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Evaluation Procedures for Deicing Chemicals and Improved Sodium Chloride

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Abstract

This report describes the studies pursued in defining, developing, and documenting protocols for testing and evaluating deicing chemicals. A secondary component of the study investigated methods for improving the effectiveness of sodium chloride as an ice melting agent.

The research encompassed a literature review of prior work; established criteria for characterizing chemical deicers; and identified potential test methods for evaluating candidate deicing chemicals. Of the 62 test methods identified, 12 primary methods developed on this program specifically for chemical deicers are described in detail, and 50 supplementary standard published test methods are referenced.

A laboratory manual for conducting the test procedures was produced as part of this project. This report, *Handbook of Test Methods for Evaluating Chemical Deicers*, SHRP-H-332, is available from the Transportation Research Board.

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Summary

The overall objective of the research program was twofold:

- To define, develop, and document standardized protocols for the testing and evaluation of candidate chemical compositions for use as deicing agents; and
- To explore and develop sodium chloride-based formulations with improved deicing performance and enhanced environmental compatibility.

The program was conducted in two main segments: preliminary studies and advanced investigations.

The preliminary studies consisted of a technological review and assessment of test methods and criteria for evaluating deicing chemicals. During this phase of the program, test methods were identified, categorized by test type and deicer type, and assessed by comparative evaluation.

The three principal documents produced from the preliminary research studies are the following three reports:

A special report titled, "Evaluation and Testing of Chemical Deicers: Literature Review" (August 5, 1988). The report contains general background information including the objectives of the literature review, the strategies employed in searching the literature, and a synopsis of the state of the art of chemical deicers.

A special report titled, "Characterization and Selection of Chemical Deicers: Criteria Document" (October 7, 1988). This report contains general background information on the criteria document and the methodologies employed in developing the chemical-deicer selection criteria.

An interim report containing a major section titled, "Selected Test Methods for Evaluating Chemical Deicers" (March 14, 1989). This report contains a tentative testing protocol for the complete physicochemical and ecological characterization of a chemical deicer.

The advanced investigations concentrated on three main areas: test method development, improved sodium chloride formulations, and development of the Test Methods Handbook. The scope of the research in these three areas is summarized as follows:

Test method development was the major thrust of the advanced investigations. Several promising test methods which required further experimental development and validation, were identified in the following areas: deicing performance, concrete compatibility, frictional characteristics, concrete reinforcement corrosion, and ecological effects.

Three deicing performance tests, namely ice-melting rate and capacity, ice penetration, and ice undercutting, were modified and validated by numerous laboratory tests using both solid and liquid deicers.

A concrete compatibility test based on ASTM C-672-84 was adapted for evaluating spalling characteristics.

A mini-concrete compatibility test was developed for the rapid evaluation of degradative effects.

A friction-characterization test, utilizing the British Pendulum Tester as a friction test device, was developed for measuring frictional properties.

A concrete-reinforcement corrosion test was developed, one which utilized mortar-encased rebar test specimens and simulated-concrete pore solutions.

An ecological effects screening protocol, which included a battery of aquatic and terrestrial toxicity tests, was developed.

Improved sodium chloride was the secondary exploratory thrust in the advanced investigation. The two main exploratory studies focused on deicing performance improvement via physicochemical techniques, and compatibility enhancement via corrosion inhibition and via surfactant addition.

Improvement of the deicing performance of sodium chloride was studied by formulating selected hybrid systems and evaluating the ice-melting capacities at 1 hr and 0°F. Chemicals used in these studies included: $CaCl_2$, $MgCl_2$, formamide, ethylene glycol, and selected acetate salts.

Enhancement of the performance and compatibility of sodium chloride was studied by incorporating selected corrosion inhibitors and surfactants in NaCl deicer formulations. Effects of the additives were evaluated by selected deicer performance and compatibility tests.

The major output of the advanced investigation phase was the Test Methods Handbook. The handbook contains 12 primary test methods and 50 supplementary test methods for characterizing chemical deicers, and for evaluating the impacts of chemical deicer usage. The first draft of the handbook was issued on November 9, 1990, for review and evaluation by SHRP and selected State Departments of Transportation. The final approved version of the Handbook was issued on July 31, 1991.

1

Introduction and Research Approach

1.1 Introduction

The Strategic Highway Research Program (SHRP) has as its general objective the development of procedures and approaches which will materially advance the nation's capabilities to construct, maintain, and operate its highway systems. The overall program addresses several important aspects of a highway system, with a general emphasis on highway materials, highway safety, and responsiveness to environmental concerns.

This report covers the work done by Midwest Research Institute (MRI) and its subcontractor on SHRP Contract No. H-205, "Evaluation Procedures for Deicing Chemicals and Improved Sodium Chloride."

1.1.1 Problem Statement

Deicing chemicals employed in highway winter maintenance operations have a pervasive, deleterious effect on the roadway and the environment. The cause of the deicing chemical problem is twofold: a lack of knowledge concerning the characteristics of chemicals that should be used for deicing and a lack of adequate testing protocols that yield data suitable for establishing application criteria to minimize environmental impact.

Experience gained in the evaluation of calcium magnesium acetate (CMA), which has been the subject of numerous tests over many years, points to the clear need for a standard method of testing and evaluation of candidate deicing chemicals which can be used by individual states in the absence of a central testing laboratory. This methodology will also serve to stimulate the search for new, effective deicing chemicals because the time from development to market will be reduced.

Sodium chloride will undoubtedly continue to be used in large quantities as a deicer because of its ready availability, effectiveness at commonly experienced temperatures, and low cost. Thus there exists a dual need (a) to explore methods of improving its effectiveness over a wider range of temperatures by enhancing its physicochemical properties, and (b) to develop techniques and practices for reducing the environmental stresses that its use has introduced.

1.1.2 Program Objectives

The overall objective of SHRP program H-205, "Evaluation Procedures for Deicing Chemicals and Improved Sodium Chloride," was twofold:

- To define, develop, and document standardized protocols for the testing and evaluation of candidate chemical compositions for use as deicing agents; and
- To explore and develop sodium chloride-based formulations with improved deicing performance and enhanced environmental compatibility.

1.2 Research Approach

The program was conducted in two main segments: a set of preliminary studies and a series of structured advanced investigations.

1.2.1 Preliminary Studies

Work on the preliminary studies was completed in January 1989. The objectives, scope of work, research approach, and principal products of these studies are discussed below.

1.2.1.1 *Objectives*

The preliminary studies had three primary objectives:

- To review prior research conducted in the United States and in other countries on the evaluation and testing of various types of chemical deicers.
- To establish the criteria necessary for a complete characterization of a chemical proposed for use as a deicing chemical.
- To identify potential test methods for evaluating the properties of candidate deicing chemicals necessary to meet these criteria.

1.2.1.2 *Scope of Work*

The scope of work of the preliminary studies involved a technological review and assessment of test methods and criteria for evaluating deicing chemicals. Test methods for evaluating the critical properties of candidate deicing chemicals were identified, categorized by test type and deicer type, and assessed by comparative evaluation. The most promising test procedures were selected and recommended as tentative test procedures for use in evaluating and/or developing certain types of deicing chemicals.

1.2.1.3 *Research Approach*

The preliminary studies consisted of four parts: (a) review of the research on evaluation and testing of deicing chemicals; (b) establishment of criteria for complete characterization of chemical deicers; (c) identification of relevant test procedures for evaluating properties of candidate deicing chemicals; and (d) preparation of an interim report and formulation of a work plan for the advanced investigations.

- <u>Review of Research on Evaluation and Testing of Deicing Chemicals</u>. The purpose of this work was to conduct a critical review of the scientific, trade, and transportation literature relative to the evaluation and testing of deicing chemicals, both in the United States and abroad. The goals of the review were to identify relevant knowledge, to provide a critical assessment, to find the common elements, and to point out discrepancies. The search covered the research conducted in both the United States and other countries. Research results from both laboratory and field testing of chemicals used or proposed as deicing agents were sought. In addition, research results were obtained on investigations of chemical and physical approaches to modify sodium chloride in order to reduce its undesirable environmental effects and to enhance its performance as a deicer.

- Establishment of Criteria for Complete Characterization of Chemical Deicers. The purpose here was to (a) establish sets of criteria for the complete characterization of chemical deicers; (b) develop standards and guidelines for the quantification of the criteria; and (c) identify test procedures for determining criteria/standards compliance. Seven categories of chemical deicer criteria were established and/or considered: (1) fundamental properties, (2) deicer performance, (3) materials compatibility, (4) environmental effects, (5) engineering operations, (6) meteorological and highway parameters,and (7) health and safety practices.

- Identification of Relevant Test Procedures for Evaluating Properties of Candidate Deicing Chemicals. The purpose of this study was to identify candidate test procedures, to assess their technical acceptability in terms of standard methods,and to document selected test methods in a functional format for use in criteria compliance testing. Initially, the work was organized into three main sections: deicer performance tests, deicer corrosion tests, and deicer environmental impact tests. However, in light of the criteria established for the complete characterization of a chemical deicer, six major test procedure categories were identified as follows: physicochemical characteristics, deicing performance, corrosion/compatibility characteristics, environmental effects, engineering parameters, and health and safety aspects.

- Preparation of Interim Report and Work Plan for Advanced Investigations. The final part of the preliminary investigations was the preparation of an interim report and the submission of this report for review by SHRP. The interim report included a detailed presentation of the results of all work performed and emphasized the identified methods of testing developed. The report was accompanied by a work plan for the advanced investigations phase of the research program. The work consisted of recommendations for the direction of the remaining research to be conducted under program H-205.

1.2.1.4 *Principal Products of the Preliminary Research Studies*

The preliminary research studies led to three reports: (a) a special report on the review of research and evaluation and testing of deicing chemicals, (b) a special report on the establishment of criteria for complete characterization of chemical deicers, and (c) an interim report summarizing the preliminary investigations.

- A special report titled "Evaluation and Testing of Chemical Deicers: Literature Review" was issued on August 5, 1988. The report contained general background information including the objectives of the literature review, the strategies employed in searching the literature, and a synopsis of the state of the art of chemical deicers. The major thrust of the literature review focused on the compilation, interpretation, and assessment of pertinent literature, which constitute the state of knowledge on the evaluation and testing of chemical deicer systems. A technical rationale was presented as a basis for structuring a program for the development of improved chemical deicers, including improved sodium chloride.

- A special report titled "Characterization and Selection of Chemical Deicers: Criteria Document" was issued on October 7, 1988. The report contained general background information which presents the objective of the criteria document and the methodologies employed in developing the chemical deicer criteria. The major elements of the criteria document were the definition and organization of six major criteria and 36 criteria subcategories, the establishment of standards and/or guidelines for all criteria categories, and the documentation of relevant test methods, test data, standards, and guidelines for all chemical deicer criteria categories.

- An interim report containing a major section titled "Selected Test Methods for Evaluating Chemical Deicers" was issued March 14, 1989. This report contained a tentative testing protocol for the complete characterization of a chemical deicer. Six major test procedure categories were identified as follows: physicochemical characteristics, deicing performance, corrosion/compatibility characteristics, environmental effects, engineering parameters, and health and safety aspects. A total of 55 specific test procedures was evaluated for adequacy and validity. As a result, 51 specific test procedures were recommended for use in the complete characterization of a chemical deicer: 41 ASTM test procedures, 1 OSHA test protocol, 2 nonstandard test procedures requiring documentation, and 7 tentative test procedures requiring further development.

1.2.2 Advanced Investigations

The objectives, scope of work, research approach, and principal products of the advanced investigations are discussed in this section.

1.2.2.1 *Objectives*

The advanced research investigations had two primary objectives: (a) to develop a set of standardized test methods for the evaluation of chemical deicers and (b) to investigate the deicing performance and materials compatibility enhancement of improved sodium chloride formulations.

1.2.2.2 *Scope of Work*

The scope of work for the advanced research investigations effort consisted of four main elements:

- The experimental development of a relatively small number of recommended chemical deicer test procedures and the presentation of all recommended test procedures in an acceptable, user-friendly (e.g., ASTM) format.
- An exploratory development program focused on improved sodium chloride, accompanied as appropriate by evaluation of examples of improved sodium chloride using the recommended test methods.
- The development of a Test Methods Handbook which presents in detail the methods recommended for chemical deicer evaluation and the criteria and guidelines which pertain to the selection and use of chemical deicers.
- The preparation of a Final Report summarizing all aspects of the advanced research investigations during the entire contract period.

1.2.2.3 *Research Approach*

The advanced investigations were focused on four areas: (a) test methods development, (b) sodium chloride improvement, (c) test methods documentation, and (d) final report preparation.

Test Methods Development

Development of deicer test methods was the major thrust of the advanced investigations. The literature review, combined with the definition of criteria for evaluating chemical deicers, indicated that several test methods required further experimental development and validation. The test methods were in the following areas: deicer performance properties, concrete compatibility, deicer frictional characteristics, concrete reinforcement corrosion, and ecological hazard assessment.

- Three deicer performance tests, namely ice-melting rate and capacity, ice penetration, and ice undercutting, were modified and developed. The basic procedures for each of these tests were essentially established and validated in numerous tests. Modifications involved changes deemed appropriate for highway deicing conditions plus modifications which were aimed at simplifying certain procedural operations.

- The concrete compatibility test development work involved studies of the suitability of ASTM C-672-84, "Scaling Resistance Test," as a rapid straightforward test method for evaluating the spalling characteristics of chemical deicers. This method was modified and compared with a version of the "accelerated" concrete compatibility test developed early in the program.

- The frictional characterization test development work involved an investigation of the suitability of the British Pendulum Tester as a friction test device for chemical deicers, according to the procedure described in ASTM E 303, "Standard Test Method for Measuring Surface Frictional Properties Using the British Portable Tester." Various substrates were investigated as potential test surfaces for use in the laboratory.

- The concrete reinforcement corrosion test work involved the development of mortar encased rebar test specimens exposed to simulated pore solutions containing deicing chemicals, and suitable electrochemically based corrosion state and rate measurements.

- The ecological hazard assessment protocol developed was generally patterned after accepted EPA testing protocols. A battery of aquatic and terrestrial test procedures were screened, modified, and evaluated using selected chemical deicers to obtain baseline response data.

Sodium Chloride Improvement

The development and evaluation of improved sodium chloride formulations was a second exploratory thrust in the advanced investigation phase. The two main areas of these exploratory development studies were deicing performance improvement via physicochemical techniques and compatibility enhancement via corrosion inhibition and surfactant addition.

- Improvement of the deicing performance of sodium chloride was studied by formulating selected hybrid systems and evaluating their ice melting capacities at 1 hr and 0°F. Chemicals used in these studies included: $CaCl_2$, $MgCl_2$, formamide, ethylene glycol, and selected acetate salts. Several hybrid systems exhibited improved low temperature performance.

- Enhancement of the compatibility of sodium chloride was studied by formulating selected corrosion inhibitors and evaluating the corrosion rate of metals exposed to inhibited salt solutions. The incorporation of selected surfactants in salt based deicing formulations was evaluated as a potential technique for improving the deicing performance and materials compatibility of solidum chloride deicers.

Test Methods Documentation

All recommended test methods developed during the advanced investigations were documented in a suitable ASTM type format and included in a Test Methods Handbook. This handbook which was a major output of the advanced investigation phase, contained a set of test procedures suitable for characterizing chemical deicers and evaluating the impacts of chemical deicer usage. Before the test methods handbook was finalized, the operability and acceptability of the documented test methods were reviewed and evaluated by SHRP and selected State Departments of Transportation.

Final Report Preparation

The final report was designed to describe the experimental work in detail, identify significant accomplishments and problem areas, and present an analysis and interpretation of the research findings.

1.2.2.4 *Principal Products of the Advanced Research Investigations*

The two principal products of the advanced research investigations were: (a) a test methods handbook for evaluating chemical deicers and (b) a final report which describes the exploratory developmental studies and experimental findings.

Test Methods Handbook

The *Handbook: Test Methods for Evaluating Chemical Deicers* was issued on November 9, 1990. This handbook was written for local and state highway engineers, chemists, materials scientists, technicians, and other laboratory and research personnel. Relevant background information was provided in a synopsis of current deicing materials and test methods presented in Appendix A of the handbook.

The main purpose of the handbook was to provide an organized collection of test methods for the complete characterization of deicing chemicals. Sixty-two specific test methods were defined for the evaluation of chemical deicers in eight principal property/performance areas:

- Physicochemical characteristics
- Deicing performance
- Compatibility with bare and coated metals
- Compatibility with metals in concrete
- Compatibility with concrete and nonmetals
- Engineering parameters
- Ecological effects
- Health and safety aspects

The 62 specific chemical deicer test methods are composed of 12 primary and 50 supplementary test methods. The primary test methods, which were developed on this project for conducting the more important evaluations, are described in detail in Appendix B of the handbook and identified as follows.

- SHRP H-205.1, Test Method for Ice Melting Capacity of Solid Deicing Chemicals

- SHRP H-205.2, Test Method for Ice Melting Capacity of Liquid Deicing Chemicals

- SHRP H-205.3, Test Method for Ice Penetration of Solid Deicing Chemicals

- SHRP H-205.4, Test Method for Ice Penetration of Liquid Deicing Chemicals

- SHRP H-205.5, Test Method for Ice Undercutting by Solid Deicing Chemicals
- SHRP H-205.6, Test Method for Ice Undercutting by Liquid Deicing Chemicals
- SHRP H-205.7, Test Method for Evaluation of Corrosive Effects of Deicing Chemicals on Metals
- 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
- SHRP H-205.10, Test Method for Evaluation of Frictional Characteristics of Deicing Chemicals
- SHRP H-205.11, Test Method for Preliminary Assessment of Ecological Effects of Deicing Chemicals
- SHRP H-205.12, Test Method for Rapid Evaluation of Corrosive Effects of Deicing Chemicals in Reinforced Concrete.

The 50 supplementary test methods, which were selected from the literature for performing ancillary evaluations, are listed as references in Appendix C of the handbook. The supplementary test methods are mainly ASTM standard test methods and EPA standard test procedures.

The handbook is currently being evaluated and assessed by selected state DOT laboratories. Test methods developed during this program may be revised by MRI, subject to contract limitations based on input from evaluating laboratories.

Final Report

This final report summarizes all phases of the preliminary studies and presents the experimental work and findings of the advanced research investigations on SHRP H-205, "Evaluation Procedures for Deicing Chemicals and Improved Sodium Chloride."

1.3 Organization of this Report

The remainder of this final report is organized as follows. Section 2 presents the development and modification of deicer test methods. Section 3 describes the development and evaluation of improved sodium chloride formulations. Section 4 presents the conclusions and recommendations drawn from the research. References are included with each main subsection of Sections 2 and 3, and four appendices are provided at the end of the report. For purposes of presentation, the preliminary studies and advanced investigations have been integrated in the discussion of each specific topic.

2

Development and Modification of Deicer Test Methods

This section is divided into seven subsections: Ice-Melting Studies; Ice-Penetration Studies; Ice-Undercutting Studies; Concrete Compatibility Studies; Frictional Characteristics Work; Concrete Reinforcement Corrosion Research; and Ecological Effects Research. The objectives of the research in the first six subsections was to develop test methods for evaluating known and candidate deicing materials. In the final subsection the objective was to identify and develop screening test procedures for use in the preliminary ecological hazard assessment of deicing chemicals in contact with selected terrestrial and aquatic plant and animal species. All of the test methods described in the different subsections would be useful to state Department of Transportation (DOT) laboratories in determining the properties of new, potential deicing chemicals, evaluating their potential environmental impact, and comparing them with baseline ice-melting data obtained using traditional chloride-based deicers such as sodium chloride and calcium chloride.

2.1 Ice-Melting Studies

2.1.1 Introduction and Background

2.1.1.1 *Introduction*

The objective of the ice-melting studies was to develop a standardized laboratory method for determining the ice-melting characteristics of known and candidate deicing materials. This subsection presents the experimental work and research studies undertaken to develop standardized laboratory methods for assessing the ice-melting characteristics of both liquid and solid deicers. Following the background discussion which includes a review of reported ice-melting tests and test results, the remainder of this subsection is organized as follows: Developmental Studies and Experimental Work (Section 2.1.2); Results and Discussion (Section 2.1.3); Conclusions and Recommendations (Section 2.1.4); and References (2.1.5).

2.1.1.2 *Background*

An ice-melting test involves the determination of the quantity of ice melted in a suitable deicer/ice system, as a function of time and of the quantity of deicer employed in the test. The test is sometimes called an ice-melting capacity test, but this term is both misleading and inappropriate. The ice-melting capacity of a chemical deicer is the quantity of water in a deicer/water system containing a unit weight of the deicer when the system is at equilibrium with excess ice at a temperature of interest. The ice-melting capacity so defined is usually termed the equilibrium or theoretical ice-melting capacity. Theoretical or equilibrium ice-melting capacities may, with certain limitations, be calculated from the familiar mathematical relationship which describes the effect of a solute on the freezing point of a solvent.

$$\Delta T = KwC$$

where ΔT is the freezing point depression in °C; Kw is a freezing point depression constant; and C is the deicer concentration expressed in moles or equivalents in 1,000 g water. Kw for water is ordinarily given as 1.86, which signifies that 1 mole or equivalent of a chemical in 1,000 g water will cause the freezing point to be -1.86°C. In dilute aqueous solutions, a Kw of 1.86 is adequate. In concentrated aqueous solutions a Kw of 1.86 will generally not yield true or actual freezing temperatures. In the International Critical Tables (National Research Council [1933]) freezing point depression constants are presented as a function of temperature for individual chemicals.

Ice-melting tests and test results reported in the literature universally employ a method in which ice and a deicer are placed in contact at a given temperature, and the generated brines are collected and measured at various time intervals. The test procedures accordingly rely on some method to separate ice from brine by drainage or decantation. The results obtained with such a procedure will be affected by the following factors:

- Adsorption of brines as surface films on ice
- Brine entrapment in cavities in ice

- Brine adsorbed on undissolved solid deicer particles

- The extent to which actual temperatures differ from a specified or initial test temperature, due to the endothermicity of ice-melting

- With solid-particle deicers, test results tend strongly to reflect the rate of dissolution of the particles. At low temperatures in particular, low yields of melted ice, after a given time interval, are more likely to be a consequence of incomplete dissolution of the deicer than due to slow melting of ice by the dissolved deicer. Results can accordingly be expected to differ as initial particle size ranges differ.

Ice-melting tests and test results reported in the literature are summarized below.

Keyser (1973) presents a general review of results of ice-melting tests conducted prior to 1973. *The Handbook of Snow* (Keyser 1981) presents a similar review.

Ice-melting test procedures and results obtained with various procedures are presented by Kersten et al. (1959), Brohm and Edwards (1960), Grant (1974), Dickinson (1959), and McElroy et al. (1988a,b,c). These findings are highlighted below.

Kersten et al. (1959) studied the melting of ice at temperatures from -23°F to +27°F. Deicing chemicals tested were sodium chloride, flake and pellet calcium chloride, and mixtures of sodium chloride and calcium chloride. The deicers were applied to the surfaces of ice contained in a pan. After varying time intervals, brine melts were removed by an unspecified procedure apparently consisting of decantation through an exit tube. Quantities of brine were determined by weighing brine and/or the ice-pan system before and after decantation.

Deicer application rates ranged from 32.8 g to 40 g applied to 550 g ice with a surface area of 112 in.^{2} (723 cm^2). These data correspond to an application rate of 0.45 to 0.55 kg/m^2 to ice approximately 0.75 cm thick. The application rates were approximately 15 times a representative application rate for highway deicing of 400 lb/lane mile (0.031 kg/m^2).

Results from the study showed that calcium chloride melts ice at the low temperatures at which sodium chloride is inactive; that initial melting is faster with calcium chloride than with sodium chloride; and that at high temperatures and long contact times (2 hr), the quantity of ice melted by sodium chloride tends to exceed the quantity melted by the same weight of calcium chloride. Mixtures of sodium chloride and calcium chloride yielded results that were predictable from the data obtained with the individual deicers.

Brohm and Edwards (1960) conducted a similar series of ice-melting tests with coarse crushed rock salt, fine crushed rock salt, flake and pellet calcium chloride, rock salt-calcium chloride mixtures, and sand-deicer mixtures at several application rates (0.72, 1.80, 3.60 and 7.2 lb/yard^2), at temperatures of 0°, 10°, 20°, and 30°F, and at times of 15, 20, 45, and 60 min. The application rates correspond to 0.39, 0.98, 1.96, and 3.9 kg/m^2 or approximately 12 to 120 times the representative highway deicing application rate. The series of tests generally yielded results which paralleled the comparisons in the Kersten et al. study.

In addition, Brohm and Edwards' results showed that the quantity of ice melted per unit weight of deicer decreases markedly as the application rate is increased and that fine crushed rock salt melts more ice than does coarse crushed rock salt. At comparable conditions, results obtained in the two studies differed considerably. However, one concludes that procedural differences, which were not readily apparent from the descriptions of the methods, were likely responsible for the inconsistencies.

Grant (1974) conducted a series of tests on the melting capacities of solar salt, rock salt, and mixtures of solar salt and rock salt. Three 11 x 17 in. (28 x 43 mm) trays containing 3/4 in. (19 mm) thick ice were placed one above the other, at 4-in. spacing, in a temperature controlled enclosure. The trays were tilted to give an incline of about 8 degrees in the direction of drainage holes, which permitted brine melts to drain continually to a collector. Deicing salts (100 g) were placed in a band about 2-in. (5 cm) wide along the center of the 11 in. (28 cm) dimension and extending from near the lower end to near the higher end of the 17 in. (43 cm) dimension. In these tests, the deicer was applied at a rate of 0.83 kg/m^2 for the total ice specimen. The salt was applied at a rate of about 4.6 kg/m^2, however, to the narrow (2-in., 5-cm) band of ice. A substantial fraction of the salt initially was not in contact with ice. Grant determined both the amount of ice melted and the amount of salt dissolved, at time intervals up to 6 hr and at temperatures of 10°F and 27°F (-12.2°C and -2.8°C). Test results indicated differences between solar salt and rock salt and between fine and coarse particle solar salt. Results were consistent from test to test, but do not correlate well with results reported by Brohm and Edwards and by Kersten.

Dickinson (1959) reports results of comparisons of flake calcium chloride and sodium chloride by unspecified procedures, at 0°, 10°, 20°, and 25°F (-17.8°, -12.2°, -6.7°, and -3.9°C). The chemicals were applied at a rate of 0.8 lb/yard^2 (0.434 kg/m^2). The data are reasonably consistent with the results reported by Brohm and Edwards at an application rate of 0.72 lb/yard^2 (0.391 kg/m^2), and indicate the expected differences between calcium chloride and sodium chloride, that is, faster initial melting by calcium chloride, a lower temperature threshold for calcium chloride, and equal or greater quantities of ice melted by sodium chloride at longer times and higher temperatures.

McElroy et al. (1988a,b,c) report the use of an ice-melting test similar in basic approach to those presented above. The method consists of broadcast addition of deicer particles to a 1/8-in. (3.175 mm) thick layer of ice contained in a 9-in. (22.9 cm) circular diameter Plexiglas flat-bottomed dish. At specified time intervals (usually 10, 15, 20, 25, 30, 45, and 60 min) the dish was tilted, and the liquid collected in a syringe. After being measured by volume, the liquid was reintroduced to the ice system via the melt holes. A uniform application rate of 3 oz/yard^2 (0.11 kg/m^2) was employed. Test temperatures were 0°, 5°, 10°, 15°, 20°, and 25°F (-17.8°, -15°, -12.2°, -9.44°, -6.7°, and -3.9°C). Materials tested contained the generic chemicals NaCl, $CaCl_2$, KCl, and urea as principal ingredients of commercial deicing products. Two types of calcium magnesium acetate (CMA) were also tested, as was rock salt wetted with 38% and 42% calcium chloride solutions. Quantities of brine, after 60 min, ranged from about 30 mL at 25°F to approximately 2 mL for sodium chloride deicers at 0°F and approximately 10 mL for calcium chloride deicers at 0°F. The reproducibility of results obtained with this method was considered to be good; tests conducted more than a year apart compared well. The greatest variability or apparent lack of reproducibility was observed with rock salt from two sources, which differed substantially in the proportion of fine particles.

The method employed by McElroy and coworkers (1988a,b,c) clearly demonstrated the rather substantial difference between generic classes of deicing materials at various temperatures and time intervals. Smaller differences, for example, between rock salt and rock salt wetted with liquid calcium chloride, were also satisfactorily demonstrated.

2.1.2 Developmental Studies and Experimental Work

The developmental studies and experimental work conducted are described in the following sections: Ice-Melting Test Method Selection and Development; Synopsis of Developed Ice-Melting Test Procedures; Facilities Requirements for Ice-Melting Test; Investigations of Ice-Melting at Various Solid Deicer Application Rates; and Development of an Ice-Melting Test for the Evaluation of Liquid Deicers.

2.1.2.1 *Ice-Melting Test Method Selection and Development*

All of the approaches described in the literature involved the addition of solid deicers to an ice specimen, followed by collection and measurement of generated brines at specific time intervals. No reasonable alternatives to this general approach were evident. Further, the results obtained by McElroy et al. (1988a,b,c) indicate that with a relatively simple overall procedure using inexpensive and simple equipment, satisfactory results with acceptable reproducibility can be obtained and that differences between chemical deicers can be reliably documented.

The principal deterrent to acceptance of a specific test method documented in the literature is the fact that the deicers were usually applied at quite high rates compared to standard highway-deicing application rates. The lowest rate utilized in the literature studies was 1,320 lb/lane mile, or 101.8 g/m^2; this rate was universally employed in studies reported by McElroy and coworkers (1988a,b,c). Rates employed in the remaining literature studies ranged from 390 g/m^2 to 3,900 g/m^2. A majority of the results were obtained with application rates of about 400 g/m^2. A representative highway application rate of 400 lb/lane mile corresponds to about 31 g/m^2.

It was decided to use the ice-melting test equipment and procedures employed by McElroy et al. (1988a,b,c) with the following areas designated for evaluation.

- The use of lower application rates, that is, rates of the order of 400 lb/lane mile or 30 g/m^2
- Assessment of the suitability of the test method for use with liquid deicers

The use of lower application rates is constrained or limited primarily by the lower volumes of brines generated in an ice-containing apparatus sufficiently small that it can be handled and manipulated with reasonable ease. A further size constraint is imposed by the stated need for a test which could be conducted in a reasonably conventional freezer. The 9-in. diameter Plexiglas dish employed by McElroy et al. (1988a,b,c) yielded about 2 to 4 mL of brine at 0°F (-17.8°C) to 5°F (-15°C), in 1 hr, with a sodium chloride deicer application rate of 1,320 lb/lane mile (101 g/m^2). At 400 lb/lane mile (31 g/m^2), the quantities of brine generated by sodium chloride in 1 hr would be vanishingly small; a 16-in. diameter dish would be required to generate 2 to 4 mL brine in 1 hr at the low temperatures with sodium chloride. It also was probable that brines would be less effectively recovered at the low application rates due to the dispersion of the brines over larger surface areas and retention of the brines as adsorbed films on the ice. For these reasons retention of the 9-in. diameter test dish was judged to be preferred. No deterrent was envisioned relative to the applicability of the test method to fluid deicers.

Before advancing the overall recommendation for an ice-melting test, it is appropriate to restate what an ice-melting test is and to consider its limitations. First, an ice-melting test consists of an attempt to physically separate melted ice and dissolved deicer from nonmelted ice, followed by measurements so that quantities of brine or melted ice can be related to the quantity of deicer. The separation process is necessarily flawed because complete separation cannot be effected. The completeness of separation will vary from deicer to deicer and from one temperature to another as brine concentration varies, and will be affected by the quantity of brine in relation to exposed surface areas of the ice.

No reasonable technique or procedure that permits a straightforward measurement of quantities of melted ice is obvious. One possible technique consists of the measurement of the concentration of the deicing chemical in a brine at various time intervals. This technique with solid deicers will, however, give meaningful results only after the solid is completely dissolved, and accordingly would be of no value for the numerous time intervals (particularly at lower temperatures) when solids are not completely dissolved. In this context, the ice-melting test is often more a measure of the rate of dissolution of a solid deicer than it is of the rate of ice-melting.

Given these basic limitations of an ice-melting test, one concludes that the preferred overall procedure should meet three requirements:

- A set of conditions and parameters that are conducive generally to a comparison of deicers, emphasizing both the time dependency of ice-melting and the comparative quantities of ice melted within a reasonable time frame, that is, 1 hr
- A set of conditions and parameters that permit the development of comparisons over temperature ranges of interest
- A reproducibility of results sufficient to permit reliable comparisons of deicers where differences are small, exemplified by comparisons of nonwetted rock salt with wetted rock salt

The principal thrust of experimental studies performed with the objective of defining the parameters of an ice-melting test involved the effect of deicer application rates. These studies particularly addressed the feasibility and practicability of a test utilizing an application rate of the order of 400 lb/lane mile (31 g/m^2). These tests, which are described in Sections 2.1.2.4 and 2.1.3 were concerned with the effect of deicer application rate on the quantity of brine collected per unit weight of deicer, and with the experimental limitations of tests based on low deicer application rates.

Results obtained in the experiments indicate that quantities of collectible brine per unit weight of deicer are apparently determined to a considerable extent by physical factors exemplified by the ratio of ice surface areas to brine volumes, and that the effects of such physical factors differs from deicer to deicer (specifically sodium chloride and calcium chloride). The results further support a conclusion that higher percentages of generated brines may be decanted and measured when brine volumes are higher relative to ice quantities and surface areas.

The recommended ice-melting test accordingly utilizes a deicer application rate of 1,320 lb/lane mile (101 g/m_2), with deicers applied to an ice specimen with a surface area of 63.62 in^2 (410.4 cm^2). These parameters will permit tests with sodium chloride at temperatures as low as 5°F (-15°C) to 0°F (-17.8°C) and will accommodate other deicers in the temperature ranges where they are potentially useful. Adherence to these parameters will also permit the general comparison of deicers under a uniform set of conditions.

It is appropriate, however, to consider and to present for possible use other test parameters which should give acceptable results.

As a general rule, the theoretical quantities of ice melted by a deicer at 30°F (about -1°C) are about three times the quantities theoretically melted at 25°F (-3.9°C). At 30°F, melting tests with an application rate of 1,320 lb/lane mile (101 g/m^2) would result in inconveniently high brine volumes. With calcium chloride and sodium chloride, ice-melting tests could be conducted with an application rate of 150 to 200 lb/lane mile (11.5 to 15.4 g/m^2); 200 lb/lane mile (15.4 g/m^2) would generally be acceptable for testing and comparing most deicers at 30°F.

At 25°F (-3.9°C) an application rate of about 500 lb/lane mile (38.5 g/m^2) would be generally acceptable; brine yields with a low melting capacity deicer such as urea will, however, be on the verge of being too low to permit accurate collection. For this reason it would appear that the rate of 1,320 lb/lane mile (101 g/m^2) is the preferred rate for temperatures of 25°F (-3.9°C) and lower.

2.1.2.2 *Synopsis of Developed Ice-Melting Test Procedures*

The ice-melting test utilizes a smooth layer of ice, 1/8 in. (3.175 mm) thick, frozen in a 9-in. (22.86 cm) diameter Plexiglas dish. The ice specimen is equilibrated to the specified test temperature, and a weighed quantity of deicer is placed as uniformly as possible on the surface of the ice. With solid deicers, the weight tested is 4.17 g, which corresponds to 1,320 lb/lane mile (101.5 g/m^2). With liquids, measured test sample weights correspond to a volume of about 3.8 mL. Prior to addition of deicer, the deicer is cooled to the test temperature, except in cases when cooling of liquid deicers will result in composition changes. Three replicate tests are specified.

At time intervals of 10, 20, 30, 45, and 60 min, brines are decanted to the perimeter of the dish, collected in a syringe; collected volumes are recorded; and the brines are returned to the ice specimens.

Data treatment:

- Brine volumes are divided by deicer weights
- Standard errors are determined for the three replicates
- Brine volumes are converted to quantities of ice melted per unit weight of deicer

The ice-melting test procedure includes, as required, determination by standard procedures, of brine densities or specific gravities in detail sufficient to permit calculation of quantities of melted ice.

2.1.2.3 *Facilities Requirements for Ice-Melting Test*

Ice-melting test results vary about 5% to 10% per degree Fahrenheit. Temperature control to within ±0.5°F (±0.3°C) is therefore important. This degree of control will not normally be possible in a cold room or freezer, and temperature control will be compromised by specimen manipulation requiring operator access.

For this reason, a regulated temperature enclosure placed either in a walk-in cold room or in a freezer is required. Specifications for an enclosure designed for use in a cold room were developed, as were specifications for an enclosure designed for use in an upright freezer. Temperature regulation in both enclosures is achieved by maintaining the cold room or freezer at a temperature a few degrees lower than the test temperature and by supplying thermal energy through a temperature-sensing and regulating system as required to maintain an operating temperature. All of the specifications are detailed in the Handbook: *Test Methods for Evaluating Chemical Deicers* in Annexes 1 and 2 of Method SHRP H-205.1, pp. B-17 to B-24.

Both systems (cold room and upright freezer enclosures) perform satisfactorily with the ice-melting, ice-penetration, and ice-undercutting tests. The cold-room system has a considerable advantage with respect to the ease of manipulation of test samples and generally permits the more effective use of manpower. If a walk-in cold room is not available, facilities costs are considerably less with an upright freezer.

Other facilities or equipment requirements are either generally available in a laboratory or are commercially available at nominal costs. These include a temperature regulator, an auxiliary freezer or refrigerator/freezer, timers, balances, syringes, sample vials, and calibrated thermometers.

2.1.2.4 *Investigations of Ice-Melting at Various Solid Deicer Application Rates*

Investigations of ice-melting at reduced deicer application rates were undertaken with two objectives in mind:

- Determination of whether or not ice-melting results differed substantially as application rates were lowered, thereby providing a basis for determining whether a low application rate (e.g., 400 lb/lane mile [31 g/m^2]) should be proposed for general use in a recommended test
- Determination of a practical lower limit for an application rate, based on the experimental limits of brine collection and measurement

We expected that the quantities of ice actually melted per unit weight of deicer would increase as the application rate is lowered, due to the lessened impact of the endothermic melting of ice. For the same quantities of ice melted per gram of deicer, the endothermic cooling from ice-melting at 1,320 lb/lane mile is 1,320/400 times the endothermic cooling at 400 lb/lane mile.

We also expected that quantities of recovered brine relative to quantities of brine formed by ice-melting would tend to decrease as application rates were lowered, that is, that surface films of brine retained by the ice would be higher in proportion to brine quantities actually formed as these quantities were reduced.

It was possible also that the two effects might counterbalance one another and that higher actual yields of brine accompanying a reduction in application rate would be counterbalanced by lower brine-collection efficiencies.

Ice-melting tests were conducted with sodium chloride (rock salt) at 1,320, 600, and 400 lb/lane mile at 25°F (-3.9°C); and at 1,320 and 600 lb/lane mile at 15°F (-9.44°C).

Tests were conducted with calcium chloride pellets at 5°F (-15°C), 15°F, (-9.44°C); and 25°F (-3.9°C) at 1,320 and 600 lb/lane mile. Corresponding metric system application rates were 101.5 g/m^2 (1,320 lb/lane mile); 61.5 g/m^2 (800 lb/lane mile); 46.2 g/m^2 (600 lb/lane mile); and 30.8 g/m^2 (400 lb/lane mile). Results of these tests are presented and discussed in Section 2.1.3.

2.1.2.5 *Development of an Ice-Melting Test for the Evaluation of Liquid Deicers*

The ice-melting test for liquid deicers differs only in procedural details from the test employed with solid deicers. The procedural difference relative to the test for solids consists of the utilization of a standard deicer test volume (3.8 mL ± about 0.05 mL), but with actual test weights being determined by weighing sample containers before and after discharge of liquid deicer to the ice specimen.

Because liquids melt ice primarily at the surface, the cavity-pocked ice formed with solid deicers is avoided. Liquids are completely uniform compared to the diversity in particle size and particle purity of solid deicers. Liquids further have a kinetic advantage over solids, which must dissolve before ice can be melted. The inherent differences between liquid and solid deicers potentially should translate into a greater result reproducibility for liquids and to rate vs. time plots essentially free of melting induction periods which are most marked when temperatures approach the eutectic temperatures of deicers.

Ice-melting tests were conducted at 25°F (-3.9°C), 15°F (-9.44°C), and 5°F (-15°C) with ethylene glycol, a 37.3% solution of calcium chloride in water and, a 26.3% solution of sodium chloride. Reagent purity chemicals were employed. Results of these tests are presented and discussed in Section 2.1.3.

2.1.3 Results and Discussion

2.1.3.1 *Experimental Results*

Results of ice-melting tests at various solid deicer application rates tests are presented in Table 2.1-1, with brine volumes converted to milliliters brine per gram deicer. Results of the ice-melting tests with liquid deicers are presented in Tables 2.1-2, 2.1-3, and 2.1-4. Methods employed to calculate quantities of ice melted as reported in the tables are presented in Section 2.1.3.2.3.

Table 2.1-1. Ice-melting capacities as a function of application rate

	Rock salt, 25°F (-3.9°C), mL/g deicer			Rock salt, 15°F (-9.44°C), mL/g deicer	
Time (min)	1,320 lb/ lane mile[a]	800 lb/ lane mile	400 lb/ lane mile	1,320 lb/ lane mile	600 lb/ lane mile
10	2.08	1.87	1.95	0.74	0.83
20	3.68	3.78	3.77	1.45	1.53
30	5.11	5.15	5.22	2.24	2.20
45	6.18	6.69	6.27	3.03	2.92
60	7.01	7.64	7.06	3.76	3.80

	$CaCl_2$ pellets, 5°F (-15°C), mL/g deicer		$CaCl_2$ pellets, 15°F (-9.44°C), mL/g deicer		$CaCl_2$ pellets, 25°F (-3.9°C), mL/g deicer	
Time (min)	1,320 lb/ lane mile	600 lb/ lane mile	1,320 lb/ lane mile	600 lb/ lane mile	1,320 lb/ lane mile	600 lb/ lane mile
10	0.98	0.98	1.81	1.25	2.84	2.82
20	1.96	1.73	2.94	2.07	4.72	4.57
30	2.45	1.95	3.46	2.27	5.64	5.38
45	2.65	2.11	3.77	2.41	6.48	6.19
60	2.72	2.25	4.00	2.54	7.00	6.56

[a] Metric system application rates:
1,320 lb/lane mile = 101.5 g/m^2
800 lb/lane mile = 61.5 g/m^2
600 lb/lane mile = 46.2 g/m^2
400 lb/lane mile = 30.8 g/m^2

Table 2.1-2. Ice-melting test data for ethylene glycol (EG)

Time (min)	25°F[a]		15°F[a]		5°F[a]	
	mL Brine per g EG	Ice melted, g/g EG	mL Brine per g EG	Ice Melted, g/g EG	mL Brine per g EG	Ice melted, g/g EG
10	3.85	2.97[b]	2.87	1.99[b]	2.54	1.66[b]
20	4.77	3.89	3.22	2.34	2.55	1.67
30	5.31	4.43	3.44	2.56	2.64	1.76
45	5.81	4.93	3.60	2.72	2.72	1.84
60	6.12	5.24	3.71	2.83	2.77	1.89
Equilibrium,[c] calculated	8.72	7.83	4.32	3.43	3.16	2.28

[a] Test information, average deicer weight

25°F, 4.1704 g (four replicates)
15°F, 4.2193 g (four replicates)
5°F, 4.137 g (three replicates)
Standard error, percent
25°F: range 0.3 to 2.3
average, 1.0
15°F: range 0.5 to 0.9
average, 0.7
5°F: range 0.3 to 2.2
average 1.0

[b] Gram ice melted/g EG = mL brine/g EG -0.885.

[c] Equilibrium g ice melted/g EG calculated from literature values for EG concentrations in solutions at equilibrium with ice:

25°F: $\frac{1 \text{ g EG}}{0.1132} - 1 = 7.83$

15°F: $\frac{1 \text{ g EG}}{0.226} - 1 = 3.43$

5°F: $\frac{1 \text{ g EG}}{0.3046} - 1 = 2.28$

Table 2.1-3. Ice-melting test data for 37.3% $CaCl_2$

	25°F[a]		15°F[a]		5°F[a]	
Time (min)	mL Bring/g solution	g Ice melted/g solution	mL Bring/g solution	g Ice melted/g solution	mL Brine/g solution	g Ice melted/g solution
10	2.37	1.65[b]	1.82	1.10[b]	1.50	0.78[b]
20	2.75	2.03	2.01	1.29	1.58	0.86
30	3.07	2.35	2.10	1.38	1.61	0.89
45	3.28	2.56	2.17	1.45	1.62	0.90
60	3.45	2.73	2.20	1.48	1.63	0.91
Equilibrium,[c] calculated	4.74	4.01	2.46	1.73	1.812	1.08

[a] Test information, average of three replicates
Average deicer wt.
25°F, 5.2193 g
15°F, 5.1843 g
5°F, 5.2649 g
Standard error, percent
25°F: range 1.6 to 3.6
average, 2.1
15°F: range 0.3 to 0.7
average, 0.5
5°F: range 0.3 to 1.6
average 0.9

[b] Gram ice melted/g deicer solution = mL brine/g EG -0.725.

[c] Equilibrium quantities of ice melted per g deicer solution calculated from literature equilibrium brine concentration:

25°F: $\frac{0.373}{0.0745} - 1 = 4.007$

15°F: $\frac{0.373}{0.1365} - 1 = 1.73$

5°F: $\frac{0.373}{0.17925} - 1 = 1.08$

Table 2.1-4. Ice-melting test data for 26.3% NaCl

	25°F[a]		15°F[a]		5°F[a]	
Time (min)	mL Brine/g solution	g Ice melted/g solution	mL Brine/g solution	g Ice melted/g solution	mL Brine/g solution	g Ice melted/g solution
10	1.97	1.15[b]	1.46	0.64[b]	1.06	0.24[b]
20	2.33	1.51	1.51	0.69	1.09	0.27
30	2.51	1.69	1.57	0.75	1.09	0.27
45	2.63	1.81	1.62	0.80	1.10	0.28
60	2.81	1.99	1.62	0.80	1.11	0.29
Equilibrium,[c] calculated	4.01	3.19	1.79	0.96	1.23	0.40

[a] Test information, average of three replicates
Average deicer wt.,
25°F, 4.6273 g
15°F, 4,6633 g
5°F, 4.5916 g
Standard error, percent
25°F: range 0.6 to 1.7
average, 1.1
15°F: range 1.0 to 1.8
average, 1.2
5°F: range 0.3 to 1.5
average 1.1

[b] Gram ice melted/g deicer solution = mL brine/g -0.825.

[c] Equilibrium quantities of ice melted per g deicer solution calculated from literature equilibrium brine concentration:

25°F: $\frac{0.263}{0.0628} - 1 = 3.188$

15°F: $\frac{0.263}{0.1345} - 1 = 0.955$

5°F: $\frac{0.263}{0.1882} - 1 = 0.3974$

Typical ice-melting test results for calcium chloride pellets and sodium chloride particles are presented in Tables 2.1-5 and 2.1-6.

2.1.3.2 *Discussion of Results*

2.1.3.2.1 Investigations of Ice-melting at Various Solid Deicer Application Rates. With sodium chloride, the results presented in Table 2.1-1 indicate that brine yields are essentially the same with the different deicer application rates at 15°F (-9.44°C) and 25°F (-3.9°C). It would appear that if actual quantities of melted ice per gram deicer are greater with the lower application rate, they are essentially counterbalanced by lower brine recovery efficiencies.

The results with pellet calcium chloride show that recovered quantities of brine per gram deicer are higher at 1,320 lb/lane mile (101.5 g/m^2) than at 600 lb/lane mile (46.2 g/m^2), at 25°F (-3.9°C), 15°F (-9.44°C), and at 5°F (-15°C). Yields of brine per gram deicer at 600 lb/lane mile are about 95% of the yields at 1,320 lb/lane mile (101.54 g/m^2) at 25°F (-3.9°C), 67% at 15°F (-9.44°C), and about 80% at 5°F (-15°C). This general behavior is consistent with the fact that calcium chloride reacts exothermically with water and ice. Lowering the application rate should, therefore, have a lesser effect on quantities of ice melted than it does with sodium chloride, which reacts somewhat endothermically with water and ice. However, it is believed the lower yields, particularly at 15°F (-9.44°C) are primarily due to adsorption of calcium chloride brines on ice surfaces. This effect will be greater, on a relative basis, when brine quantities are lower in proportion to the area of ice surfaces.

Relative to the advisability or need to conduct ice-melting tests with rates of the order of highway deicing application rates, the data indicate the following.

- With sodium chloride at 25°F (-3.9°C) and at 15°F (-9.44°C), yields of collected brine per unit weight of sodium chloride are not appreciably different at the tested deicer application rates. The similarity of the results may be due in part to a counterbalancing of increased actual yields per gram deicer, as rates are lowered, by reduced recovery efficiencies. It was concluded, nevertheless, that the higher application rate of 1,320 lb/lane mile (101.5 g/m^2) is preferred for sodium chloride. This rate permits the conduct of melting tests with sodium chloride over the range of temperatures of interest (e.g., as low as 5°F [-15°C], and 0°F [-17.8°C], utilizing an apparatus sized for reasonable manipulative convenience. This consideration applies

Table 2.1-5. Typical ice-melting capacity test results

Test Parameters
  Deicers:
    $CaCl_2$ pellets
    NaCl, Morton-Thiokol Safe-T-Salt™
    Deicer weights: 4.17 g
  Temperatures:
    -3.89°C (25°F)
    -9.44°C (15°F)
    -15°C (5°F)
  Replicates: 3

	NaCl		$CaCl_2$	
Time (min)	Brine[a] volume (mL)	Standard error (%)	Brine[a] volume (mL)	Standard error (%)
		-3.89°C (25°F)		
10	8.7	5.2	11.8	12
20	15.3	5.4	19.7	1.4
30	21.3	4.7	23.5	1.5
45	26.2	3.3	27.0	1.2
60	29.7	3.8	29.2	1.4
		-9.44°C (15°F)		
10	3.1	4.0	7.5	8.3
20	6.0	2.8	12.3	3.9
30	9.3	0.4	14.4	3.3
45	12.7	0.5	15.7	1.9
60	15.7	2.1	16.7	2.0
		-15°C (5°F)		
10	1.0	11.0	4.9	6.0
20	1.5	5.8	10.6	3.0
30	2.6	6.2	12.0	1.2
45	3.8	5.3	12.8	1.0
60	5.2	5.0	13.1	0.3

[a] Average of 3 replicates.

Table 2.1-6. Typical ice-melting capacity test results
(Milliliters of brine per gram of deicer)(grams of ice melted per gram of deicer)[a]
test parameters: specified in Table 2.1-5.

Time	-3.89°C (25°)		-9.44°C (15°F)		-15°C (5°F)	
(min)	mL/g	g ice melted/ g deicer	mL/g	g ice melted/ g deicer	mL/g	g ice melted/ g deicer[a]
			$CaCl_2$ pellets			
10	2.83	2.75	1.80	1.75	1.18	1.14
20	4.72	4.58	2.95	2.86	2.54	2.46
30	5.64	5.47	3.45	3.35	2.88	2.79
45	6.47	6.28	3.76	3.65	3.07	2.98
			Sodium chloride			
10	2.09	2.03	0.74	0.70	0.24	0.22
20	3.67	3.56	1.44	1.37	0.36	0.33
30	5.11	4.96	2.23	2.12	0.62	0.58
45	6.28	6.09	3.04	2.89	0.91	0.85
60	7.12	6.91	3.76	3.57	1.25	1.16

[a] g ice melted per g deicer = (mL brine/g deicer) x (g H_2O/mL brine)
g H_2O/mL brine are as follows:

$CaCl_2$ at all temperatures: 0.97 g H_2O/mL brine
NaCl at 25°F (-3.9°C): 0.97 g H_2O/mL brine
NaCl at 15°F (-9.44°C): 0.95 g H_2O/mL brine
NaCl at 5°F (-15°C): 0.93 g H_2O/mL brine

also to other deicers for melting tests conducted at temperatures approaching either the eutectic temperature or a temperature at which quantities of melted ice diminish to small values. Examples of such deicers are urea, potassium chloride, and CMA.

- With calcium chloride the quantities of generated and collectible brine are high enough at low temperatures to permit reasonable tests at 400 lb/lane mile at 5° to 0°F (-15° to -17.8°C). However, the fact that collectible yields of brine per unit weight of deicers decrease somewhat as the application rate is lowered indicates that a better measure of ice melting is obtained at higher application rates because a higher percentage of the generated brine can be collected and measured at the higher application rates. For this reason, the higher rate (1,320 lb/lane mile, 101.5 g/m^2) is preferred for an ice-melting test with calcium chloride.

2.1.3.2.2 Ice-Melting Test Results With Liquid Deicers. The results obtained with liquid deicers were considered to be satisfactory relative to the recommended procedure for use with liquid deicers. The standard errors given in Tables 2.1-2, 2.1-3, and 2.1-4 for liquid deicers are generally about 1% of the average values, compared to standard errors generally in the range of 2% to 10% for solid deicers. Results obtained with liquid deicers are thus more reproducible than results with solid deicers. Results with liquid deicers also indicate that initial rates of melting are higher with liquids than with solid deicers. This behavior is particularly evident with sodium chloride at low temperatures; the effect can be attributed to the low rate of dissolution of a solid deicer which becomes pronounced for sodium chloride at low temperatures.

2.1.3.2.3 Modification of Ice-Melting Data Analysis Procedures. Investigations with liquid deicers prompted the adoption of data analysis and reporting practices which had not previously been used with solid deicers.[1] The first step in data analyses consists of calculation of the volume, in milliliters, of the brine collected per gram of deicers for each of the three replicates. The second, and normally final, step consists of calculation of the quantity of ice melted per gram of deicer.

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[1] With solid deicers, the volume of brine collected is a reasonably straightforward measure of ice melting, when deicer weights are the same in all cases. With liquid deicers, the initial liquid volume may be as much as 67% of the volume calculated for theoretical ice melting (e.g., 26.3% NaCl at 5°F [-15°C]); collected brine volumes can be misleading and have no consistent relation to quantities of ice melted by liquid deicers.

Raw data obtained in the ice-melting test consist of brine volumes, which can either be related to the total weight of charged deicer or to a unit weight of deicer. Calculations of quantities of ice melted, as signified by collected brine volumes, may in principle be carried out by multiplying brine volumes by brine densities, followed by multiplying the resultant brine weights by the percentage of water in the brines (100-wt % deicer in brines). While such a procedure is simple in principle, its use is hindered by the general lack of data on specific gravities at low temperatures as a function of deicer concentrations and by uncertainties regarding deicer concentrations in brines. The procedure becomes more manageable, and less dependent on precise physical property data, if one considers the fact that the weight of water contained in a unit volume of brine is relatively insensitive to changes in deicer concentration and to changes in temperature. For calcium chloride brines, the weight of water in 1 mL brine ranges from 0.956 g H_2O/mL for an 18% solution at 5°F (-15°C) to 0.9805 g H_2O/mL for a 10% solution at 23°F (-5°C). For sodium chloride brines with concentrations expected at 5°F (-15°C), 15°F (-9.44°C), and 25°F (-3.9°C), 1 mL brine contains 0.93, 0.95, and 0.97 g H_2O/mL brine.

Solutions of solid inorganic chemicals generally conform to the above relationships, that is, the addition of solute is roughly accompanied by density increases so that the weight of water in a unit volume of brine remains relatively constant. From a limited amount of data on specific gravity as a function of solute concentration and temperature, appropriate factors may be developed which permit the calculation of the weight of water contained in a unit volume of brine.

For solid calcium chloride deicers, 0.97 g H_2O/mL brine is appropriate for temperatures ranging from 5°F (-15°C) to 25°F (-3.89°C). For solid sodium chloride deicers, the appropriate numbers are 0.97 at 25°F (-3.89°C), 0.95 at 15°F (-9.44°C), and 0.93 at 5°F (-15°C).

Results with liquid deicers are more conveniently treated on the basis that dilution of a given volume of deicer with 1 g of water (as melted ice) results in a volume increase very close to 1 mL. This means that if the volume of 1 g of liquid deicer is known (i.e., the specific volume), the change in volume, in milliliters, accompanying dilution with melted ice can be equated with the weight of dilution water in grams. The quantity of ice melted in grams by 1 g of liquid deicer in any specified time interval can accordingly be calculated by subtracting the specific volume (mL/g) of the deicer from the collected volume of brine.

Specific volumes of ethylene glycol, 37.3% aqueous $CaCl_2$, and 26.3% NaCl, at several temperatures are shown in Table 2.1-7. The values given for lower temperatures are extrapolated. From the data in the table, it can be seen that specific volume changes about

1% over a temperature range of +20° to -15°C. Specific volumes at about 25°F (-3.9°C) will accordingly be satisfactory for calculations of quantities of melted ice over the temperature ranges of interest in ice-melting tests.

Table 2.1-7. Specific volumes of liquid deicers

	Temperature	mL/g
Ethylene glycol	20°C	0.896
	25°F (-3.9°C)	0.888
	15°F (-9.44°C)	0.886
	5°F (-15°C)	0.884
37.3% $CaCl_2$	20°C	0.733
	25°F (-3.9°C)	0.726
	15°F (-9.44°C)	0.725
	5°F (-15°C)	0.723
26.3% NaCl	10°C	0.830
	0°C	0.827
	25°F (-3.9°C)	0.825
	15°F (-9.44°C)	0.824
	5°F (-15°C)	0.822

Calculations of quantities of melted ice give values based on collected brine volumes. Calculated results are accordingly conservative to the extent that some fraction of generated brines remain adsorbed on the ice.

2.1.4 Conclusions and Recommendations

- A basic procedure and associated equipment have been developed and evaluated for an ice-melting test which is recommended as a standard test method. The procedure consists of the application of solid or liquid deicer to an ice surface and decantation, collection, and measurement of generated brines at several time intervals over a 1-hr period.

- For solid deicers, an application rate of 101.5 g/m^2 (1,320 lb/lane mile) is recommended. For liquid deicers, a uniform volume of liquid is applied at a rate which corresponds approximately to a rate of 101.5 g/m^2 (1,320 lb/lane mile).

- Procedures have been developed that permits the conversion of volumes of brine recovered in the tests to the quantities of ice melted per unit weight of deicer.

- The recommended deicer application rate represents a compromise between an objective of a test which might yield generally acceptable results at representative application rates for highway deicers and a set of test parameters which will result in collectible and measurable quantities of brine from reasonably sized test specimens, over temperature ranges of interest.

- Results from the ice-melting test are subject to the uncertainties and variability of the effectiveness with which generated brines can be collected and measured. For this reason, the test is most appropriately viewed as a procedure which permits the comparison of deicers with tests conducted under uniform conditions, but with temperature varied to gather data within the temperature ranges of interest.

- The recommended ice-melting test methods developed during this program are given in the *Handbook: Test Methods for Evaluating Chemical Deicers*, as SHRP H-205.1, Test Method for Ice-melting Capacity of Solid Deicing Chemicals, and SHRP H-205.2, Test Method for Ice-melting Capacity of Liquid Deicing Chemicals.

2.1.5 References

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2.2 Ice-Penetration Studies

2.2.1 Introduction and Background

2.2.1.1 *Introduction*

The objective of the ice-penetration studies was to develop a standard laboratory method for determining the ice-penetration characteristics of known and candidate deicing materials.

This section presents the experimental work and research studies undertaken to develop a standard laboratory method for assessing the ice-penetration characteristics of both liquid and solid deicers. Following the background discussion, which includes a review of reported ice-penetration tests and test results, the remainder of this section is organized as follows: Developmental Studies and Experimental Work (Section 2.2.2); Ice-Penetration Results (Section 2.2.3), Conclusions and Recommendations (Section 2.2.4), and References (Section 2.2.5).

2.2.1.2 *Background*

Particles of solid deicers, when placed on the surface of ice, tend strongly to melt in the downward direction, creating roughly cylindrical cavities. The dimensions of the cavity at the surface are determined largely by the dimensions of the original particles. Cavity diameters generally decrease as the particles diminish in size and they continue to sink in the brine created by melting. In the final stages the cavities may be less than 1 mm in diameter at the lower extremities. With a block or cube of ice, the cavities tend to be directionally irregular, that is, develop what can be described as a corkscrew configuration.

The penetration property is important from a deicer performance standpoint in that, with a sufficiently thin layer of ice (or packed snow), the deicer is afforded a means to attain the ice/pavement interface. Subsequent ice-melting occurs in part at the interface, thereby disbonding the ice from the pavement. The penetration properties of a deicer, accordingly, provide a measure of its usefulness in ice and snow control. Ice-penetration tests are designed to provide information on this aspect of the performance properties of chemical deicers.

Trost, Heng, and Cussler (1988) conducted penetration tests at -5°, -10°, and -20°C with sodium chloride, calcium chloride, urea, and CMA. A major objective of this work was the development and testing of mathematical formulas which might account for the physical processes involved in ice-melting and ice penetration. Water was frozen in cylinders 6 cm in diameter and 5 cm high. After equilibration to test temperatures, weighed quantities of the deicer (either 0.1 g or 1.8 g) were placed on the surface of the ice. A drop of water was added to the deicers, and depths of penetration were measured with a cathetometer. Reagent grade calcium chloride, reagent grade sodium chloride, commercial rock salt (halite), fertilizer grade urea and RAD Chemicals CMA were tested. Rock salt and regent grade sodium chloride gave similar results. After 1 hr at -5°C the following approximate penetration depths were reported for 0.1 g samples: (a) $CaCl_2$ = 38 mm, (b) NaCl = 19 mm, (c) urea = 5 mm, and (d) CMA = 3 mm.

At -10°C, sodium chloride penetrated to a depth of about 7 mm in 60 min. At -20°C, 0.1 g sodium chloride penetrated to a depth of about 3 mm in 60 min.

Deicer particle sizes or particle weights were not specified. It is probable that each test sample contained multiple deicer particles. Trost et al. report that penetration rates and depths are independent of the amount of chemicals applied.

Dickinson (1959) reports depths of penetration of ice at temperatures from 30°F to approximately -20°F for sodium chloride, calcium chloride, and 25% $CaCl_2$-75% NaCl mixture. Calcium chloride penetrated to greater depths than did sodium chloride after 2 hr at 10°F and lower, and the mixture penetrated to greater depths than either single material at all temperatures.

Keyser (1981) cites penetration data obtained by Amberg and Williams (1948) on rates and depths of penetration of ice by salt particles of various sizes (maximum size 0.1 m g) at 0°C and -10°C.

Sinke and Mossner (1976) describe a method for observing deicer penetration as part of a study of undercutting. Particles coated with fluorescein dye were placed on the surface of 1/8-in. thick ice layers on concrete near one edge, so that the penetration cavity could be observed visually. No data on penetration rates were reported.

Larrimore et al. (1979) employed the Sinke and Mossner technique, with 2-in. thick block of ice, to determine the penetration characteristics of rock salt, and rock salt wetted with 30% liquid calcium chloride, 59% propylene glycol in water, 56% ethylene glycol in water, and water. It was found that the wetting agents increased initial rates of penetration and depths of penetration up to 1 hr after application.

Penetration cavities in ice tend to vary in diameter and sometimes to develop partially in a horizontal direction. This behavior makes it somewhat difficult to compare deicers. Sodium chloride penetration cavities thus differ in dimension and shape from calcium chloride penetration cavities. To circumvent this difficulty, McElroy et al. (1988a,b) developed a procedure which employed ice frozen in a 1/8-in. diameter cavity in Plexiglas. The upper section of the cavity was conically enlarged to provide an ice surface with a diameter of about 6 mm (1/4 in.). Pellets were placed on the top of the cavity. The pellets were lightly dusted with a water-soluble dye, or alternatively, a drop of aqueous dye was frozen on the ice surface.

Penetration data were obtained by this approach for rock salt; several commercial products composed principally of sodium chloride, urea, potassium chloride, sodium chloride-potassium chloride mixtures; and two sources of calcium magnesium acetate. Temperatures ranged from 5° to 25°F. Penetration rates and depths essentially mirrored ice-melting test results with respect to the response of deicer type to temperature and time. Reproducibility of results was considered to be acceptable.

The equipment and the associated procedure employed by McElroy and coworkers (1990) is simple and can be used to test 10 to 15 pellets at one time. Results can be documented and preserved photographically. However, the procedure has one possible defect. The melting process is artificially confined to a relatively small surface area, and thus it tends to force the deicer to melt vertically rather than horizontally. The same consideration applies to the relatively small diameter penetration cavity.

McElroy et al. (1990) conducted extensive tests of ice undercutting by solid particle deicers that indirectly yielded ice penetration data. In these tests, solid particles were placed on the surface of 1/8-in. (3.175 mm) thick layers of ice frozen on mortar substrates. The surface of the ice was spotted with a dye, and photographs were taken from above at several time intervals up to 60 min. The photographs showed the surface of small diameter cavities (about 4 mm in diameter) which were generated as the deicer particle melted through the ice to the substrate. Shortly after the ice/substrate interface was reached, the diameter of the approximately circular dye pattern began to increase as the ice was undercut. Visual observations of successive photographs in combination with curve fits of plots of undercutting versus time, served to identify times required for penetration through 1/8-in. (3.175 mm) depths of ice. Data generated on this basis represent a completely nonartificial set of conditions. The surface brines generated by initial melting were permitted to flow naturally away from the particle; the penetration cavity was not artificially constrained; and the surrounding environment consisted of ice and mortar. The times developed in this manner for penetration to a depth of 1/8 in (3.175 mm) are shown in Table 2.2-1.

Table 2.2-1. Time, minutes for penetration through 1/8-in. (3.175-mm) ice

Deicer[a]	25°F (-3.9°C)	20°F (-6.7°C)	15°F (-9.44°C)	10°F (-12.2°C)	5°F (-15°C)	0°F (-17.8°C)
Pellet $CaCl_2$	4-6	6-7	6-8	9-11	10-12	12-13
Flake $CaCl_2$	4-6	6-7	7-8	10-12	14-16	18-20
Rock salt	7-8	11-12	14-15	19-21	27-30	38-42
Potassium chloride	11-13	24-26				
Urea	24-26	30-35				
CMA	43-46					

[a] Particle sizes:

Pellet $CaCl_2$	21-23 mg
Flake $CaCl_2$	14-16 mg
Rock salt	30-35 mg
Potassium chloride	30-35 mg
Urea	14-16 mg
CMA	15-17 mg

The penetration results of Table 2.2-1 agree well with results obtained by McElroy et al. (1988b) with ice contained in Plexiglas cavities.

2.2.2 Developmental Studies and Experimental Work

2.2.2.1 *Test Method Selection*

The stated needs for a penetration test were procedures and equipment suitable for use with liquid and solid deicers. Since the literature contained no information on a method for liquid deicers, a substantial fraction of developmental efforts dealt with liquid deicers. The developmental efforts initially emphasized, however, studies of ice configurations and associated equipment. Some of the effort was devoted to tests of optional marking dyes and to procedures for applying the dyes.

The following guidelines were judged to be important or appropriate for selection of an ice penetration test method:

- For solid deicers, the test should if at all possible be a single particle test.
- Particle weights should be representative of weights of particles in commercial or other available materials. To the extent possible, particle weights should be essentially the same for different deicers.
- The equipment should permit the ready observation or measurement of ice penetration.
- The ice specimen should be configured so that the deicer particle occupies a relatively small fraction of the ice surface. The cross sectional area of the cavities formed in ice by the melting/penetration should furthermore be less than the cross sectional area of the ice.

In this regard, deicer particles of the size and weight employed in penetration tests are of the order of 2 to 3 mm in diameter or length, and the surfaces of the cavities formed by melting are of the order of 4 mm in diameter. Cavity diameters generally decrease as the depth of penetration increases. Behavior in this regard varies from deicer to deicer: calcium chloride pellets tend to produce relatively uniform cavities that have little tendency to drift in the horizontal direction; sodium chloride particles yield cavities that generally decrease in diameter with depth of penetration and are likely to be less than 1 mm in diameter at the lower extremities. The sodium chloride cavities also have a much greater tendency to wander in the horizontal direction--enough so that on occasion a depth measuring probe could not be inserted to the bottom of the cavity.

- The ice should be of sufficient quality to preclude variability in results which can be anticipated with ice which is stressed or exhibits faults. A preferred technique and associated equipment would permit the formation of ice both simply and reproducibly.

The Plexiglas-cavity method employed by McElroy et al. (1988b) was judged to be the simplest from an operational standpoint, and the consistency and reproducibility of the results were found to be satisfactory. However, the surface area (6 mm diameter) of the conically shaped segment of the ice was only 2.5 to 3 times the area of penetration cavities at the surface, and the cross sectional area of the 1/8 in. (3.175 mm) diameter cavity below the surface cone was approximately the same as the cross sectional of areas of penetration cavities at depths of 3 to 4 mm.

2.2.2.2 *Test Method Development*

2.2.2.2.1 Ice Configuration Studies. A series of exploratory penetration tests was conducted with various configurations of ice.

Initial tests involved ice specimens frozen in cavities in Plexiglas ranging from 1/4 in. (6.35 mm) to 1/2 in. (12.7 mm) in diameter. Other specimens were frozen in conically shaped cavities 1/2 in. (12.7 mm) in diameter at the top. Penetration tests with such systems, with sodium chloride particles at 25°F (-3.9°C) gave results generally consistent with prior results obtained by McElroy et al. (1988b) with smaller diameter cavities in Plexiglas. The results were variable, however, and it was apparent that the quality of the ice was both variable and unacceptable.

The majority of the developmental tests were conducted with cavities in Plexiglas consisting of an upper conical section 10 mm in diameter at the surface. The test cavities were constructed by drilling holes in a 1/2-in. (12.7 mm) wide x 2-in. (50 mm) tall section of Plexiglas, to a depth of 40 mm, followed by countersinking with a 60-degree angle, 1/2 in. diameter body center reamer to a depth which yielded a surface diameter of 10 mm. The cone intersected with the small diameter cavity 5 mm below the surface. Three diameters: 1/8 in. (3.175 mm); 5/32 in. (3.97 mm); and 6/32 in. (4.76 mm) were tested for the lower segments of the cavities. With these ice specimens, deicer pellets at initiation of penetration tests occupy about 10% of the available surface area of the ice, and the tops of penetration cavities occupy about 15% of the available surface area.

The cross-sectional areas of ice below the cone (i.e., at penetration depths of 5 mm and greater) range from approximately the same as the cross-sectional areas of ice-penetration cavities at 5 mm, to approximately 20 times the cross-sectional areas of ice-penetration cavities at greater depths.

Ice formed in conical sections of these configurations and confined by rigid Plexiglas walls is not acceptable for use in its original or as-frozen condition. Some ice always protrudes above the surface of the Plexiglas, and ice in the cone is usually separated from the walls. The ice at or near the surface must be prepared for penetration tests by a process which involves melting the protruding ice with a metal iron, followed by refreezing and one or two additional remelt and surface leveling operations. Final surface leveling is usually effected by the addition of small droplets of water via a glass rod. The conditioning/leveling process establishes ice contact with the walls of the cone and appears to anneal or melt out flaws in the ice. In this regard, ice specimens in the larger, 6/32 in. (4.76 mm) diameter cavities were somewhat more difficult to prepare for penetration tests.

Deicer penetration tests were conducted with a Plexiglas apparatus containing five of each cavity types described above. Sodium chloride particles and calcium chloride pellets were tested at 25°F (-3.9°C), 20°F (-6.7°C), 15°F (-9.44°C), and 5°F (-15°C). Penetration results were essentially the same with cavities 1/8 in. (3.175 mm), 5/32 in. (3.97 mm), and 6/32 in. (4.79 mm) in diameter. The intermediate diameter (5/32 in. [3.97 mm]) was selected as the preferred diameter for a penetration test. Results obtained with the selected apparatus are presented in Section 2.2.3.

The intermediate diameter cavity with a conically enlarged upper section provides an ice specimen several times the cross-sectional area of ice penetration cavities for the first 3 to 5 mm of penetration, and ice below the conical section has a cross-sectional area which ranges from about the same to substantially greater than the cross-sectional areas of penetration cavities. The ice in the conical section of the intermediate diameter cavity is more readily converted by melting/refreezing to the condition judged acceptable for penetration tests, than is the ice formed in the larger diameter (6/32 in., 4.76 mm) system.

2.2.2.2.2 Dye Studies. Penetration depths are in effect manually measured at various time intervals. A dye material is essential to provide a sharp, visible outline of the penetration cavity. A technique in general use consists of dusting solid deicers with a relatively minor quantity of powder-form dye. Dye substances sufficiently soluble in water or brines at low temperatures are limited in number. The dusting procedure was discarded by McElroy et al. (1988b) when it was found that rock salt and other similar solid deicers coated with even small quantities of dye were in effect insulated from ice at temperatures of 15°F (-9.44°C) and lower.

This difficulty was circumvented by preparing a dilute water solution of the dye, and freezing a small droplet of dye solution on the surface of the ice. With Rhodamine B as the dye, no difficulties attributable to the dye were experienced (an identical procedure was employed in undercutting tests). Unfortunately, Rhodamine B has been designated as a cancer suspect dye, and its recommendation for use in a penetration test is precluded. Other alternative dye materials and dye introduction procedures were investigated and generally found to be unacceptable, usually due to poor or erratic color.

The Bulls-Eye™ dye material has been designated as nonhazardous. This dye is available in a 50% solution in water. This dye has proved to be satisfactory when added in very small proportions to liquid deicers. However, when droplets of dilute aqueous solutions are frozen on ice surfaces, and solid deicers placed on top of the frozen droplets, the initial rate of deicer dissolution is inhibited. Satisfactory results were obtained, however, when deicer particles were placed on ice surfaces adjacent to small frozen dye droplets. The procedure finally adopted consists of placement of two to three pin head size droplets of neat (i.e., 50% in water as received) Bulls Eye™ dye slightly off center on the surface of ice prepared for the penetration tests.

2.2.2.2.3 Test Method Modifications for Liquid Deicers. A need was stated for a penetration test adapted for use with liquid deicers. Given the inherent tendencies of liquid deicers to become dispersed as thin films over an ice surface and to melt ice uniformly from the surface downward, a penetration test for liquids is basically an artificial test.

A penetration test for liquids most directly comparable to the test for solid particles probably consists of placing 20 to 25 mg (approximately 30 μL) in a preformed surface cavity in ice about 4 mm in diameter and 3 mm deep. Such a test would approximate the entrapment of a small quantity of liquid in a depression in ice.

The configuration tested utilized ice frozen in the cavities employed for solid deicers, with the ice surface slightly concave so that the 30 μL of liquid deicer was contained on ice 10 mm in diameter. With this configuration, the liquid deicer is deposited in a liquid layer about 0.4 mm thick on the surface of the ice. From 15 to 20 mg of neat Bulls-Eye™ dye was added to 5 mL of liquid deicer, so that the configuration of melted ice could be observed.

Liquid deicers tested were ethylene glycol, aqueous calcium chloride saturated at 0°C (37.3% $CaCl_2$), and aqueous sodium chloride saturated at 0°C (26.3% sodium chloride). The ethylene glycol was precooled to test temperatures. The aqueous solutions were precooled to 0°C to prevent precipitation of dissolved salts. Results from these tests are presented in Section 2.2.3

Ice penetration in the test was evidenced chiefly by uniform melting downward from the surface of the ice. An occasional small projecting node was observed at 25°F (-3.9°C). At 15°F (-9.44°C), and 5°F (-15°C), no deviations from a uniform front were observed. Ice penetration results obtained with the three liquids are acceptably reproducible. The recommended procedure for testing the penetration properties of liquid deicers accordingly consists of placement of 30 μL of the liquid on the surface of ice formed in a cavity in Plexiglas which is 10 mm in diameter at the surface and tapers to a diameter of 3.97 mm at a depth of 5 mm.

2.2.2.2.4 Synopsis of Developed Ice Penetration Test Procedures. Ice penetration test procedures for solid and liquid deicers are described in detail in the *Handbook: Test Methods for Evaluating Chemical Deicers* as SHRP H-205.3 and SHRP H-205.4, respectively. A synopsis of the test methods is given below.

- Test Apparatus

The apparatus is constructed from a 1/2-in. thick Plexiglas specimen by drilling 10 holes, 5/32 in. (4.0 mm) in diameter and 40 mm deep, and countersinking each cavity with a 60-degree center reamer to a depth such that the surface of the cavity is 10 mm in diameter. This apparatus is provided with a clear millimeter scale, taped to one side, so that penetration depths can be measured.

- Ice Preparation

Deaerated, deionized water is introduced into the cavities, and the water is frozen in a conventional freezer. After freezing, the upper sections of ice are prepared for penetration tests by approximately a three-step procedure consisting of melting excess surface ice, refreezing, and a final adjustment of the surface so that it is flush with the tops of the cavities. With liquid deicers, surface ice in the final step is made slightly concave, in order to confine liquid deicers to the surface.

- Dye Addition

With solid deicers, a very small quantity of neat Bulls-Eye™ dye is placed off center on the surface of the ice. With liquid deicers, neat Bulls Eye™ is admixed with a small inventory of liquid deicer in proportions of 15 to 20 mg dye in 5 mL deicer.

- Penetration Test

After the ice specimens have been equilibrated to test temperatures, deicers are placed on the surface of the ice. Solid deicer particles are centered on the ice surface; deicer weights are 25 ± about 2 mg. Liquid deicers are added via a micropipette in 30 μL quantities to each ice specimen. Penetration depths are recorded at 5- to 15-min intervals over a 60-min test period.

- Data Presentation

Five replicates are recommended. Data handling consists of calculation of average penetration depths of the five replicates for each time interval, calculation of standard errors, and presentation of the results in tabular and/or graphical form.

2.2.3 Ice-Penetration Test Results

2.2.3.1 *Experimental Results*

Representative ice penetration test results with rock salt (sodium chloride) particles and calcium chloride pellets are presented in Table 2.2-2.

Representative ice penetration test results for liquid deicers are presented in Table 2.2-3. Liquid deicers tested were ethylene glycol, 37.3% calcium chloride in water, and 26.3% sodium chloride in water.

2.2.3.2 *Discussion of Results*

While the results in Table 2.2-3 have been designated as ice-penetration results, that is, as depths of penetration after specified time intervals, the numbers are more appropriately viewed as measures of the quantities of ice melted. The deicer to deicer differences are in fact essentially the differences predicted from theoretical ice-melting capacities. The penetration results found with the aqueous sodium chloride solution illustrate this point.

At 5°F(-15°C), penetration by the sodium chloride solution was barely detectable, consistent with the low ice-melting capacity (0.4 g ice melted per gram NaCl solution) of the solutions at this temperature. At 15°F (-9.44°C), the theoretical ice-melting capacity of the sodium chloride solution is 0.96 g ice melted per gram solution, and penetration in 1 hr was 0.3 to 0.4 mm. Depths of ice melting calculated from theoretical ice-melting capacities are 0.19 mm at 5°F (-15°C) and 0.45 mm at 15°F (-9.44°C).

It should be pointed out that all of the penetration results reported for liquid deicers are valid only for the configuration tested. Thus ethylene glycol would melt/penetrate to greater depths if the same quantity of liquid was confined to a smaller surface area of ice, and penetration would be substantially less if the ethylene glycol was permitted to disperse freely over an ice surface.

Table 2.2-2. Example ice-penetration test results

Time (min)	Rock salt particles (22-27 mg)						Calcium chloride pellets			
	15°F		20°F		25°F		5°F		25°F	
	Penetration depth avg. (mm)	Standard error (%)	Penetration depth avg. (mm)	Standard error (%)	Penetration depth avg. (mm)	Standard error (%)	Penetration depth avg. (mm)	Standard error (%)	Penetration depth avg. (mm)	Standard error (%)
3	0.5	30	1.0	6	1.6	9	1.4	12	2.8	5
5	1.3	22	1.9	11	3.0	5	2.3	7	4.9	3
10	2.1	13	3.6	13	5.1	4	4.2	12	9.7	4
15	3.2	12	5.1	9	8.7	9	6.2	11	14.5	4
20	4.0	13	6.7	13	11.2	9	7.6	11	14.9	4
30	5.7	8	10.0	18	15.9	7	9.3	8	15.8	4
45	8.9	11	13.1	10	17.5	6	9.4	9	16.3	4
60	10.4	12	13.4	9	18.5	6	9.5	8	17.6	4

Table 2.2-3. Ice penetration test results with liquid deicers

Test parameters
Deicers:
Ethylene glycol (EG), 31-34 mg
37.2% $CaCl_2$, 41-43 mg
26.3% NaCl, 35-38 mg
Test results
mm penetration, average of 5 tests

-15°C (5°F)

	EG		37.3% $CaCl_2$		26.3% NaCl	
Time (min)	Avg. depth (mm)	Standard error (%)	Avg. depth (mm)	Standard error (%)	Avg. depth (mm)	Standard error (%)
5	0.42	4.8	0.62	6.0	Barely detectable penetration	
10	0.78	4.8	0.73	4.1		
15	0.97	2.1	0.86	4.7		
20	1.12	3.3	0.99	2.5		
30	1.12	3.3	1.01	2.4		
60	1.21	3.3	1.08	3.1		

-9.44°C (15°F)

	EG		37.3% $CaCl_2$		26.3% NaCl	
Time (min)	Avg. depth (mm)	Standard error (%)	Avg. depth (mm)	Standard error (%)	Avg. depth (mm)	Standard error (%)
5	0.76	5.3	0.76	3.2	Maximum penetration 0.3-0.4 mm	
10	1.06	3.8	1.10	2.9		
15	1.26	3.2	1.16	2.1		
20	1.82	4.4	1.50	3.0		
30	2.10	1.5	1.58	3.7		
45	2.23	1.3	1.78	2.1		
60	2.88	2.8	1.95	1.6		

-3.89°F (25°F)

	EG		37.3% $CaCl_2$		26.3% NaCl	
Time (min)	Avg. depth (mm)	Standard error (%)	Avg. depth (mm)	Standard error (%)	Avg. depth (mm)	Standard error (%)
5	1.32	7.3	1.2	11	0.2	-
10	1.96	3.7	1.6	6.0	0.3	-
15	2.28	3.2	2.1	7.3	0.4	-
20	2.60	4.7	2.3	4.7	0.6	-
30	3.50	3.1	3.1	5.5	1.0	-
45	4.72	4.6	3.3	5.1	1.1	3
60	5.48	3.8	3.5	4.3	1.6	7

2.2.4 Conclusions and Recommendations

Based on the ice-penetration test research conducted during this program, the following conclusions and recommendations are drawn:

- Equipment and associated procedures for determination of the penetrating characteristics of solid and liquid deicers have been developed. The recommended apparatus permits the use of simple procedures for preparing multiple ice specimens for the test. The apparatus provides an ice specimen that is large in proportion to the dimensions of surface melting and ice penetration cavities to a penetration depth of about 5 mm. At depths below 5 mm, penetration cavities are directionally constrained in the vertical direction in an ice specimen with a cross-sectional area greater than normal ice penetration cavities.

- The significance of ice-penetration results arises from a combination of the rate of penetration and the ultimate depth of penetration. The initial rate of penetration serves to indicate the time required to penetrate through ice to the substrate, so that the undercutting and disbondment process can commence. The ultimate depth of penetration, that is, after about 1 hr, provides a new semiquantitative measure of the melting capacity available for undercutting and disbondment. In this regard the ultimate depths of penetration may be misleading as some deicers tend to form small and elongated cavities.

- The ice-penetration test is perhaps the simplest of the three deicer performance tests from an operational standpoint. It can be considered the preferred test for the preliminary screening test for a deicer and for observing characteristics exemplified by rates of deicer particle wetting, surface melting vs. melting via penetration, and the lower temperature limits for a deicer.

- The ice-penetration test with a liquid deicer is an artificial test in that the liquid is artificially contained on a specified ice-surface area. Melting takes place chiefly via a uniform front propagated in the downward direction. Results obtained in the test are thus specific for the dimensions of the test configuration.

2.2.5 References

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2.3 Ice-Undercutting Studies

2.3.1 Introduction and Background

2.3.1.1 *Introduction*

The objective of the ice-undercutting studies was to develop a standard laboratory method of determining the ice-undercutting characteristics of known and candidate deicing materials.

