is warranted in order to make the environmental evaluation of snow and ice control materials more robust.
- Information related to environmental monitoring in conjunction with application of snow and ice control materials is weak. To be relevant to the direct evaluation of snow and ice control materials, such monitoring needs to be designed to answer specific questions. Examples of relevant questions include the following: for specific climatic conditions and application rates, what are the characteristic rates of dilution for application materials after they leave the roadway? What are the conditions under which stagnant or slowly moving waters are significantly impaired by application materials? What kinds of assessment or monitoring methods would be appropriate for routine use as insurance against environmental impairment?
- Metals mobilization in soils has been identified as a potential concern for roadside soils; however, limited field evidence is available linking metals mobilization in soils to applications of snow and ice control materials.
- Heavy metal ions can be displaced by specific ions such as calcium and magnesium. These metal ions may bioaccumulate in the food chain; however, information is lacking in public literature relating this potential effect to snow and ice control materials.
- The literature indicates that reductions in soil stability and potential for soil erosion are concerns related to sodium applications, but limited field evidence is available.
- When considering soil microbial communities, limited literature was found directly assessing exposures and effects of these snow and ice control materials to soil microbial communities.
- There is no conclusive field evidence demonstrating whether or not snow and ice control materials increase animal deaths though toxicosis or through vehicle collisions.
- Radioactivity has been linked to well brines associated with oil and gas production; however it is unknown what levels can generally be expected from similarly obtained brines and mined material.

6.3.2 Information Gaps—Infrastructure

6.3.2.1 Atmospheric Corrosion

Atmospheric corrosion processes related to snow and ice control chemicals are extremely complex and it is difficult to provide generalized evaluations. The following information gaps exist:

- Comparison of the reviewed literature shows wide-ranging conclusions that in some cases contradict one another.
- Many laboratory study conclusions are based on very specific assessment conditions, including type and concentration of snow and ice material; presence, type and concentration of corrosion inhibitor; type of alloy materials; corrosion type being monitored; and specific test method/conditions used.
- The literature is not decisive in providing relative corrosion rates between snow and ice control material for various metal types, and even between alloys within the same metal group.
- The effectiveness of common corrosion inhibitors outside of controlled laboratory conditions (i.e., under field conditions, with dilution) is not fully supported in the literature.
- Although the main types of impairment related to snow and ice control materials seem to have been identified, actual documentation and modeling of these types of impairment under specific field conditions are not available.

The variability and uncertainty surrounding atmospheric corrosion processes is, therefore, considered a significant weakness in information.

6.3.2.2 Concrete Reinforcing and Concrete Paste

The following information gaps exist with respect to effects of snow and ice control materials on concrete:

- Many of the studies reviewed through this assessment have made conclusions based on information provided through laboratory studies. These studies often used mortar and cement paste or used poorer quality concrete than is typically used for infrastructure applications.
- The information indicates that magnesium can affect the concrete matrix, but the degree of deterioration risk is uncertain.
- There is insufficient evidence to support the claimed effectiveness of common corrosion inhibitors (typically organic biomass) added to snow and ice control chemicals in preventing corrosion in reinforcing steel. These products have not been designed to penetrate concrete and will likely have short-lived duration because of biodegradation.

- Limited information is available that assesses the effects of cations on the pore structure of concrete paste. The potential effects are twofold: (1) cations can, to some degree, affect the durability of concrete pore structure, which can affect strength and chloride ion penetration; and (2) cations can affect the pH of the concrete pore solution, which may depassivate the reinforcing at the rebar level.
- Although the main types of impairment seem to have been identified, the actual documentation of these types of impairment under specific field conditions is not available. Currently, the history of use for many snow and ice control products is less than 15 years. It may take many more years before effects related to their use are evident.

6.3.2.3 Other Infrastructure

Evidence supports the suggestion that snow and ice control materials, specifically chloride-based materials, can influence the proper operation of railway traffic control signaling and power distribution lines. Although processes for impairment have been identified, actual documentation is not available.

6.3.3 Information Gaps—Materials

Many products available for snow and ice control are proprietary, making it difficult to obtain specific test information. Significant variability may exist in these products in terms of additive types and percentages. This has not been well-documented in the literature.

6.4 Revised Work Plan

The Phase II work plan covered Tasks 7 through 13 of the NCHRP Project 06-16 research plan.

6.4.1 Task 7 (Analytical Testing Program)

6.4.1.1 Product Selection

Agency surveys determined common snow and ice control materials were found to include one or more of the following base products:

- Chloride salts—NaCl, $MgCl_2$, $CaCl_2$, and various proprietary blends;
- Acetates—calcium magnesium acetate; and
- Organic Products—typically agriculturally derived biomass.

Subsequent testing efforts focused on these materials. Other products (e.g., glycols, alcohols, K_2CO_3, and potassium formate) were used too infrequently for roadway applications to warrant any consideration for analytical testing. It was also unlikely that these materials would be used beyond very limited applications given their significant costs when compared with more common products. Regardless, these materials could still be considered at a later date using the framework established in Phase II of this study.

Samples were obtained through cooperation with producers and suppliers only. Collection of samples from user sources was avoided so as to address issues related to possible contamination or mishandling.

To develop a list of significant properties for common snow and ice control materials, an analytical testing program was proposed for chemical analysis, aquatic toxicity, concrete corrosion, and atmospheric corrosion. Materials were selected to represent a cross section of the present market in terms of product types, additives, and vendors. Chemical products (Table 6-8) were selected for each of the proposed test programs. Most products represented commercially available products identified in the agency survey (Section 2.4.1), although manufacturers' names have not been disclosed. Products listed in Table 6-8 represent the current situation and therefore depend on materials availability.

Up to 50 samples were tested for chemical analysis. Efforts were reduced for aquatic toxicity, atmospheric corrosion, and concrete corrosion testing. For these groups, efforts focused on $CaCl_2$ and $MgCl_2$. These selected products represent the most-used snow and ice control materials and corrosion inhibitor combinations as well as most of the available products. KA and a CMA-KA blend were included in Table 6-8 because of their widespread use on automated bridge snow and ice control systems. The use of these chemicals on bridges presents unique corrosion and environmental issues given that many bridges are over waterways.

Commercial product blends are continually evolving and, in many cases, product-specific test data become obsolete when formulations are modified. This is especially true where inhibitors and additives are present. It was, therefore, not the purpose of this study to provide a comprehensive classification of all available products. Proposed testing efforts were to provide an initial data set of commonly used products. This study was not intended to determine variance in each manufacturer's production. To conduct such an effort with an acceptable level of statistical significance would be beyond the scope of this study. Concerns of product variability could, however, be addressed indirectly through the application of the quality assurance program, although this would require continued management through a parent organization.

Table 6-8. Proposed test samples.

Chemical	Description	Testing Effort			
		Chemical Analysis (6.4.1.2)	Aquatic Toxicity (6.4.1.3)	Concrete Corrosion (6.4.1.4)	Atmospheric Corrosion (6.4.1.5)
$CaCl_2$	Liquid	X	X	X	X
	Corrosion Inhibited Liquid	X	X	X	X
	Corrosion Inhibited Liquid	X	X	X	X
	Corrosion Inhibited Liquid	X	X	X	X
	Corrosion Inhibited Liquid	X			
	Corrosion Inhibited Liquid	X			
	Solid Pellet	X			
	Solid Flake	X			
	Solid Flake	X			
$MgCl_2$	Liquid	X	X	X	X
	Corrosion Inhibited Liquid	X	X	X	X
	Corrosion Inhibited Liquid	X	X	X	X
	Corrosion Inhibited Liquid	X	X	X	X
	Corrosion Inhibited Liquid	X			
	Corrosion Inhibited Liquid	X			
	Corrosion Inhibited Liquid	X			
	Corrosion Inhibited Liquid	X			
	Corrosion Inhibited Liquid	X			
	Corrosion Inhibited Liquid	X			
	Corrosion Inhibited Liquid	X			
	Solid Flake	X			
	Solid Crystal	X			
NaCl	Solid (ASTM Spec)	X	X	X	X
	Solid	X			
	Corrosion Inhibited Solid	X	X	X	X
	Corrosion Inhibited Solid	X			
	Corrosion Inhibited Solid	X			
	Corrosion Inhibited Solid	X			
	Corrosion Inhibited Solid	X			
Blended Chloride	Mined	X	X	X	X
	Well Brine Liquid	X	X		
	Corrosion Inhibited Solid	X	X	X	X
	Corrosion Inhibited Solid	X			
	Corrosion Inhibited Solid	X			
	Corrosion Inhibited Solid	X			
	Corrosion Inhibited Solid	X			
	Corrosion Inhibited Liquid	X			
	Corrosion Inhibited Liquid	X			
CMA	Manufactured Solid	X	X	X	X
KA	Manufactured Liquid	X	X	X	X
CMAK	Blended Liquid	X		X	X
Organic	Manufactured Liquid (Biomass)	X			
	Manufactured Liquid (Biomass)	X			
	Totals	43	15	15	15

6.4.1.2 Chemical Analysis

Chemical analyses were conducted to characterize the snow and ice control products and to determine the presence of any trace chemicals that might occur as impurities. It was expected that up to 50 test samples (Table 6-8) would be analyzed as part of the chemical testing program. These samples represented different base chemicals, mix ratios, and additives.

Each test sample was subjected to a range of applicable analytical test parameters. The study team recognized that not all sample types needed to be tested for all chemical analysis parameters (i.e., it was unlikely that appreciable amounts of chloride would be found in potassium acetate). However, it was proposed that all samples requiring chemical analysis be subjected to the same suite of testing, except where this was physically impossible. This approach was taken to ensure completeness of the data set and to account for cases where unexpected analytes were shown to be present. Table 6-9 indicates the product types and associated chemical analyses.

6.4.1.3 Aquatic Toxicity Testing

Aquatic test procedures were proposed for 15 snow and ice control products (Table 6-8). Standard test methods as indi-

Table 6-9. Chemical analysis.

Test Parameters	Method Reference
Metals • Arsenic, Barium, Cadmium, Chromium, Copper, Iron, Lead, Manganese, Mercury, Molybdenum, Nickel, Selenium, Silver, Zinc	APHA
Cations • Sodium, Calcium, Magnesium, Potassium	APHA
Phosphorus • Total Phosphorus, Total Soluble Phosphorus	APHA
Nitrogen • Nitrate & Nitrite, Ammonia, Total Kjeldahl Nitrogen (TKN)	APHA
Chloride	APHA
Biochemical Oxygen Demand (BOD)	APHA
Chemical Oxygen Demand (COD)	APHA
pH	APHA
Cyanide, Ferrocyanide	APHA
Specific Gravity	ASTM D 1429

APHA – American Public Health Association (*67*)
ASTM – American Society for Testing and Materials

cated in Table 6-10 were followed and represented chronic exposure assessments to various levels of aquatic biota, including vertebrates, invertebrates, and algae.

Chronic exposure tests were selected over more commonly used acute test procedures (i.e., Rainbow trout 96-hour LC_{50}) because they provided more information related to potential long-term impacts. Both Environment Canada and the U.S. EPA recognize the 7-day fathead minnow test as a chronic bioassay for freshwater fish whereas the 96-hour test is recognized as an acute test. It has been judged that the 7-day test is sufficient in length to evaluate chronic toxicity. In addition, this test assesses the life stage of the representative fish that is considered to be most sensitive to adverse effects from chemicals and provides endpoints for growth and survival.

By conducting a 7-day test, one can determine the 96-hour LC_{50} and 7-day LC_{50} as well as a 7-day EC_{50} on growth, in addition to other endpoints, including LC_{25}, EC_{25}, lowest observable effect concentration (LOEC), and no observable effect concentration (NOEC).

6.4.1.4 Concrete Reinforcing Corrosion

The properties of the concrete that required evaluation, and the gaps in our current ability to conduct the evaluation, are outlined in Section 6.3.2.2. It was proposed that a minimum of 15 snow and ice control products be selected for concrete corrosion testing (Table 6-8). It was beyond the scope of this study to develop completely new test methods. It was intended to take existing methods, possibly combinations or

Table 6-10. Aquatic toxicity testing.

Test Method	Standard Reference Method
Fathead Minnow 7-day Survival and Growth Test (will also include acute toxicity data for Fathead Minnow 96-hour Survival Test)	U.S. EPA, 1994, Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to Freshwater Organisms, 3rd Edition, EPA/600/4-91/002
Ceriodaphnia dubia 3-brood Survival and Reproduction Test	U.S. EPA, 1994, Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to Freshwater Organisms, 3rd Edition, EPA/600/4-91/002
Selenastrum capricornutum 96-hour (US EPA) Growth Test	U.S. EPA, 1994, Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to Freshwater Organisms, 3rd Edition, EPA/600/4-91/002

modifications of those discussed in Section 5.4, and apply them to the needs here. Results were in relative performance only. In this regard, a single ice control chemical, presumably NaCl at some established dosage, was selected as a control for reference of others. It was expected that test sample concentrations would be selected to match routine application exposure concentrations.

As indicated in Section 5.4.4.1, it was necessary to define a standard concrete (not mortar) mixture proportion from which evaluation of the relative performance of ice control chemicals could be made. It should have been representative of the quality of the concrete used in transportation works. As an initial effort in this regard, the AASHTO specification for such concretes was used. Concrete exposed to snow and ice control chemicals proposed for testing were to have

- Air entrainment producing adequate bubble spacing factors to ACI 318 requirements; and
- A maximum w/c ratio of 0.45.

A test method was designed to evaluate, simultaneously, the susceptibility of a surface-applied chemical's potential to cause deterioration of the paste and/or corrosion of the rebar. The test was similar to ASTM C 1556 (refer to Section 5.4.4.2) but included wetting and drying cycles. In addition to the assessment of the rebar corrosion, ion diffusion profiles were obtained and the two aspects correlated. Again, opinion on the method was sought from other researchers.

The study team had informal discussions with researchers assessing the effects of snow and ice control chemicals on concrete and concrete reinforcing. Detailed discussions were held with these to obtain the benefit of their experience on test method development. Such discussions also avoided duplication of effort between this program and existing programs.

6.4.1.5 Atmospheric Corrosion Testing

Various options are available to assess atmospheric corrosion; however most accelerated laboratory tests do not correlate with field experience, particularly where the predominant form of degradation is localized corrosion and galvanic corrosion. The following represented the development of the proposed test program.

Immersion corrosion tests, such as the PNS corrosion test (*43*), are rapid tests that provide an acceptance ranking for snow and ice control chemicals based on a single sample, typically steel, and single concentrations of chemical and inhibitor. However, test results do not necessarily bear any relationship to field conditions. In addition, immersion corrosion tests have shown significant variability between test coupons used and between laboratories. The validity of the immersion tests to predict uniform or general corrosion field conditions could be improved by running duplicate samples, controlling temperature and humidity, and running the test at a number of dilution ratios to try and simulate field conditions. These changes still did not provide correlation with field conditions because of localized corrosion, galvanic corrosion, or corrosion of metals other than steel.

Salt-spray (fog) tests are primarily for the evaluation of organic coatings on steel. They could be adapted to evaluate forms of localized corrosion by using snow and ice control chemicals and inhibitors for the test media instead of the normal salt solutions in environmental chambers with programmed drying periods. However, drawbacks include method development (particularly for tests of solutions exceeding 5-percent concentration) and duration of time required for testing. Salt-spray (fog) tests are quality control tests for coatings and not a viable tool for evaluating degradation of infrastructure.

The literature and study team experience indicated that laboratory poultice corrosion tests using various dilutions of chemicals and inhibitors would provide good correlation with field experience for crevice corrosion, poultice corrosion, pitting, and galvanic corrosion of the various metals and combinations of metals used in motor vehicles and metal bridge structures. Despite limited evidence of correlation with various forms of localized attack, the poultice test had drawbacks—it was not a standardized (and therefore not widely applied) test; moreover, comparatively long exposure times would be necessary.

Rapid evaluation of the corrosive properties of snow and ice control chemicals and inhibitors could best be carried out using electrochemical techniques (i.e., linear polarization resistance (LPR) testing). Electrochemical corrosion tests could be used to evaluate general corrosion of snow and ice control chemicals and corrosion inhibitors over various concentrations. The effectiveness of a corrosion inhibitor is influenced by concentration (i.e., as affected by roadway dilution). In part this also addressed manufacturer corrosion claims. Further benefits of LPR were that it

- Was a mature, proven technology and had been used extensively to field-monitor corrosion of equipment and infrastructure;
- Was considered suitable for evaluating the effect of inhibitors with roadside dilution;
- Had good correlation with weight loss measurements for near-neutral pH solutions; and
- Was considered to be most well adapted to aqueous corrosion.

As with the drawbacks of immersion and salt-spray corrosion testing, LPR had limited applicability with respect to evaluating localized corrosion and galvanic corrosion, but the benefits of this technique outweighed these.

The study team proposed to conduct LPR measurements in accordance with the criteria established in ASTM G 96. The test program would comply with the conventions acknowledged in ASTM G 3 while the calculation of corrosion rates would be carried out per ASTM G 102. Measurements would be conducted on five commonly available alloys:

1. Steel is used in the following functions: reinforcing bar, structural steel bridges, motor vehicle frames, bumpers, brake line fittings, body panels, general roadside infrastructure, guard rails, sign posts, and lamp standards. A wide range of steel grades is used, but most will have similar corrosion rates, except for weathering steels. A standard structural steel such as ASTM A 36 will be used for testing.
2. Wrought aluminum is used in the following functions: motor vehicle frames, diesel fuel tanks, body panels, roadside infrastructure, building cladding, signage and so forth. Wide ranges of aluminum alloys are used and have varying degrees of corrosion resistance. Aluminum alloy 6061-T6 will be used for testing because it is one of the most common alloys used.
3. Cast aluminum is used in motor vehicle wheel rims, transmission cases, engines, and so forth. Cast aluminum alloy 356.0 will be used for testing because it is one of the most common aluminum alloys used.
4. Cast magnesium is used primarily for motor vehicle wheel rims and transmission housings. Die cast magnesium alloy AM60A-F samples will be used for testing because it is one of the most common alloys used for wheel rims.
5. Brass is typically used for brake line fittings and for electrical contacts. A typical leaded free-machining brass such as copper alloy C360 will be used for testing.

It was proposed that a minimum of 15 snow and ice control products be selected as candidates for corrosion testing (Table 6-8). Testing for each sample/alloy combination would be conducted at three concentration ranges that represented snow and ice control material concentrations expected under typical roadway exposure conditions:

1. As applied, no dilution. For solid products, solutions would be prepared approximating liquid equivalents. For example, solid NaCl would be prepared as an approximate 21-percent (w/w) solution.
2. Diluted to 10 percent (w/w) of the "as applied" product. This represented the initial stages of roadway dilution.
3. Diluted to 1 percent (w/w) of the "as applied" product. This represented later stages of roadway dilution.

The proposed test program would produce 225 individual determinations (15 samples × 5 alloys × 3 concentrations). Expected results would provide general corrosion comparisons of metals, dilution ratios, chemicals, and inhibitors.

6.4.1.6 Abrasive Testing

The original work plan accounted for testing of 15 abrasive products using gradation and abrasion tests. From an environmental perspective, the current body of information was well developed (i.e., abrasive use can degrade air quality and lead to turbidity and sedimentation concerns for aquatic systems). The agency survey (Section 2.4) also indicated that most material was obtained through an extremely wide range of regional sources, making it extremely difficult to obtain a good representation. Current information was sufficient to warrant no further testing of abrasive materials.

6.4.2 Task 8 (Matrix of Significant Properties)

The matrix consisted of a series of tables that cross-referenced a specific base product or blended material with a measured parameter as developed through Task 7. In cases where non-tested attributes were a concern, efforts were made to include a descriptive rating that could be applied in place of a numerical test result. The matrix was to display the test results and information that would ultimately be applied to the development of the decision tool. It was difficult to describe the exact formatting and organization of these tables, except that efforts would be made to ensure that the tables were understandable and organized logically. A simple conceptualization of the matrix is indicated in Table 6-11.

6.4.3 Task 9 (Purchase Specification)

The developed purchase specifications probably would be similar to those used by the Pacific Northwest Snowfighters (PNS) (*43*), modified by the findings of this project. These would include recommended specifications for product qualification based on environmental issues and product properties. This process had been successful and had been used as a template by other jurisdictions. One area needing review was the maximum acceptable product concentrations for certain contaminants developed by PNS that were based on U.S. EPA water quality criteria and a "rule-of-thumb"

Table 6-11. Matrix of significant properties.

Test Parameter	Product			
	Product A	Product B	Product C	Etc.
Metals				
Cyanide				
Chloride				
Biochemical Oxygen Demand (BOD)				
Phosphorus				
Nitrogen				
Toxicity				
Atmospheric Corrosion Attribute				
Concrete Corrosion Attributes				
Etc.				

hundredfold expected dilution after roadway application. It was not the purpose of the purchase specification to dictate regulations—ideally, sufficient information related to products and environmental-related factors would be provided by the decision tool (Task 10) to allow managers to assess product risks.

6.4.4 Task 10 (Decision Tool Guidelines)

Task 10 involved the development of guidelines that incorporated all the components of the decision framework (Section 6.2); the matrix of significant properties (Task 8, Section 6.4.2); and the purchase specification (Task 9, Section 6.4.3). Of these tasks, the development of the decision framework into a practical decision tool involved the following tasks.

6.4.4.1 Develop Product Rankings

Products were ranked based on their ability to impair an area of concern. These included product-specific environmental attributes known to present possible problems or advantages for snow and ice control. It quantified those that reasonably yielded to testing (parameter matrix) and also addressed non-tested attributes and how they should be considered. The project team developed a set list of rankings that incorporated the matrix of significant properties with factors identified in the agency inventory. A score was given on a scale of 1 to 5, where a higher score designated less potential for impact. This process was described in detail in Section 6.2.4.1.

6.4.4.2 Incorporate Decision Tool into Software

The decision tool was anticipated to consist of a relatively simple software application prepared through use of a commercial spreadsheet program such as Microsoft Excel™. The tool includes rankings of products and specific conditions developed through the study work and allows the user to assign weights for a number of categories of criteria that are important in selection of the product. This is essentially a comparison tool. The final output is a product score that can be compared with other materials for a given set of conditions.

6.4.4.3 Generate Guidance Document

A straightforward user manual that explains the rationale for the use of the software and potential limitations of the software and provides step-by-step instructions for using the software and ways of interpreting the results accompanies the software. This incorporates a guidance tool that will assist agencies in developing objectives and applying significance though weighting to issues such as cost, performance, environmental impacts, and corrosion impacts. This process was described in detail in Section 6.2.4.2.

6.4.4.4 Quality Assurance Program

The quality assurance program takes the general form of a suite of qualifying tests and submittals, allowing the agency to "qualify" and characterize the product before use. This is followed by procedures to determine suitability, along with sampling and random testing to ensure product quality.

Quality control test requirements focus on chemical analysis parameters. Chemical analysis provides a great deal of valuable information on a product's potential environmental impact at a price that is not restrictive when compared with common corrosion and toxicity testing. However, it is suggested that toxicity and corrosion testing be conducted at a reduced frequency or as product concerns dictate.

6.4.5 Phase II Reporting

6.4.5.1 Task 11 (Draft Task 10 Report and Review)

A draft report incorporating the elements of Task 10 (Section 6.4.4) was prepared and submitted for review to the NCHRP and to a project advisory panel established by the study team that included industry experts representing DOT maintenance managers from U.S. states and Canadian provinces, the PNS, and AASHTO's Winter Maintenance Policy Coordinating Committee. Researchers involved in related issues were also included. This document provided sufficient supporting information for reference and use by transportation managers so that they could make informed decisions about user-specific requirements.

6.4.5.2 Task 12 (Compilation of Review Process)

The results of the review steps were compiled and a technical memorandum was submitted to the NCHRP indicating how comments were to be addressed where possible.

6.4.5.3 Task 13 (Final Report)

A final report incorporating review revisions was submitted to the NCHRP and included

- Documentation of the entire research effort;
- A stand-alone guidance document for the selection of snow and ice control products that incorporates the review;
- An Executive Summary outlining the research results; and
- Recommendations for research required for refining the established guidelines.

CHAPTER 7

Analytical Program Overview

The analytical test program for NCHRP Project 06-16 was designed to help address gaps in current information and establish a matrix of significant properties for common snow and ice control chemicals in the areas of environmental chemistry, aquatic toxicity, concrete corrosion, and atmospheric corrosion. Producers and suppliers of snow and ice control chemicals provided 42 products for testing (Table 7-1). These materials represented the current U.S. and Canadian market in terms of product type (e.g., NaCl, $MgCl_2$, $CaCl_2$, CMA, and KA), manufacturers, regional sources and additives. Commercial products continue to evolve, especially with respect to additives, and variability can exist between product batches. The data and information presented in this report provide a snapshot of the materials available for use in 2004. Abrasives were not included in the test program because material sources are too numerous and varied. Testing efforts are also listed in Table 7-1. All 42 products received full chemical analysis. Fifteen materials representing each material type and common additive combination were selected for aquatic toxicity, concrete corrosion, and atmospheric corrosion assessments. Conducting a large-scale analytical assessment on a wide range of snow and ice control materials using the same test methods provides data that can be directly compared for trends and significant material attributes can be identified.

Both solid and liquid snow and ice control materials were assessed in the analytical test program. Liquid materials were tested as received. Solid materials were dissolved in deionized water at room temperature at concentrations equivalent to common liquid counterparts (Table 7-2). This approach allowed testing of solids and liquids using the same test methods and further allowed direct comparison of data between matrix types. Where insoluble solid material existed, additional efforts were made to dissolve this material; these efforts included extended mixing and further addition of water. Where insoluble material remained, only the liquid component was tested. Water hydration was unknown for the three solid $CaCl_2$ products tested and the sample dilution scheme underestimated the target concentration by about 25 percent. These samples underwent chemical analysis only, and test data were in the same general range as for liquids. Samples were transferred into test bottles and logged into a laboratory information management system to track sample analysis steps, quality control efforts, and data management tasks. The following chapters describe and assess test results:

- Chapter 8, Chemical Analysis
- Chapter 9, Aquatic Toxicity Testing
- Chapter 10, Concrete Reinforcing Testing
- Chapter 11, Atmospheric Corrosion Testing

Table 7-1. Analytical program testing effort.

Lab ID	Base Chemical	Matrix	Additive[1]	Analytical Program			
				Chemistry	Aquatic Toxicity	Concrete Corrosion	Atmospheric Corrosion
1	NaCl	Liquid	-	X			
2	NaCl	Liquid	OMB	X	X	X	X
3	NaCl	Liquid	OMB	X	X	X	X
4	NaCl	Solid	-	X			
6	NaCl	Solid	-	X	X	X	X
7	NaCl	Solid	-	X			
8	NaCl	Solid	OMB	X			
9	NaCl	Solid	OMB	X			
10	NaCl	Solid	P	X	X	X	X
11	NaCl	Solid	P	X			
12	NaCl	Solid	Unknown	X			
13	$CaCl_2$	Liquid	-	X	X	X	X
14	$CaCl_2$	Liquid	-	X			
15	$CaCl_2$	Liquid	-	X			
16	$CaCl_2$	Liquid	-	X			
17	$CaCl_2$	Liquid	OMB	X	X	X	X
18	$CaCl_2$	Liquid	OMB	X			
19	$CaCl_2$	Liquid	OMB	X			
20	$CaCl_2$	Liquid	C, A	X	X	X	X
21	$CaCl_2$	Liquid	OMB	X	X	X	X
22	$CaCl_2$	Solid	-	X			
23	$CaCl_2$	Solid	-	X			
24	$CaCl_2$	Solid	-	X			
25	$MgCl_2$	Liquid	-	X			
26	$MgCl_2$	Liquid	-	X	X	X	X
27	$MgCl_2$	Liquid	-	X			
28	$MgCl_2$	Liquid	OMB	X			
29	$MgCl_2$	Liquid	OMB, TEA	X	X	X	X
30	$MgCl_2$	Liquid	OMB	X			
31	$MgCl_2$	Liquid	OMB	X			
32	$MgCl_2$	Liquid	OMB	X	X	X	X
33	$MgCl_2$	Liquid	OMB	X			
34	Blended Chloride	Liquid	OMB	X			
35	Blended Chloride	Liquid	OMB	X			
36	Blended Chloride	Solid	-	X			
37	Blended Chloride	Solid	OMB, P	X	X	X	X
38	Blended Chloride	Solid	-	X			
40	CMA	Liquid	-	X	X	X	X
41	CMAK	Liquid	-	X	X	X	X
42	KA	Liquid	-	X	X	X	X
43	KA + OMB	Liquid	KA, OMB blend	X			
44	NAAC	Solid	-	X			

[1] OMB – Organic Matter from Biomass, P – phosphate, TEA – triethanolamine, C – polyhydroxycarboxylate, A – polyalkoxylated amine

‘ - ’ indicates not present

Table 7-2. Solid snow and ice control material dilution scheme.

Solid Material Type	Concentration Target (% w/w)
NaCl	23 %
Blended Chlorides	30 %
$CaCl_2$	30 %
NAAC	30 %

CHAPTER 8

Chemical Analysis

The chemical analysis program provided data for chemical attributes of environmental concern so that trends and significant material attributes could be identified. All 42 snow and ice control materials were subjected to the analytical test parameters shown in Table 8-1. Test parameters were selected based on a literature assessment of known potential environmental concerns conducted during Phase I of this study. Standard methods employed for testing were referenced from "Standard Methods for the Examination of Water and Wastewater," 20th Edition, 1998, American Public Health Association, American Waterworks Association, Water Environment Federation (APHA).

APHA contains well-recognized standard environmental test methods commonly used at environmental laboratories throughout the United States and Canada. For some parameters, APHA lists multiple analytical techniques. Those shown in Table 8-1 were selected based on suitability for the test matrix; existing quality test programs, such as the PNS program; and the testing laboratory's experience conducting similar testing.

Chemical test data is tabulated in Tables 8-2 through 8-15. Data is organized based on analyte level. Detection limits indicate limits of quantitation. APHA tests used for testing are designed for water and wastewater matrixes, whereas snow and ice control chemicals are concentrated salts. Where dilutions were necessary before testing and where interferences existed, detection limit adjustments were necessary. If an analyte was detected, it was not necessarily a cause for concern. If an analyte was not detected, it was not a cause for concern if the detection limit was below the threshold of adverse effects, but it could be a concern if the detection limit was near or above this threshold.

Guidelines for Maximum Concentration (GMCs) developed through the NCHRP Project 06-16 purchase specification will be referenced throughout chemical analysis data discussions to identify where areas of environmental concern may exist. These values have been developed based on existing U.S. EPA water quality criteria, site-specific factors, and assumptions about snow and ice control material transport in the field.

Analytical data is presented in milligrams per liter (mg/L), which is the mass-to-liquid equivalent of parts per million. This convention was selected based on the processes used to develop the purchase specification GMC values. These units can be converted to the mass-to-mass equivalent of parts per million (mg/kg) by applying a specific gravity conversion.

8.1 Organic Matter (BOD and COD)

Organic matter in snow and ice control materials was assessed using Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) analyses (Table 8-2). COD measures the oxygen consumed after chemical oxidation; BOD measures oxygen consumed after biological oxidation. By this convention, COD is greater than or equal to BOD. The standard BOD test determines oxygen consumed over a 5-day period at 20°C. If a material is slowly biodegradable, higher values could be obtained for longer test periods.

Data shows that the highest organic matter levels are associated with acetate materials (e.g., CMA and KA). BOD values ranged from 110,000 to 310,000 mg/L, and COD values ranged from 180,000 to 550,000 mg/L for these materials.

Liquid products containing organic matter from biomass (OMB) as an additive also showed high organic matter levels. BOD values ranged from 1,000 to 120,000 mg/L, and COD values ranged from 6,800 to 230,000 mg/L for these materials. The wide range in levels probably is related to the concentration of additives in the blended material.

For solid snow and ice control materials containing OMB additives, BOD values for test solutions were generally less than 2,400 mg/L, and COD values were less than 10,000 mg/L. Lower values probably are related to the lower proportion of OMB product added to solid materials than to liquids.

A high BOD/COD ratio may indicate more readily biodegradable materials. Conversely, a lower BOD/COD

Table 8-1. Chemical analysis and standard methods.

Test Parameters	Method Based On:	Section
Organic Matter • Biochemical Oxygen Demand (BOD) • Chemical Oxygen Demand (COD)	• APHA 5210 B • APHA 5220 D	8.1
Nitrogen • Nitrate & Nitrite • Ammonia • Total Kjeldahl Nitrogen (TKN)	• APHA 4500-NO_3^- H • APHA–NH_3 F • APHA-N_{org} B	8.2
Phosphorus • Total Phosphorus • Total Soluble Phosphorus	• APHA 4500-P B, E • APHA 4500-P E	8.3
Cyanide (total)	• APHA 4500-CN- C	8.4
Heavy Metals • Arsenic, Cadmium, Chromium, Copper, Lead, Mercury, Nickel, Selenium, Silver, Zinc	• APHA 3125	8.5

APHA – Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998, American Public Health Association, American Waterworks Association, Water Environment Federation

ratio may indicate materials that are not biodegradable or are slowly biodegradable. The BOD/COD ratio was between 56 and 76 percent for acetate materials and between 4 and 63 percent for materials containing organic additives.

8.2 Nitrogen

Analysis was conducted for various forms of nitrogen, including ammonia, nitrate and nitrite, and total Kjeldahl nitrogen (TKN) (Table 8-3). The total nitrogen composite (sum of ammonia, nitrate and nitrite, and TKN) is the main index by which nitrogen content should be evaluated from an environmental standpoint. Ammonia and nitrate content is important as well because ammonia can be toxic to aquatic life at high concentrations, and nitrite can affect drinking water supplies.

Concentrations of total nitrogen showed little evidence of pattern across the different types of snow and ice control materials. Elevated nitrogen levels showed a direct relationship to additive type, particularly OMB additives; however, the spread of values for these materials is broad. The same was true for ammonia and nitrate, although only a few materials had high concentrations of these substances.

From an environmental standpoint, the most restrictive purchase specification GMC for ammonia is 3,000 mg/L and for total nitrogen is 75 mg/L. None of the materials tested exceeded the ammonia GMC, whereas about one-half of the materials exceeded the total nitrogen GMC. Values above the GMC levels may be cause for concern for some aquatic systems. The general conclusion for nitrogen is that each snow and ice control material type provided by a specific vendor must be tested if nitrogen is to be evaluated as a component of that material.

8.3 Phosphorus

Both orthophosphate (reported as phosphorus) and total phosphorus were determined (Table 8-4). Orthophosphate is highly available for uptake by plants, while total phosphorus includes complexed and organic phosphorus, which can be mobilized after breakdown through biological processes. When assessing potential for environmental impairment, evaluation should be in terms of total phosphorus loading, rather than specific phosphorus fractions.

Three materials containing phosphate-based corrosion inhibitors showed high phosphorus levels of 460, 690, and 780 mg/L. Materials with OMB additives also showed elevated phosphorus levels, although the spread in values was broad, ranging from <2 to 690 mg/L. This probably is related to the proportion of OMB additives in the blend and/or the level of phosphorus in the OMB materials themselves. Certain acetate products (i.e., one KA source and a NAAC material) also had somewhat elevated phosphorus levels of 160 and 340 mg/L.

From an environmental standpoint, the most restrictive purchase specification GMC for total phosphorus is 3.5 mg/L. Values above this may be cause for concern for some aquatic systems. The general conclusion for phosphorus is that each snow and ice control material type provided by a specific vendor must be tested if phosphorus is to be evaluated as a component of that material.

8.4 Cyanide

Iron-cyanide compounds are commonly added to solid NaCl as an anti-caking agent. Evidence suggests these materials have limited bioavailability under natural field conditions; however, readily applicable standard methods for the direct measurement of these compounds do not exist. Therefore, as a conservative measure of potential environmental impact, total cyanide content was measured (Table 8-5).

From an environmental standpoint, the most restrictive purchase specification GMC for cyanide is 3.5 mg/L. Total cyanide was detected in seven samples. Of these, two solid NaCl products (17 and 18 mg/L) and one with blended chloride product (9.4 mg/L) were above the GMC value.

8.5 Heavy Metals

8.5.1 Arsenic

All samples tested for arsenic were below the reported detection limit of 2 mg/L, and below the most restrictive purchase specification GMC value of 5 mg/L (Table 8-6). The data suggests that arsenic was not a significant attribute of environmental concern.

Table 8-2. Organic matter (BOD and COD) analysis data.

Lab ID	Matrix	Material Type	Additive [1]	BOD (mg/L)	COD (mg/L)
0406064-43	Liquid	Acetate	OMB	310000	550000
0406064-42	Liquid	Acetate		220000	290000
0406064-41	Liquid	Acetate		180000	280000
0406064-31	Liquid	$MgCl_2$	OMB	36000	250000
0406064-29	Liquid	$MgCl_2$	OMB, TEA	120000	230000
0406064-40	Liquid	Acetate		160000	220000
0406064-44	Solid	Acetate		110000	180000
0406064-03	Liquid	NaCl	OMB	86000	160000
0406064-28	Liquid	$MgCl_2$	OMB	100000	160000
0406064-02	Liquid	NaCl	OMB	35000	76000
0406064-17	Liquid	$CaCl_2$	OMB	5700	66000
0406064-18	Liquid	$CaCl_2$	OMB	21000	43000
0406064-19	Liquid	$CaCl_2$	OMB	4200	38000
0406064-35	Liquid	Blended Chloride	OMB	17000	37000
0406064-34	Liquid	Blended Chloride	OMB	13000	33000
0406064-20	Liquid	$CaCl_2$	C, A	7400	30000
0406064-21	Liquid	$CaCl_2$	OMB	2400	30000
0406064-33	Liquid	$MgCl_2$	OMB	11000	27000
0406064-25	Liquid	$CaCl_2$		4200	21000
0406064-30	Liquid	$MgCl_2$	OMB	1100	20000
0406064-32	Liquid	$MgCl_2$	OMB	670	19000
0406064-26	Liquid	$MgCl_2$		<10	12000
0406064-13	Liquid	$CaCl_2$		<10	11000
0406064-14	Liquid	$CaCl_2$		<10	11000
0406064-16	Liquid	$CaCl_2$		<10	9900
0406064-37	Solid	Blended Chloride	OMB, P	2400	9500
0406064-27	Liquid	$MgCl_2$		<10	8500
0406064-24	Solid	$CaCl_2$		<10	8100
0406064-08	Solid	NaCl	OMB	910	7000
0406064-09	Solid	NaCl	OMB	940	6800
0406064-15	Liquid	$CaCl_2$		<10	6800
0406064-11	Solid	NaCl	P	<10	6200
0406064-23	Solid	$CaCl_2$		<10	6200
0406064-01	Liquid	NaCl		<10	5900
0406064-12	Solid	NaCl	Unknown	<10	5600
0406064-07	Solid	NaCl		<10	5300
0406064-10	Solid	NaCl	P	<10	4900
0406064-04	Solid	NaCl		<10	4800
0406064-22	Solid	$CaCl_2$		<10	4700
0406064-06	Solid	NaCl		<10	<4000
0406064-36	Solid	Blended Chloride		<5	<4000
0406064-38	Solid	Blended Chloride		<5	<4000

[1] Additive: OMB – Organic Matter from Biomass
P – Phosphate
TEA – triethanolamine
C – polyhydroxycarboxylate
A – polyalkoxylated amine

Table 8-3. Nitrogen analysis data.