This section presents the experimental work and research studies undertaken to develop a standard laboratory method for assessing the ice undercutting characteristics of both liquid and solid deicers. Following the background discussion, which includes a review of reported ice-undercutting tests and test results, the remainder of this section is organized as follows: Developmental Studies and Experimental Work (Section 2.3.2); Results and Discussion (Section 2.3.3), Conclusions and Recommendations (Section 2.3.4), and References (Section 2.3.5).

2.3.1.2 *Background*

Ice undercutting is the term used to describe the melting, by a chemical deicer, of relatively thin layers of ice between a pavement substrate and ice formed on the surface of the substrate. The undercutting process serves to disbond ice from the pavement; the degree of disbondment is a function of temperature, of deicer characteristics and the quantity available at an undercutting site, of the properties of ice at the interface, and of the physical characteristics of the pavement surface.

Of the deicer performance tests, an undercutting test provides information and data which most directly relate to ice and snow control. The test permits the direct comparison of deicers in a function (ice disbondment), which is a key to ice and snow control.

An undercutting test involves the measurement of the area of the ice melted between ice and pavement when isolated, measured quantities of a deicer are positioned so that ice-melting can occur at the ice/pavement interface. With solid-particle deicers, the particle must initially be provided a degree of contact with ice sufficient both to initiate the melting process and to provide for continuing dissolution of the solid in ice melts. With liquid deicers, the deicer must initially be localized at the undercutting site in artificially constructed cavities or holes in the ice. In all of the tests, undercutting is part of an overall process which may include melting through a given thickness of ice. It always involves some melting of the walls of a cavity in ice which serves to contain and localize the deicer.

There is a need for an undercutting test method to be used with solid particle deicers, with liquid deicers, and with different types of substrates.

Two specific requirements are methods suitable to be used with dark substrates (e.g., asphaltic) and light substrates (e.g., portland cement concrete). These two types of substrates require different approaches if the undercut patterns are to be made visible and measurable.

Sinke and Mossner (1976) used 1/8-in. thick specimens of ice in a study of ice penetration followed by undercutting with rock salt (sodium chloride) and calcium chloride particles. The particles were dusted with the sodium salt of fluorescein, which dissolved in the melt and was fluorescent under ultraviolet light. Photographs of the undercut areas were used to determine the undercut area. Time and temperature were the variables in addition to deicer type. Results were expressed as undercut area per unit weight of deicer (cm^2/g). Temperatures were in the 0° to 25°F range.

Larrimore et al. (1979) employed the Sinke method to compare sodium chloride and sodium chloride prewet with 30% liquid calcium chloride.

McElroy et al. (1990) used the same technique with a different dye (Rhodamine B) to investigate undercutting by 10 deicers based on the generic materials $CaCl_2$, NaCl, KCl, urea, and calcium magnesium acetate (CMA).

The preformed cavity technique was employed with solid deicers by Trost et al. (1987) in an extensive fundamental study focused on the development of mathematical models to describe the several physical and chemical processes in melting and undercutting.

The preformed cavity technique was employed with liquid deicers by Blackburn et al. (1990) in SHRP H-203 as a means to determine and define surface and interfacial properties as they pertain to ice bonding and ice/surface disbondment, and in extensive studies of undercutting on several types of pavement substrates.

2.3.2 Developmental Studies and Experimental Work

2.3.2.1 *Test Method Selection*

2.3.2.1.1 Test Guidelines. The basic features of undercutting test procedures described in the literature were deemed to be generally acceptable. The principal considerations relative to selection of specific or preferred procedures were as follows:

- The method employed to prepare ice/substrate specimens was considered to be critical. With improperly frozen ice, undercutting can be erratic and quite extensive. Although information on undercutting with ice poorly bonded to a substrate can be viewed as important, a standardized test should be based on ice/substrate specimens which can be depended upon to yield reproducible results.

- With solid deicers, undercutting tests should be conducted with single particles, sized to be representative of available deicing chemicals.

- With solid deicer particles, the particles should be placed on the surface of a specific thickness of ice. This practice will satisfy the following requirements:
  (a) representation of expected undercutting when a deicer is placed on the surface of ice on highway, and (b) provision of an environment in which a deicer particle can melt ice until its melting capacity is exhausted by a combination of undercutting and melting ice on the surfaces of cavities in the ice.

- An undercutting test with liquids should resemble as closely as possible the undercutting test with solid particles. Such a condition could best be met by placing the liquid in an ice cavity of the approximate size (diameter of 4 mm) of cavities formed by solid particle deicers. Selection of such a configuration was prompted in part by the observation that undercutting areas per unit weight of liquid deicers found in SHRP H-203 were less than areas predicted by comparison with results reported by McElroy et al. (1990) with solid particle deicers. Liquid deicer test quantities employed in the SHRP H-203 study were of the order of 300 mg; these were placed in a conical cavity in ice approximately 10 mm in diameter at the ice/substrate interface.

- While an undercutting test should be suitable for use with ice formed on a variety of substrates, a test designed primarily for comparison of deicers should be based on a standardized substrate which can be fabricated reproducibly and can be expected to give reproducible results. A second consideration is the achievement of undercut patterns which can be measured without resort to the use of a planimeter or its equivalent.

With reasonably smooth substrates, undercut patterns are near perfect circles, and areas can be reliably determined by diameter measurement--manually during a test or from photographs.

Lightly broomed portland cement substrates yield irregularly shaped undercut patterns which must be measured with a planimeter. Very irregular or rough surfaces yield variously shaped undercut patterns; undercut areas are significantly affected by the physical nature of such substrates.

- The test procedure should, however, be suitable for use with various substrates, including core samples from highways.
- Suitable procedural techniques are needed to permit the observation and measurement of undercutting with various types of substrates.

2.3.2.1.2 Basic Features of the Selected Test Method. The selected undercutting test method basically is as follows:

2.3.2.1.2.1 *Substrate*. In principle, the substrate may be any available representative material. Substrate specimens should be 1 in. to 2 in. (2.5 cm to 5.0 cm) thick, have a surface area in the range of about 20 in.^{2} to 50 in.^{2} (100 cm^2 to 300 cm^2), and have a level, though not necessarily smooth, surface. The dimensions given above are not critical; they are convenient for laboratory operations and are large enough for replicated tests with one to two deicers.

The above generalized description of a substrate is presented in order to indicate that undercutting tests may be conducted with a wide variety of materials which either are or represent highway construction materials. In the next section of this report, the characteristics of a substrate designed for a standardized test are presented. This substrate is preferred for use in tests focused on comparison of deicers.

2.3.2.1.2.2 *Ice Characteristics*. Carefully frozen ice with a thickness of 1/8 in. (3.175 mm) has been designated for all tests. Adherence to the designated thickness is important for tests with solid particle deicers in which the solid particles are placed on the surface of the ice and must melt and penetrate through the ice before undercutting can commence.

With liquid deicers, ice thickness is less critical, but the ice must be thick enough that artificially formed cavities in the ice are large enough to contain designated test volumes of deicers.

2.3.2.1.2.3 *Synopsized Procedure*. Undercutting tests are conducted as follows:

- Single solid particles of known weights are placed on the surface of the ice together with a dye material which will serve to define the ice undercutting pattern as it develops.
- Measured quantities of liquid deicers are placed in cavities in the ice which extend to the substrate. A dye material is also provided.
- Undercut areas are measured at selected time intervals over a 1-hr period. The preferred approach involves photographic recording and measurement of areas from projected slides.
- Undercut areas are usually expressed as area undercut per unit weight of deicer, that is, as cm^2/g.

Test developmental studies conducted in the program were based on the above generalized method and procedures.

2.3.2.2 *Test Method Development*

2.3.2.2.1 Substrate Development. A smooth, level, lightly textured portland cement mortar surface was considered to be the appropriate substrate for use in a standardized test designed for elucidation and comparison of undercutting properties of deicers.

Test specimens were prepared as follows. The bottoms of Rubbermaid™ plastic trays, 6 in. x 9 in. x 2 in. deep, were sand-blasted to yield a surface with indentations approximately 1.7 mil, peak to valley. A mortar, prepared in accordance with ASTM C109-84, Standard Test Method for Comprehensive Strength of Hydraulic Cement, was cast in the trays and removed and cured as specified. The bottoms of the specimens, in contact with the sand blasted plastic surface, were smooth, but with a texture corresponding to peak and valley indentations of about 2 mils.

These substrates were used in numerous undercutting tests with liquids and solids. Undercutting patterns were near perfect circles, and circle areas were reliably determined by diameter measurement, principally on projected slides.

From the results of undercutting tests with the mortar substrate, it was concluded that the substrate was suitable for use in a standardized undercutting test. Undercutting results obtained with the smooth textured mortar surfaces were consistent with results obtained previously with lightly broomed mortar surfaces (McElroy et al., 1990).

2.3.2.2.2 Ice Preparation. Ice specimens employed in undercutting tests for both liquid and solid deicers were 1/8 in. (3.175 mm) thick layers of ice frozen on the substrate of choice.

Limited tests of optional ice growing techniques were conducted. The selected method is that employed by McElroy et al. (1990). Both the mortar substrate and water are precooled separately to about 35°F (2°C); the mortar specimen is placed on a level metal plate cooled to about 15°F (-10°C) in the bottom of an insulated chamber or box. The box is closed; air in the box heated to slightly above the freezing point of water; and this condition is maintained for 3 to 4 hr as the ice freezes in a bottoms-up mode. Ice frozen in this manner is apparently stress-free. Most important, however, is the fact that the method avoids flash or rapid freezing of water at the substrate/ice interface.

2.3.2.2.3 Marking Dye Development.

2.3.2.2.3.1 *Dye for Solid Deicer Test with Light Substrates*. As with the penetration test, Rhodamine B is the dye of choice in terms of color intensity, ease of use, and apparent absence of interference with melting processes. A felt tip marker may be used to deposit a small quantity of dilute aqueous Rhodamine B on the ice surface. The desired color develops quite well when deicer particles are placed on the frozen dye spots.

Several alternatives to Rhodamine B (a cancer suspect material) were tested. The selected dye is Malachite Green, which is sparingly soluble in water. A double application of dye spots from a saturated aqueous solution of Malachite Green gave satisfactory results in undercutting tests with solid particle deicers.

2.3.2.2.3.2 *Dye for Use with Dark (Asphaltic) Substrates*. The only acceptable dye for dark substrates identified in the investigations is the disodium salt of fluorescein. Under strong UV radiation, this dye yields brilliant yellow patterns which photograph well.

With solid particle deicers, placement of the fluorescein dye at the ice surface (by freezing an aqueous dye droplet or dusting the deicer particle) was precluded by the fact that dye dispersed over the surface in initial melts obscures the fluorescein undercut pattern.

This difficulty was circumvented by melting 4 mm diameter cavities in the ice extending to the substrate, placing 5 µL of an aqueous solution of fluorescein (150 mg in 5 mL H_2O) in the bottom of the cavity, and allowing it to freeze. The cavity is then filled with 0°C water, which is frozen. Deicer particles are placed over the visible dye in the center of a crater formed by ice refrozen from water expelled from the cavity by the warm rod.

This procedure worked well and is in fact superior to placement of dye on the surface. (With dyes on the surface, initial dispersion of ice melt on the ice surface surrounding the particle obscures the core cavity until the surface dye fades out. With deicers that have propensity for surface melting, identification of the onset and propagation of undercutting can be difficult.)

The dye material and procedure developed for use on dark substrates with liquid deicers are identical to that presented above, with the exception that the 4-mm cavity in the ice is not refilled with ice, 30-µL quantities of liquid deicer are placed in the cavity over the frozen fluorescein dye droplet.

2.3.2.2.3.3 *Dye for Use with Liquid Deicers on Light Substrates*. The preferred dye for use with liquid deicers on light substrates is Bulls-Eye™. The dye is added to inventories of liquid deicers in a proportion of 15 to 20 mg of neat dye in 5 mL of deicer.

2.3.2.2.4 Modification of Test Method for Liquid Deicers. The only available reference or literature information on undercutting by liquid deicers was that generated in SHRP H-203 prior to and concurrent with tests conducted in this study.

In the SHRP H-203 study, conically shaped Teflon plugs, 10 mm in diameter at the small end, were lightly pressed against the surface of the substrate. Water was added and frozen in the bottoms-up mode. The plugs were removed, and 0.25-mL (250-µL) quantities of deicer plus trace amounts of indicating dyes were placed in the resulting cavities. Deicers tested were ethylene glycol, 37.3% $CaCl_2$ in water, and 26.3% NaCl in water. Deicer test weights ranged from about 280 mg with ethylene glycol to 340 mg with the calcium chloride solution.

The SHRP H-203 procedure is the only reasonable option for undercutting studies with liquid deicers. However, the extents of undercutting found with calcium chloride and sodium chloride solutions were less than predicted from undercutting results obtained with the solid forms of calcium chloride and sodium chloride. In addition, the quantities of deicers employed in the SHRP H-203 studies were 8 to 10 times greater than quantities employed with solid particle deicers. The cross-sectional areas of the cavities in ice of the SHRP H-203 technique were 6 to 7 times the cross-sectional area of cavities generated by penetration of solid particle deicers through the ice.

No obvious explanation of the apparent discrepancy between SHRP H-203 results and results obtained with solid particle deicers was evident. However, the two procedures differed substantially in the size or magnitude of the tests. Further, comparisons of liquid and solid deicer undercutting would be more valid if test configurations and deicer test quantities were approximately the same. For these reasons, tests with liquids were undertaken with 30-µL quantities of the liquid placed in 4 mm diameter cavities in ice 1/8 in. (3.175 mm) thick.

The technique tested and adopted for formation of 4 mm diameter cavities in ice is as follows:

The end (0.5 cm in length) of a 1/4-in. aluminum rod was machined to a nominal diameter of 5/32 in. (3.97 mm). The measured diameter was 3.86 mm. The rod was warmed in water to 65° to 70°C, and the machined end is used to melt a hole in the ice. Water not forced out by the rod was removed with a plastic syringe with the needle removed. Normally, one repeat of this operation yielded an essentially bare or ice-free substrate at the bottom of the cavity. Cavity diameters were uniformly close to 4 mm.

With the mortar substrate, 15 to 20 mg of neat Bulls-Eye™ dye was added to a 5-mL inventory of the liquid deicers. An undercutting test set consisted of five cavities; in each cavity, 30 µL of deicer was deposited with a micropipette. Before and after weighings were used to determine the weight of deicer placed in five cavities. The total weight and the sums of the five undercut areas were employed to calculate undercut areas in cm^2/g deicer.

Results obtained with this procedure were quite satisfactory from the standpoint of reproducibility. Worthy of particular note is the fact that undercutting capacities were substantially higher than the capacities found in H-203. The differences or apparent discrepancies in undercutting capacities may in part be attributed to differences in substrate physical characteristics. Tests conducted in H-203 utilized substrates ranging from reasonably smooth portland cement concrete to the highly variable surface of core samples of open-graded asphalt. From a fundamental standpoint, the differences in undercutting capacities appear to be attributable to scale or size of individual undercutting tests. Undercutting results are presented and discussed relative to such considerations in the following section.

2.3.3 Results and Discussions

2.3.3.1 *Typical Experimental Results*

Typical ice-undercutting results obtained with solid-particle deicers on a smooth textured mortar substrate are presented in Tables 2.3-1 and 2.3-2 for pellet calcium chloride and sodium chloride particles, respectively.

Undercutting results with liquid deicers on mortar substrates are presented in Tables 2.3-3, 2.3-4, and 2.3-5 for ethylene glycol, 37.3% $CaCl_2$, and 26.3% NaCl. The data in Tables 2.3-4 and 2.3-5 are the undercut areas per unit dry weight of calcium chloride and sodium chloride.

2.3.3.2 *Discussion of Experimental Results*

Undercutting results obtained in the present study (H-205), in SHRP H-203, by McElroy et al. (1990) and by Trost et al. (1988) constitute a substantial inventory of data on this aspect of deicer performance. A cursory examination of results from these sources indicate that certain results are in conflict with other results. The inconsistencies or differences might be taken as an indication that one or more of the approaches to determination of undercutting is flawed, and that the results should be considered suspect. The apparent inconsistencies are as follows:

- With three liquid deicers, less undercutting was found in the SHRP H-203 study than in this study (SHRP H-205).
- Undercutting results obtained with solid calcium chloride and solid sodium chloride and results obtained with aqueous solutions of sodium chloride and calcium chloride are in apparent conflict.

Table 2.3-1. Typical ice-undercutting test results with solid $CaCl_2$ using a mortar substrate

	$CaCl_2$ pellets (90% $CaCl_2$)			
	25°F (-3.9°C)		5°F (-15°C)	
Time (min)	Average of 5 replicates (cm^2/g)	Std. error (%)	Average of 5 replicates (cm^2/g)	Std. error (%)
5	16.8	2.0	-	-
10	46.5	4.4	7.6	-
15	61.0	5.0	11.6	11.0
20	66.2	4.0	15.6	3.8
30	71.7	4.1	25.4	4.8
45	76.9	3.1	28.1	5.6
60	77.3	3.0	28.7	5.5

Table 2.3-2. Typical ice-undercutting test results with solid NaCl using a mortar substrate

	Sodium chloride (rock salt) particles			
	25°F (-3.9°C)		5°F (-15°C)	
Time (min)	Average of 5 replicates (cm^2/g)	Std. error (%)	Average of 5 replicates (cm^2/g)	Std. error (%)
5	8.1	-	0	-
10	24.6	15.0	0	-
15	46.0	6.1	0	-
20	58.8	4.7	0	-
30	79.5	3.5	5.7	14
45	84.9	1.6	7.5	7.7
60	86.5	2.5	10.7	8.7

Table 2.3-3. Typical ice-undercutting test results with ethylene glycol using a mortar substrate

Time (min)	Undercut area (cm^2/g ethylene glycol)				Standard error (%)
	Set No. 1	Set No. 2	Set No. 3	Average	
25°F (-3.9°C)					
5	22.7	24.9	20.2	22.6	7.4
10	39.6	40.7	34.7	38.3	4.8
15	48.3	51.4	43.2	47.6	5.0
20	54.2	55.6	48.0	52.6	4.4
30	58.0	61.1	51.9	57.0	4.7
45	60.2	63.3	56.4	60.0	3.3
60	60.5	64.1	57.3	60.6	3.2
20°F (-6.7°C)					
5	17.8	17.0		17.4	2.3
10	29.8	28.1		28.9	2.9
15	36.3	34.5		35.9	4.0
20	40.0	38.3		39.2	2.1
30	45.6	-		45.6	-
45	49.5	44.7		47.1	5.1
60	49.6	44.7		47.2	5.2
15°F (-9.44°C)					
5	6.8	8.0	5.3	6.7	1.2
10	16.9	15.7	14.6	15.7	4.2
15	22.4	20.5	21.9	21.6	2.6
20	26.8	23.7	24.0	24.8	3.9
30	29.5	27.1	26.8	27.8	3.0
45	31.5	28.6	29.6	29.9	2.8
60	32.0	30.5	29.7	30.7	2.2
5°F (-15°C)					
5	3.6	2.1		2.9	26
10	5.4	3.3		4.4	24
15	8.0	7.4		7.7	5.2
20	9.8	8.5		9.2	7.1
30	12.6	12.4		12.5	0.8
45	14.6	14.9		14.8	1.0
60	15.2	15.3		15.3	0.3

Table 2.3-4. Typical ice-undercutting test results with 37.3% $CaCl_2$ solution using a mortar substrate

Time (min)	Set No. 1	Set No. 2	Set No. 3	Average	Standard error (%)
	Undercut area (cm^2/g $CaCl_2$)				
25°F (-3.9°C)					
5	-	66.5	64.7	65.6	1.4
10	89.4	91.8	84.2	88.5	2.5
15	94.0	96.8	90.9	93.9	1.8
20	97.8	96.8	91.4	95.3	2.1
30	101.7	98.3	93.4	97.8	2.5
45	102.9	98.3	93.6	98.3	2.7
60	103.8	102.2	95.3	100.4	2.6
20°F (-6.7°C)					
5	50.6	52.2		51.4	1.5
15	63.1	63.9		63.5	0.6
20	65.2	64.7		64.9	0.4
30	69.6	67.4		68.5	1.6
45	70.3	-		70.3	-
60	71.1	70.4		70.7	0.5
	71.6	72.1		71.9	0.4
15°F (-9.44°C)					
5	37.4	35.3	33.4	35.4	3.3
10	46.4	44.8	43.8	45.0	1.7
15	52.2	49.3	46.7	49.4	3.2
20	53.3	50.4	48.0	50.6	3.0
30	53.7	51.1	50.1	51.6	2.1
45	53.9	52.0	50.1	52.0	2.1
60	54.6	52.0	50.1	52.2	2.5
5°F (-15°C)					
5	22.6	11.0		16.8	35
10	31.1	18.2		24.7	25
15	31.9	21.7		26.8	19
20	32.2	22.7		27.5	17
30	32.9	24.0		28.5	16
45	33.0	25.4		29.2	13
60	33.9	25.8		29.5	12

Table 2.3-5. Typical ice-undercutting test results with 26.3% NaCl solution using a mortar substrate

	Undercut area (cm^2/g NaCl)				
Time (min)	Set No. 1	Set No. 2	Set No. 3	Average	Standard error (%)
			25°F (-3.9°C)		
5	73.2	72.9	66.6	70.9	3.0
10	89.0	92.3	87.5	89.6	1.6
15	99.3	104.6	94.0	99.3	3.1
20	101.0	107.8	97.0	101.9	3.1
30	103.3	108.2	98.6	103.4	2.7
45	104.0	108.2	100.1	104.1	2.3
60	104.0	108.2	100.9	104.4	2.0
			20°F (-6.7°C)		
5	39.6	43.4		41.5	4.6
15	55.7	57.0		56.4	1.1
20	59.2	61.6		60.4	2.0
30	60.7	-		60.7	-
45	64.4	64.5		64.5	0.1
60	68.5	64.5		66.5	3.0
	69.4	64.5		67.0	3.7
			15°F (-9.44°C)		
5	23.7	19.6	20.9	21.4	5.8
10	28.0	29.0	27.6	28.2	1.5
15	32.9	31.6	29.6	31.4	3.1
20	34.2	32.8	31.0	32.7	2.8
30	34.9	33.0	34.8	34.2	1.8
45	37.3	35.6	35.2	36.0	1.8
60	37.6	35.6	35.2	36.1	2.1
			5°F (-15°C)		
5	3.7	4.9		4.3	14
10	5.2	6.0		5.6	7.1
15	6.0	6.3		6.2	2.4
20	6.5	6.8		6.7	2.2
30	6.8	7.1		7.0	2.1
45	6.8	7.1		7.0	2.1
60	6.8	7.1		7.0	2.1

- With solid forms of calcium chloride and sodium chloride, results obtained by Trost et al. (1987) range from being essentially the same as results obtained in SHRP H-205 and by McElroy et al. (1990), to being different by factors of two to three.

Some of the differences may be associated with experimental differences. Thus, Trost et al. (1987) placed multiple particles of solid deicers in the bottoms of preformed cavities in ice; McElroy et al. (1990) and the SHRP H-205 studies utilized single particles placed on the surface of the ice 1/8 in. (3.175 mm) thick. The SHRP H-203 undercutting procedure with liquids utilized a comparatively large cavity (10 mm diameter) and comparatively large quantities (250 µL) of deicer; in SHRP H-205, 30-µL quantities were placed in 4 mm diameter cavities.

The major procedural difference appear to be the substantial differences in the quantities of deicers utilized in individual undercutting tests. Some comparisons involve as much as a 15-fold difference in the quantities of deicers employed in the tests. With certain comparisons involving aqueous solutions of calcium chloride or sodium chloride with solid forms of these deicers, a 40- to 50-fold difference exists in the theoretical ice-melting capacities of the test samples.

The total inventory of undercutting results in the above enumerated studies involve slightly different temperatures, for example, -5°C vs. -3.89°C (25°F), as well as varied experimental techniques. Interpretation and comparison of the results is difficult in the absence of a reasonable and valid approach which permits comparisons on the basis of a property common to all deicers and which further might be expected to be independent of temperature.

Trost et al. (1987) interpreted both the magnitudes and the rates of undercutting in terms of a factor which basically consists of the theoretical ice-melting capacity of deicers at test temperatures. This fundamentally interesting and useful concept has been utilized in the present study to normalize available data. With this approach, undercut areas are expressed as cm^2 undercut per gram ice-melting capacity. The ice-melting capacities utilized in the normalization process are the theoretical or equilibrium ice-melting capacities of each deicer at each temperature, as calculated from literature freezing point/composition data.

Conversion of undercutting data to the normalized basis yields sets of data which show how effectively the inherent melting capacities are translated to undercutting.

Undercutting results germane to the comparisons and analyses undertaken in this study are presented in several tables as follows (all results represent undercutting at 60 min):

- In Table 2.3-6, undercutting results reported by Trost et al. (1987) with multiple particles of sodium chloride placed in cavities in ice at -5°C (23°F) are presented. The results are expressed as cm^2 undercut per gram sodium chloride.

Table 2.3-6. Literature undercutting results,[a] solid NaCl, at -5°C (23°F)

mg NaCl	Undercut area (cm^2/g)
50	69
100	55
200	40
316	45
500	34

[a] From Trost et al. (1987); multiple sodium chloride particles placed in a cavity in ice.

The results in Table 2.3-6 are considered significant in that the undercutting area per unit weight of sodium chloride decreases substantially as test sample weight is increased, that is, by a factor of two as weights are increased by a factor of 10. Trost et al. (1987) suggests that undercutting is limited or controlled by diffusion; the data are consistent with this interpretation.

- In Table 2.3-7, H-205 and H-203 undercutting results with three liquid deicers are tabulated. The results are expressed as cm^2 undercut per gram deicer. From the data in this table, it is evident that undercutting per unit weight of deicer increases by a factor of about 1.5 as deicer test weight is decreased by a factor of 8.33. The results with 26.3% sodium chloride at 5°F (-15°C) are an exception to this trend; this deicer has a very low melting capacity at 5°F (-15°C), and undercutting patterns are correspondingly small.

The results shown in Table 2.3-7, accordingly, indicate a consistent difference that would appear to be related to test sample size.

- In Table 2.3-8, undercutting results obtained with liquid deicers have been normalized with respect to deicer ice-melting capacities. The normalized data exhibit the trends attributed to test sample weights identical to the trends in Table 2.3-7. When either the 30 µL or 250 µL sets of data are examined, it is evident that the three deicers are

Table 2.3-7. Ice-undercutting results with liquid deicers (60-min), cm^2 undercut/g deicer

	Ethylene glycol		37.3% $CaCl_2$[a]		26.3% NaCl[a]	
	30 µL[b]	250 µL[b]	30 µL[b]	250 µL[b]	30 µL[b]	250 µL[b]
25°F (-3.89°C)	60.6	38	100.4	79	104.4	68
15°F (-9.44°C)	30.7	20	52.2	34	36.1	24
5°F (-15°C)	15.3	11	29.5	19	7.0	9.5

[a] Undercutting results expressed as cm^2 undercut per gram dry weight $CaCl_2$ and NaCl.

[b] SHRP H-203: 250-µL test sample.
SHRP H-205: 30-µL test samples.

Table 2.3-8. Ice-undercutting results with liquid deicers (60-min), cm^2 undercut/g ice melting capacity

	Ethylene glycol		37.3% $CaCl_2$		26.3% NaCl	
	30 µL[a]	250 µL[a]	30 µL[a]	250 µL[a]	30 µL[a]	250 µL[a]
25°F (-3.89°C)	7.8	4.9	9.2	7.2	8.7	5.7
20°F (-6.67°C)	10.1		11.0		11.0	
15°F (-9.44°C)	9.1	5.9	11.5	7.5	10.0	6.6
5°F (-15°C)	6.7	4.9	10.2	6.6	4.6	6.2

[a] SHRP H-203: 250-µL test samples
SHRP H-205: 30-µL test samples

quite similar at each of the three higher temperatures with respect to a capability to translate theoretical melting capacities into undercutting. The data do, however, support a conclusion that the order of decreasing effectiveness is $CaCl_2$ > NaCl > ethylene glycol.

Comparisons involving temperature generally indicate that on a normalized basis, ice-melting capacities are most effectively translated to undercutting at intermediate temperatures (15°F [-9.44°C] and 20°F [-6.7°F]). The calcium chloride solution is substantially more effective at 5°F (-15°F) than ethylene glycol and the sodium chloride solution, in keeping with other results obtained with calcium chloride at low temperatures.

- In Table 2.3-9, undercutting results obtained with solid deicers are presented on a normalized basis, with test sample weights indicated.

The -5°C (23°F) results were obtained with multiple particles of sodium chloride placed in ice cavities extending to the substrate. The remainder of the results were obtained with deicer particles placed on the surface of 1/8 in. (3.175 mm) thick ice. When comparable test weights were employed (50 mg NaCl vs. 30 to 35 mg NaCl), it can be seen that undercutting results were essentially the same at -5°C (23°F) and 25°F (-3.89°C), that is, 5.9 vs. 6.4 cm^2 undercut per gram ice-melting capacity. When deicer test weights at -5°C (23°F) are increased from 50 mg to 500 mg, undercut areas decrease from 5.9 to 2.9 cm^2/g ice-melting capacity.

At 25°F (-3.8°C), the normalized data with $CaCl_2$, KCl, NaCl, and urea range from 6.0 to 6.9 cm^2 undercut per gram ice-melting capacity.

Pellet calcium chloride is indicated to be somewhat superior to sodium chloride particles at the three higher temperatures and substantially better (6.7 vs. 2.9 cm^2 undercut per gram ice-melting capacity) at 5°F (-15°C).

The undercutting results presented in Tables 2.3-6, 2.3-7, 2.3-8, and 2.3-9 consistently indicate that undercutting areas are sensitive to test sample weights: undercutting decreases substantially as test weights increase which is consistent with the Trost et al. (1987) suggestion that diffusion limits undercutting. A satisfactory explanation accordingly exists for the apparent discrepancies or inconsistencies in results cited earlier. Further, it is evident that the relatively small test weights or liquid volumes specified in the recommended undercutting procedure are to be preferred to larger test specimens.

Table 2.3-9. Ice-undercutting results with solid deicers, 60 min, cm^2 undercut per gram ice melting capacity

	Solid deicers				
	25°F (-3.89°C)	23°F (-5°C)[a]	20°F (-6.67°C)	15°F (-9.44°C)	5°F (-15°C)
Sodium chloride					
30-35 mg	6.4		7.8	8.1	2.9
50 mg		5.9			
100 mg		4.7			
200 mg		3.4			
316 mg		3.8			
500 mg		2.9			
CaCl2					
22 mg	6.9		8.6	8.7	6.7
KCl					
30-35 mg	6.0		4.9		
Urea					
15-16 mg	6.8		7.9		

[a] From Trost et al. (1987).

Undercutting results available for analysis and interpretation support a conclusion that the extent of undercutting can be estimated from ice-melting capacity data with the following stipulations:

- The mass of the deicer considered falls within a range for which undercutting data are available.
- Calculated results generally will be more reliable at higher temperatures than at lower temperatures. At temperatures approaching the eutectic temperatures of a deicer, calculated results are likely to differ substantially from experimental results.
- All deicers do not respond equally in proportion to theoretical ice-melting capacities; this stipulation applies particularly to a new or unknown deicer.

As a generalized rule, when deicer test quantities fall within the range of 15 mg to 35-40 mg, undercutting areas can be expected to be as follows:

- For solid particles placed on the surface of 1/8 in. (3.175 mm) thick area: 6 to 8 cm^2 undercut per gram ice-melting capacity at temperatures of 15° to 25°F (-10° to -4°C).

- For liquid deicers placed in small cavities: 8 to 11 cm^2 undercut per gram ice-melting capacity at 15° to 25°F (-10° to -4°C).

The difference between liquid and solid deicers reflects the fact that solid deicers are required to melt the ice before undercutting commences.

2.3.4 Conclusions and Recommendations

Tests methods and procedures have been developed for determination of the undercutting capabilities of deicers. The method, with adaptations as referenced, is acceptable for use with a variety of substrates and with both liquid and solid deicers.

- Two factors are particularly important, namely the adherence to procedures which reproducibly yield ice properly and uniformly bonded to the substrate and the use of deicer test quantities which fall within a specified range. When the objective is the comparison of deicers, it is important to use a substrate with uniform and reproducible characteristics; for this purpose, a smooth, lightly textured mortar substrate is recommended.

- The simplest mode to depict undercutting results consists of calculation of the area undercut by a unit weight of deicer, that is, cm^2 undercut per gram of deicer. Such results permit the estimation of undercutting and disbondment to be expected from a specified rate of application for a deicer. From a practical standpoint, however, undercutting results obtained with the recommended procedure should be viewed as conservative, undercutting with poorly bonded ice can be much more extensive than the undercutting which occurs with ice/substrate specimens prepared by the recommended procedure.

- Conversion of undercutting data to the areas undercut per unit of deicer melting capacity provides information of fundamental interest. This conversion is also useful to compare an aqueous solution of a deicer with the solid form of the deicer. Conversely, the theoretical or equilibrium ice-melting capacity of a deicer may be employed, with certain limitations, to estimate the undercutting capability of a deicer.

Relative to the practical aspects of snow and ice control (more specifically, ice control), the following may be advanced.

- The most effective use of solid particle deicers for undercutting and disbondment of ice should be realized with the uniform distribution of relatively small deicer particles on the ice surface.

- The best option for ice disbondment should consist of application of deicer prior to ice formation for both liquid and solid deicers. Undercutting/disbondment (or prevention of bonding) will be substantially greater when chemicals are applied to the substrate surface rather than to the ice surface, because ice formed over a deicer-laden surface will be weakly bonded to the substrate and thus more susceptible to extensive undercutting.

- Although liquid deicers are shown by undercutting data to be effective with regard to undercutting and disbondment, their use as surface additions to ice is precluded because liquids have little tendency to penetrate through ice. Liquids should be particularly effective when applied to highway substrates prior to a storm.

2.3.5 References

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2.4 Concrete Compatibility

2.4.1 Introduction and Background

2.4.1.1 *Introduction*

The objective of the concrete compatibility studies was to develop a laboratory method of assessing the scaling/spalling effects of known and candidate deicing materials on concrete test specimens.

This section presents the experimental work and research studies undertaken to develop standardized laboratory test methods for assessing chemical deicer compatibility with concrete. Following the background discussion, which includes a review of reported concrete compatibility tests, the remainder of this section is organized as follows: Developmental Studies and Experimental Work (Section 2.4.2); Results and Discussion (Section 2.4.3); Conclusions and Recommendations (Section 2.4.4); and References (2.4.5).

2.4.1.2 *Background*

A driving force in the search for new or improved deicers is the corrosive or material-degrading characteristics of chloride-based deicers. Major costs associated with chemical deicers are those of maintaining and replacing bridge structures and pavements. Substantial costs are also associated with practices employed to minimize chemical deicer degradation effects on concrete, exemplified by the use of air-entrained concrete for pavement construction, increased overlayment thickness, and concrete surface treatments.

Concrete is subject to some degree of degradation in a nondeicer-impacted environment, and generally to more extensive degradation when chemicals are present. Some chemicals are quite incompatible with concrete, and these are clearly unacceptable in a deicer. The mechanical forces attending freezing and thawing of wetted concrete are clearly the cause of degradation; this effect is more severe when the water contains chemicals. Air-entrained concrete is susceptible to considerably less freeze/thaw damage than non-air-entrained concrete. Degradation of concrete also occurs under wet/dry exposure to chemical solutions, that is, in the absence of freeze/thaw cycles.

The mechanism of the deterioration of portland cement concrete caused by deicing chemicals is not well understood, but sufficient factors are known to allow the selection of a test method. Some of the major factors which influenced the choice of the test methods have been summarized by Boies and Bortz (1965) as follows:

- Some damage to the surface occurs when water without deicing chemicals is used in the freeze-thaw cycle. The damage, however, is greatly increased if the water contains a deicing chemical. Damage has been found with sodium chloride, calcium chloride, alcohol, and urea, with generally more damage in medium-strength solutions than in high-strength solutions. These factors indicate that the damage does not depend primarily on the formation of ice crystals, inasmuch as the damage with plain water is low. Furthermore, the damage experienced with various types of chemicals is less severe in more concentrated solutions.

- Properly cured air-entrained concrete has heightened resistance to the action of deicing chemicals. However, the use of an absorbent aggregate or variations in the surface air entrainment of the concrete can result in scaling even when the concrete is prepared properly. The amount of air entrained in the surface mortar layer is often considerably below that in the bulk mortar. This results in increasing the aggressiveness of deicing chemicals in the area most susceptible to damage.

- Continuous immersion of concrete in salt solutions without freezing results in some damage, indicating that there may be some chemical deterioration in addition to the physical damage.

- Damage appears to be greatest when water or deicer solution is in contact with the surface during the freezing portion of the cycle.

- There also are some indications that damage may occur during drying, caused by the recrystallization of the deicing agent.

The compatibility tests which are reported in the literature are both laboratory (controlled environment) and field (uncontrolled environment) evaluations to determine the type and rate of deterioration of nonmetals. The compatibility tests can be divided into two main types and then further broken down by specific test:

- Exposure tests
    - Freeze/thaw
    - Wet/dry
    - Outdoor exposure
    - Penetration/impregnation

- Degradation evaluation tests
    - Abrasion resistance
    - Mechanical strength
    - Ultrasonic/velocity
    - Visual/spectroscopic

Exposure tests are defined as those tests in which nonmetallic samples are subjected to a harmful or deterioration-producing environment. Degradation evaluation tests are defined as those tests measuring the severity of deterioration of a nonmetal sample subjected to a harmful environment.

2.4.1.2.1 Exposure Tests.

Brief descriptions of the use of each of the exposure tests as reported in the literature follow.

2.4.1.2.1.1 *Freeze-Thaw Tests*. An extensive amount of testing has been conducted using the freeze-thaw technique. The American Society for Testing and Materials (ASTM) has recommended a standard method to test the resistance of concrete to rapid freeze-thaw cycles (ASTM C666-84, 1987). This method determines the resistance of concrete samples exposed to rapidly repeated cycles of freezing and thawing in a laboratory using two different procedures: (a) rapid freezing and thawing in water, and (b) rapid freezing in air and thawing in water.

Each procedure is used to determine the effects of variations in the properties of concrete when subjected to specified freeze-thaw cycles. The recommended freezing-thawing cycle of test specimens consists of lowering the temperature from 40° to 0°F (4.4° to -17.8°C) and raising it from 0° to 40°F (-17.8° to 4.4°C) for 2 to 5 hr.

Several investigations have been conducted using the ASTM recommendation for freeze-thaw testing with a few variations. Minsk (1977) conducted an investigation in which concrete specimens (6 x 8 x 3 in. or 6 x 10-1/2 x 3 in.) were covered with 1/4 in. of chemical solutions and placed in a 0°F cold room for 16 hr. The specimens were removed and placed in a room at 70°F for 8 hr. At the end of every fifth cycle, the chemicals were poured off and a visual graded inspection of the specimens was conducted using a visual rating scheme. Specimens were photographed before the freeze-thaw tests, after 30 cycles, and at the end (60 cycles). Weight loss changes of each specimen were also recorded.

Eck et al. (1983) subjected 15 portland cement concrete specimens (three groups of five specimens) to freeze-thaw tests. One group was subjected to a distilled water freeze-thaw; another group was subjected to sodium and calcium chloride freeze-thaw; and a third group was subjected to a natural brine freeze-thaw.

Ozycdirim (1987) used the freeze-thaw testing procedure outlined in ASTM C666-84 (procedure A) with a few modifications. One modification consisted of the addition of 2% sodium chloride to the test water. The other modification consisted of moist curing the samples for 2 weeks and air drying for 1 week before testing.

Other experiments using freeze-thaw testing include Gonnerman (1944); Zaman, Ridgway, and Ritchie (1982); Mather (1982); Kallas (1963); and Pitt, Schluter, Lee, and Dubberke (1987).

Nadezhdin et al. (1988) reported an accelerated freeze-thaw test on small concrete specimens. The specimens, if prepared correctly, produced data on the relative effects of deicer formulations in a time period as short as 5 days. Briefly outlined, the test consists of placing concrete specimens the size of ice cubes in a Tupperware® dish (with lid) with a deicer solution and subjecting the specimens to a freeze-thaw process. After five or seven freeze-thaw cycles, the specimens are weighed and data analyzed.

2.4.1.2.1.2 _Wet-Dry Ponding Tests_. These tests (also referred to as immersion tests) are closely associated with the freeze-thaw testing procedures. Briefly described, wet-dry testing consists of submerging (partially or completely) specimens in a liquid substance for a specified time. The specimens are then removed and left to dry. The process is repeated several times and observations are recorded.

Several investigations have been conducted using the wet-dry testing process on concrete subjected to distilled water, sodium chloride, brine, and calcium chloride. Eck, Usmen, Sack, Adar, and Atefi (1983) used a wet-dry testing cycle on bituminous concrete and portland cement concrete. Specimen groups were totally immersed in a deicing solution (brine, sodium chloride, or $CaCl_2$) for 24 hr followed by a washing-drying period for 24 hr. Gonnerman (1944) subjected concrete specimens not only to a freeze-thaw process but also to a wet-dry process. Specimens were immersed in a 10% calcium chloride solution and tap water. Zaman, Ridgway, and Ritchie (1982) also used a combination of freeze-thaw and wet-dry testing procedures. Specimens were totally immersed in sodium chloride solutions ranging from 0% to saturation. An article published in *Better Roads* (1974) reported a test procedure in which portland cement concrete specimens were subjected to partial and full immersion. Billott (1978) reported a partial immersion test. Specimens were continuously immersed in water, NaCl (5% and saturation), $CaCl_2$ (5% and saturation), and $MgSO_4$ (4% and saturation). All specimens were subjected to 7 days of immersion in water before immersion in solutions.

2.4.1.2.1.3 *Outdoor Exposure Tests*. Closely related to freeze-thaw tests and wet-dry tests are the outdoor environmental exposure tests. Outdoor exposure test procedures differ from experiment to experiment. Basically, the test includes exposing concrete slabs to regular outdoor environmental conditions for a few years. Winter exposure usually includes ponding of water and/or deicing chemical solutions and permitting a freeze-thaw process to occur. Warmer seasons usually include a wet-dry process. Test results are usually derived using a concrete surface visual rating system.

Brink, Russell, Grieb, and Woolf (1967) created 115 concrete slabs (4 ft x 5 ft x 6 in) and placed them on columns 3-1/2 ft above ground for an outdoor exposure test. The slabs were covered with 1/4 in. water each night that freezing was expected. The following morning, NaCl and $CaCl_2$ were spread uniformly on each ice-encrusted slab. After 4 or 5 hr, the ice and chemicals were removed by flushing with water. The slabs went through a total of 140 cycles of freezing and thawing during a 3-year interval. All specimens were periodically examined and rated for the amount and depth of scaling. The studies revealed that outdoor exposure tests are not practical if there is a time constraint. Extensive time, space, and labor are needed to conduct an outdoor test.

2.4.1.2.1.4 *Penetration and Impregnation Tests*. There are many studies dealing with the penetration of deicing chemicals into concrete. While test procedures vary from experiment to experiment, most tests measure penetration of chloride concentrations in concrete specimens over a period of specified time. ASTM C114-84, "Chemical Analysis of Hydraulic Cement," outlines a test procedure for determining chloride content by the potentiometric titration of chloride with silver nitrate (ASTM C114-85, 1987).

Pitt, Schluter, Lee, and Dubberke (1987) used the hydrochloric acid dissolution techniques and the sulfur trioxide evaluation listed under ASTM C114-85. Beratsson and Chandra (1982) reported the mean content of chloride in concrete. Specimens were taken from dry borings at 100 mm from the surface and at 45 to 55 mm from the surface. Collepardi, Marcialis, and Turriziani (1972) report a procedure in which samples were cut lengthwise to measure the penetration of deicing agents on the interior of the samples.

Unlike Collepardi's method, Cavalier and Vassie (1982) tested samples by using the Quantab method for chloride content determination. Clear and Harrigan (1977) report step-by-step procedures for determining the amount of chloride ions in concrete. The potentiometric titration and the grade plot method of testing are outlined. Employing a different technique, Weyers, Blankenhorn, Lady, and Kline (1975) determined the effects of unidirectional pressure impregnation at relatively low pressures and the effects of deicer salts on the degree and rate of impregnation.

2.4.1.2.2 Degradation Evaluation Tests.

Brief descriptions of the use of the degradation evaluation tests as reported in the literature follow.

2.4.1.2.2.1 *Abrasion Resistance Tests*. Abrasion testing of concrete/cement surfaces is not a recently created testing procedure. However, only three references were discovered in the literature search that employed some sort of abrasion test. Currently, there are three recommended procedures for abrasion testing through ASTM: (a) C418-81, "Abrasion Resistance of Concrete by Sandblasting"; (b) C779-82, "Abrasion Resistance of Horizontal Concrete Surfaces"; and (c) C944-80, "Abrasion Resistance of Concrete or Mortar Surfaces by the Rotating-Cutter Method."

Minsk (1977) conducted an abrasion test that he developed to simulate the scraping action of a snowplow blade. Hoff (1987) briefly mentions an abrasion test conducted in a Canadian study. The test was conducted in accordance with ASTM C799-82 (987) under the ball bearing subprocedure. Nadezhdin et al. (1988) used the "Minsk Abrasion Technique" to compare the effects of various deicer formulations on concrete.

2.4.1.2.2.2 *Mechanical Strength Tests*. The mechanical strength tests are used to predict the behavior of concrete subjected to deicing chemicals under a freeze-thaw condition.

Eck, Usmer, Sack, Arar, and Atefi (1983) used compressive strength and pulse velocity tests. Zaman, Ridgway, and ritchie (1982) conducted compression tests on portland cement specimens cured underwater. Ozycdirim (1987) used compressive strength tests in which neoprene pads in steel end caps were used for capping. Flexural strengths were determined using third-point loading. Flexural tests were also conducted on test specimens.

Based on the literature findings, it was decided that mechanical tests should be considered for evaluating the effects of deicer chemicals on concrete and, when employed, that they should follow ASTM guidelines.

2.4.1.2.2.3 *Sonic and Ultrasonic Tests*. Only a few references on ultrasonic and sonic testing were found. Two references specified a standard test procedure for ultrasonic pulse velocity, ASTM C597-83, "Pulse Velocity Through Concrete."

Eck, Usmen, Sack, Arar, and Atefi (1983) subjected concrete specimens to pulse velocity tests immediately after curing. Pitt, Schluter, Lee, and Dubberke (1987) also employed pulse velocity testing in accordance with ASTM C597-83. Manning and Holt (1980) list two methods of acoustical detection of concrete delamination. Both methods are more suited for field testing.

2.4.1.2.2.4 *Visual and Spectroscopic Tests*. A wide variety of visual inspection procedures are employed. Most inspections are based on a rating system. ASTM test procedure C672-84, "Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals," is widely accepted for visual evaluation. Pitt, Schluter, Lee, and Dubberke (1987) and Beratsson and Chandra (1982) mention the use of spectroscopy. Pitt analyzed concrete specimens for pore structure. Beratsson and Chandra also analyzed samples by X-ray diffraction. Power and Hammersley (1978) examined polished concrete specimens to identify the various cement mineral phases in unhydrated clinker particles contained in hardened concrete.

2.4.2 Developmental Studies and Experimental Work

The objective of these experimental studies was to develop a laboratory method to assess scaling/spalling effects of deicer materials on concrete test specimens. The principal elements of these concrete compatibility experimental studies were (1) review applicable concrete compatibility test methods, (2) select the most appropriate methods, (3) modify and standardize available methods into acceptable SHRP-H205 laboratory test methods, (4) compare standardized test methods for correlation of results, and (5) publish the developed test methods in a handbook for state and local highway maintenance departments.

2.4.2.1 *Review of Concrete Compatibility Test Methods*

The available literature relating to compatibility of deicer materials and concrete was reviewed. The results were published as a part of a special report to SHRP, "Evaluation and Testing of Chemical Deicers, Literature Review," August 5, 1988. This review provided a basis for the selection of candidate concrete compatibility test methods.

2.4.2.2 *Selection of Appropriate Test Methods*

Criteria were developed for the selection of the most appropriate candidate test methods to assess the compatibility of deicer materials with concrete. Criteria used for selection were as follows:

1. Test method must be adaptable to use in a laboratory.
2. Test method must be relatively rapid, requiring not more than 3 months including curing of the concrete test specimens.
3. Test method must yield easily interpretable test results.
4. Test method must be within the scope of most, if not all, state highway maintenance laboratories and personnel.
5. Test method must not require expensive capital equipment.

Based on these criteria, the test method published by Nadezhdin et al. (1988) was selected for development and standardization. The Nadezhdin method met all of the criteria of selection, initially. The ASTM C672 test method was selected as an alternate method, meeting most of the criteria except length of time for completion and ease of interpretation of the results.

Both of these test methods involved freeze/thaw (F/T) cycling of concrete test specimens in contact with deicing brines. The concrete test specimens in the Nadezhdin method were small, about 50 cc, and were evaluated by weighing the test specimens after removing loose concrete material.

The ASTM C672 test specimens were much larger, but still the tests could be conducted in the laboratory using conventional refrigeration equipment. Evaluation of the scaled/spalled test specimens was somewhat subjective and consisted of visual examination and estimation of the scaling/spalling severity on a scale of 0 to 5. However, since ASTM C672 had been developed specifically for determining the scaling effects of deicer materials on concrete, the method was chosen as an alternate method for study.

2.4.2.3 *Modification and Standardization of Candidate Test Methods*

A rapid test method for determining the relative effects of deicer materials on the scaling/spalling resistance of concrete was reported by Nadezhdin et al. (1988). This method was selected as the "best available" test for a rapid evaluation of the concrete compatibility of chemical deicers. ASTM C672 was also chosen for modification as an additional method to determine the scaling/spalling effects of deicer materials on concrete test specimens.

2.4.2.3.1 Rapid Method to Determine Concrete Compatibility. Development of an accelerated test was prompted by the length of time and amount of labor required to conduct the standard test (ASTM C672) for determining the scaling resistance of concrete surfaces exposed to deicing chemicals. One of the significant features of the accelerated test was that the test specimens utilized in the Nadezhdin method were concrete, without air entrainment, whereas in the standard ASTM method, air-entrained concrete test specimens are usually employed.

Standardization of the accelerated test method was required to enhance its utility. It was evident that the test method and specimen preparation, as presented in the Nadezhdin paper, allowed for considerable latitude in the design of the concrete mix and the preparation of the test specimens. Therefore, in an attempt to standardize these variables, several modifications were made to the original test scheme.

2.4.2.3.1.1 <u>*Concrete Mix Design*</u>. Four aspects of the test specimen concrete mix design are discussed in this subsection: original mix design, modified mix design, sand used in modified mix design, and coarse aggregate used in modified mix design.

- Original mix design. The original concrete mix as specified by Nadezhdin was as follows:

Component	Parts w/w	Normalized to 100%
Type I portland cement	1.0	14.925
Water	0.7	10.448
Sand	2.25	33.582
Aggregate (-4/+20 mesh)	2.75	41.045

Water/cement ratio = 0.7
Sand/aggregate ratio = 45/55

ASTM C672-84, "Scaling Resistance Test," suggests a cement content of 564 ± 9.4 lb/yd^3. This translates into 14.92 wt % ± 0.25% for a concrete with a 140-lb/ft^3 density. Thus it seems reasonable that this was the basis for the original mix design.

- Modified mix design. The original mix design was modified by MRI with respect to the sand/aggregate ratio of 50/50 versus the 45/55 ratio used by Nadezhdin. In addition, the percentages were rounded for convenience to produce the following mix proportioning:

Component	Parts w/w	Wt %
Type I portland cement	1.0	15.00
Water	0.7	10.50
Sand (C-109 Ottawa)	2.48	37.25
Aggregate (limestone, washed, -4/+20 mesh)	2.48	37.25

Water/cement ratio = 0.7
Sand/aggregate ratio = 50/50

- Sand used in modified mix design. Sand from different sources with different gradations can possess different characteristics. Therefore, a standard-graded sand with a uniform composition was desirable. A graded Ottawa sand designated ASTM C-109 was selected. This natural silica sand was graded as follows:

U.S. Standard Sieve Size	Cumulative Percentage Retained
No. 16 (118 mm)	None
No. 30 (600 μm)	2 ± 2
No. 40 (425 μm)	30 ± 5
No. 50 (300 μm)	75 ± 5
No. 100 (150 μm)	98 ± 2

Ottowa sand is available in 50-lb bags from Soiltest Inc. or local building material suppliers throughout the United States.

- Coarse aggregate used in modified mix design. Due to restrictions imposed by ASTM C192-88, "Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory," a reduction in the maximum size of aggregate normally used to prepare concrete for highway pavement was employed in the modified mix design. The size of the aggregate is governed by the size of the test specimen. The minimum diameter of the beaker selected as a test specimen mold (configured in the shape of an inverted truncated cone) was 1.325 in. ASTM C192-88, paragraph 4.4, states that the minimum diameter of the mold shall be at least three times or more than the nominal maximum size of the coarse aggregate. The gradation (-4/+20 mesh) used by Nadezhdin appears to fit these specifications and blended well with the grading of the ASTM C109 Ottawa sand to produce a gradation curve which approaches the curve of a maximum density material.

  The coarse aggregate was prepared according to the ASTM C192-88 guidelines. Crushed limestone (referred to by the supplier as limestone dust) was secured and dry-sieved to remove most of the material greater than the No. 4 sieve and finer than the No. 20 sieve. This presieved material was then water washed on the No. 20 sieve and dried. The following gradation analysis resulted:

U.S. Standard Sieve Size	Cumulative Percentage Retained
No. 4	0
No. 6	24.3
No. 10	62.7
No. 16	87.1
No. 20	100.0

This material was crushed, angular, and sound, just as the larger-sized aggregate used in standard highway mixes, and it blended well with the ASTM C109 Ottawa sand. Thus it was recommended that an aggregate graded similarly (±2%) and processed as described above be utilized in the preparation of the rapid method test specimens.

2.4.2.3.1.2 *Preparation of Test Specimens*. Three aspects of test specimen preparation are discussed in this subsection: mold size and configuration, mixing of concrete, and consolidation of cast concrete.

- Mold size and configuration. Ice cube trays were specified as the molds for the concrete test specimens in the original rapid test method. Since ice cube trays vary in size and configuration, it was decided that a mold having a standard size, configuration, and availability countrywide should be used in the rapid test. To this end, 30-mL Nalgene beakers (No. 1201-0030) were initially selected as a standard. The beakers were in the shape of an inverted truncated cone, with a height of 1.800 in. The large diameter measured 1.520 in., and the small diameter measured 1.325 in. Specimens prepared from beaker molds are referred to as conical test specimens.

  Using these dimensions, the volume of the beaker mold was calculated to be 2.9 in.^3 (47 cm^3), and the inner surface area was determined to be 11.3 in.^2 (72.6 cm^2). The volume at 77°F (25°C) was confirmed experimentally by filling a beaker completely full with water dispensed from a 60-mL syringe.

  In addition, a mold support fixture was designed to provide solid and substantial support for the beaker mold so that the sides of the thin wall beaker would not distort during consolidation. To accomplish this and avoid the cost of machining a holding fixture, a hollow cylinder (bronze bushing) was secured. The holding fixture was made by inserting a beaker into the void of the cylinder and pouring liquid cerometal (melting point--150°F) into the void and around the beaker. A hole was drilled in the bottom of the fixture to facilitate the removal of the molded specimen by means of a plunger insert in the bottom.

An alternate procedure for molding the rapid test specimens was employed in tests conducted during the later phases of the research. The mold was changed from the 30-mL Nalgene® beaker to a 1 1/2-in. ID x 1 7/8-in. piece of PVC pipe designated ASTM 2665. The pipe mold was split through the outside wall with a vertical axial cut to facilitate demolding and taped with duct tape. Twenty of these molds were held in a plywood box during concrete placing and consolidation. Specimens prepared using PVC pipe molds are referred to as cylindrical test specimens.

- Mixing of concrete. Although the Nadezhdin paper made no mention of the method used for mixing the concrete, ASTM C672 does specify machine mixing in conformance with the provisions of ASTM C192. Since the availability of mechanical mixers among various researchers might well be limited, according to ASTM Method C192, paragraph 6.1.1, "General Procedure for Mixing Concrete," hand-mixing is allowed for batches of 1/4-ft^3 volume or less, which for 140 lb/ft^3 concrete would amount to approximately 35 lb or 15 kg of mix.

  ASTM C192 details the procedure for hand-mixing concrete in paragraphs 6.1.3 through 6.1.4. This procedure was employed to mix the concrete for the conical test specimens. Concrete for cylindrical tests specimens was machine-mixed as part of concrete batches for ASTM test specimens described later (Section 2.4.2.3.2.3).

- Consolidation and cure of the cast concrete. Again, no guidance was detailed in the original test method for the consolidation of the cast specimens, so ASTM C192 was referred to for this information. Paragraph 6.4.2, titled "Rodding," specifies the use of a 3/8-in. diameter rod with the tamping end rounded to a 3/16-in. radius and the mix being placed in three equal layers and consolidated with 25 strokes uniformly distributed over the cross section of the mold for each layer. This method was used for conical test specimens. Cylindrical test specimens were consolidated on a vibrating table, after initial consolidation with a screw driver.

  The test specimens were cured for 28 days at 75° ± 3°F (23.9° ± 1.7°C) and 100% relative humidity.

2.4.2.3.1.3 *Batch-to-Batch Reproducibility of Concrete Properties*. Nadezhdin reports reproducible data when the test specimen cubes are made from the same batch of concrete. However, if a study was conducted that required a larger number of test specimens, several concrete batches would be required.

In order to determine the similarity of one concrete batch to another, three control cubes measuring 2 x 2 x 2 in. were prepared from two separate batches of the standard concrete mix. ASTM C109, "Standard Test Method for Compressive Strength of Hydraulic Cement Mortars," was used as a guide with respect to (a) the apparatus required (excluding the mechanical mixer and the flow table and flow mold), (b) consolidation of cast concrete, (c) storage of test specimens, and (d) determination of compressive strength after 3 days of cure. A 3-day cure was selected in order to establish at an early date if the batches were similar.

Two sets of control concrete cubes were cast from two separate batches of concrete. Two cubes from the first batch and three cubes from the second batch were tested after 3 days of cure and gave average compressive strengths of 1,660 psi and 1,700 psi, respectively. (Note: Compressive strength of concrete with a water/cement ratio of 0.7 and a density of ~ 140 lb/ft^3 after 3 days' cure is approximately 30% of the 28-day strength.) Since the average strength of the two batches differed by only 1.2%, the requirement for a difference of less than 10.7% of their average was met as required in the precision statement of ASTM C109, paragraph 11.1.2, for a single-laboratory coefficient of variation.

An additional indication of the similarity of multiple mixes (repetitive batches of the same mix design) was obtained by comparison of the density of the two sets of control cubes. The control cubes from the first batch of concrete had an average density of 140.1 lb/ft^3 as compared to an average density of 141.9 lb/ft^3 for the cubes from the second batch of concrete.

2.4.2.3.1.4 *General Experimental Protocol*. The general experimental protocol for conducting accelerated concrete compatibility tests is given as follows. Concrete test specimens prepared and cured as specified previously were allowed to dry 24 hr in lab air at 75° ± 3°F (23.9° ± 1.7°C) and 50% ± 5% relative humidity, and then weighed to the nearest 0.1 g. Specimens were then presoaked in deionized water or deicer solution for 24 hr prior to testing. Four specimens were placed (large end down if conical) on a sponge in a test cell containing 310 mL of a given test or control solution. Test cells were covered with a tight-fitting lid and placed in a chest freezer for 16 to 18 hr until specimens and solutions were completely frozen (0° to 5°F). Test cells were then removed from the freezer and allowed to thaw completely (6 to 8 hr) in lab air.

This cycle of freezing and thawing was repeated for the specified number of times. After complete thawing at the end of the specified number of cycles, the test specimens were carefully removed from their test cells, hand-crumbled under running tap water to loosen degradative material, and allowed to dry in 75° ± 3°F (23.9° ± 1.7°C) and 50% ± 5% relative humidity lab air 24 hr before weighing. Final weights of specimens were then determined to the nearest 0.1 g, and percent weight losses calculated and averaged for each test cell. Control cells containing deionized water as a test solution were included with each set of tests conducted, as were test cells with 3 wt % NaCl solution to serve as an internal control with which to compare the other solutions. The density of each specimen was calculated before testing. The compressive strength of test cubes prepared with each batch of concrete specimens was determined after a specified length of cure in order to compare batches of concrete prepared at different times.

2.4.2.3.2 Modification of ASTM C672 Test Method. ASTM C672 test method to determine the scaling effects of deicer materials on concrete surfaces was selected as an additional method to determine concrete compatibility. ASTM C672 was a secondary choice because of (a) the long amount of time required to run the test and (b) the subjective evaluation of the effects of the deicer materials on the concrete surfaces.

Two modifications were made to ASTM C672 to shorten the time required to complete the concrete compatibility tests by this method. The first was the use of concrete without purposely entrained air. Air-entrained concrete has been used for about 30 years to mitigate the scaling effects of chloride-based deicers on concrete.

The second modification was to cast the dam into the top of the test specimens during placement of the concrete. A stainless steel band was cast in the concrete to form a dam that was resistant to corrosion, physical abuse, and expansion/contraction effects during freeze/thaw cycling.

This second modification then necessitated that the size of the coarse aggregate be reduced to provide proper fill on the outside of the stainless steel band. Limestone aggregate designated 3/8 in. maximum was substituted for the larger aggregate specified in ASTM C672.

2.4.2.3.2.1 *Concrete Mix Specifications*.

Water (tap)	9.11
Cement (Portland Type 1)	17.79
Sand (50/50 coarse/fine)	31.13
Aggregate (3/8 in. maximum limestone--surface dry, saturated)	41.97
Non-air-entrained	
Water/cement ratio	0.51
Slump (ASTM C143)	2.5 ± 1.0 in.
Density (lb/ft^3)	144
Compressive strength (psi)	4,900 ± 300

2.4.2.3.2.2 *Specimen Mold Specification*. A 4 1/2-in. x 10 1/2-in. x 3/4-in. plywood block was wrapped with Saran® wrap and centered on the bottom of the regular specimen mold. Care was taken to pull the Saran wrap tight and smooth to prevent the concrete test surface from being compromised by grooves or wrinkles. This spacer block was then secured to the mold bottom with two 1 1/4-in. wood screws. Stainless steel banks, 1 1/2-in. wide, were bent into 4 1/2-in. x 10 1/2-in. ID rectangles and silver-soldered in one corner. These bands were then fitted onto the spacer blocks.

2.4.2.3.2.3 *Concrete Mixing and Placement*. Seven batches of 105.61 lb were made as follows: (a) aggregate and sand mixed; (b) cement added and mixed; (c) water added and mixed 5 min; (d) slump measured according to ASTM C143, and concrete returned to mixer; and (e) concrete allowed to mix an additional 2 min. When filling the ASTM C672 molds, care was taken to fill the area between the mold walls and the stainless steel-surrounded spacer block first. Initial consolidation of this area was aided with a paint scraper. One batch of concrete was adequate to fill five ASTM specimens. Specimens were vibrated for 5 min, and then tapped with a hammer as described earlier. All specimens were then struck off and finished with a trowel. Two ASTM specimens had thermocouples embedded in them during filling to allow monitoring of the core temperature of the concrete during freeze/thaw cycling. Proctor cubes were made with batches 4 and 7. Specimens were demolded after 24 hr. All specimens were well consolidated and considered suitable for testing.

2.4.2.3.2.4 *Concrete Curing*. The modified ASTM C672 test specimens were allowed to stand in the mold for 20 to 24 hr. After demolding, the test specimens were placed in 100% relative humidity, at ambient temperature, for 13 additional days. The specimens were then moved to 45% to 50% relative humidity and 75° ± 3°F (23.9° ± 1.7°C) for at least 14 additional days.

2.4.2.3.2.5 *General Experimental Protocol*. After concrete placement and curing, the ASTM C672 test specimens were subjected to freeze/thaw (F/T) cycling with various deicer brines in the dam. Freeze/thaw conditions were 16 to 18 hr at 0° ± 5°F (-17.8° ± 2.8°C) followed by 6 to 8 hr at 75° ± 5°F (23.9° ± 2.8°C). After each five cycles, the specimens were evaluated for scaling/spalling effects of the deicer brine. Fresh brine was added at the beginning of each five cycles. Each specimen was covered with Saran® to minimize evaporation losses.

2.4.2.3.2.6 *Evaluation Procedures*. After each five F/T cycles, the ASTM C672 concrete test specimens were evaluated by two methods. The first method was the visual rating scheme published as a part of ASTM C672. Visual ratings were:

Rating	Condition of Surface
0	No scaling
1	Very slight scaling [1/8 in. (3.2 mm) depth, max., no coarse aggregate visible]
2	Slight to moderate scaling
3	Moderate scaling (some coarse aggregate visible)
4	Moderate to severe scaling
5	Severe scaling (coarse aggregate visible over entire surface)

The second evaluation procedure included weighing the scaled/spalled concrete material, after drying. The test specimen surface was brushed and rinsed with brine to remove loosened concrete. The resulting rinse was filtered and rinsed, then dried. Evaluation included the individual weight lost after each five cycles, as well as the cumulative weight lost.

2.4.2.4 *Comparison of Rapid Test Method and Modified ASTM Test Method*

In order to ascertain whether the two standard methods developed would yield comparable results for a given set of deicers under specified conditions, a set of parallel tests was conducted. Cylindrical specimens were used in the rapid test. Specimens for both methods were prepared, cured, and freeze/thaw cycled simultaneously to eliminate as many variables as possible. Detailed descriptions of the test matrices appear along with the results in Section 2.4.3.2.

2.4.2.5 *Publication of the Developed Test Methods*

The two test methods for evaluating the compatibility of deicers with concrete were published in Appendix B of the *Handbook: Test Methods for Evaluating Chemical Deicers* as SHRP H-205.8, Test Method for Rapid Evaluation of the Effects of Deicing Chemicals on Concrete, and SHRP H-205.9, Test Method for Evaluation of Scaling Effects of Deicing Chemicals on Concrete Surfaces. Method SHRP H-205.8 uses small cylindrical concrete test specimens. Method SHRP H-205.9 is a modification of ASTM C672 and uses larger rectangular test specimens.

2.4.3 Results and Discussion

2.4.3.1 *Experimental Results*

The experimental results of the concrete compatibility tests conducted during this study are presented in Tables 2.4-1 through 2.4-5 in the appropriate subsections.

2.4.3.2 *Discussion of Experimental Results*

The experimental results of concrete compatibility tests conducted during this study are discussed as follows: Rapid Test Method Results Using Concrete Conical Concrete Specimens (2.4.3.2.1), and Results of the Modified ASTM C672 Method Compared with Results of Rapid Method Using Cylindrical Concrete Test Specimens (2.4.3.2.2).

2.4.3.2.1 Rapid Test Method Results Using Conical Concrete Specimens. The detailed results of the rapid test method to determine concrete compatibility using conical test specimens are presented in this section. Typical results are presented in Table 2.4-1.

Table 2.4-1. Typical results of the rapid concrete compatibility test method using conical test specimens

Deicer solution	Additive (wt % of solids)	Presoak solution	Average spalling weight loss (%)	Coefficient of variation (%)
3% NaCl	None	3% NaCl	5.1	42
3% NaCl	None	DI water	20.2	35
3% CMA	None	DI water	1.5	19
3% NaCl	5% sodium erythorbate	DI water	13.3	10
3% NaCl	5% calcium phosphate	DI water	16.4	36
3% NaCl	5% zinc sulfate[a]	DI water	22.1	19
3% NaCl	5% zinc chloride[a]	DI water	21.6	7

[a] Plus 5 wt % sodium tripolyphosphate ($Na_5P_3O_{10}$).

Following is a presentation and discussion of the results of the studies conducted in developing a rapid method to determine concrete compatibility.

2.4.3.2.1.1 *First Set of Tests*. The initial set of tests were conducted using conical test specimens under the following specified conditions:

- The test specimens were made from concrete batches 1 and 2 (modified mix design) which were prepared on the same day. Cement content was 15%. Water-to-cement ratio was 0.7.
- The number of test cells was 5.
- Each test cell contained specimens prepared from only one concrete batch.

- The compressive strength of concrete after 3 days of cure was 1,660 lb/in^2 for batch 1. The compressive strength of batch 2 was not determined.

- The test specimens were presoaked in a solution of the same composition as that which they were exposed to during freeze/thaw cycling.

- The number of freeze/thaw cycles was 5.

The test specimens exposed to 3 wt % NaCl showed an average weight loss of 5.1% ± 1.2%. Specimens exposed to deionized water or to 3 wt % CMA showed no measurable weight loss. Specimens exposed to 3 wt % urea had an average weight loss of 1.7% ± 0.4%. Specimens exposed to 3 wt % NaCl with 5 wt % of solids each $ZnSO_4$ and $Na_5P_3O_{10}$ had an average weight loss not significantly different from that of specimens exposed to uninhibited 3 wt % NaCl.

2.4.3.2.1.2 _Second Set of Tests_. This set of tests was conducted because of the low degree of degradation noted in the first series of tests, and the high degree of degradation (30% to 45%) reported in the literature under similar test conditions. It was also desirable to determine the effects of increasing the number of freeze/thaw cycles to 10 and the effects of 4 wt % NaCl versus 3 wt % NaCl. The second set of tests was conducted using the conical test specimens under the following conditions.

- The test specimens were prepared from concrete batches 2 and 3 (modified mix design) on different days. The cement content was 15%. The water-to-cement ratio was 0.7.

- Each test cell contained specimens from either concrete batch 2 or 3. (A defect in labeling prevented test specimens from being identified as to specific batch.)

- The compressive strength of the concrete was not determined for batch 2.

- The compressive strength of the concrete after 3 days of cure for batch 3 was 1,700 lb/in^2.

- All test specimens were presoaked in deionized H_2O except for two sets which were presoaked in 4 wt % NaCl.

- The number of test cells subjected to 5 freeze/thaw cycles was 4.

- The number of test cells subjected to 10 freeze/thaw cycles was 3.

This study yielded the observation that presoaking specimens in deionized water could potentially predispose the concrete to a more serious degree of degradation than presoaking in solutions of the same composition as those employed in the test cells during freeze/thaw cycling. The test specimens exposed to deionized water for 10 freeze/thaw cycles had no degradation measurable by weight loss. Those exposed to 3 wt % NaCl solution and presoaked in deionized water had an average weight loss of 30.4% ± 6.6%. This was significantly greater than the degradation measured in the first set of tests for specimens exposed to the same solution for both presoaking and freeze/thaw cycling. The specimens presoaked in deionized water or 4 wt % NaCl and exposed to 4 wt % NaCl during 5 freeze/thaw cycles had similar degrees of degradation, and their average weight losses were only slightly greater than the 3 wt % NaCl exposed test specimens presoaked in deionized water. After 10 freeze/thaw cycles, the 4 wt % NaCl exposed specimens which had been presoaked in either 4 wt % NaCl or deionized water had similar average weight losses. Test specimens presoaked in deionized water and exposed to 3 wt % CMA showed very little degradation, with average weight losses being 2.4% ± 0.7%.

2.4.3.2.1.3 *Third Set of Tests*. This set of tests was conducted to evaluate the ability of certain corrosion inhibitors to protect concrete against degradation during exposure to NaCl and freeze/thaw cycling. This set of accelerated tests was conducted using the conical test specimens under the following specified conditions.

- The test specimens were prepared from concrete batches 4 and 5 (modified mix design) on different days. The cement content was 15%, and the water-to-cement ratio was 0.7.

- Each test cell contained specimens from only one batch of concrete.

- The compressive strength of concrete in batch 4 and batch 5 was not determined.

- All test specimens were presoaked in deionized water except one set from batch 4 which was presoaked in 3 wt % NaCl.

- The number of freeze/thaw cycles was 5.
- The number of test cells was 11.

Test specimens from concrete batch 4 which had been presoaked in deionized water and exposed to 3 wt % NaCl had an average weight loss of 22.3% ± 5.1%. Those from concrete batch 5 had an average weight loss of 13.1% ± 4.1%. Test specimens from concrete batch 4 exposed to 3 wt % NaCl to which $Ca(H_2PO_4)_2$ had been added at 3.5 and 1.5 wt % of solids had average weight losses of 24.8% ± 6.5% and 14.0% ± 4.9%, respectively. For test specimens exposed to 3 wt % NaCl containing 10 wt % of solids CMA, the average weight loss was 14.1% ± 4.6%. Test specimens from batch 5 exposed to 3 wt % NaCl containing 5 wt % of solids each of $ZnCl_2$ and $Na_5P_3O_{10}$ or 3.5 wt % of solids each of Na_2FPO_3 and $N[CH_2P(O)(OH)_2]_3$ or 5 wt % of solids $MgCl_2$ or 5 wt % of solids $C_7H_{14}O_{26}$ had average weight losses nearly the same as those for test specimens exposed to 3 wt % NaCl alone. Test specimens from batch 5 exposed to 3 wt % CMA again showed negligible weight loss.

2.4.3.2.1.4 *Fourth Set of Tests*. A fourth set of tests was undertaken to ascertain the effect of varying the cement content and/or water-to-cement ratio of concrete on susceptibility to freeze/thaw degradation when exposed to 3 wt % NaCl. This set of tests was conducted using conical test specimens under the following conditions.

- The test specimens were prepared from concrete batches 6 and 7. Concrete batch 6 had a cement content of 11.1% and a water-to-cement ratio of 0.7. Concrete batch 7 had a cement content of 11% and a water-to-cement ratio of 0.82.
- Each test cell contained specimens from only one batch of concrete.
- The compressive strength of the concrete after 7 days of cure was 850 lb/in^2 for batch 6 and 1,600 lb/in^2 for batch 7.
- All test specimens were presoaked in deionized water.
- The number of freeze/thaw cycles was 5.
- The number of test cells was 12.

The test specimens from concrete batch 6 exposed to 3 wt % NaCl had average weight losses of ~ 24% ± 2%. Concrete batch 7 specimens had average percent weight losses of ~ 37% ± 5% under the same conditions. Deionized water exposed test specimens from concrete batches 6 and 7 had average weight losses in the 3% to 4% range. Test specimens from concrete batch 6 exposed to 3 wt % NaCl containing either 5 wt % of solids sodium erythorbate or 5 wt % of solids each of $ZnSO_4$ and $Na_5P_3O_{10}$ demonstrated average weight losses nearly the same as the 3 wt % NaCl exposed test specimens. Concrete batch 7 test specimens exposed to 3 wt % NaCl solutions containing either 5 wt % of solids $Ca(H_2PO_4)_2$ or 5 wt % of solids each of $ZnCl_2$ and $Na_5P_3O_{10}$ also were unprotected against the degradative effects noted with 3 wt % NaCl solutions containing no additives. Test specimens from concrete batches 6 and 7 which were exposed to 3 wt % CMA solutions, showed average weight losses in the same range as the deionized water control test specimens.

2.4.3.2.1.5 *Fifth Set of Tests*. A final set of tests was conducted using conical test specimens under the following conditions.

- The test specimens were prepared from concrete batches 8 and 9 (modified mix design) on different days. The cement content was 15% and the water-to-cement ratio was 0.7.
- Each test cell contained specimens from only one batch of concrete.
- The compressive strength of the concrete after 7 days cure was 1,940 lb/in^2 in batch 8 and 2,820 lb/in^2 in batch 9.
- All test specimens were presoaked in deionized water.
- The number of freeze/thaw cycles was 5.
- The number of test cells was 10.

Test specimens from concrete batch 8 exposed to 3 wt % NaCl had average weight losses of ~ 21.5% ± 4%. Those from concrete batch 9 demonstrated average weight losses of ~ 19% ± 4%. Concrete batch 8 test specimens exposed to 3 wt % NaCl containing 5 wt % of solids sodium erythorbate had an average weight loss of 13.3% ± 1.3%. A 5 wt % of solids each addition of $ZnSO_4$ and $Na_5P_3O_{10}$ to 3 wt % NaCl demonstrated no ability to protect concrete batch 8 test specimens from the degradative effects of 3 wt % NaCl alone.

Additions of either 5 wt % of solids $Ca(H_2PO_4)_2$ or 5 wt % of solids each of $ZnCl_2$ and $Na_5P_3O_{10}$ also were ineffective at protecting test specimens from concrete batch 9.

2.4.3.2.2 Comparison of the Modified ASTM C672 Test Method with the Rapid Test Method Using Cylindrical Test Specimens. The results of the modified ASTM C672 test method to determine concrete compatibility are presented and discussed in this section. Results of rapid test studies conducted with cylindrical specimens are also presented and discussed in this section.

2.4.3.2.2.1 *Comparison of Test Methods Using a Chest Freezer*. The modified ASTM C672 test method for evaluating the scaling resistance of rectangular concrete test specimens was compared with a test method for the rapid evaluation of the effects of deicing chemicals on cylindrical test specimens. Principal modifications to the ASTM method were use of a stainless steel lined embedded reservoir to hold ponded deicer solutions, and the inclusion of a procedure for quantification of scaled materials by weighing.

- Deicers tested: 3 wt % solutions of NaCl, $CaCl_2$, $MgCl_2$, and CMA.
- Test specimens were from concrete batches 2 and 5.
- Number of test specimens and cells:
    - Modified ASTM C672: 2 specimens per deicer solution (one from each concrete batch) plus 1 control specimen with deionized water
    - Rapid evaluation test: 2 test cells (one with test specimens from concrete batch 2 and one with test specimens from concrete batch 5) per deicer and 2 control test cells with deionized water. The number of test specimens per cell was 4.

After addition of appropriate deicer or control solution, the 9 modified ASTM specimens and the 10 rapid evaluation test cells were arranged on a three-shelf aluminum rod rack which had been placed in a Sears chest freezer. The rack aided air circulation in the freezer and prevented test cells or specimens from contacting the freezer and walls. Modified ASTM test specimens were subjected to 15 freeze/thaw cycles and rapid evaluation test specimens to 10 cycles, with evaluation taking place after each five cycles. Test specimens and test cells were placed on different shelves when being returned to the freezer after each cycle in order to mitigate any temperature gradient effects due to the various heights of the shelves. Thermocouples embedded in the deionized-water-exposed test specimens allowed monitoring of test specimen core temperatures during the tests. A thermometer was also placed on the same shelf as the test specimens containing thermocouples to monitor the ambient freezer temperature. Temperature measurements made during the tests are summarized as follows:

- Range of temperature monitored at the end of each freeze cycle:
    - Ambient freezer: -2°F to 3°F (-17.8° to -11.1°C)
    - Modified ASTM test specimen core: 0°F to 7°F (-17.8° to -13.9°C)
    - Rapid evaluation test specimen core: 3°F to 12°F (-16.1° to -11.1°C)
- Range of temperatures monitored at the end of each thaw cycle:
    - Ambient laboratory: 69°F to 73°F (20.6° to 22.8°C)
    - Modified ASTM test specimen core: 64°F to 72°F (17.8° to 22.2°C)
    - Rapid evaluation test specimen core: 66°F to 75°F (18.9° to 23.9°C)
- Time for core to reach lowest temperature during freeze cycle:
    - Modified ASTM test specimen: 10.7 to 13.7 hr
    - Rapid evaluation test specimen: 14.0 to 16.3 hr

The modified ASTM test specimens and test cells containing the cylindrical test specimens were placed on metal shelves outside the freezer during thaw cycles. When evaluating the rapid-test specimens, two specimens were taken from each test cell to mitigate differences due to concrete batch variability.

Results from these two sets of tests which were run concurrently are given in Tables 2.4-2 and 2.4-3.

2.4.3.2.2.2 _Comparison of Test Methods Using an Upright Freezer_. The test matrix presented in the previous section using specimens from concrete batches 1 and 6 was repeated in a similar manner using a Puffer-Hubbard upright freezer. The upright freezer was equipped with four equidistant shelves and a fan for circulation. Test specimens and test cells were placed on a paper-covered cart during thaw cycles. Modified ASTM test specimens were evaluated after 5 and 10 cycles. Rapid evaluation test specimens were evaluated after 10 cycles only. Initial weights of the rapid evaluation test specimens were recorded after

Table 2.4-2. Results of modified ASTM C672 concrete scaling resistance test

Deicer solution or control	Number of F/T cycles[a]	ASTM visual rating	Avg. cumulative weight[b] of spalled material removed from test specimens[c] (g)
3 wt % NaCl	5	3 to 4	40.6
	10	5	144.6
	15	5	222.9
3 wt % $CaCl_2$	5	3	25.7
	10	4 to 5	56.4
	15	5	92.3
3 wt % $MgCl_2$	5	0 to 1	1.2
	10	1	2.7
	15	1 to 3[d]	3.5
3 wt % CMA	5	0	< 0.1
	10	0	0.6
	15	1	1.7
Deionized water	5	0	ND[e]
	10	0	0.1
	15	0	ND[e]

[a] Sears chest freezer.

[b] Duplicate test specimens.

[c] Prepared from concrete batches 2 and 5.

[d] Spalling was localized in pits.

[e] ND = not determined.

Table 2.4-3. Results of test for rapid evaluation of effects of deicing chemicals on concrete using cylindrical test specimens

Deicer solution or control	Number of F/T cycles[a]	Mean wt % of spalled material removed from test specimens[b] (g)	Standard deviation[c]
3 wt % NaCl	5	10.7	±4.4
	10	31.2	±7.7
3 wt % $CaCl_2$	5	2.7	±1.2
	10	9.3	±1.0
3 wt % $MgCl_2$	5	0	0
	10	0	0
3 wt % CMA	5	0	0
	10	0.7	±1.4[d]
Deionized water	5	0	0
	10	0	0

[a] Sears chest freezer.

[b] Prepared from concrete batches 2 and 5.

[c] For four test specimens.

[d] One test specimen had weight loss and three test specimens had weight gain.

having been presoaked for 24 hr. Temperature measurements made during the tests are summarized as follows.

- Range of temperatures monitored at the end of each freeze cycle:
  - Ambient freezer: 0°F to 2°F (-17.8° to -16 7°C)
  - Modified ASTM test specimen core: 3°F to 7°F (-16.1° to -13.9°C)
  - Rapid evaluation test specimen core: 2°F to 9°F (-16.7° to -12.8°C)

- Range of temperatures monitored at the end of each thaw cycle:
  - Ambient laboratory: 75°F (23.9°C)
  - Modified ASTM test specimen core: 43°F to 59°F (6.11° to 15.0°C)
  - Rapid evaluation test specimen core: 63°F to 70°F (17.2° to 21.1°C)
- Time for core to reach lowest temperature during freeze cycles:
  - Modified ASTM test specimen: 7.7 to 8 hr
  - Rapid evaluation test specimen: 5.3 to 6.3 hr

Results of these tests are presented in Table 2.4-4 and 2.4-5.

Examination of these two sets of tests shows that, in all cases, sodium chloride-exposed specimens exhibited a much higher degree of spalling than calcium chloride-exposed specimens. Specimens exposed to magnesium chloride, CMA, or deionized water exhibited essentially no spalling. The degree of spalling in the second set of tests (Tables 2.4-4 and 2.4-5) was consistently less than in the first set of tests (Tables 2.4-2 and 2.4-3), but the ranking of the chemical deicers was the same for both sets of tests.

2.4.4 Conclusions and Recommendations

2.4.4.1 *Conclusions Drawn from Experimental Work Conducted Using the Test Method for Rapid Evaluation of the Effects of Deicing Chemical on Concrete (Conical or Cylindrical Test Specimens)*

- Deionized water presoaking prior to freeze/thaw cycling increases the amount of spalling exhibited by test specimens.
- Use of deionized water for presoaking test specimens prior to freeze/thaw cycling permitted a significantly higher degree of spalling than use of deicer brine presoaking.
- Increasing the sodium chloride test solution concentration from 3 wt % to 4 wt % only marginally increased the degree of spalling observed in test specimens.
- No antispalling additives to 3 wt % sodium chloride test solutions were found to be effective using this test.

Table 2.4-4. Results of modified ASTM C672 concrete scaling resistance test

Deicer solution or control	Number of F/T cycles[a]	ASTM visual grade	Avg. cumulative weight[b] of spalled material removed from test specimens[c] (g)
3 wt % NaCl	5	3 to 4	47.4
	10	5	104.6
3 wt % $CaCl_2$	5	1 to 3	19.5
	10	3 to 5	48.8
3 wt % $MgCl_2$	5	0 to 1	0.6
	10	1	1.5
3 wt % CMA	5	0	0.6
	10	0 to 1	0.9
Deionized water	5	0	0
	10	0	0

[a] Puffer-Hubbard upright freezer.