Lab ID	Matrix	Material Type	Additive [1]	Ammonia (mg/L)	Nitrate & Nitrite (mg/L)	TKN (mg/L)	TN-calc (mg/L)
0406064-31	Liquid	$MgCl_2$	OMB	4	<5.0	8900	8904
0406064-03	Liquid	NaCl	OMB	150	<5.0	6350	6500
0406064-17	Liquid	$CaCl_2$	OMB	2200	<5.0	3860	6060
0406064-29	Liquid	$MgCl_2$	OMB, TEA	<5	<5.0	3000	3000
0406064-11	Solid	NaCl	P	1400	<5.0	1550	2950
0406064-18	Liquid	$CaCl_2$	OMB	44	94	2040	2178
0406064-33	Liquid	$MgCl_2$	OMB	450	<5.0	1290	1740
0406064-34	Liquid	Blended Chloride	OMB	280	320	933	1533
0406064-10	Solid	NaCl	P	710	<5.0	699	1409
0406064-19	Liquid	$CaCl_2$	OMB	12	<5.0	1220	1232
0406064-21	Liquid	$CaCl_2$	OMB	16	260	773	1049
0406064-35	Liquid	Blended Chloride	OMB	14	<5.0	889	903
0406064-09	Solid	NaCl	OMB	330	<5.0	502	832
0406064-30	Liquid	$MgCl_2$	OMB	35	<5.0	620	655
0406064-32	Liquid	$MgCl_2$	OMB	15	<5.0	629	644
0406064-25	Liquid	$CaCl_2$		1	<5.0	589	590
0406064-16	Liquid	$CaCl_2$		150	<5.0	136	286
0406064-02	Liquid	NaCl	OMB	50	<5.0	126	176
0406064-20	Liquid	$CaCl_2$	C, A	2	<5.0	155	157
0406064-28	Liquid	$MgCl_2$	OMB	2	<5.0	89.8	91.8
0406064-26	Liquid	$MgCl_2$		2	<5.0	73	75
0406064-37	Solid	Blended Chloride	OMB, P	<0.2	<5.0	53.7	53.7
0406064-38	Solid	Blended Chloride		2	<5.0	25.6	27.6
0406064-14	Liquid	$CaCl_2$		14	<5.0	11.3	25.3
0406064-24	Solid	$CaCl_2$		9	<5.0	7.24	16.24
0406064-41	Liquid	Acetate		4	<5.0	10.5	14.5
0406064-01	Liquid	NaCl		11	<5.0	3.25	14.25
0406064-40	Liquid	Acetate		<0.2	<5.0	10	10
0406064-13	Liquid	$CaCl_2$		6	<5.0	2.86	8.86
0406064-27	Liquid	$MgCl_2$		0.6	<5.0	8.14	8.74
0406064-42	Liquid	Acetate		0.3	<5.0	7.6	7.9
0406064-08	Solid	NaCl	OMB	<0.2	<5.0	7.36	7.4
0406064-07	Solid	NaCl		3	<5.0	3.65	6.65
0406064-12	Solid	NaCl	Unknown	3	<5.0	3.47	6.5
0406064-23	Solid	$CaCl_2$		3	<5.0	2.29	5.29
0406064-15	Liquid	$CaCl_2$		2	<5.0	1.6	3.6
0406064-06	Solid	NaCl		2	<5.0	0.83	2.83
0406064-43	Liquid	Acetate	OMB	<0.2	<5.0	<0.50	<5.0
0406064-44	Solid	Acetate		0.4	<5.0	<0.50	<5.0
0406064-36	Solid	Blended Chloride		1	<5.0	1.54	2.54
0406064-22	Solid	$CaCl_2$		1	<5.0	<0.50	1
0406064-04	Solid	NaCl		0.2	<5.0	<0.50	0.2

[1] Additive: OMB – Organic Matter from Biomass
P – Phosphate
TEA – triethanolamine
C – polyhydroxycarboxylate
A – polyalkoxylated amine

Table 8-4. Phosphorus analysis data.

Lab ID	Matrix	Material Type	Additive [1]	Ortho-Phosphate as P (mg/L)	Total Phosphorus (mg/L)
0406064-10	Solid	NaCl	P	780	780
0406064-37	Solid	Blended Chloride	OMB, P	98	690
0406064-33	Liquid	$MgCl_2$	OMB	23	540
0406064-11	Solid	NaCl	P	440	460
0406064-34	Liquid	Blended Chloride	OMB	5.6	430
0406064-09	Solid	NaCl	OMB	370	420
0406064-35	Liquid	Blended Chloride	OMB	270	420
0406064-42	Liquid	Acetate		340	370
0406064-21	Liquid	$CaCl_2$	OMB	230	350
0406064-44	Solid	Acetate		160	190
0406064-31	Liquid	$MgCl_2$	OMB	<20	110
0406064-30	Liquid	$MgCl_2$	OMB	22	76
0406064-29	Liquid	$MgCl_2$	OMB, TEA	<2.0	56
0406064-32	Liquid	$MgCl_2$	OMB	34	52
0406064-03	Liquid	NaCl	OMB	<20	50
0406064-17	Liquid	$CaCl_2$	OMB	<20	44
0406064-28	Liquid	$MgCl_2$	OMB	4.8	28
0406064-43	Liquid	Acetate	OMB	<2.0	19
0406064-02	Liquid	NaCl	OMB	<2.0	14
0406064-40	Liquid	Acetate		<2.0	13
0406064-41	Liquid	Acetate		2.5	11
0406064-20	Liquid	$CaCl_2$	C, A	<10	10
0406064-38	Solid	Blended Chloride		<2.0	8.7
0406064-25	Liquid	$CaCl_2$		<2.0	7.2
0406064-36	Solid	Blended Chloride		<2.0	6.5
0406064-18	Liquid	$CaCl_2$	OMB	<2.0	3.4
0406064-26	Liquid	$MgCl_2$		<2.0	3.2
0406064-04	Solid	NaCl		<2.0	2.5
0406064-01	Liquid	NaCl		<2.0	<2.0
0406064-06	Solid	NaCl		<2.0	<2.0
0406064-07	Solid	NaCl		<2.0	<2.0
0406064-08	Solid	NaCl	OMB	<2.0	<2.0
0406064-12	Solid	NaCl	Unknown	<2.0	<2.0
0406064-13	Liquid	$CaCl_2$		<2.0	<2.0
0406064-14	Liquid	$CaCl_2$		<2.0	<2.0
0406064-15	Liquid	$CaCl_2$		<2.0	<2.0
0406064-16	Liquid	$CaCl_2$		<2.0	<2.0
0406064-19	Liquid	$CaCl_2$	OMB	<2.0	<2.0
0406064-22	Solid	$CaCl_2$		<2.0	<2.0
0406064-23	Solid	$CaCl_2$		<2.0	<2.0
0406064-24	Solid	$CaCl_2$		<2.0	<2.0
0406064-27	Liquid	$MgCl_2$		<2.0	<2.0

[1] Additive: OMB – Organic Matter from Biomass
P – Phosphate
TEA – triethanolamine
C – polyhydroxycarboxylate
A – polyalkoxylated amine

8.5.2 Cadmium

Cadmium was detected in seven samples, although values were low and near the detection limit of 0.02 mg/L (Table 8-7). The most restrictive purchase specification GMC for cadmium is 0.12 mg/L for NaCl and KA products and 2.5 mg/L for $CaCl_2$, $MgCl_2$, and CMA. The highest three samples (i.e., 0.09, 0.06, and 0.04 mg/L) were associated with $CaCl_2$ from one source; however, from an environmental protection standpoint these levels were not a concern.

8.5.3 Chromium

Chromium was common in most materials and was detected in all but two samples. Chromium levels ranged between 0.05 mg/L and 1.4 mg/L (Table 8-8). These levels are below the most restrictive purchase specification GMC for chromium of 5.5 mg/L and are not a significant environmental concern.

The data suggests a relationship between chromium levels and OMB additive materials. Twelve of the sixteen high

Table 8-5. Cyanide analysis data.

Lab ID	Matrix	Material Type	Additive [1]	Cyanide (mg/L)
0406064-12	Solid	NaCl	Unknown	18
0406064-07	Solid	NaCl		17
0406064-36	Solid	Blended Chloride		9.4
0406064-35	Liquid	Blended Chloride	OMB	0.94
0406064-40	Liquid	Acetate		0.41
0406064-34	Liquid	Blended Chloride	OMB	0.38
0406064-02	Liquid	NaCl	OMB	0.32
0406064-01	Liquid	NaCl		<0.15
0406064-03	Liquid	NaCl	OMB	<0.15
0406064-04	Solid	NaCl		<0.15
0406064-06	Solid	NaCl		<0.15
0406064-08	Solid	NaCl	OMB	<0.15
0406064-09	Solid	NaCl	OMB	<0.15
0406064-10	Solid	NaCl	P	<0.15
0406064-11	Solid	NaCl	P	<0.15
0406064-13	Liquid	$CaCl_2$		<0.15
0406064-14	Liquid	$CaCl_2$		<0.15
0406064-15	Liquid	$CaCl_2$		<0.15
0406064-16	Liquid	$CaCl_2$		<0.15
0406064-17	Liquid	$CaCl_2$	OMB	<0.15
0406064-18	Liquid	$CaCl_2$	OMB	<0.15
0406064-19	Liquid	$CaCl_2$	OMB	<0.15
0406064-20	Liquid	$CaCl_2$	C, A	<0.15
0406064-21	Liquid	$CaCl_2$	OB	<0.15
0406064-22	Solid	$CaCl_2$		<0.15
0406064-23	Solid	$CaCl_2$		<0.15
0406064-24	Solid	$CaCl_2$		<0.15
0406064-25	Liquid	$CaCl_2$		<0.15
0406064-26	Liquid	$MgCl_2$		<0.15
0406064-27	Liquid	$MgCl_2$		<0.15
0406064-28	Liquid	$MgCl_2$	OMB	<0.15
0406064-29	Liquid	$MgCl_2$	OMB, TEA	<0.15
0406064-30	Liquid	$MgCl_2$	OMB	<0.15
0406064-31	Liquid	$MgCl_2$	OMB	<0.15
0406064-32	Liquid	$MgCl_2$	OMB	<0.15
0406064-33	Liquid	$MgCl_2$	OMB	<0.15
0406064-37	Solid	Blended Chloride	OMB, P	<0.15
0406064-38	Solid	Blended Chloride		<0.15
0406064-41	Liquid	Acetate		<0.15
0406064-42	Liquid	Acetate		<0.15
0406064-43	Liquid	Acetate	OMB	<0.15
0406064-44	Solid	Acetate		<0.15

[1] Additive:
OMB – Organic Matter from Biomass
P – Phosphate
TEA – triethanolamine
C – polyhydroxycarboxylate
A – polyalkoxylated amine

Table 8-6. Arsenic analysis data.

Lab ID	Matrix	Material Type	Additive [1]	Arsenic (mg/L)
0406064-01	Liquid	NaCl		<2.0
0406064-02	Liquid	NaCl	OMB	<2.0
0406064-03	Liquid	NaCl	OMB	<2.0
0406064-04	Solid	NaCl		<2.0
0406064-06	Solid	NaCl		<2.0
0406064-07	Solid	NaCl		<2.0
0406064-08	Solid	NaCl	OMB	<2.0
0406064-09	Solid	NaCl	OMB	<2.0
0406064-10	Solid	NaCl	P	<2.0
0406064-11	Solid	NaCl	P	<2.0
0406064-12	Solid	NaCl	Unknown	<2.0
0406064-13	Liquid	$CaCl_2$		<2.0
0406064-14	Liquid	$CaCl_2$		<2.0
0406064-15	Liquid	$CaCl_2$		<2.0
0406064-16	Liquid	$CaCl_2$		<2.0
0406064-17	Liquid	$CaCl_2$	OMB	<2.0
0406064-18	Liquid	$CaCl_2$	OMB	<2.0
0406064-19	Liquid	$CaCl_2$	OMB	<2.0
0406064-20	Liquid	$CaCl_2$	C, A	<2.0
0406064-21	Liquid	$CaCl_2$	OMB	<2.0
0406064-22	Solid	$CaCl_2$		<2.0
0406064-23	Solid	$CaCl_2$		<2.0
0406064-24	Solid	$CaCl_2$		<2.0
0406064-25	Liquid	$CaCl_2$		<2.0
0406064-26	Liquid	$MgCl_2$		<2.0
0406064-27	Liquid	$MgCl_2$		<2.0
0406064-28	Liquid	$MgCl_2$	OMB	<2.0
0406064-29	Liquid	$MgCl_2$	OMB, TEA	<2.0
0406064-30	Liquid	$MgCl_2$	OMB	<2.0
0406064-31	Liquid	$MgCl_2$	OMB	<2.0
0406064-32	Liquid	$MgCl_2$	OMB	<2.0
0406064-33	Liquid	$MgCl_2$	OMB	<2.0
0406064-34	Liquid	Blended Chloride	OMB	<2.0
0406064-35	Liquid	Blended Chloride	OMB	<2.0
0406064-36	Solid	Blended Chloride		<2.0
0406064-37	Solid	Blended Chloride	OMB, P	<2.0
0406064-38	Solid	Blended Chloride		<2.0
0406064-40	Liquid	Acetate		<2.0
0406064-41	Liquid	Acetate		<2.0
0406064-42	Liquid	Acetate		<2.0
0406064-43	Liquid	Acetate	OMB	<2.0
0406064-44	Solid	Acetate		<2.0

[1] Additive:
OMB – Organic Matter from Biomass
P – Phosphate
TEA – triethanolamine
C – polyhydroxycarboxylate
A – polyalkoxylated amine

chromium values were associated with materials containing OMB materials; however, other OMB-containing materials had much lower chromium values, suggesting the concentration depends on the specific material.

8.5.4 Copper

Copper was detected in 26 of 42 samples and ranged between the detection limit of 0.1 mg/L and 0.91 mg/L (Table 8-9). The most restrictive purchase specification GMC for copper is 4.5 mg/L for NaCl and KA products and 15 mg/L for $CaCl_2$, $MgCl_2$, and CMA. Test sample levels were not considered to be of significant environmental concern. The data indicates no obvious trends associated with material types and additives and higher values probably depend more on material source than type.

8.5.5 Lead

All samples displayed lead levels below the reported analytical detection limit of 0.5 mg/L (Table 8-10). The most restrictive purchase specification GMC for lead is 1.3 mg/L for NaCl and KA products, and 5.5 for $CaCl_2$, $MgCl_2$, and CMA. Based on the data, lead was not a significant attribute of environmental concern for the samples tested.

Table 8-7. Cadmium analysis data.

Lab ID	Matrix	Material Type	Additive [1]	Cadmium (mg/L)
0406064-15	Liquid	$CaCl_2$		0.09
0406064-20	Liquid	$CaCl_2$	C, A	0.06
0406064-22	Solid	$CaCl_2$		0.04
0406064-09	Solid	NaCl	OMB	0.02
0406064-10	Solid	NaCl	P	0.02
0406064-11	Solid	NaCl	P	0.02
0406064-43	Liquid	Acetate	OMB	0.02
0406064-01	Liquid	NaCl		<0.02
0406064-02	Liquid	NaCl	OMB	<0.02
0406064-03	Liquid	NaCl	OMB	<0.02
0406064-04	Solid	NaCl		<0.02
0406064-06	Solid	NaCl		<0.02
0406064-07	Solid	NaCl		<0.02
0406064-08	Solid	NaCl	OMB	<0.02
0406064-12	Solid	NaCl	Unknown	<0.02
0406064-13	Liquid	$CaCl_2$		<0.02
0406064-14	Liquid	$CaCl_2$		<0.02
0406064-16	Liquid	$CaCl_2$		<0.02
0406064-17	Liquid	$CaCl_2$	OMB	<0.02
0406064-18	Liquid	$CaCl_2$	OMB	<0.02
0406064-19	Liquid	$CaCl_2$	OMB	<0.02
0406064-21	Liquid	$CaCl_2$	OMB	<0.02
0406064-23	Solid	$CaCl_2$		<0.02
0406064-24	Solid	$CaCl_2$		<0.02
0406064-25	Liquid	$CaCl_2$		<0.02
0406064-26	Liquid	$MgCl_2$		<0.02
0406064-27	Liquid	$MgCl_2$		<0.02
0406064-28	Liquid	$MgCl_2$	OMB	<0.02
0406064-29	Liquid	$MgCl_2$	OMB, TEA	<0.02
0406064-30	Liquid	$MgCl_2$	OMB	<0.02
0406064-31	Liquid	$MgCl_2$	OMB	<0.02
0406064-32	Liquid	$MgCl_2$	OMB	<0.02
0406064-33	Liquid	$MgCl_2$	OMB	<0.02
0406064-34	Liquid	Blended Chloride	OMB	<0.02
0406064-35	Liquid	Blended Chloride	OMB	<0.02
0406064-36	Solid	Blended Chloride		<0.02
0406064-37	Solid	Blended Chloride	OMB, P	<0.02
0406064-38	Solid	Blended Chloride		<0.02
0406064-40	Liquid	Acetate		<0.02
0406064-41	Liquid	Acetate		<0.02
0406064-42	Liquid	Acetate		<0.02
0406064-44	Solid	Acetate		<0.02

[1] Additive: OMB – Organic Matter from Biomass
P – Phosphate
TEA – triethanolamine
C – polyhydroxycarboxylate
A – polyalkoxylated amine

8.5.6 Mercury

Of the samples tested, mercury was detected in one $MgCl_2$ sample at 0.02 mg/L (Table 8-11). This value was well below the most restrictive purchase specification GMC value of 0.39 mg/L. Based on the data, mercury was not a significant attribute of environmental concern for the samples tested.

8.5.7 Nickel

Nickel was detected in two samples, although levels were near the detection limi of 1 mg/L (Table 8-12). These levels were well below the most restrictive purchase specification GMC value of 26 mg/L. Based on the data, nickel was not a significant attribute of environmental concern for the samples tested.

Table 8-8. Chromium analysis data.

Lab ID	Matrix	Material Type	Additive [1]	Chromium (mg/L)
0406064-43	Liquid	Acetate	OMB	1.40
0406064-29	Liquid	$MgCl_2$	OMB, TEA	1.10
0406064-28	Liquid	$MgCl_2$	OMB	0.91
0406064-31	Liquid	$MgCl_2$	OMB	0.79
0406064-44	Solid	Acetate		0.76
0406064-18	Liquid	$CaCl_2$	OMB	0.68
0406064-17	Liquid	$CaCl_2$	OMB	0.64
0406064-33	Liquid	$MgCl_2$	OMB	0.58
0406064-26	Liquid	$MgCl_2$		0.55
0406064-30	Liquid	$MgCl_2$	OMB	0.52
0406064-25	Liquid	$CaCl_2$		0.46
0406064-19	Liquid	$CaCl_2$	OMB	0.45
0406064-03	Liquid	NaCl	OMB	0.43
0406064-20	Liquid	$CaCl_2$	C, A	0.40
0406064-40	Liquid	Acetate		0.40
0406064-32	Liquid	$MgCl_2$	OMB	0.37
0406064-27	Liquid	$MgCl_2$		0.30
0406064-42	Liquid	Acetate		0.29
0406064-22	Solid	$CaCl_2$		0.28
0406064-10	Solid	NaCl	P	0.27
0406064-41	Liquid	Acetate		0.27
0406064-15	Liquid	$CaCl_2$		0.26
0406064-14	Liquid	$CaCl_2$		0.25
0406064-35	Liquid	Blended Chloride	OMB	0.25
0406064-06	Solid	NaCl		0.24
0406064-34	Liquid	Blended Chloride	OMB	0.24
0406064-13	Liquid	$CaCl_2$	OMB	0.23
0406064-09	Solid	NaCl		0.21
0406064-38	Solid	Blended Chloride		0.21
0406064-02	Liquid	NaCl	OB	0.20
0406064-23	Solid	$CaCl_2$		0.19
0406064-24	Solid	$CaCl_2$		0.19
0406064-12	Solid	NaCl	Unknown	0.17
0406064-16	Liquid	$CaCl_2$		0.14
0406064-07	Solid	NaCl		0.13
0406064-08	Solid	NaCl	OMB	0.13
0406064-04	Solid	NaCl		0.12
0406064-11	Solid	NaCl	P	0.12
0406064-37	Solid	Blended Chloride	OMB, P	0.11
0406064-21	Liquid	$CaCl_2$	OMB	0.09
0406064-01	Liquid	NaCl		<0.05
0406064-36	Solid	Blended Chloride		<0.05

[1] Additive:
OMB – Organic Matter from Biomass
P – Phosphate
TEA – triethanolamine
C – polyhydroxycarboxylate
A – polyalkoxylated amine

8.5.8 Selenium

Selenium was detected in 10 samples, at levels between 1 and 1.6 mg/L (Table 8-13). These levels were below the most restrictive purchase specification GMC value of 2.5 mg/L and were thus not considered a significant environmental concern. Some caution should be exercised with the conclusion in that the detection limit capability for selenium was near limits for environmental concern.

Table 8-9. Copper analysis data.

Lab ID	Matrix	Material Type	Additive [1]	Copper (mg/L)
0406064-44	Solid	Acetate		0.91
0406064-17	Liquid	$CaCl_2$	OMB	0.68
0406064-33	Liquid	$MgCl_2$	OMB	0.63
0406064-31	Liquid	$MgCl_2$	OMB	0.58
0406064-16	Liquid	$CaCl_2$		0.51
0406064-32	Liquid	$MgCl_2$	OMB	0.35
0406064-37	Solid	Blended Chloride	OMB, P	0.34
0406064-34	Liquid	Blended Chloride	OMB	0.31
0406064-36	Solid	Blended Chloride		0.31
0406064-40	Liquid	Acetate		0.31
0406064-25	Liquid	$CaCl_2$		0.28
0406064-21	Liquid	$CaCl_2$	OMB	0.26
0406064-30	Liquid	$MgCl_2$	OMB	0.23
0406064-41	Liquid	Acetate		0.23
0406064-18	Liquid	$CaCl_2$	OMB	0.22
0406064-06	Solid	NaCl		0.21
0406064-20	Liquid	$CaCl_2$	C, A	0.20
0406064-26	Liquid	$MgCl_2$		0.20
0406064-29	Liquid	$MgCl_2$	OMB, TEA	0.20
0406064-35	Liquid	Blended Chloride	OMB	0.20
0406064-09	Solid	NaCl	OMB	0.17
0406064-27	Liquid	$MgCl_2$		0.17
0406064-28	Liquid	$MgCl_2$	OMB	0.16
0406064-19	Liquid	$CaCl_2$	OMB	0.12
0406064-38	Solid	Blended Chloride		0.12
0406064-07	Solid	NaCl		0.10
0406064-01	Liquid	NaCl		<0.10
0406064-02	Liquid	NaCl	OMB	<0.10
0406064-03	Liquid	NaCl	OMB	<0.10
0406064-04	Solid	NaCl		<0.10
0406064-08	Solid	NaCl	OMB	<0.10
0406064-10	Solid	NaCl	P	<0.10
0406064-11	Solid	NaCl	P	<0.10
0406064-12	Solid	NaCl	Unknown	<0.10
0406064-13	Liquid	$CaCl_2$		<0.10
0406064-14	Liquid	$CaCl_2$		<0.10
0406064-15	Liquid	$CaCl_2$		<0.10
0406064-22	Solid	$CaCl_2$		<0.10
0406064-23	Solid	$CaCl_2$		<0.10
0406064-24	Solid	$CaCl_2$		<0.10
0406064-42	Liquid	Acetate		<0.10
0406064-43	Liquid	Acetate	OMB	<0.10

[1] Additive:
OMB – Organic Matter from Biomass
P – Phosphate
TEA – triethanolamine
C – polyhydroxycarboxylate
A – polyalkoxylated amine

8.5.9 Silver

Silver was detected in one sample at the detection limit of 0.1 mg/L (Table 8-14). The most restrictive purchase specification GMC for silver is 0.32 mg/L for NaCl and KA products and 3.5 mg/L for $CaCl_2$, $MgCl_2$, and CMA. Based on the data, silver was not a significant attribute of environmental concern for the samples tested; however, detection limit capability for silver was near limits for environmental concern.

Table 8-10. Lead analysis data.

Lab ID	Matrix	Material Type	Additive [1]	Lead (mg/L)
0406064-01	Liquid	NaCl		<0.5
0406064-02	Liquid	NaCl	OMB	<0.5
0406064-03	Liquid	NaCl	OMB	<0.5
0406064-04	Solid	NaCl		<0.5
0406064-06	Solid	NaCl		<0.5
0406064-07	Solid	NaCl		<0.5
0406064-08	Solid	NaCl	OMB	<0.5
0406064-09	Solid	NaCl	OMB	<0.5
0406064-10	Solid	NaCl	P	<0.5
0406064-11	Solid	NaCl	P	<0.5
0406064-12	Solid	NaCl	Unknown	<0.5
0406064-13	Liquid	$CaCl_2$		<0.5
0406064-14	Liquid	$CaCl_2$		<0.5
0406064-15	Liquid	$CaCl_2$		<0.5
0406064-16	Liquid	$CaCl_2$		<0.5
0406064-17	Liquid	$CaCl_2$	OMB	<0.5
0406064-18	Liquid	$CaCl_2$	OMB	<0.5
0406064-19	Liquid	$CaCl_2$	OMB	<0.5
0406064-20	Liquid	$CaCl_2$	C, A	<0.5
0406064-21	Liquid	$CaCl_2$	OMB	<0.5
0406064-22	Solid	$CaCl_2$		<0.5
0406064-23	Solid	$CaCl_2$		<0.5
0406064-24	Solid	$CaCl_2$		<0.5
0406064-25	Liquid	$CaCl_2$		<0.5
0406064-26	Liquid	$MgCl_2$		<0.5
0406064-27	Liquid	$MgCl_2$		<0.5
0406064-28	Liquid	$MgCl_2$	OMB	<0.5
0406064-29	Liquid	$MgCl^2$	OMB, TEA	<0.5
0406064-30	Liquid	$MgCl_2$	OMB	<0.5
0406064-31	Liquid	$MgCl_2$	OMB	<0.5
0406064-32	Liquid	$MgCl_2$	OMB	<0.5
0406064-33	Liquid	$MgCl_2$	OMB	<0.5
0406064-34	Liquid	Blended Chloride	OMB	<0.5
0406064-35	Liquid	Blended Chloride	OMB	<0.5
0406064-36	Solid	Blended Chloride		<0.5
0406064-37	Solid	Blended Chloride	OMB, P	<0.5
0406064-38	Solid	Blended Chloride		<0.5
0406064-40	Liquid	Acetate		<0.5
0406064-41	Liquid	Acetate		<0.5
0406064-42	Liquid	Acetate		<0.5
0406064-43	Liquid	Acetate	OMB	<0.5
0406064-44	Solid	Acetate		<0.5

[1] Additive:
OMB – Organic Matter from Biomass
P – Phosphate
TEA – triethanolamine
C – polyhydroxycarboxylate
A – polyalkoxylated amine

8.5.10 Zinc

Of the materials tested, zinc was detected in all but five samples and levels ranged from the detection limit of 1 mg/L to 20.6 mg/L (Table 8-15). The most restrictive purchase specification GMC for zinc is 59 mg/L for NaCl and KA products and 190 mg/L for $CaCl_2$, $MgCl_2$, and CMA. Based on the data, zinc was not a significant attribute of environmental concern.

Table 8-11. Mercury analysis data.

Lab ID	Matrix	Material Type	Additive [1]	Mercury (mg/L)
0406064-31	Liquid	$MgCl_2$	OBM	0.02
0406064-01	Liquid	NaCl		<0.01
0406064-02	Liquid	NaCl	OBM	<0.01
0406064-03	Liquid	NaCl	OBM	<0.01
0406064-04	Solid	NaCl		<0.01
0406064-06	Solid	NaCl		<0.01
0406064-07	Solid	NaCl		<0.01
0406064-08	Solid	NaCl	OBM	<0.01
0406064-09	Solid	NaCl	OBM	<0.01
0406064-10	Solid	NaCl	P	<0.01
0406064-11	Solid	NaCl	P	<0.01
0406064-12	Solid	NaCl	Unknown	<0.01
0406064-13	Liquid	$CaCl_2$		<0.01
0406064-14	Liquid	$CaCl_2$		<0.01
0406064-15	Liquid	$CaCl_2$		<0.01
0406064-16	Liquid	$CaCl_2$		<0.01
0406064-17	Liquid	$CaCl_2$	OBM	<0.01
0406064-18	Liquid	$CaCl_2$	OBM	<0.01
0406064-19	Liquid	$CaCl_2$	OBM	<0.01
0406064-20	Liquid	$CaCl_2$	C, A	<0.01
0406064-21	Liquid	$CaCl_2$	OBM	<0.01
0406064-22	Solid	$CaCl_2$		<0.01
0406064-23	Solid	$CaCl_2$		<0.01
0406064-24	Solid	$CaCl_2$		<0.01
0406064-25	Liquid	$CaCl_2$		<0.01
0406064-26	Liquid	$MgCl_2$		<0.01
0406064-27	Liquid	$MgCl_2$		<0.01
0406064-28	Liquid	$MgCl_2$	OBM	<0.01
0406064-29	Liquid	$MgCl_2$	OBM, TEA	<0.01
0406064-30	Liquid	$MgCl_2$	OBM	<0.01
0406064-32	Liquid	$MgCl_2$	OBM	<0.01
0406064-33	Liquid	$MgCl_2$	OBM	<0.01
0406064-34	Liquid	Blended Chloride	OBM	<0.01
0406064-35	Liquid	Blended Chloride	OBM	<0.01
0406064-36	Solid	Blended Chloride		<0.01
0406064-37	Solid	Blended Chloride	OBM, P	<0.01
0406064-38	Solid	Blended Chloride		<0.01
0406064-40	Liquid	Acetate		<0.01
0406064-41	Liquid	Acetate		<0.01
0406064-42	Liquid	Acetate		<0.01
0406064-43	Liquid	Acetate	OBM	<0.01
0406064-44	Solid	Acetate		<0.01

[1] Additive:
OMB – Organic Matter from Biomass
P – Phosphate
TEA – triethanolamine
C – polyhydroxycarboxylate
A – polyalkoxylated amine

8.6 Chemical Analysis Summary

The following general conclusions can be made from the chemical analysis program:

- High organic matter concentrations are associated with acetate materials and with materials containing OMB. For the latter, levels depended on the proportion of OMB in the blend. Solids with OMB generally had much lower organic matter levels than liquid counterparts.

Table 8-12. Nickel analysis data.

Lab ID	Matrix	Material Type	Additive [1]	Nickel (mg/L)
0406064-31	Liquid	$MgCl_2$	OMB	3
0406064-03	Liquid	NaCl	OMB	1
0406064-01	Liquid	NaCl		<1
0406064-02	Liquid	NaCl	OMB	<1
0406064-04	Solid	NaCl		<1
0406064-06	Solid	NaCl		<1
0406064-07	Solid	NaCl		<1
0406064-08	Solid	NaCl	OMB	<1
0406064-09	Solid	NaCl	OMB	<1
0406064-10	Solid	NaCl	P	<1
0406064-11	Solid	NaCl	P	<1
0406064-12	Solid	NaCl	Unknown	<1
0406064-13	Liquid	$CaCl_2$		<1
0406064-14	Liquid	$CaCl_2$		<1
0406064-15	Liquid	$CaCl_2$		<1
0406064-16	Liquid	$CaCl_2$		<1
0406064-17	Liquid	$CaCl_2$	OMB	<1
0406064-18	Liquid	$CaCl_2$	OMB	<1
0406064-19	Liquid	$CaCl_2$	OMB	<1
0406064-20	Liquid	$CaCl_2$	C, A	<1
0406064-21	Liquid	$CaCl_2$	OMB	<1
0406064-22	Solid	$CaCl_2$		<1
0406064-23	Solid	$CaCl_2$		<1
0406064-24	Solid	$CaCl_2$		<1
0406064-25	Liquid	$CaCl_2$		<1
0406064-26	Liquid	$MgCl_2$		<1
0406064-27	Liquid	$MgCl_2$		<1
0406064-28	Liquid	$MgCl_2$	OMB	<1
0406064-29	Liquid	$MgCl_2$	OMB, TEA	<1
0406064-30	Liquid	$MgCl_2$	OMB	<1
0406064-32	Liquid	$MgCl_2$	OMB	<1
0406064-33	Liquid	$MgCl_2$	OMB	<1
0406064-34	Liquid	Blended Chloride	OMB	<1
0406064-35	Liquid	Blended Chloride	OMB	<1
0406064-36	Solid	Blended Chloride		<1
0406064-37	Solid	Blended Chloride	OMB, P	<1
0406064-38	Solid	Blended Chloride		<1
0406064-40	Liquid	Acetate		<1
0406064-41	Liquid	Acetate		<1
0406064-42	Liquid	Acetate		<1
0406064-43	Liquid	Acetate	OMB	<1
0406064-44	Solid	Acetate		<1

[1] Additive:
OMB – Organic Matter from Biomass
P – Phosphate
TEA – triethanolamine
C – polyhydroxycarboxylate
A – polyalkoxylated amine

Table 8-13. Selenium analysis data.

Lab ID	Matrix	Material Type	Additive [1]	Selenium (mg/L)
0406064-25	Liquid	$CaCl_2$		1.6
0406064-19	Liquid	$CaCl_2$	OMB	1.5
0406064-26	Liquid	$MgCl_2$		1.3
0406064-14	Liquid	$CaCl_2$		1.2
0406064-32	Liquid	$MgCl_2$	OMB	1.2
0406064-34	Liquid	Blended Chloride	OMB	1.2
0406064-16	Liquid	$CaCl_2$		1.1
0406064-27	Liquid	$MgCl_2$		1
0406064-29	Liquid	$MgCl_2$	OMB, TEA	1
0406064-30	Liquid	$MgCl_2$	OMB	1
0406064-01	Liquid	NaCl		<1.0
0406064-02	Liquid	NaCl	OMB	<1.0
0406064-03	Liquid	NaCl	OMB	<1.0
0406064-04	Solid	NaCl		<1.0
0406064-06	Solid	NaCl		<1.0
0406064-07	Solid	NaCl		<1.0
0406064-08	Solid	NaCl	OMB	<1.0
0406064-09	Solid	NaCl	OMB	<1.0
0406064-10	Solid	NaCl	P	<1.0
0406064-11	Solid	NaCl	P	<1.0
0406064-12	Solid	NaCl	Unknown	<1.0
0406064-13	Liquid	$CaCl_2$		<1.0
0406064-15	Liquid	$CaCl_2$		<1.0
0406064-17	Liquid	$CaCl_2$	OMB	<1.0
0406064-18	Liquid	$CaCl_2$	OMB	<1.0
0406064-20	Liquid	$CaCl_2$	C, A	<1.0
0406064-21	Liquid	$CaCl_2$	OMB	<1.0
0406064-22	Solid	$CaCl_2$		<1.0
0406064-23	Solid	$CaCl_2$		<1.0
0406064-24	Solid	$CaCl_2$		<1.0
0406064-28	Liquid	$MgCl_2$	OMB	<1.0
0406064-31	Liquid	$MgCl_2$	OMB	<1.0
0406064-33	Liquid	$MgCl_2$	OMB	<1.0
0406064-35	Liquid	Blended Chloride	OMB	<1.0
0406064-36	Solid	Blended Chloride		<1.0
0406064-37	Solid	Blended Chloride	OMB, P	<1.0
0406064-38	Solid	Blended Chloride		<1.0
0406064-40	Liquid	Acetate		<1.0
0406064-41	Liquid	Acetate		<1.0
0406064-42	Liquid	Acetate		<1.0
0406064-43	Liquid	Acetate	OMB	<1.0
0406064-44	Solid	Acetate		<1.0

[1] Additive:
OMB – Organic Matter from Biomass
P – Phosphate
TEA – triethanolamine
C – polyhydroxycarboxylate
A – polyalkoxylated amine

- Nutrient (nitrogen and phosphorus) levels found in many of the materials tested can be considered a potential environmental concern. Nutrient levels had a strong relationship to the presence of OMB materials in the product blend. Higher nutrient levels were also present in other material types. The range in nutrient levels was broad, suggesting that each material should be assessed independently if nutrients are to be evaluated.
- Cyanide could be an environmental concern for materials such as solid NaCl that routinely contain iron-cyanide anti-caking agents. More research and information is necessary to assess the bio-availability of iron-cyanide materials under field conditions conclusively.
- Overall, metals levels were below levels considered to be a significant environmental concern. The literature does indicate that higher metals levels have routinely been

Table 8-14. Silver analysis data.

Lab ID	Matrix	Material Type	Additive [1]	Silver (mg/L)
0406064-01	Liquid	NaCl		<0.1
0406064-02	Liquid	NaCl	OMB	<0.1
0406064-03	Liquid	NaCl	OMB	<0.1
0406064-04	Solid	NaCl		<0.1
0406064-06	Solid	NaCl		<0.1
0406064-07	Solid	NaCl		<0.1
0406064-08	Solid	NaCl	OMB	<0.1
0406064-09	Solid	NaCl	OMB	<0.1
0406064-10	Solid	NaCl	P	<0.1
0406064-11	Solid	NaCl	P	<0.1
0406064-12	Solid	NaCl	Unknown	<0.1
0406064-13	Liquid	$CaCl_2$		<0.1
0406064-14	Liquid	$CaCl_2$		<0.1
0406064-15	Liquid	$CaCl_2$		<0.1
0406064-16	Liquid	$CaCl_2$		<0.1
0406064-17	Liquid	$CaCl_2$	OMB	<0.1
0406064-18	Liquid	$CaCl_2$	OMB	<0.1
0406064-19	Liquid	$CaCl_2$	OMB	<0.1
0406064-20	Liquid	$CaCl_2$	C, A	<0.1
0406064-21	Liquid	$CaCl_2$	OMB	<0.1
0406064-22	Solid	$CaCl_2$		<0.1
0406064-23	Solid	$CaCl_2$		<0.1
0406064-24	Solid	$CaCl_2$		<0.1
0406064-25	Liquid	$CaCl_2$		<0.1
0406064-26	Liquid	$MgCl_2$		<0.1
0406064-27	Liquid	$MgCl_2$		<0.1
0406064-28	Liquid	$MgCl_2$	OMB	<0.1
0406064-30	Liquid	$MgCl_2$	OMB	<0.1
0406064-31	Liquid	$MgCl_2$	OMB	<0.1
0406064-32	Liquid	$MgCl_2$	OMB	<0.1
0406064-33	Liquid	$MgCl_2$	OMB	<0.1
0406064-34	Liquid	Blended Chloride	OMB	<0.1
0406064-35	Liquid	Blended Chloride	OMB	<0.1
0406064-36	Solid	Blended Chloride		<0.1
0406064-37	Solid	Blended Chloride	OMB, P	<0.1
0406064-38	Solid	Blended Chloride		<0.1
0406064-40	Liquid	Acetate		<0.1
0406064-41	Liquid	Acetate		<0.1
0406064-42	Liquid	Acetate		<0.1
0406064-43	Liquid	Acetate	OMB	<0.1
0406064-44	Solid	Acetate		<0.1
0406064-29	Liquid	$MgCl_2$	OMB, TEA	0.1

[1] Additive:
OMB – Organic Matter from Biomass
P – Phosphate
TEA – triethanolamine
C – polyhydroxycarboxylate
A – polyalkoxylated amine

Table 8-15. Zinc analysis data.

Lab ID	Matrix	Material Type	Additive [1]	Zinc (mg/L)
0406064-16	Liquid	$CaCl_2$		20.6
0406064-31	Liquid	$MgCl_2$	OMB	15.4
0406064-03	Liquid	NaCl	OMB	6.6
0406064-35	Liquid	Blended Chloride	OMB	5
0406064-33	Liquid	$MgCl_2$	OMB	4.7
0406064-17	Liquid	$CaCl_2$	OMB	2.8
0406064-18	Liquid	$CaCl_2$	OMB	2.6
0406064-30	Liquid	$MgCl_2$	OMB	2.6
0406064-32	Liquid	$MgCl_2$	OMB	2.4
0406064-06	Solid	NaCl		2.3
0406064-26	Liquid	$MgCl_2$		2.3
0406064-20	Liquid	$CaCl_2$	C, A	2.2
0406064-41	Liquid	Acetate		2.1
0406064-37	Solid	Blended Chloride	OMB, P	2
0406064-40	Liquid	Acetate		2
0406064-28	Liquid	$MgCl_2$	OMB	1.9
0406064-34	Liquid	Blended Chloride	OMB	1.9
0406064-25	Liquid	$CaCl_2$		1.8
0406064-09	Solid	NaCl	OMB	1.7
0406064-29	Liquid	$MgCl_2$	OMB, TEA	1.7
0406064-44	Solid	Acetate		1.7
0406064-11	Solid	NaCl	P	1.6
0406064-27	Liquid	$MgCl_2$		1.6
0406064-38	Solid	Blended Chloride		1.6
0406064-43	Liquid	Acetate	OMB	1.6
0406064-01	Liquid	NaCl		1.5
0406064-13	Liquid	$CaCl_2$		1.4
0406064-15	Liquid	$CaCl_2$		1.3
0406064-19	Liquid	$CaCl_2$	OMB	1.3
0406064-04	Solid	NaCl		1.2
0406064-08	Solid	NaCl	OMB	1.2
0406064-10	Solid	NaCl	P	1.1
0406064-12	Solid	NaCl	Unknown	1.1
0406064-22	Solid	$CaCl_2$		1.1
0406064-42	Liquid	Acetate		1.1
0406064-02	Liquid	NaCl	OMB	1
0406064-14	Liquid	$CaCl_2$		1
0406064-07	Solid	NaCl		<1.0
0406064-21	Liquid	$CaCl_2$	OMB	<1.0
0406064-23	Solid	$CaCl_2$		<1.0
0406064-24	Solid	$CaCl_2$		<1.0
0406064-36	Solid	Blended Chloride		<1.0

[1] Additive:
OMB – Organic Matter from Biomass
P – Phosphate
TEA – triethanolamine
C – polyhydroxycarboxylate
A – polyalkoxylated amine

observed in snow and ice control materials. Continual monitoring of snow and ice materials received in the field over a longer time would provide a more realistic assessment of metals levels.

- The variability in the data between products and the general lack of strong trends outside of those already listed suggest that it is important to continue to monitor chemical attributes of snow and ice control materials through a quality assurance plan. The Purchase Specification provided in the attached Guidebook provides further guidance on quality monitoring plans.

CHAPTER 9

Aquatic Toxicity Testing

Aquatic toxicity testing was conducted on 15 snow and ice control products following U.S. EPA standard test methods for chronic exposure to various levels of aquatic biota, including vertebrates, invertebrates, and algae (Table 9-1). Chronic exposure tests were selected over more commonly used acute test procedures because chronic exposure tests provide more information related to potential long-term effects. Both the U.S. EPA and Environment Canada recognize these tests to be sufficient in length to evaluate chronic effects. For fathead minnows, by conducting a 7-day test, one can also determine the 96-hour LC_{50}, as well as a 7-day IC_{50} and IC_{25}, on growth. Aquatic toxicity test data is presented in Tables 9-2 through 9-4. The data shows the concentration of material required to achieve a desired endpoint (e.g., LC_{50} and IC_{50}) over the test duration. Lower values represent higher toxicity levels (i.e., less material is required to achieve the test endpoint).

The extensive toxicity testing reported in Tables 9-2 through 9-4 provided data for comparisons across snow and ice control material types, comparisons for a given material type, and comparisons of sensitivity among different kinds of organisms. In addition, the tables can be used to show what fraction of the snow and ice control material might be considered environmentally damaging at a given dilution ratio on the roadway (e.g., 500:1).

The fathead minnow was more tolerant than *Ceriodaphnia* and *Selenastrum*, especially for chloride-based snow and ice control materials. Although there is considerable variation among chloride materials, there is no evidence that the associated cation (e.g., sodium, calcium, or magnesium) makes a difference in toxicity. CMA falls within the same range of thresholds as chloride-based deicers. CMAK and KA, however, produce surprisingly low toxicity thresholds for fathead minnows. This may be an important finding, given that low toxicity thresholds (i.e., higher toxicity) for CMAK and KA have not been reported in the literature, nor would they be expected. The implication of the data is that potassium is not tolerated as well as other cations associated with snow and ice control materials. Verification will, however, require further research, given that only two of the materials tested contained potassium as a major ingredient. Another interesting aspect of Table 9-2 is the relatively small separation between thresholds involving acute mortality and chronic suppression of growth.

Selenastrum capricornutum, a green alga often used as a test organism, proved to be substantially more sensitive than fathead minnows to most snow and ice control materials. For *Selenastrum*, there was no detectable difference between potassium-containing materials and other materials, in contrast to the results for fathead minnows.

Ceriodaphnia dubia, a water flea known to have low toxicological tolerance, showed tolerances lower than those of *Selenastrum* and much lower than those of the fathead minnow. *Ceriodaphnia*, like *Selenastrum*, was not especially sensitive to potassium-containing snow and ice control materials.

It might be expected that snow and ice control materials of a certain class (e.g., NaCl) would show essentially the same thresholds of tolerance for a given kind of organism. This is not always the case, as shown by the test data. Differences between materials are partly a matter of variance in the testing methods, but undoubtedly extend beyond this to include effects of additives and contaminants that may differ from one type of material to another.

From the viewpoint of applications in the field, it is important to know how the tolerance thresholds shown in Tables 9-2 through 9-4 compare with the expected dosage that organisms would receive in the field. Although the concentrations of snow and ice control materials at the time of application vary, the roadway dilution of 500:1 can be applied to a solid. The threshold for solids is shown in Figure 9-1. 500:1 dilutions for liquids would produce a line that falls below the one for solids. Materials with toxicity thresholds above the 500:1 dilution line would, according to

Table 9-1. Aquatic toxicity testing.

Test Method	Standard Reference Method
Fathead Minnow 7-day Survival and Growth Test (will also include acute toxicity data for Fathead Minnow 96-hour Survival Test)	U.S. EPA, 1994, Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to Freshwater Organisms, 3rd Edition, EPA/600/4-91/002
Ceriodaphnia dubia 3-brood Survival and Reproduction Test	U.S. EPA, 1994, Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to Freshwater Organisms, 3rd Edition, EPA/600/4-91/002
Selenastrum capricornutum 96-hour (US EPA) Growth Test	U.S. EPA, 1994, Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to Freshwater Organisms, 3rd Edition, EPA/600/4-91/002

Table 9-2. Fathead minnow toxicity testing endpoints (mg/L) (95% confidence limits).

Lab ID	Base Chemical	Matrix	Additive[1]	Endpoint Concentration (mg/L)			
				Fathead Minnow 96-h LC50[2]	Fathead Minnow 7-d LC50[2]	Fathead Minnow 7-d IC25 (Growth)[3]	Fathead Minnow 7-d IC50 (Growth)[4]
2	NaCl	Liquid	OMB	18,415 (16,951, 20,202)	15,324 (3,201, 20,958)	8,574 (3,810, 15,349)	13,545 (N/A)
3		Liquid	OMB	11,691 (10,465, 12,822)	10,927 (9769, 12,149)	5923 (5026, 6681)	8663 (7323, 10,303)
6		Solid	-	8287 (8002, 8593)	7598 (7057, 7914)	3352 (620, 5126)	5606 (4213, 6435)
10		Solid	P	4598 (4440, 4841)	4398 (4079, 4659)	2071 (989,3375)	3857 (N/A)
13	$CaCl_2$	Liquid	-	13,893 (10,672, 16,368)	10,656 (8246, 13,720)	7707 (6805, 8752)	10574 (9457, 12,278)
17		Liquid	OMB	11,609 (10,779, 13,378)	10,971 (10,486, 12,002)	5810 (4548, 6581)	8434 (7599, 9004)
20		Liquid	C, A	79.9 (N/A)	48.6 (36.9, 98.5)	>25	>25
21		Liquid	OMB	11002 (9648, 12,666)	9315 (8787, 9904)	7195 (6212, 8221)	9946 (8637, 11340)
26	$MgCl_2$	Liquid	-	3691 (3480, 3883)	3639 (3417, 3852)	2631 (N/A)	>3038 (N/A)
29		Liquid	OMB, TEA	6000 (4690, 6575)	5664 (4316, 6755)	>2400	>2400
32		Liquid	OMB	3528 (3306, 3803)	3326 (3023, 3650)	1887 (1494, 2391)	3045 (N/A)
37	Blended Chloride	Solid	OMB, P	7692 (6924, 10,377)	6402 (5735, 7127)	3666 (2897, 4441)	5388 (N/A)
40	CMA	Liquid	-	22,093 (15,182, 27,767)	12,586 (11,771, 13,283)	6337 (4541, 7745)	9493 (7022, 12,152)
41	CMAK	Liquid	-	2711 (2593, 2930)	2596 (2459, 2891)	1308 (884, 1762)	2143 (N/A)
42	KA	Liquid	-	1033 (963, 1085)	907 (835, 926)	>788	>788

[1] OMB – Organic Matter from Biomass, P – Phosphate, TEA – triethanolamine, C – polyhydroxycarboxylate, A – polyalkoxylated amine

[2] LC50 = concentration at which 50% of the population exposed would survive

[3] IC25 = concentration which would cause a 25% inhibition in reproduction or growth

[4] IC50 = concentration which would cause a 50% inhibition in reproduction or growth

‘ - ’ indicates not present

Table 9-3. ***Selenastrum capricornutum*** **toxicity testing endpoints (mg/L) (95% confidence limits).**

Lab ID	Base Chemical	Matrix	Additive[1]	Endpoint Concentration (mg/L)	
				Selenastrum 96-h IC25[2] (Growth)	*Selenastrum* 96-h IC50[3] (Growth)
2	NaCl	Liquid	OMB	224 (206, 253)	2100 (1335, 2741)
3		Liquid	OMB	<747	<747
6		Solid	-	1439 (764, 1715)	2956 (1302, 4115)
10		Solid	P	1306 (867, 1417)	1990 (1694, 2194)
13	$CaCl_2$	Liquid	-	1295 (803, 9814)	18993 (9707, 27314)
17		Liquid	OMB	928 (242, 1111)	1489 (1148, 4123)
20		Liquid	C, A	23.9 (6.5, 49.4)	50.5 (17.1, 67.5)
21		Liquid	OMB	569 (374, 889)	1146 (910, 1447)
26	$MgCl_2$	Liquid	-	1031 (0, 3371)	3365 (370, 5424)
29		Liquid	OMB, TEA	623 (0, 964)	1206 (907, 1424)
32		Liquid	OMB	941 (69, 1158)	1593 (1115, 2812)
37	Blended Chloride	Solid	OMB, P	1184 (697, 1493)	1892 (1557, 2075)
40	CMA	Liquid	-	1001 (57.8, 2273)	3443 (1666, 5346)
41	CMAK	Liquid	-	1326 (0, 1920)	2480 (1884, 2865)
42	KA	Liquid	-	2373 (1640, 2660)	3535 (3128, 3789)

[1] OB – Organic Matter from Biomass, P – Phosphate, TEA – triethanolamine, C – polyhydroxycarboxylate, A – polyalkoxylated amine

[2] IC25 = concentration which would cause a 25% inhibition in reproduction or growth

[3] IC50 = concentration which would cause a 50% inhibition in reproduction or growth

‘ - ’ indicates not present

the toxicity data, be unlikely to harm the representative organisms used in these tests.

Figure 9-1 makes clear that a dilution to 500:1 would be insufficient to prevent nonlethal chronic effects of most snow and ice control materials on the most sensitive organisms (i.e., *Selenastrum* and *Ceriodaphnia*), although other organisms might not be affected at these concentrations (i.e., fathead minnow). Dilution at the margin of a roadway varies, but 500:1 would be close to the amount of dilution for many applications.

Figure 9-2 shows that these lethal effects under acute exposures at a dilution of 500:1 would affect sensitive organisms for a number of snow and ice control materials but not for others. Acute exposure might be the most meaningful guide for field applications, given that transport of materials with melt following application probably would not extend for a long period. The suitability of acute or chronic criteria would depend on the location and type of application.

Although it appears likely that the most sensitive organisms would be affected in some way at dilutions that could be expected at the margin of a roadway for many snow and ice control materials, it is also true that dilutions greater than 500:1 can be expected within a relatively short distance beyond the roadway. Therefore, the toxicity data suggest that there could be an impact zone relatively close to the roadway, bounded by dilutions that offset acute or chronic toxicities close to the roadway. Dilution rates characteristic for a specific site could be determined easily from dominant marker substances in a given type of material (e.g., chloride).

Table 9-4. *Ceriodaphnia dubia* toxicity testing endpoints (mg/L) (95% confidence limits).

Lab ID	**Base Chemical**	**Matrix**	**Additive**[1]	**Endpoint Concentration (mg/L)**		
				3-brood LC50[2]	**3-brood IC25**[3] **(Reproduction)**	**3-brood IC50**[4] **(Reproduction)**
2	NaCl	Liquid	OMB	3889 (3461, 4330)	564 (464, 809)	1659 (1325, 2098)
3		Liquid	OMB	180 (160. 253)	107 (90.6, 132)	159 (130, 215)
6		Solid	-	2349 (2187, 2555)	659 (371, 1153)	1598 (738, 2204)
10		Solid	P	2353 (2130, 3118)	1082 (829, 1227)	1561 (1356, 1777)
13	$CaCl_2$	Liquid	-	2937 (1872, 3740)	<570	1885 (1535, 2196)
17		Liquid	OMB	997 (724, 1300)	246 (184, 295)	367 (327, 400)
20		Liquid	C, A	380 (252, 440)	76.0 (55.6, 118.6)	170 (132, 232)
21		Liquid	OMB	2040 (1248, 3326)	258 (171, 362)	900 (754, 1022)
26	$MgCl_2$	Liquid	-	3202 (3013, 4234)	272 (175, 439)	1250 (526, 1885)
29		Liquid	OMB, TEA	1983 (1525, 2529)	697 (374, 862)	1306 (1076, 1546)
32		Liquid	OMB	3358 (3149, 4025)	442 (321, 555)	1804, 1283, 2131)
37	Blended Chloride	Solid	OMB, P	372 (118, 754)	<118	<118
40	CMA	Liquid	-	6311 (414, 8651)	305 (73.8, 723)	1030 (660, 1236)
41	CMAK	Liquid	-	4961 (N/A)	435 (285, 597)	1033 (718, 1614)
42	KA	Liquid	-	1994 (N/A)	<25	<25

[1] OMB – Organic Matter from Biomass, P – Phosphate, TEA – triethanolamine, C – polyhydroxycarboxylate, A – polyalkoxylated amine

[2] LC50 = concentration at which 50% of the population exposed would survive

[3] IC25 = concentration which would cause a 25% inhibition in reproduction or growth

[4] IC50 = concentration which would cause a 50% inhibition in reproduction or growth

‘ - ’ indicates not present

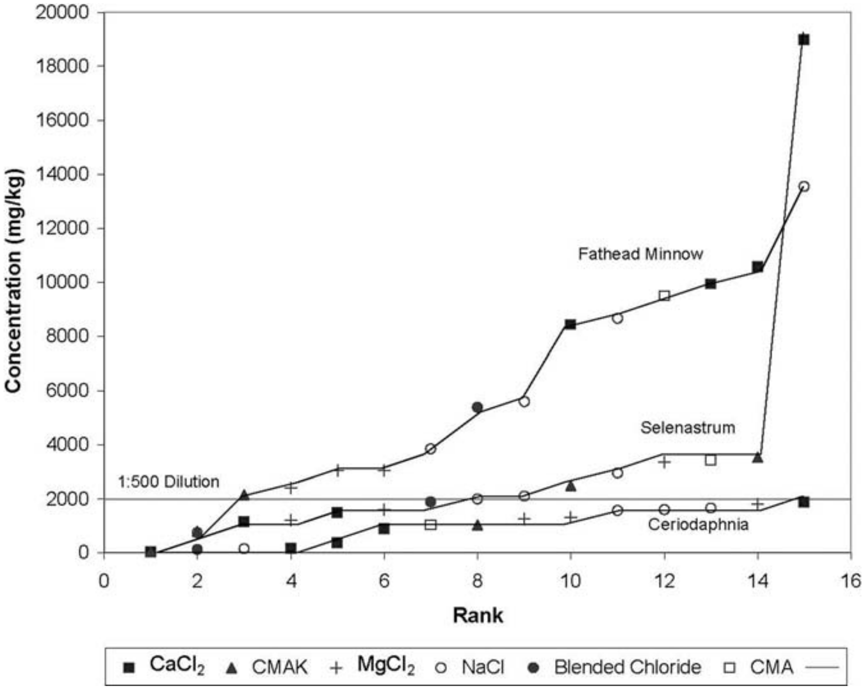


Figure 9-1. Sub-lethal (chronic) aquatic toxicity.

Summary of the chronic sub-lethal bioassay data on fathead minnow, *Selenastrum*, and *Ceriodaphnia*. For each species, each source is assigned a rank and the threshold concentrations corresponding to the ranks are shown in the graph. The data used in this graph are for chronic toxicity involving growth or reproduction (not mortality). The solid line near the bottom of the graph shows the concentration corresponding to a 500:1 dilution of a snow and ice control chemical. Points falling well above the line are unlikely to present any danger of toxicity for the combinations of species and snow and ice control materials in this test.

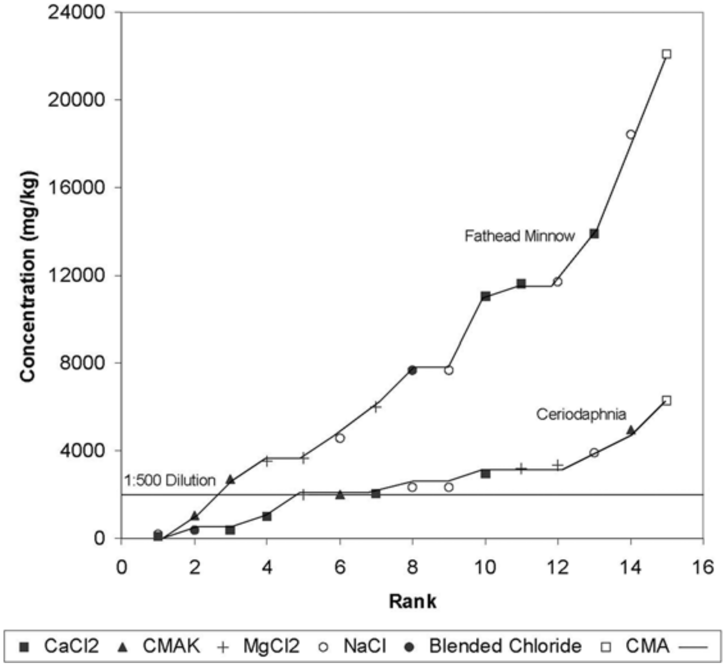


Figure 9-2. Lethal (acute) aquatic toxicity.

Summary of the acute lethal bioassay data on fathead minnow, and *Ceriodaphnia* (no data available for *Selenastrum*). For each species, each source is assigned a rank and the threshold concentrations corresponding to the ranks are shown in the graph. The data used in this graph are for acute toxicity involving mortality thresholds. The solid line near the bottom of the graph shows the concentration corresponding to a 500:1 dilution of a snow and ice control chemical. Points falling well above the line are unlikely to present any danger of toxicity for the combinations of species and snow and ice control materials in this test.

CHAPTER 10

Effects of Snow and Ice Control Materials on Reinforcing Steel Corrosion

10.1 Introduction

In addition to environmental impacts, snow and ice control materials can be detrimental to the durability of concrete structures (e.g., bridges, concrete pavements, and parking garages). The effects of these materials on concrete can be twofold—either by attacking the concrete itself or by penetrating the concrete cover and corroding the reinforcing steel. Deterioration of the concrete was not included in the scope of this project because a study by the South Dakota DOT is in progress (Project SD2002-01). That study focuses on the effects of magnesium chloride and other concentrated salt solutions on pavement and structural Portland cement concrete. Considering that the South Dakota study is not addressing reinforcing steel corrosion, a laboratory testing program was included in this project.

Corrosion effects related to snow and ice control materials are a recognized and costly consequence of use. A U.S. FHWA report conducted in 1999 on "Corrosion Costs and Prevention Strategies in the United States" estimated annual dollar effect of corrosion on steel highway bridge components to be $2 billion for maintenance and the cost of capital for bridge substructures and superstructures, and approximately $500 million for maintenance painting on steel bridges.

Sodium chloride has been used for roadway snow and ice control for more than 50 years. In recent years, alternative products such as magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$), calcium magnesium acetate (CMA), and potassium acetate (KA) have gained popularity. Manufacturers also blend snow and ice control materials with various materials intended to inhibit corrosion, including phosphates, amines, and agriculturally derived organic matter from biomass (OMB).

The objective was to determine the rate at which snow and ice control materials penetrate the concrete cover and initiate active corrosion of the reinforcing steel as well as to determine corrosion rates once corrosion has been initiated. The analytical program involved the relative evaluation of corrosion rates of concrete reinforcing steel under exposure to 15 common snow and ice control materials, including those with corrosion inhibitors. The methodology was based on ASTM G 109 ponding tests, modified to represent field-applied material concentrations. In addition, chloride ion diffusion properties were tested for chloride-based snow and ice control materials using ASTM C 1556. Testing was initiated in June of 2004 and results to June of 2006 are discussed.

10.2 Background

Snow and ice control materials are known to affect concrete structures—either through corrosion of reinforcing steel or deterioration of the concrete paste. Corrosion of reinforcing steel has typically been the primary deterioration mechanism and has been linked to use of chloride-based snow and ice control materials (e.g., NaCl, $CaCl_2$, and $MgCl_2$). NaCl has been used for more than 50 years and associated long-term effects to reinforced concrete are fairly well understood. Although there has been extensive research into the use of alternative materials (e.g., $MgCl_2$ and $CaCl_2$), there is limited data about their long-term effects.

Concrete is a composite material consisting of stone and sand held together in a matrix of hydrated cement paste. The two major components of the hydrated cement paste are calcium-silicate-hydrate (C-S-H) and calcium hydroxide ($Ca(OH)_2$). The C-S-H phase provides the bond strength of concrete. The $Ca(OH)_2$ buffers the pH of the pore solution to about 12.5. At this pH, reinforcing steel embedded in concrete is protected against corrosion by a "passive" layer (i.e., chemical coating) that forms on its surface. Degradation of the passive layer initiates active corrosion and can be caused by the presence of chloride ions. The typical threshold value (i.e., concentration) for chloride in concrete to initiate corrosion of black steel is 0.4 percent by weight of cement, but values as low as 0.15 percent may be considered dangerous.

The threshold value also depends somewhat on the pH of the concrete pore solution at the reinforcing steel level. Both $MgCl_2$ and $CaCl_2$ cause a drop in pH—not typically observed to the same extent with NaCl. This suggests that the chloride threshold for NaCl may be somewhat higher than for $MgCl_2$ and $CaCl_2$. However, this argument requires that the cation diffuses through the concrete at a rate similar to that of chloride. If the diffusion rate of the cation is lower than for chloride, the pH effects will not necessarily influence the corrosion initiation threshold value.

Considering that chloride-induced corrosion is independent of the associated cation, there is no reason to consider any relative differences in corrosivity between various chloride salts (i.e., the steel does not differentiate between the source of chloride). However, the amount of chlorides that will penetrate the concrete and their rate of penetration do affect corrosion, and evidence suggests this may be related to the associated salt cation.

Chloride is a relatively small, negatively charged anion that can diffuse through concrete as a result of concentration gradients. Concrete quality, pore structure, and micro-cracks will influence diffusion rates. Evidence also suggests that chloride ion diffusion depends on the type of salt used.

10.3 Laboratory Program

The objective was to assess relative effects of various snow and ice control materials on concrete reinforcing steel, including those with corrosion inhibitor additives, for their potential to initiate corrosion in concrete reinforcing. It was beyond the scope of the work to develop completely new test methods; therefore, two existing standard test methods were used:

- Macrocell corrosion/ponding testing to assess time to corrosion was conducted in accordance with ASTM G 109-99a (2005) *Standard Test Method for Determining the Effects of Chemical Admixtures on the Corrosion of Embedded Steel Reinforcement in Concrete Exposed to Chloride Environment*.
- Chloride-ion diffusion testing was conducted in accordance with ASTM C 1556-04, *Standard Test Method for Determining the Apparent Chloride Diffusion Coefficient of Cementitious Mixtures by Bulk Diffusion.*

10.3.1 Concrete Properties

Many previous laboratory studies used mortar or cement paste samples instead of concrete, thus not representing the actual material used in structures. Review of the literature has shown that observations in the field and laboratory were significantly different with more severe deterioration being observed in laboratory studies. Therefore, it was decided to use concrete representative of actual structures. A standard concrete (not mortar) mix design was used to evaluate the relative performance of snow and ice control materials. As an initial effort in this regard, the AASHTO specification for such concrete was used. Given the variability in the type, use, and availability of supplementary cementing materials (e.g., fly ash, slag, and silica fume), it was decided to omit these materials from the concrete mixture.

Table 10-1. Concrete mixture proportions.

Cement content (Type I)	405 kg/m^3
w/c	0.37
Plastic air content	6.4 %
Slump	140 mm
Compressive Strength	43.2 MPa @28 days 48.3 MPa @ 56 days 50.2 MPa @ 90 days
Rapid Chloride Ion Permeability (ASTM C1202)	3116 Coulombs (moderate) @ 28 days 2611 Coulombs (moderate) @ 90 days

Properties of the concrete used in this study are presented in Table 10-1. All samples were cured for 28 days in a standard moist curing room at 100-percent relative humidity. Hardened concrete samples were analyzed in accordance with ASTM C 114 for acid-soluble chloride ion content to determine total chloride ion background. Total chloride ion content in the concrete was determined at 0.004 percent by mass of concrete.

10.3.2 Snow and Ice Control Materials

The snow and ice control materials used for assessment were selected based on currently available common materials. Although the overall project has a broader selection of snow and ice control materials, 15 products were selected that represent the current U.S. and Canadian market in terms of product type (i.e., e.g., NaCl, $MgCl_2$, $CaCl_2$, CMA, and KA), and common additive combinations were selected for this assessment (Table 10-2). The same materials were also used to study atmospheric corrosion effects (Chapter 5). Primarily chloride-based materials were selected because these are most commonly used for snow and ice control on public roads, primarily because of cost. Also, chloride-based materials, when compared with other materials, are more likely to cause corrosion of the reinforcing steel.

The benefit of conducting a large-scale analytical assessment on a wide range of snow and ice control materials using the same test methods was that a direct comparison for trends

Table 10-2. Snow and ice control material description.

Lab ID	Base Chemical[1]	Matrix	Approximate Salt Concentration %	Additive[2]
2	NaCl	Liquid	23	OMB
3	NaCl	Liquid	23	OMB
6	NaCl	Solid	23	-
10	NaCl	Solid	23	P
13	CaCl2	Liquid	32	-
17	CaCl2	Liquid	32	OMB
20	CaCl2	Liquid	32	C, A
21	CaCl2	Liquid	32	OMB
26	MgCl2	Liquid	29	-
29	MgCl2	Liquid	29	OMB, TEA
32	MgCl2	Liquid	29	OMB
37	Blended Chloride	Solid	30	OMB, P
40	CMA	Liquid	25	-
41	CMAK	Liquid	37.5	-
42	KA	Liquid	50	-

[1] NaCl - Sodium Chloride, CaCl2 - Calcium Chloride, MgCl2 - Magnesium Chloride, CMA - Calcium Magnesium Acetate, KA - Potassium Acetate, Blended Chloride - mixture of NaCl, MgCl2, and CaCl2.

[2] OMB – Organic Matter from Biomass, P – phosphate, TEA – triethanolamine, C – polyhydroxycarboxylate, A –polyalkoxylated amine

‘ - ’ indicates not present

could be made. Commercial products continue to evolve, especially with respect to additives, and variability can exist between product batches.

Liquid materials were tested as received. Solid materials were dissolved in deionized water at room temperature at concentrations approximately equivalent to common liquid counterparts. These concentrations are typical for use in roadway applications. This approach was conservative and provided an unbiased representation of field exposure.

10.3.3 ASTM G 109 Exposure

The ASTM G 109 ponding test was selected to provide a relative assessment of the potential of various snow and ice control materials to initiate corrosion by means of diffusion of chlorides or other ionic species through the concrete. Once active corrosion was initiated, the macrocell corrosion current (i.e., corrosion rate) could be measured between the anode and cathode bars of the specimens. The effects of the snow and ice control materials on the cement and concrete properties could also be assessed. However, the samples were not subject to freezing and thawing cycles and, as such, the combined effects of freezing and thawing and snow and ice control materials could not be assessed.

Concrete test specimens were prepared in accordance with ASTM G 109 with a clear concrete cover to the top bar (anode) of 25 mm. Figure 10-1 is a schematic illustration and photograph of the specimens. In addition, for each material an additional sample without reinforcing bars was cast to determine chloride penetration at the end of the exposure experiment. Triplicate samples were prepared for all 15 snow and ice control materials, which included three distilled water control samples, resulting in 48 specimens. Figure 10-2 shows the setup of all samples.

Samples were ponded with snow and ice control materials for 2 weeks followed by 2 weeks of drying per ASTM specifications. Macrocell currents were measured every 2 weeks when the samples were filled and drained, and half-cell potential values (ASTM C 876) were measured monthly when draining the samples. Half-cell potentials provided information about the probability of corrosion as shown in Table 10-3 and generally provided an indication when corrosion was initiated. The main deviation from the specified ASTM procedure was the solution concentration. Although ASTM G 109 specifies a 3-percent NaCl solution, much higher concentrations were used to represent actual field conditions. The 3-percent NaCl concentration is typically used to assess the performance of different types of concretes whereas the objective of this study was to assess different types of solutions with identical concrete specimens. Macrocell currents were calculated by measuring the potential between the bottom two bars (cathode) and the top bar (anode) across a 100-ohm resistor and using Ohm’s law:

$$I = E/R$$

Where

R = resistance in ohms (100-ohm resistor installed)

E = potential in volts

I = current in amperes

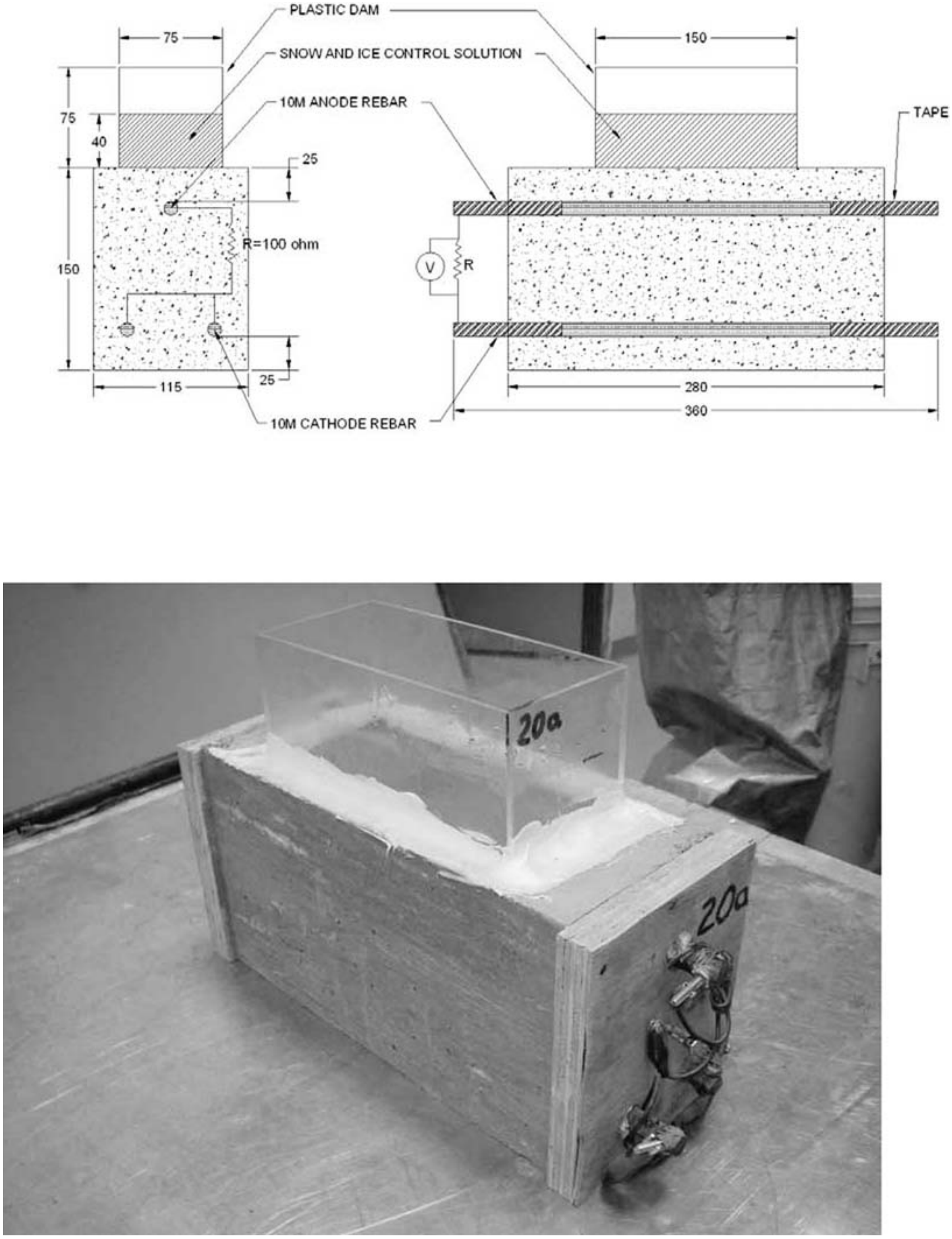


Figure 10-1. ASTM G 109 specimen illustration.

Figure 10-2. ASTM G 109 specimen setup.

Table 10-3. Probability of corrosion (ASTM C 876).

E_{corr} vs. (mV_{CSE}*)	Probability of Corrosion
More positive than -200 mV	10%
-200 to -350 mV	Uncertain
More negative than -350 mV	90%

*CSE – Copper/copper-sulfate reference electrode

Samples were cast in April of 2004 and exposure of the G109 samples to snow and ice control material solutions started in June of 2004.

10.3.4 Chloride Diffusion—ASTM C 1556

In addition to ponding samples, the ASTM C 1556 method was selected to assess the relative diffusion rate of several chloride-based snow and ice control materials. Most research has assessed diffusion coefficients of various concrete types and has assumed that diffusion rates depend primarily on concrete properties and have generally not considered the possibility that diffusion may be affected by the associated salt cation. Concrete cylinders were used for diffusion testing in accordance with ASTM C 1556 to obtain a relative assessment of chloride diffusion properties of different chloride-based snow and ice control materials. Duplicate samples were prepared with $MgCl_2$ (~29 percent), $CaCl_2$ (~32 percent), and NaCl (~23 percent) products only, because the primary objective was to determine chloride ion diffusion through the concrete. Continual concrete specimen exposure to the snow and ice control materials began in September of 2004 and one set of each duplicate sample was tested for chloride penetration in May of 2006. The second set will be left for future testing to assess further chloride penetration. Concrete powder samples were collected at 1- to 3-mm increments using a 25-mm diamond core bit and a milling machine. Samples were removed by drilling without any cooling liquids.

10.4 Results and Discussion

After 2 years of ponding, corrosion has not been initiated for any of the snow and ice control materials—ions have not yet diffused through 25 mm of concrete cover causing active corrosion of the top reinforcing bar. Thus, it is not possible to comment on the relative differences in chloride ion diffusion and corrosion activity of the various chloride-based materials based on the ASTM G 109 ponding samples. Similarly, non-chloride materials have not corroded the reinforcing steel.

Figure 10-3 shows half-cell potential values for one sample each of all 15 materials for approximately 2 years of exposure. Potential values for replicate samples for each material were essentially identical, with differences in potentials being typically less than 10 mV_{CSE}. Half-cell potential values are in the passive (less than 10-percent probability) and transitional ranges for all materials when compared with ASTM C 876 specifications shown in Table 10-3. Initial negative values for some materials are most likely associated with the passivation of the reinforcing steel. Over time, these values have stabilized in the passive and transitional ranges, indicating that active corrosion has not been initiated.

For clarification, Figure 10-4 shows half-cell potentials for one sample of each type of snow and ice control material, as well as one control sample (water exposure). Half-cell potentials are comparable for all snow and ice control materials with no significant difference in values.