[b] Duplicate test specimens.

[c] Prepared from concrete batches 1 and 6.

Table 2.4-5. Results of test for rapid evaluation of effects of deicing chemicals on concrete using cylindrical test specimens

Deicer solution or control	Number of F/T cycles[a]	Mean wt % of spalled material removed from test specimens[b] (g)	Standard deviation[c]
3 wt % NaCl	10	14.4	±3.3
3 wt % $CaCl_2$	10	2.9	±1.9
3 wt % $MgCl_2$	10	0.4[d]	±0.8
3 wt % CMA	10	0.7[e]	±1.9
Deionized water	10	0	-

[a] Puffer-Hubbard upright freezer.

[b] Prepared from concrete batches 1 and 6.

[c] For eight test specimens.

[d] Four test specimens had weight loss and four test specimens had weight gain.

[e] Two test specimens had weight loss and six test specimens had weight gain.

- Ball mill tumbling during evaluation of conical test specimens had no effect on the observed weight loss due to spalling after freeze/thaw cycling.

- Adjusting the cement content of the concrete used to make the test specimens from 15 wt % to 11 wt % had only a marginal effect on the degree of spalling.

2.4.4.2 *Conclusions Drawn from Experimental Work Conducted Using the Modified ASTM Method for Evaluation of the Scaling Effects of Deicers on Concrete*

- Use of non-air-entrained concrete in test specimens permits the scaling effects caused by exposure to deicing chemicals during freeze/thaw cycling to become manifest in a much shorter period of time (5 to 10 days or cycles) than use of air-entrained concrete.

- Use of embedded stainless steel dams on test specimens provided easier handling, increased resistance to accidental physical abuse, and mitigation of expansion/contraction effects on the ponding reservoir during testing.

- Removal and weighing of scaled material from test specimens as an adjunct evaluation procedure provides a consistent way of quantitating the degree of scaling observed.

2.4.4.3 *Conclusions Drawn from Experimental Work Conducted for Comparing Standard Methods SHRP H-205.8 and SHRP H-205.9*

- Test specimens exposed to 3 wt % solutions of magnesium chloride, CMA, or deionized water during freeze/thaw cycling showed essentially no spalling.

- The degree of spalling noted for specimens exposed to 3 wt % sodium chloride varied over a wide range, both between various batches of concrete and within the same batch of concrete.

- Both of these concrete compatibility tests are valid for comparisons of spalling activity where specimens are from the same batch of concrete.

- Both of these concrete compatibility test methods are consistent in that they rank conventional deicers in the same order as to their ability to cause concrete to scale during freeze/thaw cycling: $NaCl > CaCl_2 > MgCl_2 \geq CMA \geq$ deionized water.

- Both of these concrete compatibility tests can be used to distinguish between deicers with low spalling activity and those with high spalling activity.

2.4.4.4 *Recommendations*

- Since the magnitude of scaling observed may vary when tests are replicated even under controlled conditions, it is strongly recommended that sodium chloride always be included in the test matrix as an internal control with which to compare other chemical deicers.

- SHRP H-205.8, Test Method for Rapid Evaluation of the Effects of Deicing Chemicals on Concrete, is preferred over SHRP H-205.9, Test Method for Evaluation of Scaling Effect of Deicing Chemicals on Concrete Surfaces, for the following reasons: (a) test specimens are on a much smaller scale; (b) the overall method is much less labor-intensive; (c) loss or spillage of test solutions during testing is minimized; and (d) evaluation of test specimens requires less time.

2.4.5 References

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2.5 Frictional Characteristics Work

2.5.1 Introduction and Background

2.5.1.1 *Introduction*

The experimental work and supporting background studies undertaken to investigate and finalize a standard test method for evaluating the frictional characteristics of chemical deicers in the laboratory is presented in this section. Following the background discussion, which includes a review of pertinent literature citations, the remainder of the section is organized as follows: Developmental Studies and Experimental Work (Section 2.5.2); Results and Discussion (Section 2.5.3); Conclusions and Recommendations (Section 2.5.4); and References (Section 2.5.5).

2.5.1.2 *Background*

The safe movement of vehicles upon our nation's highways depends, in part, on an adequate level of friction (or coefficient of friction) between the vehicle tires and the driving surface. This statement holds true whether the driving surface is a dry, wet, or ice/snow-covered pavement. A universally accepted definition of an adequate level of friction remains unresolved. What is adequate depends upon many parameters, such as vehicle speed, tire tread and condition, roadway grade, friction demand, pavement surface condition, ambient conditions, and so forth. Researchers and state highway departments generally agree informally on what constitutes a good or high level of friction and what levels are poor or unacceptable. However, the division between the two extremes is ill-defined.

Research has shown that the friction coefficients of wet pavements are generally less than those of dry pavements. Also, the friction coefficients for snow-covered pavements are about half those of wet pavements (Schaerer, 1970), and the coefficients of friction of ice-covered roads are about half those for snow-covered roads, especially near 32°F (0°C) (Ichihara and Mizoguchi, 1970). The coefficient of friction of chloride-treated snow tends to be slightly higher than that of untreated snow. These results suggest a basis by which we may judge the impact a chemical deicer has on the level of friction available to the friction demand of a vehicle.

An important consideration for a deicer is that its use should not appreciably degrade the friction level associated with an untreated pavement condition. It is recognized that under certain conditions, a transient reduction of pavement friction coefficient can occur due to deicer application. This temporary effect is not considered in the following general criteria:

- The friction coefficient of a dry, wet, or ice/snow-covered pavement treated with a dry or pelletized form of a deicer should not be less than the friction coefficient of the same, but untreated pavement.

- The friction coefficient of a wet or ice/snow-covered pavement treated with a liquid or brine form of a deicer should not be less than the friction coefficient of the same, but untreated pavement.

Friction testing of snow and/or ice-coated surfaces has ranged from studies of braking distances with vehicles to instrumented, relatively small-scale systems which can be viewed as laboratory test systems. Minsk (1982) presented in detail the equipment, test procedures, and results obtained with laboratory-type friction equipment. Hu (1979) reported the results of field tests under controlled conditions.

Many field test techniques have been used to evaluate the friction values of deicer-treated bare and snow/ice-covered pavements. These techniques include: a Tapley decelerometer mounted in a light truck (Schaerer, 1970), a specially instrumented highway vehicle (Ichihara and Mizoguchi, 1970), the skidding car method (Stratfull et al., 1974), the stopping distance method (Minsk, 1982; ASTM E445-82), the Penn State Mark II Road Friction tester with an ASTM E524-82 smooth-tread tire (Minsk, 1982), and a skid test trailer operated generally in accordance with ASTM E274-79 (Forbes et al., 1970; Ernst, 1984; DeFoe, 1984; Wieman, 1987). Varying degrees of success have been achieved with this spectrum of techniques. Evaluations of wet skid resistance on bare pavement treated with deicing solutions have been reported using the locked wheel method (Wambold, 1983) and the ASTM E274-79 full tire method (Shultz, 1984).

There is no standard laboratory technique for evaluating the effects of chemical deicers on the friction coefficient of a wet or ice-covered pavement surfaces. In fact, there are only three standard laboratory methods (ASTM E303-83, E-510-79, and E707-79) for measuring the surface frictional properties of highway materials. However, none of these techniques provides results that correlate well with field methods of measuring tire-pavement friction. Developmental concepts and discussions of the use and performance of the British Pendulum Tester, as specified in ASTM E303, have been reported by Kummer and Moore (1963) and Giles et al. (1964).

Minsk (1982) described two devices developed primarily for use in the laboratory to measure changes of surface friction with time. One device was a rotating rubber annulus for making point measurements; the other consisted of a slipping wheel for measuring the effects of trafficking on a circular test track. Both devices are considered research tools and are not readily available to highway agencies. A prototype version of the first device was used in limited outdoor tests with mixed results (Minsk, 1982).

2.5.2 Developmental Studies and Experimental Work

The principal elements of the developmental studies and experimental work on frictional characterization of deicers are Collection and Review of Current or Proposed Laboratory Methods for Measuring the Frictional Properties of Various Materials, Preliminary Investigations Using the Horizontal Slip Tester (ASTM D-21, Proposal 125), Investigation and Adaptation of Test Method ASTM E303-83 Using the British Pendulum Tester, and Finalization of a Standard Test Method.

2.5.2.1 *Collection and Review of Current or Proposed Laboratory Methods*

2.5.2.1.1 Literature Search. A search was made of all available literature. The following 15 standard or proposed methods used to determine the static and kinetic coefficients of friction of various materials and surfaces were collected and reviewed.

- Floor Surfaces; Horizontal Slip Tester (ASTM D21, P125)
- Floor Surfaces; NBS-Brungraber Articulated Arm Tester (ASTM D21, P126)
- Floor Surfaces; NBS-Sigler Pendulum Impact Tester (ASTM D21, P127)
- Floor Surfaces; Topeka Slip Tester (ASTM D21, P128)
- Plastic Film and Sheeting (ASTM 1894-78), revised 1986
- Wood Finish Flooring (ASTM D2394-83)
- Wax Coatings (ASTM D2534-73)
- Plastic Solids and Sheeting (ASTM D3028-72)
- Fiberboard; Horizontal Plane (ASTM D3247-73)
- Fiberboard; Inclined Plane (ASTM D3248-73)
- Paved Surfaces; Full-Scale Tire (ASTM E274-85)
- Surface Friction; British Pendulum Tester (ASTM E303-83)
- Paved Surfaces; Side Force, MU-Meter (ASTM E670-79)
- Paved Surfaces; Variable-Speed Friction Tester (ASTM E707-79)
- Carbon Paper (ASTM F254-79)

2.5.2.1.2 Review criteria. The following criteria were used in selecting candidate test methods for further evaluation.

- Appropriateness and adaptability of test design for evaluating frictional characteristics of deicer solutions
- Cost and availability of equipment
- Complexity of equipment setup and calibration
- Simplicity of test design
- Ease of test execution by a technician
- Directness of measurement and data collection

2.5.2.1.3 Test methods selected for further evaluation. Based on the above criteria, two candidate test methods were selected for further evaluation: ASTM D21, P125 using the Horizontal Slip Tester and ASTM E303-83 using the British Pendulum Tester. The investigations conducted in evaluating these methods as potential standard laboratory procedures for use with chemical deicers are detailed in the two subsections which follow.

2.5.2.2 *Preliminary Investigations Using the Horizontal Slip Tester*

ASTM D-21, Proposal P125, "Test Method for Static and Dynamic Coefficients of Friction of Polish-Coated Floor Surfaces as Measured by the Horizontal Slip Tester," was initially selected because of its simple design, modest equipment cost, ability to directly measure static and kinetic coefficients of friction, ease of execution, and adaptability to deicer solution testing. In this method, a 10-lb sled connected to a force gauge and fitted on the bottom with three small rubber pads was pulled across a horizontal surface. Coefficients of static and kinetic friction were obtained by observing the force gauge readings during the test.

Results of the investigations with the Horizontal Slip Tester are presented and discussed in Section 2.5.3.1 and Appendix A.

2.5.2.2.1 Special Equipment. A horizontal slip tester of the type specified in the chosen test method was obtained from Technical Products Company, North Caldwell, New Jersey (Model 80 Floor Friction Tester). This tester kit included the sled, force gauge, calibration weight, and a set of leather pads. A set of hard rubber pads was also obtained, as rubber was considered to be a more suitable material to test frictional properties of deicers.

2.5.2.2.2 Test Surface and Test Temperature. A test surface was desired which would be nonporous, be easy to clean and recondition between tests, and have some degree of texture. Sand-blasted glass was chosen as the initial test surface. A 1-ft x 3-ft panel of this glass was placed in a shallow Plexiglas tray and clamped to the top of a lab bench. Later the glass panel was secured directly to the surface of a lab bench using double-sided tape. Some tests were also conducted on the smooth (nonblasted) surface of the glass. Tests were conducted at 73° to 75°F (22.8° to 23.9°C).

2.5.2.2.3 Test Solutions. All test solutions were prepared using deionized water. Selected deicers were tested at 3 wt %. NaCl, $CaCl_2$, and CMA were also tested at 25 wt %.

2.5.2.2.4 Application of Test Solution to Test Surface. Various methods of applying test solution to the glass surface prior to using the horizontal slip tester were considered. These included spraying, spreading with a wood block or rubber glove, immersion of the test surface panel until just covered by test solution, and use of a 10-mil steel latex spreader to draw a thin film of solution along the test surface. Immersion was not investigated, because it required greater quantities of solution and presented undesirable containment and cleanup problems. The 10-mil latex spreader gave the most desirable application.

2.5.2.2.5 General Experimental Procedure. The test surface was cleaned, rinsed, and dried, and secured on the top of a level lab bench. Rubber pads were placed in the bottom of the slip tester sled and were abraded by drawing the tester across 400-grit sandpaper. The force gauge was calibrated and connected to the tester. Thirty to forty milliliters of test solution were spread over the test surface. The sled was immediately placed on the wetted surface and pulled in a straight line a distance of 2 ft in ~ 6 sec. The gauge reading was noted when the tester first began to move. The average gauge reading during the 6-sec pulling period was noted. Solution was respread after each test. After three tests, the sled pads were cleaned, dried, and reabraded. The glass surface was cleaned, and test solution reapplied.

2.5.2.3 *Investigation and Adaptation of Test Method Using the British Pendulum Tester*

ASTM E303-83, Measuring Surface Frictional Properties Using the British Pendulum Tester, was investigated after tests conducted with the horizontal slip tester proved unsatisfactory. Although the equipment cost is considerable (~ $8,000), the method was found to be easy to set up and simple to execute; it is capable of producing replicable results. In this method a rubber slider attached to a pendulum is allowed to contact a test surface wetted with a deicer solution along a set path length. A pointer, which travels with the pendulum arm, indicates a scale reading (British Pendulum No. BPN).

Results of investigations using the British Pendulum Tester are presented and discussed in Section 2.5.3.2.

2.5.2.3.1 Special Equipment. Arrangements were made to borrow a British Pendulum Tester from the Federal Highway Administration (FHWA). A trip was made to FHWA laboratories in McLean, Virginia, to pick up the tester. Instructions for using the tester were provided by Mr. Steven Forster, Acting Chief, Pavements Divisions.

2.5.2.3.2 Test Surfaces and Test Temperatures. Tests were conducted on the following surfaces at the indicated temperatures.

- Sand-blasted glass, 1.5-mil profile: 75°, 30°, and 20°F (23.9°, -1.11°, and -6.67°C)
- Molded mortar, smooth and textured: 75°F (23.9°C)
- Concrete patio block: 75°F (23.9°C)
- Molded concrete slab: 75°F (23.9°C)
- Molded asphalt/sand composite: 75°F (23.9°C)
- Asphalt parking lot (field trials): 82°F (27.8°C)

2.5.2.3.3 Test Solutions. All solutions were prepared using deionized water. Deicers were tested at 10 and 25 wt %.

2.5.2.3.4 General Experimental Procedure. The general experimental procedure was as described in ASTM E303-83. Five consecutive pendulum swings, yielding BPNs which differed by no more than 1 unit, were required for determination of the BPN for a given deicer solution on a given surface.

2.5.2.3.5 Specific Considerations.

2.5.2.3.5.1 *Testing of Deicer Solutions on Sand-Blasted Glass at Low Temperatures*. Frictional characteristics tests were conducted using the British Pendulum Tester with deicer solutions on sand-blasted glass at 75°, 30°, and 20°F (23.9, -1.11, and -6.67°C). The test surface, apparatus, and solutions were allowed to equilibrate overnight at the test temperature. Tests at 30°F (-1.11°C) and 20°F (-6.67°C) were performed in the cold room facility used for other deicer performance tests. Deionized water was used as a control and as a rinse solution between tests conducted at 75°F (23.9°C). A 3 wt % NaCl solution was used as a control and as a rinse solution between tests conducted at 30°F (-1.11°C). For tests at 20°F (-6.67°C), residual deicer from the previous trial was sponged from the surface, and the surface was wetted and sponged three times with the next deicer to be tested. Only deicer solutions which showed no signs of freezing, ice crystal formation, or precipitation after temperature equilibration at 30°F or 20°F (-1.11° or -6.67°C) were used in those tests. Test conditions were as follows:

- Test surface profile: 1.5 mils
- Rubber slider: No. 81D, Side 1
- Test temperatures: 75°F ± 1°F (23.9° ± 0.56°C), 30° ± 1°F (-1.11° ± 0.56°C), and 20° ± 1°F (-6.67° ± 0.56°C)
- Test solutions and materials: See Table 2.5-1

2.5.2.3.5.2 *Repeatability of Test Data Obtained for Deicers on Sand-Blasted Glass*. Tests using selected deicers were repeated on a different piece of sand-blasted glass at 75°F (23.9°C) in order to ascertain reproducibility of test data. Test conditions were as follows:

- Test surface: Sand-blasted glass, 1 ft x 3 ft x 1/8 in.; mean profile, 1.5 mils
- Rubber slider: No. 81D, Side 1
- Temperature: 75°F (23.9°C)

2.5.2.3.5.3 *Testing of Selected Deicers on an Asphalt Pavement*. In order to determine to what extent the frictional characteristics of deicers on sand-blasted glass were representative of those which might be determined on actual pavement, selected deicers were tested on an asphalt parking lot surface. The area chosen was as even and uniform as could be determined visually and by touch. The area was marked off into three equal sections. A separate section was used to test each deicer so as not to risk residual surface contamination. The test area was swept to remove any loose dirt and grit. Each test section was washed several times using deionized water and a rag. Test conditions were as follows:

- Temperature 1/4 in. from surface: 82°F (27.8°C)
- Wind: Calm
- Sunlight: Indirect
- Time: 9 to 10:30 a.m.
- Place: South of receiving dock in line of driveway
- Rubber slider: 81-D, Side 1

2.5.2.3.5.4 *Investigation of Other Potential Laboratory Test Surfaces*. Several other pavement-like substrates were evaluated as potential standard surfaces for use with deicer frictional characteristics tests. These included smooth and textured mortar, molded concrete slab, and molded asphalt/sand composites and concrete patio blocks. A summary of these investigations follows. Test temperature was 75°F (23.9°C).

Lime-water-cured mortar specimens, 8 1/2 in. x 5 1/2 in. x 2 in., of the type used in ice undercutting tests, were presoaked in deionized water for 28 days. The surface profile of the smooth molded side of one specimen was 1.7 mils. A similar mortar sample having a more textured surface was also tested.

Three concrete slabs, 6 in. x 12 in. x 1 1/2 in., which were prepared and cured along with specimens for scaling resistance tests, were used as frictional characteristics test substrates. The molded side was used as the test surface. To eliminate possible residual effects during successive tests, a separate slab was used for each deicer tested. Attempts to repeat the BPN for deionized water after deicer testing were not successful. A concrete patio block surface was also investigated as a test substrate.

Attempts were made to prepare asphalt/sand composite surfaces for testing. The asphalt was Shell VAC-20. Mixes of 50/50 (wt/wt) asphalt and sand were tested.

2.5.2.4 *Test Method Finalization*

Based on experimental work with the British Pendulum Tester described above, a standard laboratory procedure for use in determining the frictional characteristics of deicer solutions at rubber/substrate interfaces was finalized. After finalization, the test method was written and arranged in a format typically used in ASTM standards, and included in the handbook: *Test Methods for Evaluating Chemical Deicers*.

2.5.2.5 *Materials Specifications*

Materials specifications for frictional characteristics testing are given in Table 2.5-1.

2.5.3 Results and Discussion

2.5.3.1 *Results of Preliminary Investigations Using the Horizontal Slip Tester*

Results of all frictional characteristics tests using the horizontal slip tester on sand-blasted and smooth glass wetted with various deicer solutions are given in Table 2.5-2. These results were analyzed statistically for significant differences versus appropriate deionized water controls. A detailed discussion of this statistical treatment and a table (Table A-1) summarizing the statistical values are presented in Appendix A.

No differences were detected between the static and kinetic coefficient of friction values measured for rubber/sand-blasted glass surfaces wetted with deicer solutions when using the horizontal slip tester. Also, no differences were detected between the coefficient of friction values for rubber/sand-blasted glass surfaces wetted with solutions of different deicers at similar concentration levels, or when wetted with solutions of the same deicer at different concentration levels. Kinetic coefficient of friction values measured for rubber/smooth glass surfaces wetted with deicer solutions were judged to be unreliable because of the slip-stick behavior of the horizontal slip tester.

Table 2.5-1. Materials[a] and test solutions[b] used for friction characteristics test

Test Solution	Composition
Deionized water	Control
Sodium chloride	3 wt %; 10 wt %; 25 wt %
Calcium chloride	10 wt %; 25 wt %
Rock salt	10 wt %; 25 wt %
Magnesium chloride[c]	10 wt %; 25 wt %
Sodium chloride + PCI	10 wt % NaCl with PCI at 10 wt % of solids
Sodium chloride + calcium phosphate	3 wt % NaCl with calcium phosphate at 1.5 wt % and 3.5 wt % of solids
Sodium formate	10 wt %; 25 wt %
Urea	10 wt %; 25 wt %
Ethylene glycol	3 wt %; 10 wt %; 25 wt %; 100 wt %
CMA[d]	3 wt %; 10 wt %; 25 wt %

[a] Materials
Sodium chloride (NaCl): Fisher S-271
Calcium chloride ($CaCl_2$): Mallinckrodt 4132--anhydrous, 8-mesh
Rock salt: Morton Safe-T-Salt
Magnesium chloride ($MgCl_2 \bullet 6H_2O$): Fisher F-33
Calcium phosphate monobasic [$Ca(H_2PO_4)_2 \bullet H_2O$]: Baker 1426-01
PCI (a calcium lignosulfonate): Great Salt Lake
Sodium formate (HCOONa): Fisher S 648
Urea (NH_2CONH_2): Fisher U15-500
Ethylene glycol ($HOCH_2$-CH_2-OH): Aldrich 10, 246-6
CMA (calcium and magnesium acetate, 91%): Ice-B-Gon, Chevron

[b] All solutions prepared using deionized water.

[c] Magnesium chloride hexahydrate; weight adjusted so that solutions were 10 and 25 wt % $MgCl_2$.

[d] CMA 91% calcium and magnesium acetate; weight adjusted so that solutions were 10 and 25 wt % calcium and magnesium acetate.

Table 2.5-2. Coefficients of static and kinetic friction measured by horizontal slip tester method on sand-blasted and smooth glass surfaces wetted with deicer solutions at 75°F (23.9°C)

Solution	Mean static coefficient of friction	Mean kinetic coefficient of friction	Number of trials
Sand-blasted glass surface (profile: 2.0 ± 0.2 mils)			
Dry	0.69 ± 0.01	0.68 ± 0.01	9
Deionized H_2O	0.65 ± 0.02	0.64 ± 0.02	19
3 wt % NaCl	0.60 ± 0.02	0.60 ± 0.02	13
3 wt % CMA	0.64 ± 0.02	0.64 ± 0.02	4
3 wt % ethylene glycol	0.60 ± 0.02	0.60 ± 0.02	5
3.5 wt % $Ca(H_2PO_4)_2$ in 3% NaCl	0.59 ± 0.01	0.59 ± 0.01	8
1.5 wt % $Ca(H_2PO_4)_2$ in 3 wt % NaCl	0.59 ± 0.01	0.59 ± 0.01	4
Sand-blasted glass surface (profile: 1.6 ± 0.1 mils)			
Deionized H_2O	0.59 ± 0.01	0.59 ± 0.02	6
25 wt % NaCl	0.59 ± 0.01	0.59 ± 0.02	6
25 wt % $CaCl_2$	0.59 ± 0.01	0.59 ± 0.01	6
25 wt % CMA	0.62 ± 0.02	0.62 ± 0.02	6
Smooth glass surface (profile: ND)			
Deionized H_2O	0.33 ± 0.01	0.16 ± 0.02	6
3% NaCl	0.26 ± 0.01	0.16 ± 0.02	9
3% CMA	0.30 ± 0.01	0.21 ± 0.01	6
3% ethylene glycol	0.32 ± 0.01	0.25 ± 0.02	6

± = standard deviation.

2.5.3.2 *Results of the Investigation and Adaptation of Test Method ASTM E303-83 Using the British Pendulum Tester.*

Graphs of frictional characteristics test data obtained using the British Pendulum Tester are presented in Figures 2.5-1 through 2.5-3 below. Data tables supporting these figures, as well as tables summarizing other test results discussed in this subsection are given in Appendix A. The values shown in the tables and figures are British Pendulum Numbers (BPN). The lower the value of the BPN, the more likely skidding would occur. The BPN values presented are the mean of five consecutive pendulum swings, all within a range of 1 BPN.

A plot of frictional characteristics (BPN) of sand-blasted glass (profile 1.5 mils) wetted with 0, 10, or 25 wt % solutions of NaCl, $MgCl_2$, CMA, or ethylene glycol at 75°F (23.9°C) is shown in Figure 2.5-1. At 10 wt % all solutions show a relatively small but detectable differentiation from the deionized water control BPN value except NaCl. At 25 wt % the change in the BPN is much more marked for $MgCl_2$ and CMA than for NaCl or ethylene glycol. The lower the BPN, the lower the friction, or the greater the degree of slipperiness of a test surface. AT 10 wt % the potential of test solutions to cause a greater degree of slipperiness would be $MgCl_2$ > CMA > ethylene glycol > NaCl. At 25 wt % the order becomes CMA > $MgCl_2$ >> ethylene glycol > NaCl.

A bar graph comparing the frictional characteristics of sand-blasted glass wetted with 25 wt % solutions of selected deicers at 75°, 30°, and 20°F (23.9°, -1.11°, and -6.67°C) is shown in Figure 2.5-2. As shown in this figure, the BPN for $MgCl_2$ was not significantly affected by decreasing the test temperature, whereas decreases in BPN for NaCl and CMA were more pronounced. It is also significant that regardless of the test temperature, the potential of the solutions tested to increase slipperiness is CMA > $MgCl_2$ > NaCl.

A bar graph comparing the frictional characteristics (BPN) of a sand blasted glass surface at 75°F (23.9°C), molded concrete slab surfaces at 75°F (23.9°C), and asphalt pavement surfaces at 82°F (27.8°C) wetted with 25 wt % solutions of selected deicers is shown in Figure 2.5-3. The potential of the solutions tested to increase slipperiness regardless of the substrate is CMA > $MgCl_2$ >NaCl > DI H_2O. Of the three substrates tested under these conditions, molded concrete and sand-blasted glass were found to yield similar BPN values for a given test solution. The asphalt pavement surface yielded BPN values substantially lower for a given test solution than either concrete or sand-blasted glass.

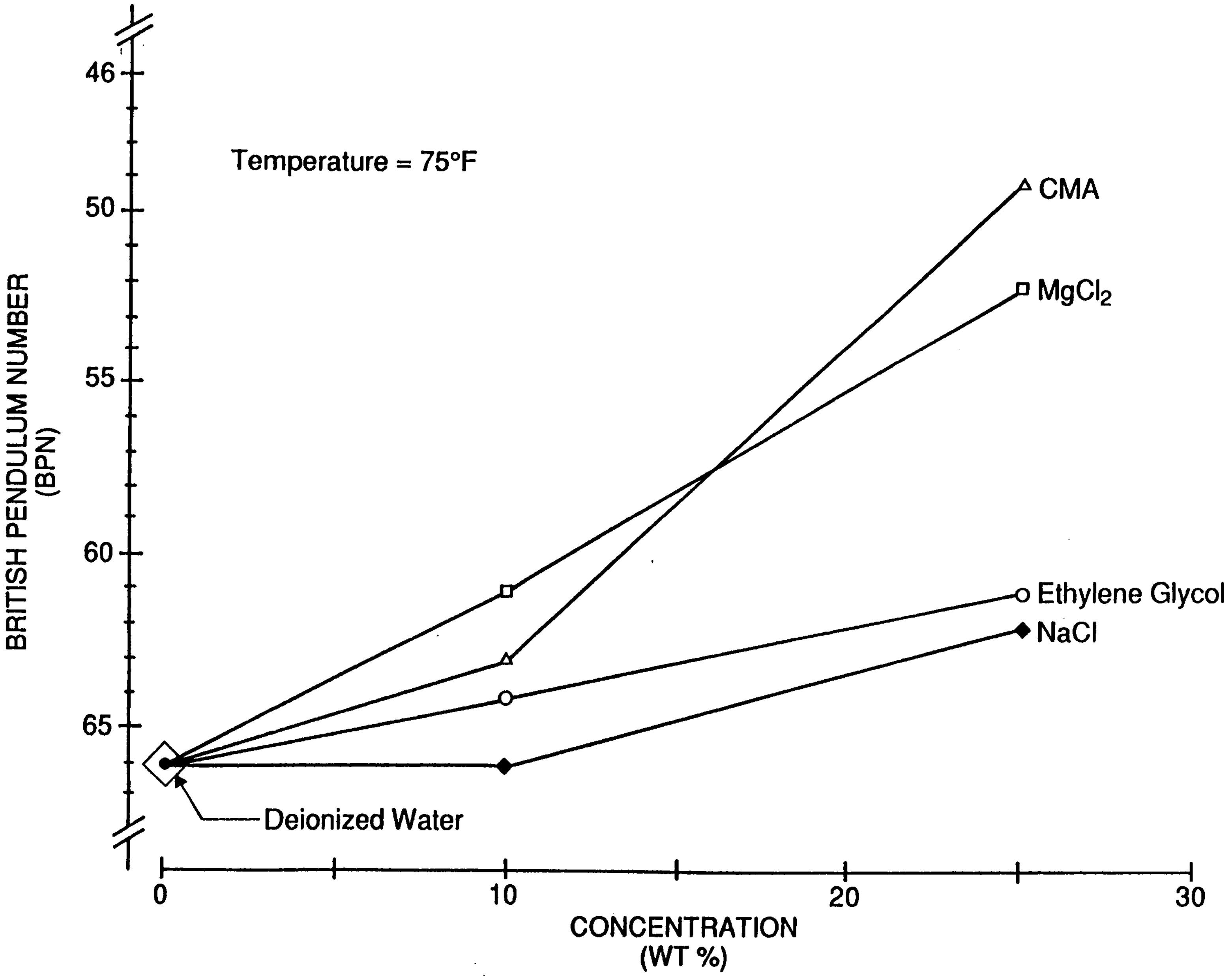

Figure 2.5-1. Frictional characteristics of sand-blasted glass wetted with selected deicer solutions at 75°F (23.9°C).

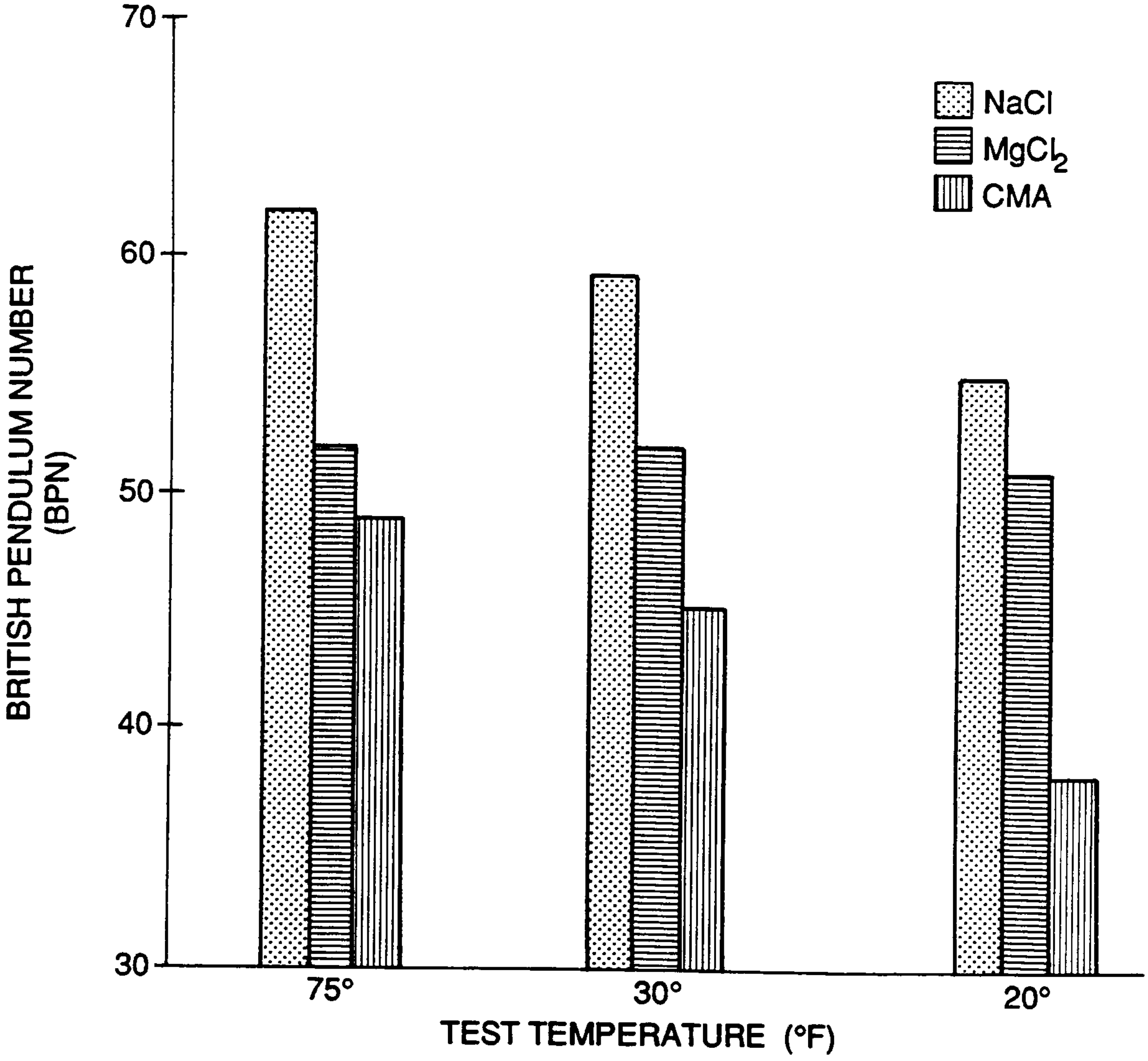

Figure 2.5-2. Frictional characteristics of sand-blasted glass wetted with 25 wt % solutions of NaCl, $MgCl_2$, and CMA at 75°, 30°, and 20°F (23.9°, -1.11°, -6.67°C).

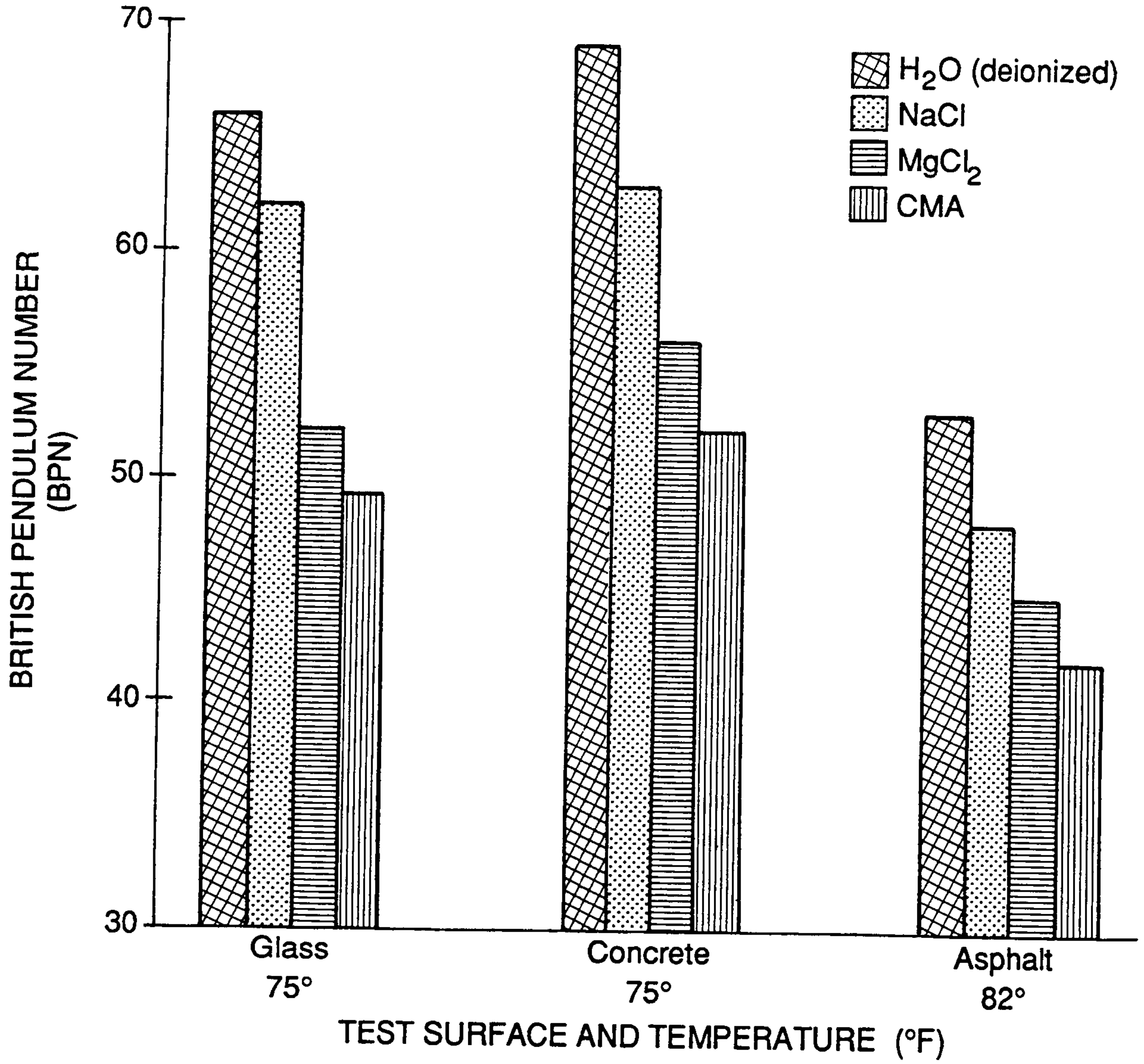

Figure 2.5-3. **Frictional characteristics of sand-blasted glass, molded concrete, and asphalt parking lot surfaces wetted with 25 wt % solutions of NaCl, $MgCl_2$, and CMA at 75° to 82°F (23.9° to 27.8°C).**

The frictional characteristics (BPN) of two different pieces of sand blasted glass wetted with selected deicer solutions at 75°F (23.9°C) to assess the repeatability of test data (given in Appendix A) demonstrate that consistently reproducible data can be obtained using sand-blasted glass as the test substrate.

The frictional characteristics (BPN) of deionized water and 10 wt % $MgCl_2$ on the lime-water-cured mortar sample (smooth) described in Section 2.5.2.3.5.5 were determined to be 30 and 24, respectively. Attempts to repeat the BPN deionized water control value after testing with $MgCl_2$ were not successful even after repeated flushing and sponging of the surface. Because there was the potential for residual additive effects to cause false results for successive deicer tests on this surface, the surface was found to be not acceptable.

A similar mortar sample having a more textured surface would not yield an acceptable BPN for deionized water even after 27 pendulum swings, perhaps because of $Ca(OH)_2$ leaching to the surface.

Asphalt/sand mixtures resulted in specimens which were too soft and tacky at 75°F (23.9°C) to be useful. Some specimens which seemed sufficiently hard gave BPN values for deionized water of 14 to 22. These values would indicate the frictional characteristics of a very slippery surface. Such surfaces would not leave any appreciable range for deicer comparison.

A concrete patio block surface also was found to be unsuitable as a test substrate, because it tended to erode the pendulum rubber slider and control values could not be reestablished during testing.

2.5.4 Conclusions and Recommendations

2.5.4.1 *Preliminary Investigations Using the Horizontal Slip Tester*

The following conclusions can be drawn from results of frictional characteristics tests using the horizontal slip tester:

- No differences were detected between the static and kinetic coefficient of friction (COF) values for rubber/sand-blasted glass surfaces wetted with deicer solutions.

- No differences were detected between the static COF values for rubber/sand-blasted glass surfaces wetted with:

  - Solutions of different deicer at similar concentration levels
  - Solutions of the same deicer at different concentration levels

- Kinetic COF values for rubber/smooth glass surfaces wetted with deicer solutions cannot be measured accurately because of slip-stick behavior.

Recommendation: The horizontal slip test method in its present configuration and state of development is not recommended as a test for chemical deicers.

2.5.4.2 *Investigation and Adaptation of Test Method ASTM E303-83 Using the British Pendulum Tester*

The following conclusions can be drawn from the results of frictional characteristics tests using the British Pendulum Tester:

- Differences in frictional characteristics can be determined for several deicer materials.

- The test procedure is not difficult to perform.

- Sand-blasted glass yields the most consistent results and is the easiest to clean.

- Results are repeatable on sand-blasted glass.

- High brine solutions (25 wt %) yield significantly lower BPN values than deionized water on sand-blasted glass.

- The same order of BPN values is obtained for 25 wt % solutions of NaCl, $MgCl_2$, and CMA at 75°, 30°, and 20°F (23.9°, -1.11°, and -6.67°C) on sand-blasted glass; at 75°F (23.9°C) on molded concrete; and at 82°F (27.8°C) on asphalt parking lot, that is, NaCl > $MgCl_2$ > CMA.

Recommendation: The British Pendulum Tester, when used in conjunction with procedures adapted and developed during this research, is recommended as a valid apparatus for evaluating the frictional characteristics of chemical deicers in the laboratory.

2.5.4.3 *Recommended of Standard Test Method*

A standard test method for determining the frictional characteristics of deicer solutions was developed and finalized. The procedure was adapted from ASTM E303-83 using the British Pendulum Tester and sand-blasted glass as the test substrate. The test method is presented in *The Handbook: Test Methods for Evaluating Chemical Deicers* as SHRP H-205.10, Method for Evaluation of Frictional Characteristics of Deicer Chemicals. A procedure for checking the calibration of the tester is included in the method.

The British Pendulum Tester is a dynamic pendulum impact-type tester used to measure the energy loss when a rubber slider edge is propelled over a test surface, in this case wetted with a selected deicer solution. The values measured, British Pendulum (tester) Numbers expressed as BPN, represent the frictional characteristics obtained with the apparatus on a given surface, and do not necessary agree or correlate with those obtained using other slipperiness-measuring equipment.

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2.6 Concrete Reinforcement Corrosion Research

2.6.1 Introduction and Background

2.6.1.1 *Introduction*

The objective of this research was to develop tests for accurately predicting the effects of deicing chemicals on the corrosion of steel in reinforced concrete structures. The research encompassed the development and evaluation of a standard test specimen and the use of three deicing chemicals to determine the sensitivity of both corrosion potential and macrocell corrosion to molal ion concentrations ranging from 0.4 to 12.8.

This section presents the experimental work and supporting background studies undertaken to develop and finalize test methods for use in predicting the effects of deicing chemicals on the corrosion of steel in concrete. Following a background discussion, the remainder of the section is organized as follows: Developmental Studies and Experimental Work (Section 2.6.2); Results and Discussion (Section 2.6.3); Conclusions and Recommendations (Section 2.5.4); References (Section 2.6.5).

2.6.1.2 *Background*

The adverse effects of deicing chemicals on the corrosion of reinforcing steel and reinforced concrete structures are well known. The deicers, principally calcium chloride and sodium chloride, cause reinforcing steel to lose the passive protection which it naturally attains in the alkaline concrete environment. The increased concentration of chloride ions directly contributes to the loss of passivity. Calcium chloride has the additional deleterious effect of reducing the pH of the pore solution within the concrete, further contributing to the loss of passivity.

Some new deicing chemicals have been developed in an attempt to produce one that is noncorrosive. Calcium magnesium acetate (CMA) is of special interest (Chollar 1984; Locke, Kennelley, Boren and Luster 1987; Chollar and Virmani 1988) because it is less corrosive to exposed metals than calcium chloride and sodium chloride (Dunn and Schenk 1980;, Locke et al. 1987). However, there is some indication that CMA produces a corrosive environment for reinforcing steel in concrete (Locke et al. 1987).

With any new deicing chemical, it is important to evaluate its effects on the corrosion of reinforcing steel. Ideally, that evaluation should simulate the effects of the deicing chemical on reinforcing steel in an environment similar to that in actual structures. The evaluation should also be completed in a relatively short amount of time. The most widely used test in current application, the so-called time-to-corrosion accelerated laboratory test (Pfeifer, Landgren, and Zoob 1987), satisfies the first criterion but requires 6 to 12 months.

The main thrust of this research was to develop tests that can be used to accurately predict the effects of deicing chemicals on reinforcing steel in actual structures in a short time period, preferably weeks rather than months. The steps taken to develop and evaluate the test specimen and the results obtained with three deicing chemicals, sodium chloride, calcium chloride, and calcium magnesium acetate, at molal ion concentrations ranging from 0.4 to 6.4, are detailed. The test procedures are described in the experimental work section and also presented in ASTM format in Appendix B, Part 1. Additional details of the study can be found in Martinez (1990).

2.6.2 Developmental Studies and Experimental Work

2.6.2.1 *Test Specimen*

The test specimen (Figure 2.6-1) consisted of a 5-in. (127 mm) long reinforcing bar, symmetrically embedded 3 in. (76 mm) into a 1.18-in. (30 mm) diameter mortar cylinder. The mortar cylinder was 4 in. (102 mm) long, and the overall specimen length was 6 in. (152 mm). This configuration was selected based, in part, on the experience obtained by Yonezewa, Ashworth, and Procter (1988) in their study of the pore solution composition and effects of chlorides on the corrosion of steel in concrete. Modifications were made to the square cross-section "lollipop" specimen used by Yonezewa et al. (1988) to provide for uniform cover and easier fabrication.

The mold for the specimen (Figure 2.6-2) was made from standard PVC pipe and fittings (full details in Appendix B, Part 1). The reinforcing steel was positioned with laboratory grade rubber stoppers to accurately maintain proper cover. The PVC mold was held together in a Plexiglas/bolt fixture which allowed for ease of construction and disassembly.

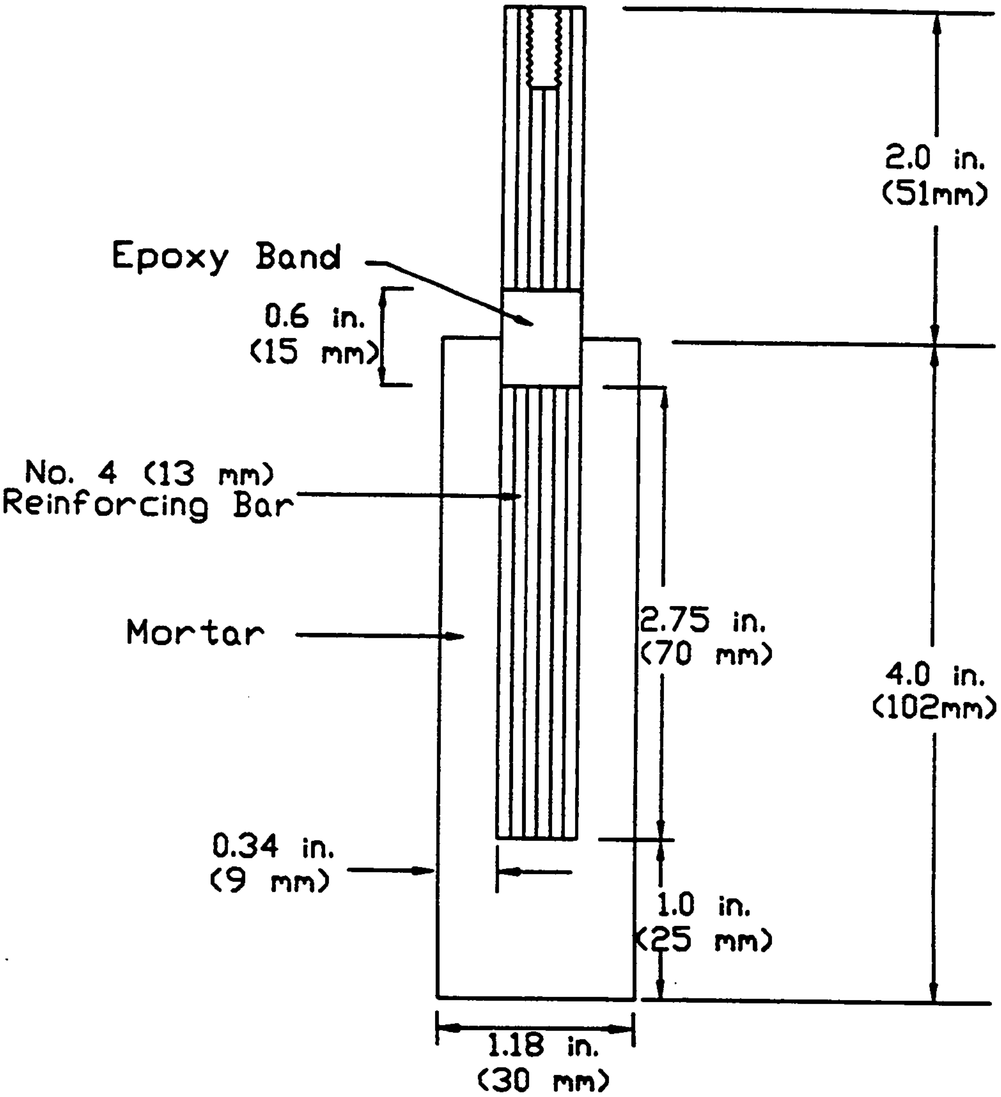

Figure 2.6.1. Cross section of test specimens.

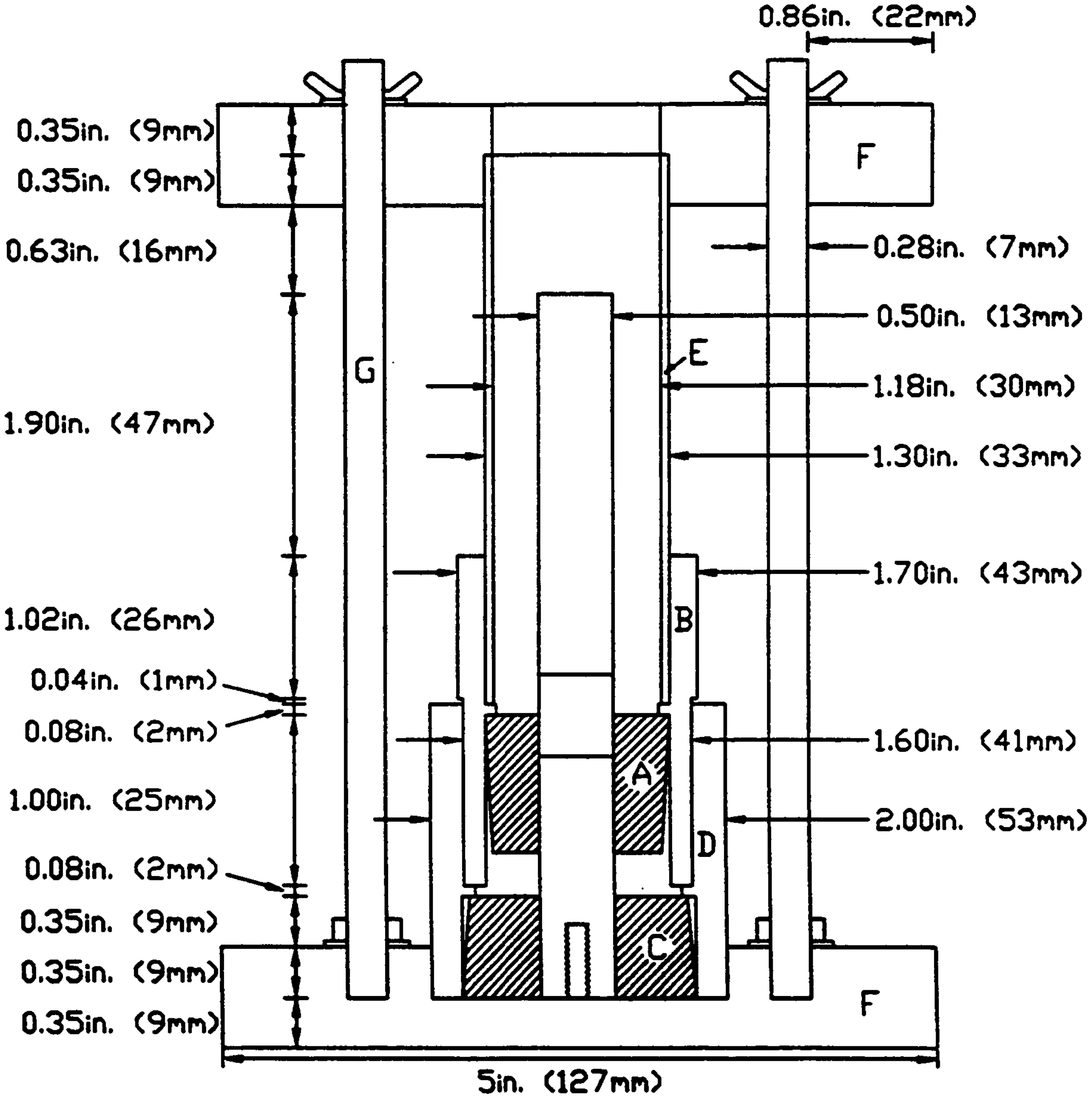

Figure 2.6-2. Cross section of mold for test specimens.

To prepare the specimen, the 5 in. (127 mm) long reinforcing bar was cut and tapped at one end to receive a steel screw to provide an electrical connection. The bar was then cleaned with acetone, and a 0.6 in. (15 mm) wide band of epoxy was applied around the bar, 2.75 in. (70 mm) from the nontapped end of the bar. The purpose of the epoxy band was to prevent crevice corrosion of the steel at the interface between the steel and the surrounding mortar. The liquid epoxy coating applied around the bar (Scotchkote 309 by 3M) was mixed and applied following the manufacturer's instructions.

To cast the specimen, the bar was assembled in the mold, as illustrated in Figure 2.6-2, by inserting the tapped end of the reinforcing bar into a hole centered in the small rubber stopper, A (wider end first). The distance between the nontapped end of the bar and the stopper was set at 3 in. (76 mm). The rubber stopper was then inserted into a machined PVC connector, B. The widest end of the stopper was in contact with the internal surface of the connector.

The large rubber stopper, C, was inserted in the large connector, D, and positioned as shown in Figure 2.6-2. The end of small connector, B, was then inserted into connector, D, while the tapped end of the reinforcing bar was inserted into the opening in rubber stopper, C. The 1.18 in. (30 mm) inside diameter PVC pipe, E, was then inserted into connector, B, until it was flush with rubber stopper, A. The assembled mold was inserted into the Plexiglas disks, F, and the assembly was tightened using threaded rods, G. The reinforcing bar was centered in the PVC pipe, E, by controlling the tension on the threaded rods. The openings in the rubber stoppers were enlarged to match the size of the reinforcing bar, and the 1.18 in. (30 mm) pipe, E, was split longitudinally (for easy disassembly) and taped before the mold was assembled.

2.6.2.2 *Materials*

2.6.2.2.1 Reinforcing Steel. ASTM A 615-87a Grade 60 No. 3, No. 4, and No. 5 bars were initially evaluated for use in the test specimen. No. 4 bars were used for the final configuration.

2.6.2.2.2 Mortar. The mortar mixture was made with Type I portland cement and ASTM C 778-87 graded Ottawa sand. The mixture proportions of the mortar represent the mortar constituent of concrete with a design strength of 4000 psi. The mortar had a water-cement ratio of 0.5 and a sand-cement ratio of 2.0 by weight. Both tap water and deionized water were evaluated for use in the specimens. The final design specimens used deionized water. The mortar was mixed following the procedures in ASTM C 305-87.

2.6.2.3 *Specimen Fabrication*

The specimens were cast in three layers. Each layer was vibrated on a vibrating table at an amplitude of 0.006 in. (0.15 mm) and a frequency of 60 cycles/sec for 15 sec. The upper surface of the mortar was finished with a trowel. Specimens were placed in a standard laboratory curing room (ASTM C 511-85) for two days. After one day, the Plexiglas disks were removed. After two days, the specimen was removed from the mold and, during this study, either left in the curing room or placed in lime-saturated water until the time of test. The final procedures required curing in lime-saturated water. Electrical cable was connected to the tapped end of the reinforcing bar using a steel screw, and the connection was covered with epoxy to prevent the formation of a corrosion cell due to the presence of dissimilar metals (steel specimen and copper wire).

2.6.2.4 *Test Procedure*

2.6.2.4.1 Corrosion Potential Test. The corrosion potential test was used to evaluate initial test specimen configurations and to determine the relative aggressiveness of deicing chemicals. The test schematic is shown in Figure 2.6-3.

The test required two plastic containers. The test specimen was placed in a 5-L container along with crushed mortar fill and either simulated pore solution or pore solution containing a deicing chemical. A standard calomel reference electrode was placed in a second container along with a saturated potassium chloride (KCl) solution. The two containers were connected by a salt bridge, and the potential difference between the specimen and the calomel electrode was measured at selected time intervals using a digital voltmeter.

The mortar fill consisted of the same mixture as used in the test specimen. The fill was used primarily to serve as a buffer and to help simulate the relative amount of cementitious material that exists in an actual structure. The fill was cast in a 1 in. (25 mm) thick layer using a metal cookie sheet as the form. The form was vibrated for 15 sec on the vibration table. The fill was cast at the same time as the test specimen. At the time of test, the mortar was broken into pieces, with nominal sizes of 0.75 to 1.5 in. (19 to 38 mm); 7.75 lb (3,500 g) of crushed mortar was used as fill in each test.

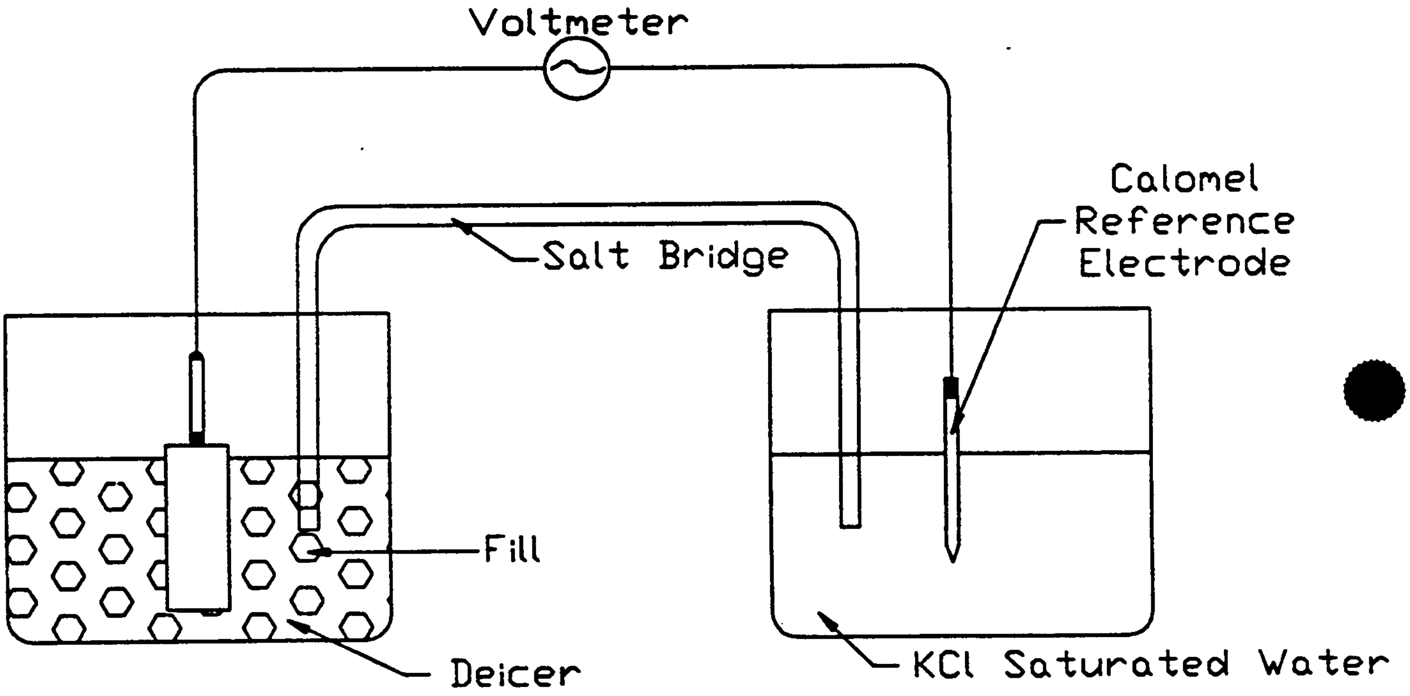

Figure 2.6-3. Schematic of corrosion potential test configuration.

The 5-L container allowed three specimens to be evaluated at one time, with at least a 1 in. (25 mm) between specimens and under each specimen. The polymer used for the container was insensitive to both the caustic pore solution and the deicing chemicals. The constituents in the simulated pore solution were selected based on the analyses of expressed pore solution performed by Farzammehr (1985). Each liter of pore solution contained 0.14 g of NaCl, 18.81 g of KOH, and 17.84 g of NaOH.

To complete the corrosion cell, the two containers were connected by a salt bridge. The salt bridge was prepared, following procedures described by Steinbach and King (1950): A gel is prepared by stirring 4.5 g of agar in 100 ml of deionized water over a double boiler. After the solution becomes clear, 30 g of KCl is dissolved in the gel, while the mixture is stirred and heating continues. The gel is then poured into 5 mm inside-diameter tygon rubber tubing, which serves as the salt bridge.

A standard calomel reference electrode (Fisher model 13-639-51) was used to measure corrosion potential. The electrode was submerged in a saturated KCl solution (15 g of KCl per 100 cc of water).

Laboratory grade sodium chloride (NaCl) and calcium chloride ($CaCl_2$) and commercially produced calcium magnesium acetate (CMA, 3 moles of calcium acetate per 7 moles of magnesium acetate) were used to evaluate the effects of various concentrations of deicing chemicals. The effects of the chemicals were compared on a isomolal ion basis (equal number of ions), since ion concentration in moles per unit volume of water controls ice-melting capacity. Molal ion concentrations of 0.4, 0.8, 1.6, 3.2, 6.4, and 12.8 were used. The weights of materials in grams per liter of pore solution for each molal concentration and deicing chemical are presented in Table 2.6-1.

Table 2.6-1. Quantities of deicing chemicals in grams per liter of simulated pore solution

Deicers	Molal ion concentration in simulated pore solution[a]					
Molal ion concentration (chemical)	0.4 m (g/L)	0.8 m (g/L)	1.6 m (g/L)	3.2 m (g/L)	6.4 m (g/L)	12.8 m (g/L)
NaCl	11.4	22.8	45.6	91.2	182.3	364.6
$CaCl_2$	14.4	22.8	57.7	115.4	230.7	461.5
CMA[b]	20.8	41.7	83.4	166.7	333.4	666.9

[a] Simulated pore solution: 0.14 g of NaCl, 18.81 g of KOH, and 17.84 g of NaOH per liter of solution. Solvent = deionized water.

[b] Three moles of calcium acetate per 7 moles of magnesium acetate.

At the desired age, a specimen was taken from the curing room or the curing tank. The tapped end of the reinforcing bar was thoroughly dried using compressed air, the shielded cable was connected to the bar with a steel screw, and the connection was covered with epoxy. The cable was then passed through a hole in the lid of the container. A layer of mortar fill was placed on the bottom of the container; up to three specimens were placed, bar up, on the layer; and the balance of the fill material was added to the container. The salt bridge was placed in the container through a second hole in the lid. The other end of the salt bridge was placed in the second container. To have a good ionic path, the gel in the tubing had to be continuous, without interruption by an air bubble. The respective solutions were then placed in the containers. For the tests reported here, the simulated pore solution, with or without the deicing chemical, was added until it reached a level 0.08 in. (2 mm) from the top edge of the mortar. The container with the test specimen was sealed for the duration of the test to prevent carbon dioxide from neutralizing the simulated pore solution, and to prevent evaporation of the liquid.

2.6.2.4.2 Macrocell Test. The macrocell test is used to evaluate the relative corrosion properties of deicing chemicals by setting up an active macrocell. The elements used in this test are the same as elements described for the corrosion potential test. A schematic of the test setup is shown in Figure 2.6-4.

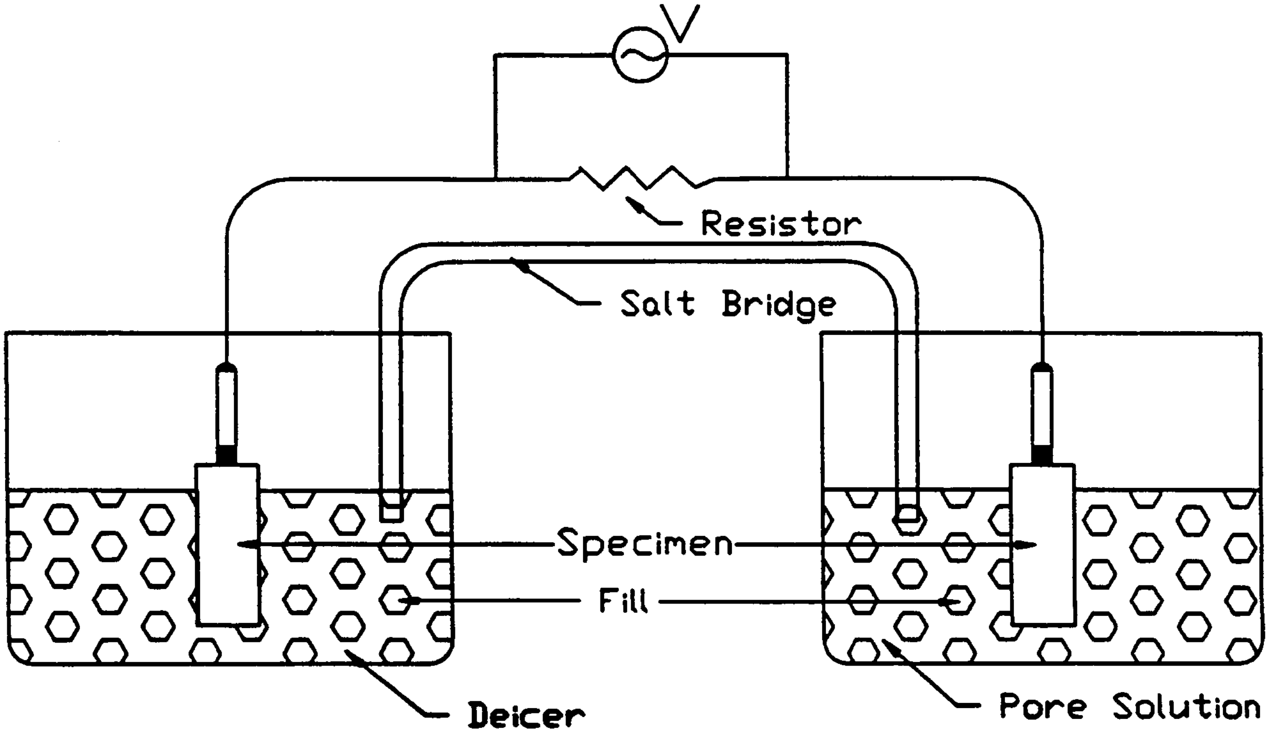

Figure 2.6-4. Schematic of macrocell test configuration.

In this test, two lollipop test specimens, located in separate containers, were electrically connected across a 100,000 ohm resistor. Electrical conductivity between the solutions in the two containers was provided by a salt bridge. Standard fill material was placed in both containers. One specimen was exposed to simulated pore solution, while the other was exposed to simulated pore solution containing a deicing chemical. The 100,000 ohm resistor allows corrosion to proceed while providing a measurable potential drop.

For the macrocell tests, the specimens and fill were removed from the curing tank and prepared in the same manner as the corrosion potential specimens. The pore solution was then added to one container, while the pore solution and deicing chemical were added to the other container. Both containers were sealed for the duration of the test. The potential drop across the resistor (a measure of the corrosion current) was then measured at regular intervals.

2.6.3 Results and Discussion

2.6.3.1 *Test Specimen Development and Evaluation*

2.6.3.1.1 Experimental Results. The results of the test specimen development and evaluation studies are presented in Figure 2.6-5 of this section and in Figures B-1 through B-6 in Appendix B.

2.6.3.1.2 Discussion of Results. Prior to the initiation of the corrosion potential and macrocell tests using deicing chemicals, the test specimens were subjected to a series of evaluation steps to determine the best combination of materials and preparation techniques. Initial evaluation of the test specimens involved determining the optimum reinforcing bar diameter, the length of curing, the method of curing, the types of sand and water to be used, and the best configuration for the epoxy coating.

Ideally, the largest possible bar diameter should be used, because it provides the minimum cover, which in turn provides the most rapid penetration of the deicing chemicals to the bar surface. No. 3, No. 4, and No. 5 bars were evaluated.

Tests should be initiated immediately following the curing period. The length of curing must be long enough for the specimens to reach a passive condition. The shorter the time period, however, the lower the density the cement paste and the faster the test solution can reach the surface of the bar. For this reason, curing ages ranging from 3 to 28 days were evaluated.

Like the age of curing, the method of curing is important because it also must allow the reinforcing bar to reach a passive condition. Specimens were cured in both a standard moist room and in lime-saturated water.

It was considered desirable to make specimen fabrication as easy and as economical as possible: the initial specimens were fabricated using local river sand and tap water. Results from early portions of the study indicated that there were some problems with the local materials. These observations prompted a switch to ASTM C 778-87 graded Ottawa sand and deionized water for the standard test configuration. However, some additional comparisons were made using tap water in the specimen, fill material and simulated pore solution, and river sand in the fill material only, to determine if specimen passivation was specifically sensitive to these materials.

- Effect of rebar size--Specimen configurations were evaluated based on the rate at which the reinforcing bars reached a passive condition. Generally speaking, there was no difference between the rate of passivation for the three size bars evaluated. The mortar in the specimens containing the No. 5 bars, however, had a tendency to crack at the end of the bar during demolding. For that reason, No. 5 bars were eliminated from further consideration. Both the No. 3 and No. 4 bars performed well. No. 4 bars were selected for the final specimen configuration because of the lower cover they provided.

- Effect of using tap water for curing test specimens--The earliest test specimens were cast using tap water. Typical results are illustrated in Appendix B, Part 2, Figure B-1 for bars cured in the moist room for 3, 7, or 28 days. As can be seen, none of the specimens had reached the passive condition, corresponding to a potential more positive than -0.30 volts with respect to calomel, at the conclusion of curing. In fact, the longer the curing period, the less passive (the more negative) the potential. It was only after being placed in the pore solution for a period of time that the specimens attained a passive condition. At this point in the study, it was concluded that the initial corrosion state of the steel was dominated by corrosion on the exposed portion of the reinforcing bar, and for that reason, the balance of the tests used specimens that were cured in lime-saturated water.

- Effect of curing in lime-saturated water--The results for the specimens cured in lime-saturated water (Appendix B, Part 2, Figure B-2) show that the longer the curing period, the closer the corrosion potential is to the passive condition. Specimens cured for 28 days are fully passive, while those cured for 3 and 7 days typically do not reach a passive condition until at least 10 days after casting. Based on these results, a standard curing time of 14 days was selected for the main battery of tests.

- Effect of epoxy configuration--Another aspect of the tests involved the epoxy configuration, that is, the location of epoxy on the test specimen. The three configurations considered are shown in Figure 2.6-5. Configuration A consisted of epoxy at the interface between the steel and the concrete, plus epoxy at the embedded end of the bar. This configuration was considered because of concern that the surface of the bar covered by mill scale would react differently in the presence of deicing chemicals than a surface exposed by a saw cut. Configuration B consisted of a full coating of epoxy on the exterior portion of the bar, plus coverage on the embedded end of the bar. Configuration C, the one finally selected for the tests, consisted of a single ring of epoxy at the exposed interface between the steel and the mortar. Test results showed that epoxy configuration, B, full coverage of the exposed steel, results in specimens that rarely attain a passive condition and often exhibit a high negative potential instead. The reason, in all likelihood, was that small holes in the epoxy coating allowed some moisture under the coating and resulted in crevice corrosion (Fontana 1986). Thus, for configuration B, it was impossible to evaluate the achievement of a passive condition for the portion of the bar that was in contact with the mortar. Therefore, full epoxy coverage of the exposed steel was eliminated as an option. Of the remaining epoxy configurations, specimens with configuration A, epoxy at the interface and on the embedded end of the bar, occasionally exhibited high negative corrosion potentials. Here again, crevice corrosion may have been the cause. Based on these results, configuration C was selected, because it provides the most consistent results.

- Effect of using tap water and river sand--The effects of using tap water in the specimen, fill, and simulated pore solution and the effects of using river sand in the fill material are illustrated in Appendix B, Part 2, Figures B-3 and B-4. These figures show that, while a passive state was attained for specimens cured for 7 and 14 days, it was not consistently attained for specimens cured for 28 days. The lack of passivity at 28 days was likely due to the presence of chlorides in the tap water and river sand. Thus, standard Ottawa sand and deionized water were selected for use in all portions of the test setup. Typical curves for specimens using these materials and exposed to the simulated pore solution are illustrated in Appendix B, Part 2, Figure B-6.

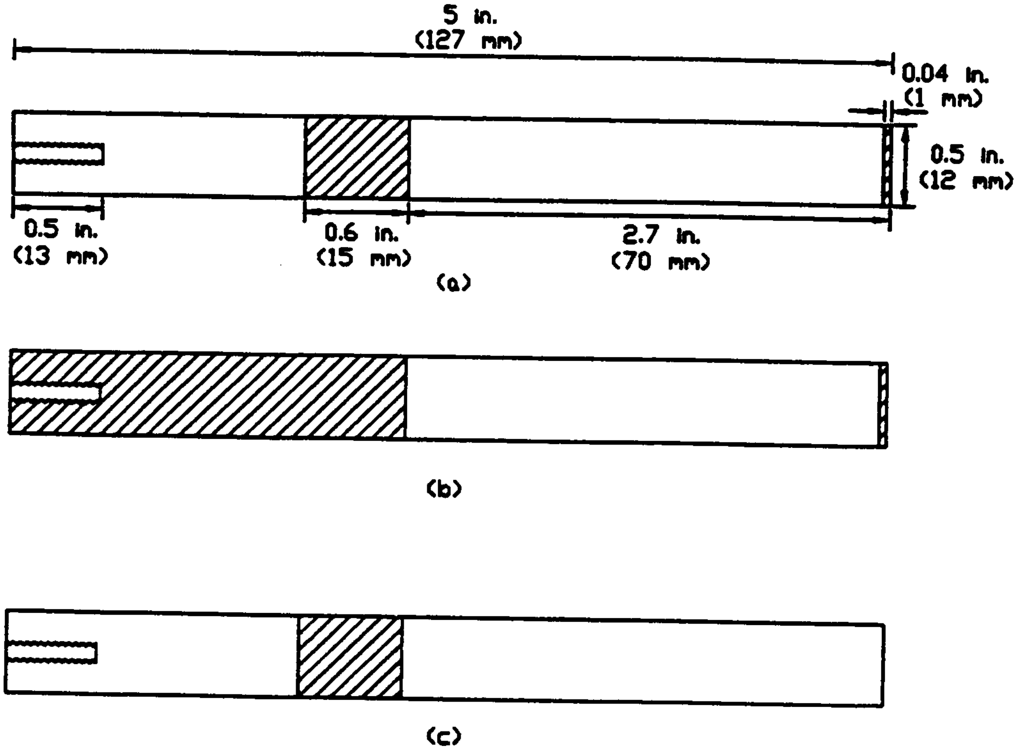

Figure 2.6-5. Epoxy configurations. (a) Configuration A, (b) Configuration B, (c) Configuration C.

- Effect of test specimen immersion depth--The standard specimen configuration provided only 0.08 in. (2 mm) of mortar above the top of the solution. As the corrosion potential and macrocell tests proceeded, there was some concern that the pore solution with the deicing chemical might be moving over the top of the specimen and down the epoxy interface to reach the steel, rather than diffusing through the mortar cover. To evaluate this possibility, a series of "dip" tests were carried out in which specimen corrosion potential was measured for different heights (or freeboard) of mortar above the top of the solution. Values of 2, 1.5, 1, 0.5, and 0.08 in. (51, 38, 25, 13 and 2 mm) were evaluated. The test solution for the dip tests consisted of the simulated pore solution with a 6.4 molal ion concentration of NaCl. Specimens with just 0.08 in. (2 mm) of freeboard attained the maximum corrosion potential by the second or third day, while the other configurations approached the maximum corrosion potential somewhat more gradually. The results, illustrated in Appendix B, Part 2, Figure B-6, show a strong similarity between specimens with freeboards of 0.5 to 2 in. (13 to 51 mm). After 50-60 days, all specimens exhibited approximately the same corrosion potential. There was enough difference between specimens with 0.5 in. (13 mm) freeboard and specimens with 0.08 in. (2 mm) freeboard that, for future evaluations, it would appear wise to run the tests with 0.5 in. (13 mm) freeboard to ensure that no portion of the solution moves over the top of the specimen and down the interface between concrete and the epoxy.

2.6.3.2 *Corrosion Potential Tests*

2.6.3.2.1 Test Results. The results of the corrosion potential tests are illustrated in Appendix B, Part 2, Figures B-7 to B-11.

2.6.3.2.2 Discussion of Test Results.

- Effect of test specimen cure time--Figure B-7 illustrates the response of specimens cured for 3, 7, or 28 days and exposed to a simulated pore solution with a 12.8 molal ion concentration of NaCl (saturated NaCl solution). The figure illustrates the relative insensitivity of the long-term corrosion potential to the age at which the test is initiated. The main difference observed in these tests appears to be the state of passivation at the initiation of the test. The 28-day-old specimens had achieved a passive state, whereas the 7-day and 3-day specimens had not yet become passive. However, after about 10 days in the solution, little difference was exhibited based on the age at which the test was initiated. The balance of the tests discussed in this report represent specimens that were cured for 14 days and had, in most cases, reached a passive condition (corrosion potential more positive than −0.30 volt) prior to the initiation of the tests.

- Effect of deicer concentration--Corrosion potential tests were run with molal ion concentrations of deicers of 6.4, 3.2, 1.6, 0.8, and 0.4 in the simulated pore solution. Results for six specimens placed in pore solution only are illustrated in Appendix B, Part 2, Figures B-5(b) and B-8. All specimens were passive or nearly passive at the initiation of the tests, and maintained the passive condition throughout the duration of the tests, 68 days after casting.

- Electrochemical behavior--For the specimens exposed to the deicers, several clear trends can be observed (Appendix B, Part 2, Figures B-9 to B-11). As a general rule, the specimens exposed to NaCl and CMA exhibited a decreasing (less negative) corrosion potential with decreasing concentrations of deicing chemical, while those containing calcium chloride showed only a slight drop in corrosion potential with decreasing concentration. Specimens in NaCl (Figure B-9) showed a gradual drop in corrosion potential, from −0.55 volt, at an ion concentration of 6.4 m, to −0.35 volt, at a concentration of 0.4 m. Specimens exposed to CMA (Figure B-11) exhibited a drop from −0.60 volt, at a concentration of 6.4 m, to a fully passive condition, −0.25 volt, at a concentration of 0.4 m. Specimens exposed to $CaCl_2$ (Figure B-10) exhibited corrosion potentials ranging only from −0.60 volt, at a concentration of 6.4 m, to −0.55 volt at 0.4 m, with the exception of the 0.8 m concentration which exhibited a long term potential of about −0.35 volt.

- Physicochemical behavior--The corrosion potential tests provided useful insight into the effects of the three deicing chemicals evaluated in this study. When the CMA and the $CaCl_2$ were initially added to the pore solution, a precipitate was observed. The CMA causes both calcium hydroxide and magnesium hydroxide to precipitate (Locke et al. 1987), while, presumably, $CaCl_2$ causes calcium hydroxide to precipitate. In both cases, the pH of the solution is decreased, which has the effect of reducing the passive protection provided by the pore solution. Both $CaCl_2$ and NaCl provide chloride ions, which also reduce passive protection.

- Effects of calcium chloride--For the calcium chloride, the dual effect of the reduced pH and chloride ion resulted in a nearly uniform corrosion potential, independent of the ion concentration over the full concentration range of 6.4 m to 0.4 m, indicating that of the three chemicals, $CaCl_2$ should be the most detrimental to reinforcing steel.

- Effects of calcium magnesium acetate (CMA)--At high concentrations, CMA appeared to act in a similar manner to $CaCl_2$. At lower concentrations CMA was less detrimental, and at the lowest concentration evaluated, 0.4 m, CMA allowed a fully passive condition to be attained. This large difference in behavior as a function of concentration may explain conflicting observations (Locke et al. 1987, Chollar and Virmani 1988) as to the effect of CMA on the corrosion of reinforcing steel. The different concentrations used in these tests can be looked upon as representing the different concentrations that are attained at the surface of reinforcing bars as deicing chemicals penetrate a thick concrete cover over time. Clearly, small amounts of $CaCl_2$ rapidly change the corrosion potential of reinforcing steel, whereas low concentrations of CMA have no effect. The overall result is that in the field, reinforcing bars exposed to CMA should not corrode until the concentration reaches higher values, while bars exposed to $CaCl_2$ will begin to corrode at low concentrations.

- Effects of sodium chloride--The effect of NaCl on corrosion appeared to fall between that of the other two deicing chemicals. NaCl had little effect on the pH of the pore solution, but did expose the reinforcement to chloride ion. Overall, NaCl appeared to provide reduced corrosion potential as its concentration is decreased. Low concentrations had the effect of reducing the passivity, but were not as detrimental as low concentrations of $CaCl_2$. Considering the sensitivity of the corrosion potential to different concentrations of some deicers, a standard test would include comparisons at molal ion concentrations of 6.4, 1.6, and 0.4. NaCl would be a good standard for comparison, because it produces a corrosion potential that is a function of deicer concentration.

- General observations--The corrosion potential versus time curves exhibited a noticeable amount of scatter. However, after 50 days the results appeared to stabilize. To get a reasonably complete picture, the standard tests should run 60 days following the time of casting (46 days after test initiation for a 14 day cure), although useful results may be obtained within 30 days of casting. The test was found to be considerably more rapid than the time-to-corrosion test (Pfeiffer et al. 1987). The relatively high consistency obtained with the corrosion potential tests and the general agreement of these tests with results observed in the literature (Locke et al. 1987) suggest that the standard corrosion potential test employing a calomel reference electrode would be useful and relatively easy to implement in the field.

2.6.3.3 *Macrocell Tests*

2.6.3.3.1 Test Results. The results of the macrocell tests using simulated pore solution and molal ion concentrations of deicer of 6.4, 3.2, 1.6, 0.8 and 0.4 are illustrated in Appendix B, Part 2, Figures B-12 to B-14. The figures show the potential drop across the resistor, which is directly related to the corrosion current. All tests were performed with two specimens. In a number of cases, the salt bridges were not functioning during the early stages of the tests, which prevented active macrocell corrosion from occurring. Cases in which this problem occurred are evident in those plots where the macrocell potentials provided by the two specimens gave values that were symmetrical about 0 volts. Once the salt bridges were fixed, active corrosion resumed.

2.6.3.3.2 Discussion of Test Results. The results shown in Figures B-12 to B-14 demonstrate that the effects of the deicing chemicals are qualitatively similar, but not as consistent as those observed in the corrosion potential tests.

- Test results with NaCl--Inconsistency in the test results are shown in Figure 12(a), the negative potential drop across one resistor exceeds –0.2 volt for one of the specimens exposed to the 6.4 m NaCl solution, but is essentially zero for the other specimen. For lower concentrations of NaCl [Figures B-12(b)-(e)], the potential drop across the resistor does not decrease monotonically with decreasing deicer concentration, as observed in the corrosion potential tests (Figure B-9).

- Test results with $CaCl_2$--The results for $CaCl_2$ (Figure B-13) are much more consistent than those for NaCl and exhibited a smooth, but nonmonotonic, variation with concentration. The negative potential drop across the resistor was greatest for the 3.2 m $CaCl_2$ solution, exceeding –0.2 volt. The potential drop decreased for concentrations below 3.2 m, with the 0.8 m and 0.4 m concentrations [Figures B-13(d) and (e)] producing similar results, between 0 and –0.1 volt. The drop in corrosion with the decrease in deicer concentration differed from the apparent insensitivity to concentration observed for $CaCl_2$ in the corrosion potential tests (Figure B-10).