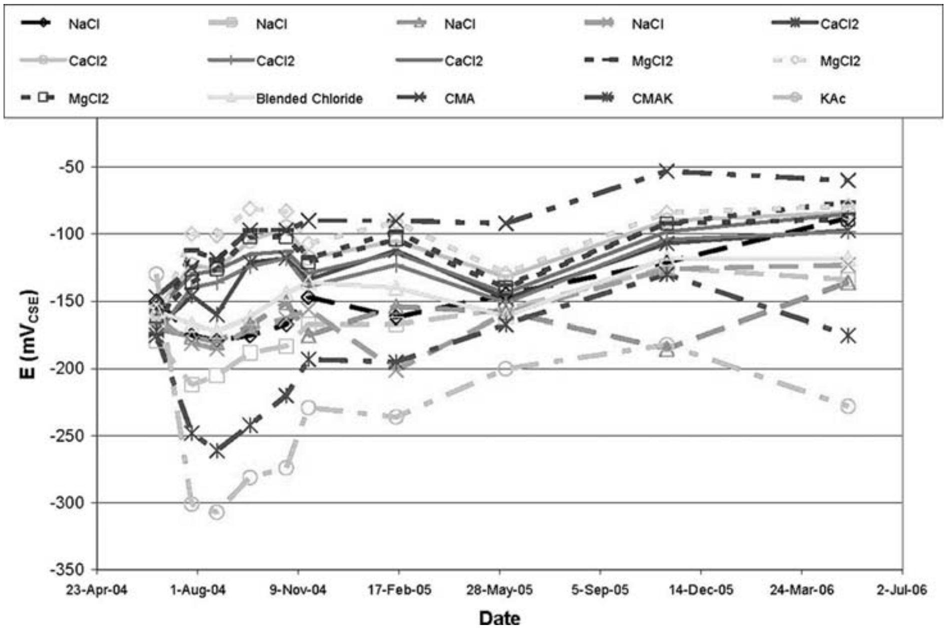


Figure 10-3. Half-cell potential values.

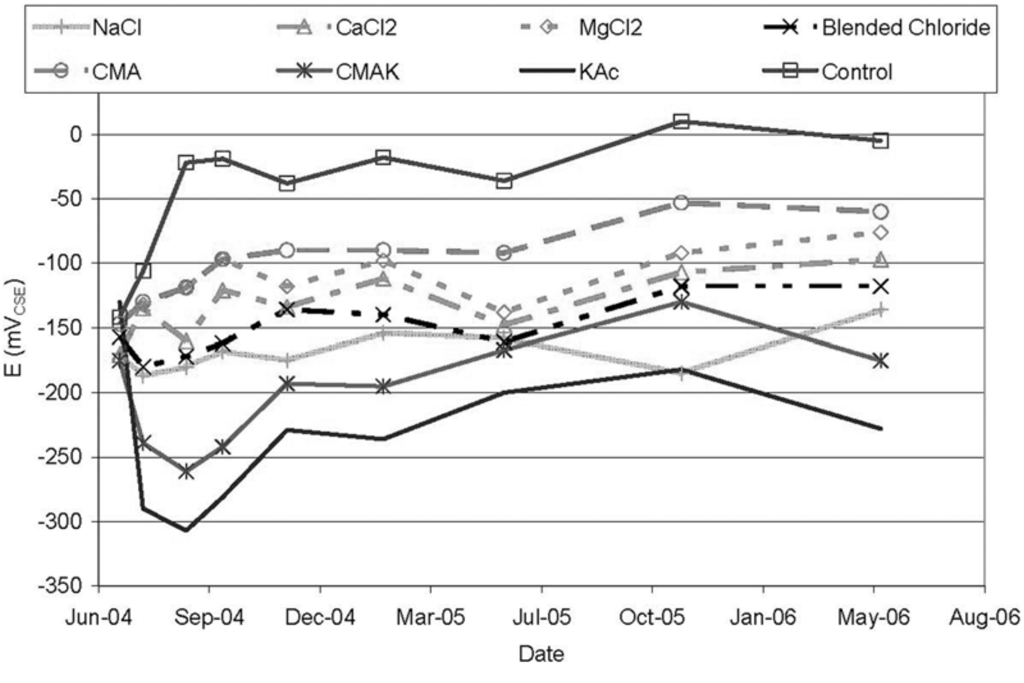


Figure 10-4. Half-cell potential values after 2 years' exposure (ASTM G 109 specimens).

Potentials across the 100-ohm resistor remained at 0 V throughout the 2-year exposure period, thus no macrocell currents were recorded. This suggests that chlorides have not yet reached the top steel and corrosion has not been initiated.

Over time, the half-cell potentials for these materials have stabilized. Visual observation of the samples did not identify any deterioration of the concrete at the exposed surface.

Chloride penetration for the ASTM C 1556 samples was measured to a depth of 18 mm by drilling concrete powder samples. Acid-soluble chloride concentrations were very high at the exposed concrete surface. The highest chloride concentration at 18 mm depth of 1.02 percent by mass of cement was measured for the $CaCl_2$ sample and the lowest concentration at the same depth was measured for the $MgCl_2$ sample (Figure 10-5). Generally, at 18-mm depth, the acid-soluble chloride concentrations are above the threshold concentration to initiate corrosion. There appears to be some evidence of inconsistent results with some higher concentrations at 18 mm than at smaller depths. This is most likely a result of large aggregate particles in the specimens.

Results shown in Figure 10-5 suggest that chloride ion concentrations at a depth of 25 mm have not yet reached the corrosion initiation threshold. The duplicate samples will be tested at the same exposure age that corrosion initiation is observed. Initial results indicate that $CaCl_2$ and NaCl are migrating faster that $MgCl_2$ and blended chlorides. Although similar results were reported in other studies for $CaCl_2$, the slower penetration of $MgCl_2$ is contrary to previous studies.

10.5 Conclusions and Recommendations

After approximately 2 years of exposure to various chloride-based and non-chloride snow and ice control materials, active corrosion has not been initiated for ponding of ASTM G 109 samples using concrete with a clear cover over the top bar of 25 mm. ASTM C 1556 samples suggest that chlorides have migrated through the concrete to a depth beyond 18 mm; however, concentrations at a depth of 25 mm remain below the threshold to initiate active corrosion.

These results are generally supported by observations made for real structures where corrosion initiation normally takes several years. Corrosion-related damage in shorter periods is often attributed to cracking of the concrete cover. The relatively slow process of chloride migration through the concrete provides the service life for reinforced concrete structures. Generally, good-quality concrete and control of cracking is essential to slow penetration of chlorides. The intent of this study was to use a concrete mix design representative of concrete used in the field rather than laboratory conditions that would accelerate the testing process. As such, longer exposure times will be required to obtain results showing corrosion initiation and measure corrosion rates once initiated.

Chloride diffusion testing (ASTM C 1556) shows chloride penetration for NaCl, $CaCl_2$ and $MgCl_2$ to a depth of at least 18 mm, with $CaCl_2$ showing the highest chloride concentration at that depth. The lowest concentration was measured for the $MgCl_2$ sample, which is contrary to findings in the literature. Longer term exposure and comparison of the diffusion and ponding tests will provide more conclusive results.

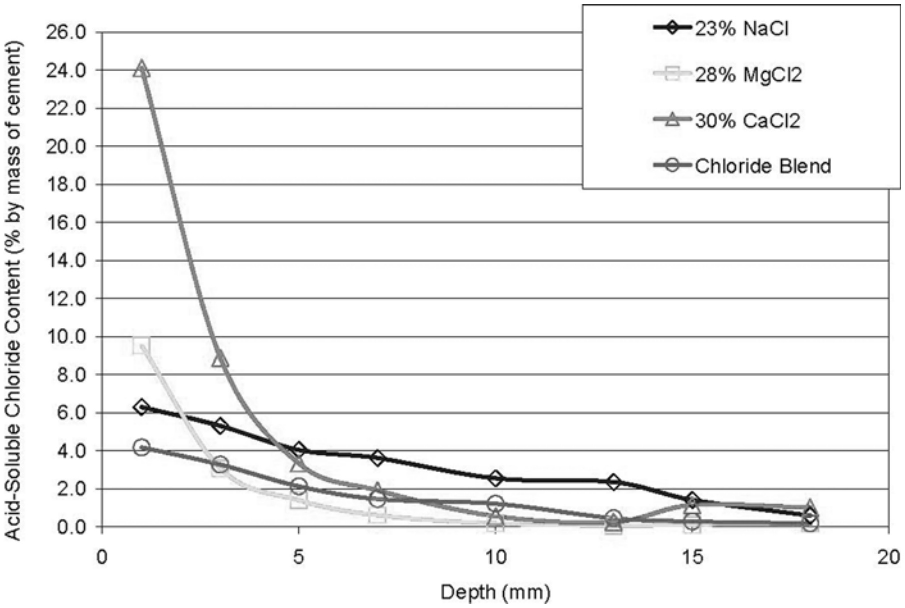


Figure 10-5. Chloride ion concentrations after 20 months of exposure.

It is recommended that the testing continue so as to determine time to initiation of active corrosion. Based on the diffusion experiments, it is anticipated that this may require at least one more year of exposure. Once initiated, corrosion rates should be monitored to determine the corrosivity of the different snow and ice control materials. Corrosion rate measurements should include macrocell corrosion rates between the top bar (anode) and the bottom bars (cathode) as well as microcell corrosion rates using the linear polarization resistance technique.

Autopsy of the samples after evidence of corrosion damage has become obvious (i.e., corrosion staining and cracking) is also recommended. It is anticipated that the overall experiment should continue for an additional 2 to 4 years.

CHAPTER 11

Atmospheric Corrosion Testing

11.1 Introduction

In conjunction with a larger study relating to the chemistry and toxicity of snow and ice control materials and corrosion of concrete from snow and ice control materials, electrochemical corrosion testing of 15 snow and ice control products of varied concentrations with five engineered alloys was completed. The objective of the study was to conduct relative assessments of snow and ice control materials corrosivity on various alloys on the basis of both dilution and chemical family type. Embedded in the general test scheme, it was anticipated that the effect of corrosion inhibitor additives could be assessed.

Corrosion, an inherently slow process, is often initiated after an incubation period, may be comparatively rapid after onset, and tends to slow over time. Various standard methods are available to assess atmospheric corrosion, including immersions tests, poultice corrosion tests, and salt-spray tests. Generally, the most accurate corrosion tests are weight-loss measurements used to estimate an average penetration rate, although they are very time-intensive (i.e., weeks, months, or years in duration).

The accuracy of weight loss measurements depends significantly on the summation of effects over time (essentially an integration). Corrosion penetration estimations based on weight loss can seriously underestimate the corrosion penetration caused by localized processes (e.g., pitting, cracking, and crevice corrosion). In addition, bias in corrosion test results may result from the following factors:

- Inappropriate exposure time to represent corrosion conditions accurately;
- Film formation whereby precipitates or complexes form on the test specimen that may inhibit corrosion;
- Inadequate corrosion product removal or excessive metal removal before final weighing of test specimens; and
- Depletion of corrodant.

Furthermore, the relevance of laboratory-based corrosion rate determinations is deeply rooted in the relationship of the test environment to the service environment and does not necessarily represent conditions that exist in the field environment.

Electrochemical techniques, such as Linear Polarization Resistance (LPR), can also be used to assess corrosion rates. Given that LPR is a mature, rapid, and sensitive corrosion rate measurement technique, LPR augmented by weight loss determinations was used for the study. The test program involved developing a rapid and reliable test protocol that was more robust than traditional electrochemical techniques. Of particular benefit was the potential suitability of LPR for evaluating the corrosiveness of inhibited snow and ice control materials and the effect of roadside dilution.

Fifteen snow and ice control material/inhibitor combinations were selected for the study and are described in Table 11-1. These materials represent common snow and ice control material chemical type and additive combinations being used in the United States and Canada for roadway snow and ice control. Testing of each snow and ice control material was conducted on five commonly available alloys representative of materials used in highway infrastructure and vehicles (Table 11-2).

To represent snow and ice control material concentrations expected in the field (i.e., application concentration through dilution), LPR assessments were conducted on liquid snow and ice control materials at 100-percent (v/v) (as received), 10-percent (v/v), and 1-percent (v/v) concentrations for each snow and ice control material with each alloy. Solid snow and ice control materials used in this test program were prepared into solutions at concentrations equivalent to common liquid counterparts (refer to Chapter 7).

Corrosion rate data was reviewed for test method robustness, and trends were assessed that related to alloy type, snow and ice control material type, test solution concentration, and the effectiveness of corrosion inhibitors. Conclusions were summarized and recommendations for further research have been made.

Table 11-1. Snow and ice control material description.

Lab ID	Chemical Type	Matrix	Additive[1]
2	NaCl	Liquid	OMB
3	NaCl	Liquid	OMB
6	NaCl	Solid	-
10	NaCl	Solid	P
13	$CaCl_2$	Liquid	-
17	$CaCl_2$	Liquid	OMB
20	$CaCl_2$	Liquid	C, A
21	$CaCl_2$	Liquid	OMB
26	$MgCl_2$	Liquid	-
29	$MgCl_2$	Liquid	OMB, TEA
32	$MgCl_2$	Liquid	OMB
37	Blended Chloride	Solid	OMB, P
40	CMA	Liquid	-
41	CMAK	Liquid	-
42	KAc	Liquid	-

[1] OMB = Organic Matter from Biomass, P = Phosphate, TEA = Triethanolomine,
C = Polyhydroxycarboxylate, A = Polyalkoxylated amine

‘ - ’ indicates not present

Table 11-2. Alloy description.

Alloy Type	Designation
Structural Steel	ASTM A 36
Wrought Aluminum Alloy	AA6061-T6
Cast Aluminum Alloy	AA356.2
Free Machining Brass	CDA 360
Magnesium Alloy	AZ91C-T6

11.2 Technology Overview

11.2.1 Electrochemistry

Metallic corrosion is the consequence of a redox reaction whereby oxidation of the anode liberates electrons and reduction at the cathode consumes electrons. Oxidation is always accompanied by reduction in an electrochemical cell. Electrical potential is the driving force for a redox reaction and is an effective measure of the thermodynamic (energetic) state of the system. Electron flow (i.e., current) is the result of a redox reaction and is an effective measure of the kinetics or rate of the corrosion reaction. Electrochemical potential measurements may be considered an indication of system equilibrium.

11.2.2 LPR

The essence of a potentiostatic test such as LPR is the alteration of a system electrical potential in some systematic manner and the measurement of current response. Corrosion current cannot be measured directly. The change in potential of an electrode (polarization) causes a redox reaction to occur. The measured corrosion current will be indicative of the rate (kinetics) of the reaction and may be readily related to current density and corrosion rate.

The ratio of a small potential shift of a corroding metal surface to the current required (ΔI) to maintain this potential displacement (ΔE) is called the polarization resistance and is inversely proportional to corrosion current (I_{corr}).

$$\frac{\Delta E}{\Delta I} \alpha \frac{I}{I_{corr}}$$

The potentiostat controls the potential between the working electrode and the reference electrode while it measures the current between the working electrode and the counter (auxiliary) electrode. Although the step interval for LPR testing may be varied, the method should be considered one of pseudo-instantaneous measurement.

11.2.3 Weight Loss

To supplement LPR, measurements of electrode mass were made before and after each test. In the absence of localized corrosion, weight loss may be used as a principal measure of uniform corrosion. In this study, estimates of average penetration by weight loss were completed as a quality control for comparison with the LPR data.

Instances whereby negative corrosion rates are suggested by the weight loss data may be indicative of corrosion product retention on the specimens or errors in weighing. Alternately, the formation of durable complexes (not corrosion products) may occur on the electrode surface which, when not removed by cleaning, cause the electrodes to gain weight.

11.3 Test Method

Corrosion rate determinations were made during the period of August 2004 to April 2005. The general measurement process involved immersing test electrodes made from the various alloys into snow and ice control material solutions and taking LPR measurements over time. All LPR measurements were completed using a Metal Samples MS1500L handheld measurement and data collection device configured for Three-Electrode Linear Polarization. Additionally, electrode mass was recorded before and after each test.

The general test protocol is described in Appendix A, which is available for download from the TRB website. Of specific interest to the conduct of the testing was

- Configuration of the MS1500L to complete cathodic polarization (cathodic control is considered more likely to be linear than anodic control).
- The use of 15-minute LPR test cycle times for all diluted (1- and 10-percent) solution measurements and 3-minute LPR test cycle times for all testing of concentrated solu-

tions. Systems exhibiting passive behavior and lower corrosion rates mandate longer cycle times.

- Testing of coupons in 1- and 10-percent concentration solutions at intervals of 3, 6, 24, 48, and 72 hours (five readings) following immersion; coupons immersed in 100-percent solutions were tested at 1, 3, 6, and 24 hours (four readings) following immersion.
- Surveillance of electrodes for pitting corrosion (corrosion current measurement is surface-area-dependent; pitting renders surface area unreliable).
- The MS1500L uses different working electrode surface areas for different alloys. Surface area is varied in proportion to the ratio of equivalent weight of the corroding metal to corroding metal density rather than input of the constant K (related to Tafel slope).
- Surface preparation by ultrasonic cleaning followed by abrasion.

Uniformity of the sample preparation and data collection were considered paramount to develop a basis of comparison in the data sets. The data collected are described in the "Corrosion Test Work Sheet and Summary" (refer to Appendix B, which is available for download from the TRB website).

11.4 Test Program Evaluation

Before evaluating data for specific trends (related to alloy type, snow and ice control materials type, snow and ice control materials concentration, and corrosion inhibitor performance), the overall robustness of the test program was evaluated. This involved various statistical assessments of the data and comparison of LPR corrosion rate data with corrosion rate data obtained through supplementary weight loss measurements on the test electrodes. The data set is presented in Appendixes C and D, which are available for download from the TRB website.

Replicate LPR measurements were made over time for each snow and ice control material/concentration/alloy system. A minimum of four LPR readings (concentrated snow and ice control materials at 1, 3, 6, and 24 hours) or five LPR readings (diluted snow and ice control materials at 3, 6, 24, 48, and 72 hours) were conducted. Comparison of corrosion potential measurements at the outset and finish of the test generally showed minimal changes in most instances, suggesting that the measured corrosion rate of the alloy/snow and ice control material systems tested was relatively constant over the duration of the test (24 or 72 hours).

There are various possible methods for assessing replicate corrosion rate data. The practice of characterizing corrosion rates using average values was applied to the replicate data and is consistent with ASTM G 16, *Standard Guide for Applying Statistics to Analysis of Corrosion Data*. In corrosion testing, average corrosion rates are frequently used in characterizing corrosion rates, particularly where replicate measurements are as likely to overestimate the experimental rate as to underestimate it. For data that span several orders of magnitude, the median is less sensitive to extreme values and provides a stable statistic that reflects the center of the distribution. When considered together, the mean and median provide an indication of the influence of extreme values in a data set. If the two measures of central tendency are close to one another, extreme values in the data set are not considered influential. Such comparison was considered for analysis of data samples from the population linked by alloy type and snow and ice control materials concentration.

Relative standard deviation (RSD) values were calculated for the replicate values for each alloy-snow and ice control materials-concentration system (Appendix C, which is available for download from the TRB website). Average RSD values for each alloy-concentration system are shown in Table 11-3. RSD values indicate the relative precision (i.e., measurement variability) that exists for the replicate measurements made. Overall, the discrete corrosion rate values obtained for replicate measurements were within about one standard deviation (100-percent RSD) of the average value. RSD values of 15 percent are considered excellent, and RSD values of 50 percent are considered good. Extremely high RSD values were typically associated with low corrosion rate values as test method uncertainty increases at the lower limits of the corrosion test.

Table 11-4 summarizes statistical values calculated for each alloy tested. Average, minimum, and maximum corrosion rate values indicate the range of values obtained for each alloy/concentration system. Median values and average corrosion rates integrated over time were also calculated and are generally consistent with average corrosion rate values. Plots of cumulative probability versus corrosion rate (measured using a logarithmic scale) and linear probability versus corrosion rate (measured using a linear scale) were prepared to graphically characterize the pooled corrosion data as to symmetry.

Table 11-3. Average relative standard deviations for each alloy and solution concentration system.

Alloy	Average (%) (minimum (%), maximum(%)) RSD Values for each Test Solution Concentration		
	100% Solution	**10% Solution**	**1% Solution**
Structural Steel, ASTM A 36	64% (0, 200)	68% (17, 137)	60% (8, 196)
Wrought Aluminum Alloy, AA6061-T6	17% (3, 86)	26% (3, 70)	108% (68, 163)
Cast Aluminum Alloy, AA356.2	28% (2, 119)	34% (3, 108)	110% (51, 170)
Free Machining Brass, CDA 360	62% (2, 115)	50% (11, 134)	100% (10, 258)
Magnesium Alloy, AZ91C-T6	54% (15, 104)	50% (17, 83)	55% (9, 91)

Table 11-4. Univariate descriptive statistics corrosion rate by alloy and snow and ice control material concentration.

Alloy	SICM Concentration	Corrosion Rate – MPY							Solution ID	Distribution Characteristic
		Max.	Min.	Population Mean	Population Median	Average of Rate by Area Under Curve	Population Standard Deviation	Aberrant Value*		
AA6061-T6	1%	0.87	0.01	0.215	0.110	0.158	0.276	-		Likely log normal
	10%	52.23	0.05*	29.74	34.40	29.30	15.49	0.05	40	Appears normal
	100%	94.88	2.27	59.57	66.23	57.19	25.06	2.27 82.2	13 10	Likely normal
AA356.2	1%	7.27*	0.01	0.663	0.06	0.27	1.850	7.27	20	Likely log normal
	10%	79.07	0.05*	28.08	26.09	26.65	23.00	0.05	40	Likely normal
	100%	80.41	0.00	46.64	52.30	47.36	30.93			Likely normal
A36	1%	16.96*	0.02*	3.20	2.21	2.17	4.02	0.02 0.03 16.96	41 42 29	Inconclusive
	10%	7.38	0.02	2.49	2.38	2.14	2.00	-		Likely normal
	100%	9.06	0.06	2.32	1.58	2.25	2.79	0.06 0.06	40 41	Likely log normal
CDA 360	10%	13.82	0.09	3.23	1.41	2.94	4.19	-		Likely log normal
	10%	97.54	0.13	28.72	24.28	30.38	31.46	-		More likely normal
	100%	85.57	0.20	14.30	3.39	12.31	24.60	-		Likely log normal
AZ91C-T6	1%	19.54	0.67	5.28	3.10	4.62	5.34	-		Likely log normal
	10%	79.74	4.98	36.48	36.98	36.51	27.22	-	**	Likely log normal
	100%	124.38	5.39	57.39	57.17	78.13	38.74	-	***	Likely log normal

MPY is equivalent to 0.001 inch per year.
* Aberrant Value – anomalous or extreme data value
** Magnesium alloy exposure to 100% SICM 3, 17, 20, 21, 26, 29 and 32 exhibited corrosion rates exceeding 200 MPY
*** Magnesium alloy exposure to 10% SICM 3, 6 and 21 exhibited corrosion rates exceeding 200 MPY
“ - ” indicates no value observed
Note: Individual corrosion rates were derived from the average of four or five LPR measurements.

Quality control was conducted by comparing LPR corrosion rate determinations with corrosion rates determined by weight loss measurement on the test electrodes (refer to Table 11-5 and Appendix D, which is available for download from the TRB website). To determine equivalency between the two corrosion rate test methods, a two-tailed "t-test" was conducted at the 95-percent confidence interval (refer to ASTM G 16, Clause 7). Populations (i.e., all possible items possessing one or more common characteristics) are often too large to be studied adequately. This is particularly true when the population is conceptual as it is in an engineering experiment or when the collection of the data requires alteration of items such as corrosion of the electrodes. Despite the complexity of the test matrix, data was compiled into sample groupings based on alloy type and snow and ice control material solution concentration. This allowed reasonable groupings of adequate size to allow performance of the statistical test. Equivalency analysis indicated that

- In approximately 53 percent (8 of 15) of the cases examined, the corrosion rate determined by LPR was similar to the corrosion rate determined by weight loss.
- The strongest correlations between the two tests occurred where LPR corrosion rate values were low. This included measurements made for carbon steel and measurements made for 1-percent solution concentrations.
- There tended to be poor correlation between the two tests where LPR measurements were high. Weight loss measurements underestimated LPR measurements at 100-percent and 10-percent concentration levels, except for magnesium alloy at the 100-percent concentration level.

11.5 Data Assessment

Complete LPR corrosion rate data for each alloy type, snow and ice control materials type, and concentration level are tabulated in Appendix C, which is available for download from the TRB website, including replicate LPR measurements, maximum and minimum values, averages values, standard deviation values, and relative standard deviation values. Data summaries of average values are represented both graphically and in tabular form in Figures 11-1 through 11-5.

Trend analysis was conducted using average LPR corrosion rate values. The population is diverse and difficult to study adequately, but the testing did provide comparative analysis of a comprehensive matrix of snow and ice control materials. It was also important to consider measurement precision and variability as expressed by RSD when comparing LPR values. Overall, standard deviation values for replicate LPR measurements were of the same order of magnitude as average values. Therefore, trends in average LPR data had to exist at a resolution of at least an order of magnitude or greater to be considered significant.

Overall, mean corrosion rate increased with increasing snow and ice control material concentration for all alloys except for the brass (CDA 360) alloy where the intermediate (10-percent) snow and ice control materials concentration was most corrosive. Corrosion rates for carbon steel (A36) also did not

Table 11-5. Comparison of corrosion rate by LPR versus weight loss.

Alloy	Solution Concentration	LPR	Weight Loss	t-stat	Tc	Null Hypothesis	Remark
AA356.2	100	46.63	3.56	5.30	2.14	Accept	Significant differences exist
	10	29.71	1.69	4.23	2.16	Accept	Significant differences exist
	1	0.64	0.96	-0.27	2.14	Reject	Negligible difference
A36	100	2.18	2.30	-0.19	2.14	Reject	Negligible difference
	10	2.61	2.43	0.25	2.16	Reject	Negligible difference
	1	3.19	2.54	0.63	2.14	Reject	Negligible difference
AA6061-T6	100	59.58	4.29	8.27	2.14	Accept	Significant differences exist
	10	31.45	4.26	4.79	2.16	Accept	Significant differences exist
	1	0.21	0.29	-0.13	2.14	Reject	Negligible difference
CDA 360	100	14.28	0.60	2.13	2.14	Reject	Statistic indicates similarity
	10	30.76	0.63	3.54	2.16	Accept	Significant differences exist
	1	3.22	0.50	2.65	2.14	Accept	Significant differences exist
AZ91C-T6	100	57.39	91.47	-0.96	2.16	Reject	Negligible difference
	10	33.40	10.94	3.36	2.16	Accept	Differences exist
	1	5.29	1.30	1.46	2.14	Reject	Negligible difference

Null Hypothesis: A difference between LPR and weight loss exists; Alternative Hypothesis: No difference between LPR and weight loss; Alpha = 0.05; Two tailed test demonstrate overall increasing corrosion rates with increasing snow and ice control material concentration. In this instance, corrosion rates were lower than for the other alloys and any trends were likely obscured by measurement variability at these levels. The comparative arrangement of alloys which experienced the least to greatest corrosion rates were as follows:

• Carbon steel (A36)	Least corrosion
• Brass (CDA 360)	
• Cast aluminum (AA356.2)	
• Wrought aluminum (AA6061-T6)	
• Magnesium (AZ91C-T6)	Greatest corrosion

The following sections describe key observations and trends in the data for each metal alloy tested as they pertain to snow and ice control material type, concentration level, and additive ability to inhibit corrosion.

11.5.1 Structural Steel, A36

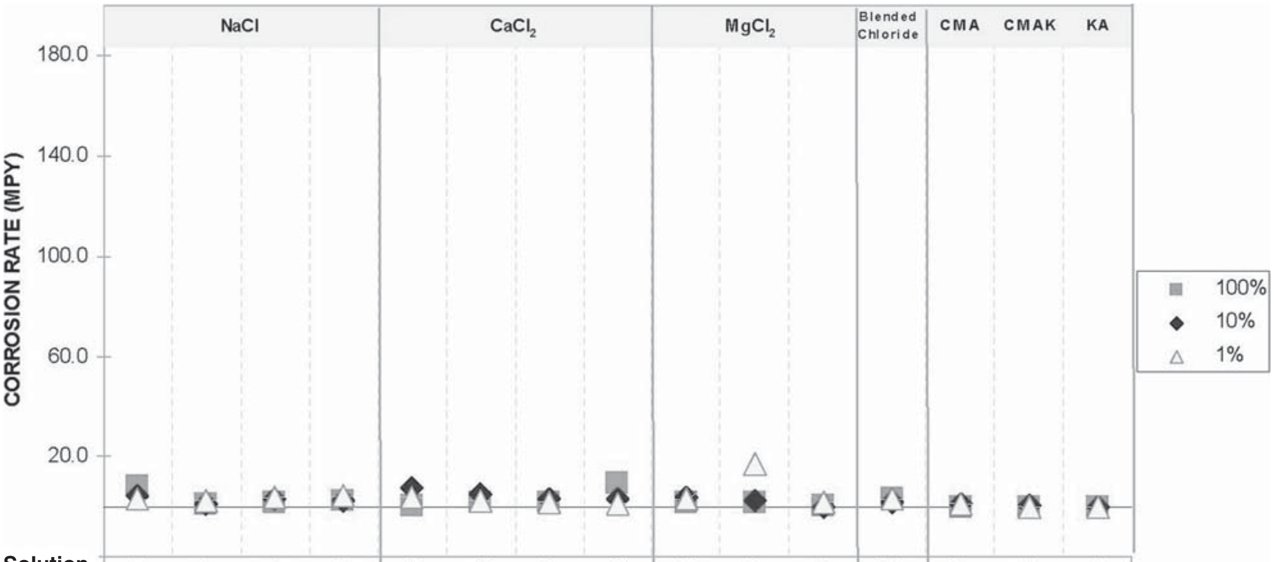
Refer to Figure 11-1 for data.

- Corrosion rates measured for structural steel (A36) were lower than for the other alloy materials tested. At lower corrosion rate levels, variability in measurement can be greater or equal to the test method resolution, making trend identification difficult.
- Chloride-based snow and ice control materials (2, 3, 6, 10, 13, 17, 20, 21, 26, 29, 32, and 37) had roughly equivalent average corrosion rates at each concentration level (100, 10, and 1 percent). This data suggests little differences in corrosivity of various chloride-based snow and ice control materials.
- Corrosion rates for acetate-based snow and ice control materials (40, 41, 42) were much lower than those for chloride-based snow and ice control materials. Observed values bordered on the minimum practical detection ability of test instrumentation.

11.5.2 Wrought Aluminum, AA6061-T6

Refer to Figure 11-2 for data.

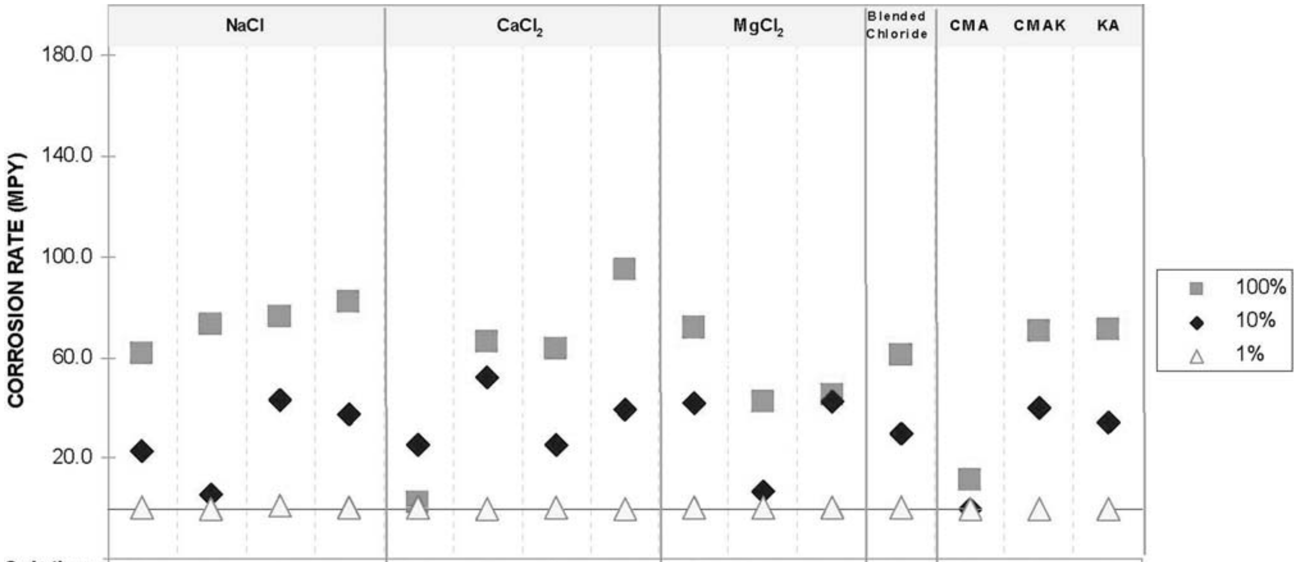
- With the exception of the uninhibited $CaCl_2$ solution (13), the chloride-based snow and ice control materials (2, 3, 6, 10, 17, 20, 21, 26, 29, 32, and 37) had roughly equivalent average corrosion rates at each concentration level (100, 10, and 1 percent). This suggests little difference in the



Solution	2	3	6	10	13	17	20	21	26	29	32	37	40	41	42
100%	8.3	1.2	1.6	2.1	0.5	1.6	1.6	9.1	1.6	1.6	0.6	2.7	0.1	0.1	0.0
10%	4.1	0.8	3.2	2.4	7.4	4.7	2.8	3.0	3.6	2.2	0.0	1.5	1.2	0.4	0.0
1%	3.3	2.2	3.6	4.3	3.8	2.1	1.7	1.2	2.7	17.0	1.8	3.1	1.1	0.0	0.0
Additive	OMB	OMB	---	P	---	OMB	C,A	OMB	---	OMB TEA	OMB	OMB,P	---	---	---

OMB=Organic matter from biomass TEA=Triethanolamine C=Poly Hydroxycarboxylate A=Polyalkoxylated Amine P=Phosphate
Circled symbol indicates average calculated on discrete measurements less than 200 MPY

Figure 11-1. Summary of average corrosion rates (MPY) for carbon steel A36.



	NaCl				$CaCl_2$				$MgCl_2$			Blended Chloride	CMA	CMAK	KA
Solution	2	3	6	10	13	17	20	21	26	29	32	37	40	41	42
100%	61.7	72.9	76.5	82.2	2.3	66.2	63.6	94.9	72.0	42.3	45.2	60.9	11.5	70.4	71.1
10%	22.6	5.8	43.2	37.5	25.2	52.2	25.1	39.0	41.9	6.7	42.7	29.7	0.0	40.1	34.4
1%	0.2	0.1	0.9	0.1	0.7	0.0	0.6	0.0	0.2	0.1	0.1	0.1	0.0	0.0	0.0
Additive	OMB	OMB	---	P	---	OMB	C,A	OMB	---	OM B TEA	OMB	OM B,P	---	---	---

OM B=Organic matter from biomass TEA=Triethanolamine C=Poly Hydroxycarboxylate A=Polyalkoxylated Amine P=Phosphate
Circled symbol indicates average calculated on discrete measurements less than 200 M PY

Figure 11-2. Summary of average corrosion rates (MPY) for wrought aluminum alloy AA6061-T6.

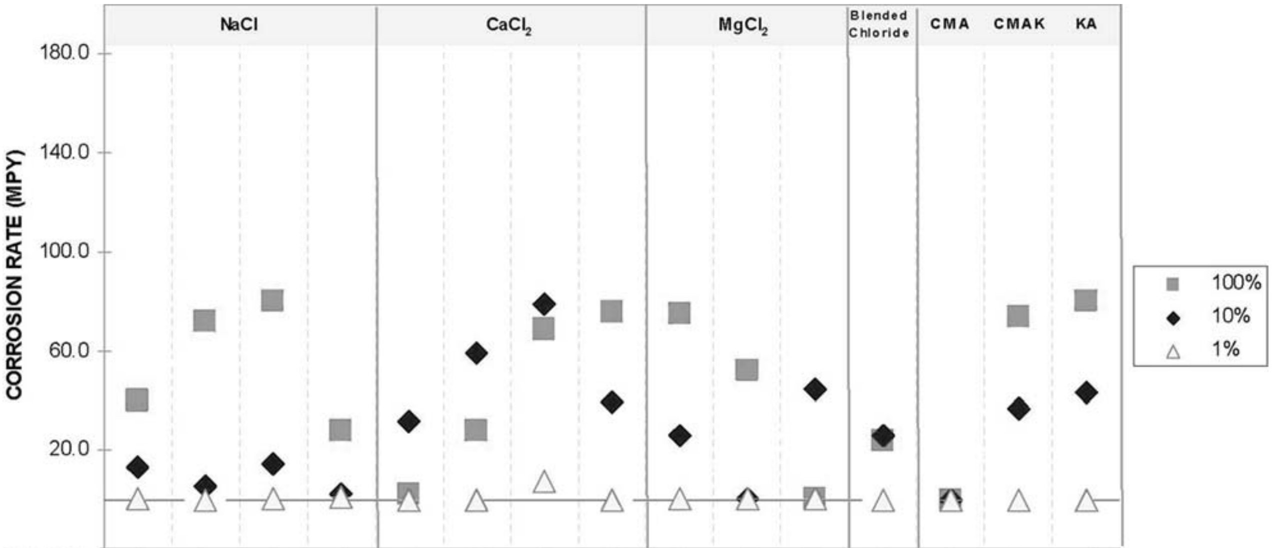
corrosivity of various chloride-based snow and ice control materials on wrought aluminum.

- Uninhibited $CaCl_2$ (13) had a comparatively low corrosion rate at the 100-percent concentration level when compared with inhibited $CaCl_2$ snow and ice control materials (17, 20, 21) and other chloride-based snow and ice control materials. However, corrosion rates were consistent between inhibited and uninhibited $CaCl_2$ snow and ice control materials at 10- and 1-percent concentration levels. Similar trends were observed for cast aluminum (AA356.2). A potential explanation may be that the 100-percent solution was sufficiently aggressive that a corrosion product barrier was formed on the measurement electrodes that prevented further corrosion and corrosion measurements.
- Acetate-based snow and ice control materials containing potassium (CMAK (41) and KA (42)) demonstrated corrosion rates similar to chloride-based snow and ice control materials at all concentration levels. Conversely, the CMA snow and ice control materials (40) had comparatively lower corrosion rates. A similar trend was also observed for cast aluminum (AA356.2) and is contrary to general opinion that all acetate products are equally non-corrosive to metals.

11.5.3 Cast Aluminum AA356.2

Refer to Figure 11-3 for data.

- NaCl-based snow and ice control materials with corrosion inhibitors (2, 3, 10) demonstrated corrosion rates similar to the NaCl snow and ice control materials without a corrosion inhibitor (6) at 100-, 10-, and 1-percent concentration levels. The NaCl snow and ice control materials containing a phosphate inhibitor (10) demonstrated the lowest corrosion rate at 100- and 10-percent concentration levels; however the magnitude of this difference borders on the precision limits of the test and thus cannot be conclusively attributed to corrosion performance or measurement variability.
- Uninhibited $CaCl_2$ (13) had a comparatively low corrosion rate at the 100-percent concentration level when compared with inhibited $CaCl_2$ snow and ice control materials (17, 20, 21) and other chloride-based snow and ice control materials. Corrosion rates were consistent between inhibited and uninhibited $CaCl_2$ snow and ice control materials at 10- and 1-percent concentration levels. Similar trends were observed for wrought aluminum (AA6061-T6). A potential explanation may be that the 100-percent solution was sufficiently aggressive that a corrosion product barrier was formed on



Solution	2	3	6	10	13	17	20	21	26	29	32	37	40	41	42
100%	40.2	71.9	80.3	27.7	2.1	27.6	68.9	75.4	75.0	52.3	0.2	23.9	0.0	73.6	80.4
10%	13.5	5.4	14.3	2.2	32.0	58.9	79.1	39.6	25.9	0.4	44.3	26.1	0.1	36.6	43.0
1%	0.4	0.1	0.3	0.9	0.0	0.0	7.3	0.0	0.2	0.2	0.2	0.0	0.0	0.0	0.0
Additive	OMB	OMB	---	P	---	OMB	C,A	OMB	---	OMB TEA	OMB	OMB,P	---	---	---

OMB=Organic matter from biomass TEA=Triethanolamine C=Poly Hydroxycarboxylate A=Polyalkoxylated Amine P=Phosphate
Circled symbol indicates average calculated on discrete measurements less than 200MPY

Figure 11-3. Summary of average corrosion rates (MPY) for cast aluminum alloy AA356.2.

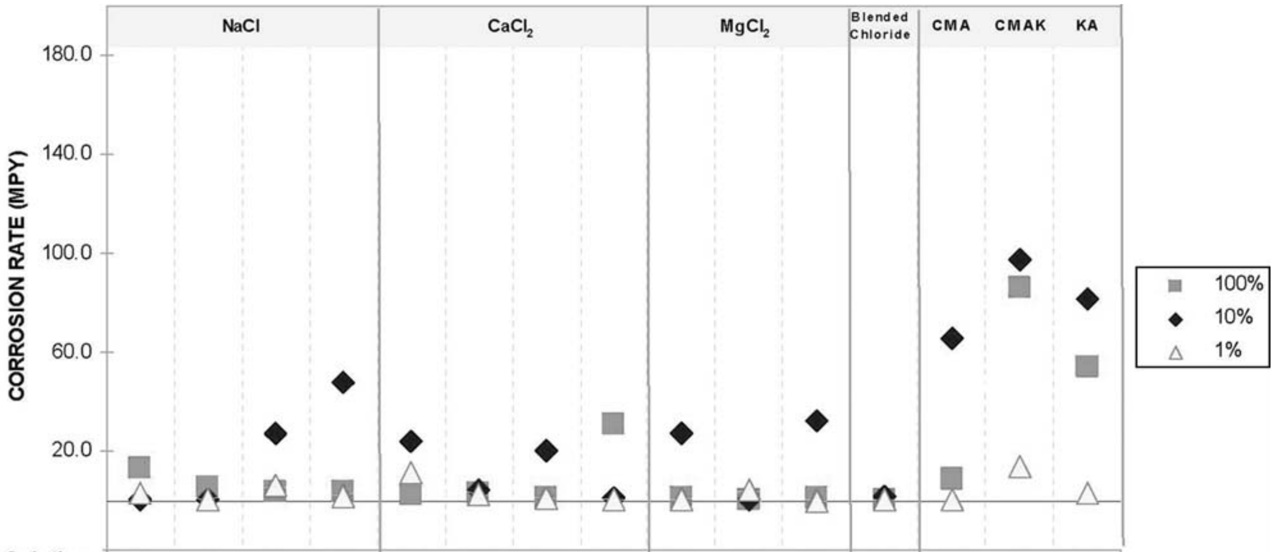
the measurement electrodes that prevented further corrosion and corrosion measurements.

- Corrosion rates for $MgCl_2$-based snow and ice control materials (26, 29, 32) varied greatly among test solutions. Product 32 contained an OMB inhibitor and displayed a low corrosion rate at the 100-percent concentration level, but had a corrosion rate consistent with uninhibited $MgCl_2$ (26) at the 10-percent concentration level. Product 29 contained an OMB/TEA corrosion inhibitor and displayed a corrosion rate similar to uninhibited $MgCl_2$ (26) at the 100-percent concentration level, but a much lower corrosion rate at the 10-percent concentration level. A possible explanation for these observations may be that corrosion inhibitor effectiveness depends on snow and ice control material and/or inhibitor concentration.
- Acetate-based snow and ice control materials containing potassium (CMAK (41) and KA (42)) demonstrated corrosion rates similar to chloride-based snow and ice control materials for all test concentrations. Conversely, the CMA snow and ice control materials (40) had comparatively lower corrosion rates. A similar trend was also observed for wrought aluminum (AA6061-T6) and is contrary to general opinion that all acetate products are equally noncorrosive to metals.

11.5.4 Free Machining Brass, CDA 360

Refer to Figure 11-4 for data.

- Brass is recognized for its ability to resist electrochemical corrosion because of the formation of a relatively thin film of corrosion product, though this ability can be influenced by other chemical interactions that may exist in the corrosion system.
- For 12 of the 15 snow and ice control materials tested, the corrosion rate was greater at the 10-percent concentration level than at the 100-percent concentration level (6, 10, 13, 17, 20, 21, 26, 32, 37, 40, 41, 42). This is contrary to the trends observed for the other alloys tested, where corrosion rates increased with concentration.
- For NaCl-based snow and ice control materials, the two products with OMB-type additives (2, 3) demonstrated comparatively low corrosion rates at the 10-percent concentration level. However, a similar trend was not observed at the 100-percent concentration level. A similar corrosion reduction effect was observed for $CaCl_2$ snow and ice control materials containing OMB corrosion additives (17, 21).
- The $MgCl_2$-based snow and ice control material containing an OMB additive (32) did not demonstrate low corrosion



Solution	2	3	6	10	13	17	20	21	26	29	32	37	40	41	42
100%	13.2	5.7	3.8	3.4	2.2	3.0	1.0	31.3	0.7	0.2	1.0	0.3	9.0	85.6	53.8
10%	0.2	0.1	26.9	47.6	24.3	4.4	20.5	1.1	26.9	0.2	32.4	1.8	65.4	97.5	81.5
1%	2.9	0.6	6.0	1.4	11.4	2.4	1.2	0.4	0.2	3.9	0.1	0.7	0.2	13.8	3.1
Additive	OMB	OMB	---	P	---	OMB	C,A	OMB	---	OM B TEA	OMB	OM B,P	---	---	---

OM B=Organic matter from biomass TEA=Triethanolamine C=PolyHydroxycarboxylate A=Polyalkoxylated Amine P=Phosphate
Circled symbol indicates average calculated on discrete measurements less than 200 M PY

Figure 11-4. Summary of average corrosion rates (MPY) for free matching brass 360.

rates as was observed for similarly blended NaCl-based and $CaCl_2$-based snow and ice control materials. However, the $MgCl_2$ snow and ice control material containing TEA (29) demonstrated a reduced corrosion rate at the 100-percent concentration level and a very low corrosion rate at the 10-percent concentration level.

- Acetate snow and ice control materials generated corrosion rates that were similar and/or higher than chloride-based snow and ice control materials for all concentration levels tested.

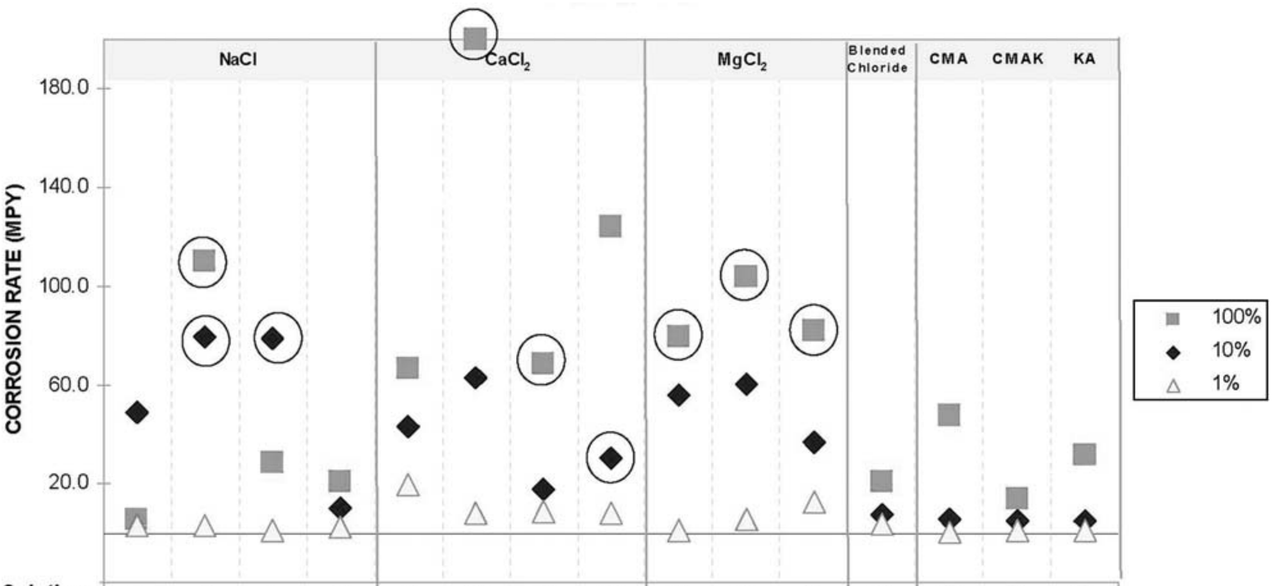
11.5.5 Magnesium Alloy, AZ91C-T6

Refer to Figure 11-5 for data.

- Magnesium is an extremely reactive metal, and higher corrosion rates were measured than for the other alloys tested in the study. Given the exposure of the magnesium alloy to 100-percent concentration levels for snow and ice control materials 3, 17, 20, 21, 26, 29, and 32, in addition to 10-percent concentration levels for snow and ice control materials 3, 6, and 21, resulted in corrosion rates exceeding 200 MPY (the MS1500L maximum capacity), the mean and median corrosion rates for magnesium alloy underestimate the true corrosion rate in these exposures. Estimates of corrosion rate by area under curve (integration) are considered more meaningful in the 100- and 10-percent concentration levels.
- Chloride-based snow and ice control materials (2, 3, 6, 10, 13, 17, 20, 21, 26, 29, 32, 37) had roughly equivalent corrosion rates at each concentration level (100-, 10-, and 1-percent). This suggests little difference in the corrosivity of various chloride-based snow and ice control materials on magnesium alloy based purely on electrochemical corrosion processes.
- Acetate-based snow and ice control materials demonstrated corrosion rates that were slightly lower than the chloride-based snow and ice control materials. However, from the standpoint of potential impairment from corrosion, acetate snow and ice control materials would still be considered corrosive.

11.6 Conclusions

The study of commercially significant alloys and 15 snow and ice control materials was consistent with the following conclusions based on the average LPR corrosion rate data obtained through this study:



Solution	2	3	6	10	13	17	20	21	26	29	32	37	40	41	42
100%	5.4	109.8	28.4	21.0	66.7	200.0	68.9	124.4	79.2	103.5	82.0	21.1	47.7	14.0	31.4
10%	48.7	79.7	78.6	10.1	42.9	62.8	17.8	30.3	56.1	60.5	37.0	7.2	5.5	5.0	5.1
1%	2.8	3.1	1.2	2.5	19.5	7.9	8.8	8.0	1.3	5.4	12.8	3.4	0.7	1.2	0.8
Additive	OMB	OMB	---	P	---	OMB	C,A	OMB	---	OM B TEA	OMB	OM B,P	---	---	---

OM B=Organic matter from biomass TEA=Triethanolamine C=PolyHydroxycarboxylate A=Polyalkoxylated Amine P=Phosphate
Circled symbol indicates average calculated on discrete measurements less than 200 MPY

Figure 11-5. Summary of average corrosion rates (MPY) for magnesium alloy AZ91C-T6.

1. LPR is a viable corrosion rate measurement technique to relatively assess corrosion rates of various snow and ice control materials. Average corrosion rates may not be the most precise indicators of central tendency, particularly for asymmetrical distributions. Comparison of the mean and median provide an indication of the influence of extreme values in the data set (similar means and medians suggest negligible extreme value influence).
2. Overall, the structural steel alloy (A36) demonstrated the lowest corrosion rate values while the magnesium alloy (AZ91C-T6) demonstrated the highest corrosion rate values. Wrought aluminum alloy (AA6061-T6), cast aluminum alloy (AA356.2), and brass alloy (CDA 360) demonstrated intermediate corrosion rate values.
3. With the exception of structural steel (A36) and brass (CDA 360), corrosion rates increased with increasing snow and ice control material concentration. Structural steel corrosion rates were sufficiently low that identification of trends may have been obscured by measurement variability at these levels. Brass corrosion rates were highest when snow and ice control materials were at the 10-percent concentration level.
4. Overall, chloride-based snow and ice control materials (i.e., NaCl, $CaCl_2$, $MgCl_2$ and blended chlorides) displayed similar corrosion rates for each metal type tested at each concentration level. This suggests little difference in corrosion rates among chloride-based snow and ice control materials. Field conditions along with other snow and ice control material properties (e.g., hygroscopicity) may contribute more to the relative corrosiveness of these materials in the service environment. Other corrosion mechanisms not emulated by aqueous testing may be significant.
5. Acetate materials (i.e., CMA, CMAK, and KA) demonstrated a range of LPR corrosion rates for the alloys assessed:

- The lowest corrosion rates were for structural steel (A36). Observed values bordered on the minimum practical detection ability of test instrumentation for all acetate types.
- Acetates were equally or slightly less corrosive than chlorides to magnesium (AZ91C-T6).
- Acetates were equally or slightly more corrosive than chlorides to brass (CDA 360).
- For aluminum alloys (AA356.2 and AA6061-T6), acetates containing potassium demonstrated corrosion rates equal to chloride-based snow and ice control mate-

rials. CMA demonstrated a much lower corrosion rate for these alloys.

6. The effectiveness of corrosion inhibitors was varied and poorly quantified. In some cases, these materials provided no detectable corrosion improvement; in other cases, corrosion improvement appeared to depend on the concentration level of the test solution. This suggests that, although some benefit may be realized from the use of these materials, the overall effectiveness under field conditions (including dilution) and after exposure to numerous potential alloy types is questionable.

11.7 Proposed Testing Program

Based on the study team's experience with the snow and ice control material corrosion test program thus far, refinements of the initial test parameters are recommended as follows:

1. Use an LPR corrosion rate meter (i.e., electrochemical measurement) calibrated to read metal loss directly. Corrosion rate measurement capacity exceeding 200 MPY is preferred for reactive metals, particularly magnesium alloys.
2. Confine testing to 10-percent snow and ice control material concentrations. 100-percent snow and ice control material solution concentrations are not present for long in the service environment because of dilution and excess reactants at these concentrations manifest atypical corrosion rates for the short term. One-percent snow and ice control material solution concentrations developed corrosion rates that were essentially unresolvable.
3. Test snow and ice control material/alloy combinations in triplicate; assess corrosion rate with a single LPR measurement at a maximum test time of 24 hours.
4. Consider confining future studies to the most commercially relevant alloys (i.e., structural steel, wrought aluminum, and cast aluminum).

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Guidebook to the Decision Tool, Purchase Specification, and Quality Assurance Monitoring Program

CONTENTS

CHAPTER 1

General Overview

1.1 Introduction

Every year, considerable quantities of snow and ice control products are applied to highways, and environmental and regulatory agencies have questioned the environmental effects of these products. Transportation agencies are asked to use "environmentally-friendly" or less toxic alternatives wherever possible, but there is no commonly accepted guidance for determining which products meet these criteria. The traditional use of roadsalt has been prohibited in some locations, leaving highway agencies uncertain about how traffic safety can be maintained in winter conditions.

Studies of the most common chemical alternatives—sodium chloride (salt, NaCl), magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$), and acetate-based materials—have focused on performance and cost under various weather conditions without evaluating their relative effects on the environment. Several new chemical preparations, including some that are proprietary formulations, have entered the market as snow and ice control chemicals for use by transportation agencies, but there is limited information about their environmental impacts.

There is a need for rational decision-making guidelines to assist winter maintenance managers in selecting the most appropriate snow and ice control materials for the conditions in their jurisdictions. A transportation agency must consider a range of factors when assessing snow and ice control materials for use. These include performance, cost, potential for the material to impair the natural receiving environment, and potential for the material to impair infrastructure. Each agency will have unique objectives and conditions that influence the importance of each of these factors in the decision process.

The overall objective of this project is to develop guidelines for selection of snow and ice control materials based on their properties, together with common site-specific conditions near roadways on which these products would be used. This report expands on the information developed through the information assessment conducted for Phase I of NCHRP Project 06-16 and provides a practical snow and ice control material selection process (decision tool), including supporting technical information and contributing thought processes.

1.2 Material Selection Process Framework

When selecting a snow and ice control material, the factors affecting the decision processes can be numerous and complex. The framework provided here is relatively straightforward and addresses the most common and significant items. The product is a practical tool that generates a numerical evaluation that can be used to compare snow and ice control materials. Although the research team has established the primary steps in the decision process, user input is a key element to ensure that maintenance area conditions are represented. Users will gather and input a range of information associated with materials and maintenance area conditions. Even though some information may be unfamiliar or considered irrelevant to agency conditions, a "complete" data set is necessary so that relative rankings can be developed for materials. A secondary benefit is that users will research and develop knowledge in new areas, further increasing their understanding of the elements involved in snow and ice control material selection.

The overall process for selecting snow and ice control materials is illustrated in Figure 1-1. Each agency will have unique objectives and priorities that will affect selections. These objectives and priorities will be expressed through percentage weightings of the categories and subcategories that form the framework for the snow and ice control material selection process (Table 1-1). Decision categories include cost, performance, potential to impair the natural environment, and potential to impair infrastructure. These balance economic value related to cost and performance with potential consequences of use related to environmental and corrosion impacts.

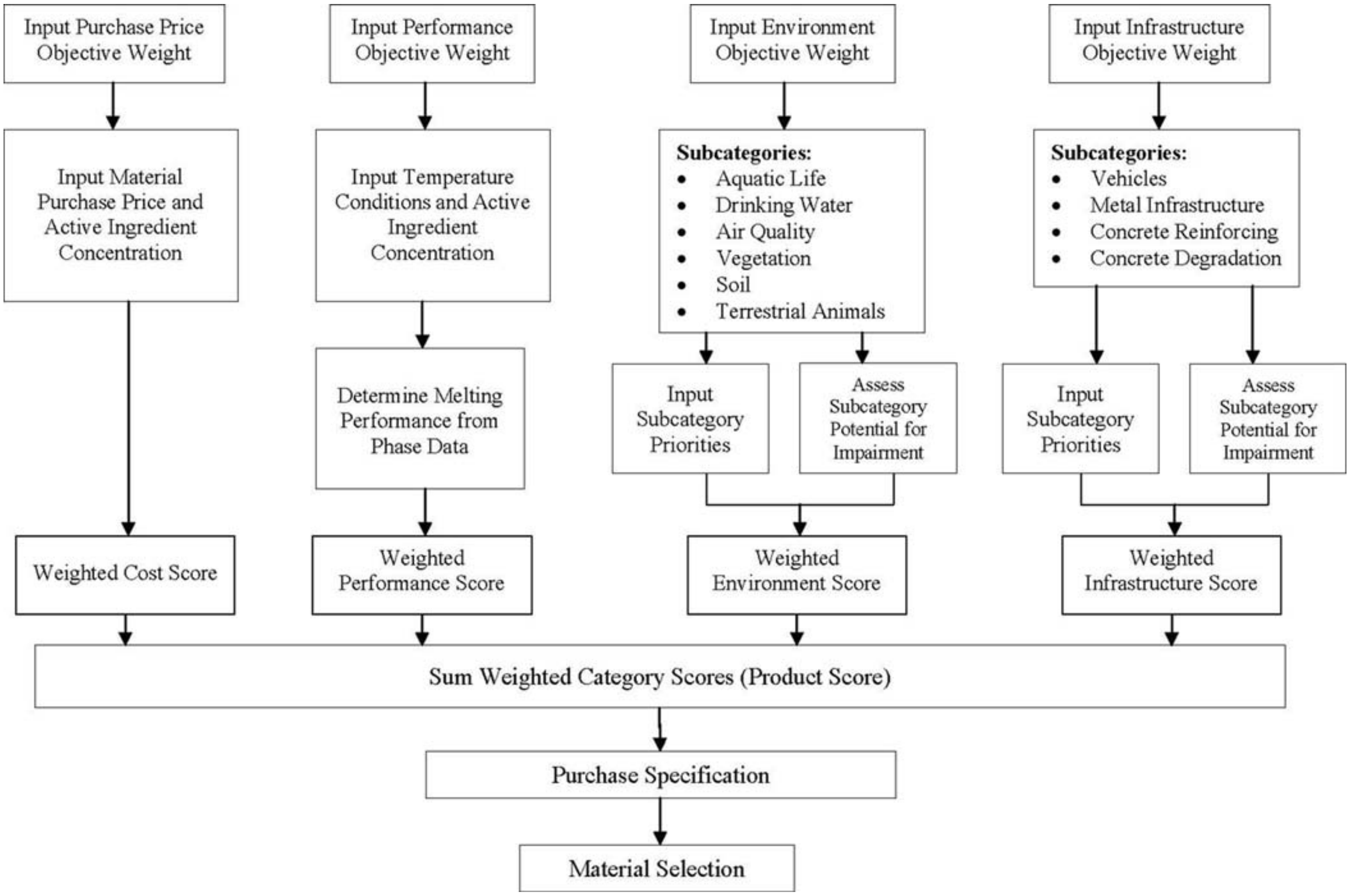

Figure 1-1. Decision tool process flow chart.

Decision subcategories that support the natural environment and infrastructure decision categories are relatively straightforward and represent the most significant components contributing to the higher level decision category.

To quantify risks of impairment for environmental and infrastructure subcategories resulting from each snow and ice control material type, numerical rankings were developed. These rankings are based on a material's potential to elicit an effect on a receptor, as developed from a comprehensive information review and analytical test results. These values are applied where sensitive receptors exist in the maintenance area as identified through user-completed receptor inventory worksheets.

Table 1-1. Decision tool framework.

Decision Category (Policy Objectives)	Decision Subcategory (Operational Objectives)
Purchase Price	Not Applicable
Performance (as Melting Potential (MP))	Not Applicable
Natural Environment	Aquatic Life
	Drinking Water
	Air
	Vegetation
	Soil
	Terrestrial Animals
Infrastructure	Vehicles
	Metals Infrastructure
	Concrete
	Concrete Reinforcing

When assessing relative cost and performance of snow and ice control materials, many factors are influential and considerable research continues to be done here. The decision tool uses the following approaches:

- Cost is based on the purchase price of the dry active ingredient. Active ingredients include the five primary snow and ice control chemicals: NaCl, $MgCl_2$, $CaCl_2$, CMA, and KA. Section 2.5 provides further discussion of cost quantification.
- Performance is based on melting potential derived from phase curve information and expected winter temperature in the maintenance region. Section 2.6 provides further discussion of performance quantification.

These approaches may not be ideal; however, they provide a standard, practical method that reasonably represents the dominant component for each decision category.

For each decision category, a weighted score is generated. These are summed for each material to produce a numerical product score that is used to compare snow and ice control material types objectively. Once a material type has been selected, various sources may exist. Considerable variation in certain attributes can exist among materials from different sources, or between batches from the same source. A purchase specification containing concentration-based guidelines for key attributes will allow transportation agencies to screen out unsuitable products (Chapter 3). The purchase specification is supported by a quality assurance monitoring program to assess received materials and by standard test methods to measure these attributes (Chapter 4).

Product selection occurs after a review of the purchase specification and supplemental considerations that may include, but are not limited, to product availability (e.g., delivery times and quantities), quality testing results, and equipment availability.

CHAPTER 2

Decision Tool

The following sections detail the development of the snow and ice control material selection tool and discuss how it is to be used, including required inputs. Application notes are included in the text and identify key steps in the decision tool process.

2.1 Policy Objectives

Application Note 1 – Agency Objectives

Identify policy objectives for decision categories through numerical weighting.

Transportation agencies have unique objectives and concerns specific to their maintenance areas that affect selection of snow and ice control materials. Users will express these objectives through percent weightings for the decision categories shown in Table 2-1. These categories represent the most significant items influencing the snow and ice control material selection process. When combined, purchase price and performance represent economic value in the snow and ice control material (i.e., performance per unit cost). Natural environment and infrastructure categories represent potential consequences of use and long-term costs. Decision makers must balance value with consequences. As an example, agencies wishing to reduce environmental concerns by using alternate materials should ensure that cost and performance objectives are also met.

Assignment of weights to the decision categories should be conducted at the beginning of the snow and ice control material selection process by management staff familiar with agency policy decisions. By setting clear objectives at the onset of the decision process, managers can demonstrate transparency in their decision criteria and establish a baseline to monitor and communicate the effectiveness of future policy changes.

2.2 Operational Objectives

Application Note 2 – Operational Objectives

Identify operational objectives for decision subcategories through numerical weighting.

Natural environment and infrastructure decision categories are supported by decision subcategories representing the most significant components contributing to the higher level decision criteria (Table 2-2). Users will apply percent weightings to these according to agency priorities. Subcategory (operational) weightings enable users to prioritize areas of greatest concern. The potential extent or severity of damage is greatest for aquatic ecosystems, rather than for other environmental subcategories—an exception may be for abrasives where road dust contributes to air quality concerns. Therefore, it is recommended that the aquatic life subcategory not be assigned a weighting less than 25 percent, unless reasonable information suggests otherwise.

2.3 Snow and Ice Control Strategy and Material Selection

Significant research has been applied toward developing guidelines for selecting snow and ice control application methods (i.e., NCHRP Project 06-13). Application methods can influence volumes of materials used, which can influence performance and the potential for negative impacts. A challenge when developing a material selection process is to ensure that potential impairments related to a material type are considered independently of application methods.

Table 2-1. Policy objectives.

Decision Category	Decision Weighting (%)
Purchase Price[1]	Sum = 100 %
Performance as Melting Potential (MP)[2]	
Natural Environment	
Infrastructure	

[1] The Decision Tool uses purchase price per dry unit of active ingredient, including shipping as a cost benchmark. This is a practical approach and yields a consistent and unbiased assessment of the dominant cost element (refer to Section 2.5 for further discussion).

[2] Given that the primary objective of winter maintenance is controlling snow and ice, it is recommended that performance weighting not be assigned a value below 25%.

Table 2-2. Operational objectives.

Decision Category (Policy Objectives)	Decision Subcategory (Operational Objectives)	Decision Weighting (%)
Natural Environment	Aquatic Life[1]	Sum = 100 %
	Drinking Water	
	Air Quality	
	Vegetation	
	Soil	
	Animals	
Infrastructure	Vehicles	Sum = 100 %
	Metal Infrastructure	
	Concrete Corrosion	
	Concrete Degradation	

[1] It is recommended that aquatic life weighting not be assigned a value below 25%

Establishing the application method before material selection normalizes application method-based influences between materials, allowing the materials to be assessed based on their specific properties.

2.3.1 Strategies

Application Note 3 – Application Method Selection

Identify the primary application method for the material evaluation.

Most winter maintenance practices follow one or a combination of the snow and ice control strategies shown below. It is assumed that mechanical removal of snow and ice is used as appropriate within all strategies. Further information on the selection and use of snow and ice control strategies is presented in *NCHRP Report 526*.

- **Deicing,** a reactive strategy, involves application of a chemical on top of a layer of snow, ice, or frost already bonded to the surface of the pavement. Typical application rates for dry chemicals range from 25 kg per lane kilometer (100 lbs. per lane mile) to 100 kg per lane kilometer (400 lbs. per lane mile), and sometimes more, depending on conditions. Deicing typically involves the application of solid NaCl and, as with any dry application, traffic action can result in a significant loss of material to the roadside environment.
- **Anti-icing,** a proactive strategy, involves application of snow and ice control materials before a snow, ice, or frost event. This strategy delays or can prevent precipitation from bonding (i.e., freezing) with the pavement surface. When only a delay in the bonding of the ice is achieved, it weakens the bonds that form, allowing easier removal than with deicing. Anti-icing applications are not limited to liquid chemicals. Properly timed applications of either dry or pre-wetted chemicals can achieve the goal of preventing bond formation if these materials can be held in place and not removed by traffic action.
- **Abrasive** use has long been a strategy of choice by many agencies because it is a very visible and assumed to be a low-cost approach to managing pavement friction. However, when abrasives are placed "dry" on the road surface (i.e., without significant pre-wetting) they provide, at best, a very short-term increase in road surface friction. As roadway

traffic levels increase, and vehicle speeds are greater than 30 mph (50 kph), any benefit from abrasive use diminishes.

- **Pre-wetting** is injecting or spraying a liquid chemical on solid chemicals or abrasives so as to enhance their effectiveness. It is a viable and desirable alternative to dry application of solid materials. Pre-wetting may be conducted to support anti-icing, deicing, or abrasive use. Using standard application rates, the pre-wet liquid has little contribution to the overall chemical loading. For example, when solid NaCl is pre-wet with liquid $CaCl_2$ at a rate of 10 gallons per ton, the chloride contribution from $CaCl_2$ is less than 0.2 percent of total chloride loading.

2.3.2 Material Selection

Application Note 4 – Snow and Ice Control Materials Selection

> Select the specific material for evaluation, in addition to standard products.

Several types of materials are used for snow and ice control, and new products continue to emerge in the marketplace. However, most materials used for roadway snow and ice control contain or will continue to contain one or more of the material types shown in Table 2-3. The potential for impairment to the natural environment or infrastructure is linked to the properties (i.e., components and attributes) of each snow and ice control material. The decision tool addresses effects from the primary components and attributes of snow and ice control material types. Secondary components and attributes are addressed though the purchase specification (Chapter 3).

Table 2-4 lists common snow and ice control strategy and material combinations. Materials are denoted as being primary or secondary. For example, when pre-wetting NaCl with liquid $MgCl_2$, NaCl is the primary product, and $MgCl_2$ is the secondary product. Using typical application rates, secondary materials contribute little to total material loading. Therefore only primary materials are considered in the decision tool process. Organic matter from biomass (OMB) materials are generally not used alone for snow and ice control and will typically exist as an additive or a secondary product to the other chemical materials.

2.3.2.1 Blended Materials

Blends of snow and ice control materials are common and are generally prepared with specific goals in mind, such as corrosion inhibition or performance enhancement. Commercial blends of chloride-based chemicals generally contain between 5 and 25 percent of an OMB material, although OMB levels up to 50 percent are also commercially available. Blended snow and ice control materials pose certain challenges when assessing potentials for impairment to the environment and infrastructure, because it is not always clear what concentrations are present or which materials are active ingredients. The decision tool defines standard active ingredients for snow and ice control as being

- Sodium Chloride (NaCl);
- Calcium Chloride ($CaCl_2$);
- Magnesium Chloride ($MgCl_2$);
- Calcium Magnesium Acetate (CMA);
- Potassium Acetate (KA); and
- Abrasives.

Table 2-3. Primary components and secondary attributes of selected snow and ice control materials.

Material Type	Snow and Ice Control Material	Primary Components and Attributes	Secondary Components and Attributes
Chloride Salts	Sodium Chloride (NaCl)	Na, Cl	Heavy metals, Cyanide (CN), Nutrients (N, P)
	Calcium Chloride ($CaCl_2$)	Ca, Cl	Heavy metals, Nutrients (N, P)
	Magnesium Chloride ($MgCl_2$)	Mg, Cl	Heavy metals, Nutrients (N, P)
Acetates	Calcium Magnesium Acetate (CMA)	Ca, Mg, Organic Matter (acetate) as BOD[1]	Heavy metals, Nutrients (N, P)
	Potassium Acetate (KA)	K, Organic Matter (acetate) as BOD[1]	Heavy metals, Nutrients (N, P)
Organic Products	Organic Matter from Biomass (OMB), Agricultural By Products	Organic Matter as BOD[1]	Heavy metals, Nutrients (N, P)
Abrasive	Abrasives	Particulate – Air Quality (PM-10) Sediments – Water Quality	Heavy metals, P

[1] Biochemical Oxygen Demand

Table 2-4. Common snow and ice control strategy & material combinations.

Strategy		NaCl	$CaCl_2$	$MgCl_2$	Acetates			Organic Matter from Biomass	Abrasives
					CMA	KA	CMAK		
Deicing	Solid Only	P	P	P[1]	P	-	-	-	-
	Liquid Only	P	P	P	P	P	P	S	-
	Pre-wet Solid	P, S	S	S	S	S	S	S	-
Anti-Icing	Solid Only	P	P	P[1]	P[1]				-
	Liquid Only	P	P	P	P	P	P	S	-
	Pre-wet Solid	P, S	S	S	S	S	S	S	-
Abrasive Use	Abrasive Only	-	-	-	-	-	-	-	P
	Pre-wet abrasive	S	S	S	S	S	S	S	P

P = denotes a primary material
S = denotes a secondary product material
[1] Not Commonly Used
‘ - ’ denotes not applicable

These materials are the primary snow and ice control materials, as identified through a comprehensive literature review and industry survey conducted in Phase I of this study. These materials also have a proven ability to melt ice under field conditions. Recent information suggests that OMB materials may also contribute to melting performance, but information is limited. Any measurable performance benefits of OMB materials should be assessed on a case-by-case basis through development of material-specific phase curves. Abrasives have no snow and ice melting potential, but are an established winter maintenance strategy for many agencies.

For commercially available blends, it is necessary for suppliers to provide complete, accurate, and independently developed data that identifies product components. Preliminary qualification may include basic physical and chemical data and MSDS information. Where transportation agencies prepare blended products in house, chemical and physical properties can be calculated through proportional summation. In either case, it is recommended that further verification be conducted by a laboratory using approved methods (refer to Chapter 4).

Table 2-5 provides molecular weights and primary component proportions for standard snow and ice control materials. Chloride-based materials (NaCl, $MgCl_2$, and $CaCl_2$) have chloride concentrations within a close relative range (61- to 74-percent chloride) implying that chloride-related effects for these materials would generally be of the same order of magnitude. The following example shows how to calculate the chloride content of a blend that is 75-percent NaCl and 25-percent $MgCl_2$:

Material	% Chloride	% of Mixture	Chloride Contribution
NaCl	61 %	75 %	$0.75 \times 0.61 = 45$ %
$MgCl_2$	74 %	25 %	$0.25 \times 0.74 = 19$ %
	Total Chloride		64 %

Table 2-5. Molecular weights and constituent proportions of five standard snow and ice control materials.

Material	Ion	Na	Mg	Ca	K	Cl	Acetate
	Molecular Weight	22.99	24.31	40.08	39.01	35.45	59.04
NaCl	58.44	39 %	-	-	-	61 %	-
$MgCl_2$	95.21	-	26 %	-	-	74 %	-
$CaCl_2$	110.99	-	-	36 %	-	64 %	-
KA	98.14	-	-	-	40 %	-	60 %
CMA[1]	90[1]	-	15 %[1]	15 %[1]	-	-	60 %[1]

[1] Concentration may vary depending on manufacturing processes.
‘ - ’ denotes not applicable

This mixture contains 64-percent chloride, which is within the 61- to 74-percent chloride range typically exhibited by the chloride-based products. Similar principles can be applied to other components and blended materials.

2.4 Maintenance Area Information

Application Note 5 – Maintenance Area

Identify and briefly describe the roadway section or region undergoing assessment. Inventory potential maintenance area receptors using Tables 2-6 through 2-15 and develop potential for impairment scores specific to receptors and materials.

The decision tool can assess maintenance area sizes ranging from small areas with specific concerns (e.g., bridges or environmentally sensitive areas) to entire maintenance regions. Users must clearly define maintenance area limits in order to set the constraints for establishing an inventory of site-specific considerations.

For impairment to occur, snow and ice control materials must contact a receptor in a concentration significant enough to elicit a negative response. Predicting transport processes from the roadway and identifying all possible receptors in a maintenance area can be challenging and some broad assumptions are necessary.

Many historical problems related to snow and ice control materials are associated with chemical overuse that resulted in higher than necessary loadings to the environment. Subsequent assessments provided in this decision tool are based on normal use of snow and ice control products. The following references provide suggestions for normal application rates of snow and ice control materials:

- Ketcham, S. A., L. D. Minsk, R. R. Blackburn, and E. J. Fleege. *Manual of Practice for an Effective Anti-Icing Program – A Guide for Highway Winter Maintenance Personnel*, US Army Cold Regions Research and Engineering Laboratory Corps of Engineers for the FHWA, Hanover, New Hampshire, 1996.
- Blackburn, R. R., D. E. Amsler, S. E. Boselly, and A. D. McElroy. *Guidelines for Snow and Ice Control Materials and Methods*, NCHRP Project No. 06-13. National Cooperative Highway Research Program, Transportation Research Board, National Research Council, 2003.
- Salt Institute, *The Snowfighters Handbook*, July 1999.

The transport process for snow and ice control materials from the roadway involves movement of liquid (through splashing, spraying, runoff, surface water movement, and groundwater movement) and movement of dry material or residue mobilized or resuspended by traffic action and wind. Although it is important to understand all possible transport processes, they have little practical application to a material selection tool that is broadly applied. It is necessary to simplify the transport processes into the following generalizations developed through a comprehensive technical assessment of information reviewed during Phase I of this study:

- Assessment of numerous studies investigating snow and ice control material movement over roadside soil (from splash, spray, and runoff) shows that the effects on soil concentrations typically drop quickly beyond the first 10- to 20-m-wide strip of land bordering the roadway or along paths of overland flow.
- Many studies have attempted to model the concentrations of direct water runoff; however, findings are highly variable and depend on site-specific factors, including precipitation amounts, first flush effects, soil infiltration, hydraulic conductivity, and dilution effects. A conservative estimate is that snow and ice control materials will be diluted 500-fold at the point they leave the roadway. In certain instances, lower dilution rates are possible, although dilution will increase substantially as the distance from the roadway increases.
- Air quality effects can be further reaching than effects on soil, water, vegetation, and animals and should be assessed on a local to regional level.

The decision tool applies a conservative approach to identify potential at-risk receptors in the maintenance area. This involves a series of checklists used to inventory common and significant areas of concern for the environmental and infrastructure subcategories. The inventory should be conducted by individuals with a broad understanding of the conditions that exist in the maintenance region. Suitable individuals will include supervisory and management staff with knowledge of snow and ice control operations and environmental and infrastructure conditions and concerns. This step may direct further investigation, which if necessary, would require input by additional professionals trained in the area of concern.

Tables 2-6 through 2-15 are practical worksheets that summarize common and significant maintenance area receptors that may be impaired by snow and ice control materials. These tables address the primary components and attributes of snow and ice control materials (refer to Table 2-4). Secondary components and attributes are addressed through a purchase specification (Chapter 3).

Each snow and ice control material will have a certain potential to impair an environmental or infrastructure

Table 2-6. Aquatic life—material/receptor potential for impairment worksheet.