- Test results with CMA--Like the results for NaCl, the results for CMA (Figure B-14) were erratic, with little apparent corrosion occurring for the 6.4 m solution (potential drop ≈ 0). The potential drop increased to about –0.05 volt at 3.2 m, decreased again at 1.6 m, and then increased significantly for one specimen at 0.8 m. At 0.4 m, one specimen exhibited slight corrosion, while the other exhibited a small positive potential change, under +0.1 volt.

- Comparative corrosivity of deicers tested--Overall, $CaCl_2$ provided the greatest macrocell corrosion. NaCl caused less macrocell corrosion, and CMA, with one exception [Figure B-14(d)], caused the least corrosion.

- Possible causes of testing inconsistencies--One reason for the lack of consistency in the observed degree of macrocell corrosion could be the salt bridges that did not function during the early stages of some tests. Another cause for the greater scatter observed in these tests may be the fact that the "reference electrode" (the specimen in the pure pore solution) was not manufactured under the same controlled conditions as was the standard calomel electrode used for the potential tests.

- Additional evaluations and modifications--The results illustrated in Appendix B, Part 2, Figures B-12 to B-14, suggest that additional evaluation is necessary before this test procedure can be finalized. The macrocell test should ultimately prove to be more useful than the corrosion potential test, since it compares the effects of deicing chemicals on an active corrosion cell. Modifications to consider include improved methods for making the salt bridge and the use of a much lower resistance in the circuit to obtain a greater degree of corrosion in the macrocell. The very high resistance used in the current tests greatly limited the corrosion current and partially defeated the purpose of using a macrocell.

2.6.4 Conclusions and Recommendations

2.6.4.1 *Conclusions*

- The corrosion potential test appeared to provide more consistent results and should prove to be a useful tool for comparing the effects of deicing chemicals on the corrosion of reinforcing steel.

- Based on limited test data using sodium chloride, calcium chloride, and calcium magnesium acetate, calcium chloride appeared to be the most detrimental, followed in order by sodium chloride and calcium magnesium acetate.

- Corrosion in the presence of calcium magnesium acetate appeared to be highly sensitive to relative concentration, with no corrosion occurring at a molal ion concentration of 0.4.

- Test specimens exposed to both calcium chloride and sodium chloride exhibited measurable corrosion potential at a concentration of 0.4 m.

- At the highest concentration for which comparisons were made (6.4 m), both the CMA and the $CaCl_2$ appeared to be equally detrimental, while the NaCl appeared to cause somewhat less corrosion.

2.6.4.2 *Recommendations*

- Additional developmental work is recommended before the macrocell test can be applied effectively to compare the effects of deicing chemicals on reinforcing steel. However, the rapid reaction of the test specimens, as demonstrated by the corrosion potential tests, shows that significant advantages will be obtained if the specimens can be incorporated within a macrocell test system.

- In addition to the recommended modifications to the salt bridge and resistor discussed earlier, it is recommended that the use of multiple (and perhaps longer) specimens connected in parallel be investigated to increase the surface area of the reinforcing steel and, thus, increase the measurable corrosion current.

- The incorporation of a zero resistance ammeter is also recommended.

- Recommended future work should include the use of deicing chemicals without simulated pore solution at the anode. The use of a straight deicer solution may be more realistic than the procedure used in the current study and would, in all likelihood, be a more severe test of the deicer.

- Finally, the system should be checked to ensure that the results are not affected by oxygen starvation because sealed containers are used for the tests.

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2.7 Ecological Effects Research

2.7.1 Introduction and Background

2.7.1.1 *Introduction*

The basic objective of the ecological effects research was to identify and develop screening test procedures for use in the preliminary ecological hazard assessment of deicing chemicals in contact with selected terrestrial and aquatic plant and animal species.

This section presents the background research and experimental work undertaken to identify and develop ecological effects screening tests. A synopsis of ecological testing protocols within the Environmental Protection Agency (EPA) is presented in Appendix C, Part 1. Following a background discussion, the remainder of this section is organized as follows: Developmental Studies and Experimental Work (Section 2.7.2); Results and Discussion (Section 2.7.3); Conclusions and Recommendations (Section 2.7.4); and References (Section 2.7.5).

2.7.1.2 *Background*

Evaluation procedures for determining the ecological effects of deicers are in principle available in the general inventory of methods developed by the U.S. Environmental Protection Agency (EPA) and others. These methods primarily address materials such as pesticides and require adaptation or modification for testing of the effects associated with deicing chemicals and the ways they are introduced to and disseminated into the environment. Some of these tests were examined and adapted to provide a screening protocol to assess the potential ecological effects of deicers.

The U.S. Environmental Protection Agency (EPA) can require the use of a variety of biological/ecological tests for assessing the ecological risks of chemicals such as pesticides and industrial effluents that are or could be introduced into the environment. These tests identify the toxicity of the chemical to wildlife by using particular test organisms in the laboratory. Also required are determinations of the estimated environmental concentrations (EEC) expected under certain uses or releases of the chemical. Possible regulation of the chemical occurs after a risk/benefit analysis is performed. This analysis considers the ecological risk assessment (developed in part from the ecological effects testing) along with risks to humans, as identified by other prescribed procedures. The analysis takes into account the economic, social, and environmental costs and benefits of the use of the product (e.g., pesticide) or of the product or activity associated with the production of the effluent chemical. The authority and procedures for making the ecological risk assessments and the other assessments are registered within EPA in various ways, including the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) for pesticides, the Toxic Substances Control Act (TSCA) for industrial chemicals primarily as effluents, and the Clean Water Act for chemicals more generally.

It is important to make a distinction between some terms that EPA uses in the risk analysis process. First, a distinction can be made between "risk assessment" and "hazard evaluation." The terms "risk" and "hazard" are sometimes used interchangeably, but technically they do have different meanings. "Risk" can be viewed as a function of hazard and exposure and is thus assessed by determining the probability of adverse impacts. Therefore, in this context "hazard" is the intrinsic toxicity of the chemical (i.e., results of effects test) causing adverse effects under a particular set of circumstances. Hazard must then be quantified to determine risk. In the other case, "hazard" is considered to be a function of toxicity (i.e., results of effects test) and exposure, and thus refers to a qualitative measure of potential harm. "Risk" then is limited in this context to a probabilistic measure of potential harm. The former is more generally the way all of this is considered by EPA, but even within the Agency both meanings appear and the terms are sometimes used interchangeably. During this research, tests were developed for some initial measurement of toxicity or effects only. An overall or complete "risk assessment" or "hazard evaluation" was beyond the scope of the research.

It was useful to consider ecological risk assessment for pesticides, which in some ways is relevant to how assessments could be made for deicers because of the similar ways that these chemicals come in contact with the environment. It was important to note that pesticides are manufactured and applied to be purposely toxic and deicers are not. Deicer chemicals have relatively few types of inert or active ingredients. Pesticides in the United States have 600 active ingredients mixed with 900 inert ingredients to make 50,000 individual pesticide products.

The Ecological Effects Branch (EEB) of EPA is charged with overseeing the ecological risk assessment of pesticides from information provided by the manufacturer, including the results of ecological effects tests which the latter must provide. EEB describes its ecological risk assessment method as a quotient method which compares an estimated environmental concentration (EEC) and an effect level (i.e., ecological effects test result) based on their regulatory risk criteria (i.e., test end points rated by specific pass/fail criteria). The ecological risk assessment then becomes the integration of information obtained about the components of the environment at risk from the use of the chemical, the nature of the risk, quantitative relationships between test dose and biological response, and conditions of exposure in the test and expected in the natural environment.

Determination of the estimated environmental concentration (EEC) for deicers can also follow the methods used to make the similar calculations for pesticides. Our objective here is to describe the methods currently in use for pesticides because EEC calculations for particular deicers must be based on data generated by individual highway departments about their chemical properties, mode and quantity of application, and characteristics of the receiving environment.

Deicer chemicals are introduced into the environment not as effluents but as substances with a specific purpose, as is the case with pesticides. They are not purposely developed to be toxic to certain organisms as is also the general case for effluents but not for pesticides. Deicer chemicals differ then in this regard to the chemicals society identifies for regulation ether under FIFRA or TSCA. These chemicals have been targeted less often for ecological hazard assessment under EPA regulations, but there is increasing evidence concerning their ecological effects.

The purpose of this research was to provide test procedures for initial levels of ecological hazard assessment that state and local highway departments could use in assessing the particular chemicals they are using or might use in the future. The system of testing that EPA has established and continues to develop under FIFRA, TSCA, and elsewhere served as our source of tests. Together they provide an extensive series of tests, from initial rapid screening to the longer and more elaborate higher level tests, that provide the complete assessment. These tests are described briefly below, though this project is limited to the testing level of initial screening.

2.7.2 Developmental Studies and Experimental Work

The developmental studies and experimental work conducted during this research are discussed as follows: Selection of Ecological Effects Tests for Chemical Deicers, Ecological Effects Tests for Initial Screening of Chemical Deicers, Chemical Reagents and Test Solutions, Aquatic and Terrestrial Toxicity Test Matrix, and Finalization and Standardization of Test Methods.

2.7.2.1 *Selection of Ecological Effects Tests for Deicer Chemicals*

In selecting particular tests for chemical deicers, certain criteria were used. These criteria basically relate to how well the test organisms and modes of exposure suggested by various EPA and ASTM protocols and guidance documents (see Appendix C, Part 1) represent the contact that deicer chemicals have with the natural environment. This includes which organisms and processes are contacted by these chemicals and how this contact occurs.

In considering the organisms most likely contacted and affected by chemical deicers, the Evaluation and Testing of Chemical Deicers--Literature Review, SHRP Project H-205 was the reference. It was concluded that both aquatic and terrestrial habitats are contacted, with more widespread exposure in the former. Organisms most often contacted and affected for the former include fish and insects and for the latter plants, particularly rooted plants. The species of animals and plants from both types of habitat differ regionally. Flexibility was designed into each test to allow for selecting organisms and means of exposure which account for the particular characteristics of the region in question.

In considering the mode of exposure, it was concluded that in most cases deicer chemicals would first contact the environment periodically during the winter accompanying intermittent application and thawing periods. This initial contact is followed by a longer exposure period in the spring, and finally a possible long-term period of exposure by retention of the chemical in the habitat. This long-term period of retention will depend on other environmental conditions which may affect dilution or loss of the chemical in other ways up to the time it is applied again the following winter.

A number of EPA ecological effects tests were reviewed, selected, and modified for use in this study. These tests were conducted with a variety of deicer chemicals to determine the general suitability of the test for this type of chemical. A convenient compilation of tests has been published by EPA (1982) as Environmental Effects Test Guides--Part One and Part Two, EPA/560/6-82/002. Other tests reviewed can be found in the other EPA and ASTM documents (see Appendix C, Part 1). The 1982 EPA tests guide document describes 23 methods, including tests with both aquatic and terrestrial organisms. Of these 23 tests, 17 are for aquatic organisms including 8 for invertebrates and 5 for fish with acute and chronic effects tests for both. Of the 6 tests for terrestrial organisms 3 are for plants, the terrestrial organisms of focus. To facilitate technology transfer to highway departments engaged in this testing in the future, simple, inexpensive, yet reliable tests have been developed.

Acute toxicity tests operated in the static mode are described by Peltier and Weber (1985) in EPA/600/4-85/013 as simple and inexpensive, very cost effective, and requiring limited resources (space, manpower, equipment). Two types of acute toxicity tests are utilized by EPA: static (no flow) and flow-through. Flow-through tests require more elaborate incubation systems to provide continuous flow of the culture medium and the toxicant over the test organisms. These tests have the advantage of sometimes providing more natural culture conditions and exposure conditions for the organisms. Because of these advantages, as part of this research, a simple flow-through system that could accommodate a modified version of the flow-through acute toxicity test was designed and constructed. Details of the construction and basic flow operation are presented in Appendix C, Part 2, titled A Simplified Flow-Through System for Acute and Chronic Testing.

In spite of the advantages of flow-through testing and the more simplified system developed during this research, the static acute tests are an accepted initial tier of ecological effects testing more likely to be considered at first by highway departments. Two basic types of static acute toxicity tests were available: a nonrenewal test, in which test organisms are exposed to the same chemical solution for the duration of the test; and a renewal test, in which test organisms are exposed to a fresh solution of the same concentration of test chemical every 24 hr or at some other prescribed interval. The renewal system was preferred for tests longer than 24 hr because it diminishes toxicant adsorption on the test chambers and uptake by test organisms, both of which alter the test concentration and increase the effect of metabolites on the toxicity of the chemical.

Static acute toxicity tests described by Peltier and Weber (1985) for effluent testing in EPA/600/4-85/013 can be performed in three ways, based primarily on the duration of the exposure to the effluent concentrations. The test of shortest duration is the range-finding test lasting for 8 to 24 hr. A wide range of dilutions of the effluent is used in order to rapidly assess the initial range of toxicity. A screening test may also be conducted in which the test organisms are exposed only to a 100% concentration of the effluent for 24 hr, or less if mortality is immediate. The final test in this group of acute toxicity tests is the definitive test, which is distinguished from the range-finding and screening tests primarily by the greater length of exposure to more concentrations of the effluent. A 96-hr exposure can be required, but most of the mortality generally occurs within 24 hr or sometimes 48 hr. In the tests with multiple concentrations a point estimate of toxicity in terms of a LC_{50} can be determined.

Modified from specific EPA protocols, a 24-hr static acute toxicity test for several different aquatic animals has been developed to provide initial ecological effects testing by highway departments for deicer chemicals. Several chemicals, some currently in use and others not commonly used or being considered for use, were tested in this manner to provide an initial evaluation of the proposed method. Some comparison for one of the chemicals was made with a longer term chronic test which could also be used by highway departments. The test methods are presented in the following section.

2.7.2.2 *Ecological Effects Tests for Initial Screening of Chemical Deicers*

Seven ecological effects tests were developed for consideration by highway departments as initial screening tests for the acute effects of chemical deicers on aquatic animals and terrestrial plants.

- Test 1. Acute toxicity test (static) including an initial range-finding test performed with the fathead minnow (juveniles), *Pimephales promelas*, routinely available from EPA Cincinnati.
- Test 2. Acute toxicity test (static) including an initial range-finding test performed with the common guppy (young adults), *Lebistes reticulatus*, routinely available from aquarium supply stores.
- Test 3. Acute toxicity test (static) including an initial range-finding test performed with the bluntnose minnow (juveniles), *Pimephales notatus*, collected from the field.
- Test 4. Acute toxicity test (static) including an initial range-finding test performed with a mixture of mayflies (nymphs) of the family Heptageniidae including the genera *Stenonema* and *Stenacron* collected from the field.
- Test 5. Acute toxicity test (static) including an initial range-finding test performed with amphipods (adults) of the genus *Gammarus* routinely available from biological supply houses such as Ward Natural Science Supply.
- Test 6. Chronic toxicity test (static) with renewal daily for 7 days performed with the fathead minnow (larvae), *Pimephales promelas*, routinely available from EPA Cincinnati.
- Test 7. Seed germination/radicle elongation test performed with seeds of oats, sunflowers, soybeans, vetch, and fescue routinely available from commercial seed suppliers.

EPA procedures presented by Peltier and Weber (1985) in EPA/600/4-85/013, form the basis for the methods.

2.7.2.2.1 Acute Aquatic Toxicity Tests (Tests 1 through 5).

The acute toxicity Tests 1 through 5 are conducted in an identical manner except for some slight modifications to accommodate the different types of organisms. The basic protocol is provided for Test 1 with the juvenile fathead minnows. Modifications for other organisms are presented later.

2.7.2.2.1.1 *Range-Finding Test*. For each chemical an initial range-finding test was performed, followed by a main test which included more test fish and exposure concentrations. Each test was 24 hr in exposure duration. The range test comprised four test concentrations and a nonaddition control, each with 10 fish in a separate 1-L pyrex beaker (Pyrex No. 1040) containing 750 mL of the test solution. The four test concentrations were prepared in the following manner. The weighed-out chemical (e.g., chemical deicer) in amounts calculated to create the desired concentrations in 750 mL of synthetic dilution water was placed in a larger beaker. Approximately half the dilution water was poured over the chemical and stirred by magnetic stirrer for 5 to 10 min. This solution was then poured into a gallon jug, and the remaining half of the dilution water was used to rinse the stirring beaker and then poured into the jug. The jug was then capped and vigorously shaken for a few minutes, and emptied into the 1-L test beaker. The four test concentration beakers and the control beaker were prepared and certain water quality parameters were measured before the test fish were added.

It can be useful to measure certain water quality parameters at the beginning of both the range-finding and main test before the fish are added and then again at the end of the test after the number of surviving fish have been counted. Though not required for the final mortality versus concentration estimates, certain parameters like pH, dissolved oxygen, and conductivity, can be measured by standard instruments readily available from scientific instrument catalogues. These measurements can provide insights into water quality changes caused by the chemical and possibly affecting the test organisms. Conductivity in the case of deicer chemicals provides some measure of test concentrations that can be related to field measurements. Conductivity measurements are included with the mortality vs. concentration data in the figures in Appendix C, Part 3.

The 10 fish added to each of the five beakers were added as quickly as possible but not at the expense of handling them roughly. All fish could generally be added within 15 min of each other. In transferring the fish, a different 1-L beaker (short, larger diameter type to provide more surface area) was filled with aquarium water. Thirty to forty fish could be gently netted with a typical small aquarium net and placed in the beaker with as little air exposure and rough handling as possible. As EPA (Peltier and Weber, 1985) recommends, it is best not to handle these fish with a net but instead concentrate them by siphoning the aquarium and then transferring some to a bowl or beaker with a large-bore, fire-polished glass tube (6 mm to 9 mm i.d. x 30 cm long equipped with a bulb), or dip them out with the bowl or beaker if concentrated enough. The netting and the EPA methods were used at various times successfully but the EPA method is recommend. Also used with success was a small Plexiglas cylinder (approximately 30 mm diameter, 25 mm long, with 80 to 110 µ mesh netting attached over one end) used to "scoop up" several fish to be transferred to a test beaker. Lifting the cylinder with fish drains the water back into the beaker and then fish can be passed to the test beaker without diluting the test solution. Care must be used with the tube transfer method to expel most excess water before releasing the fish into the test beaker to minimize water transfer. The drained cylinder held with forceps was placed gently into the test beaker. It was filled with test water, resuspending the counted fish, and then tipped under the surface to release the fish. A beaker received 10 fish. The loading limits (i.e., weight of organisms per volume of test solution) set by the EPA document (Peltier and Weber, 1985) at 0.8 g/L at 68°F (20°C) or less than 0.4 g/L above 68°F (20°C) to minimize depletion of dissolved oxygen were followed. The beakers were then placed under the same room conditions as the aquarium. This was in a dimly lit room or growth chamber at 68°F (20°C). The test beakers and aquarium can be provided with one tubular fluorescent bulb four or more feet away.

After 24 hr all surviving fish were counted while still in each beaker. A fish is considered alive if it is showing any movement, including gill movement. All survivors for a test could generally be counted within 15 min. All desired water quality parameters were again measured after the test was completed. The results of the range-finding test provided an indication of concentrations at which some mortality begins, then reaches 50% and then is 100%. For the main test it was desirable, with the use of more concentrations (6 plus control), to narrow in on a span of concentrations, with the lowest above the control with no or very slight mortality, the mid-range concentrations at or near 50% mortality, and the highest concentration with close to or 100% mortality. It must be emphasized that this two-part acute test was only an initial screening test, particularly in terms of the multiple tier testing approach that EPA requires for most other potentially toxic chemicals. It provided only the first indication of the potential ecological effects of the chemical.

2.7.2.2.1.2 _Main Test Following the Range-Finding test_. Most of the procedures described above were the same here except for the greater number of fish and concentrations. Six concentrations of the chemical were generally used in addition to the control, though as was also the case in the above test, fewer or more concentrations can be used depending on prior knowledge of the potential effects of the chemical. Four test beakers were used for each concentration, each receiving 10 fish. A quantity of chemical, which when later added to 3,000 mL dilution water creates the desired concentration, was placed in the mixing beaker. Approximately half of the dilution water was added, followed by stirring and transfer to a mixing jug. The chemical solution was then equally divided into four 1-L test beakers at approximately 750 mL each. Water quality parameters were measured. Fish were transferred to the beakers, now numbering 28 with six treatments and a control. A total of 280 fish were used, compared to the 50 used in the range-find test. Test beakers were incubated under the same conditions as described previously above and after 24 hr the test was concluded in the same manner.

With the greater number of concentrations and with replication (four), the LC_{50} can be identified with greater confidence and then used as the first measure of potential ecological effects. A detailed section on data analysis is provided in the EPA document (Peltier and Weber, 1985) on pages 50 to 90.

2.7.2.2.1.3 _Basic Testing Procedures Using Fathead Minnows (Test 1)_. Juvenile fathead minnows (approximately 30 days old and 15 to 25 mm long, about half the average adult length of 50 mm) arrived a few days after ordering from the Environmental Monitoring and Support Laboratory Newtown Facility in Cincinnati, Ohio. Five-hundred to 1,000 fish were received and placed in a 30-gal. aquarium at 68°F (20°C). The fathead minnow can also be bred and reared at the testing facility as described in the EPA document (Peltier and Weber, 1985). The aquarium contained gravel and a filter and aeration system typical of systems obtained from commercial aquarium supply stores. Prior to use, the aquarium and all other glassware was cleaned according to a standard EPA procedure. Water for the aquarium was the same as the test synthetic dilution water and was prepared according to the EPA document (pp. 22, 23) as the "moderately hard" dilution water (Peltier and Weber, 1985). Fish were maintained in the aquarium for a few days for any initial mortality to occur due to transport and handling. Generally most fish will arrive and remain healthy. Initial introduction of fish into the aquarium was gradual to equilibrate temperature (container suspended in aquarium) and water quality (periodic partial mixing of aquarium water into container water after temperature equilibration) differences between the shipping container and aquarium. With a healthy aquarium condition, fish to be used for tests can be maintained for a few weeks. Fish were fed when in the aquarium, but not during 24-hr tests. Food consisted of newly hatched brine shrimp (*Artemia*) nuplii which were prepared from eggs obtained from an aquarium supply store according to the label procedures or those described in the EPA document (Peltier and Weber, 1985, page 118). Since the brine shrimp were hatched in salt water they had to be thoroughly rinsed with dilution water or distilled water to prevent a salt buildup in the aquarium.

2.7.2.2.1.4 *Modifications of the Basic Testing Procedures for Other Organisms (Test 2 though 5)*. Tests 2 through 5 for different aquatic animals were identical to Test 1 for fathead minnows except for modifications made to accommodate the different types of organisms. These modifications now are described test-by-test. Tests 2 and 3 used two other species of fish. Once these fish arrived in the laboratory they were handled identical to the fathead minnow. The EPA loading limits were followed. (If for some reason these limits are not followed, then supplemental aeration for each test beaker must be provided but must not interfere with the biological action of the chemical being tested.) The bluntnose minnow obtained from the field was collected from a local stream. It was chosen as a local species that may actually be exposed to deicing chemicals.

- Test organism considerations--Certain procedures were followed in making collections of aquatic animals; these are similar whether for fish, insects, or other small animals. The types of organisms selected for testing should be representative of the area in its uncontaminated state, excluding organisms that have colonized contaminated sites and are thus likely to have some unusual tolerance, making them less representative of the organisms that may be threatened. Particular care was taken to minimize the shock of the transfer from the field to the laboratory. Gentle collection, whether by net, hand picking, or live trap is critical, as is maintaining the organisms in near ambient conditions of water quality (particularly temperature and oxygen) during the trip back to the laboratory. Insulated boxes (e.g., ice chests) with aeration (e.g., battery operated minnow bucket aerators) were generally suitable. Once in the laboratory, the organisms were gradually transferred to a suitable holding aquarium comparable to the one described for the fathead minnows, containing the type of dilution water eventually to be used in the test. These organisms were observed for a few days for initial mortality to optimize the establishment of healthy organisms for the test. The period of initial holding and observation was a compromise. A longer period might have introduced a slowly developing, though initially minimal, stress due to the new environment to which the organisms were being exposed. Stressed test organisms may respond differently to the chemical, thus producing unrealistic ecological effects predictions.

- Bluntnose minnows for Test 3--The minnows were seined (small enough mesh size for the fish being sought) from the stream and transported to the laboratory in an aerated ice chest containing stream water. An effective way of seining a small stream, with minimal contact of the fish with the net, was to span the seine across most or all of the stream leaving slack in the net so as to form a downstream bag. Starting upstream one or more people walked downstream in a zigzag pattern herding fish into the net which was then quickly lifted tipping the bottom upward and trapping the fish in the bag. The portion of the net containing the fish could remain in the water but was brought close to the surface for examination and selection of the desired fish. Fish were scooped out with a larger version of the cylinder with a net bottom described earlier. Once in the laboratory these minnows were gradually transferred to an aquarium the day of collection.

- Mayflies for Test 4--The mayflies were collected by hand from another stream. They were captured by lifting rocks at least 10 cm wide out of the water then quickly examining the underside for moving individuals generally 5 to 15 mm in length. They were picked up individually with a small paint brush (bristles 5 mm wide and 10 mm long) by gently sliding the bristles under them or sometimes just touching them causing them to cling. (If they are common on the stream substrate, hundreds can be collected by one person in a hour or so.) As each was collected it was placed in a 1-L plastic beaker filled with stream water and kept in the stream. Some pieces of 10 mm diameter 10 cm long nylon rope weighted with steel nuts (coated with silicone seal to retard rust and leaching of metals) were placed on the bottom of the beaker to provide substrate and prevent organisms from clumping together and harming themselves. After about 15 min the entire contents (including ropes) of the beaker were transferred to a 5-gal bucket (with a secure lid for the later trip to the laboratory) or ice chest filled with stream water and aerated. When the desired number of insects had been gathered they were returned to the laboratory. They were then gradually transferred to an aerated aquarium (modified to contain the rope substrates, with no gravel, and a water depth of 15 to 20 cm) or kept in the aerated bucket for 24 hr at the test temperature. The mayflies were transferred to test beakers by first transferring several to a Pyrex pie dish filled with aquarium water, or stream water if taken from the original bucket or cooler. If they were in the dish with stream water, an equal volume of dilution water was added to provide some initial adjustment to new water quality conditions before final transfer to the test beakers. The transfer to the dish was accomplished by removing ropes on which insects were clinging and shaking or gently brushing the mayfies into the dish. Individuals were then captured with a suction tube (greater than 5 mm I.D.) and placed in pairs in 20 mL plastic vials. In this manner 10 individuals were accumulated. Each vial was drained and then dipped (using forceps keeping hands out of the test solution) into the test beaker solution and flushed out. A few rocks (inert composition so as not to affect water quality or the test chemical) were already in place to serve as refuge. The remainder of the range-finding test and main test proceeded as described for the fathead minnows.

- Amphipods for Test 5--The amphipods were obtained commercially from EPA. (They can also be cultured in-house to supply tests.) The standard EPA tests for freshwater invertebrates most often use the crustacean zooplankter, *Daphnia magna*, which is not very representative of the stream insects potentially contacted by deicers. EPA tests for stream insects are not well developed and standard supplies of such organisms are not as available as they are for fathead minnows and amphipods. Amphipods were considered to be more representative of a variety of freshwater insects for deicer evaluations than is *Daphnia*. When the amphipods were received they were placed (gradual transfer as described for fish and insects) into an aquarium with 10 to 15 cm of synthetic dilution water over a layer of gravel and with aeration but no filtering (due to small size of the organisms, approximately 5 mm). They were fed brine shrimp or a fine settling fish food. To prepare test beakers, several amphipods were sucked up with a tube and bulb as described for fathead minnows and placed in a petri dish containing aquarium water. From here they were transferred one at a time to the test beaker (500 to 1,000 mL size) containing 250 mL of the test solution. Because amphipods are sometimes cannibalistic on weaker individuals, a few small rocks (quartz or some relatively inert composition) were added for refuge. The remainder of the range-finding and main test proceeded as described for fathead minnows.

2.7.2.2.2 Chronic Aquatic Toxicity Test (Test 6). A chronic toxicity test allows effects of the chemical to develop over a longer period of time, in this case for 7 days. A 7-day test is still considered an initial level of testing compared to the tiers of testing sometimes required for other chemicals. A static renewal procedure was used in this test. The test procedure is nearly identical to that of the EPA test described by Weber et al. (1989) in EPA/600/4-89/001 (pages 33 to 40), and is described briefly as follows.

Six concentrations of the chemical were selected along with a nonaddition control with 10 fish in each of two beakers for each condition. The approximate LC_{50} can be used as the highest concentration in this test. The concentrations were prepared and added to the beakers as described above with 250 mL in each of the two beakers. Water quality parameters were measured and then the fish were added. Fish for this test were shipped as "eyed eggs" (fully developed embryo but still in the egg) from EPA in Cincinnati, hatched in the mail, and they arrived as less than 48-hr larvae. The test required that the fish be less than 48-hr-old at the start. The fish were transferred to the test beakers on the day they arrived. The shipping container was acclimated to the room temperature, and approximately 30 fish were removed by a suction tube (5 mm I.D.) and placed into a petri dish containing the dilution water. Because of the volume of water transferred with the fish, a ≈75% solution of dilution water was created. Individual fish, only a few millimeters in length, were removed using a pipette with smooth edges (4 mm I.D.) and placed in the test beaker solution. The beakers were then maintained under the usual test conditions. The fish were fed three times each day at 4 hr intervals with newly hatched brine shrimp, which were less than 24-hr-old so that they were small enough to be eaten. By adding 0.1 mL of a concentrated suspension of the shrimp (rinsed to remove salt) about 700 to 1,000 individuals were provided. At each successive 24-hr interval excess food which had settled to the bottom was removed by suction (taking care not to also remove live fish). Dead fish were removed and counted. Water quality parameters were measured carefully to avoid disturbing fish, and test solution was removed by siphoning so that about 20% remained at a 5- to 10-mm depth. New solution was added up to the 250 mL volume mark by gently pouring it in down the side of the test beaker. This procedure of cleaning, parameter measurement including mortality, and test solution renewal was performed at the end of each of the first six 24-hr intervals. At the end of the seventh interval the test was concluded with the final parameter measurements and mortality observations. Fish still alive at the end were grouped for each beaker and their dry weight measured as described in the attached EPA procedures. Various types of standard data analyses are described in Weber et al. (1989).

2.7.2.2.3 Seed Germination/Radicle Elongation Test (Test 7). The testing of seed germination/seedling emergence was considered to be particularly relevant to the ecological effects testing of deicer chemicals. The time of year for maximum exposure to deicers coincides with or immediately precedes the period of seed germination and early growth in the late winter and early spring. In this test, a variety of seed plants, generally crop plants according to EPA, were selected. Plants were chosen to be representative of this region of the country and seeds were obtained from commercial distributors. Oats, sunflowers, and soybeans were selected as crop species. Also included were vetch and fescue, two common roadside plants with seeds available commercially. EPA guidelines for this test can be found in EPA 560/6-82/002.

The test container was a Pyrex tall petri dish with lid identified as a 100 x 80 No. 3250. Three containers were prepared for each of six concentrations and a control, each to eventually receive 10 seeds of one species. Two sheets of filter paper (inert and water absorbent) were placed in each container. Ten seeds were grouped toward the center on top of the two sheets, but separated. Deicer solutions were prepared as described for the other tests, and 4 mL was added to each chamber gently around the edges so as not to dislodge the seeds. A lid was then placed on the dish, a wet paper towel placed over the dish, and the dishes placed under the same room conditions as described for the other tests. No lights were provided, thus germination was in the dark at 68°F (20°C). The seeds were checked daily to be sure drying did not occur. If necessary, another 1 to 2 mL of solution was added. The number of seeds germinated and the radicle length were determined after five days.

2.7.2.3 *Chemical Reagents and Test Solutions*

All of the chemicals with the exception of rock salt were tested in the reagent grade form. The rock salt was obtained from the supply of the City of Lawrence, Kansas, and was originally from the Independent Salt Company of Kanopolis, Kansas. Most of the chemicals were prepared for testing as dry weight/liter of test solution. Six additional deicer chemicals formulations are identified in Table 2.7-1. The five liquid deicers were tested as a percent dilution ranging from 99% to 96% (i.e., 1 part deicer/99 parts diluting water to 4 parts deicer/96 parts dilution water).

2.7.2.4 *Aquatic and Terrestrial Toxicity Test Matrix*

Summary tables of aquatic and terrestrial toxicity test matrices with specific chemical deicers are presented in this section. Acute and chronic toxicity tests for all deicers and species tested are listed in Table 2.7-2. Terrestrial seed germination/radicle elongation tests for all deicers and species tested are listed in Table 2.7-3. Both tables include the deicer test concentration ranges studied.

2.7.2.5 *Finalization and Standardization of Test Methods*

The ecological effects test methods developed and modified during this research for use in the initial screening of chemical deicers for ecological hazard potential were finalized and written in standard ASTM format. These test methods were published in the *Handbook: Test Methods for Evaluating Chemical Deicers (1990)* as SHRP H-205.11, Test Methods for Preliminary Assessment of Ecological Effects of Deicing Chemicals.

Table 2.7-1. Deicer formulations and reagents

		Formulation	
Deicer/conc.	Additive(s) (wt % of solids)	Ingredient	Weight (g)
Sodium chloride[a]	Calcium phosphate[b]	NaCl	200.00
20 wt %	3.5 wt. %	$Ca(H_2PO_4)_2 \cdot H_2O$	7.82
		Deionized H_2O	800.00
Sodium chloride	Sodium fluorophosphate[c]	NaCl	200.00
20 wt %	3.5 wt %	Na_2FPO_3 (94%)	7.72
		Deionized H_2O	800.00
Sodium chloride	Zinc sulfate[d] 5 wt %	NaCl	100.00
10 wt %	Sodium tripolyphosphate[e]	$ZnSO_4 \cdot 7H_2O$	0.88
	5 wt %	$Na_5P_3O_{10}$	5.55
		Deionized H_2O	900.00
Sodium chloride	PCI[f]	NaCl	200.00
10 wt %		PCI	22.22
		Deionized water	1,800.00
Sodium formate[g]	NA	HCOONA	NA
Ethylene glycol[h]	NA	$HOCH_2CH_2OH$	NA

[a] Sodium chloride, NaCl, Fisher S-271.

[b] Calcium phosphate, monobasic, $Ca(H_2PO_4)_2 \cdot H_2O$, Baker 1426-01.

[c] Sodium fluorophosphate, Na_2FPO_3, 94%, Aesar 14129, Lot 20339.

[d] Zinc sulfate, $ZnSO_4 \cdot 7H_2O$, Fisher Z68-500.

[e] Sodium tripolyphosphate, $Na_5P_3O_{10}$, Fisher S-645.

[f] PCI (a calcium lignosulfonate), solid, Great Salt Lake.

[g] Sodium formate, COONA, Fisher S-648.

[h] Ethylene glycol, $HOCH_2CH_2OH$, 99+%, Aldrich 10, 246-6.

Table 2.7-2. Summary of aquatic acute and chronic tests

Chemical deicer	Test organism	Test (type)	Deicer concen. range (g/L)
Calcium chloride	Amphipods	Acute (range)	2.25 to 18.0
		Acute (main)	6.10 to 18.0
	Fathead minnow	Acute (range)	2.25 to 18.0
		Acute (main)	6.0 to 18.0
CMA	Amphipods	Acute (range)	2.25 to 18.0
		Acute (main)	3.0 to 12.0
	Mayflies	Acute (range)	2.25 to 18.0
		Acute (main)	6.0 to 18.0
	Fathead minnows	Acute (range)	2.25 to 18.0
		Acute (main)	9.0 to 18.0
Sodium chloride	Amphipods	Acute (range)	2.25 to 18.0
		Acute (main)	6.0 to 18.0
	Mayflies	Acute (range)	2.25 to 18.0
		Acute (main)	6.0 to 15.0
	Fathead minnows	Acute (range)	2.25 to 18.0
		Acute (main)	8.0 to 18.0
		Chronic	0.5 to 10.0
	Guppies	Acute (range)	2.25 to 18.0
		Acute (main)	16.0 to 22.0

Table 2.7-2 (Continued)

Chemical deicer	Test organism	Test (type)	Deicer concen. range (g/L)
Rock salt	Amphipods	Acute (range)	2.25 to 18.0
		Acute (main)	6.0 to 18.0
	Mayflies	Acute (range)	2.25 to 18.0
		Acute (main)	6.0 to 18.0
	Fathead minnows	Acute (range)	2.25 to 18.0
		Acute (main)	8.0 to 18.0
Sodium chloride with calcium phosphate	Fathead minnows	Acute (range)	90 to 99% dilution
		Acute (main)	95 to 97.5% dilution
Ethylene glycol	Fathead minnows	Acute (range)	80 to 99% dilution
		Acute (main)	96 to 99% dilution
Sodium formate	Fathead minnows	Acute (range)	2.25 to 18.0
		Acute (main)	6.0 to 18.0
Sodium chloride with sodium fluorophosphate	Fathead minnows	Acute (range)	90 to 99% dilution
		Acute (main)	95 to 97.5% dilution
Sodium chloride with zinc sulfate and sodium tripolyphosphate	Fathead minnows	Acute (range)	75 to 99% dilution
		Acute (main)	90 to 99% dilution
Sodium chloride with PCI	Fathead minnows	Acute (range)	75 to 99% dilution
		Acute (main)	84 to 92% dilution

Table 2.7-3. Summary of terrestrial seed germination and radicle elongation tests

Chemical deicers tested	Seed used in tests	Deicer concentration range tested (g/L)
Calcium chloride	Fescue	3.0 to 18.0
CMA	Oats	3.0 to 18.0
Sodium chloride	Soybeans	3.0 to 18.0
Rock salt	Sunflower	3.0 to 18.0
	Vetch	

2.7.3 Results and Discussion

2.7.3.1 *Test Results*

The ecological effects test results are presented in Appendix C, Part 3 in Figures C-3 through C-30.

2.7.3.2 *Discussion of Experimental Results*

The responses of the organisms tested for effects of particular deicer chemicals were generally consistent with what little data of this type exists in the literature. Most studies of the response of fathead minnows in acute tests to NaCl report 96 hr LC_{50} values of between 4 and 12 g/L. The response of fathead minnows in our 24-hr test was within this range. The responses of other organisms to NaCl showed the guppy to be the least sensitive, with an approximate LC_{50} of 20 g/L while the amphipods and mayflies were similarly sensitive. The fathead minnow response to the other chemicals produced LC_{50}'s in the range of 8 to 12 g/L. Amphipods and mayflies displayed similar sensitivities to the other chemicals compared to the minnow responses. The response of the bluntnose minnow was not included in the data set since only the range test was performed. It would likely have an LC_{50} of less than 18 g/L and higher than 9 g/L. The liquid deicer solutions tested as percent dilutions all produced significant mortality at a 96% to 91% dilution. The seeds also responded to the deicer concentrations but more in terms of radicle length than actual percent germination. Species varied in their sensitivity, though when 50% reductions occurred, they were within the range observed for the other organisms. The chronic aquatic test was not performed as often, so we will say only that as is typically reported in the literature, longer exposure did intensify the response lowering the LC_{50} range to 2 to 5 g/L. The younger fish which are generally used in this type of chronic test are also known to be more sensitive.

Typical data from the aquatic acute and chronic toxicity trial tests are presented in Figures 2.7-1 and 2.7-2, and Tables 2.7-4 through 2.7-6.

The results of the sodium chloride range-finding acute toxicity test using fathead minnows are given in Table 2.7-4.

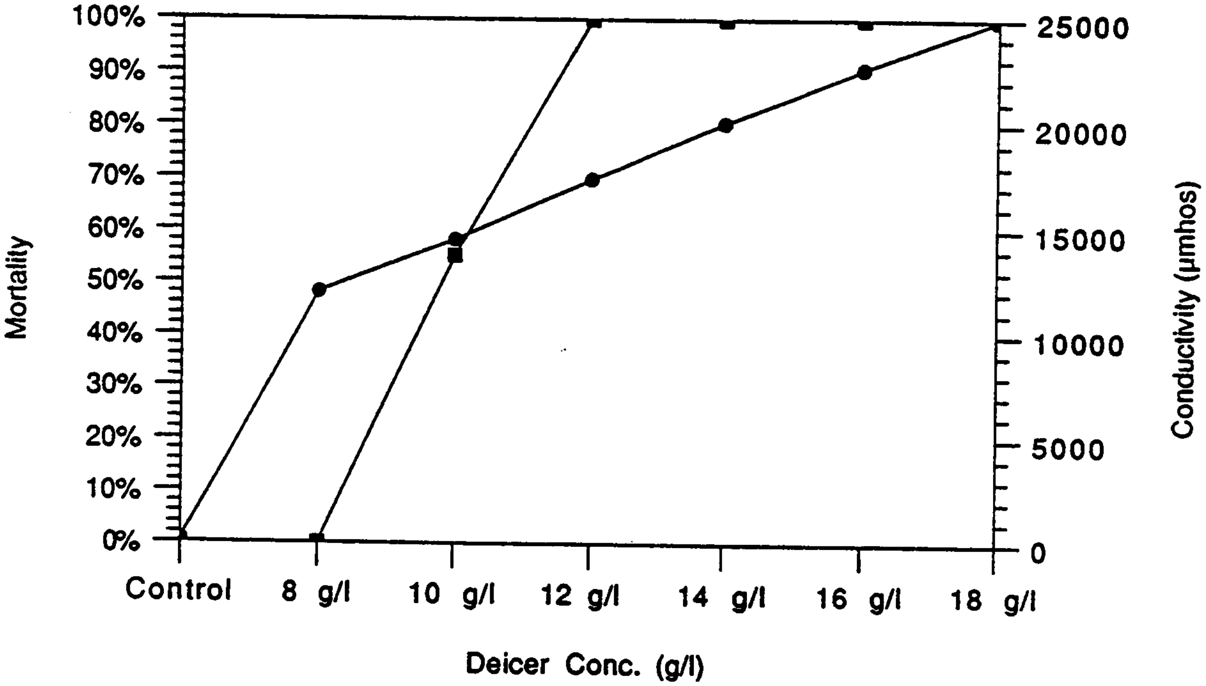
The results of the sodium chloride main acute toxicity test using fathead minnows are given in Table 2.7-5, and Figure 2.7-1 (also in Appendix C, Part 3 as Figure C-10). Percent mortality of the test organisms and conductivity of the test solutions are plotted vs. deicer concentration in the figure. The LC_{50} (concentration at which 50% of the test organisms die) can be seen to be near 10 g/L for sodium chloride.

The results of the chronic toxicity tests using sodium chloride and fathead minnows are given in Table 2.7-6 and Figure 2.7-2 (also in Appendix C, Part 3 as Figure C-12). The percent mortality after one week of exposure is plotted vs. deicer concentration. The LC_{50} for sodium chloride in this chronic toxicity study was ≈ 2.5 g/L, 75% lower than the LC_{50} for the acute exposure test.

Typical data from the terrestrial seed germination/radicle elongation trial tests are presented in Table 2.7-7 and Figures 2.7-3 and 2.7-4. Radicle elongation measurements for seeds of five species exposed to sodium chloride solutions are given in Figure 2.7-3 (also in Appendix C, Part 3 as Figure C-28). The average radicle elongation is plotted vs. deicer concentration. As seen in the figure at higher deicer concentration levels (9 g/L and above), over 50% retardation in radicle length was noted for all species.

Germination results for five species of seeds exposed to sodium chloride solution are given in Figure 2.7-4 (also in Appendix C, Part 3 as Figure C-27). The percent germination is plotted versus deicer concentration. Oats, soybeans, and sunflowers showed only about a 20% reduction in germination at the highest concentration of deicer compared to control values. Vetch plus fescue were much more susceptible to the concentration gradient.

Basically these acute tests modified from the EPA protocols produced results consistent with what little data exists in the literature for deicers using the exact protocols. The acute tests could provide the simplest initial screening, but ultimately more thorough testing and risk/benefit analysis following standard EPA test protocols and analysis procedures if encouraged.



Deicer Conc. (g/l)	Control	8 g/l	10 g/l	12 g/l	14 g/l	16 g/l	18 g/l
Conductivity	148	12025	14513	17388	20063	22625	24988
Mortality	0.0%	0.0%	55.0%	100.0%	100.0%	100.0%	100.0%

Figure 2.7-1. Results of NaCl acute toxicity main test (LC_{50}) for fathead minnows showing percent mortality (squares) and conductivity (circles).

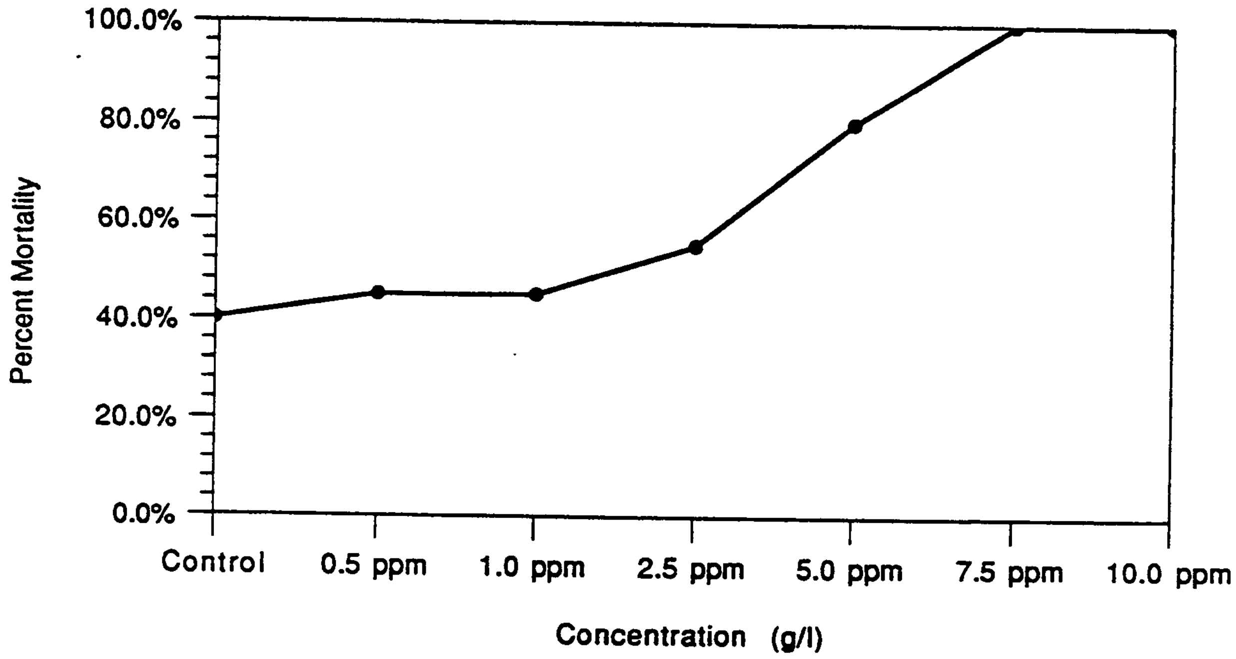


Figure 2.7-2. Results of NaCl chronic toxicity test using fathead minnows showing percent mortality after a 1-week period.

Table 2.7-4. Sodium chloride acute toxicity range-finding test results using fathead minnows

Deicer concentration (g/L)		Dissolved oxygen (mg/L)		pH		Conductivity (μmhos)		Mortality (dead/ total)
		Initial	Final	Initial	Final	Initial	Final	
Control	1	7.8	5.9	7.30	7.03	250	280	0/10
	2	6.9	5.5	7.25	6.93	248	270	0/10
2.25	1	6.5	6.5	7.55	7.31	3,620	3,890	0/10
	2	7.4	5.6	7.51	7.27	3,620	3,720	0/10
4.5	1	6.8	5.8	7.70	7.37	6,400	7,200	0/10
	2	6.9	5.7	7.57	7.35	6,400	7,200	0/10
9.0	1	6.5	5.0	7.73	7.27	13,000	13,500	0/10
	2	7.5	4.2	7.65	7.26	13,000	13,200	0/10
18.0	1	6.6	4.8	7.68	7.33	24,100	24,500	10/10
	2	6.9	4.0	7.66	7.24	24,000	25,000	10/10

Table 2.7-5. Sodium chloride acute toxicity main test results using fathead minnows

Deicer concentration (g/L)		Dissolved oxygen (mg/L)		pH		Conductivity (µmhos)		Mortality (dead/ total)
		Initial	Final	Initial	Final	Initial	Final	
Control	1	7.4	6.6	6.99	7.14	140	159	0/10
	2	7.4	6.0	7.11	7.13	140	151	0/10
	3	7.3	5.7	7.21	7.16	140	154	0/10
	4	7.7	6.2	7.21	7.18	139	158	0/10
8	1	7.9	5.5	7.47	7.17	11,700	12,300	0/10
	2	7.0	5.9	7.33	7.20	11,800	11,900	0/10
	3	6.8	5.2	7.43	7.12	11,700	12,100	0/10
	4	7.2	5.3	7.48	7.17	11,800	12,900	0/10
10	1	7.2	5.7	7.40	7.17	14,100	14,800	7/10
	2	7.4	5.6	7.44	7.13	14,100	15,000	5/10
	3	7.4	5.9	7.45	7.17	14,100	14,900	7/10
	4	6.7	5.1	7.51	7.09	14,100	15,000	3/10
12	1	6.8	3.9	7.35	7.07	16,500	18,000	10/10
	2	6.8	4.5	7.42	7.12	16,900	17,500	10/10
	3	7.2	2.9	7.55	6.99	16,900	18,000	10/10
	4	7.2	3.0	7.57	6.97	17,000	18,300	10/10
14	1	6.3	2.5	7.69	7.12	19,500	21,000	10/10
	2	6.5	2.7	7.84	7.15	19,500	20,900	10/10
	3	7.5	3.3	7.92	7.24	19,500	20,200	10/10
	4	7.1	3.2	7.94	7.27	19.700	20,200	10/10
16	1	6.7	5.0	7.88	7.42	22,000	23,400	10/10
	2	6.8	3.6	7.93	7.33	22,000	23,500	10/10
	3	6.5	3.3	7.91	7.31	22,000	23,200	10/10
	4	6.6	0.8	7.94	7.09	22,000	22,900	10/10
18	1	6.7	3.8	7.79	7.35	24,900	25,100	10/10
	2	6.5	1.1	7.81	7.11	24,800	24,900	10/10
	3	7.0	1.7	7.82	7.14	24,800	25,100	10/10
	4	6.7	2.6	7.80	7.19	24,800	25,500	10/10

Table 2.7-6. Results of NaCl chronic toxicity test using fathead minnows

Concentration (g/L)	Sample	Time	Dissolved oxygen (mg/L)	pH	Conductivity (μmhos)	Mortality (dead/total)
Control	1	Day 1	6.1	7.60	272	0/10
		Day 2	5.9	7.51	300	4/10
		Day 3	6.1	7.62	302	5/10
		Day 4	6.1	7.52	350	5/10
		Day 5	5.8	7.55	348	5/10
		Day 6	6.2	7.68	291	5/10
		Day 7	4.0	6.55	170	5/10
		Day 8	4.9	7.14	312	
	2	Day 1	6.0	7.74	252	0/10
		Day 2	6.0	7.59	292	1/10
		Day 3	6.0	7.70	282	2/10
		Day 4	5.8	7.54	290	2/10
		Day 5	5.3	7.44	288	2/10
		Day 6	5.9	7.70	288	2/10
		Day 7	4.1	6.70	122	3/10
		Day 8	3.8	7.17	300	
0.5	1	Day 1	6.5	7.80	1,070	0/10
		Day 2	5.9	7.71	1,180	2/10
		Day 3	6.1	7.82	1,180	2/10
		Day 4	6.3	7.76	1,220	2/10
		Day 5	6.2	7.76	1,180	2/10
		Day 6	5.8	7.72	1,210	3/10
		Day 7	5.2	6.96	1,020	3/10
		Day 8	4.2	7.34	1,210	
	2	Day 1	6.0	7.82	1,040	2/10
		Day 2	6.0	7.78	1,120	4/10
		Day 3	5.9	7.87	1,140	5/10
		Day 4	6.3	7.82	1,200	5/10
		Day 5	6.2	7.81	1,170	6/10
		Day 6	6.0	7.77	1,190	6/10
		Day 7	5.4	7.04	1,020	6/10
		Day 8	5.4	7.61	1,180	

Table 2.7-6 (continued)

Concentration (g/L)	Sample	Time	Dissolved oxygen (mg/L)	pH	Conductivity (µmhos)	Mortality (dead/total)
1.0	1	Day 1	6.5	7.81	1,810	0/10
		Day 2	5.7	7.76	1,900	1/10
		Day 3	6.0	7.95	1,870	4/10
		Day 4	6.1	7.79	1,900	4/10
		Day 5	6.0	7.80	1,890	4/10
		Day 6	6.1	7.85	1,890	4/10
		Day 7	5.5	7.23	1,850	4/10
		Day 8	5.8	7.72	1,910	
	2	Day 1	5.9	7.82	1,800	0/10
		Day 2	6.0	7.85	1,910	1/10
		Day 3	5.8	7.90	1,890	3/10
		Day 4	6.0	7.76	1,950	5/10
		Day 5	6.0	7.90	1,920	5/10
		Day 6	5.8	7.80	1,970	5/10
		Day 7	5.4	7.28	1,820	5/10
		Day 8	5.6	7.70	1,970	
2.5	1	Day 1	7.1	7.89	3,900	0/10
		Day 2	6.1	7.87	4,200	3/10
		Day 3	6.0	7.94	4,200	5/10
		Day 4	6.5	7.83	4,500	5/10
		Day 5	6.2	7.88	4,200	5/10
		Day 6	6.0	7.93	4,200	5/10
		Day 7	5.4	7.36	4,100	5/10
		Day 8	5.9	7.69	4,100	
	2	Day 1	6.0	7.92	3,900	0/10
		Day 2	5.9	7.85	4,100	3/10
		Day 3	6.2	7.95	4,200	5/10
		Day 4	6.1	7.79	4,200	6/10
		Day 5	5.9	7.78	4,200	6/10
		Day 6	5.9	7.87	4,300	6/10
		Day 7	5.5	7.37	4,100	6/10
		Day 8	5.7	7.69	4,200	

Table 2.7-6 (continued)

Concentration (g/L)	Sample	Time	Dissolved oxygen (mg/L)	pH	Conductivity (µmhos)	Mortality (dead/total)
5.0	1	Day 1	7.0	7.90	7,400	0/10
		Day 2	6.1	7.88	7,500	1/10
		Day 3	6.0	7.94	8,200	2/10
		Day 4	5.6	7.55	8.900	6/10
		Day 5	6.0	7.77	8,200	8/10
		Day 6	6.0	7.89	8.700	9/10
		Day 7	5.8	7.65	8,400	9/10
		Day 8	5.7	7.66	8,500	
	2	Day 1	6.3	7.91	7,400	0/10
		Day 2	6.0	7.77	7,900	1/10
		Day 3	6.1	7.95	8,200	2/10
		Day 4	5.8	7.61	8,800	5/10
		Day 5	5.8	7.77	8,300	6/10
		Day 6	5.9	7.89	8,700	7/10
		Day 7	6.1	7.63	8,300	7/10
		Day 8	5.6	7.69	8,300	
7.5	1	Day 1	6.3	7.88	10,900	6/10
		Day 2	6.2	7.84	11,800	7/10
		Day 3	6.9	7.96	11,800	8/10
		Day 4	6.2	7.84	12,200	10/10
		Day 5	6.2	7.90	12,700	
	2	Day 1	6.3	7.87	10,800	4/10
		Day 2	5.9	7.86	11,000	6/10
		Day 3	6.2	7.92	11,400	6/10
		Day 4	6.3	7.84	12,200	6/10
		Day 5	6.5	7.94	12,600	9/10
		Day 6	6.2	7.92	12,800	10/10
		Day 7	6.3	7.74	11,900	
10.0	1	Day 1	6.4	7.87	14,000	10/10
	2	Day 1	6.5	7.88	13,900	10/10

Table 2.7-7. Results of seed germination/radicle elongation test using NaCl and soybeans

Deicer concentration (g/L)		Germination (germ./total)	Radicle length (mm)	Average radicle length (mm)
Control	1	10/10	37,40,70,54,52,16,18,62,6,23	37.80
	2	10/10	49,75,32,61,38,21,31,13,35	40.60
	3	10/10	20,21,6,8,70,17,87,45,78,30	38.20
3	1	10/10	42,68,17,22,66,28,52,23,17,55	39.00
	2	9/10	15,7,31,15,52,63,56,10,47	32.89
	3	10/10	44,17,49,21,40,40,34,35,32,39	35.10
6	1	9/10	12,26,16,30,20,32,28,29,30	24.78
	2	9/10	41,44,29,34,36,33,24,37,11	32.11
	3	10/10	27,24,31,32,32,37,6,40,40,11	28.00
9	1	7/10	25,7,22,18,15,25,30	20.29
	2	8/10	27,9,9,7,28,7,17,12	14.50
	3	10/10	9,10,10,11,12,17,15,30,10,13	13.70
12	1	9/10	17,10,21,5,21,11,12,17,3	14.80
	2	10/10	20,3,11,5,21,19,6,13,16,20	13.40
	3	8/10	3,4,4,16,6,6,18,19	9.50
15	1	8/10	10,16,5,8,5,6,6,13	8.63
	2	7/10	6,4,11,18,10,11,11	10.14
	3	8/10	3,11,11,8,13,9,14,2	8.88
18	1	7/10	12,6,4,3,6,3,7	5.86
	2	5/10	5,5,9,10,10	7.80
	3	6/10	7,12,12,6,6,4	7.83

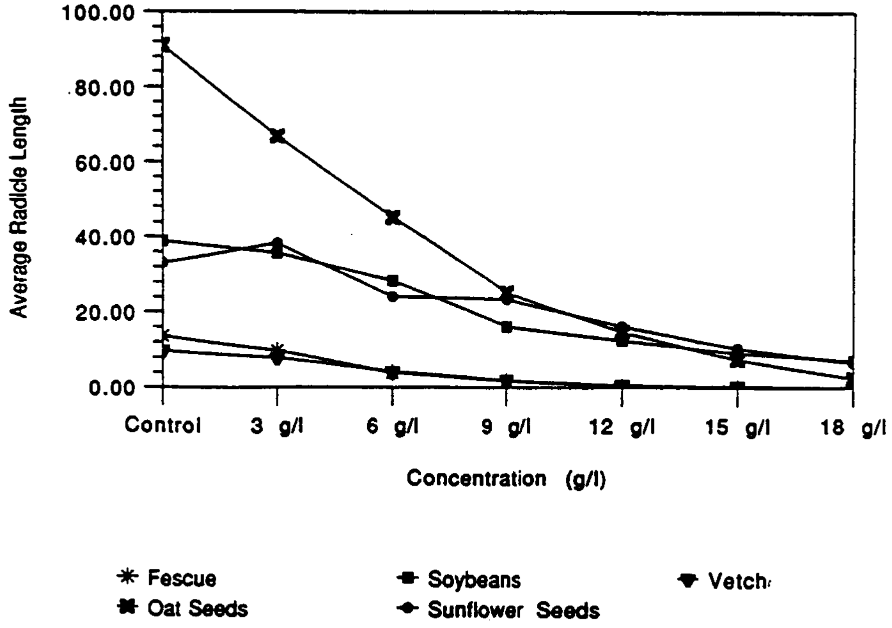


Figure 2.7-3. Results of NaCl/radicle elongation test showing average radicle length of germinating fescue, oat, soybean, sunflower, and vetch seeds.

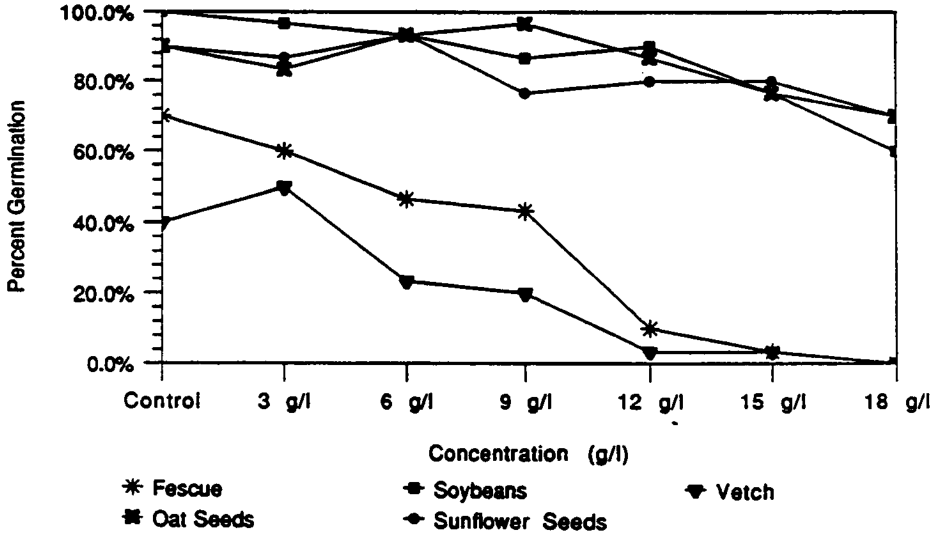


Figure 2.7-4. Results of NaCl/seed germination test showing percent germination of fescue, oat, soybean, sunflower, and vetch seeds.

2.7.4 Conclusions and Recommendations

2.7.4.1 *Conclusions*

Based on the results of the ecological effects studies the following conclusions are drawn.

- The common guppy was the organism showing least sensitivity to sodium chloride in acute aquatic toxicity tests conducted during this study.
- The sensitivities demonstrated by amphipods and mayflies to sodium chloride during this study were similar.
- The sensitivities to other deicing chemicals used during this study were similar for fathead minnows, amphipods, and mayflies.
- In terrestrial seed germination/radicle elongation tests, radicle elongation was found to be more sensitive to deicer test concentration gradients than germination.
- The test methods developed and modified during this study constitute a simple and direct means for obtaining useful information about the ecological effects of particular deicing chemicals.
- The experimental results of tests conducted during this study generally parallel estimates of aquatic toxicity reported in the literature for specified deicing chemicals.
- The test species selected for both aquatic and terrestrial ecological effects tests developed during this study are representative of those organisms likely to be exposed to deicing chemicals in the environment.
- The test species selected for use in ecological effects tests developed during this study are appropriate for these tests.

2.7.4.2 *Recommendations*

- The test methods developed and modified during this research are recommended for use as an initial screening protocol for the potential ecological hazard assessment of chemical deicers.

- The ecological effects test methods developed and modified during this study are recommended to be included in the risk/benefit analysis used to characterize chemical deicers prior to potential use.

- It is recommended that information obtained using these test methods be supplemented and augmented by use of other recognized and established EPA testing protocols when feasible or appropriate.

2.7.5 References

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3

Development and Evaluation of Improved Sodium Chloride

Sodium chloride, in a form and purity commonly known as rock salt or halite, has been the work horse chemical deicer for two principal reasons: (a) reasonably low cost compared to that of other chemicals; and (b) generally high theoretical ice-melting capacities over the usual range of ambient environmental temperatures.

Unfortunately, the efficacy of sodium chloride under field conditions does not parallel its theoretical capabilities at low temperatures. Thus at ambient temperatures lower than 20°F (-7°C), highway departments generally believe that the practical utility of sodium chloride for snow and ice control diminishes to an extent which signifies that other deicing chemicals must be employed, usually in combination with rock salt.

Sodium chloride also is viewed with disfavor for two other basic reasons: (a) its inherent corrosivity to metals, and other materials compatibility problems; and (b) certain adverse environmental effects which are primarily associated with or due to high usage rates.

Improvements in sodium chloride enhancing its use as a chemical deicer may develop along the following lines.

1. The perspective of enhancing its performance as a chemical deicer, emphasizing low temperatures, for example, down to about 0°F (-17.8°C).

2. Decreasing corrosion and generally improving compatibility with materials.

3. Reducing usage requirements, thereby reducing the potential for adverse impacts on materials and on the environment.

Approaches considered in this study, aimed at improving sodium chloride, fall into three categories.

1. Deicing performance improvement, emphasizing deicing properties at temperatures near 0°F (-17.8°C). The stated objective was the achievement of deicing characteristics at 0°F (-17.8°C) essentially equivalent to the deicing capabilities of sodium chloride at 20°F.

2. Reduction of the corrosivity of sodium chloride by incorporation of corrosion inhibitors.

3. Incorporation of surfactants, in order to achieve one or more of the following objectives: (a) enhancing the effect of corrosion inhibitors; (b) improving deicer performance properties; and (c) improving sodium chloride with respect to deleterious effects on materials, especially highway construction materials.

The results of efforts devoted to the first two research areas are presented in the following sections of the report.

3.1 Deicing Performance Improvement

3.1.1 Introduction and Background

3.1.1.1 *Introduction*

The objective of the research on the deicing performance improvement of sodium chloride was to explore and develop ways to enhance the deicing characteristics of sodium chloride at low temperatures (0°F). Information regarding enhancement of the deicing characteristics of sodium chloride would be useful to state highway departments in choosing more effective and economical ways to combat ice and snow on roadways. Following is a background discussion which includes theoretical considerations, basic approach guidelines, and relevant literature citations. The remainder of this section is organized as follows: Developmental Studies and Experimental Work (Section 3.1.2); Results and Discussion (Section 3.1.3); Conclusions and Recommendations (Section 3.1.4); and References (Section 3.1.5).

3.1.1.2 *Background*

3.1.1.2.1 Theoretical Considerations. The boundaries or limits to improvement of the ice melting capacity of sodium chloride are essentially fixed by the amply documented properties of sodium chloride-water systems at temperatures at and above the eutectic temperature. It will not be precisely true that 1 g of NaCl and 1 g of $CaCl_2$ separately will melt the same quantity of ice, at equilibrium, as that melted by 2 g of a 50-50 mixture of calcium chloride and sodium chloride. However, for all practical purposes it is reasonable to expect that the theoretical melting capacity of 1 g of sodium chloride in a mixed or modified deicer system will be essentially the same as the theoretical melting capacity of 1 g of pure sodium chloride, with the following exception: at temperatures below the sodium chloride eutectic temperature, sodium chloride in a mixture which exhibits an apparent eutectic temperature lower than the eutectic temperature of sodium chloride will melt ice in proportion to its concentration in the brine. In such a system, sodium chloride is accordingly capable of melting finite quantities of ice at temperatures below its eutectic temperature. Nevertheless, at temperatures above the eutectic temperature of sodium chloride--specifically at 0°F (-17.8°C)--the theoretical ice melting capacity of sodium chloride in any mixed or modified deicing system will essentially be that of the same quantity of sodium chloride in the pure state.

At 0°F (-17.8°C), 1 g of sodium of sodium chloride will melt 3.76 g of ice at equilibrium. At 5°F (-15°C), 1 g of sodium chloride will melt 4.35 g of ice at equilibrium. These quantities constitute theoretical limits for the ice melting capacity of sodium chloride in a modified sodium chloride system.

At 20°F (-6.67°C) the theoretical ice-melting capacity of sodium chloride is 8.984 g of ice melted per gram sodium chloride. The equilibrium ice melting capacity of sodium chloride at 20°F (-6.67°C) is thus about 2.5 times the equilibrium ice melting capacity of 0°F (-17.9°C). One cannot therefore expect to be able to modify sodium chloride so that its ice melting capacity at 0°F (-17.9°C) approaches that at 20°F (-6.67°C). A realistic objective consists of modification or improvement aimed at approaching more closely the theoretical or equilibrium ice melting limit. In this regard, sodium chloride becomes increasingly less effective relative to the equilibrium limits as the temperature is lowered. As shown in Table 3.1-1, the quantities of brine collected from sodium chloride-ice systems by decantation, in 1 hr correspond to yields of melted ice of 28% of equilibrium yields at 5°F (-15°C), and 11% of equilibrium yields at 0°F (-17.8°C). A realistic and potentially achievable goal for an improved sodium chloride would appear to be enhancement of the rate at which sodium chloride melts ice to the extent that 50% to 70% of the equilibrium quantity of ice is melted in 1 hr at 0°F (-17.8°C).

Table 3.1-1. Ice melting results at low temperatures, with solid sodium chloride, 60-min test period

Temperature	Theoretical	Found (% of theoretical)
5°F (-15°C)	4.315*	1.2* (28)
0°F (-17.8°C)	3.76*	0.43* (11)

* Grams ice melted per gram sodium chloride

More than one explanation can be offered for the slowness with which solid sodium chloride interacts with and melts ice at low temperatures. From a thermodynamic standpoint, interaction rates are low at low temperatures because thermodynamic driving forces are small, and diminish to zero at the sodium chloride-water eutectic temperatures. This effect is particularly important at 0°F (-17.8°C). Under abiatic conditions, a system consisting of 1 part sodium chloride and 10 parts ice will be cooled to the eutectic temperature of -6.03°F (-21.13°C) when 0.242 g ice has been melted. This quantity of melted ice is 6.5% of the equilibrium melting capacity of sodium chloride at 0°F (-17.9°C). Physical chemical processes which may proceed slowly range from initial particle wetting by brines generated at solid-solid interfaces, through dissolution of solid sodium chloride in surrounding brines, to melting which occurs at brine/ice interfaces. Of these, the rate of dissolution of solid sodium chloride in surrounding brines is likely to be the principal rate controlling process.

Melting at brine/ice interfaces should occur at rates approximately in proportion to the difference between deicer concentration at the brine/ice interface and the deicer concentration in adjacent brines, with rates being limited by diffusion from regions of higher to lower concentrations. This aspect of ice melting is subject to control or modification only to the extent that deicer dissolution rates can be increased.

Rate limiting factors which would appear to be subject to control or modification are as follows:

- <u>Temperature</u>

  The endothermicity of ice melting in principle may be partially counterbalanced by mixing sodium chloride with materials which dissolve exothermically in deicer brines.

- <u>Deicer dissolution rates</u>

  Elimination of the 15- to 20-min period required for sodium chloride particles to generate significant quantities of brine at low temperature should serve to increase yields of melted ice, particularly at times of 1 hr or less. Measures which serve to increase rates of dissolution of solid sodium chloride should similarly be beneficial.

Qualitative observations of ice melting and ice penetration by sodium chloride particles indicate the following: (a) at temperatures of 5°F (-15°C) and 0°F(-17.8°C) an induction period of several minutes is required to generate a quantity of brine sufficient to wet the particle; and (b) the larger particles (100 to 200 mg) are incompletely dissolved at the end of a 1-hr test period. The induction period also varies from particle to particle, presumably due to differences in shape and in the surface area in direct contact with ice. One concludes from these observations that small particles will melt ice more effectively at low temperatures than will large particles, and that some type of treatment designed to promote the rapid generation of a brine film around the particles should reduce the length of the induction period.

Potentially significant relative to an improved sodium chloride at low temperatures is the observation that potassium chloride admixed with sodium chloride contributes to ice melting at temperature below the potassium chloride eutectic temperature (12°F; -11.1°C). At 15°F (-9.44°C) potassium chloride by itself melts about 0.5 g ice per gram KCl in 1 hr. At 15°F (-9.44°C) the apparent melting capacity of potassium chloride in a 1:1 NaCl/KCl mixture is about 2.5 g ice melted per gram KCl, in 1 hr. These observations tentatively signify that sodium chloride admixed with a second material having a eutectic temperature lower than that of sodium chloride should melt ice at higher rates, at 0°F to 5°F (-17.8°C to -15°C), than it does by itself. The observations with NaCl/KCl mixed systems signify that thermodynamic constraints to ice melting at temperatures approaching a eutectic temperature are in effect released or reduced when a deicer is paired with a material having a lower eutectic temperature.

3.1.1.2.2 Basis of Approaches to Improved Sodium Chloride. The following guidelines constitute the basis for efforts to improve the deicing performance properties of sodium chloride at low temperatures.

1. The theoretical or equilibrium ice melting capacity of the sodium chloride content of a modified sodium chloride will be essentially that of sodium chloride alone, at temperatures down to the sodium chloride eutectic temperature.

2. The rate at which ice is melted by sodium chloride is, however, susceptible to improvement.

3. Approaches available for improving ice melting rates are based generally on thermodynamic and kinetic factors.

4. Specific approaches include the following:

   a. The use of small particles, and particularly the exclusion of the larger particles which comprise a substantial percentage of the weight of deicing sodium chloride (rock salt).

   b. Coating sodium chloride particle surfaces with liquid films or with ice-reactive solid materials, to reduce the time required for initiation of significant melting.

   c. Incorporation of materials which react exothermically with ice or water, with two objectives: (1) achievement of a reduction in the overall endothermicity of ice melting; and (2) utilization of the spontaneity of interactions between ice and exothermic materials in order to increase rates of interaction between sodium chloride and ice.

   d. Incorporation of materials with eutectic temperature significantly lower than the eutectic temperature of sodium chloride.

3.1.1.2.3 Relevant Literature Citations. Literature information in support of the above approaches is as follows:

- Larrimore (1979) found that penetration of ice by sodium chloride particles is enhanced by wetting particles with calcium chloride solutions, glycols, and water.

- In highway ice and snow control tests, at temperatures below 20°F (-6.7°C) with rock salt prewet with liquid calcium chloride, accelerated action and overall better results were obtained, and salt patterns and salt retention were improved (Lemon, 1974).

- Rock salt prewetted with liquid calcium chloride is effective down to 0°F (-17.8°C), and permits a 40% reduction in the normal rate of salt application at low temperatures (Huisman, 1974; Bozarth, 1973).

- In comparative tests of deicing with solid rock salt and salt brines, ice and snow control with solid rock salt required 3 to 5 times the salt required with salt brines. Substantial reduction in salt usage was observed with salt brine (Kasinskas, 1979, 1982).

- Rock salt prewetted with 42% calcium chloride enhanced ice melting capacities by 10% to 20%, with the greatest enhancement occurring at 5°F (-15°C) (McElroy, 1988b).

- Dickinson (1959) reports that a mixture of three parts salt and one part calcium chloride melts ice to greater depths in 2 hr than either chemical alone at temperatures down to -10°F (-23.3°C).

The literature thus indicates that significant improvements in the deicing characteristics of sodium chloride at low temperatures are possible via approaches which serve to accelerate the rates of interactions between ice and either solid sodium chloride or sodium chloride brines.

3.1.2 Developmental Studies and Experimental Work

The developmental studies and experimental work related to the deicer performance improvement of sodium chloride are discussed as follows: Experimental Approach and Procedures, Deicing Materials Evaluated, and Preparation of Test Samples.

3.1.2.1 *Experimental Approach and Procedures*

A simple and direct experimental approach and testing technique was selected for these studies for the following reasons:

1. Containment or localization of ice melting events and of deicing chemicals was considered to be a requirement, so that deicer-deicer effects over periods of 1 to 3 hr could be observed and measured. Thus an approach which permitted the measurement of ice melted by two deicers placed in close proximity was preferred to an approach in which several particles of each deicer were randomly spread on an ice surface.

2. The recommended standard ice melting test (SHRP H-205.1) was not considered appropriate under the anticipated test situations for the following reasons:

- Quantities of collectible brine from sodium chloride at 0°F (-17.8°C) are very small, and are less than generated quantities because surface films and brine tend to remain in ice cavities. An experimental technique which permits a more quantitative recovery of brines was needed.

- Due to the random distribution of deicers over an ice surface, the ice melting test does not permit the direct measurement of the effect of one deicer on the capacity and rate of another deicer. Collection and measurement of brines generated from contained and localized ice melting events are not possible with the recommended ice melting test.

For these reasons, preliminary tests were conducted using the following technique.

- Ice approximately 1 in. (2.5 cm) thick was frozen in a metal or plastic tray.

- Cavities in the ice were formed to a depth of about 1/4 in. (6 mm), by melting with a warm 1/2 in. (12 mm) diameter metal rod, followed by withdrawal of water with a syringe.

- Weighed quantities of deicing materials were placed in the cavities.

- After specified time intervals, brines were withdrawn via a syringe, and transferred to a tared vial. A small quantity of dye was added to each cavity to assist in observing the completeness of brine recovery.

- Brine weights were determined by weighing vials plus brine, at ambient conditions.

This basic procedure was modified to a five-cavity test, to permit the collection of larger quantities of brine. Five-cavity tests yielded brine weights ranging from 0.2 to 1.5 g. In the five-cavity test, quantities charged to and collected from each cavity were not determined, that is, only totals for the five cavities were determined.

3.1.2.2 *Deicing Materials Evaluated*

The following materials were tested, exclusively at 0°F (-17.8°C).

Individual deicers

- Sodium chloride (rock salt) particles
- Sodium chloride aqueous solutions (26.3% NaCl)
- Pellet calcium chloride
- Liquid ethylene glycol
- Solidified formamide

Two-component systems

- Sodium chloride particle/aqueous sodium chloride
- Calcium chloride solution or pellet/sodium chloride particle
- Ethylene glycol liquid/sodium chloride particle
- Ethylene glycol liquid coated on sodium chloride particles
- Solid formamide coated on sodium chloride particles

3.1.2.3 *Preparation of Test Samples*

The procedures employed to prepare test samples were as follows:

<u>Sodium Chloride (Rock Salt)</u>

Five particles approximately equal in size were placed in a vial, and total weight (150 to 220 mg) was determined. The vial was cooled to 0°F (-17.8°C), and one particle was placed in each cavity.

<u>Calcium Chloride Pellets</u>

Five pellets were placed in vials, and total weight (130 to 150 mg) determined. Precooled particles were placed in each of the five cavities.

Sodium Chloride Solution

Deionized water was saturated (26.3% NaCl) with reagent grade sodium chloride at 0°F (-17.8°C), supernatant liquid decanted, and a small quantity (0.25 mL) of liquid was transferred to a tared syringe. The syringe was cooled to 0°F (-17.8°C), the contents discharged in five approximately equal increments to test cavities, and the empty syringe reweighed.

In tests involving rock salt particles plus sodium chloride solution, five weighed particles were added to the solutions placed in test cavities.

Calcium Chloride Hexahydrate/Rock Salt

$CaCl_2 \bullet 6\ H_2O$ was prepared as liquid from reagent-grade calcium chloride dihydrate. A few drops of the liquid were added to five weighed rock salt particles in a vial, and the vial weighed. The vials were cooled immediately to crystallize the hexahydrate on and around the rock salt particles. The coated particles were cooled, placed in the cavities, and the vials reweighed to determine the quantity of hexahydrate transferred to the cavities.

Solid Formamide

A vial containing formamide was weighed and cooled to 0°F (-17.8°C). The solid formamide was fractured into small particles, five particles transferred to test cavities, and the vial reweighed to determine the weight of formamide placed in five cavities.

Rock Salt/Formamide

The procedure for this system was identical to that employed for calcium chloride hexahydrate (formamide fuses at 2°C).

Ethylene Glycol

Small volumes (0.25 mL) of ethylene glycol were transferred to syringes. The syringes were weighed, cooled to 0°F (-17.8°C), the liquid discharged in approximately equal increments to five cavities, and the empty syringes weighed to determine total weights of ethylene glycol placed in five cavities.

Rock Salt/Liquid Ethylene Glycol

Small quantities (0.25 mL) of ethylene glycol were transferred to tared syringes. The syringes were weighed, and then cooled to 0°F (-17.8°C); the contents were discharged in approximately equal increments to five cavities; and five weighed rock salt particles were added. The syringes were reweighed to determine quantities of ethylene glycol deposited in the cavities.

Rock Salt Wetted With Ethylene Glycol

A few drops of ethylene glycol were added to five rock salt particles of known weight, and the vial was weighed. Wetted particles were cooled, transferred with forceps to the test cavities, and the vial reweighed to determine the quantity of ethylene glycol transferred to the test system together with the sodium chloride particles.

Rock Salt/Calcium Chloride Brines

Five weighed calcium chloride pellets were transferred to test cavities. After 1 hr, five weighed rock salt particles were added to the cavities. Care was taken to ensure that rock salt particles were placed in cavities created by calcium chloride pellets. In a variation of this procedure, one pellet of calcium chloride and one sodium chloride particle were placed in each cavity at time zero.

3.1.3 Experimental Results and Discussion

3.1.3.1 *Baseline Studies*

Elucidations of possible enhancements of the ice melting characteristics of sodium chloride will be possible if two stipulations are met: (a) reliable data must be available for sodium chloride alone, and a baseline must be obtained with the conditions and procedures employed with mixed or modified systems; and (b) the contribution of added deicing materials to measured ice melting should be known. In this regard, one might report the ice melting of a composite deicing material, but the results will be more informative if melting due to sodium chloride can be distinguished from melting due to added deicing constituents.

To establish baseline data, ice melting tests with individual deicers were conducted at 0°F (-17.8°C) as follows:

- Sodium chloride particles at time intervals of 1, 2, and 3 hr.
- Aqueous sodium chloride (26.3% NaCl) at time intervals of 1 and 2 hr.
- Pellet calcium chloride at time intervals of 1 and 2 hr.
- Liquid ethylene glycol and solid formamide at 1 hr.

Baseline tests showed that calcium chloride, ethylene glycol, and formamide yielded essentially the theoretical or equilibrium quantities of melted ice in 1 hr at 0°F (-17.8°C). Concentrated aqueous sodium chloride yielded 70% to 80% of equilibrium quantities of melted ice in 1 hr, and essentially 100% of equilibrium quantities in 2 hr or less. These results justify the conclusion that in systems containing solid sodium chloride plus one of the other deicing materials, the quantity of recovered brine in excess of that calculated for the other deicing material may be attributed to the melting action of solid sodium chloride, for tests of 1 hr or longer.

Baseline tests with sodium chloride particles yielded the results described below. Results obtained in 1 hr with solid sodium chloride alone varied substantially, from about 15% to 35% of the theoretical or equilibrium quantity. The average of 20 tests was 23% of the equilibrium quantity. This value has been taken as representative of melting to be expected in 1 hr, but with the understanding that initial melting is variable. The initial variability is not unexpected, because sodium chloride particles vary in shape and in probable contact with ice. Other tests at low temperatures, particularly the penetration test, indicated a considerable variation in the time required for sodium chloride particles to becoming significantly wetted and surrounded by brine.

In 2 hr at 0°F (-17.8°C), six of eight tests yielded values in the range of 43% to 46% of the theoretical quantity, one value at 52%, and one at 49%. Two-hour results are thus less variable than 1-hr results. Accordingly, an average of 44% of the theoretical quantities expected has been designated as representative.

Five tests at 3 hr yielded an average of 64% of theoretical, with a range of 57% to 73%.

The results with solid sodium chloride particles indicate that essentially complete (theoretical) melting should occur in 4 to 5 hr.

The baseline studies with individual deicing materials provide the information needed to interpret ice melting results obtained with sodium chloride particles plus each of the second deicing materials for elapsed times of 1 to 3 hr. The procedure for quantifying the effects of the added materials is as follows.

- The weights of the added materials are employed to calculate the quantities of ice melted by the added materials.
- Melted ice attributed to the added material is subtracted from the total quantity of melted ice, thereby yielding the quantity melted by solid sodium chloride.
- The resulting data are compared to quantities of ice melted by unmodified solid sodium chloride to derive results which depict the effects of added materials on ice melting by sodium chloride.

Raw data collected in the melting tests consist of the weights of individual deicing materials and the weights of brine (melted ice plus dissolved deicer) after specified time intervals. The data have been converted to quantities of ice melted by the following procedure:

- The weight of brine attributed to each of the added deicing materials is calculated from equilibrium concentrations of deicer in water at 0°F (-17.8°C).
- The above weight is subtracted from the total brine weight, and the resulting brine weight attributed to solid sodium chloride.
- The weight of melted ice attributed to solid sodium chloride is calculated on the assumption that the concentration of sodium chloride in the brine (that attributed to solid sodium chloride) is slightly higher than the equilibrium concentration of 21%. From an assumed sodium chloride concentration of 22%, the calculated quantity of melted ice in 100 mg brine is accordingly 78 mg.

3.1.3.2 *Experimental Results With Sodium Chloride and Modified Sodium Chloride*

The averaged results obtained with solid sodium chloride, concentrated aqueous sodium chloride, solid sodium chloride plus aqueous sodium chloride, and solid sodium chloride plus tested forms of calcium chloride, ethylene glycol, and formamide are presented in Table 3.1-2. Results in the table consists of the mg of ice melted per mg of solid sodium chloride.