Aquatic Life Conditions	Exists? (Y/N)	NaCl	$MgCl_2$	$CaCl_2$	CMA	KA	OMB	Abrasives
Small stream with coarse substrate		4	4	4	2	2	1	1
Small stream with fine substrate		4	4	4	2	2	1	5
Intermediate stream with coarse substrate		5	5	5	3	3	2	1
Intermediate stream with fine substrate		5	5	5	3	3	2	5
Large stream with coarse substrate		5	5	5	4	4	3	3
Large stream with fine substrate		5	5	5	4	4	3	5
Wetland, nutrient poor		3	3	3	3	3	1	1
Wetland, nutrient rich		3	3	3	3	3	3	1
Small lake, nutrient poor		2	2	2	3	3	1	5
Small lake, nutrient rich		2	2	2	4	4	3	5
Intermediate lake, nutrient poor		4	4	4	4	4	1	5
Intermediate lake, nutrient rich		4	4	4	5	5	4	5
Large lake, nutrient poor		5	5	5	5	5	3	5
Large lake, nutrient rich		5	5	5	5	5	5	5
Sum of Selected Conditions								
Average of Selected Conditions								

Definition of terms:

- **Stream Size***: small stream*: average width of water surface less than 10 yards under winter flow conditions; *intermediate stream*: 10 to 30 yards*; large stream*: greater than 30 yards.
- **Lake Size**: *small lake*: < 10 acres; *intermediate lake*: 10 to 100 acres; *large lake*: > 100 acres.
- **Wetland**: aquatic body not defined as a lake or stream, i.e. marsh, ponds, etc.
- **Substrate**: *coarse substrate*: boulder, cobble, gravel; *fine substrate*: sand, clay, muck.
- **Nutrient Levels**: *nutrient poor*: total P below 15 µg/L, total N below 300 µg/L; *nutrient rich*: > 15 µg/L P, >300 µg/L N.

Table 2-7. Drinking water from groundwater—material/receptor potential for impairment worksheet.

Drinking Water Conditions	Exists? (Y/N)	NaCl	$MgCl_2$	$CaCl_2$	CMA	KA	OMB	Abrasives
Shallow ground water used for drinking		3	5	5	4	4	3	5
Sum of Selected Conditions								
Average of Selected Conditions								

Table 2-8. Air quality—material/receptor potential for impairment worksheet.

Air Quality Conditions	Exists? (Y/N)	NaCl	$MgCl_2$	$CaCl_2$	CMA	KA	OMB	Abrasives
Existing air quality concerns relevant to particulate matter (i.e. non-attainment area)		5	5	5	5	5	5	1
Poor air dispersion, closed air shed		5	5	5	5	5	5	1
Sum of Selected Conditions								
Average of Selected Conditions								

Table 2-9. Vegetation—material/receptor potential for impairment worksheet.

Vegetation Conditions	Exists? (Y/N)	NaCl	$MgCl_2$	$CaCl_2$	CMA	KA	OMB	Abrasives
Agricultural lands within 10m of the roadway		1	2	2	4	4	5	4
Protected vegetation within 10m of the roadway		1	2	2	4	4	5	4
Aesthetic objectives within 10m of the roadway		1	2	2	4	4	5	4
Sum of Selected Conditions								
Average of Selected Conditions								

Table 2-10. Soil quality—material/receptor potential for impairment worksheet.

Soil Quality Conditions	Exists? (Y/N)	NaCl	$MgCl_2$	$CaCl_2$	CMA	KA	OMB	Abrasives
Poor soil structure within 10m of the roadway[1]		2	5	5	5	5	5	5
Sum of Selected Conditions								
Average of Selected Conditions								

[1] Exchangeable Sodium Percentage (ESP) >13

Table 2-11. Terrestrial fauna—material/receptor potential for impairment worksheet.

Animal Conditions	Exists? (Y/N)	NaCl	$MgCl_2$	$CaCl_2$	CMA	KA	OMB	Abrasives
Potential for effects on terrestrial species [1]		4	4	4	5	5	5	5
Road kill for mammals or birds is a concern		4	4	4	5	5	5	5
Sum of Selected Conditions								
Average of Selected Conditions								

[1] Includes sensitive mammals, birds, amphibians, reptiles, insects, spiders, etc.

Table 2-12. Vehicles—material/receptor potential for impairment worksheet.

Vehicles	Exists? (Y/N)	NaCl	$MgCl_2$	$CaCl_2$	CMA	KA	OMB	Abrasives
Vehicles		1	1	1	4	4	5	1
Sum of Selected Conditions								
Average of Selected Conditions								

Table 2-13. Metal infrastructure—material/receptor potential for impairment worksheet.

Metal Infrastructure Conditions	Exists? (Y/N)	NaCl	$MgCl_2$	$CaCl_2$	CMA	KA	OMB	Abrasives
Steel Bridges		1	1	1	4	4	5	5
Other metal infrastructure of concern								
Sum of Selected Conditions								
Average of Selected Conditions								

Table 2-14. Concrete matrix—material/receptor potential for impairment worksheet.

Concrete Degradation	Exists? (Y/N)	NaCl	$MgCl_2$	$CaCl_2$	CMA	KA	OMB	Abrasives
Concrete pavement and structures		4	3	4	3	4	5	5
Sum of Selected Conditions								
Average of Selected Conditions								

Table 2-15 Concrete reinforcing—material/receptor potential for impairment worksheet.

Concrete Reinforcing	Exists? (Y/N)	NaCl	$MgCl_2$	$CaCl_2$	CMA	KA	OMB	Abrasives
Reinforcing Steel Bar		1	1	1	5	5	5	5
Sum of Selected Conditions								
Average of Selected Conditions								

receptor. This is reflected by product/receptor-specific numerical rankings developed based on a comprehensive technical assessment of information conducted during Phase I of this study and based on the results of analytical testing conducted during Phase II of this study. Numerical rankings correspond to the following conditions:

- 1 to 2 – undesirable,
- 2 to 3 – potential for some impairment,
- 3 to 4 – potential for minor impairment, and
- 4 to 5 – low likelihood of impairment.

These values have undergone considerable development and review. Where a user thinks that other information is more representative of the conditions in a maintenance area, these numerical rankings may be adjusted accordingly. Any adjustments must be technically defensible and conducted by individuals with knowledge of the topic area.

Instructions for use of Tables 2-6 through 2-15 are as follows:

1. A given roadway may have more than one type of potential receptor in each decision subcategory. Check the one or more types of receptors that occur along a roadway under consideration for snow and ice control.
2. Obtain a mean score for each material under consideration by summing the scores for the selected receptors and dividing by the number of selected receptors. If no selections are made, a default average score of 5 applies. The lowest score indicates the least desirable choice.
3. For snow and ice control products blended from more than one material, select the lowest (most conservative) score applicable to either material in the blend. For a material composed of $MgCl_2$ and OMB applied near a "*small coldwater stream with coarse substrate*" (refer to Table 2-6) the $MgCl_2$ score is "4," and the organic biomass score is "1." Using this approach, the applied score is "1."

2.4.1 Aquatic Life Worksheet

The rationale for the numerical scores for aquatic life is as follows:

- Small water bodies offer less dilution than large water bodies. Consequently, acceptability of any given material with a potentially adverse environmental effect tends to increase as the size of the receiving water increases.
- Abrasives block interstitial spaces within coarse substrates, thus damaging habitat. This particular category of damage is not an issue for streams with fine substrates. The same is true of wetlands.
- Organic matter and nutrients cause oxygen depletion or eutrophication where potential dilution is low, but are much less likely to be harmful where dilution is high. Higher nutrient levels tend to be associated with OMB materials. Nutrient-poor water bodies have a lower tolerance than nutrient-rich water bodies to additional nutrient loadings.
- Nutrient-poor streams typically contain organisms that are not tolerant of oxygen depletion. Nutrient-rich streams are more likely to experience oxygen depletion, and, therefore, typically contain organisms that are more tolerant of oxygen depletion. Therefore, the tolerance for oxygen-demanding substances, such as acetate and OMB, is rated lower for nutrient-poor streams than for nutrient-rich streams, particularly if the streams are small.
- The probability that the chloride standard for aquatic life will be exceeded is highest for standing waters of small volume and lowest for flowing waters of large volume.

2.4.2 Drinking Water from Groundwater Worksheet

The rationale for the numerical scores for drinking water obtained from groundwater is as follows:

- Magnesium, calcium, and chloride are not associated with impairment of human health.
- Sodium in groundwater is a potential threat to persons with cardiovascular impairment, although the threshold concentration for health effects is relatively high.
- Addition of organic carbon compounds (e.g., acetate or mixed organic matter from biomass) may cause deoxygenation of groundwater, which in turn could cause release of potentially harmful substances (e.g., heavy metals) into the groundwater and could cause taste and odor problems.

2.4.3 Air Quality Worksheet

The use of abrasives for snow and ice control can degrade air quality through increases in airborne fine particulate (i.e., PM-10). This is of greatest concern for areas with limited recharge capacity or where existing air quality issues exist. Chemical materials are not known to result in similar concerns.

2.4.4 Vegetation Worksheet

Effects associated with roadside vegetation impairment from snow and ice control materials are linked to extremely high levels of ions contacting foliage and roots and damage related to elevated chloride levels. Vegetation damage is of greatest concern in the primary material deposition zone 10 meters from the roadway. Although certain types of vegetation are more tolerant to these stresses than others, a conservative approach ensures the greatest level of environmental protection.

Chloride materials have the greatest potential to impair vegetation. Sodium can degrade soil structure, which can impede water uptake and root growth. Evidence suggests that acetate materials can also affect vegetation through osmotic stress damage, although this does not occur to the same degree as for chlorides. OMB materials pose minimal concern to vegetation when compared with inorganic salts. Abrasives are not completely innocuous and can cause smothering concerns in some instances.

2.4.5 Soil Worksheet

Snow and ice control chemicals can affect soils chemically (by affecting concentrations of available ionic components in the soil) and physically (by affecting soil structure). Chemical effects on the soil are primarily a vegetation-impact concern and are not significant when considering soil as the individual receptor. Elevated sodium levels can degrade soil structure by reducing soil particle size. This can reduce permeability and create a higher potential for soil erosion. Sodium effects are of greatest concern when poor soil conditions already exist (Exchangeable Sodium Percentage (ESP) >13) within 10 meters of the roadway.

2.4.6 Terrestrial Fauna Worksheet

Snow and ice control materials have been linked to reports of salt toxicosis from ingestion and increases in vehicle-animal collisions. Some information suggests salt toxicosis from ingestion is a concern for small animals such as birds, although most terrestrial animals have high salt tolerances, especially when adequate drinking water is available. It is unclear whether snow and ice control materials increase vehicle-animal collision rates. Some research supports this, but most current information suggests other conditions contribute much more significantly to vehicle-animal collisions.

2.4.7 Vehicles Worksheet

Chloride-based snow and ice control materials are corrosive to metallic motor vehicle components. Numerous studies have attempted to rank these materials for corrosion but complex contributing factors limited the development of definitive conclusions. From the standpoint of developing practical rankings, these materials have been ranked equally high for their potential to cause corrosion. Information suggests that acetate-based materials are less corrosive to steel than chlorides, but may lead to corrosion concerns for other alloys. Although OMB materials are accepted as being noncorrosive to metals, limited evidence suggests that these materials, used as corrosion-inhibition additives, significantly reduce corrosion rates under field conditions. Abrasives can degrade coatings that protect metals from the corrosive effects of snow and ice control materials.

2.4.8 Metal Infrastructure Worksheet

Chloride-based snow and ice control materials are corrosive to metal infrastructure components. Numerous studies have attempted to rank these materials for corrosion but complex contributing factors limited the development of definitive conclusions. From the standpoint of developing practical rankings, these materials have been ranked equally high for their potential to cause corrosion. Information suggests that acetate-based materials are less corrosive to steel than chlorides, but may lead to corrosion concerns for other alloys. Although OMB materials are accepted as being noncorrosive to metals, limited evidence suggests that these materials, used as corrosion-inhibition additives, significantly reduce corrosion rates under field conditions.

2.4.9 Concrete Matrix Worksheet

Considerable research is ongoing on the effects of snow and ice control materials on concrete paste. To date, there have been conflicting findings as to how the various materials affect the durability of the concrete. Traditional snow and ice control materials (e.g., $NaCl$ and $CaCl_2$) are known to have some detrimental effects on concrete, primarily causing scaling of the concrete surface, although no problems with the bulk properties of the concrete are known. With good-quality concrete, scaling problems can be avoided. Some laboratory studies have shown deterioration of the cement paste and bulk properties of the concrete by $CaCl_2$; however, the material is widely used and these findings do not appear to be substantiated in field applications.

Laboratory studies with magnesium-based materials (e.g., $MgCl_2$ and CMA) have found chemical degradation of the concrete matrix as a result of magnesium reacting with the calcium-silica-hydrate (C-S-H) by replacing the calcium with magnesium and, in time, resulting in strength-loss of the concrete. Although there have been some reports of $MgCl_2$ causing deterioration of the concrete in the field, there does not appear to be a widespread problem. However, $MgCl_2$ is used to a somewhat lesser extent. Considering the reactivity of magnesium, long-term effects are possible and, given the findings of past studies, future work will be required. Close monitoring of structures where $MgCl_2$ is used is also recommended.

2.4.10 Concrete Reinforcing Worksheet

Chlorides enable and/or accelerate corrosion of concrete reinforcing. Current evidence suggests that chloride associated with magnesium may have higher chloride diffusion coefficients than NaCl or $CaCl_2$. Considerable research is ongoing and, for practical purposes, all chloride materials have been ranked equally high in causing corrosion of the reinforcing steel. This study includes an analytical research program investigating the relative chloride diffusion coefficients between chloride-based snow and ice control materials. After 1.5 years of exposure testing, corrosion has not been initiated for any of the materials. The rankings will remain based on the comprehensive literature assessment, as this time of exposure can be considered short when viewed in terms of concrete durability where current service life requirements in the order of 30 to 100 years are commonly specified. Acetate-based materials, OMBs, and abrasives are not considered corrosive to concrete reinforcing.

2.5 Identified Cost

Application Note 6 – Price and Concentration

> Input price and active ingredient concentrations for standard snow and ice control materials, plus other materials under consideration.

This section provides a model to assess costs associated with snow and ice control materials. The complete cost of snow and ice control involves both direct costs (i.e., material purchase price) and indirect costs (i.e., operational costs and capital costs). Costs are dynamic and are influenced by factors difficult to predict with certainty. This is particularity true for indirect costs, which are closely related to application strategy influences (e.g., roadway retention, melting capacity at specific temperatures, and applications required per given storm event). The decision tool uses purchase price per dry unit of active ingredient, including shipping, as a cost benchmark. This is a practical approach and yields a consistent and unbiased assessment of the dominant cost element. It is necessary for the decision tool user to obtain the purchase price and active ingredient concentration of standard materials (i.e., NaCl, $CaCl_2$, $MgCl_2$, KA, CMA, and abrasives) and other candidate materials. Some standard materials may not be strong agency considerations, but the information is important to ensure completeness of the decision tool assessment. A secondary benefit is that users will research and develop knowledge of new material types, further increasing their understanding of the important elements involved in snow and ice control material selection.

Snow and ice control materials can exist in various forms (i.e., liquids and solids), concentrations, and blends. Cost must be expressed as dry weight of active ingredient. For example, NaCl may be provided as a solid material, a blended solid material, a pure liquid, or a blended liquid. Examples for calculating cost per unit of active ingredient are shown in Table 2-16. Inert substances are defined as substances that do not melt ice and primarily include insoluble substances that do not enter into solution.

Relative price rankings of products can be derived from purchase price information (Table 2-17). A high price ranking represents the preferred product for this category.

2.6 Performance

Measuring performance of snow and ice control chemicals continues to be a topic of considerable research. Several approaches for quantifying performance exist and many are not easily quantifiable. The primary considerations affecting snow and ice control material performance are as follows:

- **Chemical characteristics** of snow and ice control chemicals, primarily the concentrations of active ingredients responsible for melting snow and ice affect performance. Phase curves provide a simple method to correlate concentration with melting point.
- **Physiochemical properties**, such as solubility rates and exothermic (i.e., heat-producing) properties, can also affect melting rate and ice penetration rates, but these characteristics are difficult to quantify. Information related to measuring these characteristics is available in SHRP H-332, *Handbook of Test Methods for Evaluating Chemical Deicers*, although this document does not address all types of snow and ice control materials.

Table 2-16. Example of cost per active ingredient calculation.

Material Form and Type	Common Examples	Cost Per Active Ingredient Calculations
Solid	NaCl	(Total material weight – inert substances and moisture) ÷ purchase price
Hydrated Solid	$CaCl_2$-xH_2O, $MgCl_2$-xH_2O	(Total material weight – inert substances and moisture) ÷ purchase price
Liquid	NaCl, $CaCl_2$, $MgCl_2$, KA, CMA	(Total material weight – inert substances and moisture) ÷ purchase price
Blend	Varies	(Total material weight – inert substances and moisture) ÷ purchase price

Note: materials suppliers can supply total moisture percentage and purity for solid materials (hydrated and non-hydrated solids).

Table 2-17. Development of relative purchase price rankings.

	NaCl	$CaCl_2$	$MgCl_2$	KA	CMA	Abrasive
Purchase Price per Ton ($)[1]	$ 50	$ 130	$ 120	$ 1000	$ 1150	$ 80
Active Ingredient Concentration (%)	23 %	32 %	30 %	50 %	25 %	NA
Purchase Price per Dry Pound ($/lb)	$ 0.11	$ 0.20	$ 0.20	$ 1.00	**$ 2.30**[2]	$ 0.04
Maximum Price ÷ Material Price	21	11	12	2	1	58
Price Ranking (Maximum 100)	37	20	20	4	2	100

[1] Pricing was gathered from contracts published on the Internet and provides semi-realistic demonstration of relative purchase price calculations and rankings.

[2] Bold text indicates maximum purchase price per dry pound ($/Lb)

- **Weather** has considerable influence on material performance and includes precipitation (e.g., type, amount, and rate) and temperature. Although precipitation affects performance of chemicals through dilution, application rates will vary directly with storm magnitude—more chemical will be applied for high precipitation storms. Temperature, on the other hand, can be correlated with chemical properties to provide a practical assessment of performance.
- **Application methods**, including timing, application rates, and equipment, influence overall snow and ice control chemical performance significantly. However, when application methods are established before material selection, these influences are normalized, allowing the materials to be assessed based on their specific properties.
- **Roadway factors**, including grade, texture, and the presence of surface contaminants, can affect snow and ice control material performance. These factors are not easily quantified over a large maintenance area, but will be the same for each material assessment made.
- **Agency operational concerns** (e.g., handling, storage, ease of use, familiarity, and ease of delivery) can affect assessment of performance.

Although numerous factors can affect snow and ice control material performance, the dominant performance component remains the chemical's ability to melt ice at a specified temperature. If the application temperature and the active ingredient concentration are known, a melting potential using phase curve information can be used to assess materials. The following sections address how to apply temperature and active ingredient information to assess the relative performance of snow and ice control materials.

2.6.1 Temperature Information

Application Note 7 – Temperature Information

Input the 85th percentile cold winter temperature.

Pavement (or working) temperatures can be correlated with a chemical's phase properties to provide a practical assessment of performance. Users will input expected cold temperatures for a maintenance area. Historical pavement temperatures provide the best source of this information. Historical air temperatures can also be used if pavement temperature data is not available. Temperature information is generally obtained from Roadway Weather Information Systems (RWIS), installed recording devices, purchased weather information, or other sources the user consults for decision-making.

The selected cold temperature should represent the 85th percentile of cold temperatures occurring in the maintenance area. Higher percentiles (90th or 95th) may be selected to represent higher levels of service objectives, while lower

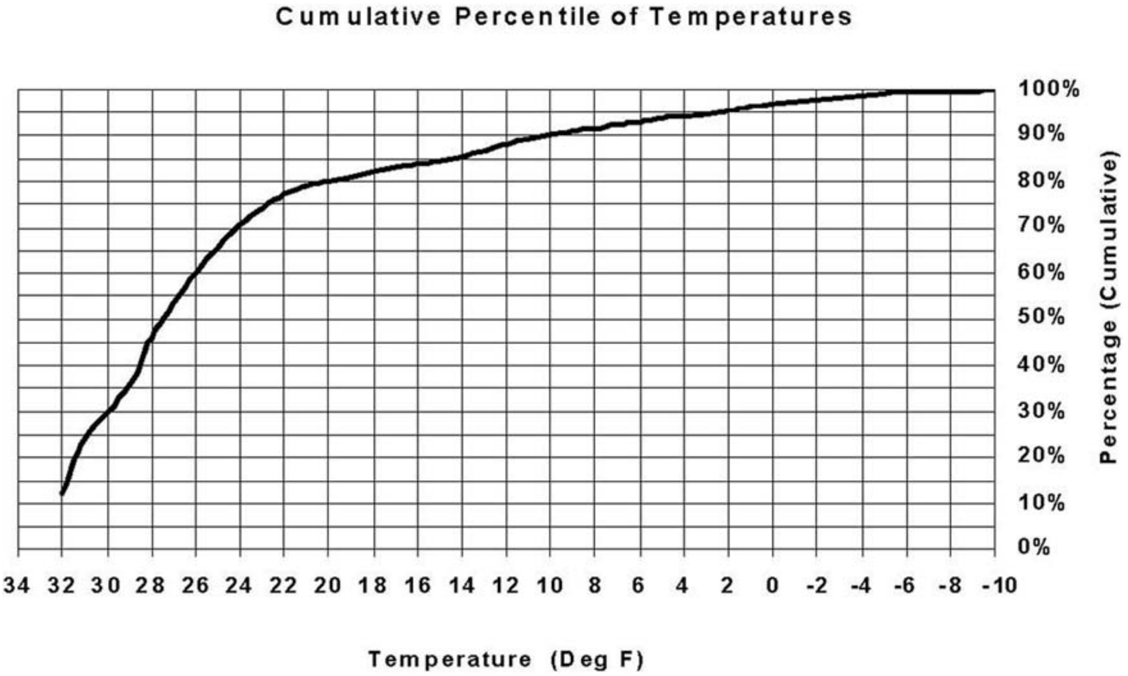

Figure 2-1. Sample cumulative temperature plot.

percentiles (80th or 75th) may be selected to represent lower levels of service objectives. Consistent use of a single temperature and service level objective throughout the decision tool process will ensure that all products will be evaluated equally.

Figure 2-1 is a sample cumulative plot of historical, subfreezing temperatures. The temperature is 16°F or higher 85 percent of the time when the temperature is below freezing. From another perspective, if a snow and ice control material is effective at 16°F, it will theoretically work in 85% of expected winter storm events. It is recommended that the user construct a chart(s) similar to that shown in Figure 2-1, ensuring that each data point represents a consistent temperature measurement time period (e.g., hourly, daily, or weekly) and historical temperatures that are at or below the freeze-point.

2.6.2 Performance Measured by Melting Potential

Application Note 8 – Material-Specific Phase Information

For non-standard or blended snow and ice control materials, input material-specific phase curve data.

Short of extensive field and laboratory testing, the only objective method of comparing snow and ice control material performance is to assess materials based on their potential to melt ice and snow as developed from phase (eutectic) curve information. Figure 2-2 and Table 2-18 show phase data for a hypothetical chemical and indicate how this material performs at different concentrations with correlating freeze-points. Each point on the phase curve in Figure 2-2 is referred to as the eutectic temperature and represents a chemical concentration and a corresponding freeze-point. The optimum eutectic temperature is the lowest freezing temperature achievable for material concentration and is typically the bottom point (the "v") on many phase curves. In this example, the optimum eutectic point occurs at 0°F at a concentration of 25 percent.

Standard phase curves for pure forms of NaCl, $MgCl_2$, $CaCl_2$, CMA, and KA exist in the scientific literature. Ice-melting properties can deviate significantly if these materials contain additional active ingredients, additives, or contaminants. For impure or blended materials, phase curves developed by an independent laboratory using standard test procedures are recommended. Section 3.2.1.2 provides a standard method for assessing the freezing point of snow and ice control materials. If independent verification is not available, the phase curve for the primary active constituent may be used until additional information can be obtained.

The snow and ice melting capacity of snow and ice control chemicals is based on their concentration and temperature in solution. As melting occurs, water is produced that dilutes the original chemical concentration. As the solution concentration reduces, the freezing point (i.e., ice/snow melting temperature) changes. The mass of ice melted (i.e., water produced) before refreezing occurs for a given chemical application at a specified temperature can be used to assess performance.

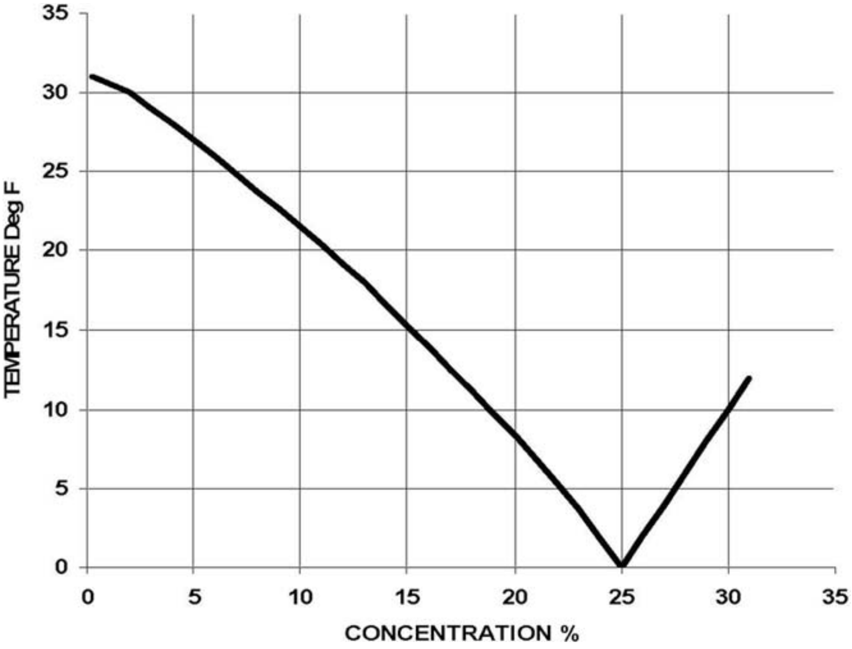

Figure 2-2. Phase/eutectic curve for hypothetical chemical X.

Melting potential (MP) is a reliable and accurate method to calculate the amount of ice and snow that can be melted at a given temperature and is represented mathematically by the following equation:

$MP = BC/EC - 1$

Where

BC = Beginning Concentration (% w/w)
EC = Ending Concentration (% w/w)
1 = Constant representing the initial application.

For liquid materials, BC is the applied concentration. For solid materials, BC is the saturated concentration (should sufficient moisture be present). The melting performance assessment compares materials independent of application rate, and only materials in solution can effectively melt ice. For solids, it is assumed that a saturated solution forms after application. Use of any value for BC greater than the saturated solution would bias the MP assessment toward materials applied as a solid. Saturated solution estimations for standard materials are based on standard solubility information at 32°F (0°C) (Table 2-19).

Once snow and/or ice melting begins, the chemical will dilute until it reaches a concentration where melting stops. This concentration is referred to as the ending concentration (EC) and is also referred to as "refreeze."

Table 2-18. Phase/eutectic data for hypothetical chemical X.

Material Concentration (%)	Specific Gravity	Freezing Temperature (F)	Material Concentration (%)	Specific Gravity	Freezing Temperature (F)
0	1	32	16	1.118	14
1	1.007	31	17	1.126	12.6
2	1.014	30	18	1.134	11.2
3	1.021	29	19	1.142	9.8
4	1.028	28	20	1.150	8.4
5	1.035	27	21	1.158	6.9
6	1.043	25.9	22	1.166	5.4
7	1.050	24.8	23	1.175	3.7
8	1.057	23.7	24	1.183	1.9
9	1.065	22.6	25	1.191	0
10	1.072	21.5	26	1.199	1
11	1.080	20.3	27	1.207	3
12	1.087	19.1	28	1.214	5
13	1.095	17.9	29	1.221	7
14	1.103	16.6	30	1.224	9
15	1.111	15.3			

Table 2-19. Solubility products for common snow and ice control materials.

Chemical	Percent Solution at Saturation[1]
NaCl	26.28 % at 0°C (32°F)
$CaCl_2$	36.70 % at 0°C (32°F)
$MgCl_2$	33.96 % at 0°C (32°F)
CMA	NA
KA ($KC_2H_3O_2$)	68.40 % at 0°C (32°F)

[1] CRC Handbook of Chemistry and Physics 85th edition.

Three examples are provided to illustrate MP calculations for Chemical X (from Table 2-18). This material has an optimum eutectic point at a 25-percent concentration and a freeze-point of 0°F. For these examples it is assumed that the roadway surface is either coated with ice or under continual snowfall.

Example 1 – Melting Potential at 27° F

- Consider a 25-percent BC solution of Chemical X applied at a temperature of 27°F. This temperature corresponds to a 5-percent EC solution.
- Every 100 pounds of 25-percent BC solution contains 25 pounds of solid active ingredient. After dilution, the 25 pounds of active ingredient generates a 5-percent EC solution with a total mass of 500 pounds. Therefore, 100 pounds of the 25-percent solution will melt 400 pounds of ice and/or snow at 27°F. Using the information from the example:

MP (27°F) = (25%/5%) − 1 = 4

Example 2 – Melting Potential at 14° F

- Consider a 25-percent BC solution of Chemical X applied at a temperature of 14° F. This temperature corresponds to a 16-percent EC solution.
- Every 100 pounds of 25-percent BC solution contains 25 pounds of solid active ingredient. After dilution, the 25 pounds of active ingredient generates a 16-percent EC solution with a total mass of 160 pounds. Therefore, 100 pounds of the 25-percent solution will melt 60 pounds of ice and/or snow at 14° F. Using the information from the example:

MP (14°F) = (25%/16%) −1 = 1.6 −1 = 0.6

Example 3 – Melting Potential at 30° F

- Consider a 25-percent BC solution of Chemical X applied at 30° F. This temperature corresponds to a 2-percent EC solution.
- Every 100 pounds of 25-percent BC solution contains 25 pounds of solid active ingredient. After dilution, the 25 pounds of active ingredient generates a 2-percent EC solution with a total mass of 1,250 pounds. Therefore, 100 pounds of the 25-percent solution will melt 1,150 pounds of ice and/or snow at 2° F. Using the information from the example:

MP (30° F) = (25%/2%) − 1 = 12.5 −1 = 11.5

Summaries of data for these examples are presented in Table 2-20.

The MP formula can also be used to evaluate hypereutectic chemical solutions—solutions with concentrations in excess of the optimum eutectic concentration. Examples of hypereutectic solutions are 30-percent magnesium chloride (optimum eutectic concentration = 21.6 percent) and 32-percent calcium chloride (optimum eutectic concentration = 28.9 percent). When compared with lower concentration solutions, hypereutectic solutions can withstand higher dilutions, helping to prolong the time of effectiveness for a chemical. However, hypereutectic solutions can have higher (i.e., warmer) freeze-points than the optimum eutectic temperature and should be used with attention to temperatures. For example, the hypothetical chemical in Figure 2-2 supplied at a 30-percent concentration will freeze at 10°F, which is much warmer than the optimum eutectic point (25-percent concentration at 10°F).

Melting potential represents an objective and easily calculated method to measure material performance at various temperatures. The MP approach can be applied to blended materials using product-specific phase information. Table

Table 2-20. Melting potential examples.

		Percent Active Ingredient	Mass of Active Ingredient	Total Solution Mass	Mass of Water
Example 1 Temperature = 27° F MP = 4	Beginning Concentration (BC)	25 %	25 lbs	100 lbs	75 lbs
	Ending Concentration (EC)	5 %	25 lbs	500 lbs	475 lbs
	Mass of Snow and Ice Melted (Water Produced)				400 lb
Example 2 Temperature = 14° F MP = 0.6	Beginning Concentration (BC)	25 %	25 lbs	100 lbs	75 lbs
	Ending Concentration (EC)	16 %	25 lbs	160 lbs	135 lbs
	Mass of Snow and Ice Melted (Water Produced)				60 lbs
Example 3 Temperature = 30° F MP = 11.5	Beginning Concentration (BC)	25 %	25 lbs	100 lbs	75 lbs
	Ending Concentration (EC)	2 %	25 lbs	1250 lbs	1225 lbs
	Mass of Snow and Ice Melted (Water Produced)				1150 lbs

2-21 shows examples of MPs for five standard snow and ice control materials using phase curves from various commercial sources. Phase curves from commercial sources can and will differ from the pure chemical data from sources such as the CRC Handbook of Chemistry and Physics because of the presence of other species of chlorides and/or chemicals. This highlights the necessity of using phase curves specific to the products being assessed, rather than depending on generalized curves.

The numeric MP value can be easily applied to determine relative performance of snow and ice control materials. MP and purchase price can be combined to generate the economic value of a snow and ice control material (i.e., MP per price per mass), which can be used to establish relative rankings of material types.

2.7 Decision Tool Application

This decision tool is designed to assist users in selecting the most appropriate snow and ice control materials based on user priorities and conditions. Decision tool steps and assumptions are summarized below:

- Users will prioritize agency policy objectives for cost, performance, environmental impacts, and infrastructure impacts. Users will further prioritize subcategory objectives that support the environmental and infrastructure objectives.
- Users will input cost and concentration information for candidate material snow and ice chemicals.
- Cost will be represented by purchase price per dry unit of active ingredient (Section 2.5). Active ingredients will include standard snow and ice control chemicals: NaCl, $MgCl_2$, $CaCl_2$, CMA, and KA.
- Performance will be represented by melting potential (Section 2.6), which is based on standard phase versus concentration data for standard active ingredients and on a user-supplied expected cold winter temperature (i.e., 85th percentile). Product-specific phase curve information will be required for non-standard chemicals such as blends.
- OMB materials are rated for environmental impact but are not included in performance assessments. If a performance assessment is desired, product-specific phase curve information will be required.
- Abrasives are rated for environmental impact, but are not included in performance assessments. Abrasives do not melt snow and ice.
- Users will complete an inventory of the most common and significant receptors that may be affected by snow and ice control materials (Section 2.4). The individual environmental impacts assigned to each chemical are subject to modification, pending new information.

The following examples demonstrate the process and results.

Table 2-21. Examples of melting potentials for standard commercial snow and ice control materials.

Temperature		NaCl		Ca Cl$_2$		Mg Cl$_2$		KAc		CMA	
		BC (%) = 23		BC (%) = 32		BC (%) = 30		BC (%) = 50		BC (%) = 25	
°F	°C	EC (%)	M P	EC (%)	M P	EC (%)	M P	EC (%)	M P	EC (%)	M P
30	-1.1	1.9	11.3	2.5	11.7	2.1	13.4	5.0	9.0	5.0	4.0
29	-1.7	2.8	7.2	3.7	7.7	3.0	8.9	6.0	7.3	6.0	3.2
28	-2.2	3.7	5.2	4.8	5.7	3.9	6.7	7.0	6.1	7.0	2.6
27	-2.8	4.6	4.0	5.7	4.6	4.7	5.4	8.0	5.3	8.0	2.1
26	-3.3	5.4	3.2	5.7	4.6	5.3	4.7	9.0	4.6	9.0	1.8
25	-3.9	6.3	2.7	6.4	4.0	6.0	4.0	10.0	4.0	10.0	1.5
24	-4.4	7.1	2.2	7.0	3.6	6.7	3.5	11.0	3.5	11.0	1.3
23	-5.0	7.9	1.9	8.0	3.0	7.3	3.1	12.0	3.2	11.9	1.1
22	-5.6	8.7	1.7	9.0	2.6	8.1	2.7	13.0	2.8	12.7	1.0
21	-6.1	9.4	1.4	9.5	2.4	8.6	2.5	13.5	2.7	13.5	0.9
20	-6.7	10.1	1.3	10.0	2.2	9.0	2.3	14.0	2.6	14.4	0.7
19	-7.2	10.8	1.1	10.5	2.0	9.5	2.2	15.0	2.3	15.0	0.7
18	-7.8	11.5	1.0	11.0	1.9	10.0	2.0	16.0	2.1	15.8	0.6
17	-8.3	12.2	0.9	11.5	1.8	10.4	1.9	16.5	2.0	16.5	0.5
16	-8.9	12.8	0.8	12.0	1.7	10.8	1.8	17.0	1.9	17.2	0.5
15	-9.4	13.4	0.7	12.5	1.6	11.1	1.7	17.5	1.9	17.7	0.4
14	-10.0	14.1	0.6	13.0	1.5	11.4	1.6	18.0	1.8	18.3	0.4
13	-10.6	14.6	0.6	13.5	1.4	11.9	1.5	19.0	1.6	18.8	0.3
12	-11.1	15.2	0.5	14.0	1.3	12.3	1.4	19.5	1.6	19.4	0.3
11	-11.7	15.8	0.5	14.5	1.2	12.7	1.4	20.0	1.5	19.9	0.3
10	-12.2	16.3	0.4	15.3	1.1	13.1	1.3	20.5	1.4	20.6	0.2
9	-12.8	16.8	0.4	15.6	1.1	13.4	1.2	21.0	1.4	21.3	0.2
8	-13.3	17.3	0.3	16.0	1.0	13.7	1.2	21.5	1.3	21.8	0.1
7	-13.9	17.9	0.3	16.3	1.0	13.9	1.2	22.0	1.3	22.3	0.1
6	-14.4	18.3	0.3	16.7	0.9	14.2	1.1	22.5	1.2	22.8	0.1
5	-15.0	18.8	0.2	17.0	0.9	14.5	1.1	23.0	1.2	23.3	0.1
4	-15.6	19.3	0.2	17.3	0.8	14.8	1.0	23.5	1.1	23.8	0.1
3	-16.1	19.7	0.2	17.8	0.8	15.2	1.0	24.0	1.1	24.3	0.0
2	-16.7	20.2	0.1	18.2	0.8	15.5	0.9	24.5	1.0	24.8	0.0
1	-17.2	20.6	0.1	18.5	0.7	15.8	0.9	25.0	1.0	NA	NA
0	-17.8	21.0	0.1	18.7	0.7	16.1	0.9	25.5	1.0	NA	NA
-1	-18.3	21.4	0.1	19.0	0.7	16.3	0.8	25.9	0.9	NA	NA
-2	-18.9	21.8	0.1	19.3	0.7	16.6	0.8	26.3	0.9	NA	NA
-3	-19.4	22.2	0.0	19.7	0.6	16.8	0.8	27.7	0.8	NA	NA
-4	-20.0	22.6	0.0	20.0	0.6	17.1	0.8	28.1	0.8	NA	NA
-5	-20.6	22.9	0.0	20.3	0.6	17.4	0.7	28.6	0.8	NA	NA
-6	-21.1	23.3	(0.0)	20.5	0.6	17.6	0.7	29.0	0.7	NA	NA
-7	-21.7	NA	NA	20.8	0.5	17.8	0.7	28.4	0.8	NA	NA
-8	-22.2	NA	NA	21.0	0.5	18.1	0.7	28.8	0.7	NA	NA
-9	-22.8	NA	NA	21.3	0.5	18.3	0.6	29.2	0.7	NA	NA
-10	-23.3	NA	NA	21.5	0.5	18.5	0.6	29.6	0.7	NA	NA
-11	-23.9	NA	NA	21.8	0.5	18.7	0.6	30.0	0.7	NA	NA
-12	-24.4	NA	NA	22.0	0.5	19.0	0.6	30.4	0.6	NA	NA
-13	-25.0	NA	NA	22.3	0.4	19.2	0.6	30.7	0.6	NA	NA
-14	-25.6	NA	NA	22.5	0.4	19.4	0.5	31.1	0.6	NA	NA
-15	-26.1	NA	NA	22.8	0.4	19.6	0.5	31.5	0.6	NA	NA
-16	-26.7	NA	NA	23.0	0.4	19.8	0.5	31.8	0.6	NA	NA
-17	-27.2	NA	NA	23.3	0.4	20.0	0.5	32.2	0.6	NA	NA
-18	-27.8	NA	NA	23.5	0.4	20.2	0.5	32.6	0.5	NA	NA
-19	-28.3	NA	NA	23.8	0.3	20.4	0.5	32.9	0.5	NA	NA
-20	-28.9	NA	NA	24.0	0.3	20.6	0.5	33.3	0.5	NA	NA

Table 2-21. Examples of melting potentials for standard commercial snow and ice control materials (Continued).