Table 3.1-2. Results of ice melting tests with sodium chloride and sodium chloride plus other materials at 0°F (-17.8°C)

Deicers	Wt. percent second deicer	1 Hr (mg ice melted per mg NaCl[a,b])	2 Hr (mg ice melted per mg NaCl[a,b])	3 Hr (mg ice melted per mg NaCl[a,b])
NaCl		0.86	1.63	2.38
<u>NaCl Plus</u>:				
26.3% NaCl in water	55-60	1.30	2.15	
$CaCl_2 \cdot 6H_2O$ (surface coat)	8-20	1.14	2.09	2.73
Ethylene glycol (surface coat)	3-8	1.27	2.22	2.89
Formamide, solid (surface coat)	6-18	1.72	2.61	3.22
Liquid ethylene glycol	55-60	2.03		
$CaCl_2$, pellet or concentrated solution[c]	40-45	2.03	2.73	

[a] In mixed systems, mg ice melted/mg NaCl = (total mg ice melted-calculated mg ice melted by second component) ÷ mg solid NaCl.

[b] Averages of all tests for each system.

[c] Percent $CaCl_2$ for concentrated solution of $CaCl_2$ based on weight of solid $CaCl_2$ pellets.

The equilibrium concentration of sodium chloride solutions in equilibrium with ice at 0°F (-17.8°C) is 21%. The equilibrium quantity of ice melted at this temperature by pure sodium chloride is accordingly 3.76 mg ice melted per mg NaCl. Results presented in Table 3.1-2 may be compared to an equilibrium ice melting capacity of the order of 3.65 to 3.70 mg/mg NaCl, for the sodium chloride employed in the test.

The effects of the various environments on the melting capacity of solid sodium chloride are shown on a relative basis in Table 3.1-3. The quantities of ice melted by 1 g of sodium chloride alone in 1, 2, and 3 hr are shown as 1.00, and quantities in the modified systems as a multiple of 1.00.

Table 3.1-4 shows the incremental quantities of ice melted per gram solid sodium chloride in 1-hr periods (i.e., from 0 to 1 hr, 1 to 2 hr, and 2 to 3 hr).

The data in Table 3.1-4 are based on the initial weight (approximately 40 mg/particle) of the solid sodium chloride particles. A more informative or meaningful set of data may be derived from calculations of the weight of solid sodium chloride remaining at the end of each 1-hr period, followed by calculation of the quantity of ice melted in 1-hr periods per gram of solid sodium chloride present at the beginning of the 1-hr period. The calculations are based on the assumption in all cases that the sodium chloride particles weighed 40 mg at test start. Results of these calculations are shown in Table 3.1-5.

The results and comparisons developed in the study were obtained with systems in which deicing materials were confined to specific melting sites. It can be expected that similar effects would result when sodium chloride is combined with another deicing material so that both are applied adjacent to one another on an ice specimen. The effects would be substantially diminished if sodium chloride and another material were randomly distributed on an ice surface such that deicer to deicer contact is limited. The widely used practice of wetting rock salt with liquid calcium chloride fulfills this requirement for melting rate or capacity enhancement.

The wetting approach would appear to be suitable with other liquid deicers. The most useful combination of sodium chloride with a second solid deicer material will consist of the two materials combined in desired proportions in discrete particles.

The combinations of materials tested in this study may be viewed as composite, modified sodium chloride deicers. The calculated 1-hr melting capacities of specific proportions of materials are shown in Table 3.1-6. Melting capacities are given as grams of ice melted per gram of composite deicing material.

Table 3.1-3. Relative quantities of ice melted per gram solid sodium chloride

Deicer	Hours 1	 2	 3
NaCl, solid	1.00	1.00	1.00
<u>NaCl plus</u>:			
26.3% NaCl (55%-60%)	1.51	1.32	
$CaCl_2 \cdot 6H_2O$ (8%-20%)	1.33	1.28	1.15
Ethylene glycol (3%-8%)	1.48	1.36	1.21
Formamide (6%-18%)	2.00	1.60	1.35
Ethylene glycol (55%-60%)	2.36		
$CaCl_2$ (40%-45%)	2.36	1.68	

Table 3.1-4. Incremental quantities of ice melted: grams ice melted/gram NaCl

Deicer	Hours 0-1	 1-2	 2-3
NaCl, solid	0.86	0.77	0.73
<u>NaCl plus</u>:			
26.3% NaCl (55%-60%)	1.30	0.85	
$CaCl_2 \cdot 6H_2O$ (8%-20%)	1.14	0.95	0.64
Ethylene glycol (3%-8%)	1.27	0.95	0.67
Formamide (6%-18%)	1.72	0.89	0.61
Ethylene glycol (55%-60%)	2.03		
$CaCl_2$ (40%-45%)	2.03	0.70	

Table 3.1-5. Incremental quantities of ice melted per gram solid sodium chloride present at the beginning of 1-hr periods

	0-1 Hr		1-2 Hr		2-3 Hr	
Deicer	Initial mg NaCl	Gram ice melted/ gram NaCl	Initial mg NaCl[a]	Gram ice melted/ gram NaCl	Initial mg NaCl	Gram ice melted/ gram NaCl
NaCl	40	0.86	30	1.02	22	1.39
<u>NaCl plus:</u>						
26.3% NaCl (55%-60%)	40	1.30	25	1.34		
$CaCl_2 \cdot 6\ H_2O$ (8%-20%)	40	1.14	27	1.40	17	1.54
Ethylene Glycol (3%-8%)	40	1.27	26	1.47	15	1.79
Formamide (6%-18%)	40	1.72	21	1.73	11	2.30
Ethylene glycol (55%-60%)	40	2.03				
$CaCl_2$ (40%-45%)	40	2.03	17	1.65		

[a] Initial mg NaCl at time zero taken as an average weight of 40 mg. Initial mg NaCl after 1 hr and 2 hr calculated from quantities of melted ice.

Table 3.1-6. **Ice melting capacities of composite deicers, 1 hr**

Deicer	
100% NaCl	0.85 g ice melted/g NaCl
50% solid NaCl: 50% NaCl solution (26.5% NaCl)	0.77 g ice melted/g total weight
50% solid NaCl: 50% NaCl solution (26.3% NaCl)	1.25 g ice melted/g NaCl
85% NaCl:15% $CaCl_2$•6 H_2O	1.20 g ice melted/g deicer
93% NaCl:7% ethylene glycol	1.31 g ice melted/g deicer
88% NaCl:12% formamide	1.73 g ice melted/g deicer
50% NaCl:50% $CaCl_2$	2.81 g ice melted/g deicer
50% NaCl:50% ethylene glycol	1.91 g ice melted/g deicer

3.1.3.3 *Discussion of Results*

Results of the studies indicate that the quantity of ice melted by solid sodium chloride may be increased by a variety of treatments which have one characteristic in common, namely, the more or less instantaneous provision of brine in which the particle is immersed. The magnitude of the enhancement is greatest when the relative quantity of the brine provided by the second constituent is greater. The results indicate that a maximum of about 55% of the equilibrium melting capacity of sodium chloride may be achieved, in 1 hr, by placing sodium chloride particles in an environment of surrounding brine which has a volume 8 to 10 times the initial volume of the particles. An initial brine of sodium chloride enhances melting by sodium chloride particles, but not to the extent which can be realized with a brine generated by deicing materials other than sodium chloride.

The degree of enhancement of melting by solid sodium chloride appears to be roughly proportional to the relative ratio of the second deicing material to solid sodium chloride. Surface coats of solids or liquids are thus less effective than considerably larger quantities of the same deicer materials.

The results obtained in the studies are considered to be too limited to justify attempts to rank the added deicing materials in terms of effectiveness. However, 1-, 2-, and 3-hr data indicate that surface coats of ethylene glycol and calcium chloride hexahydrate give similar results and are less effective than surface coats of solidified formamide. Melting enhancements resulting from immersion of sodium chloride particles in concentrated sodium chloride solutions are about the same, in 1 hr and 2 hr, as the enhancements realized from surface coats of ethylene glycol and calcium chloride hexahydrate.

Comparisons of 1-, 2-, and 3-hr results indicate that time has a leveling effect, that is, the differences between solid sodium chloride alone and sodium chloride admixed with other materials diminishes as time is increased. This trend is likely due in part to the fact that, in all the systems, the brines surrounding undissolved sodium chloride particles become increasingly enriched in dissolved sodium chloride with the passage of time; differences between brines accordingly become smaller as time lapses. However, the calculated results presented in Table 3.1-5 clearly show that yields of melted ice per unit weight of undissolved sodium chloride increase substantially as time elapses and the size or weight of the sodium chloride particle decreases. These calculated results strongly indicate that small size/high surface area sodium chloride particles should be preferred in a modified or improved sodium chloride. In this regard, an approach worthy of testing and evaluation consists of the chemical or physical aggregation of small particle sodium chloride admixed with other deicing materials, to form 30 to 60 mg particles or pellets. The added deicing materials would serve to initiate melting without delay, and thus provide an environment favoring the rapid dissolution of the small sodium chloride particles. Procedures which might be employed for the preparation or manufacture of such materials range from the use of pellet presses to the various methods employed to aggregate finely divided materials and to coat surfaces of particles. A relatively simple potential approach consists of the use of small quantities of water to aggregate small sodium chloride particles followed by wetting with concentrated aqueous solutions of calcium chloride or magnesium chloride.

Limited tests of such techniques were conducted in this study. Results indicated that small particle sodium chloride could be aggregated by tumbling the particles admixed with varying proportions of water, calcium chloride, and ethylene glycol.

3.1.4 Conclusions

The results obtained in the study substantiate the following conclusions with regard to ice melting capability of sodium chloride at low temperatures.

- The melting action of sodium chloride in both the solid form and the aqueous state, at a temperature close to the sodium chloride eutectic temperature, is less spontaneous or less rapid than the melting action of deicers which have much lower eutectic temperatures.
- Melting by concentrated aqueous sodium chloride is, however, considerably more spontaneous than melting by solid sodium chloride.
- With solid sodium chloride, the melting action is controlled by the rate of dissolution of sodium chloride particles.
- The initial dissolution of sodium chloride particles is quite variable and reflects both the low thermodynamic driving force for interaction with ice and water, and the particle-to-particle variability of the contact between the particle and ice.
- The induction period, that is, the time required for significant melting to begin, may be essentially eliminated by placing the particle in a sodium chloride brine or by adding other materials which interact spontaneously with ice.
- Melting due to solid sodium chloride particles in a 1-hr period may be increased significantly by providing more favorable environments for the initial and continuing dissolution of sodium chloride. The magnitude of the enhancement is generally proportional to the quantity of the added materials, and tentatively differs with the identity of the added materials. An aqueous sodium chloride environment is indicated to be less effective than the environments provided by calcium chloride, ethylene glycol, and formamide.
- For sodium chloride particles weighing approximately 40 mg, the maximum realized enhancement of 1 hr melting was 2.36 times the melting realized by unmodified sodium chloride in 1 hr. This result was achieved by pairing sodium chloride particles in a ratio of about 1:1 with ethylene glycol and calcium chloride. The maximum melting realized with a modified solid sodium chloride in 1 hr was about 55% of its equilibrium melting capacity of 0°F (-17.8°C).

- The spontaneity of melting by sodium chloride particles is indicated, as expected, to be favored by small size/higher surface area particles. It is accordingly likely that tests with particles approximately 10 mg in weight would yield more favorable results with both unmodified and modified forms of sodium chloride.

- Evaluation of results in terms of composite modified sodium chloride deicers indicates that, with the tested deicing materials, 1-hr ice melting will be the sum of the equilibrium melting capacity of the added deicing materials and 35% to 55% of the equilibrium melting capacity of sodium chloride at 0°F (-17.8°C). In 2 hr, 55% to 75% of the melting capacity of sodium chloride will be realized in a composite deicer.

- Finally, the results of this study define the probable limits of an improved sodium chloride for low-temperature applications, and provide guidelines upon which further research and development can be based.

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3.2 Compatibility Enhancement By Corrosion Inhibition

3.2.1 Introduction and Background

3.2.1.1 *Introduction*

This section presents the experimental work and supporting research studies undertaken to investigate and finalize a standard test method for assessing the potential enhancement of chemical deicer compatibility with bare metals by corrosion inhibition. Following the background discussion, which includes a review of corrosion test methodology, the remainder of this section is organized as follows: Developmental Studies and Experimental Work (Section 3.2.2); Results and Discussion (Section 3.2.3); Conclusions and Recommendations (Section 3.2.4); and References (Section 3.2.5).

3.2.1.2 *Background*

Chemical deicers, particularly sodium chloride, have been applied in combination with sand and other abrasives to highways since early in the 20th century . However, not until the 1950s did rock salt (sodium chloride) usage become extensive. Rock salt has for the past 30 years been a primary means of controlling snow and ice, in conjunction with snow plowing, and with the continuing use of abrasives.

Rock salt usage has been attended by more or less predictable and undesirable side effects. A major consequence of the use of salt has been increased vehicular corrosion and the corrosion of metallic materials used in the construction of highways and bridges. Consideration of its adverse side effects has prompted searches for alternative chemical deicers.

A substantial and potentially productive deicer advancement of the past several years involves calcium magnesium acetate (CMA). The major objective of the CMA work was the development of a noncorrosive and environmentally innocuous chemical deicer (Dunn and Schenk, 1979 and 1980). Also, commercial producers or suppliers of deicers are active in the development of corrosion inhibitors for inclusion in relatively minor quantities in chloride-based deicers (Neal, 1987; Wieman, 1987; Nadezhdin et al., 1988).

A driving force for seeking new deicer chemicals is the necessity of reducing corrosion damage caused by the chloride-containing chemicals. Therefore, corrosion caused by any new deicer is one of the most important properties to be determined before it is put into use. Corrosion testing can be conducted in a number of ways. There are several standard test procedures that have been accepted by various testing and professional organizations. However, no standard tests have been accepted by these organizations for corrosion evaluation of deicers.

The chloride-containing deicers, NaCl, and $CaCl_2$, damage structural metals in bridges and cause severe corrosion to automobile bodies. Although the effect of deicers on automobile bodies is more extensively reported in the literature, the consequences of bridge damage can be very great. The closing of the Williamsburg Bridge in New York City due to corrosion-caused damage on the steel structural support members is one striking example.

Corrosion of automobile body metals and bridge structural metals can be determined by similar means. The tests described below can be applied to evaluate metals used for both purposes. Evaluation of these tests as a means of determining the corrosivity of new deicers is also discussed.

3.2.1.2.1 Direct Exposure Corrosion Tests. Several aspects must be considered in developing tests used to evaluate metal corrosion tendencies in various environments. The way in which a metal is exposed to the environment can drastically affect the corrosion rate. Therefore it is important that actual "use" conditions be simulated. Exposure of metals in actual use conditions is very useful, but the conditions are difficult to control. Laboratory exposures are more easily controlled but are difficult to correlate with actual use conditions. In many cases, however, the laboratory tests can be used as a screening tool.

Evaluation of the extent of the corrosion is accomplished in several different ways. Quantitative evaluation tools are the most useful.

3.2.1.2.1.1 *Laboratory Exposure Tests*. The corrosion rate of a metal is dependent upon the environmental conditions, including the way in which the corrosive environment contacts the metal. A review of several different ways in which solutions containing deicing chemicals contact metals and an evaluation of several laboratory tests for potential new deicing chemicals is given below.

- Immersion tests. Complete and partial immersion of the test metal in a solution containing deicing chemicals has been used in several studies (Locke et al., 1987; Rowe and Chance, 1981). A standard test method for immersion tests is ASTM G31-72 (1988). This method has been used extensively for testing corrosion behavior of metals in solutions containing deicing chemicals. The test outlined in ASTM

G31-72 covers metal samples totally immersed, partially immersed, and in the vapor space above the solution. All three conditions were used in the Locke study.

Immersion tests do not accurately simulate the type of exposure that most metals undergo when in contact with deicing solutions. Thus the corrosion rates obtained in these tests cannot be used to predict performance life. However, these tests do provide comparative data. The tests are relatively inexpensive to conduct and can be used as screening methods to determine if further testing is justified.

- Dip test. Metals exposed to solutions of deicers are usually exposed intermittently. Often, wet and dry conditions which result from this intermittent exposure lead to higher corrosion rates than those found with static immersion tests. Several types of tests are described in the literature. These tests differ in the length of wet and dry cycles, temperature control in both phases, and humidity of the "dry" portion of the cycle.

One such dip test is the Cycle-Immersion Corrosion Test for Stainless Steel Molding Materials developed by General Motors to evaluate decorative trim for automobiles (Fisher Body Division, 1970). ASTM G60-86 (1988) describes a procedure of periodically immersing a metal in corrosive solution and then cycling the relative humidity of the vapor phase between 10% and 100% at 52°C. The guidelines for a dip test specified for stress corrosion cracking in ASTM G44-75 (1988) were used to conduct the study of the corrosion tendency of CMA solutions (Locke et al., 1987). A test for the effect of deicing salt on automobile exhaust materials also is described in the literature (Patterson, 1978).

Dip tests simulate some of the exposure conditions that automobiles and bridge structural materials undergo when deicers are used. The conditions for the dipping, the wet and dry time, and the environments--both wet and dry--are somewhat arbitrary. The apparatus necessary to accomplish the dipping of the samples can be mechanically complex and expensive. However, the conditions of dip tests are more severe, and would provide more realistic test conditions than do immersion tests.

- Spray tests: Several tests have been specified and conducted to evaluate the effect of sprays of deicer solutions on various metals. Several ASTM standard tests utilize a spray method of exposing metal to corrosive solutions. ASTM B117-73 (1988) was the first standard test developed. It has undergone several modifications.

Spray-type testing may come closer to simulating the conditions of actual exposure of metals to deicing chemicals. However, a continuous spray is not found under any of the field conditions affecting a automobile or bridge structural material. The metal is exposed to deicing chemical intermittently, so a modification of the spray test to include intermittent exposure would be justified.

- Poultice tests. All the tests described thus far involve exposure of the metals to liquid solutions. Since automobiles have crevices and pockets where dirt and other solid contaminants can collect, it is possible for corrosive solutions to be retained for long periods of time. Retention of the corrosive solution by porous solids can lead to development of concentration cells which will accelerate the corrosion reaction. One study has proposed a laboratory test involving artificial poultices (Baboian and Turoctte, 1985).

- Metal test specimens. Testing of new deicer chemicals should be conducted in a manner that simulates real-world exposure. In addition, the type, shape, mechanical condition, and coating of the metal being tested should also be carefully selected. Preparation of the metal surface before and after the test should be done carefully. The test specimens selected should be representative of the metals used in automobiles and bridge structures.

Tests developed by ASTM and the National Association of corrosion Engineers (NACE) specify such preparation techniques (ASTM G1-81, 1988; NACE, 1969).

Any series of tests developed for evaluation of new deicing chemicals should be conducted with several different metals in different forms. It is important to test for general corrosion, pitting, and stress corrosion cracking. A balance must be made, however, between testing every possible metal and the cost of such testing.

3.2.1.2.1.2 *Corrosion Evaluation Tests*. Exposure of metals to deicing chemicals can be accomplished in a number of different ways. A description of the different corrosion evaluation methods follows.

- Visual examination. Several investigators have used visual examination to determine the extent of corrosion. Visual examination was used to study the corrosion of an entire vehicle in Great Britain (Bishop, 1976). A study of deicing salt corrosion in Sweden used a visual comparison method to evaluate the effectiveness of various coating materials to protect the underlying metal (Westberg and Borjesson, 1981). Visual examination is not a precise method of determining the extent of corrosion; but, unless the corrosion product completely covers the metal, comparisons can be made. It can be a useful method if used in conjunction with other more quantitative methods.

- Electrical resistance. Electrical resistance probes have been used in vehicle tests but with limited success (Palmer, 1971). Based on the principle that the electrical resistance of an electronic conductor is inversely proportional to the cross-sectional area, a specially designed probe is exposed to the corrosive environment and the electrical resistance is measured throughout the test period.

- Weight loss. The most widely used and most feasible method of evaluating the extent of corrosion of metal coupons is to measure, by weight, the amount of metal corroded away. The coupon is weighed before the exposure period is begun and after the test is completed. As discussed earlier, preparation of the metal prior to exposure and after exposure must be done very carefully. The specifications for preparation appear in ASTM G1-81 (1988) and NACE (1969).

- Pitting: It is not unusual for deicers to cause pitting of metals. Pitting is a highly localized type of corrosion which can result in complete penetration of the metal with only minimal amounts of weight loss. Pitting corrosion can be evaluated by counting the number of pits in a unit area or by measuring the 10 deepest pits. The standards for both these techniques are specified by ASTM G46-76 (1988). If pitting is extensive, one of these techniques should be included in the evaluation of metal coupons exposed in the laboratory or field.

3.2.1.2.2 Electrochemical Corrosion Evaluation Tests. Corrosion is an electrochemical reaction. Therefore, electrochemical tests can be used to develop a better understanding of the mechanism of the reactions and to determine reaction rates. Several different electrochemical techniques have been used to study corrosion in a number of environments, including corrosion by deicing chemicals. Some of these techniques should be considered for use as screening tools to evaluate new deicers, but trained personnel equipped with specialized apparatus are required for some of the tests.

Two reviews of electrochemical tests appear in the literature. One review discusses electrochemical testing for any corrosion system (Siebert, 1985), and another discusses electrochemical testing for evaluating the effect of deicers on automobiles (Rowe and Chance, 1981).

3.2.1.2.2.1 *Potential Measurements*. The electrode potential of a metal compared to a standard reference electrode is indicative of the corrosion state of the metal under the conditions of the test. This test is conducted by immersing the metal and the reference electrode in a corrosive solution. The EMF difference between the metal and the electrode is measured with a high impedance voltmeter and is usually a few hundred millivolts in magnitude. The magnitude and polarity of the potential with respect to the reference electrode are significant and should be reported.

The value of the potential can be used to determine whether the metal is in the passive (noncorroding) state or if it is in an active (corroding) state. The relative values of potentials for different metals can be used to determine whether galvanic corrosion might occur if those metals were connected. As an example, copper typically has a potential of about -220 mv with respect to the saturated calomel in 3% saltwater, while steel has a potential of about -500 mv under the same conditions. Steel will therefore be -280 mv more negative than copper and will corrode rapidly when connected to copper. However, different grades of steel will have potentials that differ by only a few millivolts, and galvanic corrosion will not occur to any great extent when two types of steel are connected.

Corrosion potentials are easily measured and should be included in any electrochemical testing procedures.

3.2.1.2.2.2 *Polarization Tests*. The tests that help to determine the electrochemical state of a metal in the corrosive solutions involve determining the influence of impressed currents on the electrode potential of the metal. The potential of the metal will be shifted by the impressed currents, and this shift is called polarization. The polarization experiments can be conducted by controlling the applied current (galvanostatic) or controlling the electrode potential (potentiostatic or potentiodynamic).

3.2.1.2.2.3 *Polarization Resistance*. Another electrochemical test can be used to estimate the corrosion rate in a rapid manner. This test is based on the fact that the applied current density is a linear function of the potential within ±10 mv of the corrosion potential for many metal-corrosive solution systems. The slope of the linear plot of the potential versus current is called the polarization resistance, and is proportional to the corrosion rate. The procedure for conducting the polarization resistance tests is specified in ASTM G59-78 (1988). This technique was used in the study of CMA corrosion (Locke et al., 1987).

The advantage of the polarization resistance test is that it can be done quickly without changing the electrochemical state of the metal. In addition, commercial instruments are available that automatically measure the polarization resistance and provide a direct readout of corrosion rate. Not all corrosive systems display true linear behavior, and special testing techniques must be used for those systems.

3.2.1.2.2.4 *AC Impedance Measurements*. The surface of a corroding metal has the electrical characteristics of capacitors and resistors in series and in parallel. The properties of the electrical equivalent circuit can be determined by utilizing AC currents of varying frequency, instead of the DC currents as used in the tests described above. Tests that utilize alternating currents are known as AC or electrochemical impedance test.

The technical criteria for evaluating or comparing the compatibility characteristics of deicers and metals are simple in principle. Any alternative to rock salt should be significantly less corrosive to metals than sodium chloride, as determined by comparisons involving one or more of the several available corrosion test methods. Failure to meet this criterion should be sufficient cause for rejection. The preferred goal would be achievement of compatibilities close to natural (nondeicer-impacted) compatibilities.

3.2.2 Developmental Studies and Experimental Work

During this phase of SHRP H-205, the primary focus of the experimental work and background research activities pursuant to compatibility enhancement of chemical deicers with bare metals was the development and standardization of a laboratory test method for evaluating the corrosive effects of deicer solutions in contact with metal substrates. This method would be used to assess the potential of new deicer materials to cause corrosion, and to evaluate potential corrosion inhibitors for use with deicing chemicals. The developmental studies and experimental work related to compatibility enhancement by corrosion inhibition are detailed below.

The principal elements of the developmental studies and experimental work conducted on compatibility enhancement by corrosion inhibition were review of corrosion inhibition technology related to chemical deicers; development and evaluation of a test method to assess candidate deicers for corrosion potential and for use in evaluating the compatibility enhancement potential of selected deicer/corrosion inhibitor systems; and finalization of test method. These elements are discussed in detail in the following subsections.

3.2.2.1 *Review of Corrosion Inhibition Technology Related to Chemical Deicers*

The objective of this review was to identify and critically assess corrosion inhibitor technology relevant to sodium chloride deicer formulation. Background information was collected by structuring computerized literature searches of several data bases and manual searches of three bibliographic literature sources. These searches yielded nearly 500 citations. Abstracts of selected articles and copies of original documents were acquired, reviewed, and organized. The complete literature review, including introduction, search strategies, and an overview of corrosion inhibitor mechanisms, is presented in Appendix D, Part 1.

3.2.2.2 *Development and Evaluation of a Corrosion Test Method*

A test method was needed to assess candidate deicers for corrosion potential and to evaluate the compatibility enhancement potential of selected deicer/corrosion inhibitor systems. One method to reduce corrosivity is incorporation of corrosion inhibitors into sodium chloride deicer materials. Thus, the impetus of this laboratory work was to determine the corrosion rates of inhibited sodium chloride solutions.

3.2.2.2.1 Selection of Test Method and Candidate Inhibitors. Based on a review of laboratory methods to assess the corrosive effects of deicers on metals, a test procedure was identified and adopted. Candidate corrosion inhibitors were chosen from the literature review of corrosion inhibitor technology given in Appendix D, Part 1. The test procedure chosen was based on ASTM G1-81 for determining the corrosion rates by weight loss of metals immersed in aerated deicer solutions. The candidate inhibitors selected for the first set of laboratory tests for effectiveness of corrosion reduction on mild steel and aluminum substrates were:

- PCI (a calcium lignosulfonate)
- Sodium fluorophosphate (Na_2FPO_3)
- Sodium molybdate (Na_2MoO_4)
- Zinc sulfate ($ZnSO_4$) + sodium tripolyphosphate ($Na_5P_3O_{10}$)

The corrosion inhibitors selected for the second set of tests were:

- Calcium phosphate ($Ca(H_2PO_4)_2$)
- Sodium molybdate (Na_2MoO_4) + sodium tripolyphosphate ($Na_5P_3O_{10}$)
- Sodium fluorophosphate (Na_2FPO_3) + nitrilotris(methylene)phosphonic acid ($N[CH_2P(O)(OH)_2]_3$)
- Zinc chloride ($ZnCl_2$) + sodium tripolyphosphate ($Na_5P_3O_{10}$)
- Calcium and magnesium acetate (CMA)

3.2.2.2.2 Technical Approach. The technical approach consisted of determining (a) the corrosion rate of test metals via weight loss measurements, (b) the pH of the corrosion test solutions at selected exposure intervals, and (c) the effect of selected corrosion inhibitor levels on the corrosion rate of the test metals. Exposure times of 6 weeks were employed to attain reliable test data. Concurrently, single-electrode potentials of the immersed test specimens were determined to evaluate the relative effectiveness of the corrosion inhibitors on an electrochemical basis.

The scope of work for the corrosion rate screening is summarized by the following listing of test variable levels and constant test conditions. Two sets of tests were conducted.

Test methods:

- Corrosion rate via weight loss (ASTM G1-81)
- Electrochemical monitoring via single-electrode potential (ASTM C876-80)

Test conditions:

- Test solutions: 3.0 wt % NaCl + inhibitor
- Test specimens: Mild steel and aluminum
- Exposure mode: Completely immersed with aeration
- Test temperature: ~ 77°F (25°C)

Test measurements:

- Test specimen weight loss: Gravimetric (6 weeks total, one test specimen from each test cell, each week for the first 4 weeks and two test specimens from each test cell after the 6th week)

- Specimen/solution potential: Saturated calomel electrode (after 7, 14, 28, and 42 days)
- Test solution pH: Electronic meter (0, 7, 14, 28, and 42 days)

First Set of Tests

Number of inhibitors: 4

Inhibitor concentration: 3 levels for each inhibitor

Replication: 2

Controls: 16 tests (no inhibitor)

- 2 steel (1018 cold rolled) in 3% NaCl, 2 aluminum (7075) in 3% NaCl
- 2 steel (1018 cold rolled) in deionized water, 2 aluminum (7075) in deionized water
- 2 steel (1018 cold rolled) in 3% rock salt,[1] 2 aluminum (7075) in 3% rock salt
- 2 steel (1018 cold rolled) in 3% CMA,[2] 2 aluminum (7075) in 3% CMA

Test Matrix Variables

- Number of inhibitors: 4
- Inhibitor concentration levels: 3
- Number of metals: 2
- Replication: 2
- Number of control cells: 16

Total number of test cells:

- 4 x 3 x 2 x 2 = 48 + 16 = 64

Test specimens per test cell: 7

Total number of test specimens:

- 7 x 64 = 448

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[1] Morton Safe-T-Salt, 96.9% soluble by gravimetric analysis.

[2] Chevron ICE-B-GONE Deicer, 91%, calcium to magnesium acetate molar ratio = 3:7.

Second Set of Tests

Number of inhibitors: 5

Inhibitor concentration:
3 levels for each inhibitor except CMA
1 level for CMA

Replication: 2

Controls: 8 tests (no inhibitor)

- 2 steel (1018 cold rolled) in 3% NaCl, 2 aluminum (7075) in 3% NaCl
- 2 steel (1018 cold rolled) in deionized water, 2 aluminum (7075) in deionized water

Test Matrix Variables:

- Number of inhibitors: 4; 1
- Inhibitor concentration levels: 3; 1
- Number of metals: 2
- Replication: 2
- Number of control cells: 8

Total number of test cells:

- (4 x 3 x 2 x 2) + (1 x 1 x 2 x 2) = 52 + 8 = 60

Test specimens per cell: 5

Total number of test specimens: 5 x 60 = 300

3.2.2.2.3 General Experimental Protocol. The general experimental protocol for conducting the corrosion rate screening tests via weight loss and electrochemical potential monitoring is summarized as follows. Test specimens were purchased preweighed. The test specimens were completely immersed in the test solution, suspended from a nylon string, and positioned so that no test specimen could come in contact with another. The test solutions were contained in plastic containers and aerated during the exposure period.

All test solutions were prepared using deionized water. During the course of the testing, evaporation losses were made up by the addition of deionized water to maintain constant test solution levels.

After each specified week of complete immersion and aeration, test specimens were removed from each test solution and cleaned according to ASTM G1-81 to remove the corrosion products from each test specimen. This cleaning procedure involved rinsing with water and brushing with a nonmetallic brush to remove large, loosely bound flakes of corrosion. Then the steel test specimens were dipped into vigorously stirred, passivated acid (Clarke's solution = 20 g antimony trioxide + 50 g stannous chloride + 1,000 mL concentrated hydrochloric acid) at 77°F (25°C) for 10 sec. The aluminum test specimens were immersed in a solution of 50 mL phosphoric acid + 20 g chromium trioxide per liter of water at 194° to 212°F (90° to 100°C) for 2 min. Test specimens were then rinsed with water, rinsed with acetone, dried, and weighed to 0.1 mg. The corrosion rate of each test specimen was calculated using the equations specified in ASTM G1-81. One unexposed steel and one unexposed aluminum test specimen were cleaned with each set of corroded test specimens in order to assess the loss of free metal during the cleaning process.

After 7, 21, and 42 days of total immersion, the electrical potential of each "electrode" test specimen in the test electrolyte was determined. The potential measurements were made on the electrode test specimen by using a saturated calomel electrode (SCE) cell reference. The electrode test specimen was a steel or aluminum test specimen with an attached lead wire. The point of attachment was coated for electrical insulation. An electrode test specimen remained in each test cell for the duration of the corrosion test. The pH of the test electrolytes was also determined according to the same time schedule.

3.2.2.2.4 Detailed Experimental Procedures. The detailed procedures employed in conducting the experimental work are presented in Appendix D, Part 2.

3.2.2.3 *Finalization of Corrosion Test Method*

Based on experimental evaluation, a laboratory test method for assessment of the corrosivity of candidate deicers and inhibited deicers on metals was finalized and written in a format commonly used in ASTM standard methods. This method appears in the *Handbook: Test Method for Evaluating Chemical Deicers* as SHRP H-205.7, Test Method for Evaluation of Corrosive Effects of Deicing Chemicals on Metals. The test is designed for determination of the comparative corrosiveness of deicing chemicals, relative in particular to sodium chloride, under controlled and reproducible conditions.

3.2.3 Results and Discussion

3.2.3.1 *Experimental Results*

Graphic representations of the corrosion inhibition effectiveness of each inhibitor system tested are presented in Figures 3.2-1, 3.2-2, and 3.2-3. Each inhibitor's corrosion rate was compared to the corrosion rate of uninhibited 3 wt % sodium chloride solutions run concurrently. Bar graphs extending below the 0% inhibition line indicate that the corrosion rate of the inhibited solution was higher than for the appropriate uninhibited 3% NaCl control solution. Corrosion inhibition results for tests using high concentrations levels of inhibitors are given in Figures 3.2-1. Results for tests using medium and low inhibitor concentration levels are given in Figures 3.2-2 and 3.2-3, respectively.

These graphs clearly show that zinc sulfate and zinc chloride systems and calcium dihydrogen phosphate are effective corrosion inhibitors for both steel and aluminum exposed to aerated 3 Wt % NaCl solution.

3.2.3.2 *Discussion of Experimental Results*

3.2.3.2.1 Steel Exposed to Corrosion Test Solutions. The corrosion data for mild steel show a wide range of corrosion rate results. Discussion of the corrosion test results by test solution type follows.

First Set of Tests

- PCI (calcium lignosulfonate)

  The corrosion rates of mild steel in 3 wt % NaCl containing PCI corrosion inhibitor at 4 to 10 wt % of solids were 6 to 8 mpy. This range corresponds to about 50% to 65% reduction in corrosion versus the 3 wt % NaCl control. The pH of the solutions remained near 7 throughout the 6-week test. The electrode potential of the steel in the test solutions remained in a range of -0.68 to -0.69 V versus a saturated calomel electrode throughout the 6-week test.

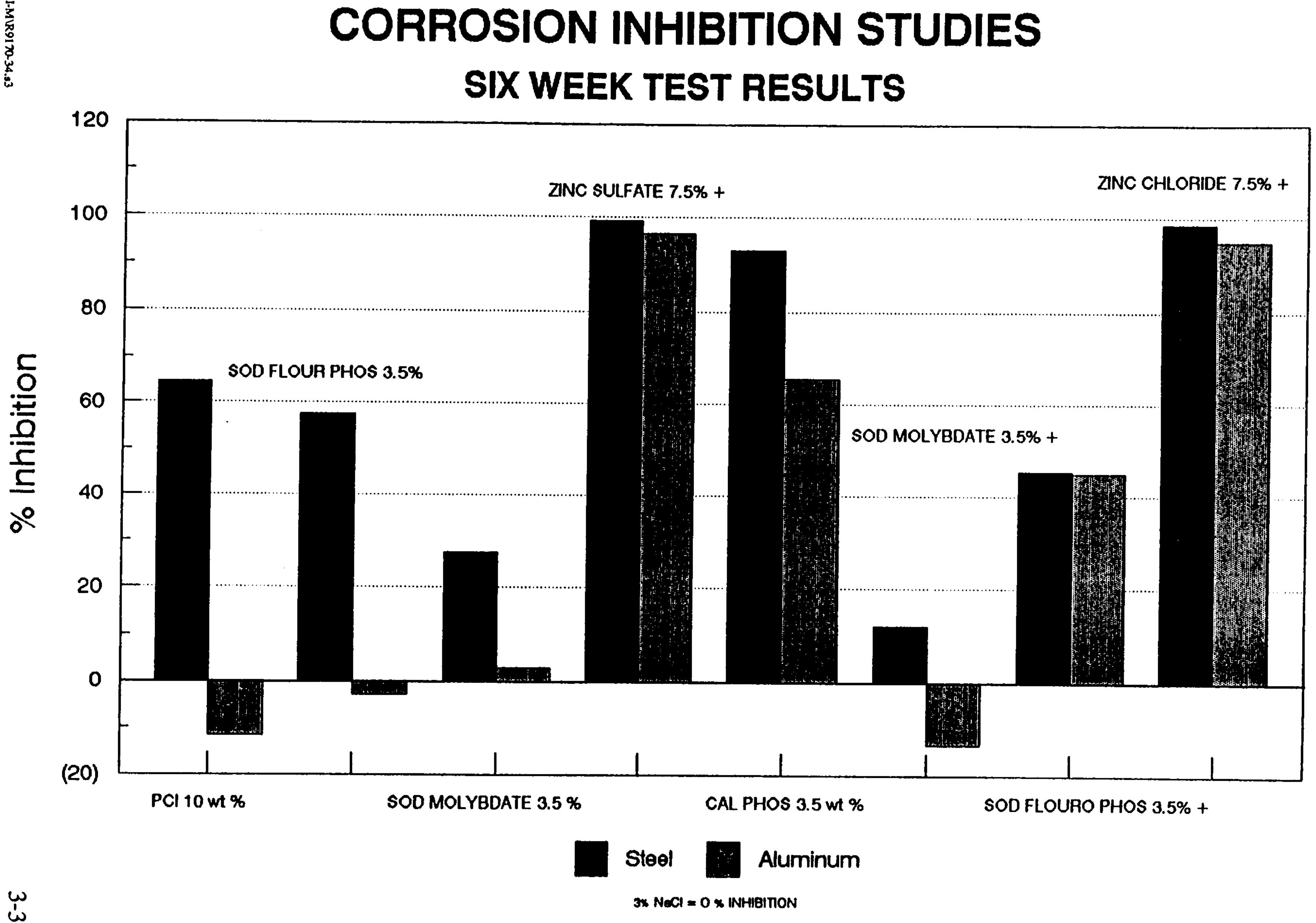

Figure 3.2-1. Corrosion inhibition test results with high concentration levels of selected inhibitors.

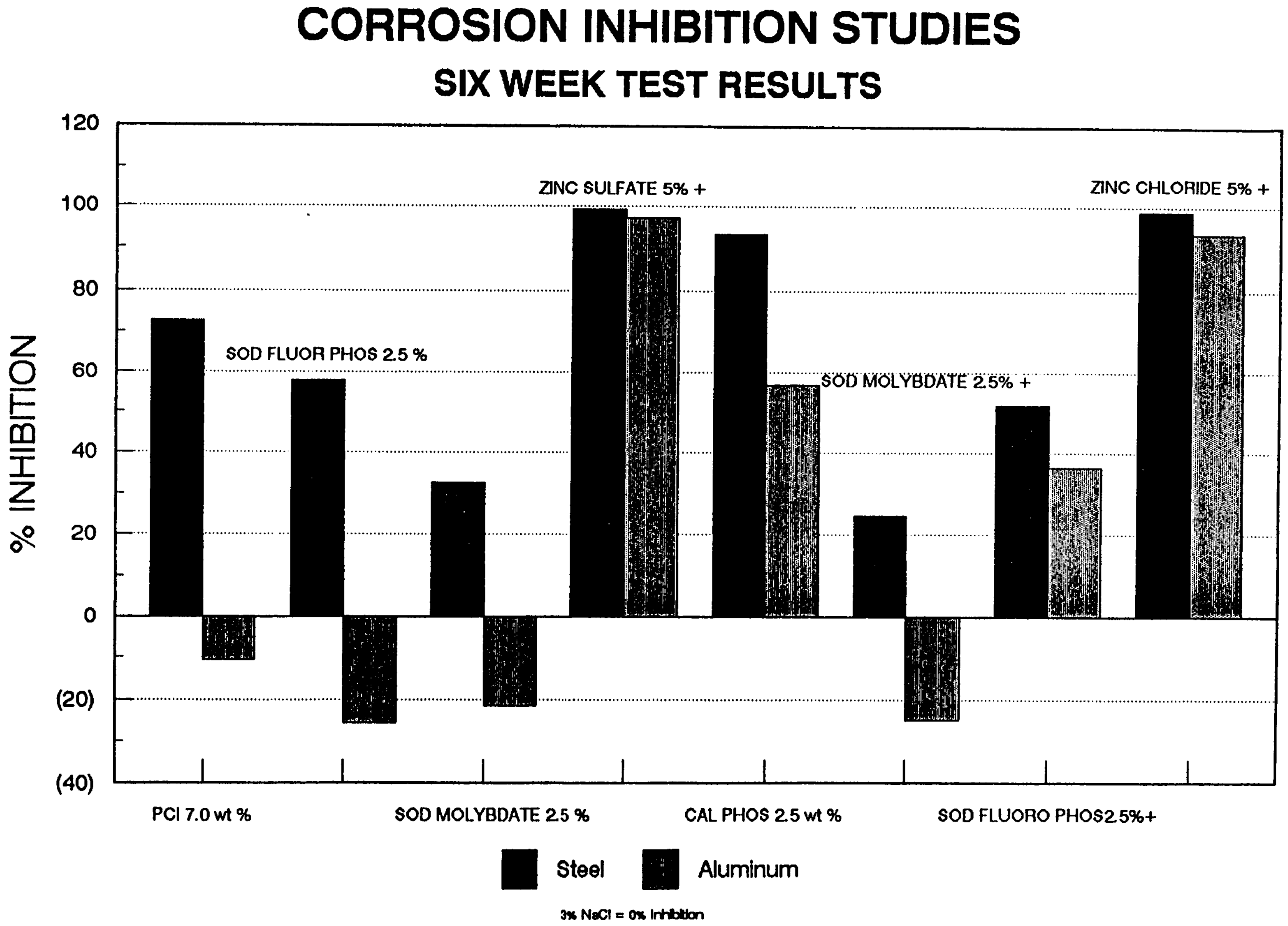

Figure 3.2-2. Corrosion inhibition test results with medium concentration levels of selected inhibitors.

CORROSION INHIBITION STUDIES

SIX WEEK TEST RESULTS

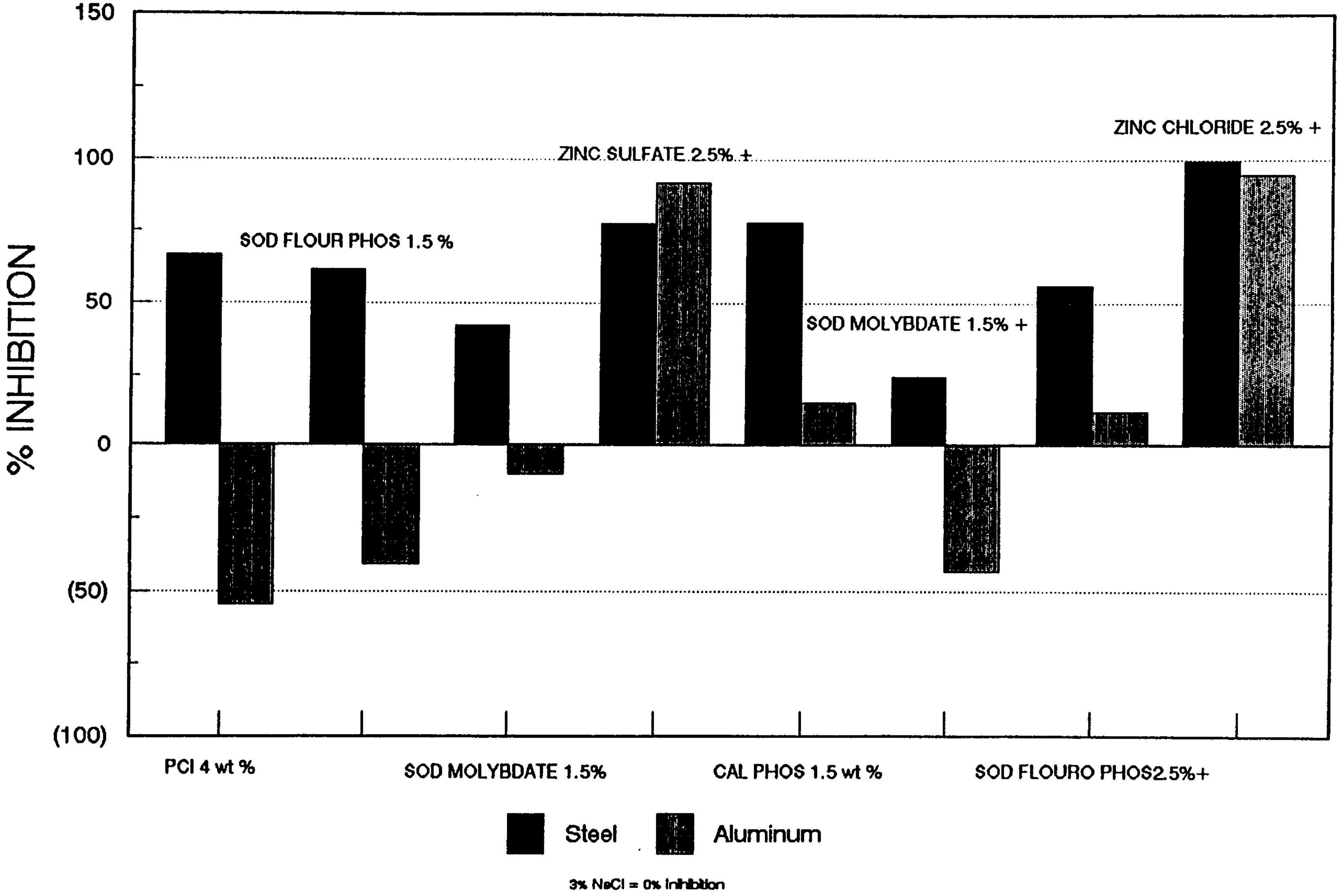

Figure 3.2-3. Corrosion inhibition test results with low concentration levels of selected inhibitors.

- Sodium fluorophosphate (Na_2FPO_3)

  The corrosion rates of mild steel in 3% NaCl containing 1.5 to 3.5 Na_2FPO_3 were similar to PCI, around 6 to 8 mpy. This rate corresponds to about 50% to 60% reduction in corrosion versus the 3% NaCl control solutions. The pH of the solutions remained near 8 through the 6-week test. The electrode potential of the steel in the test solutions remained in a range of -0.69 to -0.73 V versus an SCE electrode.

- Sodium molybdate (Na_2MoO_4)

  The corrosion rates of mild steel in 3% NaCl containing 1.5% to 3.5% Na_2MoO_4 were 10 to 11 mpy. These rates correspond to 34% to 43% reduction in corrosion versus the 3% NaCl control solutions. The pH of the solutions remained 8 to 9 through the 6-week test. The electrode potential of the steel in the test solutions ranged from -0.63 to -0.69 V.

- Zinc sulfate ($ZnSO_4$) and sodium tripolyphosphate ($Na_5P_3O_{10}$)

  Differing effects were seen in the corrosion tests with zinc sulfate and sodium tripolyphosphate. The corrosion rates of mild steel in 3% NaCl containing 7.5% and 5% each of zinc sulfate and sodium tripolyphosphate were 0.2 and 0.1 mpy, respectively. This range corresponds to 99% reduction in corrosion versus the 3% NaCl control solutions. The corrosion rate of mild steel in 3% NaCl containing only 2.5% each of zinc sulfate and sodium tripolyphosphate was 3.8 mpy. This rate corresponds to 77% reduction in corrosion versus the 3% NaCl control solutions.

  The pH of the 7.5% and 5% solutions remained near 6 and the electrode potentials remained in a range of -0.61 to -0.66 V throughout the 6-week corrosion test. The pH of the 2.5% solutions was lower, near 5. The electrode potential for the 2.5% solutions was higher, ranging from -0.70 to -0.71 V throughout the 6-week test.

- Control solutions

  Corrosion tests of mild steel were run in four duplicate control solutions. Most important was the 3 wt % reagent NaCl, to which the corrosion rates of the inhibited solutions were compared. The mean corrosion rate of the 3% NaCl control was 16.2 mpy. The pH remained near 7 to 8 throughout the 6-week test. The electrode potential ranged from -0.67 to -0.71 V.

Corrosion tests were also run on 3 wt % Morton Safe-T-Salt rock salt. The mean corrosion rate of rock salt was 12.0 mpy. The pH decreased during the 6-week tests from 6.7 to 5.2. The electrode potential ranged from -0.67 to -0.72 V.

The third control solution was deionized water. The corrosion rate of deionized water increased during the 6-week test from 4 to 12 mpy. The mean corrosion rate was 9 mpy. The pH of the deionized water solutions remained near 7. The electrode potential was low compared to all other mild steel in deicer solutions, ranging from -0.36 to -0.42 V.

The last control deicer material was 3 wt % CMA. The mean corrosion rate was 0 mpy, that is, no corrosion. The pH remained near 8, and the electrode potential remained -0.70 to -0.72 V throughout the 6-week test.

Second Set of Tests

- Calcium phosphate ($Ca(H_2PO_4)_2$)

  The corrosion rates of mild steel in 3 wt % NaCl containing $Ca(H_2PO_4)_2$ corrosion inhibitor at 1.5 to 3.5 wt % of solids were 1.0 to 1.7 mpy. This corresponds to about 86% to 92% reduction in corrosion rate versus the 3 wt % NaCl control. The pH of the 3.5 wt % solution rose from 5.3 to 5.7 during the 6-week test interval. The pH of the 2.5 wt % solution went from 5.5 to 6.2, and that of the 1.5 wt % solution went from 6.0 to 7.3. The electrode potential of the steel in the 3.5 and 2.5 wt % solutions remained in a range of -0.64 to -0.67 V versus a standard calomel electrode. The electrical potential of the steel in the 1.5 wt % solution was -0.67 to -0.72 V.

- Sodium molybdate (Na_2MoO_4) and sodium tripolyphosphate ($Na_5P_3O_{10}$)

  The corrosion rates of mild steel in 3 wt % NaCl containing 1.5 to 3.5 wt % of solids each of Na_2MoO_4 and $Na_5P_3O_{10}$ were 8.3 to 10.2 mpy. This range corresponds to about 17% to 31% reduction in corrosion rate versus the 3 wt % NaCl control solution. The pH of all inhibited solutions remained from 8.6 to 9.0 throughout the 6-week test. The electrical potential ranged from -0.53 to -0.67 V versus a standard calomel electrode.

- Sodium fluorophosphate (Na_2FPO_3) and nitrilotris(methylene)-triphosphonic acid ($N[CH_2P(O)(OH)_2]_3$)

The corrosion rates of mild steel in 3 wt % NaCl containing 1.5 to 3.5 wt % of solids each of Na_2FPO_3 and $N[CH_2P(O)(OH)_2]_3$ were 5.3 to 6.2 mpy, representing about 48% to 56% reduction in corrosion rates compared to the 3 wt % NaCl control. Except for the first week, pH of the inhibited solutions remained from 7.2 to 7.4 throughout the test. Electrical potential ranged from -0.69 to -0.71 V.

- Zinc chloride ($ZnCl_2$) and sodium tripolyphosphate ($Na_5P_3O_{10}$)

  The corrosion rates of mild steel in 3 wt % NaCl containing 2.5 to 7.5 wt % of solids each of $ZnCl_2$ and $Na_5P_3O_{10}$ were 0.1 to 0.2 mpy, representing a 98% to 99% reduction in corrosion rates compared to the 3 wt % NaCl control. The pH of the 7.5 + 5.5 wt % inhibited solution was 5.8 to 6.1; that of the 2.5 wt % solution was 6.1 to 6.4 during the test interval. The electrical potential ranged from -0.63 to -0.67 V for the duration of the test.

- Calcium and magnesium acetate (CMA)

  The corrosion rate of mild steel in 3 wt % NaCl containing 10 wt % of solids of CMA was 8.0 mpy, representing a 33% reduction in the corrosion rate compared to the 3 wt % NaCl control. The pH remained at 7.3, and the electrical potential was 0.72 to 0.74 V throughout the test.

- Control solutions

  Corrosion tests on mild steel were run in two duplicate control solutions, the 3 wt % NaCl solution to which the corrosion rates of the inhibited solutions were compared and deionized water. The mean corrosion rate of 3 wt % NaCl was 12.0 mpy, with the pH ranging from 6.7 to 7.4 and the electrical potential from -0.67 to -0.71 V. The average corrosion rate of mild steel in deionized water was 5.2 mpy. The pH range was 6.3 to 7.4, and the electrical potential ranged from -0.23 to -0.29 V throughout the test.

3.2.3.2.2 Aluminum Exposed to Corrosion test solutions. The corrosion data for aluminum also show a wide range of corrosion rate results. Discussion of the corrosion test results by test solution type follows.

First Set of Tests

- PCI (calcium lignosulfonate)

  The corrosion rates of aluminum in 3 wt % NaCl containing PCI corrosion inhibitor at 4 to 10 wt % of solids were 7 to 8 mpy. This rate corresponds to a less than 10% reduction in corrosion versus the 3 wt % NaCl control. The pH of the solutions remained near 8 throughout the 6-week test. The electrode potential of the aluminum in the test solutions remained in a range of -0.73 to -0.77 V versus a saturated calomel electrode, through the 6-week test.

- Sodium fluorophosphate (Na_2FPO_3)

  The corrosion rates of aluminum in 3% NaCl containing 1.5 to 3.5 Na_2FPO_3 were 8 to 9 mpy. This rate corresponds to no reduction in corrosion versus the 3% NaCl control solutions. The pH of the solutions remained near 9 throughout the 6-week test. The electrode potential of the aluminum in the test solutions remained in a range of -0.74 to -0.77 V versus an SCE electrode.

- Sodium molybdate (Na_2MoO_4)

  The corrosion rates of aluminum in 3% NaCl containing 1.5% to 3.5% Na_2MoO_4 were 6 to 8 mpy. This rate corresponds to less than 20% reduction in corrosion versus the 3% NaCl control solutions. The pH of the solutions remained near 8.5 throughout the 6-week tests. The electrode potentials of the aluminum in the test solutions ranged from -0.68 to -0.79 V.

- Zinc sulfate ($ZnSO_4$) and sodium tripolyphosphate ($Na_5P_3O_{10}$)

  The corrosion rates of aluminum in 3% NaCl containing 2.5% to 7.5% each of zinc sulfate and sodium tripolyphosphate were 0.2 to 0.5 mpy. This rate corresponds to 93% to 97% reduction in corrosion versus the 3% NaCl control solutions. The pH of the solutions remained 5.6 to 6.7, and the electrode potentials remained in a range of -0.73 to -0.77 V throughout the 6-week corrosion tests.

- Control solutions

  Corrosion tests of aluminum were also run in four duplicate control solutions. Most important was the 3 wt % reagent NaCl, to which the corrosion rates of the inhibited solutions were compared. The mean corrosion rate of the 3% NaCl control was 7.5 mpy. The pH remained near 8 throughout the 6-week tests. The electrode potential ranged from -0.76 to -0.79 V.

Corrosion tests were also run on 3 wt % Morton Safe-T salt, rock salt. The mean corrosion rate of rock salt was 6.7 mpy. The pH ranged during the 6-week test from 7.4 to 8.0. The electrode potential ranged from -0.61 to -0.73 V.

The third control solution was deionized water. The corrosion rate of deionized water increased during the 6-week test from 0.1 to 1.8 mpy. The mean corrosion rate was 1.0 mpy. The pH of the deionized water solutions remained near 7. The electrode potential was low compared to all the aluminum in inhibited deicer solutions, ranging from -0.42 to -0.49 V.

The last control deicer material was 3 wt % CMA. The mean corrosion rate was 0.3 mpy. The pH remained near 8, and the electrode potential, like the deionized water, was low, ranging from -0.43 to -0.49 V through the 6-week test.

Second Set of Tests

- Calcium phosphate ($Ca(H_2PO_4)_2$)

  The corrosion rates of aluminum in 3 wt % NaCl containing $Ca(H_2PO_4)_2$ corrosion inhibitor at 1.5 to 3.5 wt % were 3.3 to 4.1 mpy, representing a 45% to 59% decrease in corrosion rate compared to the 3 wt % NaCl control. Except for the 3.5 wt % solution after 1 week, the pH of the inhibited solutions ranged from 7.3 to 8.4 during the duration of the test. Electrical potential was -0.66 to -0.81 V.

- Sodium molybdate (Na_2MoO_4) and sodium tripolyphosphate ($Na_5P_3O_{10}$)

  The corrosion rates of aluminum in 3 wt % NaCl containing Na_2MoO_4 and $Na_5P_3O_{10}$ corrosion inhibitors at 1.5 to 3.5 wt % of solids each were 6.6 to 7.9 mpy, representing only an 11% decrease in corrosion rate at the low level and no effect or slight potentiation of the corrosion rate at the high level. The pH ranged from 7.9 to 8.9 during the test. The electrical potential was -0.72 to -0.75 V except for the mid-level inhibitor concentration after 6 weeks, when it was -0.58 V.

- Sodium fluorophosphate (Na_2FPO_3) and nitrilotris(methylene)-triphosphonic acid ($N[CH_2P(O)(OH)_2]_3$)

  The corrosion rates of aluminum in 3 wt % NaCl containing Na_2FPO_3 and $N[CH_2P(O)(OH)_2]_3$ corrosion inhibitors at 1.5 to 3.5 wt % of solids each were 3.3 to 4.5 mpy, representing a 39% to 55% reduction in corrosion rate compared to the 3 wt % NaCl control. The pH values were 4.2 to 7.4 for the 3.5 wt % inhibited solution, 4.8 to 8.4 for the 2.5 wt % solution, and 6.3 to 8.5 for the 1.5 wt % solution. Electrical potentials remained near -0.74 V for the duration of the test except for the 1.5 wt % inhibited solution, which was -0.64 V after 6 weeks.

- Zinc chloride ($ZnCl_2$) and sodium tripolyphosphate ($Na_5P_3O_{10}$)

  The corrosion rates of aluminum in 3 wt % NaCl containing 2.5 to 7.5 wt % of solids each of $ZnCl_2$ and $Na_5P_3O_{10}$ were 0.3 mpy. This rate represents a 96% reduction in corrosion rate compared to the 3 wt % NaCl control. The pH values remained in the range of 6.2 to 6.6 for the duration of the test. Electrical potentials were -0.76 to -0.78 V.

- Calcium and magnesium acetate (CMA)

  The corrosion rate for aluminum in 3 wt % NaCl containing 10 wt % of solids of CMA as a corrosion inhibitor was 2.2 mpy. This rate represents a 70% reduction in corrosion rate compared to the 3 wt % NaCl control. The pH range was 7.6 to 8.3, and the electrical potential range was -0.66 to -0.73 V for the duration of the test.

- Control solutions

  Corrosion tests on aluminum were also run in two duplicate control solutions: 3 wt % NaCl to which the corrosion rates of the inhibited solutions were compared, and deionized water. The corrosion rate of aluminum in the 3 wt % NaCl solution was 7.4 mpy. The pH remained near 8.0 and the electrical potential near -0.78 V for the duration of the test. The corrosion rate for aluminum in deionized water was 1.0 mpy. Except after the first week, the pH remained near 7.4. The electrical potential was -0.48 to -0.50 V.

3.2.4 Conclusions and Recommendation

Based on the results of the experimental work, the following conclusions and recommendation are drawn:

- The corrosion test method used in these studies performs well in assessing the corrosion characteristics of inhibited sodium chloride solutions.
- Zinc sulfate and zinc chloride plus sodium tripolyphosphate were the most effective inhibitors for reducing the corrosion rate of mild steel in aerated 3 wt % sodium chloride solutions.
- Zinc sulfate and zinc chloride plus sodium tripolyphosphate were the most effective inhibitors for reducing the corrosion rate of aluminum in aerated 3 wt % sodium chloride solutions.
- Calcium phosphate was also an effective inhibitor for reducing the corrosion rate of mild steel in aerated 3 wt % sodium chloride solution.
- Three weight percent CMA exhibited low corrosion rates for both mild steel and aluminum substrates.
- Calcium magnesium acetate (CMA) at 10 wt % of solids does not appear to function well as a corrosion inhibitor for mild steel in aerated 3 wt % sodium chloride solution.
- The corrosion test method developed and used during these studies is recommended as a standard test method (SHRP H-205.7) for the evaluation of the corrosive effects of deicing chemicals on metals and for the screening of candidate corrosion inhibitors for use with deicing chemicals.

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4

Conclusions and Recommendations

4.1 Conclusions

Based on this study of evaluation procedures for deicing chemicals and the development of improved sodium chloride, the following general conclusions are drawn regarding the preliminary studies and the advanced investigations.

The preliminary studies conducted during the initial phase of the research provided a sound basis for assessing the adequacy and availability of test methodologies for the characterization of chemical deicers; and for developing technical rationales for the improvement of sodium chloride as a deicing chemical. Conclusions and recommendations for the preliminary studies are presented in the following three documents: (a) Special Report, "Evaluation and Testing of Chemical Deicers: Literature Review" (August 5, 1988); (b) Special Report, "Characterization and Selection of Chemical Deicers: Criteria Document" (October 7, 1988); and Interim Report on H-205, "Evaluation Procedures for Deicing Chemicals and Improved Sodium Chloride" (March 14, 1989).

The advanced investigations led to the development of (a) standardized methodologies for the physicochemical characterization and performance evaluation of both liquid and solid chemical deicers; and (b) technical approaches for improvement of the deicing performance and materials compatibility of sodium chloride formulations.

Conclusions and recommendations regarding the advanced investigations are presented for each specific technical area, as follows:

Ice-Melting Test

- A chemical-deicer application rate equivalent to 101.54 g/m^2 (1,320 lb/lane mile) was found to be the best compromise between representative actual highway deicer application rates and test-deicer application rates. This test rate was required to yield acceptable results within the constraints imposed by brine volumes, temperature ranges of interest, and the size of test specimens in the standard ice-melting test.

Ice-Penetration Test

- The standard ice-penetration test is operationally the simplest deicer performance test to perform, and can be considered the preferred test for preliminary screening.

- The significance of ice-penetration test results arises from a combination of both the rate of penetration and the depth of penetration, yielding information on how quickly a deicer penetrates to the ice-pavement substrates to initiate undercutting and disbondment, and also as the melting capacity available for undercutting and disbondment.

Ice-Undercutting Test

- Among deicing performance tests, the standard ice-undercutting test provides information and data which most directly relates to ice control, that is, disbondment of ice from pavement.

- When considering the applications of deicers to ice surfaces for the eventual purpose of ice-undercutting and disbondment, the uniform distribution of small deicer particles is considered to be the most effective method.

- Application of liquid or solid deicers to the pavement prior to ice formation appears to be the best option for ice disbondment because ice-melting at the pavement/ice interface permits a greater transfer of thermal energy into the most critical region.

Concrete Compatibility Tests

- Both standard test methods developed and modified during the research for evaluation of the effects of deicing chemicals on concrete can be used to distinguish between deicers with low spalling activity and those with high spalling activity.

- Of the two methods, the test method for rapid evaluation of the effects of deicing chemicals on concrete is preferred because it is much less labor-intensive, and is more convenient to conduct.

Friction Characteristics Test

- The British Pendulum Tester, when used in conjunction with procedures adapted and developed during his research, is a valid apparatus for evaluating the frictional characteristics of chemical deicers in the laboratory.
- Differences in the frictional characteristics can be determined by testing solutions of deicing materials on a variety of substrates.
- Sand-blasted glass is the most suitable laboratory substrate for evaluating the frictional characteristics of deicing chemicals with the British Pendulum Tester.

Concrete Reinforcement Corrosion Tests

- The test specimen developed during the concrete reinforcement corrosion research proved to be very suitable for corrosion-potential determinations.
- The standard corrosion-potential test provides consistent results, and is a useful tool for comparing the effects of deicing chemicals on the corrosion of reinforcing steel.

Ecological Effects Tests

- The ecological effects tests developed and modified during this research provide useful information for the initial hazard assessment of chemical deicers.
- The aquatic and terrestrial toxicity tests can provide important information about the potential ecological effects of deicing chemicals contacting the environment.

Improvement of the Deicing Performance of Sodium Chloride

- The ice-melting performance of sodium chloride can be improved by combining it with other appropriate deicing chemicals in proportions from 1:1 to 20:1.

- The enhancement of ice-melting properties is achieved by increasing the rate of dissolution of sodium chloride,and reducing the time required for initiation of the melting process.

Enhancement of the Materials Compatibility of Sodium Chloride

- Research on the compatibility enhancement of sodium chloride by corrosion inhibition led to the development of a standardized laboratory procedure which can be used to compare the corrosive effects of deicing chemicals on metals, and to screen candidate corrosion inhibitors for use with chemical deicers.

4.2 Recommendations

The ice-penetration test is recommended as the preliminary screening test for evaluation of deicing performance, for determination of surface melting vs. penetration melting, and for estimation of lower temperature performance limits.

The ice-undercutting test is recommended as the most realistic deicing performance test for making direct comparisons of chemical deicers in a deicing function that is directly related to ice and snow control.

Further experimental testing with the mini-concrete compatibility test is needed to establish the effect of test specimen variation on the repeatability and reproducibility of the test results obtained with a range of deicing chemicals.

Additional work on the macrocell corrosion test is recommended to establish the proper test specimen configuration, macrocell circuitry, and electrical instrumentation for the development and/or measurement of macrocell corrosion currents.

Appendix A

Frictional Characteristics Test Data

- Part 1—Statistical Analysis of Horizontal Slip Tester Data
- Part 2—Test Data Obtained Using the British Pendulum Tester

Part 1

Statistical Analysis of Horizontal Slip Tester Data

The results of statistical analysis of test data generated using the horizontal slip tester are presented in Table A-1.

The effect of the glass substrate, including the control, on the friction coefficients was determined by an analysis of variance for each case (i.e., type of glass) and each friction coefficient separately. The overall effect of glass substrate on either friction coefficient was significant at the 5% significance level in all four analyses of variance.

Next, the treatment results were compared to their respective control results. A Bonferroni t-test was performed at the 5% experiment-wise level. In such a test, each treatment is compared to the control and the comparisons are made simultaneously to control for the overall error rate of 5%. In other words, the comparisons are not each made at the 5% level independently of the other comparisons within a group.

The simultaneous comparison results shown in Table A-1 are summarized below.

- The first column in Table A-1 lists the comparisons of interest.
- The second column gives the mean differences between control and treatment, as well as answers the question as to whether that difference is statistically different from zero.
- The third column is the standard error (SE) of the mean difference shown in the second column.

- The fourth column is the t-value calculated to test the mean difference.

The critical Bonferroni-t values are given in the header of the fourth column. These critical values are a function of the degrees of freedom of the root mean square error (RMSE), the number of comparisons made, and the chosen experiment-wise level, 5%. If the calculated t-value exceeds the critical t-value, then the difference tested is significantly different from zero.

Table A-1. Statistical analysis of friction test data generated using the horizontal slip tester.

Sandblasted glass 2.0-mil profile	Static friction coefficient		SE (diff) RMSE (df = 30) 0.015	5% t-test Bonferroni-t 2.66
	Mean diff.	Sig. ?		
Control--3% NaCl	0.012	No	0.008	1.42
Control--3% ethylene glycol	0.015	No	0.009	.59
Control--3% CMA	-0.020	No	0.010	-1.93
Control--Inhib. 3% NaCl	0.023	No	0.009	2.52

Sandblasted glass 1.6-mil profile	Static friction coefficient		SE (diff) RMSE (df = 20) 0.011	5% t-test Bonferroni-t 2.61
	Mean diff.	Sig. ?		
Control--25% NaCl	-0.007	No	0.006	-1.05
Control--25% $CaCl_2$	0.000	No	0.006	0.00
Control--25% CMA	-0.023	Yes	0.006	-3.69

Smooth glass	Static friction coefficient		SE (diff) RMSE (df = 23) 0.012	5% t-test Bonferroni-t 2.59
	Mean diff.	Sig. ?		
Control--3% NaCl	0.074	Yes	0.006	11.55
Control--3% ethylene glycol	0.007	No	0.007	0.94
Control--3% CMA	0.042	Yes	0.007	5.90

Smooth glass	Dynamic friction coefficient		SE (diff) RMSE (df = 23) 0.013	5% t-test Bonferroni-t 2.59
	Mean diff.	Sig. ?		
Control--3% NaCl	-0.010	No	0.007	-1.45
Control--3% ethylene glycol	-0.098	Yes	0.008	-13.00
Control--3% CMA	-0.053	Yes	0.008	-7.05

Part 2

Test Data Obtained Using British Pendulum Tester

The frictional characteristics (BPN) of various surfaces wetted with selected chemical deicer solutions at specified temperatures are presented in Tables A-2 through A-5. These tables provide the numerical data for the discussion in the body of the report.

Table A-2. Frictional characteristics of sand-blasted glass wetted with various deicer solutions at 20°, 30°, and 75°F.

Deicer/control	Deicer concentration (wt %)	Friction value (BPN)[a]		
		75°F (23.9°C)	30°F (−1.11°C)	20°F (−6.67°C)
Deionized water	-	66-67		
Sodium chloride	3	-	65	-
	10	66	63	-
	25	62	59	57
PCI-inhibited sodium chloride	10	66	67	62
Rock salt	10	64	64	-
	25	60	60	59
Sodium formate	10	66	63	-
	25	60	60	59
Calcium chloride	10	66	66	-
	25	61	62	58
Magnesium chloride	10	61	60	58
	25	52	52	51
Urea	10	66	63	-
	25	64	62	61
CMA	10	63	61	-
	25	49	45	38
Ethylene glycol	10	64	63	-
	25	61	59	57
	100	31	28	21

[a] BPN = British Pendulum Number.

Table A-3. Frictional characteristics of molded concrete slab surfaces wetted with 10 wt % and 25 wt % solutions of NaCl, $MgCl_2$, and CMA at 75°F (23.9°C).

Test slab no.	Test surface profile (mils)	Deicer/control	Deicer concentration (wt %)	Friction value (BPN)[a]
1	≈ 3.2	Deionized water	-	69
		Sodium chloride	10	66
			25	63
2	≈ 3.6	Deionized water	-	66
		Magnesium chloride	10	62
			25	56
3	≈ 3.4	Deionized water	-	65
		CMA	10	61
			25	52

[a] BPN = British Pendulum Number.

Table A-4. Frictional characteristics of asphalt pavement wetted with 25 wt % solutions of NaCl, $MgCl_2$, and CMA at 82°F (27.8°C).

Test section no.	Deicer/control	Deicer concentration (wt %)	Friction value (BPN)[a]
1	Deionized water	-	55
	Sodium chloride	25	48
2	Deionized water	-	55
	Magnesium chloride	25	45
3	Deionized water	-	54
	CMA	25	42

[a] BPN = British Pendulum Number.

Table A-5. Frictional characteristics of two different pieces of sand-blasted glass wetted with selected deicer solutions at 75°F (23.9°C).

Deicer/control	Deicer concentration (wt %)	Friction value (BPN)[a]	
		Glass No. 1 (original)	Glass No. 2
Deionized water	-	66	68
Sodium chloride	10	66	67
	25	62	63
Calcium chloride	10	66	66
	25	61	62
Magnesium chloride	10	61	64
	25	52	57
CMA	10	63	64
	25	49	50

[a] BPN = British Pendulum Number.

Appendix B

Concrete Reinforcement Corrosion

- **Part 1—Rapid Evaluation of Corrosive Effects of Deicing Chemicals in Reinforced Concrete: Test Methods**
- **Part 2—Rapid Evaluation of Corrosive Effects of Deicing Chemicals in Reinforced Concrete: Test Data**

Part 1

Rapid Evaluation of Corrosive Effects of Deicing Chemicals in Reinforced Concrete: Test Methods

1. Scope

1.1. These test methods cover procedures for evaluating the effects of deicing chemicals on the corrosion of reinforcing steel in concrete.

1.2 The corrosion potential test and the macrocell test are described in this standard.

1.3 Annexes covering details particular to the mold, the salt bridge and the deicing chemicals are appended to this standard.

1.4 This standard may involve hazardous materials, operations and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Significance

2.1 The test methods provide rapid and simple procedures to evaluate the corrosion effects of deicing chemicals on reinforcing steel.

3. ASTM Reference Standards

A 615	Standard Specifications for Deformed and Plain Billet-Steel Bars for Concrete Reinforcement
C 150	Standard Specification for Portland Cement
C 305	Standard Method for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency
C 511	Standard Specifications for Moist Cabinets, Moist Rooms and Water Storage Tanks Used in the Testing of Hydraulic Cements and Concretes
C 778	Standard Specification for Standard Sand
D 2241	Standard Specification for Polyvinyl Chloride (PVC) Plastic Pipe (SDR-PR)
D 2466	Standard Specification for Polyvinyl Chloride (PVC) Plastic Pipe, Fitting Schedule 40
G 1	Standard Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens
G 3	Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing

4. Definitions

Several definitions common to both testing methods are given:

4.1 Passive. State of low chemical reactivity under certain environmental conditions.

4.2 Pore Solution. Liquid constituent found in the pores of hardened concrete.

4.3 Potential. A unit of measurement of the electrical activity of an element, usually given in volts or millivolts, relative to the electrical activity of a reference element.

5. Test Specimen

5.1 General. The specimen described in this specification is common for corrosion testing Methods A and B, Corrosion Potential and Macrocell testing, respectively. The specimen consists of a reinforcing bar embedded in a mortar cylinder. In the test, the specimen is surrounded by crushed mortar fill to simulate the conditions found in reinforced concrete. The potential of the specimen is measured with respect to a reference electrode by connecting an electrical cable to the reinforcing bar using a steel screw inserted in a tapped hole in the exposed end of the bar.

5.2 The specimen consists of a 5 in. (127 mm) long, ASTM A 615 No. 4 (13 mm) reinforcing bar, drilled and tapped at one end to accept a screw. The solid end of the bar is symmetrically embedded 3 in. (76 mm) in a 1.18 in. diameter (30 mm), 4 in. (102 mm) long mortar cylinder (see Figure 2.6-1, Section 2.6.2.1 of the text). The mortar mix is made with Type I portland cement, ASTM C 778 graded sand, and deionized water. The mortar has a water-cement ratio of 0.5 and a sand-cement ratio of 2.0 by weight. The mortar is mixed in accordance with ASTM C 305. The exposed mortar-steel interface is covered by a 0.60 in. (15 mm) epoxy band. The specimen is cured for 2 days in the mold and 12 days in a lime-saturated water.

5.3 Specimen Fabrication

5.3.1 Bar preparation. The 5 in. (127 mm) long, ASTM A 615 No. 4 (13 mm) reinforcing bar is drilled and tapped to accept a 10 x 24 x 0.5 in. steel machine screw. The bar is cleaned with acetone as per ASTM G 1. A 0.60 in (15 mm) wide epoxy band is applied around the bar 2.75 in. (70 mm) from the solid end of the bar (see Figure 2.6-1 in Section 2.6.2.1 of the text).

5.3.2 Mold Preparation. The mold, shown in Figure 2.6-2 of Section 2.6.2 of the text, is assembled with the reinforcing bar according to the procedure in Annex 1 of this appendix.

5.3.3 Quantities of materials. Six specimens and the mortar fill for one container require: 1320 g of portland cement, 2640 g of sand, and 660 g of deionized water.

5.3.4 Mixing. The mortar is mixed in accordance with ASTM C 305.

5.3.5 Molding specimens. The specimens are molded in three layers. Each layer is vibrated for 15 seconds on a vibration table with an amplitude of 0.006 in. (0.15 mm) and a frequency of 60 cycles/sec. Alternate procedures providing thorough consolidation and the removal of entrapped air are acceptable.

5.3.6 Curing Procedure. After vibration, the specimens are cured in the molds in a standard curing room (ASTM C 511) for two days. After two days, the specimens are demolded and cured in lime-saturated water until the time of test.

6. Testing Elements and Apparatus

6.1 Fill. To avoid the dissolution of the constituents of the mortar layer and to provide a buffer, the specimen is tested using a fill material. The fill material is crushed mortar, with the same proportions and age as the mortar used to fabricate the specimen. The fill is cast in a 1 in. (25 mm) deep layer on a metal form and vibrated 15 seconds on the vibration table (see 5.3.5). When the specimen reaches the age to be tested, the mortar fill is crushed to sizes between 0.75 and 1.5 in. (19 mm and 38 mm). 7.75 lb (3500 g) of crushed mortar is used in each container.

Note: A standard 10 x 15 in. (250 x 380 mm) cookie sheet serves quite well as a form for the fill material.

6.2 Containers. The container used in the test is a 5.0 liter, 8.5 in. (216 mm) high container with a lid. It is made of a plastic which does not react with any of the chemical substances to be tested.

6.3 Salt Bridge. To have a complete electrical circuit, an ionic path must be formed using a salt bridge made according to Annex 2 of this appendix.

6.4 Simulated Pore Solution. The specimen is submerged in a simulated pore solution. The pore solution contains 0.14 g of NaCl, 18.81 g of KOH, and 7.87 g of NaOH per liter of solution and is made with deionized water. This composition represents the pore solution found in typical concretes.

6.5 Deicing chemicals. The deicing chemical, whose effects on the corrosion of reinforcing steel in concrete are going to be tested, is mixed with pore solution in the desired molal ion concentration according to Annex 3 of this appendix. Molal ion concentrations of 0.4, 1.6, and 6.4 are recommended. Supplementary tests may be made with molal ion concentrations of 0.8 and 3.2.

6.6 Calomel reference electrode. A standard calomel reference electrode submerged in KCl saturated water. (Required for the Corrosion Potential Test only.)

6.7 Voltmeter. The voltmeter shall have a scale that can be read to 0.001 volts without interpolation. The electrochemical measurements using the voltmeter shall be made in accordance with ASTM G 3.

7. Safety and Testing Precautions

7.1 When working with chemical products, such as the components of pore solutions, deicers, or liquid epoxy, the safety instructions for the products shall be followed.

7.2 Improper connections between the specimen and the cable may give erroneous results. Checking the connection before covering with epoxy is recommended. It is important that the tapped hole in the reinforcing bar be thoroughly dried before the connection is made.

7.3 The presence of air bubbles in the salt bridge or at the salt bridge-solution interface may give incorrect results. The salt bridge should be checked during the test.

8. Test A: Corrosion Potential Test

8.1 General. This test measures the corrosion potential of the specimen with respect to a standard calomel reference electrode submerged in potassium chloride, KCl, saturated water (15 g of potassium chloride, KCl, dissolved in 100 cc of deionized water). The specimen is submerged in a deicing chemical solution, as shown in Figure 2.6-3 of Section 2.6.2.4.1 of the text. The corrosion potential test indicates the corrosion state of the reinforcing bar in the specimen, determining if the bar is in a passive or active state.

8.2 Procedure. The specimen is removed from the lime-saturated water 14 days after casting, and the tapped end of the reinforcing bar is thoroughly dried. An electrical cable is securely connected to the reinforcing bar by a screw connection. The connection is then covered with epoxy. The cable is passed through a hole in the lid of the container. A layer of crushed mortar pieces is put on the bottom of the container. The specimen is placed, steel up, on the layer, and the rest of the fill is placed in the container. If several specimens are placed in the same container, at least 1 in. (25 mm) of fill should separate the specimens. The salt bridge is placed in the container through a second hole in the lid. The other end of the salt bridge and the calomel electrode are placed in saturated KCl solution. The solution with the deicing chemical is placed in the container up to a level 0.5 in. (13 mm) below the top edge of the mortar cylinder. While placing the solution in the container, the corrosion potential may be read. The container must be sealed to prevent carbon dioxide in the air from neutralizing the pore solution and to prevent evaporation of the liquid during the course of the test, which is run until the potential reaches a constant value, usually 5 to 9 weeks after casting (3-7 weeks after initiation of the test). Readings should be taken at intervals of 24 hours or less.

8.3 Data presentation. The potential values should be plotted against the time in days, as depicted in Appendix B, Part 2, Figure B-15. The deicing chemical being tested and its concentration should be identified on the plot.

8.4 Interpretation of results. The potential sign convention follows ASTM G 3. If the corrosion potential is more positive than -0.300 V, the electrode is considered to be in a passive state. If the value is more negative, the electrode is in an active state. The more negative the potential, the more deleterious the deicing chemical.

9. Test B. Macrocell test

9.1 General. This test measures the corrosion potential of a specimen submerged in pore solution containing a deicing chemical with respect to another specimen submerged in pore solution alone, as shown in Figure 2.6-4 in Section 2.6.2.4.2 of the text. Due to the pH and chloride ion level typical of concrete, the specimen submerged in simulated pore solution is in a passive condition. The specimen submerged in the solution containing the deicer, however, may reach an active state. The effect of the deicing chemical on corrosion of reinforcing steel is determined based on the potential difference read across a resistor that connects the two specimens.

9.2 Procedure. The specimen is removed from the lime-saturated water 14 days after casting, and the tapped end of the reinforcing bar is thoroughly dried. A shielded cable is securely connected to the reinforcing bar by a screw connection. The connection is then covered with epoxy. The specimen is placed, steel up, in the container with the fill in the same way as done for Test A, making sure that at least 1 in. (25 mm) of fill surrounds the specimen. A second specimen is placed in the same way in a second container. A salt bridge is used to connect the two containers through holes in the lids of the containers. The two specimens are connected by shielded cables across a 100 K ohm precision resistor. Once all of the elements are in place, simulated pore solution is placed in one container and the pore solution containing the deicing chemical is placed in the other container up to 0.5 in. (13 mm) below the top edge of the mortar cylinder. The containers are sealed for the reasons described in section 8.2. The potential change is measured across the resistor (Figure 2.6-4).

9.3 Data presentation. The potential should be plotted against the time in days, as depicted in Appendix B, Part 2, Figure B-16. The deicing chemical being tested and its concentration should be identified on the plot.

9.4 Interpretation of results. The potential sign convention follows ASTM G 3. If the potential measured across the resistor is negative, the electrode is in an active state. The more negative the potential, the greater the amount of corrosion. If the potential values are positive, the electrode is in a more passive state than the reference electrode and no corrosion would be expected.

Annex 1. Mold Fabrication and Assembly

1. Mold Fabrication

The mold (see Figure 2.6-2 in Section 2.6.2.1 of the text) used to make the test specimen uses standard materials for ease of duplication. The mold consists of (letters preceding each item identifies the part in Figure 2.6-2):

A. One laboratory grade No. 6 $^1/_2$ rubber stopper, with a centered 0.5 in. (12.5 mm) diameter hole.

B. One ASTM D 2466, 1 in. to 1 in. PVC fitting, 1.3 in. (33 mm) internal diameter. The fitting is turned on one end to 1.60 in. (41 mm) external diameter.

C. One laboratory grade No. 9 rubber stopper, shortened to 0.71 in. (18 mm), with a centered 0.5 in. (12.5 mm) diameter hole.

D. One ASTM D 2466, 1.25 in. to 1.25 in. PVC fitting, 1.65 in. (42 mm) internal diameter, shortened by 0.55 in. (14 mm) on one end.

E. One ASTM D 2241, SDR 21, 1 in. PVC pipe, 1.18 in. (30 mm) internal diameter, 4 in. (102 mm) long. The pipe is sliced longitudinally to allow for specimen removal. The cut in the pipe is taped on the outside with masking tape to avoid leakage during casting.

F. One 5 in. (127 mm) diameter, 0.7 in. (18 mm) thick, plexiglass disc with a centered 2.04 in. (52 mm) diameter hole through half of the thickness of the disc and four tapped holes to receive 0.25 in. (6 mm) diameter threaded rods. One 5 in. (127 mm) diameter, 0.7 in. (18 mm) thick plexiglass disc with a centered 1.3 (33 mm) diameter hole through half of the thickness of the disc and a centered 1.18 in. (30 mm) diameter hole through the other half.

G. Four 0.25 in. (6 mm) diameter threaded rods with one nut, one wing nut and two washers each.

These elements are assembled as shown in Figure 2.6-2 in Section 2.6.2.1 of the text.