Temperature		NaCl		Ca Cl$_2$		Mg Cl$_2$		KAc		CMA	
		BC (%) = 23		BC (%) = 32		BC (%) = 30		BC (%) = 50		BC (%) = 25	
°F	°C	EC (%)	M P	EC (%)	M P	EC (%)	M P	EC (%)	M P	EC (%)	M P
-21	-29.4	NA	NA	24.2	0.3	20.8	0.4	33.6	0.5	NA	NA
-22	-30.0	NA	NA	24.4	0.3	20.9	0.4	34.0	0.5	NA	NA
-23	-30.6	NA	NA	24.6	0.3	21.1	0.4	34.3	0.5	NA	NA
-24	-31.1	NA	NA	24.8	0.3	21.6	0.4	34.7	0.4	NA	NA
-25	-31.7	NA	NA	25.0	0.3	22.0	0.4	35.0	0.4	NA	NA
-26	-32.2	NA	NA	25.2	0.3	NA	NA	35.3	0.4	NA	NA
-27	-32.8	NA	NA	25.3	0.3	NA	NA	35.7	0.4	NA	NA
-28	-33.3	NA	NA	25.5	0.3	NA	NA	36.0	0.4	NA	NA
-29	-33.9	NA	NA	25.7	0.2	NA	NA	36.3	0.4	NA	NA
-30	-34.4	NA	NA	25.8	0.2	NA	NA	36.7	0.4	NA	NA
-31	-35.0	NA	NA	26.0	0.2	NA	NA	37.0	0.4	NA	NA
-32	-35.6	NA	NA	26.2	0.2	NA	NA	37.3	0.3	NA	NA
-33	-36.1	NA	NA	26.3	0.2	NA	NA	37.7	0.3	NA	NA
-34	-36.7	NA	NA	26.5	0.2	NA	NA	38.0	0.3	NA	NA
-35	-37.2	NA	NA	26.6	0.2	NA	NA	38.3	0.3	NA	NA
-36	-37.8	NA	NA	26.8	0.2	NA	NA	38.7	0.3	NA	NA
-37	-38.3	NA	NA	26.9	0.2	NA	NA	39.0	0.3	NA	NA
-38	-38.9	NA	NA	27.1	0.2	NA	NA	39.3	0.3	NA	NA
-39	-39.4	NA	NA	27.2	0.2	NA	NA	39.7	0.3	NA	NA
-40	-40.0	NA	NA	27.4	0.2	NA	NA	40.0	0.3	NA	NA
-41	-40.6	NA	NA	27.5	0.2	NA	NA	40.3	0.2	NA	NA
-42	-41.1	NA	NA	27.6	0.2	NA	NA	40.6	0.2	NA	NA
-43	-41.7	NA	NA	27.8	0.2	NA	NA	40.9	0.2	NA	NA
-44	-42.2	NA	NA	27.9	0.1	NA	NA	41.3	0.2	NA	NA
-45	-42.8	NA	NA	28.1	0.1	NA	NA	41.6	0.2	NA	NA
-46	-43.3	NA	NA	28.2	0.1	NA	NA	41.9	0.2	NA	NA
-47	-43.9	NA	NA	28.3	0.1	NA	NA	42.2	0.2	NA	NA
-48	-44.4	NA	NA	28.4	0.1	NA	NA	42.5	0.2	NA	NA
-49	-45.0	NA	NA	28.6	0.1	NA	NA	42.8	0.2	NA	NA
-50	-45.6	NA	NA	28.7	0.1	NA	NA	43.1	0.2	NA	NA
-51	-46.1	NA	NA	28.7	0.1	NA	NA	43.4	0.2	NA	NA
-52	-46.7	NA	NA	28.8	0.1	NA	NA	43.8	0.1	NA	NA
-53	-47.2	NA	NA	28.9	0.1	NA	NA	44.1	0.1	NA	NA
-54	-47.8	NA	NA	29.1	0.1	NA	NA	44.4	0.1	NA	NA
-55	-48.3	NA	NA	29.2	0.1	NA	NA	44.7	0.1	NA	NA
-56	-48.9	NA	NA	29.3	0.1	NA	NA	45.0	0.1	NA	NA
-57	-49.4	NA	NA	29.4	0.1	NA	NA	45.3	0.1	NA	NA
-58	-50.0	NA	NA	29.5	0.1	NA	NA	45.5	0.1	NA	NA
-59	-50.6	NA	NA	29.6	0.1	NA	NA	45.8	0.1	NA	NA
-60	-51.1	NA	NA	NA	NA	NA	NA	46.0	0.1	NA	NA
-61	-51.7	NA	NA	NA	NA	NA	NA	46.3	0.1	NA	NA
-62	-52.2	NA	NA	NA	NA	NA	NA	46.5	0.1	NA	NA
-63	-52.8	NA	NA	NA	NA	NA	NA	46.8	0.1	NA	NA
-64	-53.3	NA	NA	NA	NA	NA	NA	47.0	0.1	NA	NA
-65	-53.9	NA	NA	NA	NA	NA	NA	47.3	0.1	NA	NA
-66	-54.4	NA	NA	NA	NA	NA	NA	47.5	0.1	NA	NA
-67	-55.0	NA	NA	NA	NA	NA	NA	47.8	0.0	NA	NA
-68	-55.6	NA	NA	NA	NA	NA	NA	48.0	0.0	NA	NA
-69	-56.1	NA	NA	NA	NA	NA	NA	48.3	0.0	NA	NA
-70	-56.7	NA	NA	NA	NA	NA	NA	48.5	0.0	NA	NA

Table 2-22. Three example agency policy weightings.

Decision Category	Example 1 (Section 2.7.1.1) **Survey Objective Weighting**	Example 2 (Section 2.7.1.2) **Equal Objective Weighting**	Example 3 (Section 2.7.1.3) **Environment Infrastructure Priority**
Purchase Price	45 %	25 %	0 %
Performance[1]	35 %	25 %	25 %
Environment	11 %	25 %	37.5 %
Infrastructure	9 %	25 %	37.5 %

[1] Given that the primary objective of winter maintenance is controlling snow and ice, it is recommended that performance weighting not be assigned a value below 25%

Table 2-23. Example subcategory weightings.

Decision Category	Decision Subcategory	Survey Weightings
Environment	Aquatic Life[1, 2]	20 %
	Drinking Water[1]	20 %
	Air Quality	27 %
	Vegetation	20 %
	Soil	0 %
	Animals	13 %
Infrastructure	Vehicles	22 %
	Metal Infrastructure	28 %
	Concrete	20 %
	Concrete Reinforcing	30 %

[1] Agency survey addressed water quality in its entirety and did not differentiate between aquatic life and drinking water concerns. For this demonstration, equal weighting was assigned to each category.

[2] This example is based on average responses for the survey conducted in Phase I of this study. In practice, it is recommended that aquatic life weighting not be assigned a value below 25%.

This section provides three examples with differing policy objectives to demonstrate the decision tool (Table 2-22). Example 1 shows agency priorities determined from the agency survey conducted during Phase I of this study. The values represent current averaged priorities in North America. Example 2 shows equal priorities for all decision categories. Example 3 describes where environmental and infrastructure concerns are highest. A practical example may include a steel bridge with reinforced concrete decking over a sensitive wetland. Agency subcategory weightings for environment and infrastructure are based on agency survey results and will remain constant for the three examples (Table 2-23). The following conditions are also assumed for each of the three example assessments:

- Anti-icing is the selected snow and ice control strategy.
- Pricing and concentration have been obtained for all standard snow and ice control products. The price values used are semi-realistic examples obtained from contracts published on the Internet.
- Cost and performance are summed into an "Economic Objective."
- Given that temperature influences melting potential, assessments have been conducted over temperatures ranging from 30 to –20°F.
- Environmental and infrastructure potentials for impairment are based on the maintenance area inventory conditions represented in Tables 2-24 through 2-33.

The decision tool provides a numerical product score that combines user priorities and conditions with a technical assessment of potentials for impairment. Higher scores represent preferred products, but it is not necessary that an agency select the highest ranked product.

Some materials have similar properties under certain conditions and scores may have similar orders of magnitude. In such cases, considerations such as the following may influence product selection:

- Quality-testing results compared with purchase specifications;

Table 2-24. Aquatic life—material/receptor potential for impairment worksheet.

Aquatic Life Conditions	Exists? (Y/N)	NaCl	$MgCl_2$	$CaCl_2$	CMA	KA	OMB	Abrasives
Small stream with coarse substrate	Y	4	4	4	2	2	1	1
Small stream with fine substrate	N	4	4	4	2	2	1	5
Intermediate stream with coarse substrate	N	5	5	5	3	3	2	1
Intermediate stream with fine substrate	N	5	5	5	3	3	2	5
Large stream with coarse substrate	N	5	5	5	4	4	3	3
Large stream with fine substrate	N	5	5	5	4	4	3	5
Wetland, nutrient poor	N	3	3	3	3	3	1	1
Wetland, nutrient rich	N	3	3	3	3	3	3	1
Small lake, nutrient poor	Y	2	2	2	3	3	1	5
Small lake, nutrient rich	N	2	2	2	4	4	3	5
Intermediate lake, nutrient poor	N	4	4	4	4	4	1	5
Intermediate lake, nutrient rich	N	4	4	4	5	5	4	5
Large lake, nutrient poor	N	5	5	5	5	5	3	5
Large lake, nutrient rich	N	5	5	5	5	5	5	5
Sum of Selected Conditions		6	6	6	5	5	2	6
Average of Selected Conditions		3	3	3	2.5	2.5	1	3

Definition of terms:

- **Stream Size***: small stream*: average width of water surface less than 10 yards under winter flow conditions; *intermediate stream*: 10 to 30 yards*; large stream*: greater than 30 yards.
- **Lake Size**: *small lake*: < 10 acres; *intermediate lake*: 10 to 100 acres; *large lake*: > 100 acres.
- **Wetland**: aquatic body not defined as a lake or stream, i.e. marsh, ponds, etc.
- **Substrate**: *coarse substrate*: boulder, cobble, gravel; *fine substrate*: sand, clay, muck.
- **Nutrient Levels**: *nutrient poor*: total P below 15 μg/L, total N below 300 μg/L; *nutrient rich*: > 15 μg/L P, >300 μg/L N.

Table 2-25. Drinking water from groundwater—material/receptor potential for impairment worksheet.

Drinking Water Conditions	Exists? (Y/N)	NaCl	$MgCl_2$	$CaCl_2$	CMA	KA	OMB	Abrasives
Shallow ground water used for drinking	Y	3	5	5	4	4	3	5
Sum of Selected Conditions								
Average of Selected Conditions		3	5	5	4	4	3	5

Table 2-26. Air quality—material/receptor potential for impairment worksheet.

Air Quality Conditions	Exists? (Y/N)	NaCl	$MgCl_2$	$CaCl_2$	CMA	KA	OMB	Abrasives
Existing air quality concerns relevant to particulate matter (i.e. non-attainment area)	Y	5	5	5	5	5	5	1
Poor air dispersion, closed air shed	Y	5	5	5	5	5	5	1
Sum of Selected Conditions		10	10	10	10	10	10	2
Average of Selected Conditions		5	5	5	5	5	5	1

Table 2-27. Vegetation—material/receptor potential for impairment worksheet.

Vegetation Conditions	Exists? (Y/N)	NaCl	$MgCl_2$	$CaCl_2$	CMA	KA	OMB	Abrasives
Agricultural lands within 10m of the roadway	Y	1	2	2	4	4	5	4
Protected vegetation within 10m of the roadway	N	1	2	2	4	4	5	4
Aesthetic objectives within 10m of the roadway	Y	1	2	2	4	4	5	4
Sum of Selected Conditions		2	4	4	8	8	10	8
Average of Selected Conditions		1	2	2	4	4	5	4

Table 2-28. Soil quality—material/receptor potential for impairment worksheet.

Soil Quality Conditions	Exists? (Y/N)	NaCl	$MgCl_2$	$CaCl_2$	CMA	KA	OMB	Abrasives
Poor soil structure within 10m of the roadway[1]	N	2	5	5	5	5	5	5
Sum of Selected Conditions								
Average of Selected Conditions		5	5	5	5	5	5	5

[1] Exchangeable Sodium Percentage (ESP) >13

Table 2-29. Terrestrial fauna—material/receptor potential for impairment worksheet.

Animal Conditions	Exists? (Y/N)	NaCl	$MgCl_2$	$CaCl_2$	CMA	KA	OMB	Abrasives
Potential for effects on terrestrial species [1]	N	4	4	4	5	5	5	5
Roadkill for mammals or birds is a concern	N	4	4	4	5	5	5	5
Sum of Selected Conditions								
Average of Selected Conditions		5	5	5	5	5	5	5

[1] Includes sensitive mammals, birds, amphibians, reptiles, insects, spiders, etc.

Table 2-30. Vehicles—material/receptor potential for impairment worksheet.

Vehicles	Exists? (Y/N)	NaCl	$MgCl_2$	$CaCl_2$	CMA	KA	OMB	Abrasives
Vehicles	Y	1	1	1	4	4	5	1
Sum of Selected Conditions		1	1	1	4	4	5	1
Average of Selected Conditions		1	1	1	4	4	5	1

Table 2-31. Metal infrastructure—material/receptor potential for impairment worksheet.

Metal Infrastructure Conditions	Exists? (Y/N)	NaCl	$MgCl_2$	$CaCl_2$	CMA	KA	OMB	Abrasives
Steel Bridges	Y	1	1	1	4	4	5	5
Other metal infrastructure of concern	Y	1	1	1	4	4	5	5
Sum of Selected Conditions		2	2	2	8	8	10	10
Average of Selected Conditions		1	1	1	4	4	5	5

Table 2-32. Concrete matrix—material/receptor potential for impairment worksheet.

Concrete Degradation	Exists? (Y/N)	NaCl	$MgCl_2$	$CaCl_2$	CMA	KA	OMB	Abrasives
Concrete pavement and structures	Y	4	3	3	3	4	5	5
Sum of Selected Conditions		4	3	3	3	4	5	5
Average of Selected Conditions		4	3	3	3	4	5	5

Table 2-33. Concrete reinforcing—material/receptor potential for impairment worksheet.

Concrete Reinforcing	Exists? (Y/N)	NaCl	$MgCl_2$	$CaCl_2$	CMA	KA	OMB	Abrasives
Reinforcing Steel Bar	Y	1	1	1	5	5	5	5
Sum of Selected Conditions		1	1	1	5	5	5	5
Average of Selected Conditions		1	1	1	5	5	5	5

- Customer service (e.g., product availability and delivery times); and
- Other performance concerns (e.g., roadway slickness and equipment compatibility).

2.7.1.1 Decision Tool Example 1—Survey Priorities

The calculation spreadsheet for this case is provided as Table 2-34; temperature-dependent scoring is shown in Figure 2-3. Based on the selected conditions, NaCl is the preferred product between 32 and 12°F, after which $MgCl_2$ and $CaCl_2$ are preferred.

2.7.1.2 Decision Tool Example 2—Equal Priorities

The calculation spreadsheet for this case is provided as Table 2-35; temperature-dependent scoring is shown in Figure 2-4. Based on the selected conditions, NaCl is the pre-

Table 2-34. Decision tool example 1—survey.

A) Economic Weighting:	**Purchase Price:**	**45%**			
	Performance:	**35%**			
	Temperature (F):	**15**			
Material Information Parameters	**NaCl**	**CaCl2**	**MgCl2**	**KA**	**CMA**
Input Purchase Price per ton =	$ 50.00	$ 130.00	$ 120.00	$ 1,000.00	$ 1,150.00
Input Material Concentration (%) =	23	30	28	50	25
Purchase Price per dry pound ($/lb)	$ 0.11	$ 0.22	$ 0.21	$ 1.00	$ 2.30
Melting Potential (MP)	0.9	1.4	1.5	1.9	0.4
(MP)/(Purchase Price/lb)	7.9	6.5	7.1	1.9	0.2
A) Weighted "Economic" Score	**80.0**	**65.7**	**72.3**	**18.9**	**1.8**

B) Environmental Weighting:		**11%**				
		NaCl	**CaCl2**	**MgCl2**	**KA**	**CMA**
Operational Objectives (Maximum 100)		**Potential For Impairment (1=High, 5=Low)**				
Aquatic Life	20%	3	3	3	2.5	2.5
Drinking Water	20%	3	5	5	4	4
Air Quality	27%	5	5	5	5	5
Vegetation	20%	1	2	2	4	4
Soil	0%	5	5	5	5	5
Animals	13%	5	5	5	5	5
TOTAL SCORE		3.4	4.0	4.0	4.1	4.1
MAX SCORE		5.0	5.0	5.0	5.0	5.0
B) Weighted "Environment" Score		**7.5**	**8.8**	**8.8**	**9.0**	**9.0**

C) Infrastructure Weighting:		**9%**				
		NaCl	**CaCl2**	**MgCl2**	**KA**	**CMA**
Operational Objectives (Maximum 100)		**Potential For Impairment (1=High, 5=Low)**				
Vehicles	22%	1	1	1	4	4
Metal Infrastructure	28%	1	1	1	4	4
Concrete	20%	4	3	3	**3**	4
Concrete Reinforcing	30%	1	1	1	5	5
TOTAL SCORE		1.6	1.4	1.4	4.1	4.3
MAX SCORE		5.0	5.0	5.0	5.0	5.0
C) Weighted "Infrastructure" Score		**2.9**	**2.5**	**2.5**	**7.4**	**7.7**

Final Material Scores					
	NaCl	**CaCl2**	**MgCl2**	**KA**	**CMA**
Final Material Scores = A) + B) + C)	**90.4**	**77.0**	**83.6**	**35.3**	**18.5**

Temperature (F)	Final Product Scores Based on Temperature				
	NaCl	CaCl2	MgCl2	KA	CMA
30	90.4	64.8	71.1	23.9	18.2
25	90.4	76.1	76.4	31.6	19.2
20	90.4	68.8	72.7	32.4	18.8
15	90.4	77.0	83.6	35.3	18.6
10	80.8	78.2	91.3	38.1	18.2
5	57.4	76.3	91.3	38.0	17.3
0	39.3	76.0	91.3	38.7	TOO COLD
-5	12.6	73.5	91.3	37.4	TOO COLD
-10	TOO COLD	72.3	91.3	39.5	TOO COLD
-15	TOO COLD	70.0	91.3	39.9	TOO COLD
-20	TOO COLD	66.0	91.3	40.2	TOO COLD

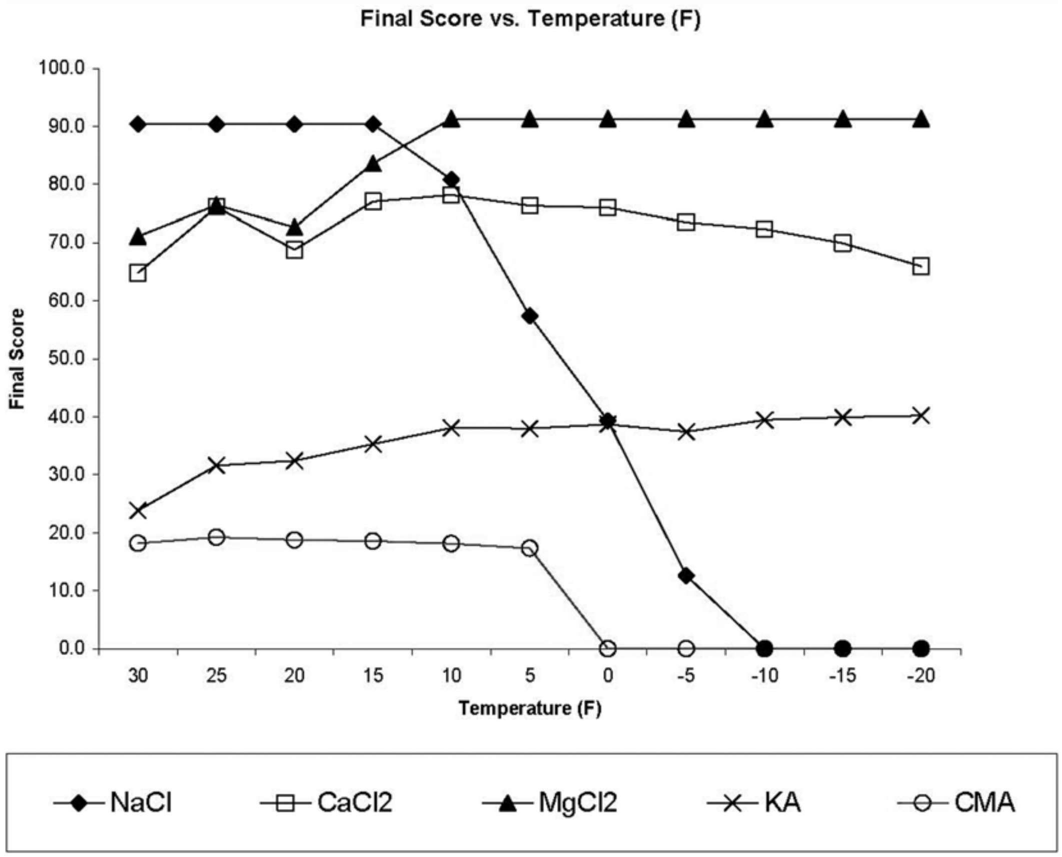

Figure 2-3. Decision tool example 1—survey priorities.

Table 2-35. Decision tool example 2—equal priorities.

A) Economic Weighting:	**Purchase Price:**		**25%**		
	Performance:		**25%**		
	Temperature (F):		**15**		
Material Information Parameters	**NaCl**	**CaCl2**	**MgCl2**	**KA**	**CMA**
Input Purchase Price per ton =	$ 50.00	$ 130.00	$ 120.00	$ 1,000.00	$ 1,150.00
Input Material Concentration (%) =	23	30	28	50	25
Purchase Price per dry pound ($/lb)	$ 0.11	$ 0.22	$ 0.21	$ 1.00	$ 2.30
Melting Potential (MP)	0.85	1.40	1.52	1.86	0.41
(MP)/(Purchase Price/lb)	7.86	6.46	7.11	1.86	0.18
A) Weighted "Economic" Score	**50.0**	**41.1**	**45.2**	**11.8**	**1.1**

B) Environmental Weighting:		**25%**				
		NaCl	**CaCl2**	**MgCl2**	**KA**	**CMA**
Operational Objectives (Maximum 100)		**Potential For Impairment (1=High, 5=Low)**				
Aquatic Life	20%	3	3	3	2.5	2.5
Drinking Water	20%	3	5	5	4	4
Air Quality	27%	5	5	5	5	5
Vegetation	20%	1	2	2	4	4
Soil	0%	5	5	5	5	5
Animals	13%	5	5	5	5	5
TOTAL SCORE		3.4	4.0	4.0	4.1	4.1
MAX SCORE		5.0	5.0	5.0	5.0	5.0
B) Weighted "Environment" Score		**17.0**	**20.0**	**20.0**	**20.5**	**20.5**

C) Infrastructure Weighting:		**25%**				
		NaCl	**CaCl2**	**MgCl2**	**KA**	**CMA**
Operational Objectives (Maximum 100)		**Potential For Impairment (1=High, 5=Low)**				
Vehicles	22%	1	1	1	4	4
Metal Infrastructure	28%	1	1	1	4	4
Concrete	20%	4	3	3	**3**	4
Concrete Reinforcing	30%	1	1	1	5	5
TOTAL SCORE		1.6	1.4	1.4	4.1	4.3
MAX SCORE		5.0	5.0	5.0	5.0	5.0
C) Weighted "Infrastructure" Score		**8.0**	**7.0**	**7.0**	**20.5**	**21.5**

Final Material Scores					
	NaCl	**CaCl2**	**MgCl2**	**KA**	**CMA**
Final Material Scores = A) + B) + C)	**75.0**	**68.1**	**72.2**	**52.8**	**43.1**

Temperature (F)	Final Product Scores Based on Temperature				
	NaCl	CaCl2	MgCl2	KA	CMA
30	75.0	60.4	64.4	45.7	42.9
25	75.0	67.5	67.7	50.5	43.6
20	75.0	62.9	65.4	51.0	43.2
15	75.0	68.1	72.2	52.8	43.1
10	69.0	68.8	77.0	54.6	42.9
5	54.4	67.6	77.0	54.5	42.4
0	43.1	67.4	77.0	54.9	TOO COLD
-5	26.4	65.8	77.0	54.1	TOO COLD
-10	TOO COLD	65.1	77.0	55.4	TOO COLD
-15	TOO COLD	63.6	77.0	55.7	TOO COLD
-20	TOO COLD	61.2	77.0	55.9	TOO COLD

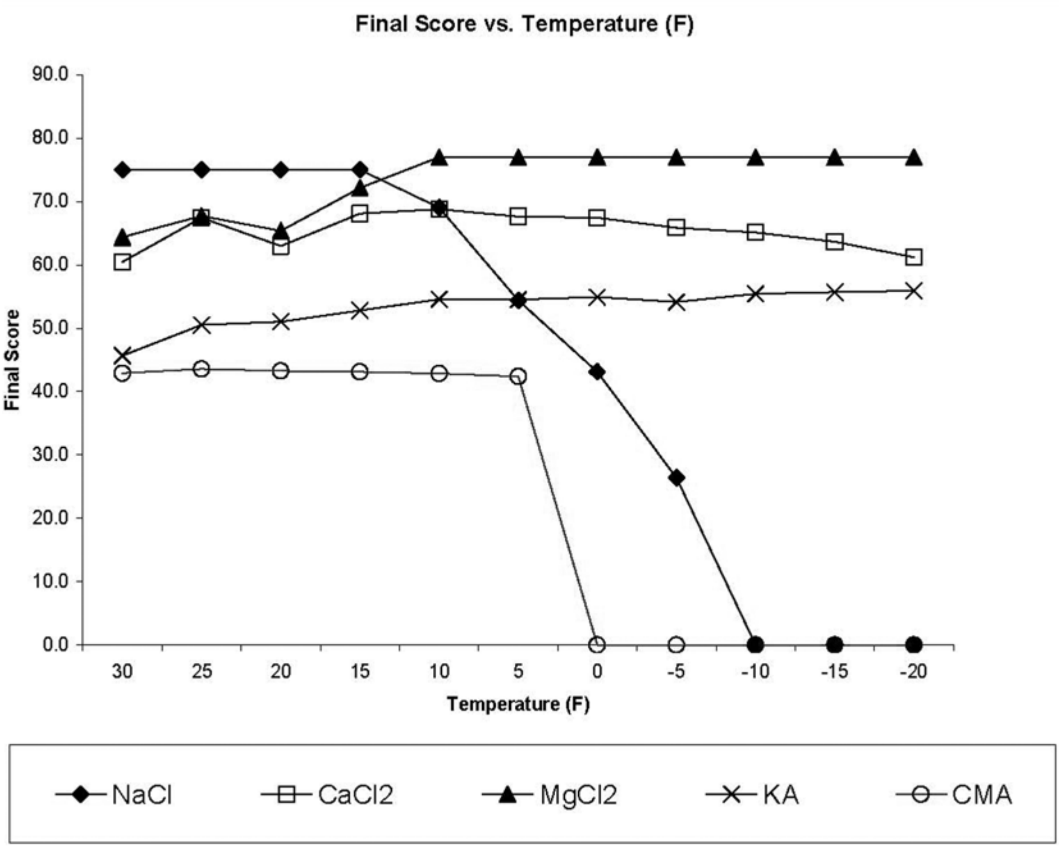

Figure 2-4. Decision tool example 2—equal priorities.

ferred product between 32 and 12°F, after which $MgCl_2$ and $CaCl_2$ are preferred.

2.7.1.3 Decision Tool Example 3—Environment/ Infrastructure Priorities

The calculation spreadsheet for this case is provided as Table 2-36; temperature-dependent scoring is shown in Figure 2-5. Based on the selected conditions, all materials have similar scores until temperatures reach below 10°F and NaCl and CMA lose performance benefits. Although KA is the preferred product, CMA also scores well at warmer temperatures.

2.8 Software

A software program was developed to assist users with applying the snow and ice control material decision tool. The software was written in "C+" programming language using Microsoft Visual Studio and requires a personal computer installed with Microsoft Windows 2000, Windows XP, or later

Table 2-36. Decision tool example 3—environmental and infrastructure priority objectives.

A) Economic Weighting:	**Purchase Price:**		**0%**		
	Performance:		**25%**		
	Temperature (F):		**15**		
Material Information Parameters	**NaCl**	**CaCl2**	**MgCl2**	**KA**	**CMA**
Input Purchase Price per ton =	$ 50.00	$ 130.00	$ 120.00	$ 1,000.00	$ 1,150.00
Input Material Concentration (%) =	23	30	28	50	25
Purchase Price per dry pound ($/lb)	$ 0.11	$ 0.22	$ 0.21	$ 1.00	$ 2.30
Melting Potential (MP)	0.85	1.40	1.52	1.86	0.41
(MP)/(Purchase Price/lb)	7.86	6.46	7.11	1.86	0.18
A) Weighted "Economic" Score	**25.0**	**20.5**	**22.6**	**5.9**	**0.6**

B) Environmental Weighting:		**37.5%**				
		NaCl	**CaCl2**	**MgCl2**	**KA**	**CMA**
Operational Objectives (Maximum 100)		**Potential For Impairment (1=High, 5=Low)**				
Aquatic Life	20%	3	3	3	2.5	2.5
Drinking Water	20%	3	5	5	4	4
Air Quality	27%	5	5	5	5	5
Vegetation	20%	1	2	2	4	4
Soil	0%	5	5	5	5	5
Animals	13%	5	5	5	5	5
	TOTAL SCORE	3.4	4.0	4.0	4.1	4.1
	MAX SCORE	5.0	5.0	5.0	5.0	5.0
	B) Weighted "Environment" Score	**25.5**	**30.0**	**30.0**	**30.8**	**30.8**

C) Infrastructure Weighting:		**37.5%**				
		NaCl	**CaCl2**	**MgCl2**	**KA**	**CMA**
Operational Objectives (Maximum 100)		**Potential For Impairment (1=High, 5=Low)**				
Vehicles	22%	1	1	1	4	4
Metal Infrastructure	28%	1	1	1	4	4
Concrete	20%	4	3	3	**3**	4
Concrete Reinforcing	30%	1	1	1	5	5
	TOTAL SCORE	1.6	1.4	1.4	4.1	4.3
	MAX SCORE	5.0	5.0	5.0	5.0	5.0
	C) Weighted "Infrastructure" Score	**12.0**	**10.5**	**10.5**	**30.8**	**32.3**

Final Material Scores					
	NaCl	**CaCl2**	**MgCl2**	**KA**	**CMA**
Final Material Scores = A) + B) + C)	**62.5**	**61.0**	**63.1**	**67.5**	**63.7**

	Final Product Scores Based on Temperature				
Temperature (F)	NaCl	CaCl2	MgCl2	KA	CMA
30	62.5	57.2	59.2	63.8	63.5
25	62.5	60.7	60.8	66.3	63.8
20	62.5	58.5	59.7	66.5	63.6
15	62.5	61.0	63.1	67.4	63.6
10	59.5	61.4	65.5	68.3	63.4
5	52.2	60.8	65.5	68.3	63.2
0	46.6	60.7	65.5	68.5	TOO COLD
-5	38.2	59.9	65.5	68.1	TOO COLD
-10	TOO COLD	59.6	65.5	68.7	TOO COLD
-15	TOO COLD	58.8	65.5	68.8	TOO COLD
-20	TOO COLD	57.6	65.5	68.9	TOO COLD

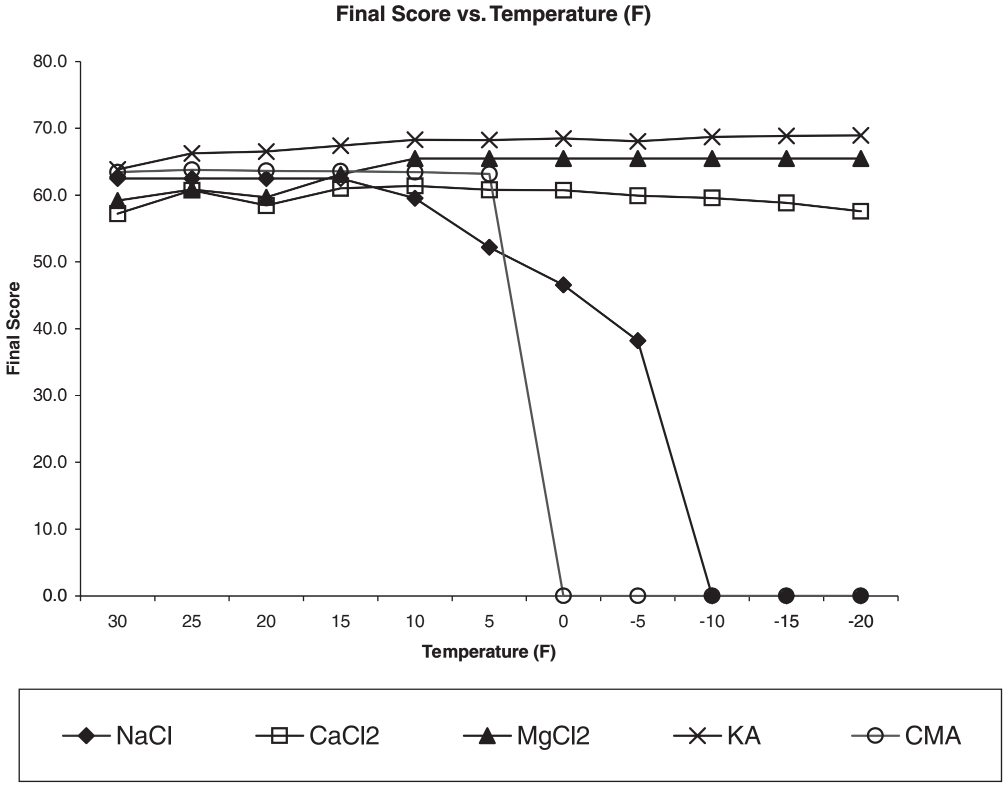

Figure 2-5. Decision tool example 3—environmental and infrastructure priority objectives.

operating systems. Some systems may require installation of Microsoft.NET runtime (available from Microsoft).

The software follows a "wizard-type" format and prompts users to populate fields with key agency and maintenance area information. Measures are built in to address inappropriate or insufficient information. The result is a numerical product score, based on input information, that can be printed on a summary report with the input information.

Appendix A, which is available for download from the TRB website, shows screen captures from the Decision Tool software program. User instructions are included on each page.

CHAPTER 3

Purchase Specification

This purchase specification is one of the steps in the snow and ice control material selection process developed through NCHRP Project 06-16. Its purpose is to assist transportation agencies with mitigating impacts to the natural environment by allowing the user to qualify and compare snow and ice control materials based on key environmental attributes. By establishing recommended material acceptance criteria, transportation agencies can screen unsuitable products. The purchase specification is to be applied after the agency has completed the NCHRP 06-16 decision tool and a snow and ice control material type has been selected for use.

Aquatic systems are the primary environmental concern associated with snow and ice control materials. The purchase specification focuses on snow and ice control material chemical attributes that can impair aquatic systems under normal use but are not addressed through the decision tool. In the overall material selection process, the decision tool addresses primary components and attributes (e.g., chlorides, cations, and organic matter from biomass), whereas the purchase specification addresses secondary components and attributes (e.g., heavy metals, nutrients, and cyanide) (refer to Table 2-3).

Existing U.S. EPA aquatic life and drinking water quality criteria are used to establish guidelines for maximum acceptable concentrations (i.e., specification limits) for snow and ice control material chemical attributes. The chemical attributes selected for assessment are easily measured using standard environmental test methods. Guidance is also provided should the agency wish to develop specifications independently for physical, toxicity, and corrosion properties of snow and ice control materials. Areas for consideration and associated test methods are referenced; however, no numerical criteria have been recommended.

Most transportation agencies have formal purchasing policies and documents in place that specify purchasing terms and conditions. This purchase specification was developed based on a comprehensive technical assessment of environmental impacts associated with snow and ice control materials and should be used to supplement existing agency purchasing policies and documents.

3.1 Chemical Specifications

Numerical criteria specific to snow and ice control materials have been established based on

- U.S. EPA numerical water quality criteria for the protection of aquatic life and drinking water (based on EPA National Recommended Water Quality Criteria: 2002, EPA-822-R-02-047, November 2002);
- Site-specific factors, specifically receiving water type, size, and current nutrient levels; and
- The default value for expected roadway runoff dilution, which is estimated to be 500 times at the point the materials leave the roadway—this may be adjusted to reflect any other assumed or measured dilution factor.

Table 3-1 lists current U.S. EPA criteria for potential chemical toxins and nutrients of general concern in snow and ice control materials. These attributes were developed based on an information assessment conducted through Phase I of this study. Other potential toxins not listed in the table may be found under unusual circumstances and may be considered in addition to those in the table. Table 3-1 includes chronic and acute criteria for the protection of freshwater aquatic life and drinking water criteria. For metal species affected by hardness, criteria have been provided for hardness values of 100 mg/L and 400 mg/L.

The Guidelines for Maximum Concentrations (GMCs) of constituents in snow and ice control materials are listed in Table 3-2. These concentrations were derived assuming that the concentrated snow and ice control materials are diluted 500 times at the point these materials leave the roadway.

Table 3-1. USEPA criteria used in calculation of guidelines for maximum concentrations for chemical constituents of concern in snow and ice control materials. Criteria are subject to change with USEPA criteria.