2. Mold Assembly

The mold is assembled in the following fashion, as shown in Figure 2.6-2 in Section 2.6.2.1 of the text.

a) The tapped end of the reinforcing bar is inserted in the hole of the small rubber stopper, A, through the widest end of the stopper. The distance between the nontapped end of the bar and the rubber stopper is 3 in. (76 mm).

b) The rubber stopper is inserted in the turned (lower) end of the small connector, B. The widest end of the small rubber stopper has to be in contact with the shoulder on the internal surface (see Figure 2.6-2) of the small connector.

c) The large rubber stopper, C, is inserted beginning with the narrow end, in the cut end of the large connector, D, until coming in contact with the shoulder on the inside surface of the connector.

d) The turned end of the small connector, B, is inserted in the free end of the large connector, D, at the same time that the tapped end of the reinforcing bar is inserted in the hole of the large rubber stopper, C.

e) The cut along one side of the PVC pipe, E, is taped with masking tape. The pipe is inserted in the free end of the small connector, B.

f) The assembled mold is inserted in the holes of the plexiglass discs, F, and tightened using the threaded rods, G.

g) Once the reinforcing bar is centered in the pipe, by controlling the tension on the threaded rods, the mold is ready for the specimen to be cast.

Annex 2

1. Salt Bridge

1.1 General. The salt bridge described in this specification is used to form an ionic path between the liquid in the two containers used in the tests.

1.2 Materials. The materials used to make four 3-ft (0.9 m) long salt bridges are 4.5 g of agar, 30 g of potassium chloride, KCl, 100 cc of distilled water, and 12 ft (3.6 m) of 0.1875 in. (5 mm) internal diameter rubber tubing.

1.3 Fabrication. The salt bridge is made by dissolving the agar in distilled or deionized water. The mix is heated in a double boiler and stirred for 20 min. After this, the KCl is added and mixed until dissolved. The agar mix is poured into the 3 ft (0.9 m) lengths of tubing when warm. Once the agar is cold, the salt bridge can be used.

Annex 3

1. Deicing Chemicals

The quantity of deicing chemical to be added to and mixed with the simulated pore solution to provide the desired molal ion concentration is calculated using Eq. B-1.

Weight of deicing chemical added to pore solution in grams per liter of pore solution

$$\left(\frac{974.8}{1000}\right)\left(\frac{A \times W}{N}\right) \qquad \text{(B-1)}$$

where

974.8 = the weight of the deionized water, in grams, in 1.0 liter of simulated pore solution
A = desired molal ion concentration
W = molecular weight of the deicer
N = number of ions in the molecule of deicing chemical

Sample Calculation

Deicing chemical: NaCl
Desired ion concentration: 0.4 m
Molecular weight of NaCl: W = 58.44
Number of ions in NaCl: N = 2

$$\text{Weight of deicing chemical added to pore solution} = \left(\frac{974.8}{1000}\right)\left(\frac{0.4 \; x \; 58.44}{2}\right)$$

= 11.39 g of NaCl added to 1.0 liter of simulated pore solution

Part 2

Rapid Evaluation of Corrosive Effects of Deicing Chemicals in Reinforced Concrete: Test Data

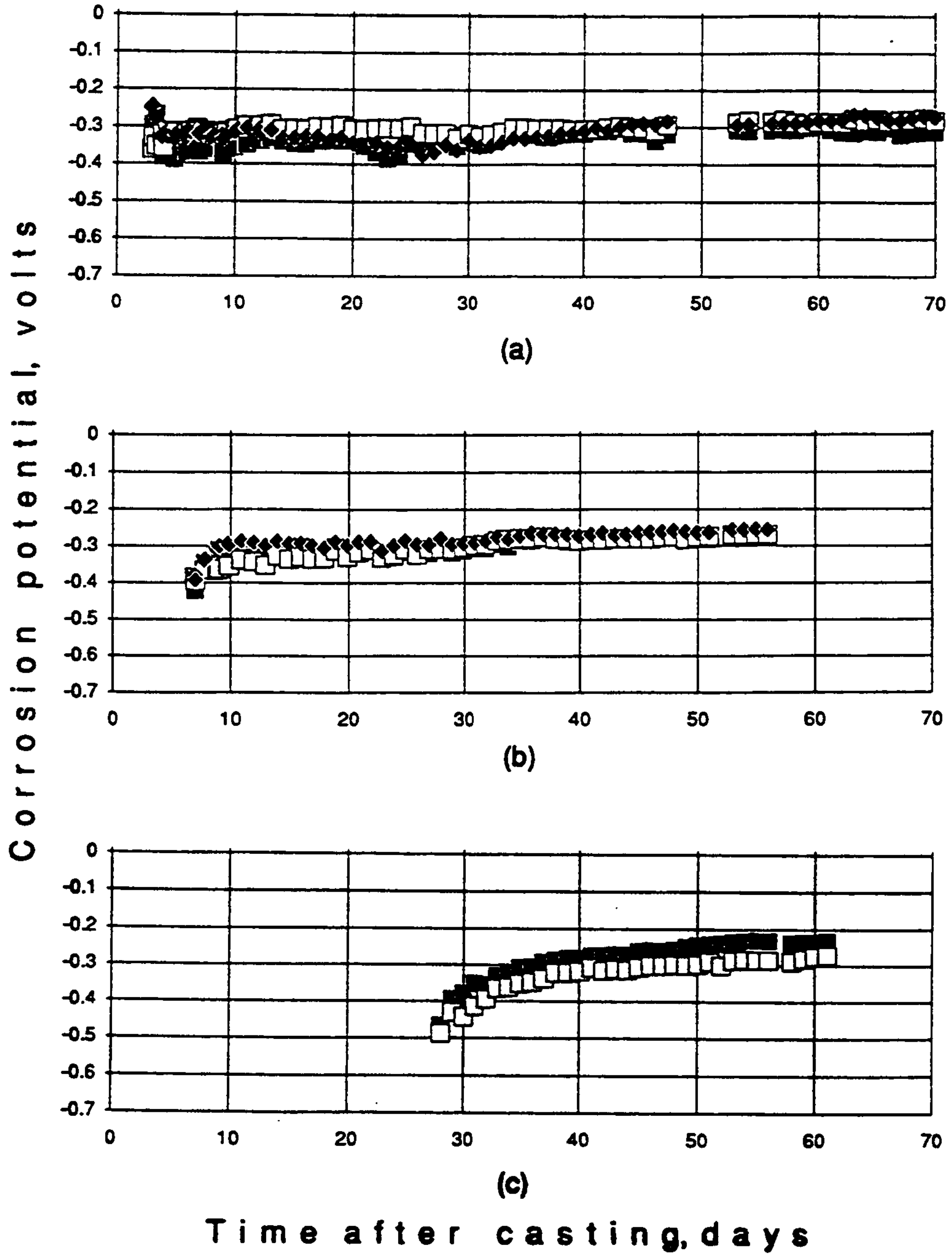


Figure B-1. Corrosion potential versus time for specimens cured for (a) 3 days, (b) 7 days, and (c) 28 days in a standard moist room and placed in simulated pore solution.

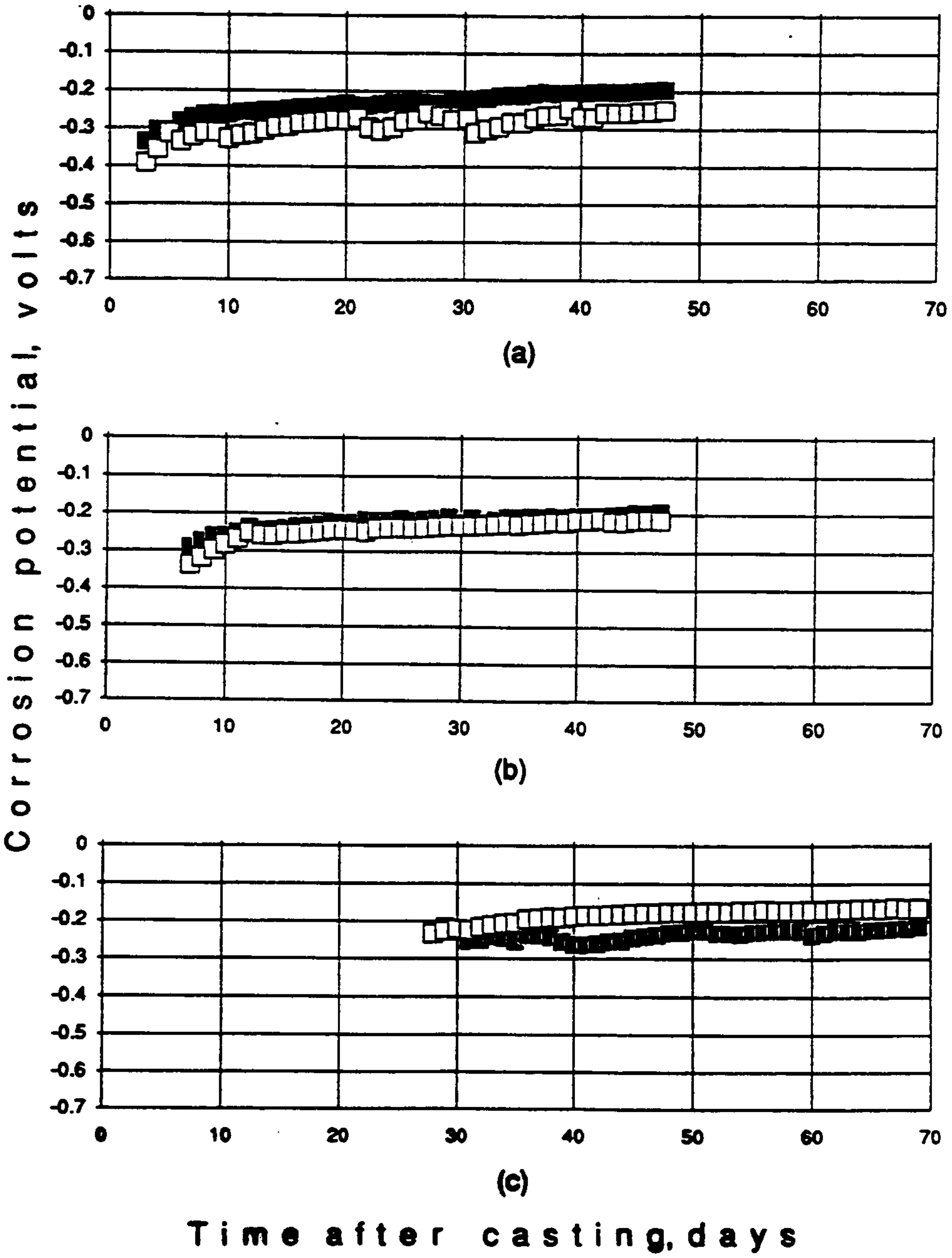


Figure B-2. Corrosion potential versus time for specimens cured for (a) 3 days, (b) 7 days, and (c) 28 days in lime-saturated water and placed in simulated pore solution.

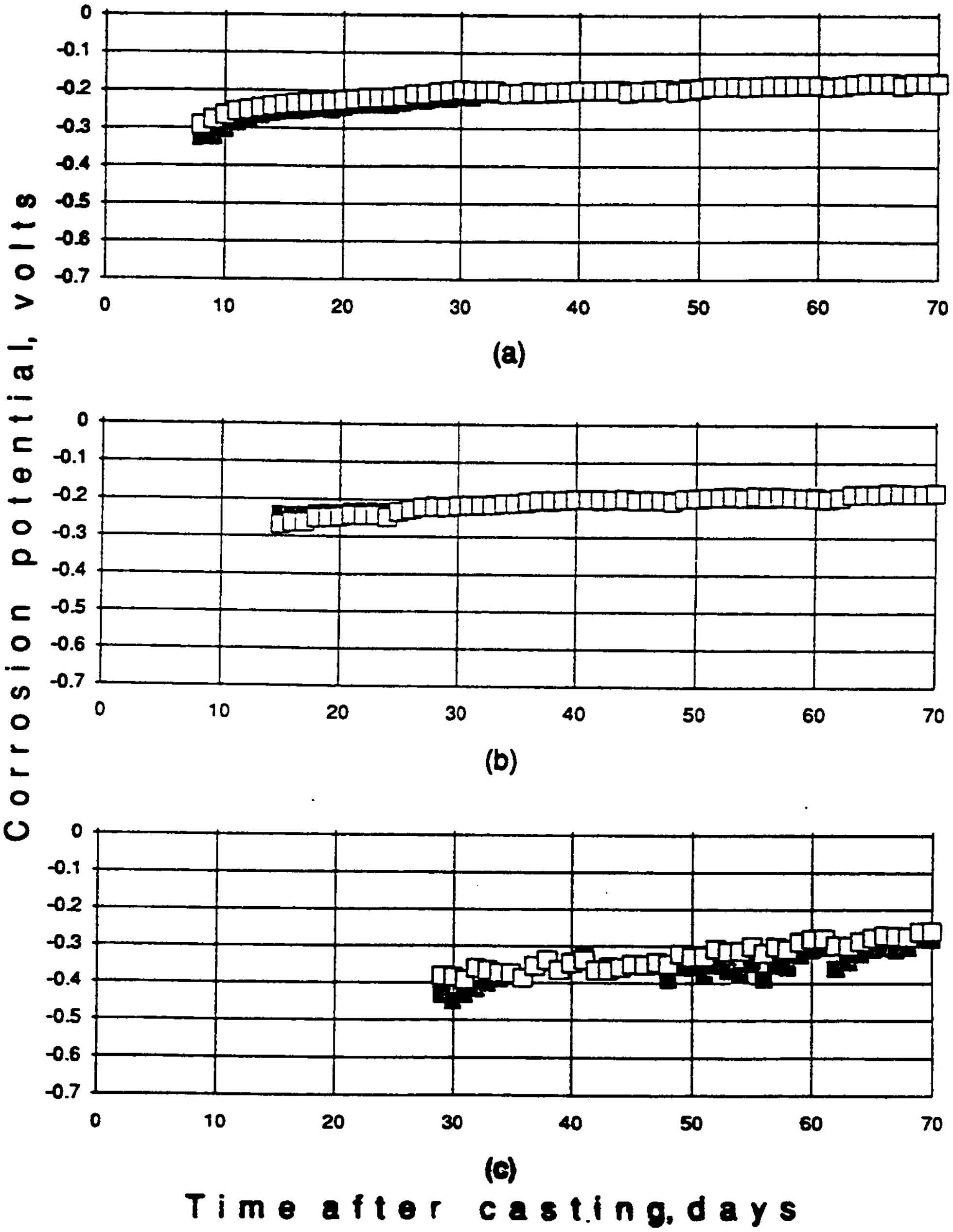


Figure B-3. Corrosion potential versus time for specimens made with tap water. Cured for (a) 7 days, (b) 14 days, and (c) 28 days.

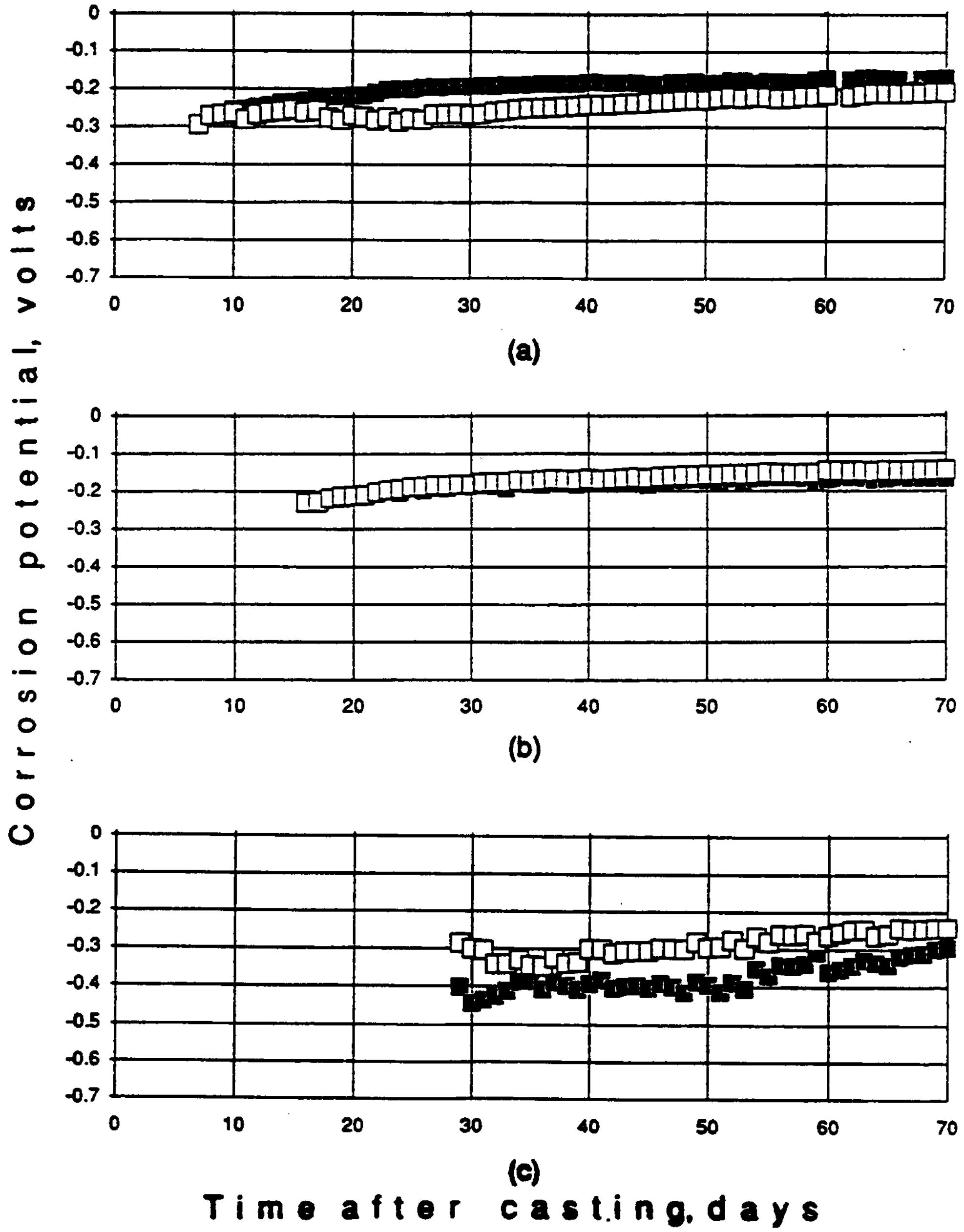


Figure B-4. Corrosion potential versus time for specimens tested with river sand in the mortar fill. Cured for (a) 7 days, (b) 14 days, and (c) 28 days.

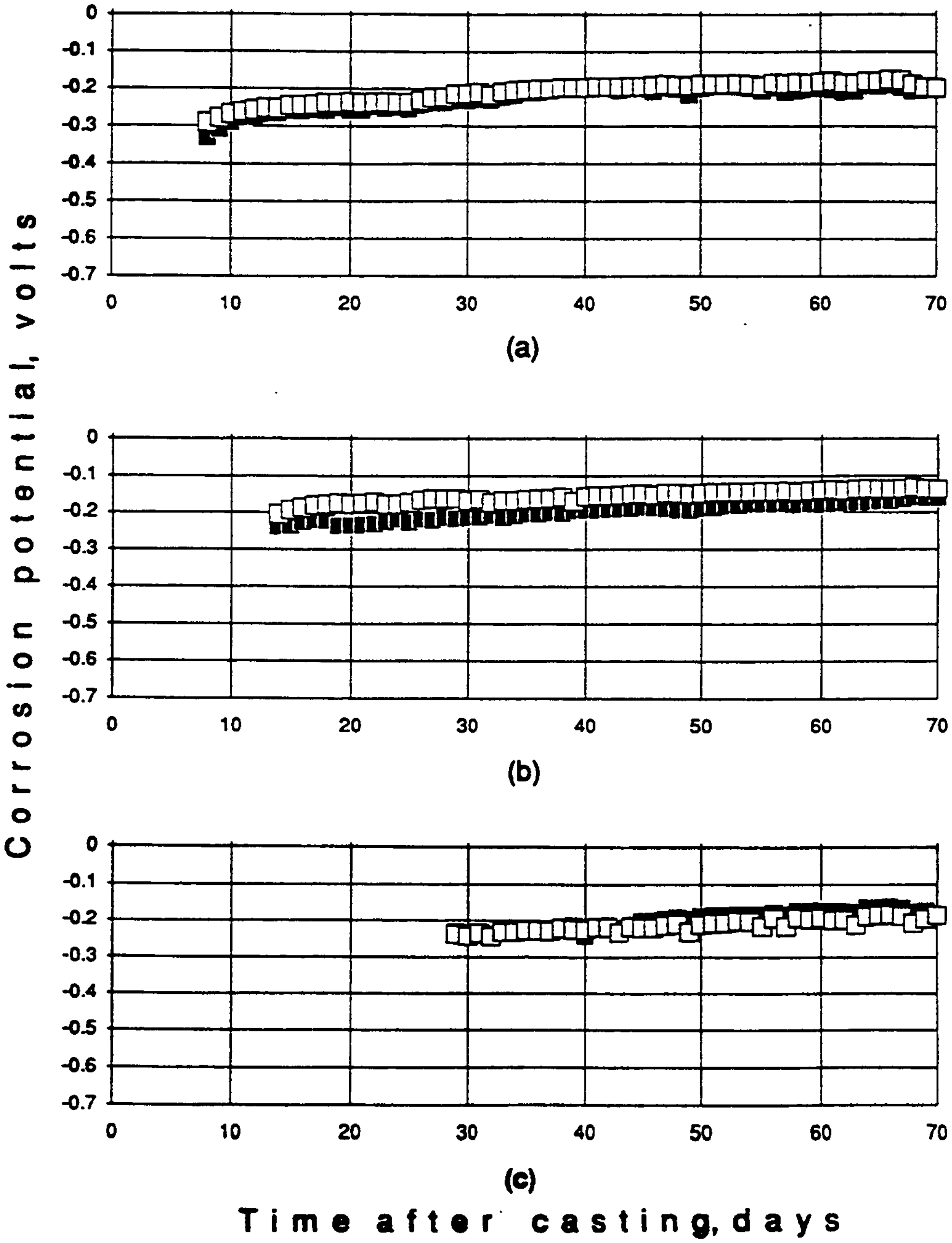


Figure B-5. Corrosion potential versus time for standard specimens. No. 4 bars, ASTM C 778 graded Ottawa sand and deionized water. Cured for (a) 7 days, (b) 14 days, and (c) 28 days.

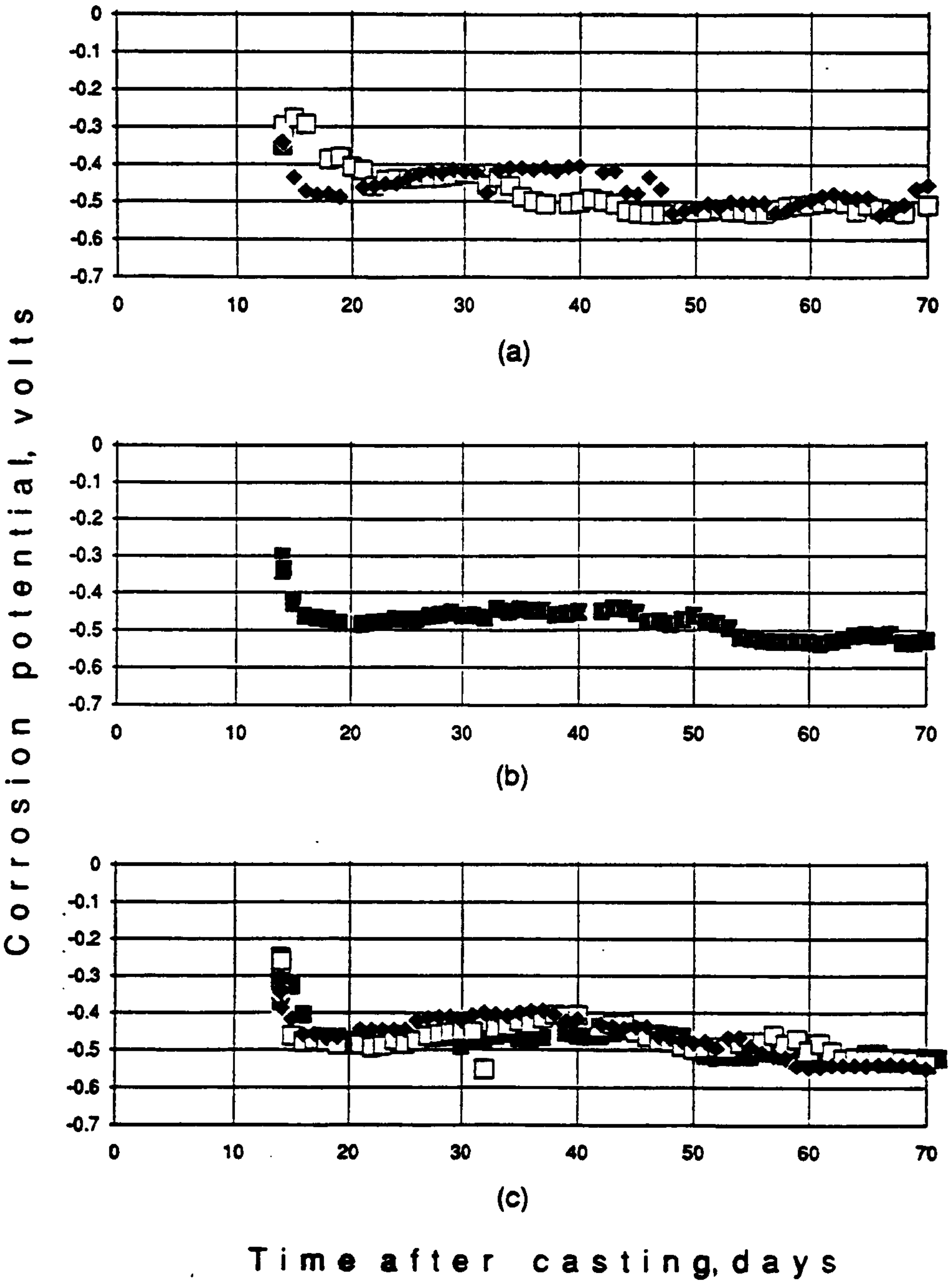


Figure B-6. Dip tests: Corrosion potential versus time for specimens cured for 14 days and exposed to 6.4 *m* ion concentration of NaCl in simulated pore solution. Freeboard (a) 2 in. (51 mm), (b) 1.5 in. (38 mm), (c) 1 in. (25 mm), (d) 0.5 in. (13 mm), and (e) 0.08 in. (2 mm).

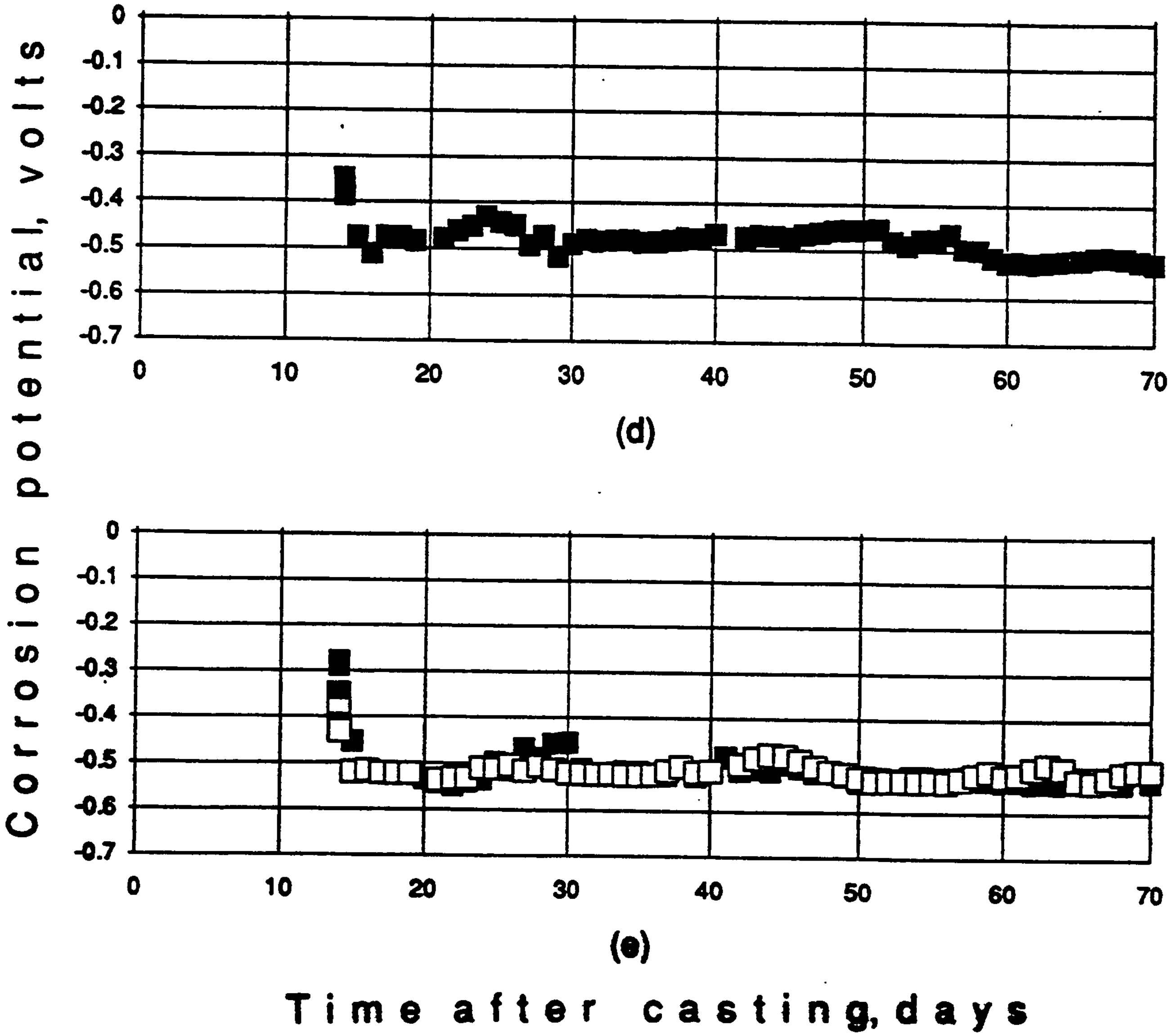


Figure B-6. (continued) Dip tests: Corrosion potential versus time for specimens cured for 14 days and exposed to 6.4 *m* ion concentration of NaCl in simulated pore solution. Freeboard (a) 2 in. (51 mm), (b) 1.5 in. (38 mm), (c) 1 in. (25 mm), (d) 0.5 in. (13 mm), and (e) 0.08 in. (2 mm).

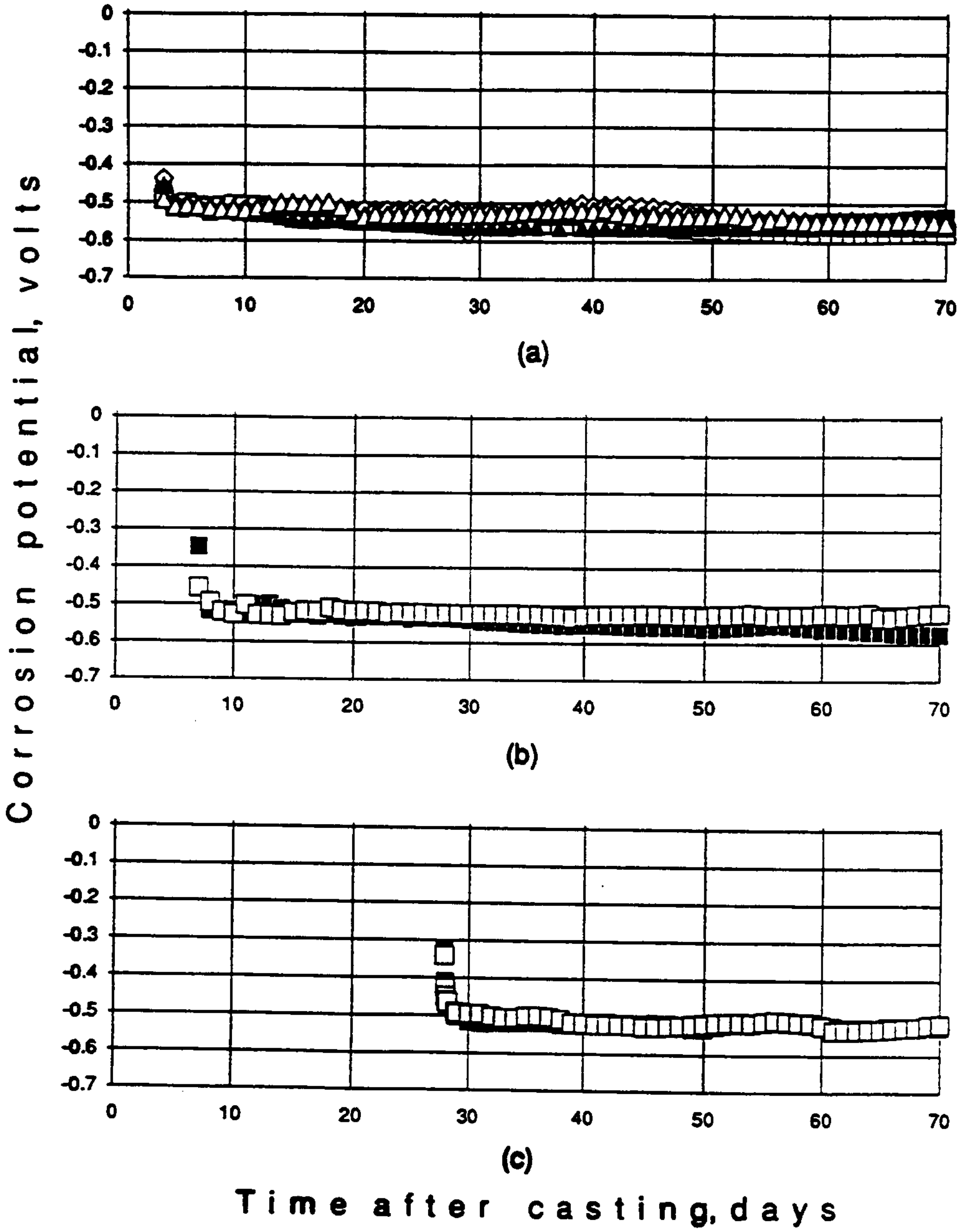


Figure B-7. Corrosion potential versus time for specimens cured for (a) 3 days, (b) 7 days, and (c) 28 days and exposed to 12.8 *m* ion concentration of NaCl in simulated pore solution.

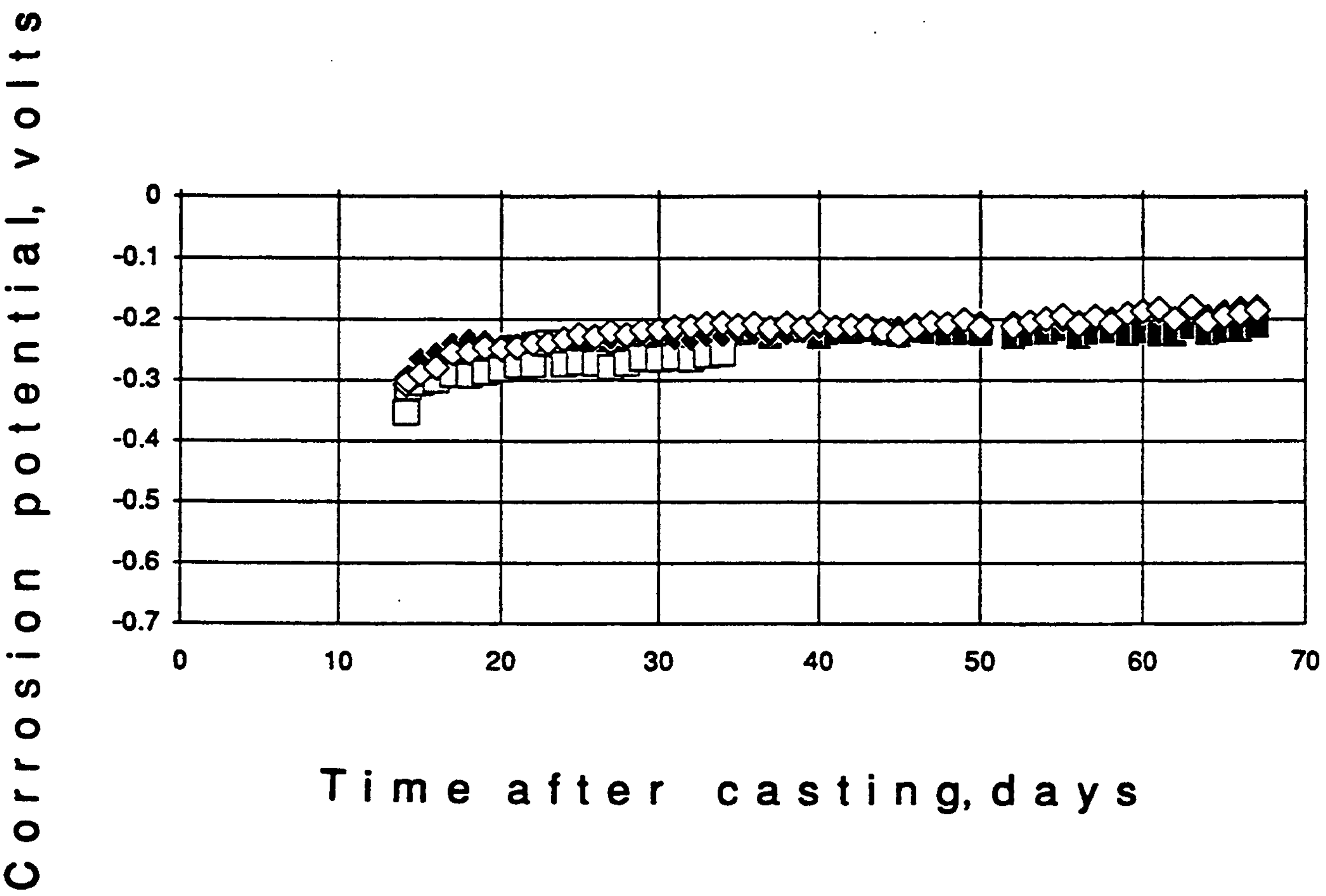


Figure B-8. Corrosion potential versus time for specimens cured for 14 days and exposed to simulated pore solution.

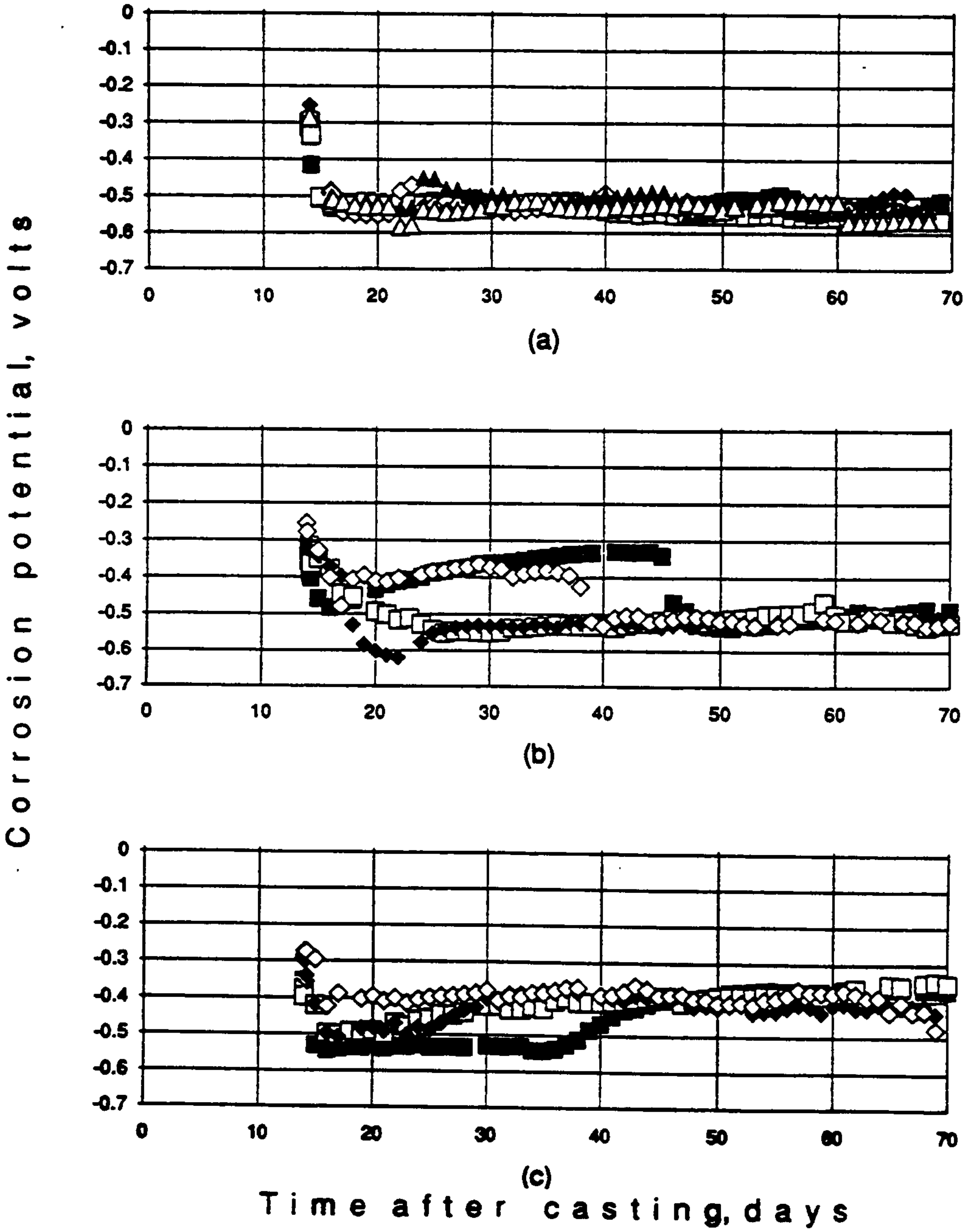


Figure B-9. Corrosion potential versus time for specimens cured for 14 days and exposed to different concentrations of NaCl in simulated pore solution. (a) 6.4 *m*, (b) 3.2 *m*, (c) 1.6 *m*, (d) 0.8 *m*, and (e) 0.4 *m*.

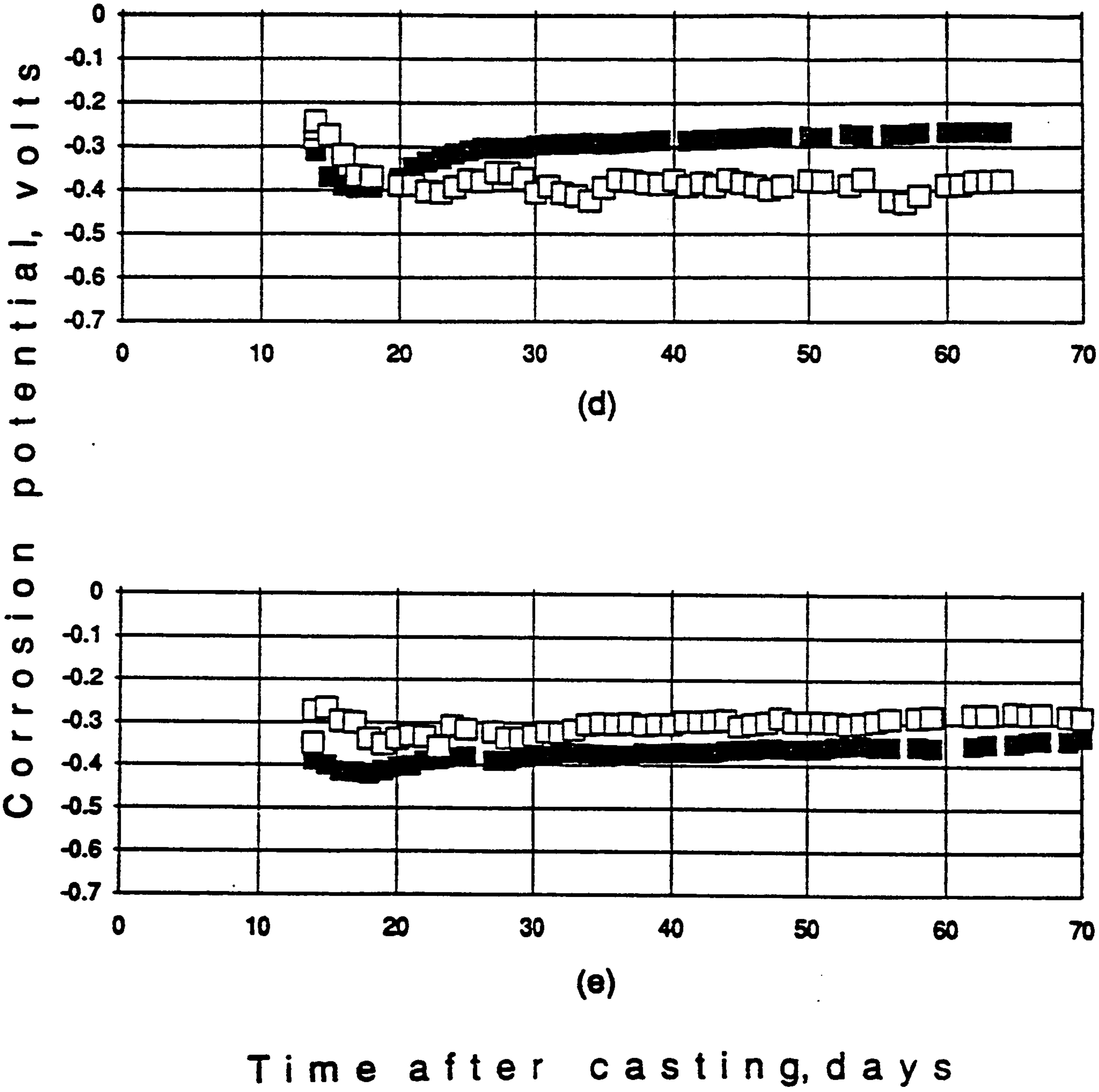


Figure B-9. (continued) Corrosion potential versus time for specimens cured for 14 days and exposed to different concentrations of NaCl in simulated pore solution. (a) 6.4 *m*, (b) 3.2 *m*, (c) 1.6 *m*, (d) 0.8 *m*, and (e) 0.4 *m*.

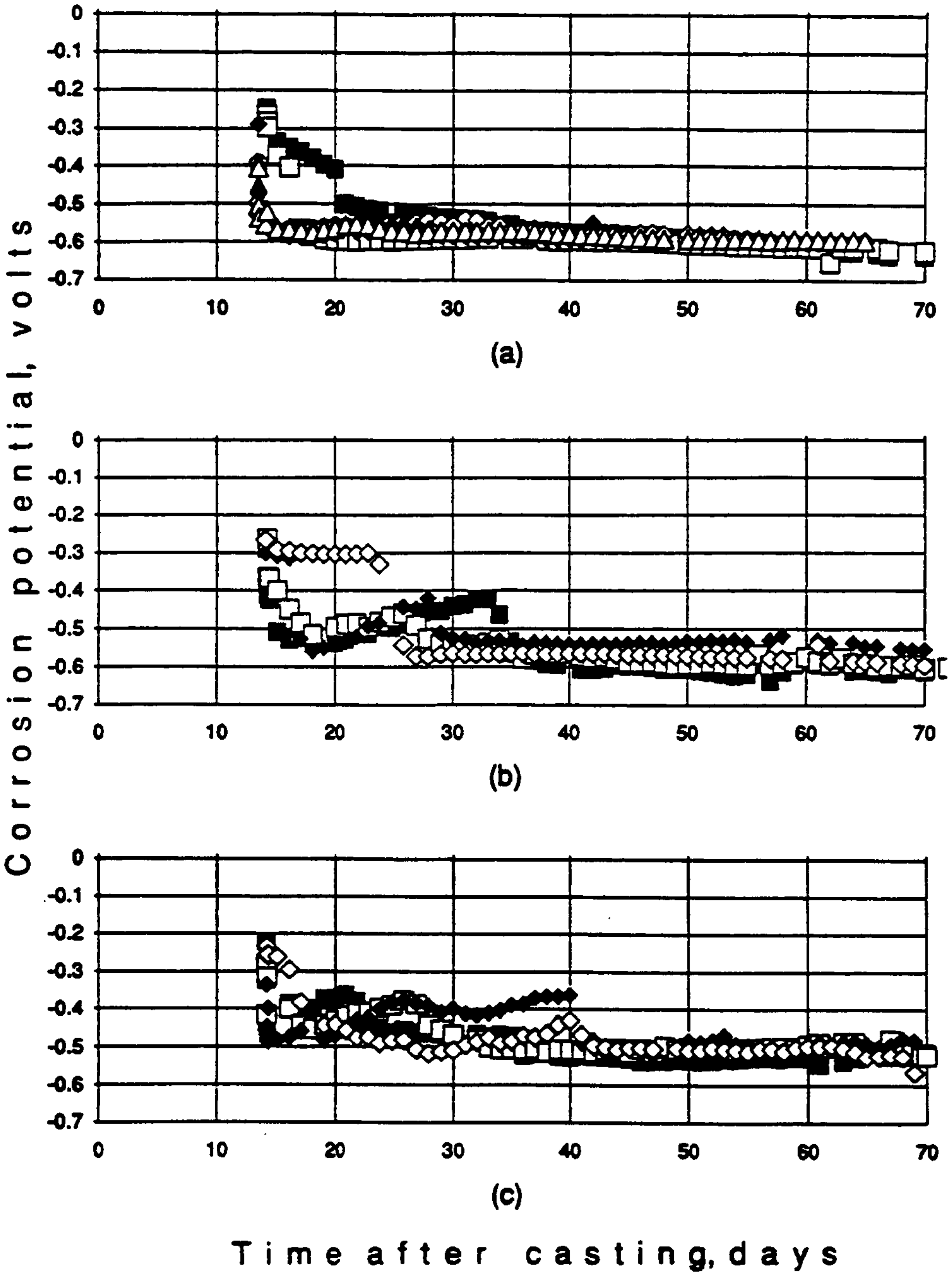


Figure B-10. Corrosion potential versus time for specimens cured for 14 days and exposed to different concentrations of $CaCl_2$ in simulated pore solution. (a) 6.4 *m*, (b) 3.2 *m*, (c) 1.6 *m*, (d) 0.8 *m*, and (e) 0.4 *m*.

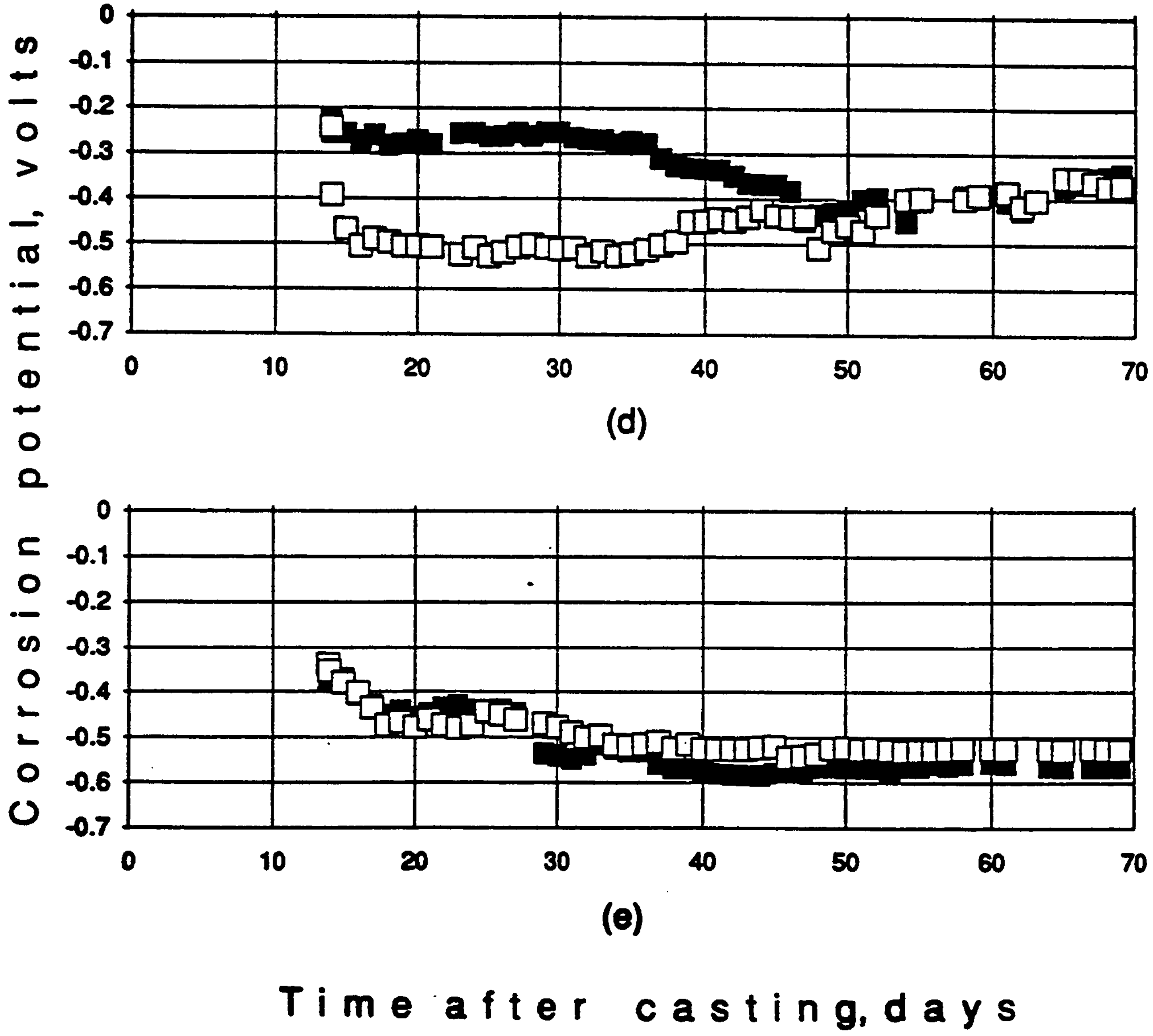


Figure B-10. (continued) Corrosion potential versus time for specimens cured for 14 days and exposed to different concentrations of $CaCl_2$ in simulated pore solution. (a) 6.4 *m*, (b) 3.2 *m*, (c) 1.6 *m*, (d) 0.8 *m*, and (e) 0.4 *m*.

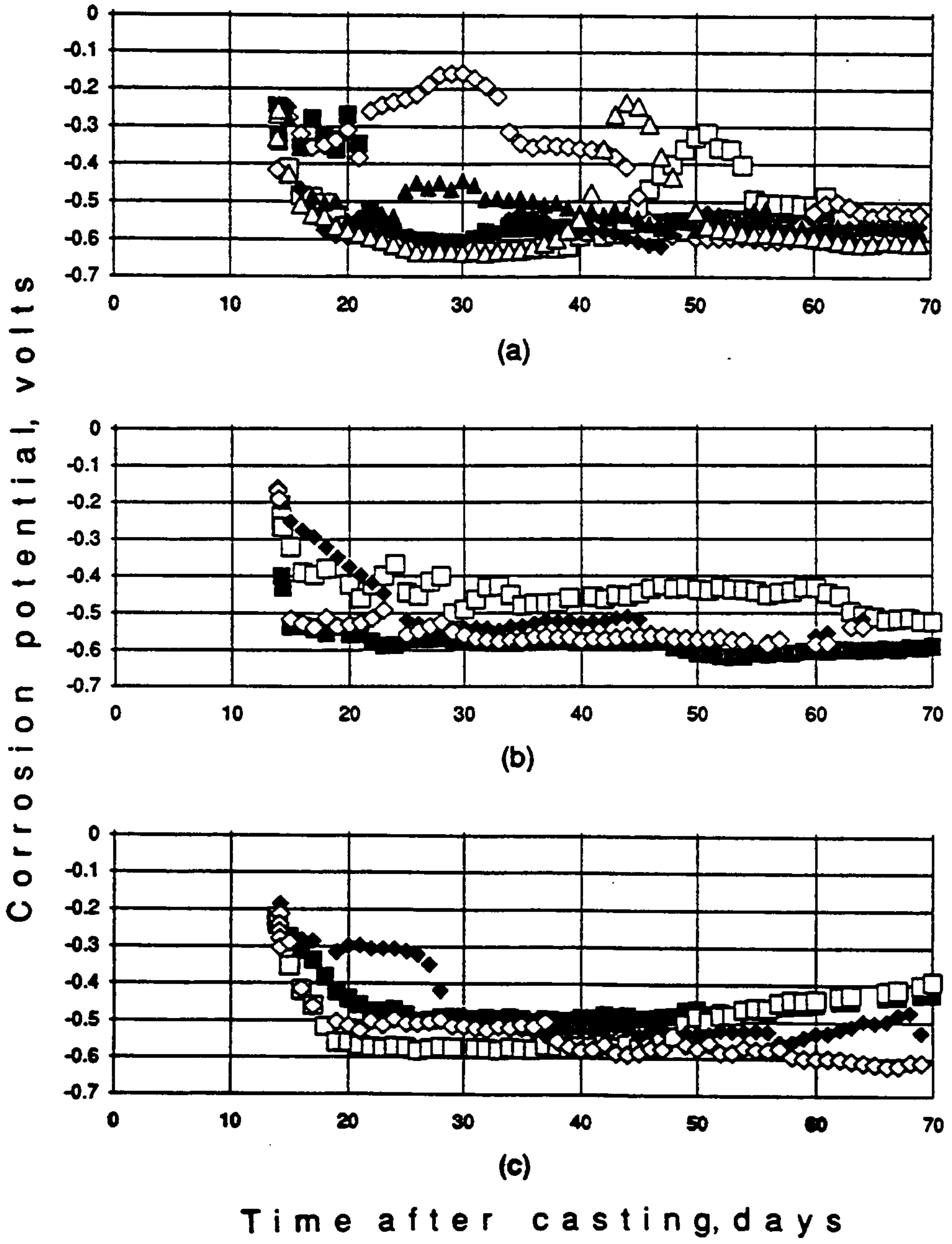


Figure B-11. Corrosion potential versus time for specimens cured for 14 days and exposed to different concentrations of CMA in simulated pore solution. (a) 6.4 *m*, (b) 3.2 *m*, (c) 1.6 *m*, (d) 0.8 *m*, and (e) 0.4 *m*.

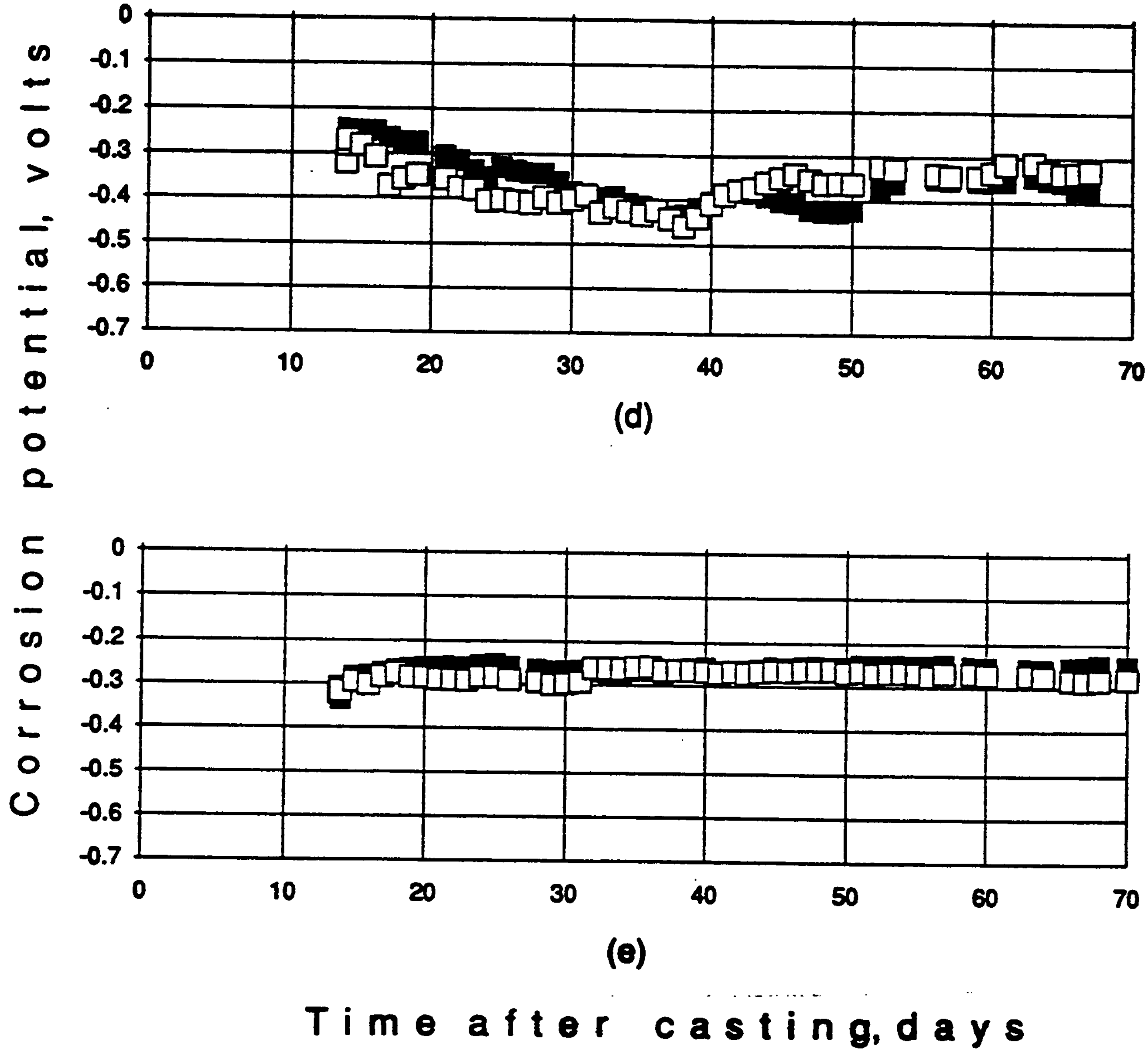


Figure B-11. (continued) Corrosion potential versus time for specimens cured for 14 days and exposed to different concentrations of CMA in simulated pore solution. (a) 6.4 *m*, (b) 3.2 *m*, (c) 1.6 *m*, (d) 0.8 *m*, and (e) 0.4 *m*.

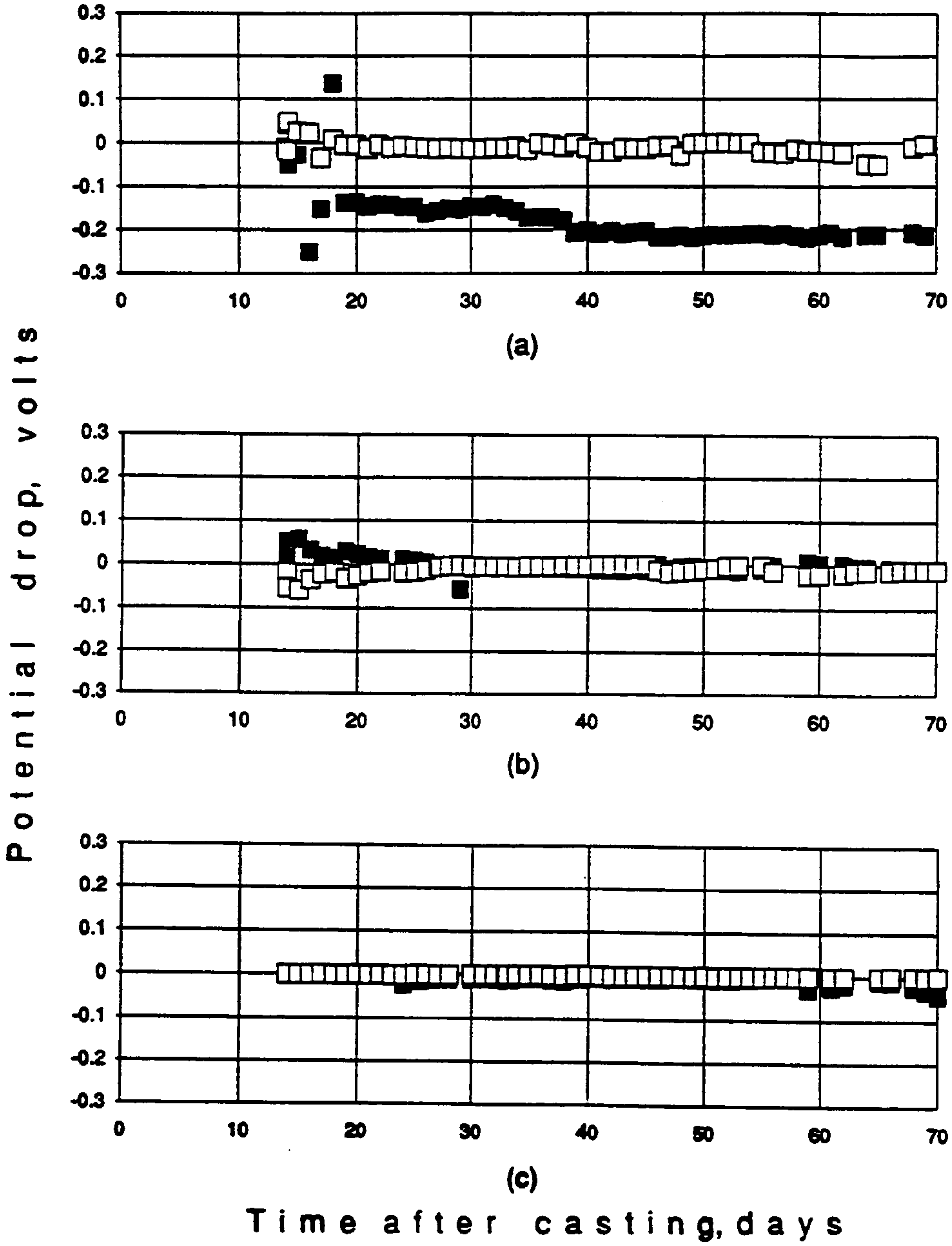


Figure B-12. Potential drop across 100,000 ohm resistor versus time for macrocells. NaCl molal ion concentrations: (a) 6.4 *m*, (b) 3.2 *m*, (c) 1.6 *m*, (d) 0.8 m, and (e) 0.4 *m*.

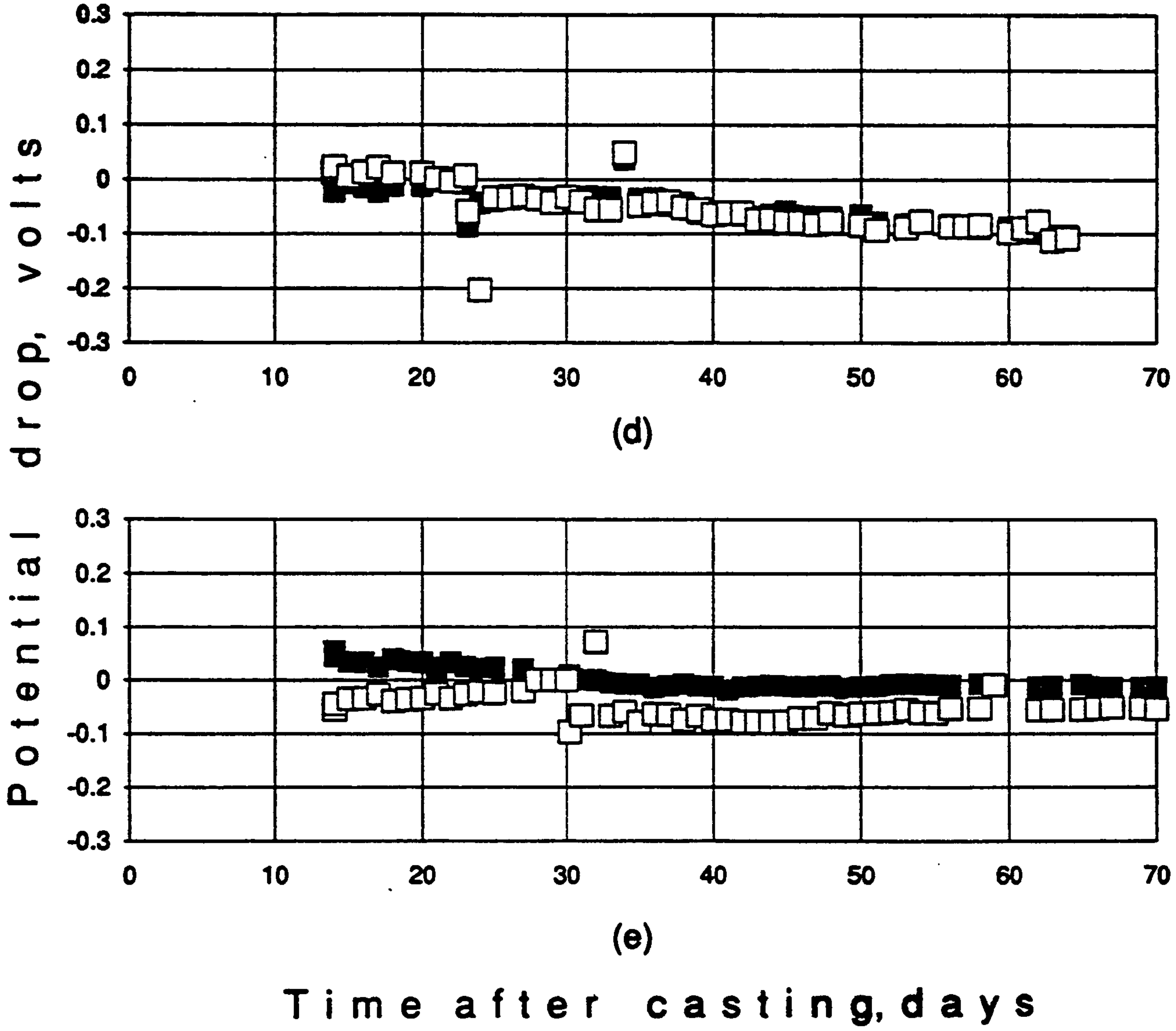


Figure B-12. (continued) Potential drop across 100,000 ohm resistor versus time for macrocells. NaCl molal ion concentrations: (a) 6.4 *m*, (b) 3.2 *m*, (c) 1.6 *m*, (d) 0.8 m, and (e) 0.4 *m*.

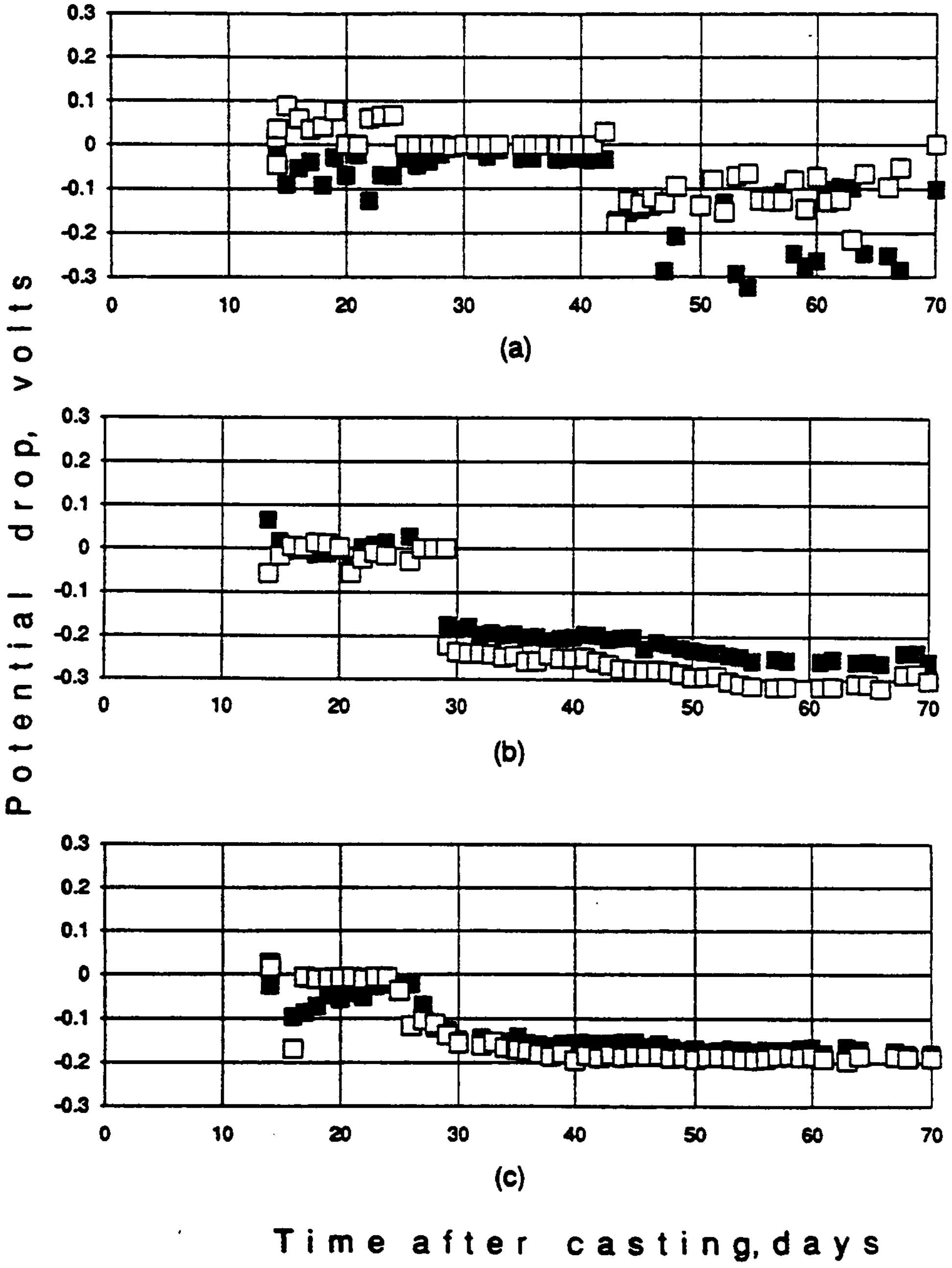


Figure B-13. Potential drop across 100,000 ohm resistor versus time for macrocells. $CaCl_2$ molal ion concentrations: (a) 6.4 *m*, (b) 3.2 *m*, (c) 1.6 *m*, (d) 0.8 *m*, and (e) 0.4 *m*.

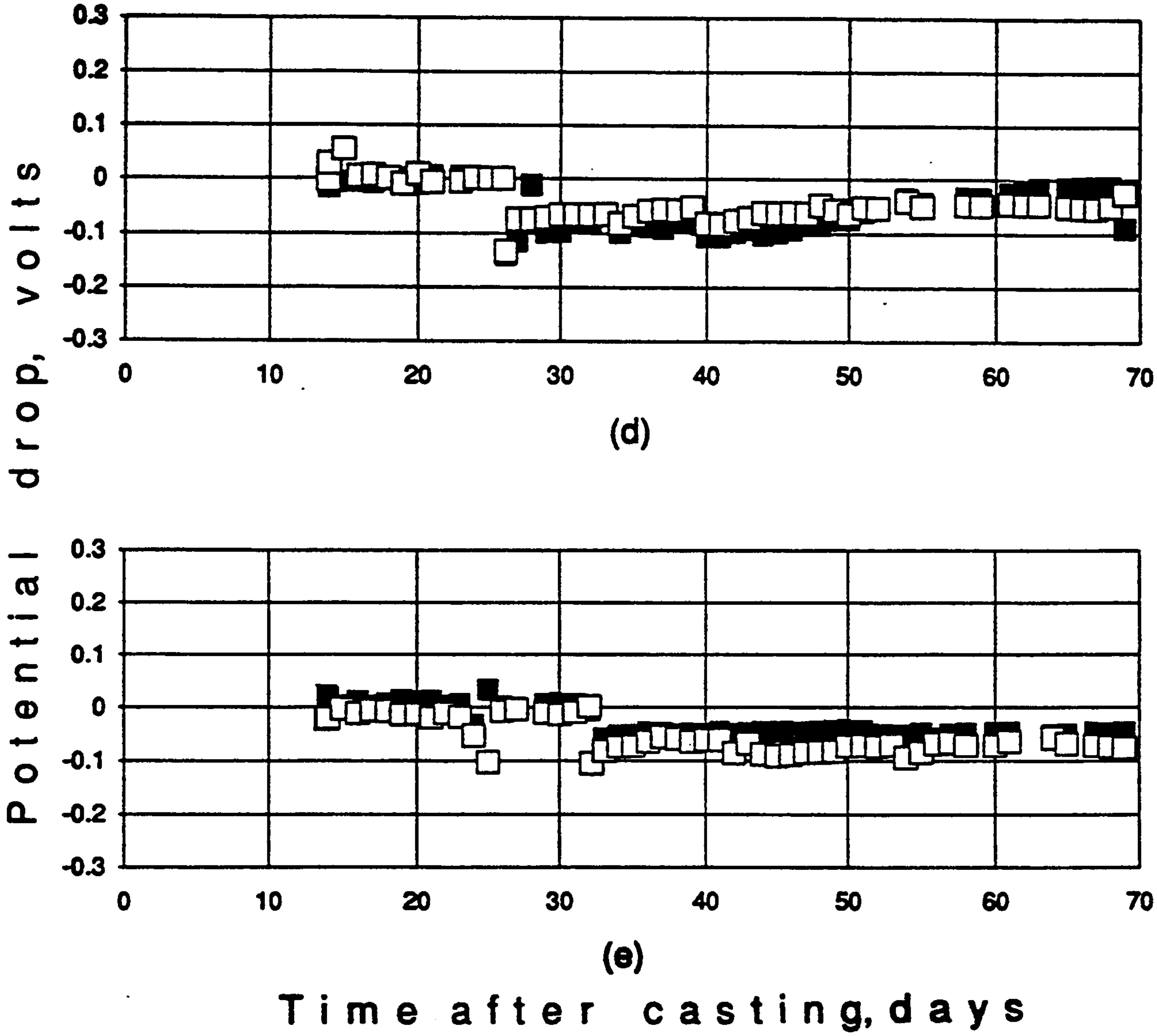


Figure B-13. (continued) Potential drop across 100,000 ohm resistor versus time for macrocells. $CaCl_2$ molal ion concentrations: (a) 6.4 *m*, (b) 3.2 *m*, (c) 1.6 *m*, (d) 0.8 *m*, and (e) 0.4 *m*.

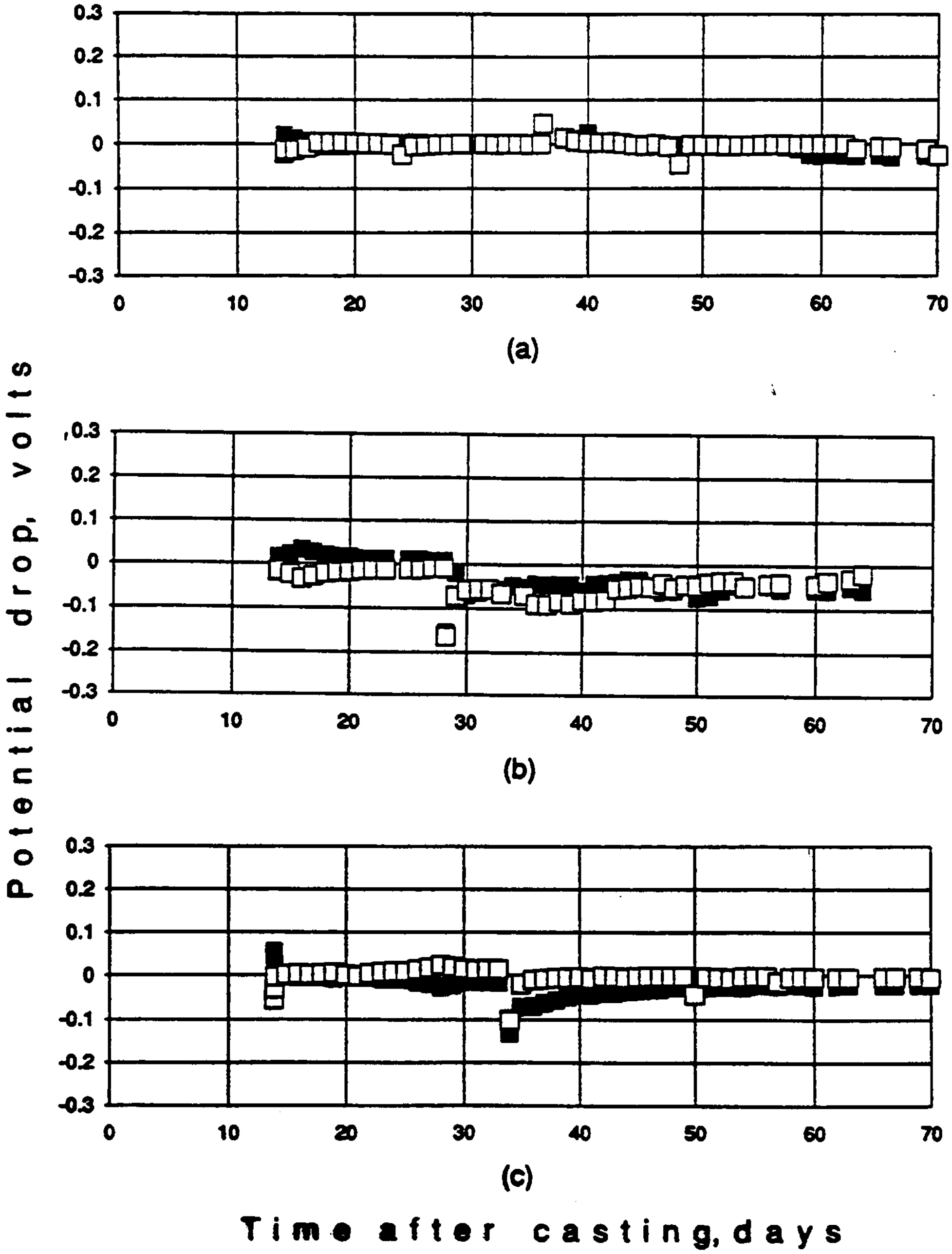
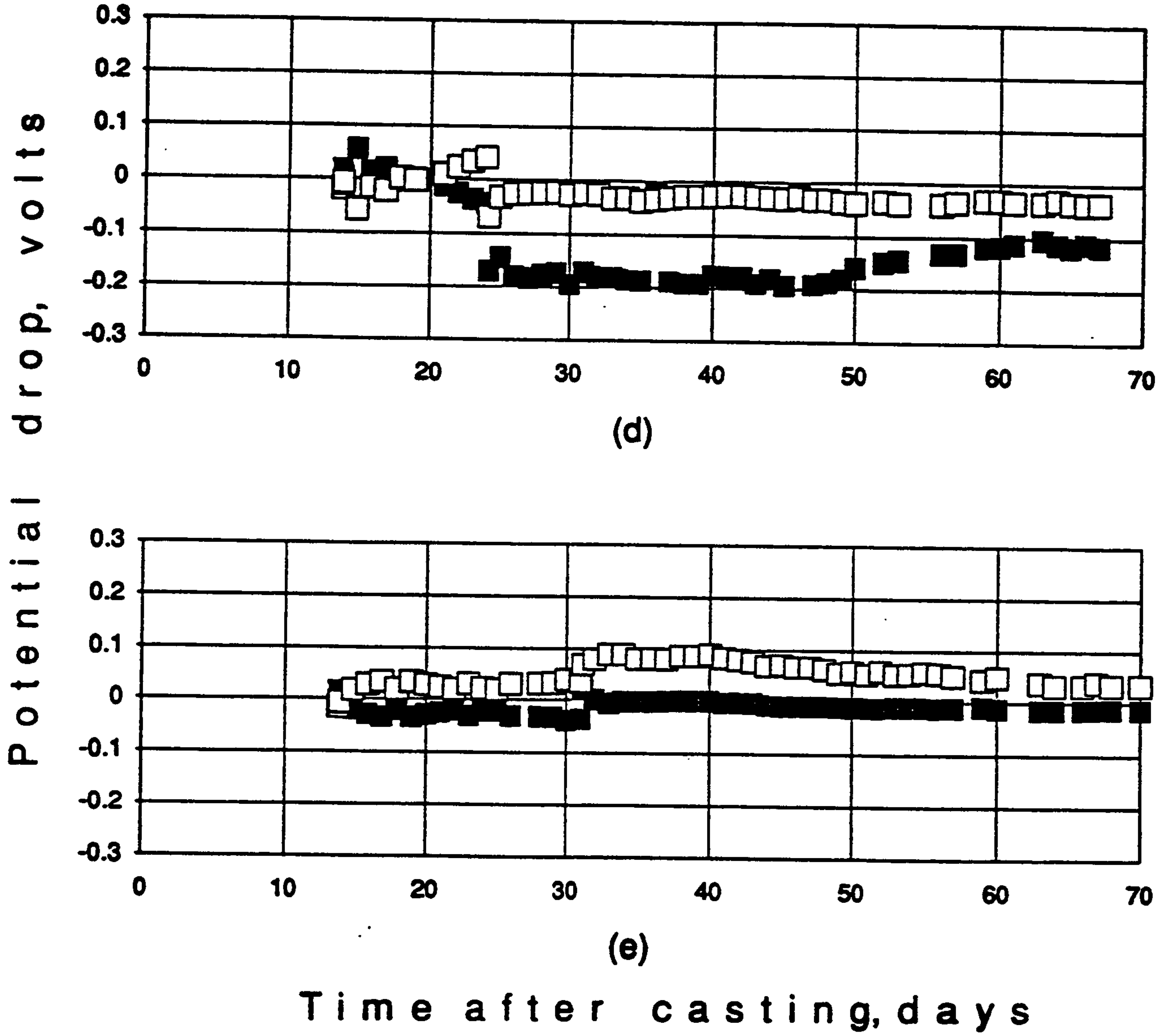


Figure B-14. Potential drop across 100,000 ohm resistor versus time for macrocells. CMA molal ion concentrations: (a) 6.4 *m*, (b) 3.2 *m*, (c) 1.6 *m*, (d) 0.8 *m*, and (e) 0.4 *m*.



(d)

(e)

Figure B-14. (continued) Potential drop across 100,000 ohm resistor versus time for macrocells. CMA molal ion concentrations: (a) 6.4 *m*, (b) 3.2 *m*, (c) 1.6 *m*, (d) 0.8 *m*, and (e) 0.4 *m*.

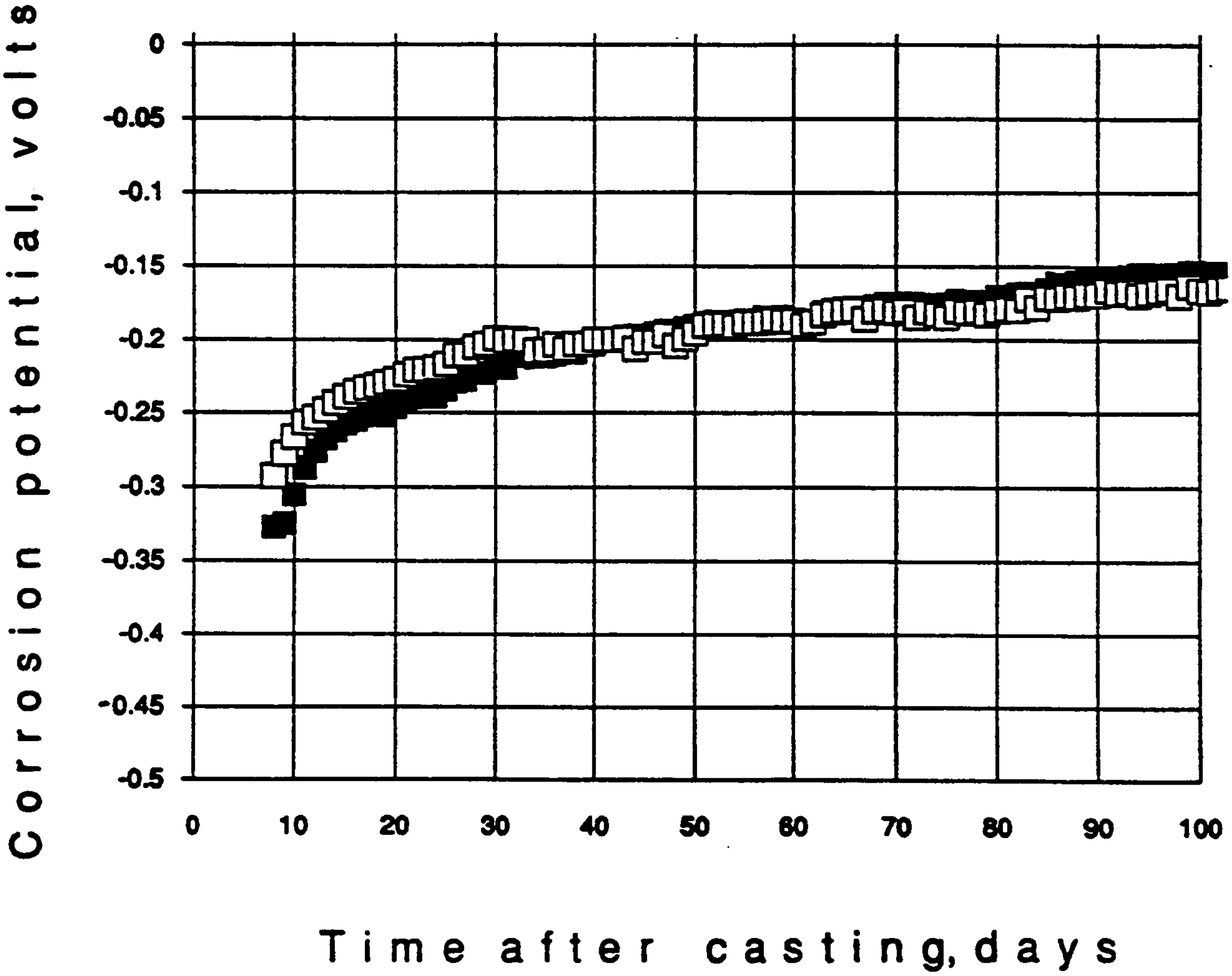


Figure B-15. Corrosion potential for specimen exposed to simulated pore solution.

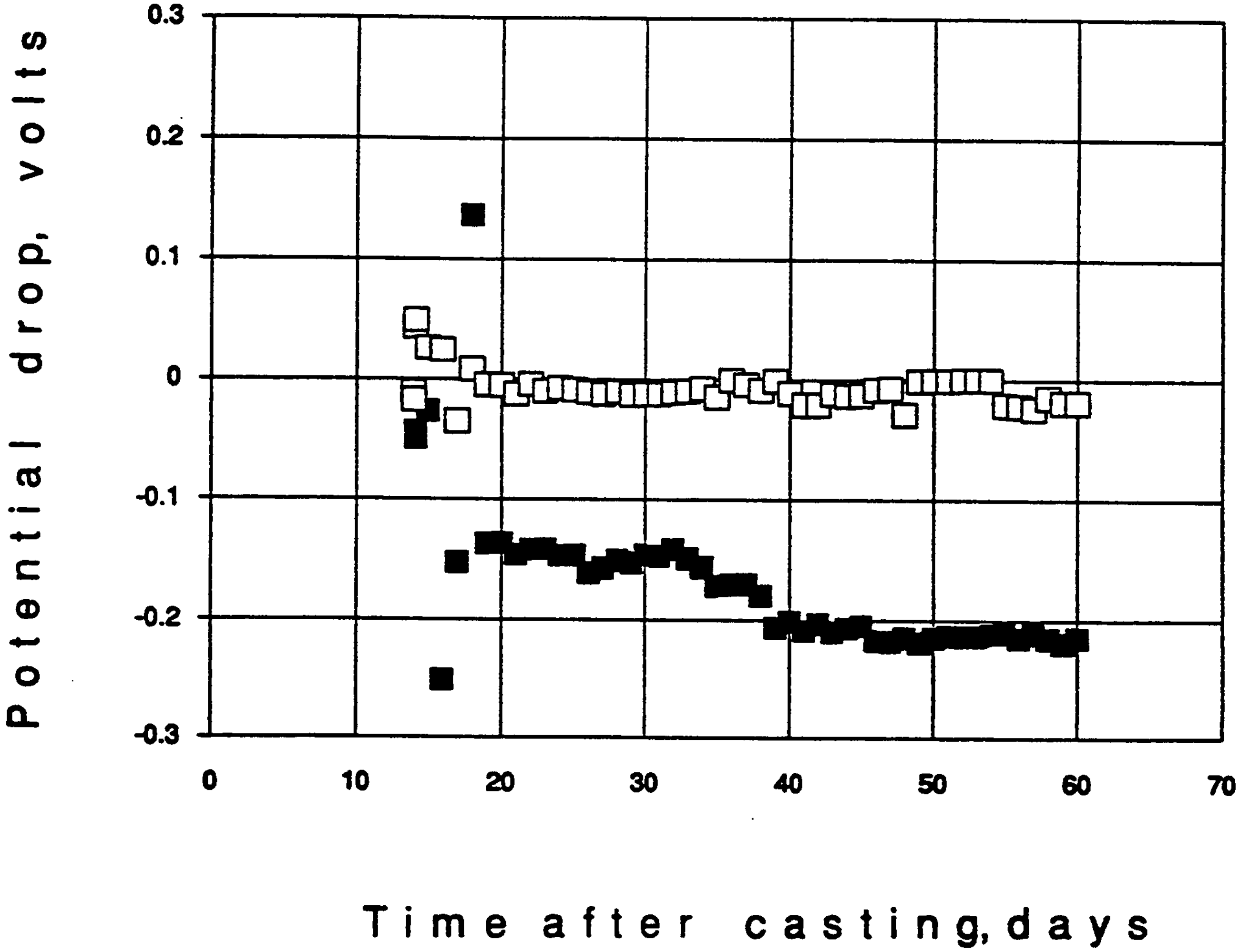


Figure B-16. Potential drop for specimen exposed to 6.4 *m* ion concentration of $CaCl_2$ in simulated pore solution.

Appendix C

Ecological Effects

- **Part 1—Ecological Effects Testing**
- **Part 2—A Simplified Flow-through System for Acute and Chronic Effects Testing**
- **Part 3—Experimental Test Data**

Part 1

Ecological Effects Testing

1.1 Introduction

A description of ecological effects testing within the various regulatory branches of EPA is presented in this section. In general, ecological effects testing is more common for the aquatic environment, for it is here that many chemicals are released or move to and accumulate. Tests used for either terrestrial or aquatic organisms are available in standard protocols, where they are outlined in detailed steps, or in guidance documents where only the general procedures are given; the specific details are left to the investigator to develop and secure approval from EPA before use. Most tests, aquatic or terrestrial, are single-species exposures to the chemical for varying periods of time in the laboratory. Acute toxicity tests measure the immediate lethal effects for a 24-, 48-, or 96-hr period, expressing the results as the LC_{50} (lethal concentration)—the concentration causing 50% mortality in the test species. Results are expressed as the EC_{50} (median effective concentration) when death is not readily detected even when occurring. Other measures of effects, such as reduced growth, are also used.

Chronic toxicity tests expose individuals of a test species to sublethal concentrations of the chemical for a longer time, one week or more. Over periods of several weeks or longer a greater portion of an organism's life cycle is exposed. This exposure has the potential to allow observation of effects on yearly growth and development, maturation, reproduction, and viability of the offspring, depending on the specific test, organism, and duration. More recently there has been increased interest from EPA to incorporate multispecies toxicity testing into the ecological effects testing process. Such tests employ a mixed assemblage of species representing aquatic or terrestrial food chains housed in laboratory enclosures or in field enclosures to include some natural prevailing conditions. Whole ecosystem tests have most recently been incorporated under FIFRA for pesticide testing and involve the use of

0.1 acre experimental ponds receiving various levels of a chemical after allowing time for natural food chains to develop. This test can be one year in duration and employs at least 12 experimental ponds.

Protocols or guidance documents for this entire range of testing are available and include some of the following: Environmental Protection Agency, 1981, Environmental Effects Test Guidelines--Part One and Part Two, EPA/560/6-82/002; Peltier and Weber, 1985, Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms, EPA/600/4-85/013; Standard Practice for Conducting Acute Toxicity Tests with Fishes, Macroinvertebrates, and Amphibians, ASTM E 729-80; Weber et al., 1989, Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms (2nd ed.), EPA/600/4-89/001; Rubenstein et al., 1975, Test Methods for Assessing the Effects of Chemicals on Plants, EPA/560/5-75/008; Cairns, 1986, Community Toxicity Testing, ASTM STP 920; Touart, 1988, Aquatic Mesocosm Test to Support Pesticide Registration, EPA/540/09-88/035.

This effects testing can be employed for the entire range of chemical contaminant conditions in the environment. This incudes purposely added toxic chemicals (e.g., pesticides), some inadvertently toxic discarded chemicals (e.g., industrial effluents), and chemicals we cause the release of or formation from natural substances due to our activities (e.g., increased turbidity from soil erosion due to certain farming practices; increased acid precipitation formed from the release of certain gaseous wastes). In some ways society's use of pesticides is comparable with that of road deicers. Although the deicer chemicals are not purposely toxic to particular organisms, their introduction into the environment is spread over large areas, and thus potential contact with the environment and effects if the deicers are toxic are comparable with pesticide use. With this in mind, ecological effects testing for the pesticides will be reviewed in greater detail, with testing for the effects of other types of chemicals described only briefly at the end.

1.2 Ecological Effects Testing for Pesticides

The EPA had developed a series of tests for the ecological risk assessment of pesticides for wildlife and aquatic organisms. They are presented here in only outline form to provide the reader with the extent and variety of testing possible for a given chemical. Details can be found in the appropriate EPA and ASTM documents, some of which were listed in the previous section. Some categories of testing contain more than one specific type of test, and new tests targeting organisms other than those listed here are in use or are being considered for use. Be aware that EPA follows a "tiered" approach, which means that testing begins at an initial level, and, depending on the test results and other information on the chemical and its use, testing may proceed to various levels through the full compliment of tests. The tiered approach will be discussed more specifically for aquatic ecological effects testing, which for deicers will be emphasized in this report for reasons also discussed later. Tiered series of tests for environmental fate of the chemical (including the EEC determination) and for toxicology data requirements (partial predictors of human effects) are also required depending on the nature and use of the chemical. Further consideration of these types of tests are not considered in this report. The following list is a summary of tests for aquatic and terrestrial organisms.

Avian and Mammalian Testing
- Avian oral LD_{50}, lethal dose (mallard or bobwhite)
- Avian dietary LC_{50}, lethal concentration (mallard and bobwhite)
- Wild mammal toxicity
- Avian reproduction (preferably mallard and bobwhite)
- Simulated and actual field testing--mammals and birds

Aquatic Organism Testing
- Freshwater fish LC_{50} (preferably rainbow trout and bluegill, sometimes fathead minnow)
- Acute LC_{50} freshwater invertebrates (preferably *Daphnia*)
- Acute LC_{50} estuarine and marine organisms
- Fish early life stage (often fathead minnow) and aquatic invertebrate life cycle
- Fish full life cycle (often fathead minnow)
- Aquatic organism accumulation
- Simulated or actual field testing for aquatic organisms

What now follows is a more detailed summary of the aquatic ecological effects tests arranged in their tiers with some consideration of the criteria used by EPA to trigger the need for higher level tests. As stated earlier, ecological risk assessment, regardless of the chemical, has been more common for the aquatic environment and, as will be discussed later, this is likely also to be the case for deicer chemicals.

Tier 1 Aquatic Testing Requirements for Pesticides
- 96-hr LC_{50} test--cold water fish (rainbow trout)
- 96-hr LC_{50} test--warm water fish (bluegill)
- 48-hr (or 96-hr) LC_{50} test--freshwater aquatic invertebrate
- 96-hr EC_{50} (effects other than death, median effective concentration)

In most cases a pesticide being considered for market will automatically receive the full compliment of Tier 1 testing. The criteria currently used by EPA to trigger Tier 2 testing for a pesticide include (1) toxicity at 1 ppm or less of the chemical, (2) continuous or recurrent exposure of wildlife, (3) EEC equal to or greater than 0.01 LC_{50}, or (4) EEC equal to or less than LC_{50} and any of the following: reproductive effects, physicochemical effects including cumulative effects, or half-life greater than 4 days.

Tier 2 Aquatic Testing Requirements for Pesticides
  Fish early life-stage toxicity
  Aquatic invertebrate life cycle
  Aquatic plant growth (algae)
  96-hr LC_{50} test--estuarine/marine fish
  96-hr LC_{50} test--estuarine/marine crustacean
  48-hr EC_{50} test--bivalve embryo/larvae
  or 96-hr EC50 test--bivalve shell deposition

The criteria currently used by EPA to trigger Tier 3 testing are more complicated than described for Tier 2 triggering. Generally this involves a combination of Tier 1 and 2 results, with the latter also having specific pass/fail criteria, including a relationship with the EEC. Some level of Tier 2 testing is common for most chemicals.

Tier 3 Aquatic Testing Requirements for Pesticides
  Fish life cycle test
  Aquatic bioaccumulation (bioavailability)

Tier 3 testing is generally reserved for chemicals demonstrated to only be marginally safe following the pass/fail criteria.

Tier 4 Aquatic Testing Requirements for Pesticides

Aquatic mesocosm test (experimental ponds or in situ enclosures preferably at least 0.1 acre in size and at least 12 in number.

Tier 4 testing is triggered by the remaining presumption of unacceptable ecological risks after completion of the lower tier testing. These presumptions of risk are based on comparisons between the singe-species laboratory data (i.e., lower tier test results) and the exposure information, including the EEC. Such chemicals are presumed hazardous to aquatic organisms and enter the remaining risk/benefit process in this evaluation condition unless the demonstrated laboratory effects are ameliorated in the whole ecosystem test which is then taken into account by the risk/benefit process.

1.3 Ecological Effects Testing for Some Other Chemicals

Ecological effects testing under the Clean Water Act, the Toxic Substances Control Act and elsewhere is generally less extensive than the testing described for pesticides under the Federal Insecticide, Fungicide, and Rodenticide Act. The tests are generally identical and can be required through a range of tests comparable to Tiers 1, 2, and 3 described previously. The minimum testing requirements suggested by EPA and sometimes altered at the state level include a series of acute tests comparable to Tier 1 for pesticides. EPA recommends acute toxicity data (e.g., LC_{50}) from freshwater animals in at least eight different families with the following included:

Salmonidae (e.g., trout)
Second family in Osteichthyes (e.g., fathead minnow, bluegill)
Third family in Chordata (e.g., fish, amphibians, birds, mammals)
Planktonic Crustacean (e.g., *Daphnia*)
Benthic Crustacean (e.g., amphipods)
Insect (e.g., midge)
Family not in Arthropoda or Chordata (e.g., worms)
Family in any order of Insecta (e.g., mayflies) or any phylum not already represented (e.g., mollusks)

1.4 Estimated Environmental Concentration Determinations Within EPA

As discussed earlier, in the ecological risk assessment process, the estimated environmental concentration (EEC) of a contaminant chemical (e.g., pesticide) is compared to the effect level (i.e., result of ecological effects test) in a quotient method. The EEC for a particular pesticide in surface waters as the result of runoff is the concentration expected to occur in the environment given particular characteristics of the chemical, application rates and other characteristics of application, and environmental conditions affecting runoff of the chemical and its persistence. It is readily noted that many of the same conditions affect the presence of deicer chemicals in a particular environment. Thus it is logical that their EECs could be determined in much the same manner. The following text contains a brief discussion of the general approach used by EPA to determine the EEC for a pesticide in surface waters as the result of runoff. This will serve as a general guideline for determinations with deicer chemicals; however, specific determinations for particular deicer chemicals is beyond the objectives of this subtask.

Generally, a two-tiered approach is followed for the determination of the EEC for a pesticide. The first tier as described by the Office of Pesticide Programs (OPP) (which contains the Ecological Effects Branch, EEB, referred to earlier), which oversees the pesticide registration process within EPA, is a first or rough-cut estimate referred to as a back-of-the-envelope (BOE) calculation. The BOE calculation sets an upper limit on the EEC for the chemical, taking into account only the application rate (i.e., amount applied per area) and solubility. Comparable information would exist for a particular deicer use, and this Tier 1 determination could be made. The specific methodology for the BOE calculation is available from the OPP. The BOE calculations are made routinely for most pesticide chemicals. A Tier 2 determination is pursued if the BOE EEC is greater than 0.01 LC_{50} (acute response from ecological effects test) or greater than the concentration causing a chronic effect, both criteria based on the responses of the most sensitive test species.

The Tier 2 determination of the EEC is a more accurate calculation using computer simulation modeling of runoff and water quality. The former is handled by two models, the Pesticide Root Zone Model (PRZM) and the Basin Scale Water Quality Model (SWRRB-WQ), and the latter by the Exposure Assessment Model (EXAMS). Basically, pesticide loading is generated from the runoff models and is used as the mass/area input loading to the water quality model. The parallels with possible deicer EEC determinations are also apparent for this tier and can be seen further with the physicochemical processes used as inputs to the models. The runoff models consider the following: rainfall, runoff/erosion, evapotranspiration, subsurface flow, percolation, soil-water partitioning, field dissipation rate (multiple nondegradative and degradative pathways such as microbial decay, hydrolysis, photolysis, volatilization, as well as transport through drift, runoff, and leaching), foliar decay, foliar washoff, solubility, and volatility. The water quality models consider the following: advection, dispersion, hydrolysis, photolysis, microbial decay, volatilization, solubility, and partitioning. The runoff models produce as output the pesticide loading as mass/area (e.g., kg/ha) as chemical dissolved and chemical sediment associated. Again, adapting such models to deicer chemicals in the environment is possible, and thus EEC determinations could become routine and then be incorporated into an ecological risk assessment process for these chemicals.

Part 2

A Simplified Flow-through System for Acute and Chronic Effects Testing

Continuous flow systems can provide, particularly for stream organisms, more natural culture or maintenance conditions and may better simulate stream toxicant exposure. Such systems can also enhance the success of maintaining and testing locally collected organisms which are more representative of local fauna and conditions but not available from supply houses. The simplest such system was designed and constructed to serve such purposes, based on considerable experience with larger and more elaborate (both in design and operation) systems used with stream plants, insects, and fish and maintained in the field, in greenhouses, and in the laboratory.

The detailed design is presented in the two accompanying figures (C-1 and C-2) which will provide an appropriate layout to follow for construction. Some further description and instruction needed for building and operating such a system follows.

The entire functional unit as shown in Figure C-1 consists of a Plexiglas [3/16 in. (4.5 mm) thickness] flow chamber (50 cm x 33.5 cm x 20 cm) subdivided into six individual flow channels (34.5 m x 5 cm x 15 cm) and a pump inserted in a 0.75 in. flexible plastic tube entering one end of the chamber and exiting from the other. The main structure of the chamber is bonded together with Plexiglas fusing glue, but the walls separating the individual channels are held (not permanently) with silicone adhesive so certain walls can be removed to form fewer wider channels to accommodate more or larger organisms. For example, the basic six unit chamber can be easily altered to three 10.45-cm wide channels, two 15.9-cm wide channels, or one 32-cm wide channel. Flow rate depends on the rate through the pump (adjustable with an adjustable pump) and the hole size (shown as 2.25-cm diameter in Figure C-2) between the common inflow section and the individual channels. Note that

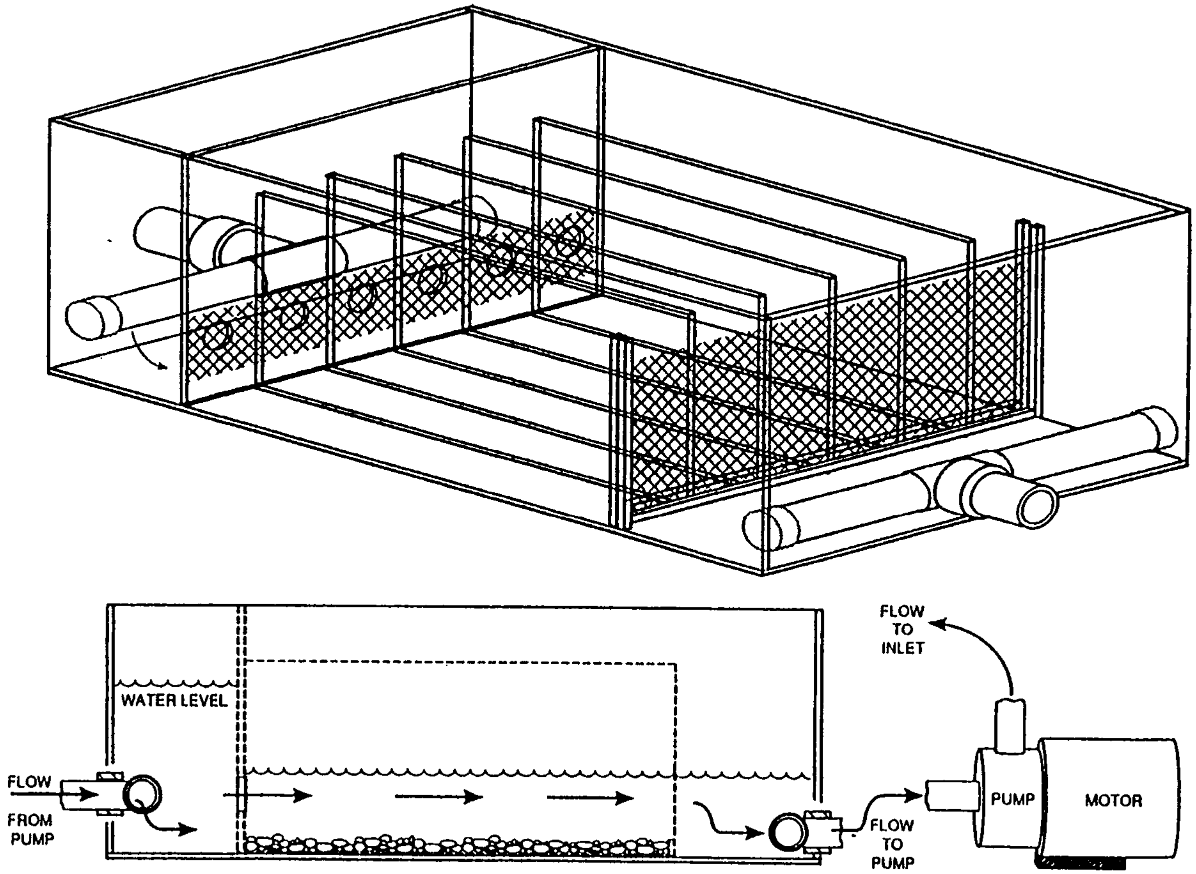


Figure C-1. Overview of the flow-through system.

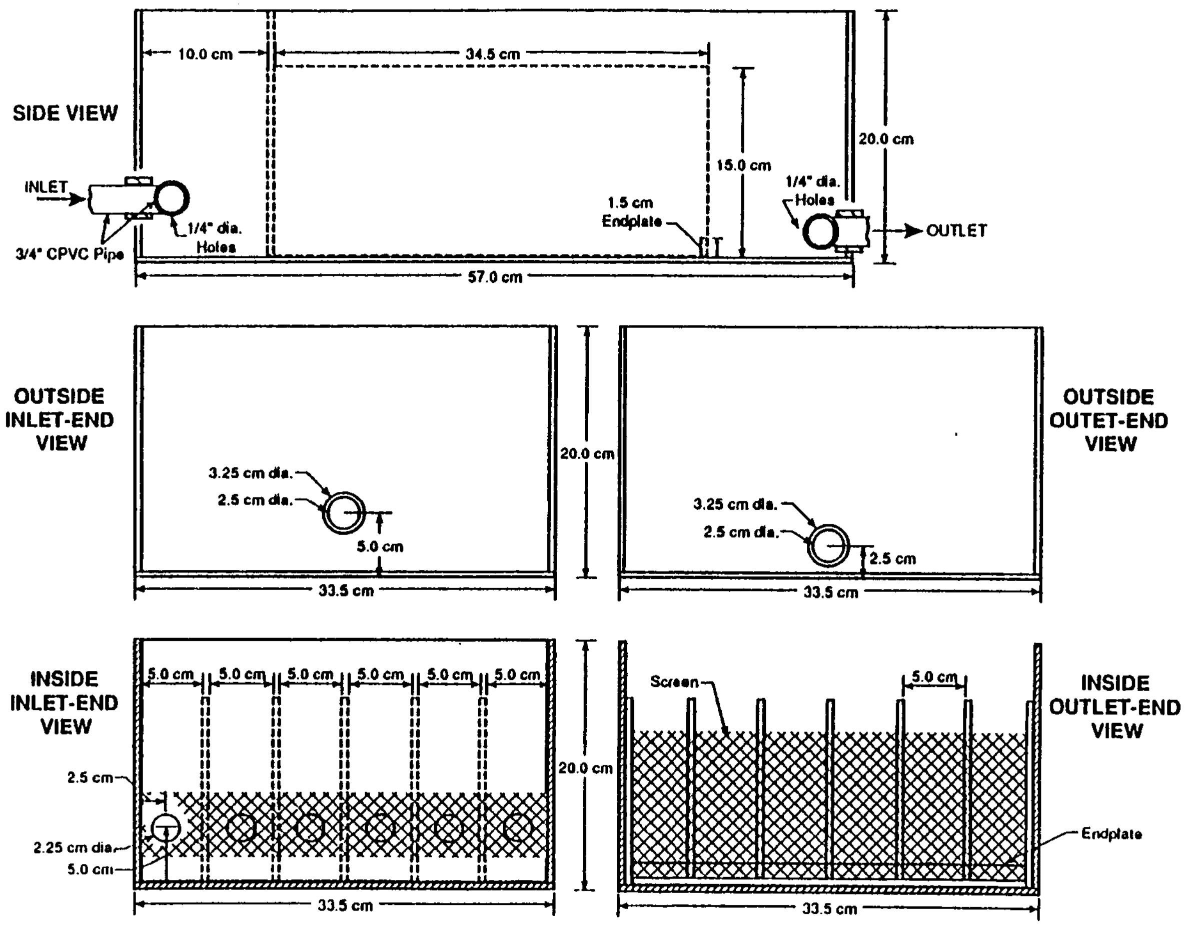


Figure C-2. Lateral and inlet views of flow-through system.

these possible adjustments will create a balanced depth in the common inflow section versus the channel depth. This is also influenced (thus flow as well) by the number and size of the holes (six 0.25 in. holes in each in this particular version) in the horizontal flow pipe extending across the width of the common inflow section and common outflow section. The pump shown (others are possible) is a Little Giant 29038 Model No. 3-MD-SC (Tecumseh Products Company, 3810 North Tulsa, Oklahoma). It is advisable to use a pump which employs a magnetic coupling between the motor and the impeller pumping the water that eliminates the conventional shaft seal (generally containing oil) and the possibility of leakage and contamination of the water with oil or other lubricant. A wide range of flow rates through the channels is possible depending on the adjustments discussed previously within the range of a few centimeters per second to over 50 cm/sec. The larger systems also operate within this range, which is acceptable for the purposes of this system.

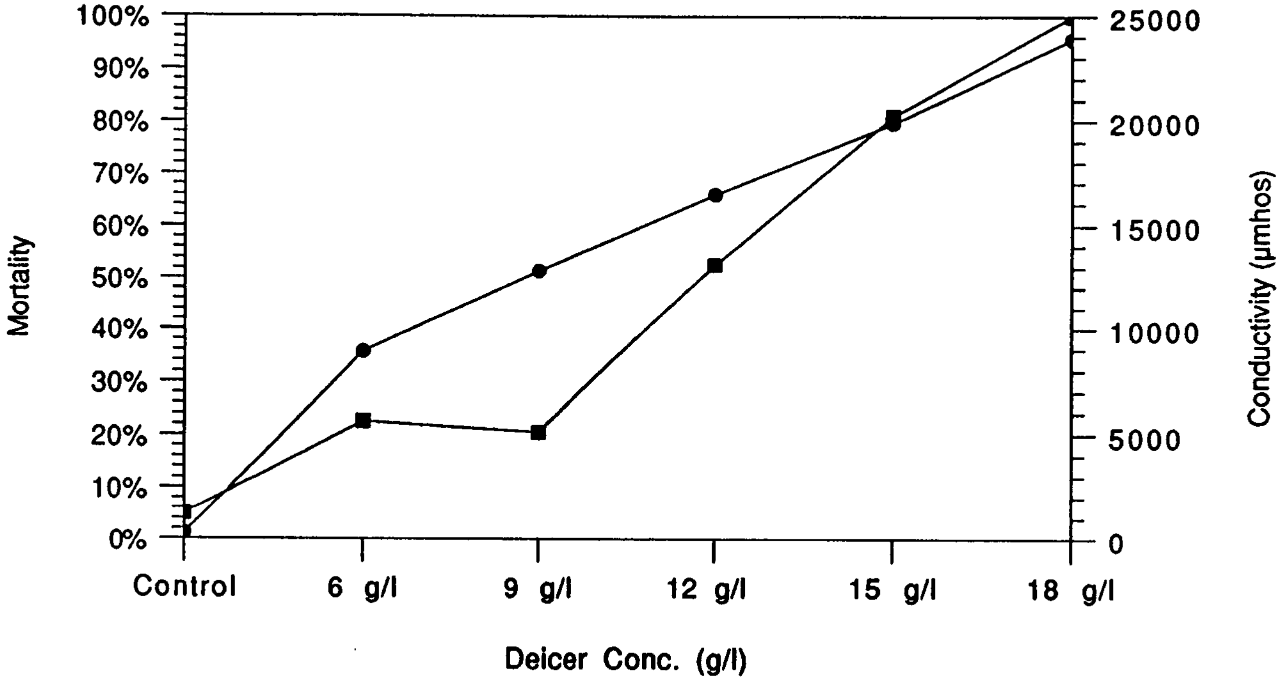
In operating this system for various uses, in one chamber with its six (3, 2, 1) channels, the same water treatment is experienced by each channel thus they serve as replicates. Different treatments are provided with other duplicate chambers.

Temperature control of the system is generally desirable particularly since pumps themselves may heat the water to various extents depending on the type of pump. One way to accomplish this is to operate the chambers in a controlled temperature chamber of the walk-in size or double-wide (approximately double-wide refrigerator size) reach-in size. Pumps can be placed on the outside of the growth chamber to reduce the heat load. Another way to cool, and perhaps more readily available to some highway departments, is to insert a cooler of some sort in the flow line between the pump and the chamber on either side of the pump. The cooler should not come in direct contact (e.g., test water flowing directly over cooling coils) with the test water because of possible contamination. One relatively simple method of cooling is to create a long coil of the 0.75 in. tubing on one side of the pump to be immersed into a container (20 to 40 gal, insulated) of ice water. By keeping a steady enough input of ice into the container so that its temperature remains constant at about 32°F (0°C) and then adjusting the length of the coil (thus contact with the coolant) the temperature of the channel water can be adjusted given the relatively constant heat input from the pump. The chambers should be housed in a room of relatively constant temperature. A more easily adjusted cooling system but more expensive and mechanically complex is possible using a thermostatically regulated cooler with its coil immersed in the cooling container. Heavy-duty coolers of this type are used for cooling large fish boxes, particularly in commercial fish rearing operations. Such coolers are available from Frigid Units, Inc. (3214 Sylvania Avenue, Toledo, Ohio).

The operation of this flow system with some locally collected insects (mostly mayflies, damselflies, and dragonflies) and fish (bluegill and various minnows and darters) was successful at maintaining these organisms over several weeks (no longer periods were attempted but are likely possible). Considering the maximum size of the organisms used in such a system, fish up to 4 cm in length adapted well to the smallest channels and larger fish to the wider channels, 6-, 8-, and 10-cm long in the three successively wider channels, respectively. The species of fish and insects, considering individual behavior and other requirements, is an important determining factor for the success of the system. Considerations like food provided and substrate (most often gravel bottom, 1- to 2-cm depth of 5- to 8-mm diameter stones) including larger stones for refuge are also important to suit the needs of particular species. For any species selected for testing, trial maintenance in the system is necessary before conducting a test with a chemical. This system can also be used to maintain organisms for a few days before use in static tests like those described earlier when aquarium maintenance is not as suitable. When attempting to adapt this flow system to the flow-through tests described by EPA in several of the documents cited in this report, it is important to carefully consider the requirements of each test to determine if they are adaptable to this system and still within the requirements set by EPA.

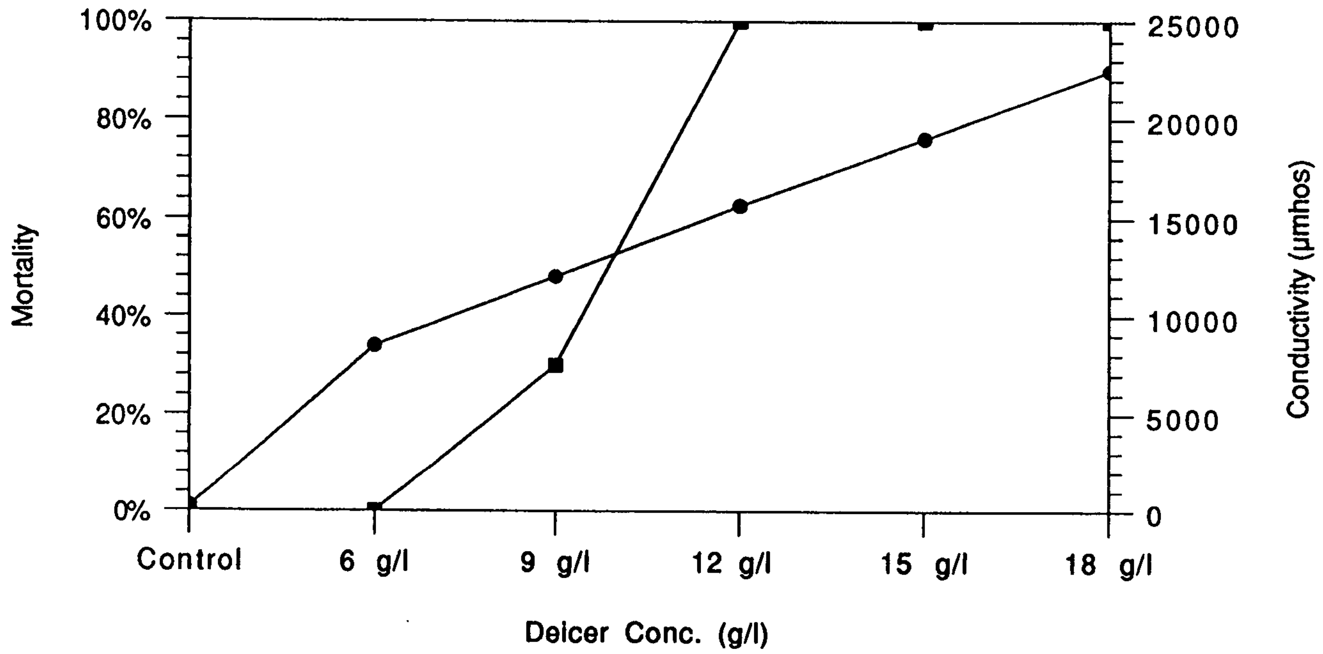
Part 3

Experimental Test Data



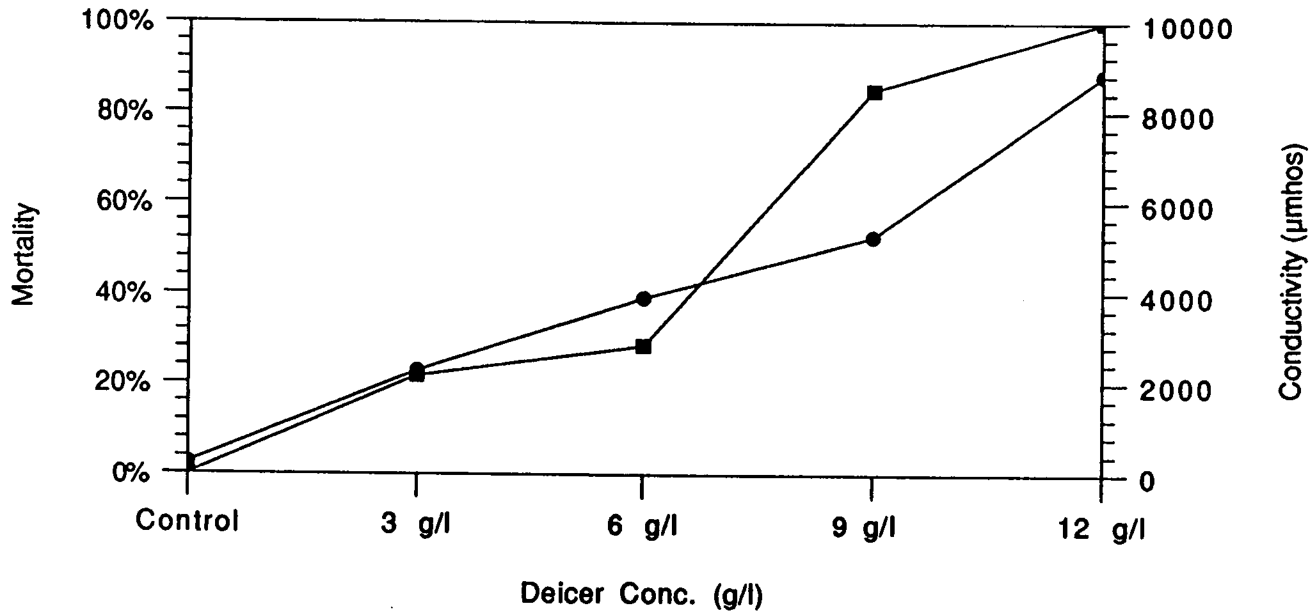
Deicer Conc. (g/l)	Control	6 g/l	9 g/l	12 g/l	15 g/l	18 g/l
Conductivity	287	8913	12825	16488	19913	23888
Mortality	5.0%	22.5%	20.5%	52.5%	81.0%	100.0%

Figure C-3. Results of $CaCl_2$ acute toxicity test for amphipods showing percent mortality (squares) and conductivity (circles).



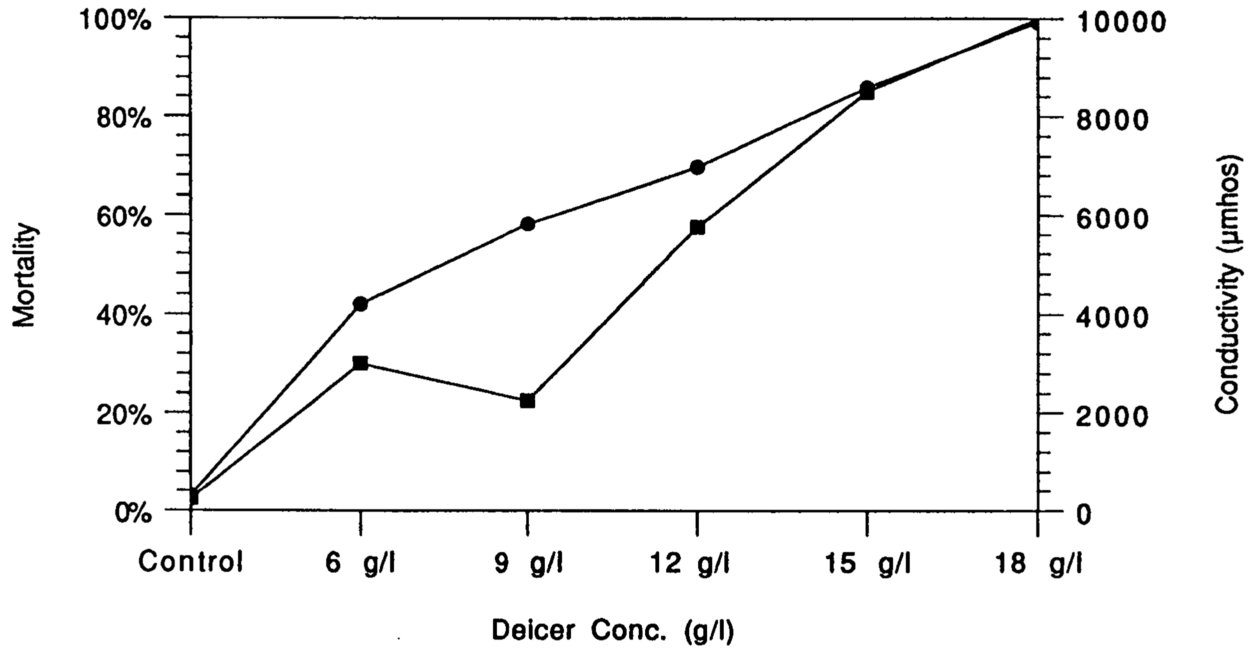
Deicer Conc. (g/l)	Control	6 g/l	9 g/l	12 g/l	15 g/l	18 g/l
Conductivity	253	8488	12013	15663	19013	22488
Mortality	0.0%	0.0%	30.0%	100.0%	100.0%	100.0%

Figure C-4. Results of $CaCl_2$ acute toxicity test for fathead minnows showing percent mortality (squares) and conductivity (circles).



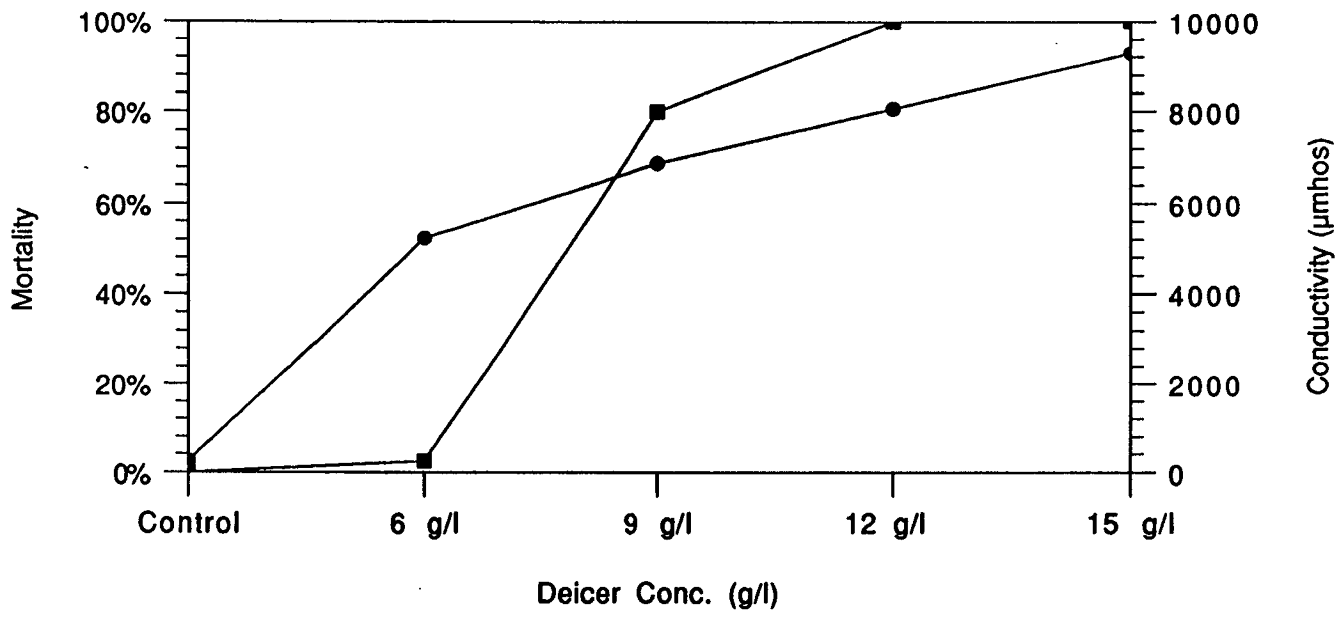
Deicer Conc. (g/l)	Control	3 g/l	6 g/l	9 g/l	12 g/l
Conductivity	253	2276	3904	5250	8813
Mortality	0.0%	20.0%	26.2%	78.6%	92.5%

Figure C-5. **Results of calcium magnesium acetate acute toxicity test for amphipods showing percent mortality (squares) and conductivity (circles).**



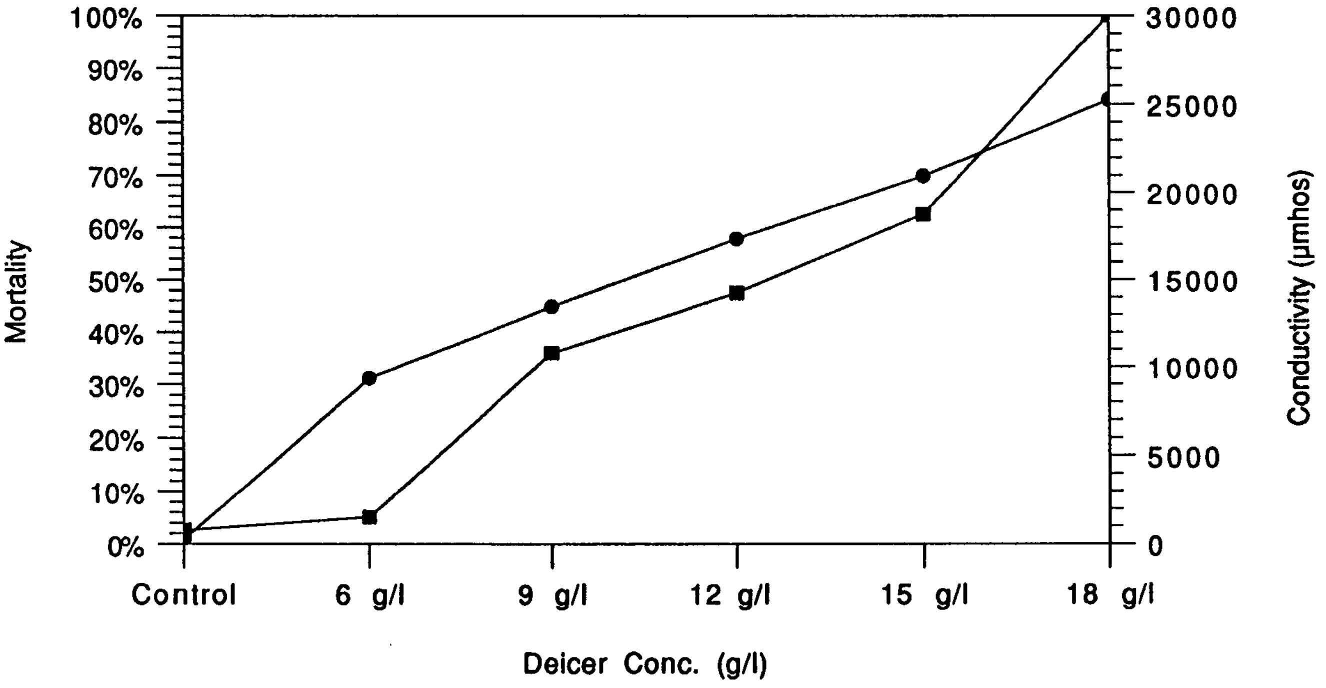
Deicer Conc. (g/l)	Control	6 g/l	9 g/l	12 g/l	15 g/l	18 g/l
Conductivity	320	4198	5813	6975	8588	9925
Mortality	2.5%	30.0%	22.5%	57.5%	85.0%	100.0%

Figure C-6. Results of calcium magnesium acetate acute toxicity test for mayflies showing percent mortality (squares) and conductivity (circles).



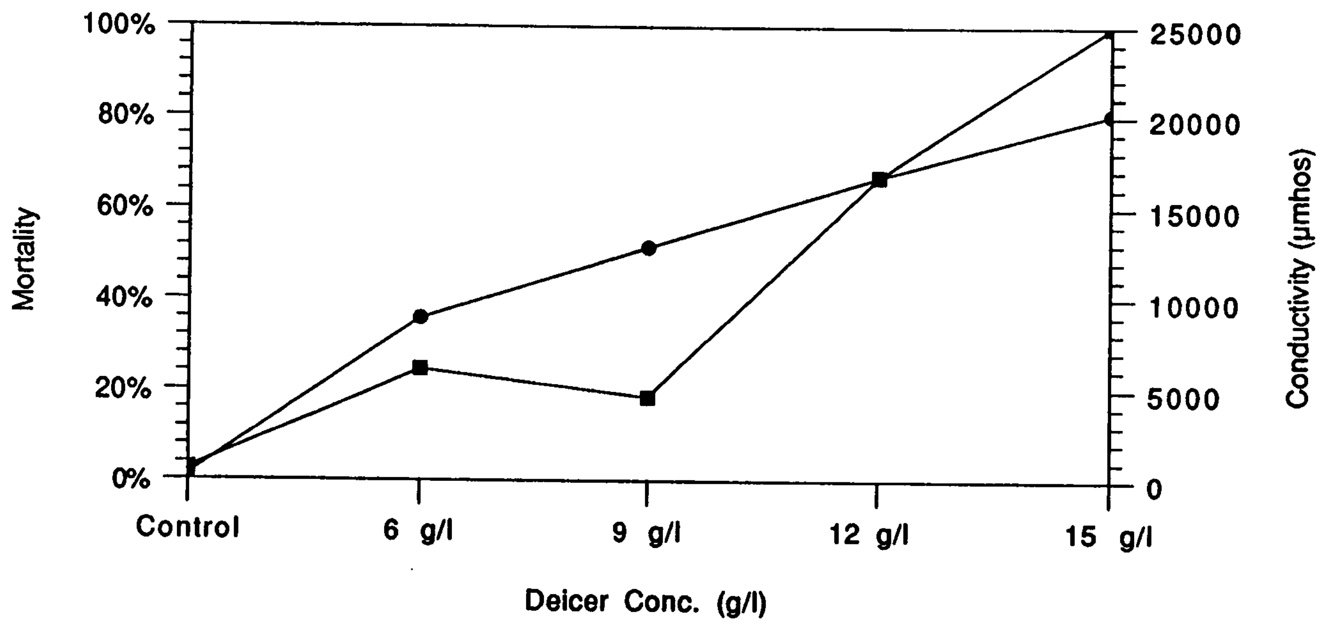
Deicer Conc. (g/l)	Control	6 g/l	9 g/l	12 g/l	15 g/l
Conductivity	250	5225	6888	8063	9288
Mortality	0.0%	2.5%	80.0%	100.0%	100.0%

Figure C-7. **Results of calcium magnesium acetate acute toxicity test for fathead minnows showing percent mortality (squares) and conductivity (circles).**



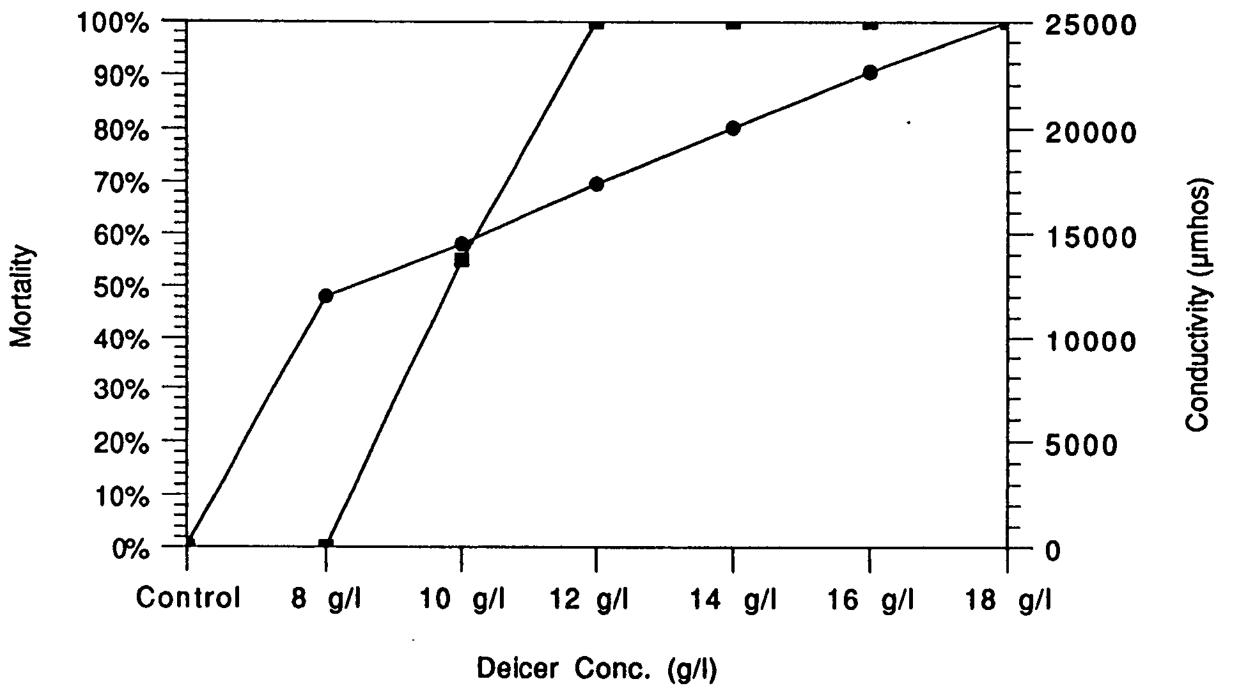
Deicer Conc. (g/l)	Control	6 g/l	9 g/l	12 g/l	15 g/l	18 g/l
Conductivity	278	9338	13463	17338	20963	25225
Mortality	2.6%	5.1%	35.9%	47.5%	62.5%	100.0%

Figure C-8. **Results of NaCl acute toxicity test for amphipods showing percent mortality (squares) and conductivity (circles).**



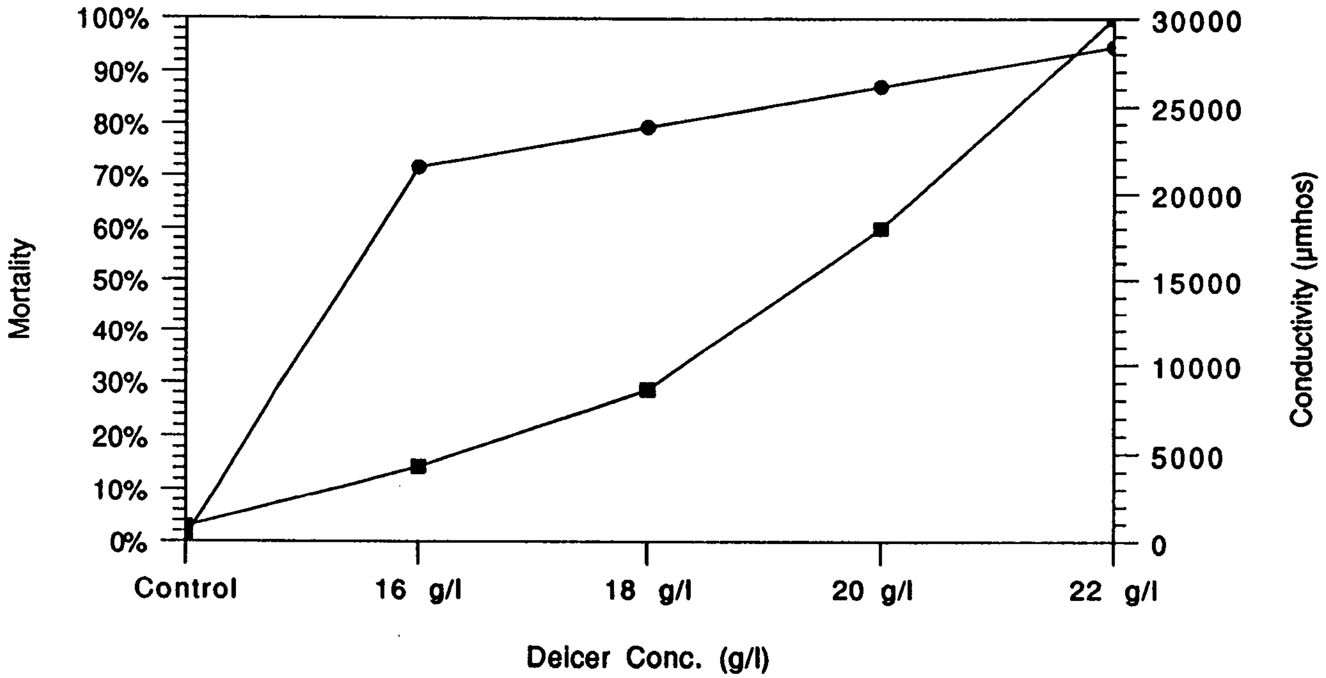
Deicer Conc. (g/l)	Control	6 g/l	9 g/l	12 g/l	15 g/l
Conductivity	322	8938	12875	16725	20138
Mortality	2.5%	23.1%	17.5%	63.4%	94.7%

Figure C-9. Results of NaCl acute toxicity test for mayflies showing percent mortality (squares) and conductivity (circles).



Deicer Conc. (g/l)	Control	8 g/l	10 g/l	12 g/l	14 g/l	16 g/l	18 g/l
Conductivity	148	12025	14513	17388	20063	22625	24988
Mortality	0.0%	0.0%	55.0%	100.0%	100.0%	100.0%	100.0%

Figure C-10. Results of NaCl acute toxicity test for fathead minnows showing percent mortality (squares) and conductivity (circles).



Deicer Conc. (g/l)	Control	16 g/l	18 g/l	20 g/l	22 g/l
Conductivity	251	21500	23825	26150	28400
Mortality	2.5%	12.5%	25.0%	52.5%	87.5%

Figure C-11. Results of NaCl acute toxicity test for feeder guppies showing percent mortality (squares) and conductivity (circles).

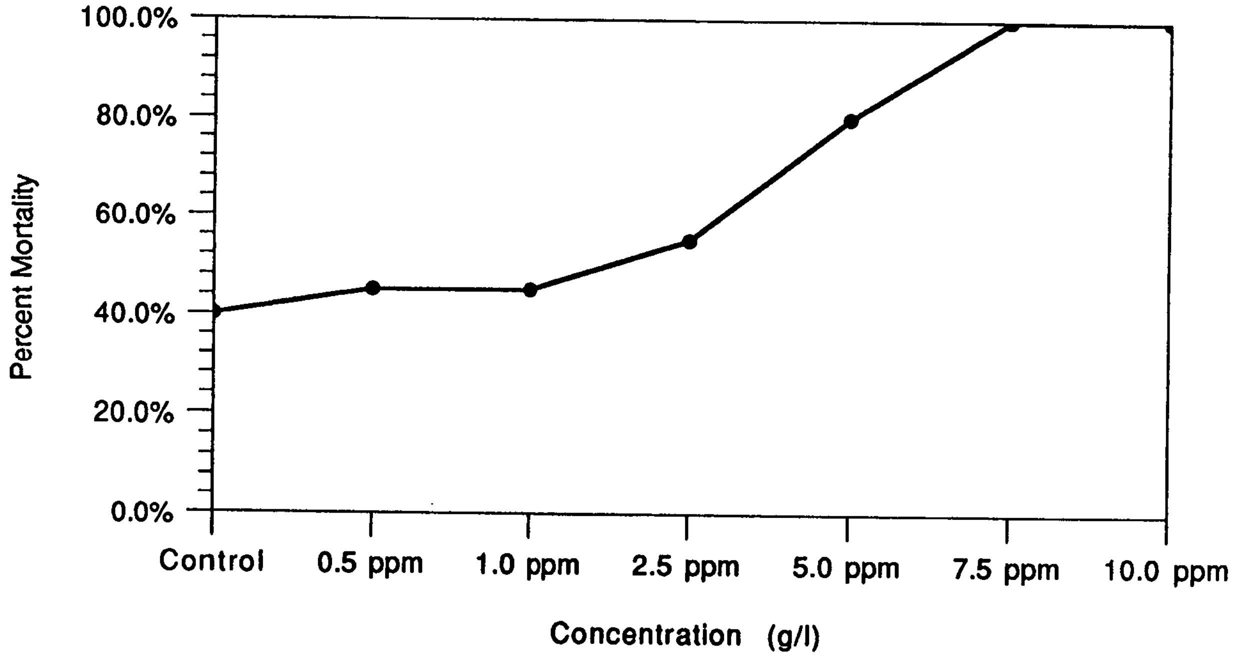


Figure C-12. Results of NaCl chronic toxicity test for fathead minnows showing percent mortality after 7 days.

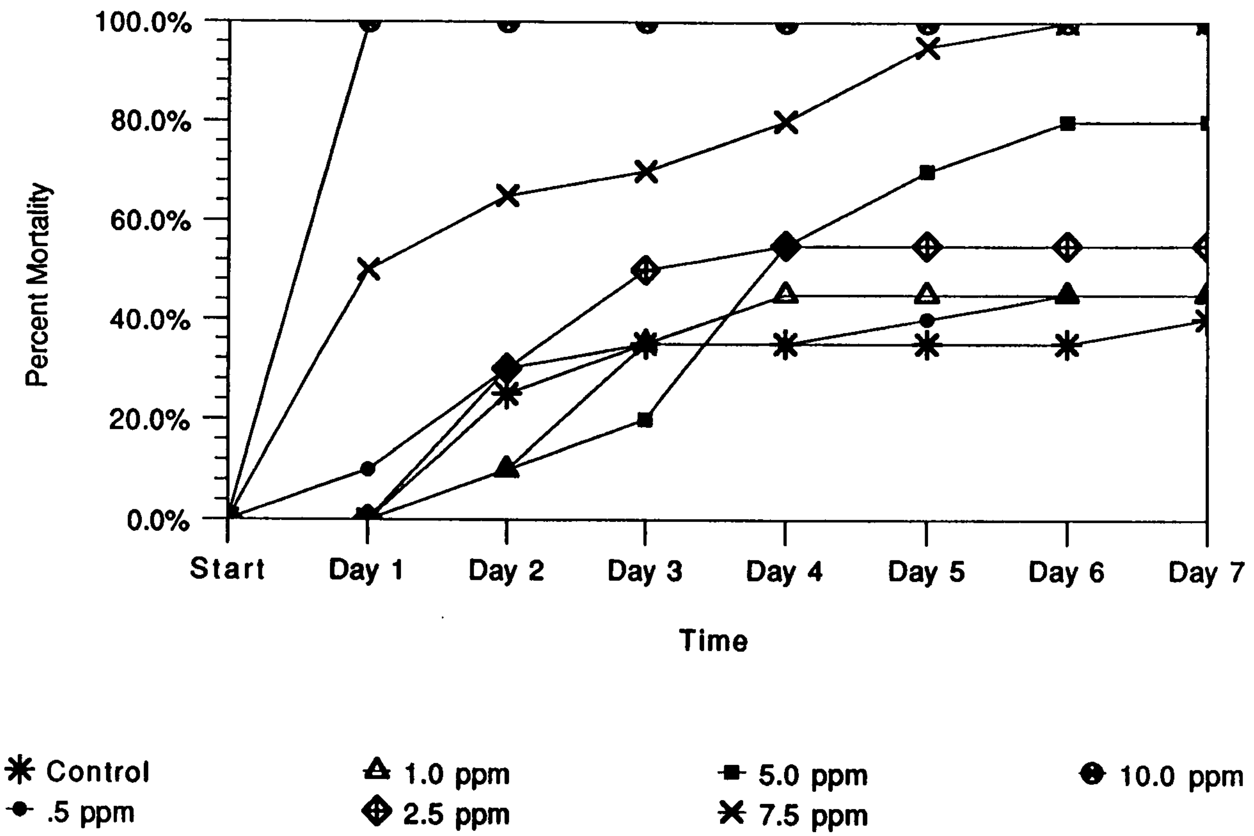
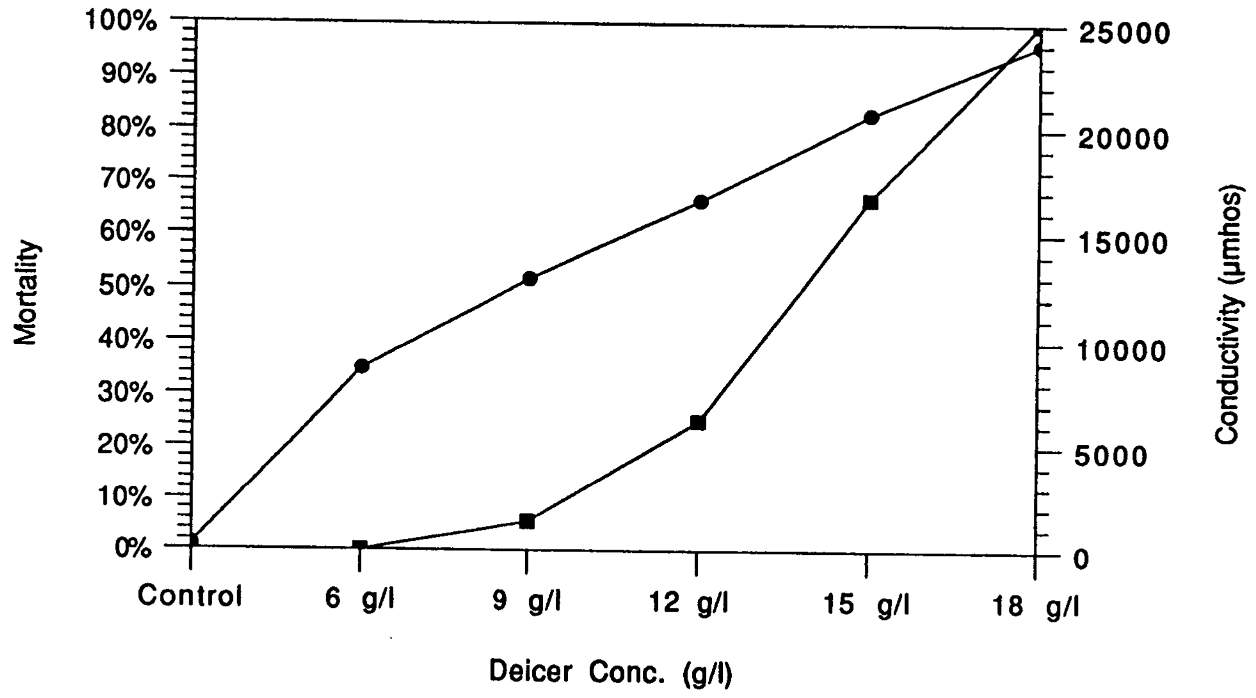
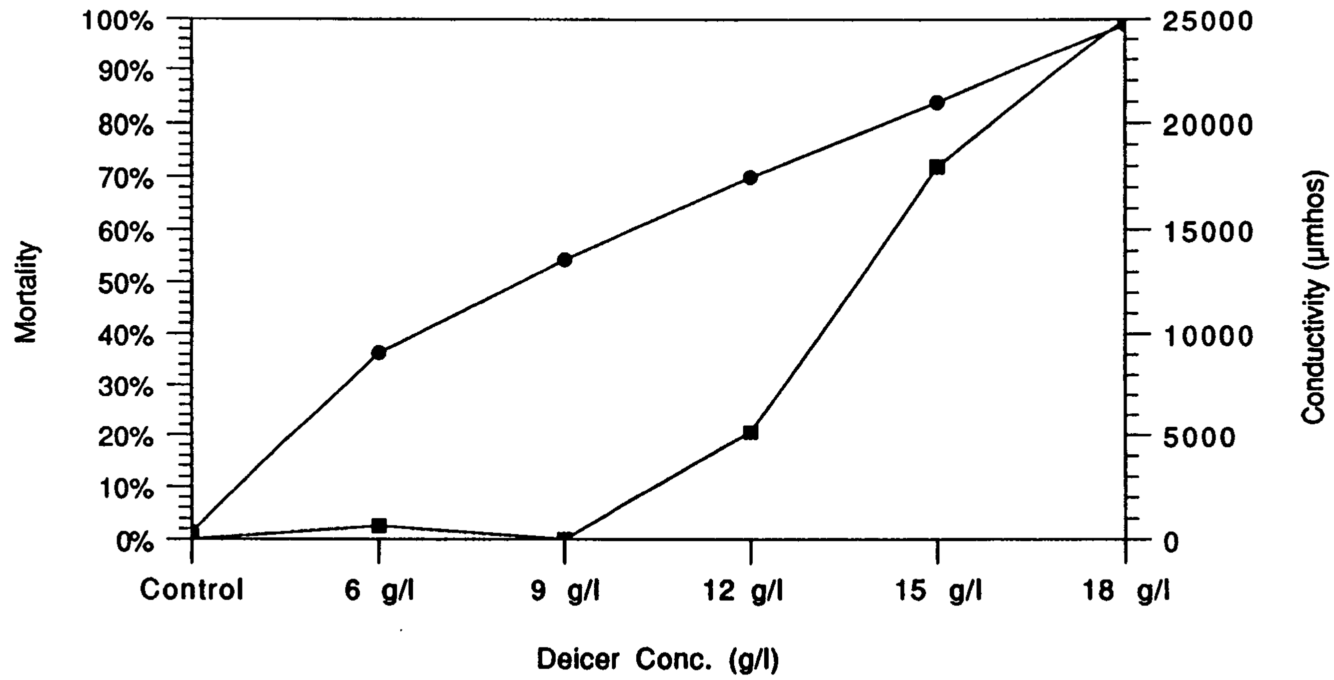


Figure C-13. Results of NaCl chronic toxicity test for fathead minnows showing percent mortality daily at six concentrations.



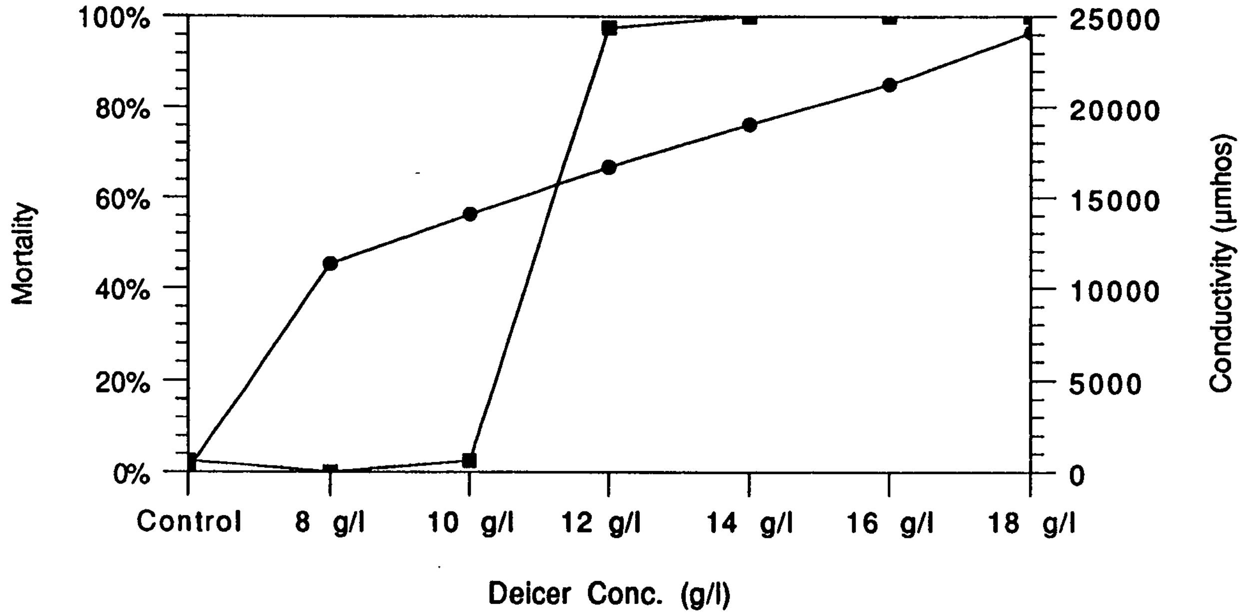
Deicer Conc. (g/l)	Control	6 g/l	9 g/l	12 g/l	15 g/l	18 g/l
Conductivity	272	8725	12925	16588	20713	24000
Mortality	0.0%	0.0%	5.0%	22.5%	60.0%	90.0%

Figure C-14. Results of rock salt acute toxicity test for amphipods showing percent mortality (squares) and conductivity (circles).



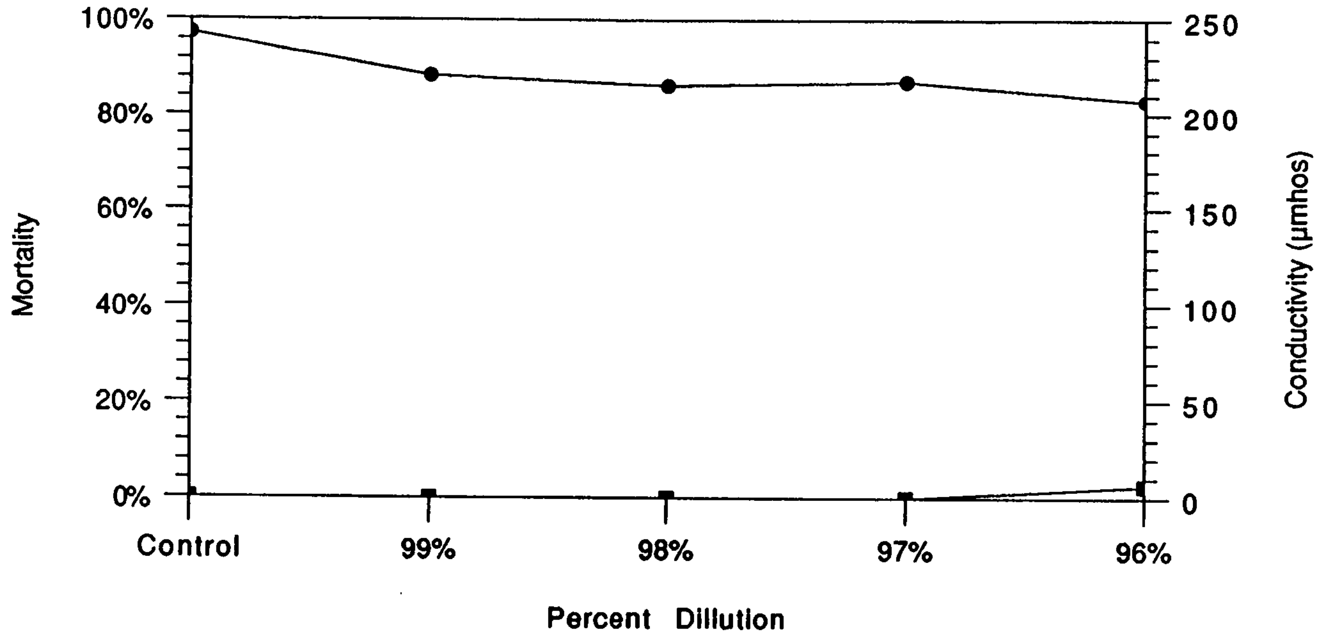
Deicer Conc. (g/l)	Control	6 g/l	9 g/l	12 g/l	15 g/l	18 g/l
Conductivity	359	9063	13575	17463	20963	24725
Mortality	0.0%	2.5%	0.0%	20.0%	70.0%	97.5%

Figure C-15. Results of rock salt acute toxicity test for mayflies showing percent mortality (squares) and conductivity (circles).



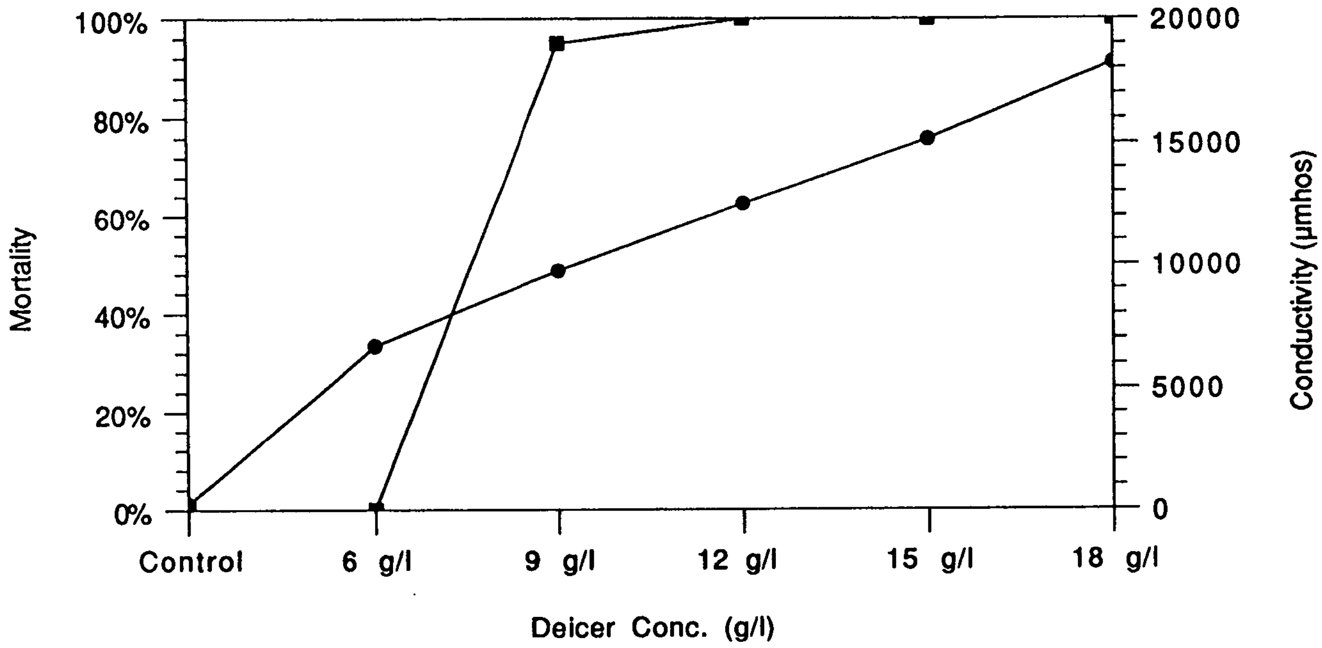
Deicer Conc. (g/l)	Control	8 g/l	10 g/l	12 g/l	14 g/l	16 g/l	18 g/l
Conductivity	144	11300	14075	16688	19025	21275	24113
Mortality	2.5%	0.0%	2.5%	97.5%	100.0%	100.0%	100.0%

Figure C-16. Results of rock salt acute toxicity test for fathead minnows showing percent mortality (squares) and conductivity (circles).



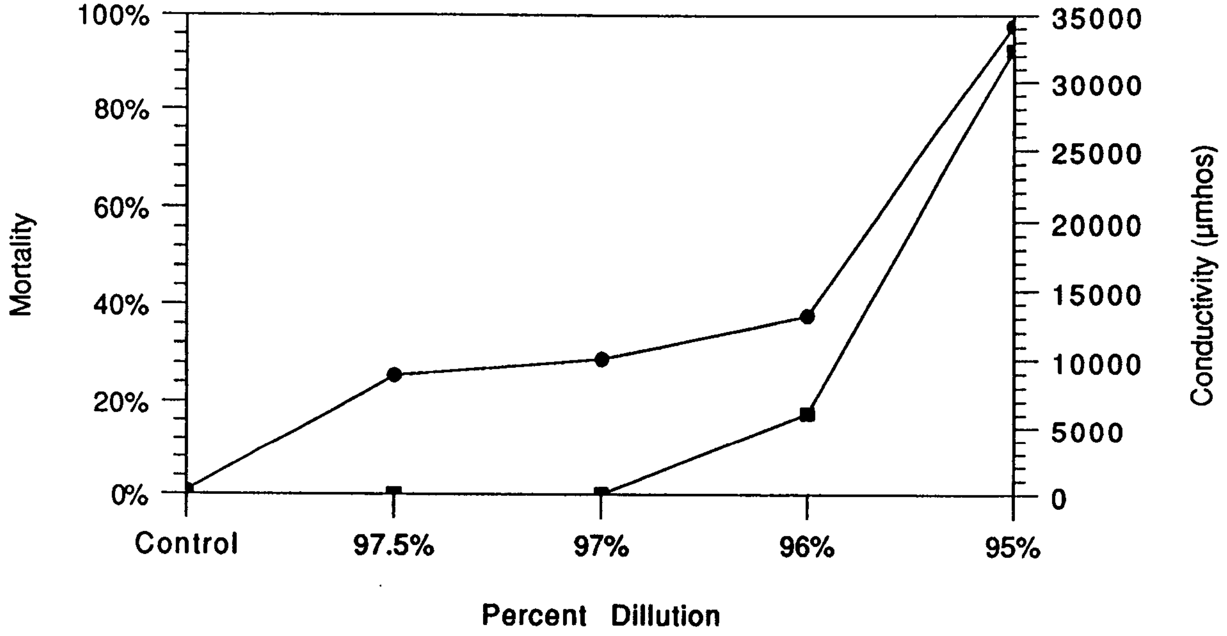
Percent Dillution	Control	99%	98%	97%	96%
Conductivity	243	221	216	218	207
Mortality	0%	0%	0%	0%	2.5%

Figure C-17. **Results of ethylene glycol acute toxicity test for fathead minnows showing percent mortality (squares) and conductivity (circles).**



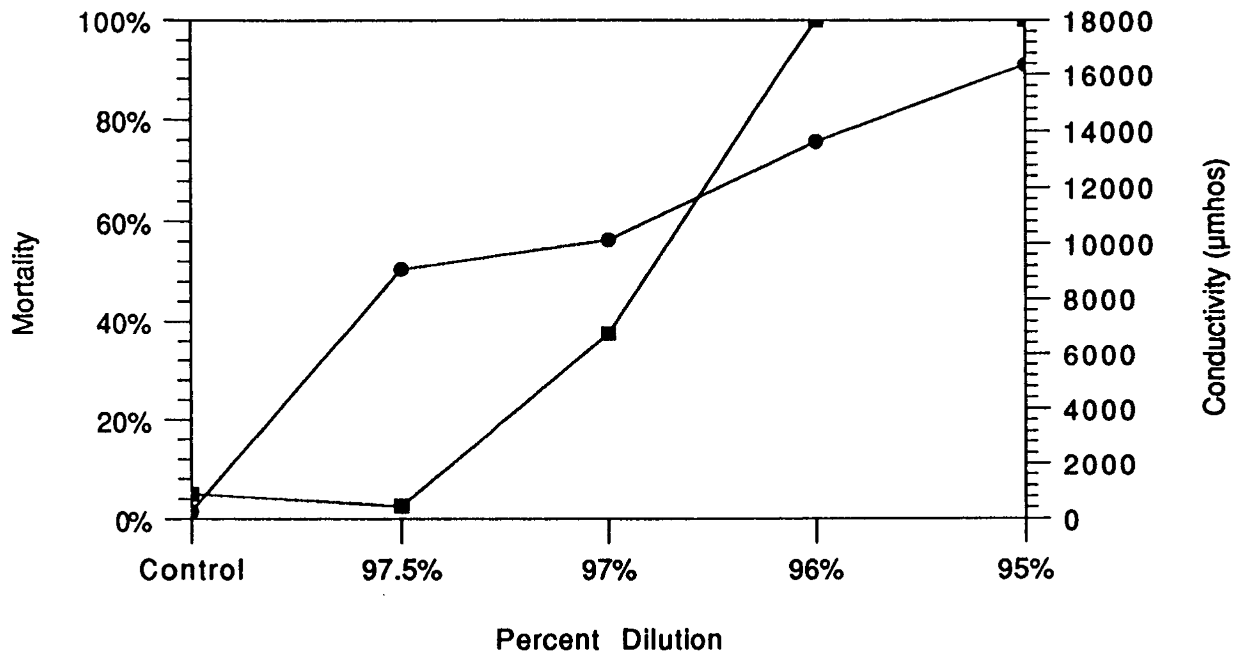
Deicer Conc. (g/l)	Control	6 g/l	9 g/l	12 g/l	15 g/l	18 g/l
Conductivity	232	6700	9738	12513	15163	18225
Mortality	0%	0%	95%	100%	100%	100%

Figure C-18. Results of sodium formate acute toxicity test for fathead minnows showing percent mortality (squares) and conductivity (circles).