Chemical	Chemical Symbol	Freshwater Aquatic Life[3]		Drinking Water, µg/L[6]
		Acute, µg/L	Chronic, µg/L	
Arsenic	As	340	150[9]	10
Cadmium[1]	Cd	3	0.25	5
Cadmium[2]	Cd	13	9.6	-
Chromium (III)	Cr (III)	570	74	100
Chromium (IV)	Cr (IV)	16	11	100
Copper[1]	Cu	13	9	-
Copper[2]	Cu	50	29	-
Lead[1]	Pb	65	2.5	15
Lead[2]	Pb	280	11	-
Mercury	Hg	1.4	0.77[9]	2
Nickel[1]	Ni	470	52	-
Nickel [2]	Ni	1520	170	-
Selenium	Se	(25)[7]	5	-
Silver[1]	Ag	3.2	(0.64) [8]	-
Silver[2]	Ag	35	(7) [8]	-
Zinc[1]	Zn	117	118	-
Zinc[2]	Zn	379	382	-
Cyanide (Free)	CN	22	5.2	140
Ammonia (Total)[4]	NH_3	30,000	6000	-
Phosphorus (Total)[5]	P	15	7.0	-
Nitrogen (Total)[5]	N	300	150	-

[1] Criterion is dependent on hardness; the value shown here is for a hardness of 100 mg/L.

[2] Criterion is dependent on hardness; the value shown here is for a hardness of 400 mg/L

[3] Concentrations are the potentially dissolved forms, except as noted. Source: http://www.epa.gov.

[4] At pH 7.5, 5°C.

[5] National criteria vary by region; see text for basis.

[6] No value is shown for constituents having more restrictive limits for protection of aquatic life; metals are as total for drinking water.

[7] Acute value for selenium does not exist. Reported value estimated as 5 times the chronic value.

[8] Chronic value for silver does not exist. Reported value estimated as 1/5th the acute value.

[9] Routine consumption of fish taken from an affected site would reduce the limit to approximately 0.001 times the indicated chronic value.

'‑' denotes not applicable

Where this is not valid, the numbers could be adjusted accordingly. Furthermore, GMC values assume that no lethal or chronic effects will be allowed to extend beyond the margin of the roadway. Small extensions beyond the roadway might allow considerably more dilution and could be judged reasonable on a site-specific basis.

The subsequent text describes the basis for the development of the GMC values. Three general categories exist according to type of snow and ice control material.

1. The first category includes chemical products with a calcium or magnesium base (i.e., with calcium or magnesium as major ingredients and not as incidental contaminants: $MgCl_2$, $CaCl_2$, CMA). Calcium and magnesium are the two components of hardness for water. Concentration limits (i.e., aquatic life criteria) for certain metals (i.e., Cd, Cu, Pb, Ni, Ag, and Zn) likely to be found in snow and ice control materials depend on hardness. The presence of calcium and magnesium in solution (i.e., hardness) reduces the relative toxicity of a given concentration of any one of these metals. Therefore, the maximum allowable concentrations for these metals are highest when calcium and magnesium are major components of ice and snow control materials.
2. A second category applies to snow and ice control chemicals that contain neither calcium nor magnesium as major constituents (i.e., NaCl, KA, agriculturally derived organic materials). Such products lack any hardness-inducing component in large quantities, which requires more restrictive limits for metals whose toxicity is affected by hardness.
3. The third category of snow and ice control materials in the table is abrasives. These materials are not soluble, but may contain contaminants that are soluble. Abrasives obtained from industrial processes (e.g., metallurgical slag, mining waste, and furnace slag.) can contain high toxicant levels. Table 3-2 reflects the assumption that abrasives to be tested will be leached in pH-adjusted (i.e., acidic) water according to U.S. EPA Method 1311, Toxicity Characteristic Leaching Procedure (Revision 0, July 1992), which incorporates a liquid-to-solid ratio of 20:1 (50 grams abrasive plus 1 liter extraction fluid).

Table 3-2 Guidelines for Maximum Concentrations (GMCs) of potential toxins and nutrients present in snow and ice control materials consistent with the protection of aquatic life and use of untreated ground water for drinking by humans.

	Maximum Allowable Potentially Dissolved Metals and Metalloids, mg/L										Other Inorganics		Nutrients	
Category of Material and Environmental Context	As	Cd	Cr[4]	Cu	Pb	Hg[1]	Ni	Se	Ag[1]	Zn	Free CN, mg/L	[2]Total NH_3, mg/L	Total P, mg/L	[2]Total N, mg/L
Chemical with Ca or Mg base:														
$MgCl_2$, $CaCl_2$, CMA - Liquid chemical or 25% w/w solid solution														
Low nutrient small stream, wetland, pond, or small lake	75	4.8	5.5	15	5.5	0.39	84	2.5	3.5	190	2.6	3000	3.5	75
High nutrient small stream, wetland, pond, or small lake	75	4.8	5.5	15	5.5	0.39	84	2.5	3.5	190	2.6	3000	3.5	75
Low nutrient large or intermediate stream, lake, or wetland	170	6.6	8.0	24	140	0.70	760	13	18	190	11	15000	7.5	150
High nutrient large or intermediate stream, lake, or wetland	170	6.6	8.0	24	140	0.70	760	13	18	190	11	15000	7.5	150
Drinking water wells near roadway[3]	5	2.5	50	-	7.5	1.0	-	-	-	-	70	-	-	-
Chemical lacking Mg or Ca base:														
NaCl, KA - Liquid chemical or 25% w/w solid solution														
Low nutrient small stream, wetland, pond, or small lake	75	0.13	5.5	4.5	1.3	0.39	26	2.5	0.32	59	2.6	3000	3.5	75
High nutrient small stream, wetland, pond, or small lake	75	0.13	5.5	4.5	1.3	0.39	26	2.5	0.32	59	2.6	3000	3.5	75
Low nutrient large or intermediate stream, lake, or wetland	170	1.5	8.0	6.7	32	0.70	235	13	1.6	59	11	15000	7.5	150
High nutrient large or intermediate stream, lake, or wetland	170	1.5	8.0	6.7	32	0.70	235	13	1.6	59	11	15000	7.5	150
Drinking water wells near roadway[3]	5	2.5	50	-	7.5	1.0	-	-	-	-	70	-	-	-
Abrasive Leachate:														
1:20 w/v leachate per EPA 1311 (TCLP)														
Low nutrient small stream, wetland, pond, or small lake	0.75	0.0013	0.055	0.045	0.013	0.004	0.26	0.025	0.0032	0.59	0.026	30	0.035	0.75
High nutrient small stream, wetland, pond, or small lake	0.75	0.0013	0.055	0.045	0.013	0.004	0.26	0.025	0.0032	0.59	0.026	30	0.0.35	0.75
Low nutrient large or intermediate stream, lake, or wetland	1.7	0.015	0.080	0.067	0.32	0.007	2.4	0.13	0.016	0.59	0.11	150	0.075	1.5
High nutrient large or intermediate stream, lake, or wetland	1.7	0.015	0.080	0.067	0.32	0.007	2.4	0.13	0.016	0.59	0.11	150	0.075	1.5
Drinking water wells near roadway[3]	0.05	0.025	0.50	-	0.075	0.010	-	-	-	-	0.70	-	-	-

[1] Fish ingestion by humans will require much lower limits.

[2] Note that ammonia limits (based on toxicity) will be overridden by total N limits (based on nutrient effects).

[3] Total for metals and metalloids.

[4] Values based on hexavalent chromium.

‘ - ’ denotes not applicable

Definition of terms:

- Small stream: average width of water surface less than 10 yards under winter flow conditions; intermediate or large stream: greater than 10 yards.
- Small lake, pond, or wetland: < 10 acres; intermediate or large lake, pond, or wetland: ≥10 acres

Nutrient poor: total P below 15 µg/L, total N below 300 µg/L; nutrient rich: P > 15 µg/L , N >300 µg/L.

U.S. EPA 1311, a widely recognized standard test method, provides a conservative estimate of leachability of contaminants contained on solid materials. Use of a less aggressive extraction fluid (e.g., deionized water) may be considered a more suitable approach to simulating highway environments.

Within each of the three categories of snow and ice control materials shown above, five possible types of environmental context are given

1. Small aquatic environment, low nutrient levels;
2. Small aquatic environment, high nutrient levels;
3. Large or intermediate aquatic environment, low nutrient levels;
4. Large or intermediate aquatic environment, high nutrient levels; and
5. Drinking water wells near the roadway.

Small aquatic environments (i.e., streams, wetlands, ponds, or lakes) account for two of these categories. For purposes of constructing the table, it has been assumed that these environments offer minimal dilution, and that the maximum allowable concentrations for potential toxins should be set on the basis of chronic toxicity criteria. The criteria are taken directly from the U.S. EPA's current list of water-quality criteria for protection of aquatic life. For metals affected by hardness, hardness is assumed to be 100 mg/L, if calcium and magnesium are not major constituents of the snow and ice control material, and 400 mg/L, if the snow and ice control material contains calcium and magnesium as major constituents. The actual hardness at the edge of the roadway probably will exceed 400 mg/L in the latter case, but the beneficial effects of hardness in reducing the toxicity of heavy metals generally is assumed to be fully expressed at about 400 mg/L hardness. For very soft waters (100 mg/L), maximum allowable concentrations can be set somewhat lower than indicated in Table 3-2, unless calcium and magnesium are added as major constituents.

The small aquatic environments fall into two categories: low-nutrient and high-nutrient. Critical concentrations for nutrients in snow and ice control materials are set on the assumption that concentrations of total phosphorus (P) and total nitrogen (N) in low-nutrient systems should not be augmented by more than about 50 percent in areas near the roadway. For environments that have high-nutrient concentrations, the amount of nutrients that can be added without substantially perturbing the ambient condition is assumed to be equal to the threshold concentrations separating low-nutrient from high-nutrient conditions.

Two additional subcategories for each type of snow and ice control material apply to aquatic environments that are of intermediate to large size, as defined in the footnote to Table 3-2. In this case, it is assumed that a substantial dilution is readily available. For this reason, acute rather than chronic criteria are used in computing maximum allowable concentrations. As in the case of small aquatic environments, this category is subdivided into low-nutrient and high-nutrient waters, and the allowable concentrations of nutrients are determined by a rationale identical to that used for smaller waters.

Total nitrogen and total phosphorus may be evaluated in a somewhat different way than other constituents listed in the tables. Unlike the other constituents shown in the table, total nitrogen and total phosphorus are nutrients, rather than toxins. The stimulating effects of nutrients on plant growth may be more tolerable in many instances than potential lethal or sub-lethal effects associated with toxins. Although all of the limits recommended in the tables are well justified from the viewpoint of preserving the integrity of aquatic ecosystems, the limits for N and P may be viewed in a more flexible, site-specific manner than limits associated with toxic substances.

A final subcategory for each category of snow and ice control material involves the presence of drinking water wells near the roadway. In this case, limits for human health are relevant and are taken directly from the U.S. EPA's Safe Drinking Water Standards. Concentrations are listed only for those substances that have human health-related standards that are near or below the aquatic life standards; in other cases, it is assumed that the more stringent aquatic life criteria will also be adequate to meet the safe drinking water standards. Because drinking water standards are subject to change, maximum allowable concentrations should be adjusted downward proportionately if they are made more restrictive in the future. Drinking water wells should be tested for contaminants, even if the table indicates that compliance with the maximum allowable limits will provide protection.

Maximum allowable concentrations for the constituents listed in Table 3-2 are computed on the assumption that a 500-times dilution occurs on the roadway (i.e., road surface plus road margins and medians) during runoff. This is a conservative estimate based on a technical assessment of information gathered in Phase I of this study. For liquid snow and ice control materials, the 500 to 1 factor is applied to U.S. EPA criteria to provide a material GMC that is directly applicable to the liquid product. Where solid chemicals are applied, the material should be tested in liquid form. A sample of the material should be dissolved in an amount of water equal to 3 times the mass of the solid (25-percent w/w solution). This allows for testing using the same standard methods as for liquid chemicals and corresponds approximately to the concentration of liquid snow and ice control materials. The produced liquid then can be evaluated as a liquid using Table 3-2. In the case of abrasives, the same overall dilution rate of

500 times still applies; however, two other factors require consideration:

1. The test solution being evaluated is a leachate extract based on a 20:1 liquid-to-solid ratio. To provide comparability with chemicals, the 500-times dilution factor must be reduced by 1/20th.
2. Abrasives are generally applied at average application rates 5 times that of chemicals (generally between 2 to 8 times). It is, therefore, necessary to reduce the 500-times dilution factor by 1/5th.

Overall the factor applied to applicable U.S. EPA water quality to develop abrasive leachate Maximum Acceptable Concentrations is as follows:

500-times dilution factor × 1/20 leachate factor (Item 1) × 1/5 times application factor (Item 2) = 5 times

If there is a site-specific basis for stricter or more lenient dilution allowance, the limits shown in Table 3-2 can be adjusted proportionately. The same reasoning applies to cyanide, total ammonia, and nutrients. The toxicity of total ammonia to aquatic life is affected by pH and temperature. For the purposes of preparing Table 3-2, it is assumed that the temperature will be 5°C and the pH will be 7.5. Large deviations from these assumptions are unlikely in winter, but if they occur, a proportionate adjustment can be made based on U.S. EPA ammonia criteria as a function of pH and temperature.

Evaluation of the GMC values shown in Table 3-2 shows there is generally not a large difference in magnitude of GMC values within each material category and environmental context. It is also likely that a maintenance area will include more than one of the possible conditions listed in Table 3-2. To ensure that the information can be applied in a practical manner, the most conservative values have been summarized in Table 3-3 and should be applied for general use.

3.2 Other Specifications

Historically, purchase specifications for snow and ice control materials have focused on physical properties, primarily to address operational and performance concerns. In recent years, specifications for corrosion properties have also been developed. Given the concern surrounding some specific environmental issues, some agencies may wish to adopt aquatic toxicity specifications as well. This purchase specification does not directly address physical, toxicological, or corrosion properties of snow and ice control materials, and no numerical criteria are suggested. However, areas of consideration have been identified, along with recommended test methods to characterize these properties. If an agency chooses to incorporate specifications for these properties, it is recommended that this be conducted under the guidance of a professional with expertise in the subject area.

3.2.1 Physical Specifications—Chemical Products

3.2.1.1 Specific Gravity

Specific gravity is a material's density (i.e., mass/volume) compared with water. Many agencies use specific gravity to monitor percentage of active ingredient in a liquid snow and ice control material using standard density versus temperature information. This approach is relevant only for pure liquid products or if product-specific data is available. ASTM D 1429, *Standard Test Methods for Specific Gravity of Water and Brine*, lists methods to determine specific gravity for brines.

3.2.1.2 Freezing Point and Eutectic Temperature

Eutectic temperature is the lowest freeze-point temperature achievable for a given product in solution. Eutectic temperature, by definition, applies to pure products; however, in practice (i.e., for commercially available blends and so forth) a material-specific phase curve can be developed over a range of material concentrations. This involves measuring the freezing characteristics of a solution with a previously identified concentration. ASTM D 1177, *Standard Test Method for Freezing Point of Aqueous Engine Coolants*, was developed to determine the freezing point of engine coolants and can be applied to liquid snow and ice control materials.

3.2.1.3 Settleable Solids

PNS has developed a method to determine percent Total Settleable Solids and Percent Solids Passing a No. 10 Sieve after a liquid chemical is stored at a specified cold temperature (−17.8 ± 1°C for $MgCl_2$ and −29 ± 1°C for $CaCl_2$) without agitation for 168 hours (i.e., 1 week). The test procedure is designed to determine the potential for solids formation under extreme-cold field temperatures. The formation of solids in liquid products can impair the operation of application equipment.

3.2.1.4 Gradation

Methods for determining particle size distribution of solid chemical products are based on methods similar to ASTM C 136, *Sieve Analysis of Fine and Coarse Aggregates*. The following test methods for gradation exist for solid chemical snow and ice control products:

- ASTM D 632, *Standard Specification for Sodium Chloride*; and
- ASTM D 98 and ASTM D 345, *Standard Specifications for Calcium Chloride.*

Table 3-3. Summary of most conservative Guidelines for Maximum Concentrations (GMCs) for general purchase specification application.

	Maximum Allowable Potentially Dissolved Metals and Metalloids, mg/L										Other Inorganics		Nutrients	
Category of Material and Environmental Context	As	Cd	Cr[4]	Cu	Pb	Hg[1]	Ni	Se	Ag[1]	Zn	Free CN, mg/L	Total NH$_3$, mg/L[2]	Total P, mg/L	Total N, mg/L[2]
Chemical with Ca or Mg base: MgCl2, CaCl2, CMA - Liquid chemical or 25% w/w solid solution	5	4.8	5.5	15	5.5	0.39	84	2.5	3.5	190	2.6	3000	3.5	75
Liquid lacking Mg or Ca base: NaCl, KA - Liquid chemical or 25% w/w solid solution	5	0.12	5.5	4.5	7.5	0.39	26	2.5	.32	59	2.6	3000	3.5	75
Abrasive Leachate: 1:20 w/v leachate per EPA 1311 (TCLP)	0.05	0.0013	0.055	0.045	0.013	0.004	0.26	0.025	0.0032	0.59	0.026	30	0.035	0.75

3.2.2 Physical Specifications—Abrasives

From the standpoint of a purchase specification, abrasives must be considered separately from snow and ice control chemicals. These materials have their own physical properties such as gradation, hardness, fracture, density, etc. which can affect performance.

3.2.2.1 Gradation and Particle Size

Gradation refers to the particle sizes in an aggregate material. Particle size, which is related to mass, is considered to affect the ability of abrasives to remain on the roadway. However, heavier particles are more likely than lighter particles to cause windshield damage. When pre-wetting fine particles, application equipment can become clogged. Fine particles also contribute to the formation of frozen lumps and/or clumps in outdoor stockpiles. The following methods may be used to assess particle size of abrasives:

- ASTM D 5444, Standard Test Method for Mechanical Size Analysis of Extracted Aggregate (AASHTO T-27 is equivalent);
- ASTM C 142, Standard Test Method for Clay Lumps and Friable Particles in Aggregates (AASHTO T-112 is equivalent); and
- ASTM D 2419, Standard Test Method for Sand Equivalent Value of Soils and Fine Aggregate (AASHTO T-176 is equivalent).

3.2.2.2 Fracture

Fracture refers to the number of manufactured fractures on an aggregate particle. Abrasives with large numbers of fractured faces are thought to remain on the pavement surface longer. ASTM D-5821, Standard Test Method for Determining the Percentage of Fractured Particles in Coarse Aggregate, may be used to assess fracture.

3.2.2.3 Particle Size—Flat/Elongated

Large flat or elongated particles (sometimes referred to as “arrow heads”) can cause tire punctures and can be assessed using ASTM D4791, Standard Test Method for Flat Particles, Elongated Particles, or Flat and Elongated Particles in Coarse Aggregate.

3.2.2.4 Mechanical Abrasion

The mechanical abrasion test, sometimes called the “LA Rattler,” is used to determine the resistance of particles to mechanical abrasion. Higher values indicate softer aggregates. Relatively soft abrasives have a greater potential to break down, which can lead to reduced performance. Traffic action on soft abrasives can create large amounts of fine particles, which can lead to air quality issues. ASTM C-131, Standard Test Method for the Resistance to Degradation by Abrasion and Impact in the Los Angeles Machine (AASHTO T-96 is equivalent), may be used to assess mechanical abrasion.

3.2.3 Toxicity Specifications

Table 3-4 lists common aquatic toxicity test methods for chronic exposure to test organisms representing aquatic vertebrates (i.e., fathead minnow), aquatic invertebrates (i.e., *Ceriodaphnia dubia*) and aquatic vegetation/algae (i.e., *Selenastrum capricornutum*). Other species of concern (i.e., threatened or endangered) can be tested as well using appropriate methodologies and under the guidance of appropriate professionals.

Table 3-4. Aquatic toxicity testing.

Test Method	Standard Reference Method
Fathead Minnow 7-day Survival and Growth Test	US Environmental Protection Agency, 1994, Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to Freshwater Organisms, 3rd Edition, EPA/600/4-91/002
Ceriodaphnia dubia 3-brood Survival and Reproduction Test	US Environmental Protection Agency, 1994, Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to Freshwater Organisms, 3rd Edition, EPA/600/4-91/002
Selenastrum capricornutum 96-hour (US EPA) Growth Test	US Environmental Protection Agency, 1994, Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to Freshwater Organisms, 3rd Edition, EPA/600/4-91/002

3.2.4 Corrosion Specifications

Corrosion properties of snow and ice control materials are related to the ionic constituents of snow and ice control materials. Chloride salts can initiate and accelerate corrosion in metals. Many commercially available snow and ice control products are modified with additives intended to inhibit corrosion. There is significant ongoing research on the effectiveness of corrosion inhibitors in the field. Users may wish to specify a corrosion inhibitor, but should weigh the added cost in relation to identified needs and current scientific literature on the subject carefully. There are numerous methods to assess corrosion potential that an agency may consider adopting if this is a significant area of concern. Key areas include atmospheric corrosion of exposed metals, concrete degradation, and corrosion of concrete reinforcing. Laboratory test results should be viewed as relative corrosion values only and not as absolute indicators of corrosion performance. Most corrosion tests reflect a particular type of corrosion under defined conditions and for a limited number of metals or alloys. The conditions that exist on the roadway can be highly variable in terms of weather, chemical application, and the presence of other contaminants not related to snow and ice control chemicals.

CHAPTER 4

Quality Assurance Monitoring Program

The Quality Assurance (QA) program is a suite of qualifying tests and submittals for the agency to characterize snow and ice control products before purchase or use. This section includes procedures for collecting and testing received snow and ice control chemicals. Standard test methods used to quantify material characteristics are also referenced. To ensure suitability of the products with agency purchase specifications, it is suggested that QA procedures be included in contract documents.

4.1 Documentation

When receiving snow and ice control materials, documentation must be maintained to ensure sufficient traceability to the materials source. This allows tracking in the event of nonperforming materials. Information may include

- Material verification information including, as applicable, active ingredient concentration, purity, and material specific phase curve information. It is recommended that the latter be prepared by an independent source.
- Shipping data with certified weights and volumes shipped.
- Lot numbers. All materials should be identified by production and/or shipping lot numbers.
- Material Safety Data Sheets (MSDS). All materials should be accompanied by an MSDS that provides sufficient safety information for handling and in case of an accident.

4.2 Field QA Procedure

Simple field observations can help ensure product suitability. It is recommended that each delivered load be subjected to the following recommended field QA procedures:

1. Specific gravity per ASTM D 1429 (refer to Section 3.2.1.1) should be conducted on liquid materials. Comparing measured values with standard curves can provide initial assurance of active ingredient concentration.
2. Visual inspection, a simple act, can sometimes detect obvious problems with a product. This may involve assessing whether the delivered material looks similar to previous products.

4.3 Sample Collection Procedure

It is recommended that each delivered load be sampled. The following sample collection procedures for snow and ice control materials reflect procedures developed by the PNS in 2002:

1. QA sampling should be conducted at the time of delivery, directly from the delivery vehicle. It is recommended that composite samples be collected by quantitatively combining discrete (i.e., grab) samples collected from several points in the material transfer process. If single grab samples are preferred, it is recommended that these be collected midway through the material transfer process. Exercise care to allow sufficient flushing of valves, fittings, and hoses to prevent potential cross contamination. Metal (specifically brass) fittings can be problematic if this step is not performed.
2. A replicate sample (i.e., two containers of the same material) is recommended for each material sampled. One replicate is for laboratory submission; the second replicate is retained by the agency in case of dispute or if further testing is required.
3. The testing laboratory should be contacted to confirm required sample volume and container type required for the requested testing. A clean quart/liter plastic bottle is generally sufficient to conduct a general chemical analysis of liquid materials. For solid products, plastic bags or wide-mouth jars (i.e., plastic or glass) capable of holding 1 pound (0.450 kg) are generally sufficient.
4. Clearly label each product sample with adequate information to ensure traceability. This will include but not be

limited to material type, product name, vendor, lot number, delivery location, lot number, date, and sampler.

Samples of abrasives can be collected based on ASTM D 75.

4.4 Laboratory Testing Effort

Chemical analysis of snow and ice control materials can provide a great deal of information in a relatively short time. Testing should correlate with agency purchase specification criteria and should include the following:

- Active ingredient concentration (i.e., NaCl, $MgCl_2$, $CaCl_2$, KA, and CMA);
- Metals (i.e., arsenic, cadmium, chromium [un-speciated], copper, lead, mercury, nickel, selenium, silver, and zinc)—All should be tested in their potentially dissolved form;
- Chloride;
- BOD;
- COD;
- Phosphorus, Total;
- Nitrogen, Total;
- Ammonia;
- pH; and
- Cyanide.

The list can be modified to suit agency needs, but should reflect the content of the agency's purchase specification. Where products are known not to contain significant amounts of a constituent (e.g., for chloride in a CMA product), it is still recommended that the full suite of testing be conducted to ensure completeness of the data set.

Overall testing frequency should be determined by the agency. Where multiple loads of a single product are received, it is recommended that at least 10 percent of the received loads be tested, selected on a random basis. When multiple product types are received, it is recommended that at least one test be conducted for each material. Additionally, any loads suspected of being out of specification should be tested. Test protocols are listed in Section 4.5.

4.5 Standard Test Methods

It is essential for a QA program to specify standard test methods to ensure data consistency among laboratories and over time. Many chemical analysis methods used for snow and ice control materials have been adapted from standard environmental test methods for water and wastewater, most notably from *Standard Methods for the Examination of Water and Wastewater*, 20th Edition, American Public Health Association, American Water Works Association, Water Environment Federation, 1998, Washington DC (APHA).

APHA methods are well-recognized and are commonly used at most environmental laboratories in the United States and Canada. For some parameters, APHA references more than one analytical technique that may be used. Trends in analytical chemistry are toward performance-based methodologies (PBMs) with specific data quality objectives (DQOs). It is the laboratory's responsibility to ensure that performance-based objectives are met for the sample matrix being tested. When adapting APHA methods to snow and ice control materials, the following considerations are necessary.

- Standard test methods for water and wastewater samples primarily involve volumetric sample aliquots. Liquid snow and ice control products are denser than water with specify gravity values generally ranging from 1.15 to 1.35. It is common to report chemical data for snow and ice control materials both volumetrically (e.g., mg/L, %w/v) and gravimetrically (e.g. mg/kg, %w/w).

  To support the purchase specification (Section 3.1), data must be reported as mg/L with the exception of active ingredient concentration, which should be reported based on weight (%w/w). Initial measurements may be taken volumetrically or, alternatively, weight-based measurements can be corrected using specific gravity values.
- Units and basis of measurement should be clearly indicated. Ambiguous units such as parts per million (ppm) or percent (%) can cause confusion and should be clarified to reflect the basis of measurement. The following measurement units are preferred: milligrams per liter (mg/L), milligrams per kilogram (mg/kg), percent volume per volume (% v/v), percent mass per volume (% w/v) or percent mass per mass (% w/w).
- Reported Method Detection Limits (MDL) should be sufficient to support purchase specification values with reasonable data confidence. It is recommended that MDLs be equal to or less than 1/5th of the purchase specification limit. If this is not possible using current and reasonably available technologies, the reported result must, at minimum, be less than the reported detection limit or the data must be qualified.
- Methods used for testing must go through sufficient method validation to ensure that the method is fit for the purpose. This will generally include an assessment of method detection limit, precision, and accuracy.
- The laboratory should also use sufficient quality samples with each batch analyzed to support the reported data. This will generally include where applicable

  1. Duplicates to monitor precision, conducted at a frequency of 5 to 10 percent with relative percent difference (RPD) targets of less than 20 percent.
  2. Laboratory control samples (e.g., blank spikes, matrix spikes, and reference materials) to assess recovery,

conducted at a frequency of 5 to 10 percent with recovery targets between 80 and 120 percent.

3. Blanks to assess contamination and interferences, conducted at a frequency of 5 to 10 percent with target acceptance levels of less than the reported detection limit.

- Test reports should include sample identification, test results, units of measurement, method detection limits, analysis methods employed, and special notes if applicable.

4.5.1 Sample Preparation

The following sections outline sample preparation steps for liquid chemical, solid chemical, and abrasive samples.

4.5.1.1 Liquid Chemicals

Liquid snow and ice control chemicals are to be tested and reported based on the received material in the units of mg/L, with the exception of active ingredient concentration, which is to be converted to percent based on weight (% w/w).

4.5.1.2 Solid Chemicals

Solid snow and ice control chemicals are to be diluted at room temperature with reagent-grade water (at minimum, ASTM D 1193, Type II) to achieve a 25-percent w/w solution (i.e., dissolve 250 grams of solid material in 750-grams of reagent-grade water). Any insoluble materials should be noted. When comparing test results with the purchase specification, test data is to be reported based on the prepared solution in mg/L, with the exception of active ingredient concentration, which is to be converted to percent based on weight (% w/w).

4.5.1.3 Abrasives

Abrasives are to be prepared based on U.S. EPA Method 1311, Toxic Characteristic Leaching Procedure, U.S. EPA SW-846, Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods, www.epa.gov/epaoswer/hazwaste/test/sw846.htm. This is an extraction method that involves a 1:20 (solid-to-liquid) leachate procedure. The leachate extract is to be tested directly, and test data is to be based on the leachate solution in units of mg/L.

4.5.2 Active Ingredient

Active ingredient refers to the primary components of the snow and ice control chemical. For present purposes, standard active ingredients include NaCl, $CaCl_2$, $MgCl_2$, CMA, and KA. An accurate assessment of the active ingredient is important to ensure that the received product concentration is equivalent to the purchased concentration. Further, product concentrations are important to help guide material performance estimations. Active ingredient concentrations may be estimated using specific gravity charts specific to each material; however, direct chemical analysis of the cationic species (e.g., Ca, Mg, Na, K) followed by a molecular weight (MW) conversion to the salt species is preferred. This approach assumes that all of the cation exists as the salt species. For example, Ca would be measured to determine $CaCl_2$ levels and Ca and Mg would be measured to determine CMA concentrations. For chloride-based chemicals, it can be helpful to balance cation concentrations with chloride concentrations as an additional check of data quality.

- NaCl (% w/w) = Na (% w/w) × 58.44 (MW NaCl)/22.99 (MW Na);
- $CaCl_2$ (%w/w) = Ca (% w/w) × 110.99 (MW $CaCl_2$)/40.08 (MW Ca);
- $MgCl_2$ (%w/w) = Mg (% w/w) × 95.21 (MW $MgCl_2$)/24.31 (MW Mg);
- KA (% w/w) = K (% w/w) × 98.14 (MW KA)/39.01 (MW K); and
- CMA (% w/w) = [Ca (% w/w) × 99.12 (MW CA)/40.08 (MW Ca)] + [Mg (% w/w) × 83.35 (MW MA)/24.31 (MW Mg)]

Simple wet chemistry techniques can be effective at measuring percent-level active ingredient concentrations common with snow and ice control products. Standard titration procedures exist for calcium and magnesium determination: ASTM E 449 Standard Test Methods for Analysis of Calcium Chloride. Procedures are given for the determination of calcium chloride, magnesium chloride, potassium chloride, sodium chloride, and calcium hydroxide.

Instrumental analysis procedures are more complex, but are generally thought to be more specific and precise than wet chemistry techniques. Ca, Mg, Na, and K are metals that can be detected by various instrumental procedures including atomic absorption spectroscopy, atomic emission spectroscopy and mass spectroscopy. Refer to Section 4.5.3 for further details.

Units of measurement for active ingredient concentration shall be percent based on weight (% w/w).

4.5.3 Metals

This purchase specification addresses the following heavy metals: arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, and zinc. These are to be tested in their potentially dissolved form. Sophisticated instrumental analysis is required to achieve the detection levels needed to meet purchase specification limits. Instrumental techniques are not without drawbacks. Snow and ice control materials contain high-percent levels of active ingredients that can interfere with precise quantification of low-level analytes. Where high-level dilutions are necessary, variances in measurement can be greatly amplified after dilution factors are applied.

Instruments used for metals analysis include the following:

- APHA 3111, Metals by Flame Atomic Absorption Spectroscopy (AA). Full range of metals analyses possible.
- APHA 3112, Metals by Cold-Vapor Atomic Absorption (CVAA). Applicable to Hg analysis.
- APHA 3120, Metals by Inductively Coupled Plasma/Optical Emission Spectroscopy (ICP/OES). Full range of metals analyses possible.
- APHA 3125, Metals by Inductively Coupled Plasma/Mass Spectroscopy (ICP/MS). Full range of metals analyses possible.

Each instrument technique listed above is technically suitable for the measurement of metals (and active ingredients) in snow and ice control products. Some methods are better suited to analyzing certain metals than others. A skilled operator with knowledge of potential analytical interferences and corrections is important in ensuring that performance objectives are met.

4.5.4 Total Phosphorus

Phosphorus can exist in various forms ranging from orthophosphate, which is readily soluble, to total phosphorus, which also includes bound and combined phosphorus. Orthophosphates are thought to be more environmentally available, although total phosphorus can degrade to orthophosphates through natural processes. Therefore snow and ice control materials should be evaluated primarily in terms of total phosphorus, rather than specific phosphorus fractions. In order to degrade total phosphorus into a more easily measurable form, APHA (*67*) includes the following total hydrolysis method:

- APHA 4500-P B, Sample Preparation, describes procedures that employ perchloric acid, sulfuric/nitric acids, or persulfate digestion.

After digestion, phosphorus may be determined colorimetrically using the following methods:

- APHA 4500-P C, Vanadomolybdophosphoric Acid Colorimetric Method
- APHA 4500-P D, Stannous Chloride Method
- APHA 4500-P E, Ascorbic Acid Method

4.5.5 Nitrogen

Various forms of nitrogen are present in snow and ice control products and include Nitrite (NO_2^-) and Nitrate (NO_3^-); Ammonia (NH_3); Organic Nitrogen (TON); Total Kjeldahl nitrogen (TKN); and Total Nitrogen (TN). Total nitrogen analysis includes all forms of nitrogen and is the preferred index to evaluate nitrogen content with respect to potential environmental impairment. A separate evaluation of ammonia is warranted because ammonia is potentially toxic to aquatic life at high concentrations.

Test methods to determine nitrogen compounds include various available options for each nitrogen compound:

- APHA 4500-N A, B, and C;
- APHA 4500-NH_3 Nitrogen (Ammonia);
- APHA 4500-NO_2^- Nitrogen (Nitrite);
- APHA 4500-NO_3^- Nitrogen (Nitrate);
- APHA 4500-N_{org} Nitrogen (Organic)—This section includes the standard Total Kjeldahl Nitrogen (TKN) methodology.

It is the responsibility of the analytical laboratory to ensure that the selected methods meet accepted performance criteria for application to snow and ice control materials.

4.5.6 Cyanide

Iron-cyanide compounds are commonly added to salt as anti-caking agents. Cyanide (CN) can exist as free cyanide, where the CN molecule is soluble and biologically available, or as complexed cyanide compounds (i.e., iron-cyanide compounds), where the CN molecule is sparingly soluble and not readily biologically available. Direct standard analytical techniques are not available for iron-cyanide compounds; therefore, total cyanide analysis provides a conservative surrogate method for their quantification.

Total cyanide analysis requires digestion using acids, reducing agents, and/or ultraviolet light to convert cyanide compounds into cyanide gas (HCN), which is distilled and adsorbed into a basic solution, from which HCN can be determined. The chemistry involved in cyanide analysis can be subject to numerous interferences. The laboratory must ensure that methods used meet acceptable performance criteria. Cyanide analysis should be based on APHA 4500-CN^- C, Total Cyanide after Distillation. This procedure details the acid digestion procedure used to liberate CN from the sample and adsorb it into a basic NaOH solution.

The following methods detail measurement of the CN ion after digestion:

- APHA 4500-CN^- E, Colorimetric Method, and
- APHA 4500-CN^- F, Selective Ion Electrode Method.

The approach taken here—measurement of total cyanide—is conservative because cyanide from iron-cyanide complexes can become available in the natural environment. Other analytical methods (e.g., measurement of cyanide-amenable chloride) may be a better indicator of readily available cyanide, but practical challenges exist. Given the high potential organic content of many snow and ice control materials, very high chlorination levels would be required to first oxidize all organic matter and then liberate the CN. In a practical sense, this may render any cyanide amenable to chlorine potentially non-detectable.

4.5.7 Organic Matter (BOD and COD)

Organic matter content influences snow and ice control material selection through the decision tool and is a recommended component of the purchase specification. Organic matter tests have environmental importance, are relatively simple to conduct, and are, therefore, recommended as part of the QA Monitoring Program. BOD is an empirical test used to determine the relative oxygen requirements of a sample subjected to biochemical oxidation. The standard 5-Day BOD test has fixed incubation conditions of 20 ± 2°C. To assess biodegradability under alternate (i.e., field) conditions, it may be desirable to conduct BOD testing over longer periods and at various temperatures. The 5-day BOD test procedure is conducted according to APHA 5210 B, 5-Day BOD Test.

Chemical oxygen demand (COD) is used to measure the oxygen equivalent of the organic matter subjected to a strong chemical oxidant. COD can be conducted relatively quickly and can be empirically related to BOD. COD values will be equal to or greater than BOD. COD can be analyzed using the following test methods:

- APHA 5220 B, Open Reflux Method
- APHA 5220 C, Closed Reflux Method
- APHA 5220 D, Closed Reflux Colorimetric Method

Abbreviations and acronyms used without definitions in TRB publications:

AAAE	American Association of Airport Executives
AASHO	American Association of State Highway Officials
AASHTO	American Association of State Highway and Transportation Officials
ACI–NA	Airports Council International–North America
ACRP	Airport Cooperative Research Program
ADA	Americans with Disabilities Act
APTA	American Public Transportation Association
ASCE	American Society of Civil Engineers
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
ATA	Air Transport Association
ATA	American Trucking Associations
CTAA	Community Transportation Association of America
CTBSSP	Commercial Truck and Bus Safety Synthesis Program
DHS	Department of Homeland Security
DOE	Department of Energy
EPA	Environmental Protection Agency
FAA	Federal Aviation Administration
FHWA	Federal Highway Administration
FMCSA	Federal Motor Carrier Safety Administration
FRA	Federal Railroad Administration
FTA	Federal Transit Administration
IEEE	Institute of Electrical and Electronics Engineers
ISTEA	Intermodal Surface Transportation Efficiency Act of 1991
ITE	Institute of Transportation Engineers
NASA	National Aeronautics and Space Administration
NASAO	National Association of State Aviation Officials
NCFRP	National Cooperative Freight Research Program
NCHRP	National Cooperative Highway Research Program
NHTSA	National Highway Traffic Safety Administration
NTSB	National Transportation Safety Board
SAE	Society of Automotive Engineers
SAFETEA-LU	Safe, Accountable, Flexible, Efficient Transportation Equity Act: A Legacy for Users (2005)
TCRP	Transit Cooperative Research Program
TEA-21	Transportation Equity Act for the 21st Century (1998)
TRB	Transportation Research Board
TSA	Transportation Security Administration
U.S.DOT	United States Department of Transportation