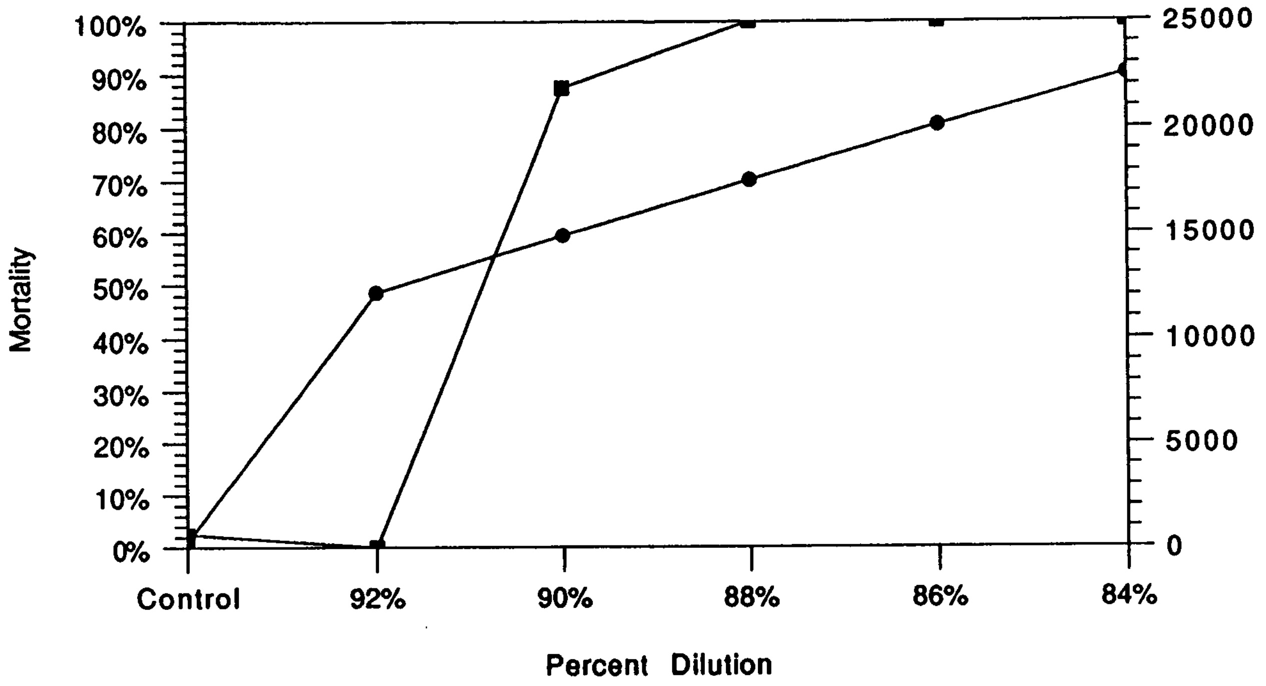
Percent Dillution	Control	97.5%	97%	96%	95%
Conductivity	251	8890	10083	13188	34163
Mortality	0.0%	0.0%	0.0%	17.5%	92.5%

Figure C-19. Results of NaCl + $Ca(H_2PO_4)_2$ acute toxicity test for fathead minnows showing percent mortality (squares) and conductivity (circles).



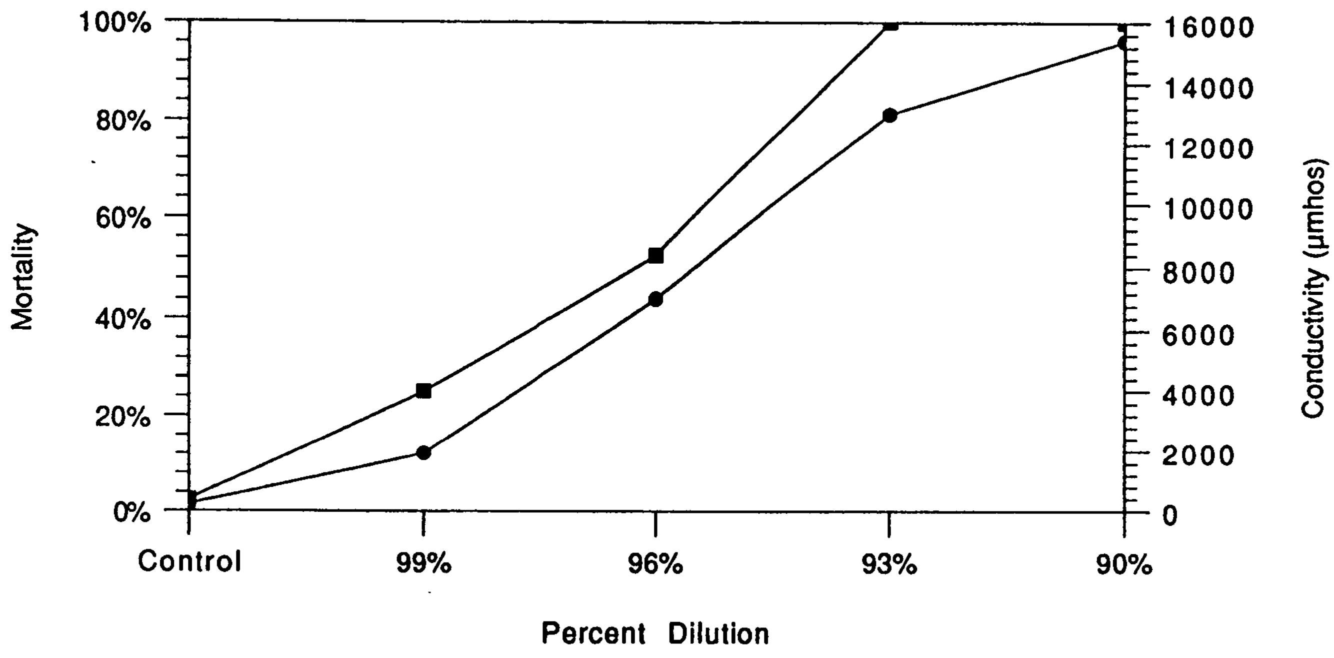
Percent Dilution	Control	97.5%	97%	96%	95%
Conductivity	256	9080	10133	13625	16350
Mortality	5.0%	2.5%	37.5%	100.0%	100.0%

Figure C-20. Results of NaCl + Na_2FPO_3 acute toxicity test for fathead minnows showing percent mortality (squares) and conductivity (circles).



Percent Dilution	Control	92%	90%	88%	86%	84%
Conductivity	256	12138	14875	17575	20150	22525
Mortality	2.5%	0.0%	87.5%	100.0%	100.0%	100.00%

Figure C-21. Results of NaCl + PCl acute toxicity test for fathead minnows showing percent mortality (squares) and conductivity (circles).



Percent Dilution	Control	99%	96%	93%	90%
Conductivity	228	1946	7025	13000	15400
Mortality	2.5%	25.0%	52.5%	100.0%	100.0%

Figure C-22. Results of NaCl + $ZnCl_2$ + $Na_5P_3O_{10}$ acute toxicity test for fathead minnows showing percent mortality (squares) and conductivity (circles).

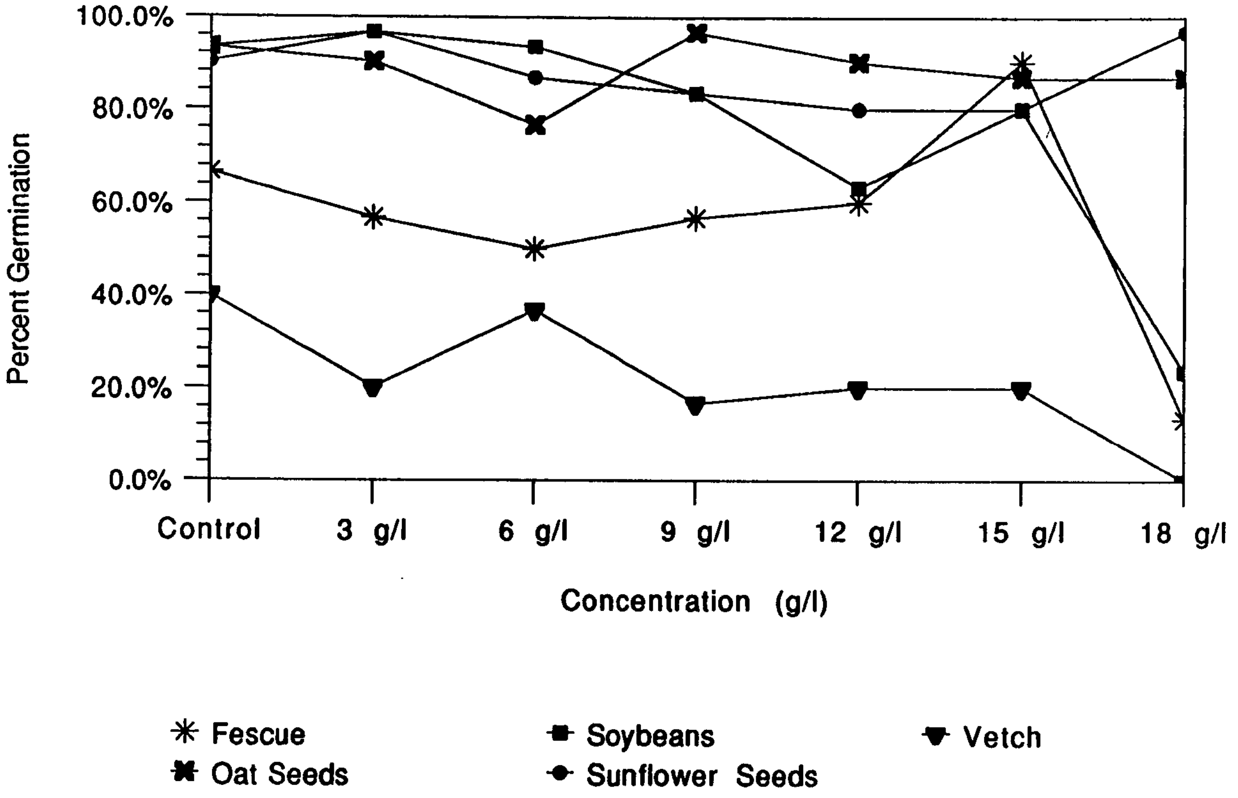


Figure C-23. Results of $CaCl_2$ seed germination test showing percent germination for fescue, oat, soybean, sunflower, and vetch seeds.

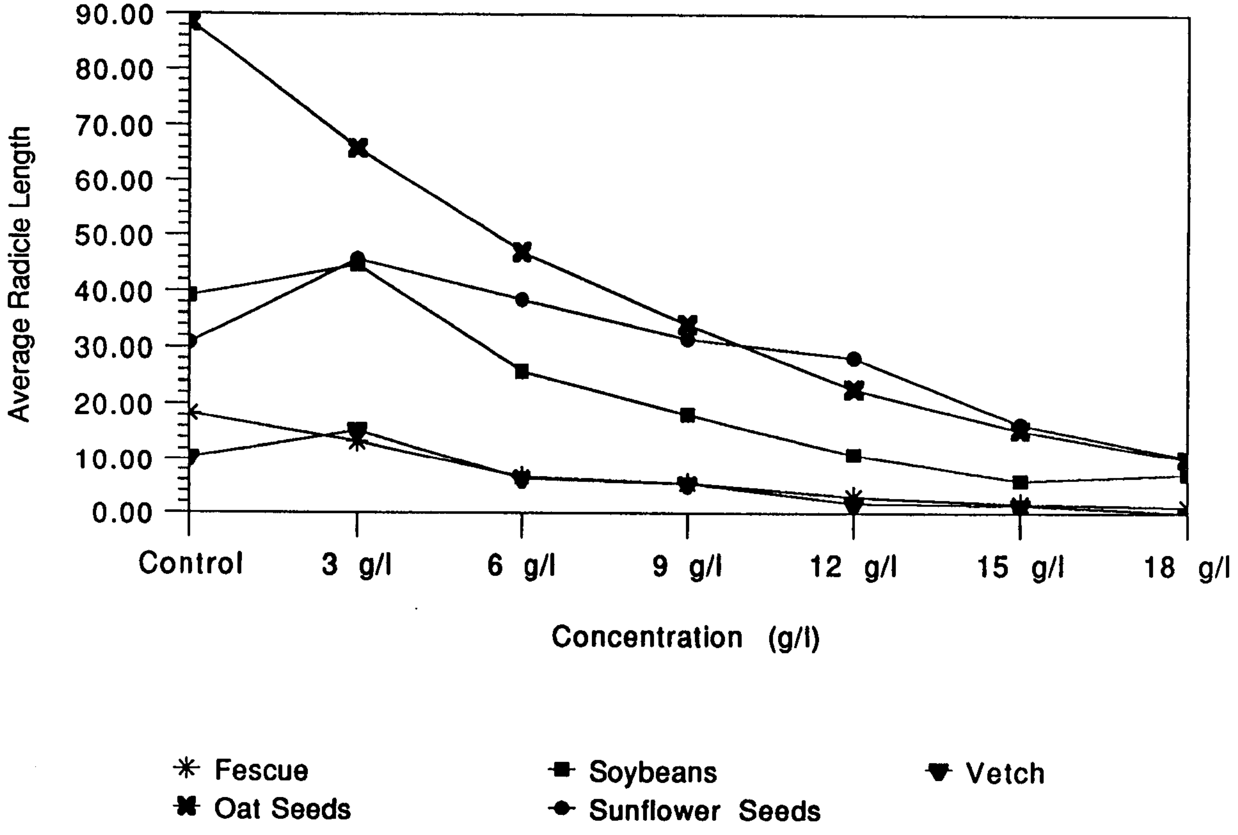


Figure C-24. Results of $CaCl_2$ radicle elongation test showing average radicle length of germinating fescue, oat, soybean, sunflower, and vetch seeds.

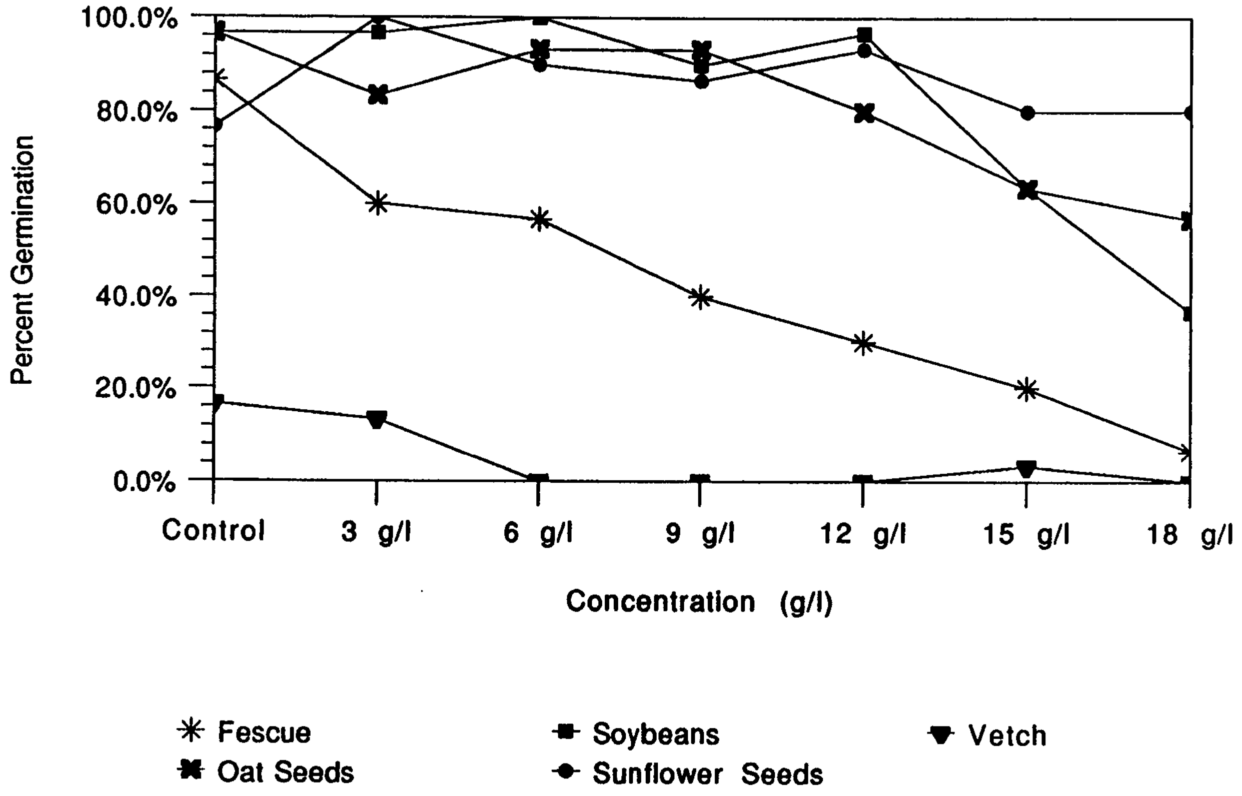


Figure C-25. Results of calcium magnesium acetate seed germination test showing percent germination for fescue, oat, soybean, sunflower, and vetch seeds.

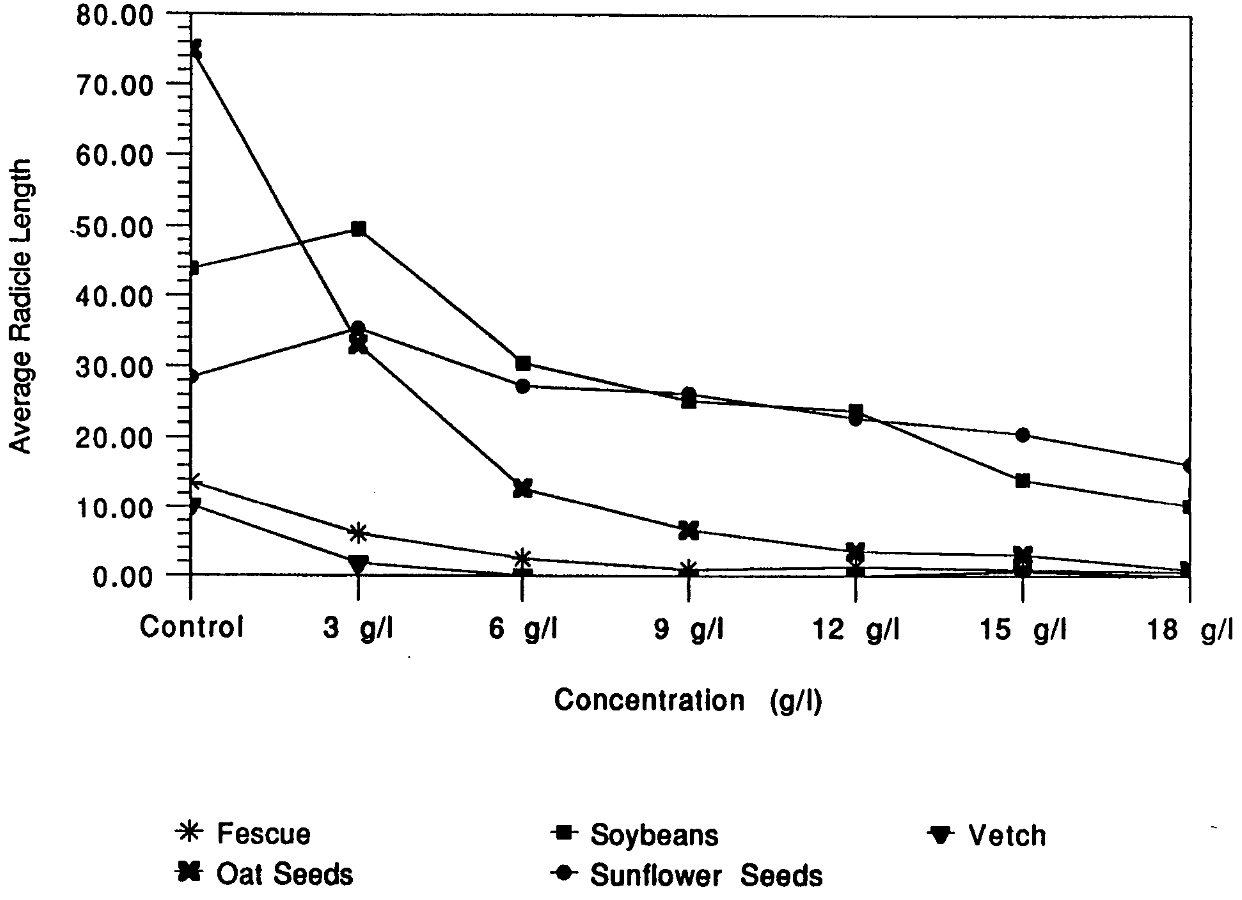


Figure C-26. Results of calcium magnesium acetate radicle elongation test showing average radicle length of germinating fescue, oat, soybean, sunflower, and vetch seeds.

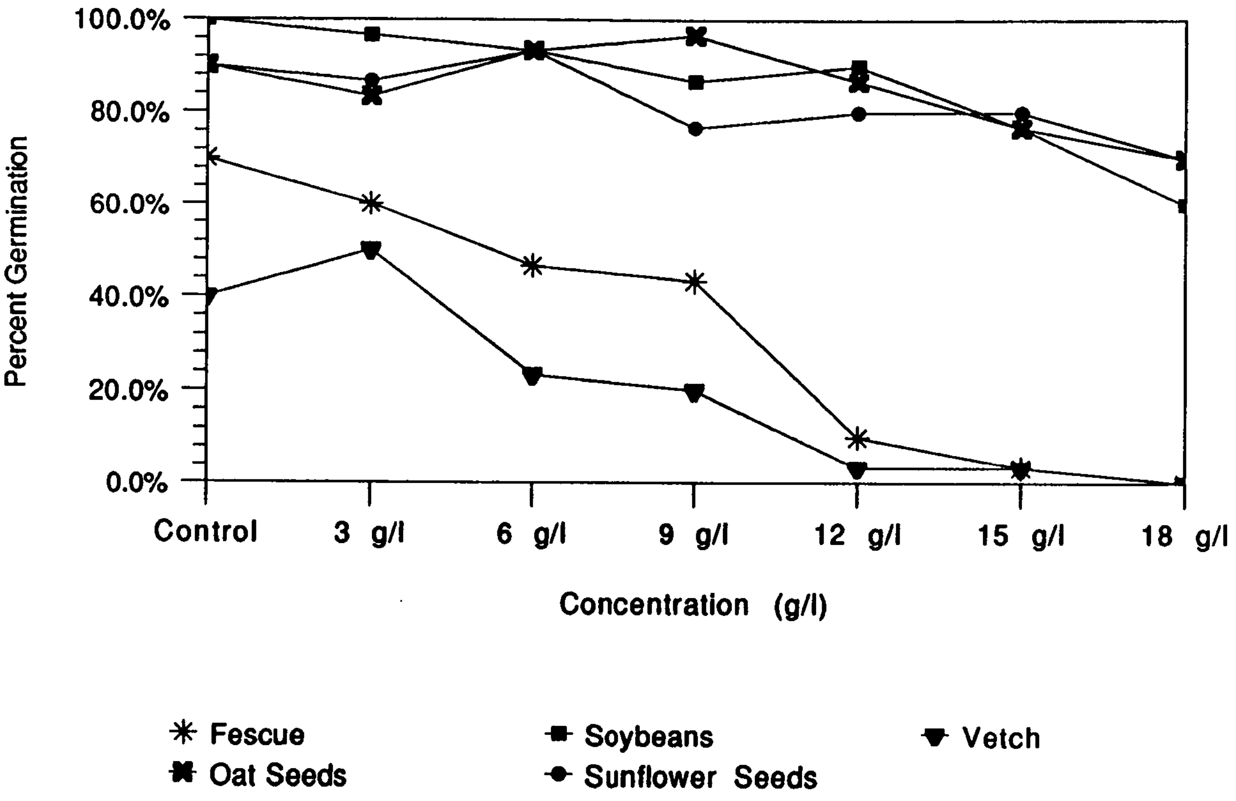


Figure C-27. Results of NaCl seed germination test showing percent germination for fescue, oat, soybean, sunflower, and vetch seeds.

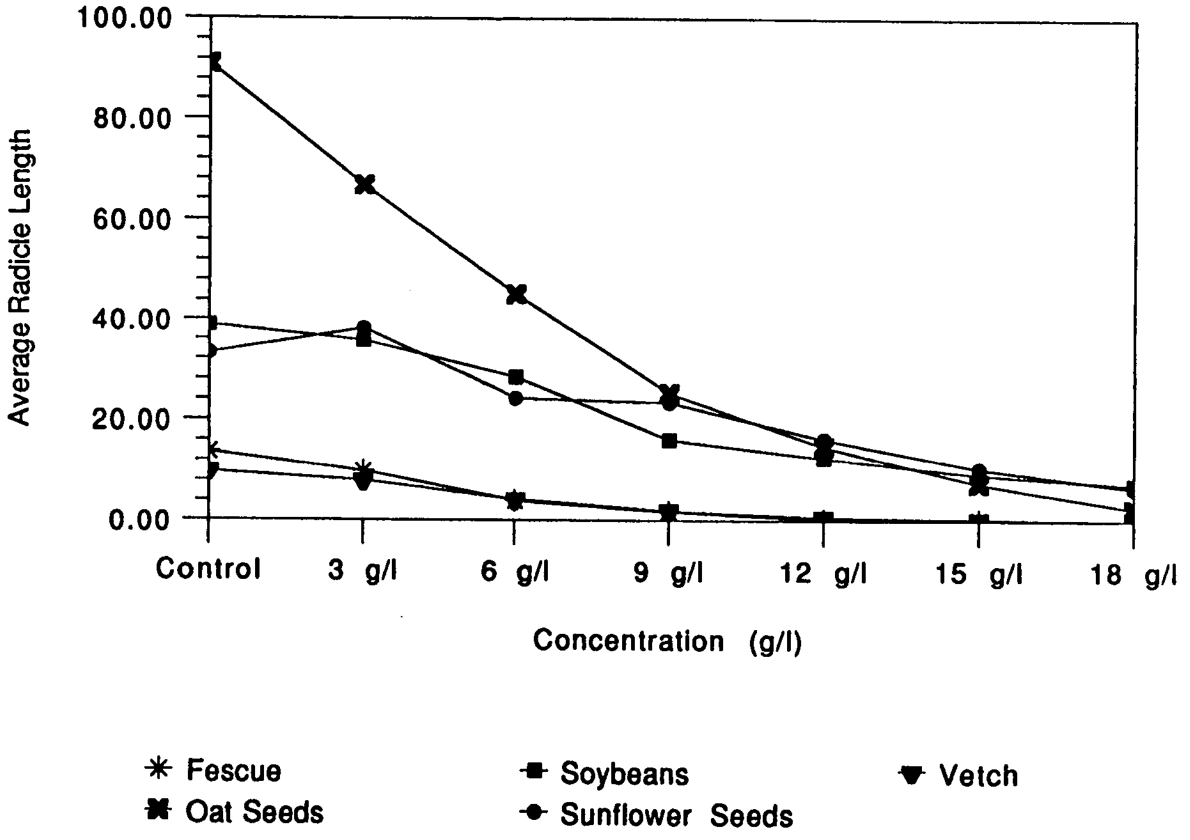


Figure C-28. Results of NaCl radicle elongation test showing average radicle length of germinating fescue, oat, soybean, sunflower, and vetch seeds.

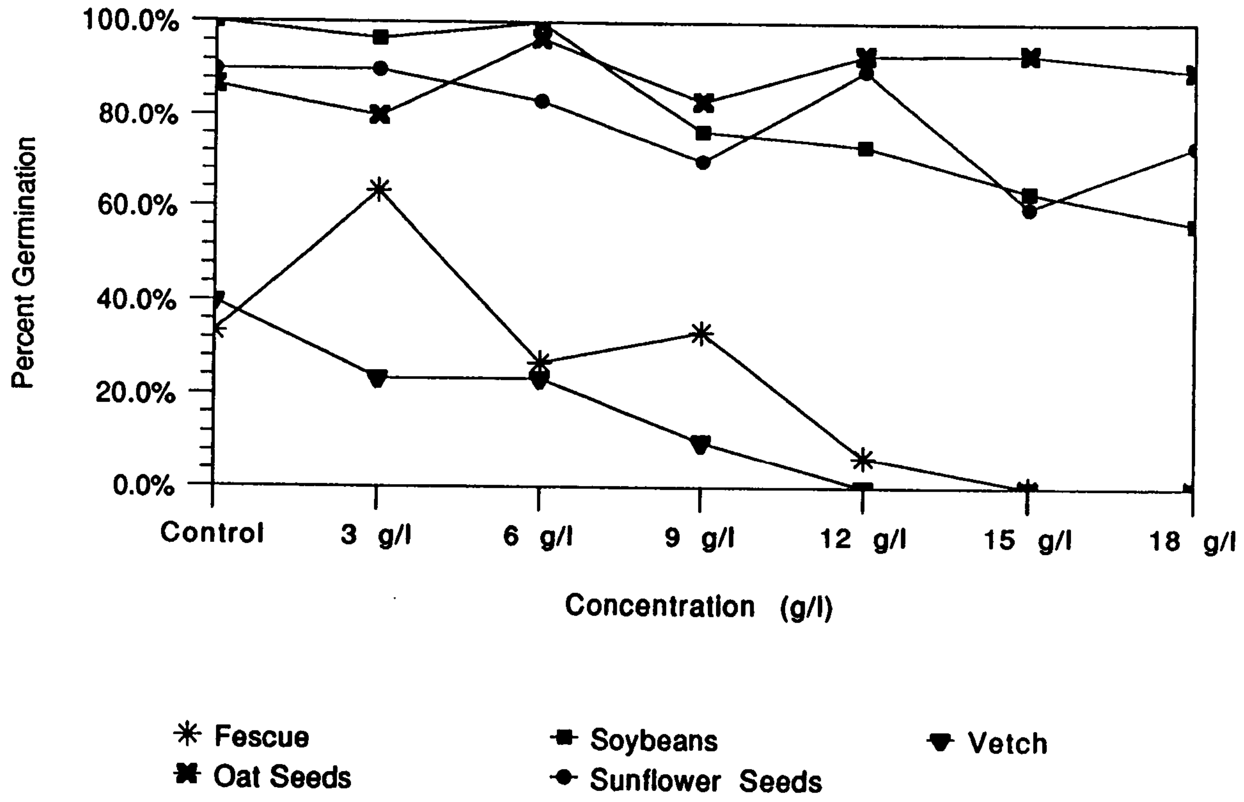


Figure C-29. Results of rock salt seed germination test showing percent germination for fescue, oat, soybean, sunflower, and vetch seeds.

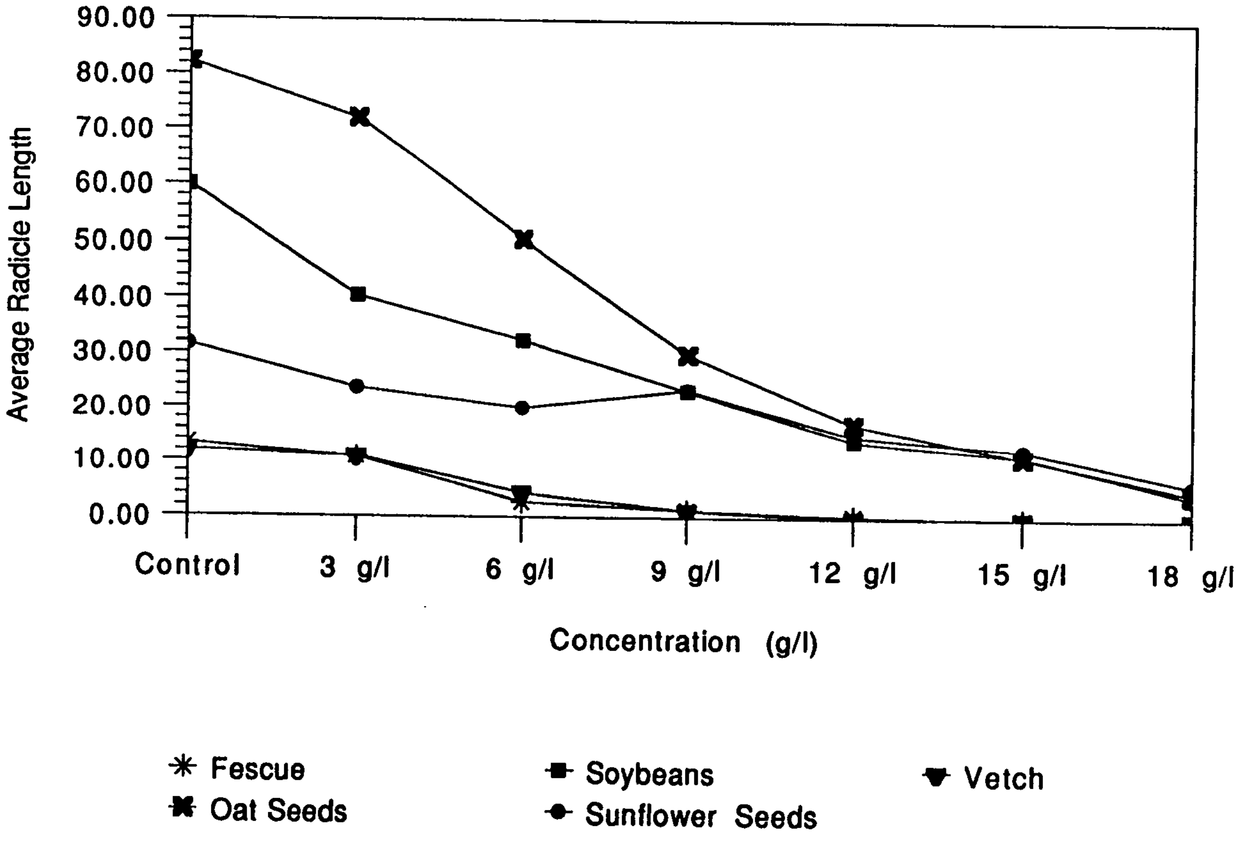


Figure C-30. Results of rock salt radicle elongation test showing average radicle length of germinating fescue, oat, soybean, sunflower, and vetch seeds.

Appendix D

Compatibility Enhancement by Corrosion Inhibition

- **Part 1—Corrosion Inhibitor Technology Related to Chemical Deicers: Literature Review**
- **Part 2—Detailed Experimental Procedures for Evaluating Corrosion Inhibitors**

Part 1—Corrosion Inhibitor Technology Related to Chemical Deicers: Literature Review

1

Introduction

1.1 Chemical Deicers and Corrosion Control

The corrosive effects of chloride-containing deicing salts on road and bridge surfaces and structures as well as on vehicles have been well documented. The annual cost of the corrosive damage to autos and bridges caused by the use of sodium chloride has been estimated to be about $3 billion (Better Roads, 1987). The magnitude of this economic impact has provided the impetus for developing and implementing a wide range of corrosion control strategies. There are several approaches to reducing the corrosion damage caused by the chloride-containing deicing salts. One general approach focuses directly on the protection of highway and automobile hardware by improved structural design, the use of protective coatings, and in certain cases, cathodic protection. A second general approach focuses on control of the chemical composition of the deicer formulations either by exclusion of chloride-containing chemicals or by incorporation of corrosion inhibitor systems (*Chemical Week*, 1989).

Nonchloride deicing substances represent one major thrust for reducing corrosion caused by chloride-containing materials. IITRI developed a urea:calcium formate (2:1) mixture as a salt substitute and a urea:calcium formate:formamide (1:1:1) mixture as a substitute for calcium chloride. However, both of these nonchloride salt substitutes proved to be too expensive for highway deicing. THAW, a urea:surfactant (99:1) mixture, was developed and promoted as a noncorrosive deicer in 1982 by Dimex Ltd. ICE-B-GON, a calcium acetate:magnesium acetate (58:42) mixture, generically known as CMA, is being developed by Chevron as an alternate deicer. The main thrust of their development work is to reduce product cost while maintaining deicer performance. Mixtures of organic acid salts derived from polysaccharide sources including waste products such as, sawdust, are claimed as deicing chemicals in a 1987 patent assigned to the State of South Dakota. OTBL is a proprietary nonchloride product of Domtar Inc. (Canada), which is in the early development stage. Its deicing and corrosion characteristics are comparable to those of CMA.

Corrosion inhibitor systems for chloride-containing deicer chemicals represent a second major thrust for alleviating corrosion damage. CARGUARD was an early attempt to produce an inhibited salt-based deicer formulation. Recently the Georgia-Pacific Corporation has developed PCI (a lignosulfonate derivative), which is reported to be an effective corrosion inhibitor for calcium chloride, sodium chloride, and magnesium chloride solutions. Utilizing this corrosion inhibitor, the Great Salt Lake Minerals and Chemicals Corporation has developed two chloride-containing deicer formulations: FREEZGARD, an aqueous solution containing 25% magnesium chloride and 5% PCI; and QUICKSALT, a granular solid formulation containing 80% sodium chloride, 5% magnesium chloride, and 15% PCI. Both formulations are reported to be effective deicers with significantly reduced corrosiveness. Domtar Inc. has recently reported the development of TCI, a corrosion-inhibited salt formulation, which has been shown to produce significantly lower levels of concrete spalling and rebar corrosion than uninhibited rock salt. Cargill has recently begun marketing GC-90, a sodium chloride-based deicer containing a proprietary corrosion inhibitor which makes it 90% to 120% effective against salt-induced corrosion of steel.

1.2 Organization of Literature Review

This review is organized in four sections. Following this introduction (Section 1.0) is the background (Section 2.0), which sets forth the literature review objectives and the literature search strategies. The major portion of the report is contained in Section 3.0, which presents the findings of the literature review and the assessments of the utility of corrosion-inhibited chemical deicer formulations and deicer-related systems. Conclusions drawn from the review process are presented in Section 4.0. The review concludes with Section 5.0, a list of cited references.

2

Background

2.1 Literature Review Objective

The objective of this review was to identify and critically assess corrosion inhibitor technology literature relevant to sodium chloride deicer formulations. Pertinent background information was collected by structured computerized searches of several literature data bases and manual searches of selected bibliographic literature sources. The literature search strategies yielded more than 500 literature citations. A review of the citations provided a basis for assessing the utility of mechanistic concepts and classification systems, the selection criteria for cited corrosion inhibitors, and the performance of inhibited chemical deicer formulations.

2.2 Literature Search Strategies

Information about inhibitors is scattered throughout the scientific and technical literature and frequently is concealed under a cloud of semantics so thick that only the most rigorous searching brings it to light. Also, like many other technical words, "inhibitor" labors under the difficulty that not everyone agrees on exactly what an inhibitor is, and few agree on all aspects of the manner in which inhibitors function.

The definition of inhibitor favored by the National Association of Corrosion Engineers (NACE, 1965) is: **"A substance which retards corrosion when added to an environment in small concentrations."** While this is not a perfect definition, it will be one of the bases on which this review of corrosion inhibitors is oriented.

Literature search strategies for computerized searches were developed by structuring several sets of descriptor terms (corrosion inhibitors, chlorides, deicers, brines, etc.) and establishing a series of combinations of these sets. Using these strategies, computer-assisted on-line searches of seven selected data bases yielded about 300 literature citations. In addition, manual searches of three selected bibliographic literature sources were conducted which yielded about 200 additional literature references, including a few duplications.

Computerized searches of the following seven literature data bases were conducted:

- Chemical Abstracts Search (CAS)
- Computerized Engineering Index (COMPENDEX)
- National Technical Information Service (NTIS)
- Transportation Research Information Service (TRIS)
- Cold Regions Research and Engineering Lab (CRREL)
- Metals Data Index (METADEX)
- Information Services for Physics, Electronics and Computing (INSPEC)

Manual searches of the following three bibliographic literature sources were conducted:
NACE-Corrosion Abstracts (1986-1988)
ACS-Chemical Abstracts (1987-1988)
ASTI-Applied Science and Technology Index (1980-1988)

Abstracts of selected articles and copies of original documents identified by the citations were acquired, reviewed, and organized into three categories (see Section 3.0).

3

Review of Literature Search Findings

The review of the literature search findings is presented in three parts: overview of corrosion inhibitors and inhibition; corrosion inhibitors for chemical deicer systems; and corrosion inhibitors for deicer-related systems.

3.1 Overview of Corrosion Inhibitors and Inhibition

Some of the general principles and practices of corrosion inhibitor technology are presented in this section to provide a general background for understanding: the fundamentals of corrosion inhibition, the common methods of inhibitor classification, and the major types of conventional inhibitors. Knowledge of this basic information should facilitate the interpretation of literature reports and the selection of potential corrosion inhibitors for chemical deicer formulations.

3.1.1 Inhibition of Corrosion

The majority of metal-corroding processes taking place in electrolytes are electrochemical in nature (Rosenfeld, 1981). The rate of any given electrochemical corrosion process depends on the rates of two conjugate reactions proceeding at the metal surface: an anodic reaction consisting of the transfer of metal ion-atoms from the lattice to the solution, with an attendant liberation of electrons, and a cathodic reaction consisting of the assimilation by some depolarizer (e.g., O_2) of the electrons liberated during the anodic reaction:

$$ne^-M^{n+} \rightarrow M^{n+} + ne^-$$

$$ne^- + Ox \rightarrow Red$$

Applying the same fundamental principles, Chandler (1984) summarized the corrosion of ferrous metals in ordinary atmospheric or immersed conditions as two simultaneous reactions, that is, the oxidation of iron at anodic sites and the reduction of oxygen at cathodic sites.

Anode: $2Fe \rightarrow 2Fe^{+2} + 4e^-$

Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Overall: $2Fe^{+2} + 4OH^- \rightarrow 2Fe(OH)_2 \rightarrow 2FeOOH$ (rust)

The cathodic reaction in an acid environment is a reduction of hydrogen instead of oxygen.
Cathode (in acid): $4H^+ + 4e^- \rightarrow 2H_2\uparrow$

Inhibitors can vary the rate of a corrosion process only if they influence the kinetics of the electrochemical reactions responsible for this process. Taking this into account, all inhibitors can be classified into anodic, cathodic, or mixed, because the first type predominantly retards the anodic reaction, the second type retards the cathodic reaction, while the third retards both reactions simultaneously.

Because inhibitors alter the kinetics of the electrochemical reactions causing the corrosion process, the actual inhibiting mechanism will be revealed most fully if the fundamental regularities of the electrochemical kinetics in the presence of inhibitors are established, as well as the molecular mechanism of their action. Research on corrosion inhibitors is concerned mainly with addressing these two fundamental issues.

The results obtained during the studies in recent years can be analyzed most suitably by considering separately inorganic inhibitors and organic inhibitors, the action mechanisms of which are quite different. Inorganic inhibitors, which are used mostly in neutral electrolytes, chiefly affect the anodic process and the passive state of the metal. The suppression of corrosion by varying only the kinetics of the cathodic reaction in neutral electrolytes rarely has any appreciable effect, unless a complete removal of the cathodic depolarizer (O_2) is envisioned.

Organic inhibitors, used mainly in acid electrolytes in which the stability of the phase layers is lower, operate according to a different mechanism. In this case, adsorption and the effect which it has on the kinetics of the cathodic reaction are of great importance. In acid electrolytes, the rate of dissolution can be reduced considerably by lowering the rate of the cathodic reaction of hydrogen-ion discharge or discharge of some other depolarizing agent. Another way to reduce the dissolution rate is to remove the intermediate product of the reduction reaction from the reaction sphere. However, some effect of the inhibitors on the anodic reaction is often observed as well.

The classification of inhibitors into organic and inorganic on the basis of the medium in which they are used (neutral, acid) is somewhat arbitrary; recently organic inhibitors have begun to be used in neutral electrolytes too, and inorganic inhibitors in acid electrolytes. However, from the methodical point of view, this classification is convenient and is frequently used.

3.1.2 Classification of Inhibitors

A number of methods for classifying inhibitors are used, but none of these is entirely satisfactory because they are not mutually exclusive and there is not always general agreement on the allocation of an inhibitor to a particular group. Some of the main classifications--used particularly for inhibitors in near-neutral pH aqueous systems--are as follows (Mercer, 1976).

- **Anodic or cathodic inhibitors:** This classification is based on whether the inhibitor causes increased polarization of the anodic reaction (metal dissolution) or of the cathodic reaction, that is, oxygen reduction (near-neutral solutions) or hydrogen discharge (acid solutions) (Thomas, 1976).

- **Organic or inorganic inhibitors:** This distinction is based on the chemical nature of the inhibitor. However, in their inhibitive action, many compounds that are organic in nature, as for example the sodium salts of carboxylic acids, often have more similarities with inorganic inhibitors (Foley and Brown, 1979).

- **Oxidizing or nonoxidizing inhibitors**: These inhibitors are characterized by their ability to passivate the metal. In general, nonoxidizing inhibitors require the presence of dissolved oxygen in the liquid phase for the maintenance of the passive oxide film, whereas dissolved oxygen is not necessary with oxidizing inhibitors (Stewart and Tulloch, 1984).

- **"Safe" or "dangerous" inhibitors:** Each inhibitor must be present above a certain minimum concentration for it to be effective, and this classification relates to the type of corrosion that will occur when the concentration is below the minimum or critical value. Thus, when present at insufficient concentration, a "safe" inhibitor will allow only a uniform type of corrosion to proceed at a rate no greater than that obtained in an uninhibited system, whereas a "dangerous" inhibitor will lead to enhanced localized attack, for example, pitting, and so in many cases make the situation worse than in the absence of an inhibitor.

- **Other classifications:** Soviet authors classify inhibitors as type A to include film-forming types, or type B for those which deactivate the medium, for example, by removal of dissolved oxygen. Type A inhibitors are then further subdivided into A(i) inhibitors that slow down corrosion without suppressing it completely, and A(ii) inhibitors that provide full and lasting protection.

  From a practical aspect, a useful classification is perhaps one based on the concentration of inhibitor used. Usually, inhibitors are used either at low concentrations, say less than approximately 50 ppm, or at rather high levels greater than 500 ppm. The determining factors in the selection of the concentration and hence the type of inhibitor, are the economics, disposal (effluent) problems, and the facilities available for monitoring the inhibitor concentration.

3.1.3 Type of Inhibitors

The scientific and technical literature has descriptions and lists of numerous compounds that exhibit corrosion-inhibiting properties. This section presents some of the major types of corrosion inhibitors according to the mechanistic classification system of Stewart and Tulloch (1984), which differs from any of the classification systems already discussed. It specifies three main types: (a) chemical passivators, (b) film-forming inhibitors, and (c) adsorption inhibitors.

3.1.3.1 *Chemical Passivators*

Also known as anodic passivators, these are oxidizing agents which produce an anodic reaction (i.e., an electron producing reaction) that is capable of passivating (balancing) the cathodic reaction (i.e., electron consuming reaction) of the electrochemical corrosion process. Chemical passivators are corrosion inhibitors for use in near-neutral pH aqueous solutions.

In these conditions, the cathodic reaction is the reduction of oxygen to form hydroxide ions, which then react with ferrous ions (the anodic reaction product) to form hydrated iron oxides. The corroding metal becomes covered with a passivating iron oxide film. The iron oxide film may be continuous or discontinuous. Passivation inhibitors either form or stabilize the iron oxide film (Thomas, 1976). Although this type of corrosion inhibitor can be very effective under certain conditions, it can have serious adverse side reactions under other conditions.

The major passivating inhibitors identified by Thomas (1976) and White (1986a) include the following:

- Chromate
- Nitrite
- Phosphate
- Phosphonate
- Silicate
- Molybdate

Other less prevalent passivating inhibitors include:

- Benzoate
- Borate
- Azelate
- Pertechnate
- Tungstenate

Chromate and nitrite passivating inhibitors are oxidizing agents and do not depend on the presence of oxygen to form the passivating iron oxide layer. Both chromate and nitrite inhibitors interfere with the anodic reaction by restricting migration of ferrous ions and are considered to be dangerous corrosion inhibitors. If the initial concentration of chromate or nitrite is too low for complete anodic passivation, or if local depletion of either inhibitor occurs, then pitting corrosion can take place (Stewart and Tulloch, 1984). Chromate is first adsorbed on the metal surface as a monolayer and slowly is incorporated into the oxide film. Chloride ions increase the concentration of chromate or nitrite necessary to completely inhibit corrosion (White, 1986a).

Phosphate inhibitors depend on the presence of oxygen to form the passivating iron oxide film. Phosphates are anodic inhibitors, becoming incorporated in the oxide film, stabilizing it, and stifling ferrous ion dissolution. Orthophosphates can precipitate with calcium ions at pH above 7. Sludges can form and create corrosion by differential oxygen cells (White, 1986b).

One disadvantage of phosphate corrosion inhibitors is that phosphates revert to the ortho structure and become ineffective as inhibitors. Phosphonates are more stable over a larger temperature and pH range. Phosphonates are not good corrosion inhibitors when used alone. Combinations of phosphonates with chromate, zinc phosphates and silicates give the best results (White, 1986b).

Silicates form hydrated gels of silica and iron oxides. High salt concentrations interfere with and coagulate the gels and interfere with the inhibition efficiency (White, 1986b).

Molybdates are mild oxidizing agents, but are considered nonoxidizing, passivating inhibitors, and require an oxidant such as air to perform efficiently. The method of corrosion inhibition may be by incorporation into the FeOOH (rust) film (Vukasovich and Farr, 1986), or by formation of an inhibiting, complex ferric molybdate (White, 1986b). Synergistic combinations of molybdate have been reported (Vukasovich and Farr, 1986). Molybdate synergistic combinations include:

Nitrite —Triazole
Zinc ion—Triazole
Nickel ion—Chromate
Manganese ion—Alkyl amine phosphonate
Triazole—Phosphate

Aliphatic amines normally would be considered as adsorption-type corrosion inhibitors. However, they can also react with iron oxide films to displace water and act as a barrier to chloride attack (White, 1986a).

3.1.3.2 *Film-Forming Inhibitors*

Film-forming inhibitors cause a barrier or blocking film of material (other than the actual inhibiting species itself) to form on the corroding metal which inhibits the electrochemical corrosion process. Film-forming inhibitors are nearly always specific to either the cathodic or anodic reaction and thus are known as cathodic or anodic inhibitors (Stewart and Tulloch, 1984).

- Cathodic film-forming inhibitors, which are also known as precipitation inhibitors (White, 1986a), appear to function by the precipitation of an insoluble material caused by the production of alkali (or the reduction of acidity) at the cathodes by such reactions as

$$2H^+ + 2e^- \rightarrow H_2, \text{ and } 1/2\ O_2 + H_2O + 2e^- \rightarrow 20H^-$$

Calcium and zinc salts are the most striking examples of this type of reaction, for example,

Ca^{++} (from cathodic inhibition)	+	$2OH_2^-$ (cathodic alkali)	→	$Ca(OH)_2$ (cathodic film precipitated)

The precipitate lessens the corrosion current, making the cathodic reaction more difficult. Cathodic inhibitors involve no risk of pitting attack and include:

Zinc ions
Calcium ions
Nickel ions
Manganese ions
Polyphosphates with zinc or calcium

Zinc, calcium, nickel, and manganese ions precipitate hydroxide ions at cathodic sites to form a barrier to oxygen permeation to the metal surface. Since the precipitated hydroxides are poor electrical conductors, oxygen cannot be reduced at the oxide film surface. Polyphosphates with zinc or calcium ions form a thin amorphous salt film. The presence of carbon dioxide in near-neutral solutions can cause precipitation of calcium carbonate, if calcium ions are present (Thomas, 1976).

The presence of an oxide film, even if discontinuous, will increase the effectiveness of cathodic film-forming inhibitors. The inhibitor may promote formation of a continuous oxide film (Stewart and Tulloch, 1984). Cathodic film-forming inhibitors do not cause pitting in anodic regions.

- Anodic film-forming inhibitors differ from anodic passivators in that it is not necessary for the E_{CRIT} to be exceeded for protection to be effective. It is believed that the charge on the metal/electrolyte surface determines whether the inhibiting species reaches the metal surface or not. Oxygen is only required to raise the potential of the corroding metal to the level to attack the inhibiting species. Anodic inhibitors react with ferrous ions produced at anodic sites. Only a few examples were mentioned in the literature.

Benzoate can act as an anodic film-forming inhibitor if the iron is connected to a more noble metal such as copper, but it cannot if connected to a more base metal such as zinc (Stewart and Tulloch, 1968).

At least some chelating agents can act similarly to anodic film-forming inhibitors. According to White (1986), sarcosine-type chelating agents react with metal ions at the oxide surface to form a precipitate.

3.1.3.3 *Adsorption Inhibitors*

These inhibitors are compounds with permanent charges (i.e., ionic) or induced charges (i.e., dipolar) which are adsorbed on metal surfaces and inhibit electrochemical reactions. The protective action of adsorption inhibitors is due to a blanketing effect over the entire metal surface on both cathodic and anodic areas (Thomas, 1980). The effectiveness of the blanketing depends on several factors, such as: (1) size of the adsorbed particles, (2) charge distribution of the particles, and (3) nature of the electrical double layer at the metal/electrolyte interface (Stewart and Tulloch, 1984).

Adsorption inhibitors may be organic compounds capable of forming an electric dipole (i.e., negative in one region and positive in another region) of the molecule. In general, nitrogen atoms in amines, quinolines, and such, will exhibit positive charge characteristics, whereas sulfur atoms in these compounds and oxygen atoms in aldehydes will exhibit negative charge characteristics.

Adsorption inhibitors are used in acid solutions where the iron surface is nearly free of an iron oxide film. Adsorption inhibitors are usually organic molecules, which are usually not effective for oxygen-based corrosion unless passivating groups such as benzoates or sulfonates are present (White, 1986a).

All organic inhibitors are surface active and diphilic. Groups with sufficiently large dipole moments for surface activity include (White, 1986b):

$-COOH$
$-OH$
$-NH_2$
$-SH$
$-CN$
$-NO_2$
$-NCS$
$-CHO$
$-SO_3$
Ring-strained cyclic hydrocarbons

The tendency of organic molecules to be adsorbed on the metal surface increases with decreasing electronegativity, that is, $O < N < S < Se$. Also, generally, inhibitive efficiency increases with greater electron density in a series of related compounds (Thomas, 1976).

Phosphonates can act as adsorption corrosion inhibitors in near neutral solutions. Phosphonates act as a barrier to oxygen reduction (White, 1986a).

3.1.3.4 *Nonclassified Inhibitors*

Some examples from recently published monographs and books indicate the wide range of chemicals that exhibit inhibitive properties.

Detailed descriptive information on corrosion inhibitors based on U.S. patents issued during 1972-1974 is contained in a book by Ranney (1976). Over 260 processes relating to all phases of corrosion control in industrial, automotive, aircraft, and other specialized application areas are described in detail. A similar book based on U.S. patents issued between January 1981 and March 1983 was prepared by Collie (1983). The subject matter is organized into seven major application areas, including aqueous system applications employing multiple use compositions.

An industrial guide to corrosion inhibitors describing approximately 750 corrosion inhibitors and rust preventives which are currently available for industrial usage was written by Flick (1987). The inhibitors identified by trade name and product number are presented by company. Listed product information includes product name, solubility, physical properties, and applications. A similar book by McCutcheon (1986) identifies more than 250 commercially available corrosion inhibitors.

3.2 Corrosion Inhibitors for Chemical Deicer Systems

In this section, literature specific to corrosion inhibitors for chemical deicers is reviewed in chronological order for the last 25 years.

3.2.1 Sodium Fluorophosphate and/or Phosphoric Acid Salt Derivatives

This corrosion inhibitor system as described in a patent issued to Johnson et al., 1989, and assigned to Domtar Inc., consists of at least one of: (a) Na fluorophosphate and (b) water-soluble salt of a phosphonic acid derivative of formula: $R_nR'N(CH_2PO_3H_2)_{2-n}$ where R and R' = alkyl, aminoalkyl or hydroxyalkyl; and n = 0 or 1. Nadezhdrin et al. (1988) report the development and evaluation of an inhibited sodium chloride-based deicer formulation containing this proprietary corrosion inhibitor which was identified by conducting a systematic series of screening/evaluation tests. Preliminary screening of candidate inhibitors consisted of immersion/weight loss tests. Advanced evaluation consisted of a series of macrocell corrosion determinations using various levels of sodium chloride admixed in the top layer of the concrete of the macrocell test units. Based on the macrocell test results, the inhibited salt mixture not only passivated the steel surface, but it appeared to be nonaggressive to rebar in fresh concrete. The authors speculate that the inhibitor diffused through the concrete and formed a passivating film on the steel rebar surface. A comparison of the performance of the inhibited salt to salt alone in immersion tests and through linear polarization and AC impedance studies is shown in Table D-1.

Table D-1. Comparison of the performance of inhibited and uninhibited sodium chloride solutions in immersion tests.

	Immersion tests[a] rate of corrosion (mpy)		Linear polarization rate of corrosion (mpy)[b]	AC impedance corrosion rates of steel electrodes[c]
	Mild steel C1010	Galvanized steel		
NaCl	2.32	0.98	2.0	8.01
NaCl + inhibitor	0.56[d]	0.11[d]	0.849	2.09

[a] Duration of tests = 214.5 hr.

[b] As measured in 10% NaCl and 10% NaCl + 0.033% inhibitor solution saturated with $Ca(OH)_2$.

[c] As measured in 1 *m* NaCl; pH 8.2; C1018 steel.

[d] 4% solution of 95:5 salt:inhibitor mixture.

3.2.2 Divalent Metal Ions and Alkali Metal Polyphosphates

Cargill is in the process of developing and commercializing CG-0-™ anticorrosive deicer product. Presently, Cargill has three developmental corrosion-inhibited deicer formulations. All three contain sodium chloride and phosphate but are differentiated by their calcium, magnesium, or zinc content. Cargill claims that research studies of CG-90 by two state highway DOTs show more than 90% anticorrosive effectiveness. The corrosion inhibitor system and the deicer formulations are the subject of a patent recently issued to Frank Garber, 1989. An example of the inhibition of the salt-water corrosion of mild steel by zinc/tripolyphosphate mixtures is shown in Table D-2.

Table D-2. Inhibition of the salt-water corrosion of mild steel by zinc/tripolyphosphate mixtures.

Coupon insertion time (days)	Salt (percent by weight of solution)	Zinc sulfate (percent by weight of salt)	Sodium Tripoly-phosphate (percent by weight of salt)	Corrosion inhibition[a] (percent)
49	0.40	5.0	5	97
11	0.80	5.0	5	93
21	1.67	2.5	2.5	97
21	0.33	2.5	2.5	93
30	3.0	5.0	5	95
9[b]	3.0	5.0	5	93
12[b]	3.0	2.5	2.5	94

[a] The corrosion inhibition due to a control solution containing the same concentration of salt without inhibition is 0%.

[b] The data resulted from spray testing of inhibited salt on corrosion coupons. Coupons were compared which were sprayed with the inhibited and uninhibited salt solution for 10 min (about 500 mL of solution) twice per day.

3.2.3 PCI, a Corrosion Control Polymer Derived from Lignin

Wieman (1987) reports studies of the corrosion inhibition of deicer salts containing PCI, a corrosion control polymer which is a lignin sulfonate material patented by the Georgia Pacific Corporation (Neal, 1987). The Washington State Department of Transportation conducted weight loss corrosion studies which confirmed the electrochemical studies indicating that PCI is an effective corrosion inhibitor in solutions of various chloride-containing deicers. The results of the 2-month corrosion rate studies are summarized in Table D-3.

Table D-3. Corrosion rate studies with PCI as an inhibitor in various chloride-containing deicer solutions.

Solution	Corrosion rate (mpy)
Distilled water	5.9
3% Urea	6.7
3% Rock salt	28.9
3% Rock salt + PCI	14.4
3% Calcium chloride	32.6
3% Calcium chloride + PCI	6.7
3% Magnesium chloride	19.0
3% Magnesium chloride + PCI	9.0

Although the reductions of the corrosion rates are significant, the concentrations of PCI in the test solutions were not reported. The effective dosage level of PCI is estimated to be 20 wt %.

A discussion of the corrosiveness of salt solutions and deicer products containing PCI which are manufactured by Great Salt Lake Minerals and Chemicals Corporation is presented in *Better Roads* (1987).

3.2.4 Synergistic Zinc/Molybdate Mixtures

The nature and origin of the synergistic interaction between zinc cations and molybdate anions in to inhibit the corrosion of mild steel in chloride solutions was investigated by Y. J. Qian and S. Turgoose (1987). It was concluded that the better inhibition obtained with mixtures than with the individual components is due to the mixture acting as a cathodic inhibitor, by precipitation of a basic zinc molybdate on the surface. Any anodic effects of the molybdate did not contribute to the reduction in corrosion rate.

3.2.5 Mixtures of Aluminum Salts and Thiourea Derivatives

Iovchev (1983) reported laboratory test data obtained during further investigations of aluminum—thiourea inhibitors in another corrosive medium, 1.0% NaCl at 20°C and under stagnant conditions. It was found that the corrosion rate of mild steel in sodium chloride solutions can be decreased markedly (by approximately 80%) if aluminum ions are used in the form of a mixture of sulfates and oxychlorides and in conjunction with thiourea, cationic surfactants and reducing agents ($SnCl_2$). Any change in the composition of the aluminum salts in the mixture, keeping a constant Al^{3+} concentration (for instance, a substitution of sulfates/oxychlorides by sulfates/chlorides or chlorides/oxychlorides), reduces the inhibitive efficiency of the formations tested. The author fails to find a satisfactory explanation of the very specific inhibitive behavior of aluminum--thiourea mixtures in 1.0% NaCl.

3.2.6 Calcium and Zinc Phosphates and Organic Inhibitors

A review article by Bishop (1976) describes the occurrence of aggressive attacks on automobiles in regions where deicing salt is used and discusses some of the mechanisms and controls. Laboratory tests with various inhibitors, including synergism of two or more inhibitors, have produced inconclusive results. On-site tests on vehicles and in outdoor test equipment also have not indicated good results unless phosphates and Ca or Zn are included. Organic inhibitors are sometimes better than phosphates but are more expensive. Track tests in Europe and England are described and economics considered. Advantages of car washing with inhibited water are discussed and various tests and results reported. Track tests indicate that the most damaging corrosive effect--inside out attack--is not substantially reduced by inhibitors. The effects of spray washing with inhibited water are measurable, but test results do not reflect what actually happens under service conditions.

3.2.7 Chromate, Polyphosphate, and Proprietary Inhibitors

Chance (1974) reviewed the problem with deicing salts and the extent of usage. A continued high rate of usage appears to correspond, at this time, with public demand for bare pavement for rapid travel and safe roadways. Investigators explored many alternatives to the use of rock salt and, except for limited use, all were found wanting. Inhibitors incorporated with deicing salts were shown to be largely ineffective for preventing corrosion of automobiles. Corrosion preventive measures that include appropriate metal selection, design, surface treatments, metallic coatings, rust preventives, and sealers are recognized and recommended by the Society of Automotive Engineers.

Environmental factors that affect corrosion were shown to vary considerably with geographic location. The most corrosive regions in the United States are in the snow belt, which must contend with deicing salts, industrial fallout, and sometimes humid and salt-laden air. Specific factors in the environment relative to corrosion are discussed, including acidity and alkalinity, dissolved oxygen, temperature, relative humidity, and atmospheric pollutants.

3.2.8 Ammonium Orthophosphate and Superphosphate

Fisons (1973) was granted a patent for a deicing composition containing an alkali-metal chloride and/or alkaline-earth metal chloride salt and less than 50% by weight of an ammonium and/or calcium orthophosphate based on the weight of the alkali-metal chloride and/or alkaline-earth metal chloride salt. The three following examples illustrate corrosion testing of typical inhibited deicing compositions cited in the patent.

Example 1: Mild steel sheets having an area of 40 cm^2 were degreased in trichloroethylene and then etched in hydrochloric acid. A sheet was then immersed in each of solutions A and B described below through which air was continuously blown.

Solution A: Aqueous solution containing 3% rock salt (96.4% NaCl, 1.6% $CaSO_4$, 0.31% KCl, and 0.23% $CaCl_2$).

Solution B: As solution A but containing, in addition, 0.8% ammonium orthophosphate based on the weight of rock salt.

After 400 hr, the plates were removed, the corrosion products scraped away, and the weight loss of each sheet measured. The weight losses are shown in the table below.

	Loss of weight in grams
Solution A:	0.9
Solution B:	0.3

Example 2 The process of example 1 was repeated except that the ammonium orthophosphate in solution B was replaced by triple superphosphate which was used in an amount of 1% based on the weight of rock salt. The results were as follows:

	Loss of weight in grams
Solution A:	0.9
Solution B:	0.05

Example 3: The process of example 1 was repeated except that the ammonium orthophosphate in solution B was replaced with by-product gypsum which was used in an amount of 33% by weight based on the rock salt. The results were as follows:

	Loss of weight in grams
Solution A:	0.9
Solution B:	0.06

3.2.9 Organic Inhibitors and Polyphosphate Blends

Bishop (1972) reported the development of a corrosion inhibitor for use as an additive to highway deicing salt. Laboratory experiments were used as screening tests, and the more promising materials were evaluated in trials on cars.

The corrosive action of salt on mild steel was almost constant over a concentration range of 10%-0.05% salt in solution. The protection given by inhibitors diminished markedly as they became diluted, and they were only effective in reducing corrosion if their initial addition was on the order of 7% of the salt. This was demonstrated both in laboratory tests and in field trials.

The use of this proportion of inhibitor would increase the expenditure on deicing salt by about £25M. Even though the cost of vehicle corrosion from salt exceeds this considerably, it seems unlikely that such an increase in public expenditure on salting could be justified unless almost complete protection from corrosion could be offered.

A cheaper way of employing the inhibitor as part of an automatic car-washing process is being examined.

3.2.10 Barium and Zinc Salts of Sulfonamide Acids

Farbwerke Hoechst (1970) was granted a British patent on a composition for thawing ice and snow, which comprises 99 parts NaCl or $CaCl_2$ and 1 part of an anticorrosive agent. The anticorrosive compound contains 10% of a barium or zinc salt $R^2(RSO_2)N(CH_2)_xCHR^1CO_2M$. The remaining 90% of the anticorrosive compound is made of a mineral oil. The anticorrosive compound has the advantage (in addition to its corrosion prevention properties) of causing an anticaking effect; agglomeration of the salt is thus avoided.

3.2.11 Polyphosphate, Emulsifier STH, and Carguard™*

Steed (1969) describes laboratory experiments to evaluate three proprietary corrosion inhibitors as additives to road deicing salt. Test panels of both bare and painted mild steel were used. Tests were carried out employing first an intermittent salt spray method, and then an intermittent immersion method. Tests were carried out at temperatures of 25° and 5°C. The inhibitors tested were sodium polymetaphosphate; emulsifier STH; and Carguard™, which contained sodium chromate.

Under spray conditions, which are considered the more realistic, no inhibitor gave a useful degree of protection to bare steel, but polymetaphosphate markedly reduced rust creep from damaged areas of painted panels. In the immersion test, the inhibitors gave a high degree of protection to bare steel.

It is concluded that the laboratory tests are useful as screening tests for preliminary evaluation, but tests of potential inhibitors using actual vehicles under realistic conditions are now required.

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* Carguard is a trademark of Cargill, Inc.

3.2.12 Organic Cathodic Passifier Plus Inorganic Anodic Passifiers

Eversole and Lee (1968) were issued a U.S. patent for a salt composition for deicing. The composition included a deicing salt and minor, but effective, amounts of an alkali metal chromate or nitrite anodic passifier and an organic compound cathodic passifier having an amino nitrogen atom and an alkyl radical of from 8 to 24 carbon atoms.

Various alkyl diamines, triamines, amino acids, quaternary ammonium compounds, alkyl ethanol amines, and imidazolines were claimed.

Six examples of anticorrosive salts gave 50%-60% protection from corrosion in 14-day tests of cars driven in simulated field tests.

3.2.13 Sodium Chromate Plus a Fatty Amine (Carguard™)

Zaremski (1968) reported on a study which was similar to the study reported by Jameston and Ireland. Stainless steel, such as used in automobile trim or mufflers, was the major focus. Test panels were mounted on 115 cars that were driven on streets treated with Carguard™-inhibited deicing salts, either in Minneapolis, Minnesota or Pittsburgh, Pennsylvania. Test panels were also mounted on 115 cars that were then driven on streets treated with uninhibited deicing salts, either in Milwaukee, Wisconsin or suburbs of Pittsburgh.

The Minneapolis versus Milwaukee tests showed Carguard™-inhibited deicing salts gave 99% protection from galvanic corrosion (stainless steel trim mounted on painted test panels) during the first year of the tests and 90% protection on samples reexposed during the subsequent winter.

Tests run in the Pittsburgh area resulted in only 61% protection from galvanic corrosion during one year of exposure. This result was attributed to increased atmospheric corrosion from air pollutants.

3.2.14 Sodium Chromate Plus a Fatty Amine (Carguard™)

Jameston and Ireland (1968) conducted a study in which test panels were mounted on 80 police cars and taxicabs. Forty cars were driven in Minneapolis, where streets were treated with Carguard™-inhibited deicing salts. Thirty cars were driven in Milwaukee, where streets were treated with uninhibited deicing salts. The remaining 10 cars were driven in suburb cities around Minneapolis where streets were treated with uninhibited deicing salts.

After 7 weeks, bare steel test panels showed a 39% reduction of corrosion for cars driven over streets treated with Carguard™-inhibited deicing salts. After 14 weeks, bare steel test panels showed 52% reduction of corrosion for cars driven over streets treated with Carguard™-inhibited deicing salts.

3.2.15 Anodic, Cathodic, and Other Corrosion Inhibitors

Fromm (1968) reports a study of three corrosion inhibitors which were incorporated with sodium chloride and evaluated by laboratory corrosion tests and in test rigs for traffic simulation tests. Test panels were also mounted on actual traffic vehicles in eight cities of Canada, but no effects of corrosion inhibitors in deicing salts were measured because none of the cities used inhibited salt.

The results of the laboratory tests are summarized as follows:

Substrate: Bare steel
Corrodant: Sodium chloride
Corrodant concentration: 1-5 wt %. The results for 3 wt % are presented here

Corrosion inhibitors
- A = impure sodium hexametaphosphate + 10% $CaCl_2$,
- B = a finely divided metal powder, electropositive to iron,
- C = anodic and cathodic corrosion inhibitors

Inhibitor concentration:
A = 1 and 2 wt %
B = 0.5 and 1 wt %
C = 0.5 and 1 wt %

Corrosion reduction (dip test):

Inhibitor at Dosage Level	Temperature 32°F	Temperature 70°F
A at 1 wt %	N.S.	40%
A at 2 wt %	95%	80%
B at 0.5 wt %	N.S.	N.S.
B at 1 wt %	N.S.	30%
C at 0.5 wt %	N.S.	N.S.
C at 1 wt %	N.S.	40%

N.S. = no significant reduction in corrosion

The traffic simulator tests showed no significant difference in corrosion rates for uninhibited and inhibited deicing salts.

3.2.16 Sodium Chromate and Sodium Hexametaphosphate

Himmelman and Parsons (1967) report the laboratory evaluation of four corrosion inhibitors in sodium and calcium chloride solutions. Bare steel panels also were attached behind the wheels of four maintenance trucks used on deicer-treated streets. Two trucks were driven on streets treated with inhibited sodium and calcium chloride deicers, and two trucks were driven over streets treated with similar uninhibited deicing salts.

The laboratory test results are summarized as follows:

Substrate: Bare steel
Corrodant: Commercial sodium chloride deicer

Corrodant concentration: 3 wt %

Inhibitor: ASI = sodium chromate + an organic inhibitor
Inhibitor: ASI = sodium hexametaphosphate

Inhibitor concentration: Not reported

Corrosion reduction:
ASI = 64.5%
ASII = 41.5%

Other factors to consider: Two other unidentified organic inhibitors were tested, but the reduction of corrosion was reported as less than 41.5%

The field tests were not conclusive due to variations in application rates of the inhibited and uninhibited deicers and also how the vehicles were driven over the deicer-treated roads.

3.2.17 Amines, Sulfonates, Polyphosphtes, and Others

This article by Boies and Bortz (1965) is a comprehensive report of laboratory studies of selected corrosion inhibitors for sodium and calcium chloride chemical deicers. The effects of inhibited and uninhibited sodium and calcium chloride on bare steel in dirt and in concrete were measured. Also, chemical additives to reduce spalling of concrete were studied.

The results of one series of corrosion inhibitor tests are presented in Table D-4 and summarized as follows:

Substrate:	Bare steel
Corrodant:	Sodium chloride solution periodically added to bare steel, partially embedded in dirt. This test was chosen to simulate auto body corrosion of bare steel and at locations where soil accumulates

Corrodant concentration: 6 wt % sodium chloride solution

Boies recommends that field tests with corrosion-inhibited deicing salts be performed as follows:

- <u>Deicer Salt No. 1</u>
  a. <u>Inhibitor Composition</u>
  62% sodium polyphosphate
  6% zinc chloride
  32% sodium metasilicate

  b. <u>Inhibitor Concentration</u>
  2 wt % on rock salt

Table D-4. Corrosion reducing effects of various inhibitors for sodium chloride solutions on bare steel partially embedded in dirt.

Inhibitor	Inhibitor concentration (wt % of NaCl)	Corrosion reduction (%)
Fatty acid amines	2	40-60
Imidazoline	2	50-70
Imidazoline quaternary	2	45
Petroleum sulfonate	2	34
Sodium polyphosphate[a] + Zn acetate 7:3	3	82
Sodium polyphosphate + $Ca(OH)_2$ 3:5	2.5	88
Sodium polyphosphate + Zn acetate + sodium metasilicate 5:1:5	2.5	76
Sodium metasilicate	17	88

[a] Boies does not identify "sodium polyphosphate." However, he does mention that a problem of polyphosphate is the tendency to revert to less active orthophosphate. Therefore, it is assumed that "polyphosphate" is hexametaphosphate.

- <u>Deicer Salt No. 2</u>
  a. <u>Inhibitor Composition</u>
  63% calcium hydroxide
  37% sodium polyphosphate

  b. <u>Inhibitor Concentration</u>
  5 wt % on rock salt

- Deicer Salt No. 3
    a. Inhibitor Composition
    100% sodium polyphosphate

    b. Inhibitor Concentration
    2 wt % on calcium chloride

- Deicer Salt No. 4
    a. Inhibitor Composition
    Armeen C or
    Duomeen S or
    Nalcamine G11 or A31

    b. Inhibitor Concentration
    2 wt % on rock salt

Boies suggests that a 5 wt % addition of either dextrose or the sodium salt of ethylene diamine tetraacetic acid (EDTA) to rock salt would reduce concrete spalling.

3.2.18 Sodium Hexametaphosphate and Supplements

Palmer (1963) reports a study in which three curbed asphalt tracks, 40 in. in diameter, were constructed in Canada. A test rig containing four wheels with simulated fender wells was driven around the tracks. Flat and V-type steel coupons were mounted inside the fender wells.

Substrate: Bare steel
Corrodant: Rock salt (NaCl)

Corrodant concentration: 1%-12%, 5.8% average

Corrosion inhibitor: Sodium hexametaphosphate supplemented by nitrites, chlorides, and a soluble zinc compound

Inhibitor concentration: 2% by weight of rock salt, average was actually 1.42%

Corrosion reduction: Range = 10.5%-77.0%, average 55.7%, depending on the type and positions of the test panel.

Other factors to consider:	The polyphosphate inhibitor at 2 wt % was effective in preventing corrosion in open, well-splashed areas, but considerably less effective in crevice areas

3.3 Corrosion Inhibitors for Deicer-Related Systems

Corrosion inhibitors used in refrigerating brines, saltwater desalination, and high-density brines are reviewed in this section.

3.3.1 Corrosion Inhibitors for Deicer-Related Systems

These brines are used as heat transfer fluids and generally are composed of aqueous solutions of either $CaCl_2$ or NaCl in a closed piping system.

Due to the limited availability of oxygen, oxidizing passivating corrosion inhibitors such as chromates and nitrites have been used. According to Bregman (1963), the American Society of Refrigerating Engineers recommends a pH from 7.0 to 8.5 and sodium dichromate corrosion inhibitor at concentrations of 2,000 ppm for calcium chloride brines and 3,200 ppm for sodium chloride brines.

A Japanese patent by Imai, Ano, and Kaisha (1987) cites the use of mixtures of chromium-based compounds (chromates and dichromates) and polyphosphates (not otherwise specified) as corrosion inhibitors for refrigerating brines. The invention claims soluble nitrites (sodium, calcium, ammonium) in combination with water-soluble silicates (sodium and calcium) as corrosion inhibitors for $CaCl_2$ brines. The best example for inhibiting corrosion was 2,000 ppm sodium nitrite with 100 ppm sodium silicate in a calcium chloride brine.

Bregman (1963) states that the American Society of Refrigerating Engineers recommends 1.6 g/L of sodium monohydrogen phosphate as a corrosion inhibitor for sodium chloride brines, where chromates cannot be used. Also, sodium silicate is effective for sodium chloride brines, but not for calcium chloride brines. Lithium and sodium molybdate are effective at a pH of 12.5 to 13.5.

3.3.2 Saltwater Desalination

In desalination plants, seawater and salt-concentrated seawater must be processed. Since most of the desalination plants are evaporative (distillation) systems, prevention of scale formation on heat exchanger surfaces is critical. Therefore, carbon dioxide generally is removed from incoming seawater by various vacuum degassing techniques. At the same time, most of the dissolved oxygen is also removed.

Oakes (1973) summarizes a report to the Office of Saline Water by the Dow Chemical Company. In this report, three inorganic corrosion inhibitor systems are described for use with oxygen-containing seawater.

- 50 ppm of sodium dichromate and sodium phosphate
- 50 ppm of sodium chromate and sodium phosphate
- 100 ppm of sodium chromate and sodium phosphate and zinc iodide

Sodium monohydrogen phosphate was the preferred source of phosphate because it did not cause pitting.

Sodium hexametaphosphate is reported to be an effective corrosion inhibitor for flowing seawater (Bregman, 1963). Also, Bregman cites work showing aniline, pyridine, and alkylated pyridine phosphates as effective corrosion inhibitors.

3.3.3 High-Density Brines

The petroleum industry uses the largest quantity, in total, of corrosion inhibitors. Anticorrosive compounds are used during drilling, field production, transportation, refining, and in consumer products.

Corrosion inhibitors generally used today in the petroleum industry are, or are similar to, the organic adsorption-type corrosion inhibitors discussed previously. Bregman (1963) presents an excellent review of the literature on the uses of corrosion inhibitors in the petroleum industry.

Of particular interest to this project are corrosion inhibitors for heavy brines. Heavy brines are used during drilling operations to flush the drill cuttings from the drill bore. Heavy brines are also used in completed wells to maintain hydrostatic pressure between a well casing and tubing within the casing.

Heavy brines are composed of aqueous solutions of sodium chloride and bromide, calcium chloride and bromide, magnesium chloride and bromide, and zinc chloride and bromide. The halide salt used is determined first by the required density of the brine. Solution densities greater than 15 lb/gal can be produced.

Son and Kuzlik (1985) claim that erythorbate salts (sodium preferred) at concentrations from 0.1 to 25 ppb are corrosion inhibitors for heavy brines. Sodium molybdate enhances the erythorbate corrosion inhibition in some heavy brines. The patent states that the erythorbate could act as an antioxidant, a reducing agent, an oxygen scavenger, and as a chelating agent in brine solutions.

Doty and Larson (1988) were granted a U.S. patent assigned to the Dow Chemical Company which claimed zinc or ammonium thiocyanate as an effective corrosion inhibitor for heavy brines. Ammonium thiocyanate could be used if a component of the heavy brine was a zinc halide. Claimed effective concentration ranged from 0.05 to 1.5 wt %.

Ezzat, Augsburger, and Tillis (1988) present laboratory and field test results for an unspecified inorganic corrosion inhibitor for heavy brines. Both laboratory and field test results showed good corrosion inhibiting properties.

4

Conclusions

- Significant progress has been made in the chemical inhibition of the corrosive effects of deicing salts on vehicles. However, improvements in automotive design and protective coatings have reduced the impact of deicing salts on vehicles.

- Several types of corrosion inhibitors have been shown to reduce significantly the corrosive effects of sodium chloride solutions on various types of bare steel, and in one case, steel in concrete.

- The health hazards and environmental impacts of corrosion inhibitors for chloride containing deicer salts are not well defined in the technical literature.

- Corrosion protection obtained by using inhibitors with deicer salts diminishes as the inhibitors become diluted. Many inhibitors are only effective in quantities on the order of 7% by weight of salt.

- A new thrust in the development of corrosion inhibitors for chemical deicers has emerged. This new thrust is targeted at the inhibition of the corrosive effects of deicer salts on highway hardware and structures, especially bridges and reinforced concrete.

- Sodium chloride-based deicers have several advantages over other chemical deicers. These advantages are: ready availability at low cost, effectiveness at low temperatures and low application rates, low-order health and environmental effects, and established application technology.

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Part 2—Detailed Experimental Procedures for Evaluating Corrosion Inhibitors

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Detailed Experimental Procedures

Detailed procedures employed in conducting the experimental work are presented in the following seven subsections: (1.1) Preparation of Test Specimens and Test Cells, (1.2) Preparation of Test Solutions and Initial pH Measurements, (1.3) Weekly Start-up Procedure, (1.4) Basic Daily Experimental Operations, (1.5) Test Specimen Cleaning Procedure, (1.6) Test Specimen Weighing Procedure, and (1.7) Equipment and Materials Specifications.

1.1 Preparation of Test Specimens and Test Cells

The procedures used to prepare the metal test specimens, "electrode" test specimens, and the test cells are outlined in the following three subsections.

1.1.1 Preparation of Metal Test Specimens

The metal test specimens which were used to determine the corrosion rates by weight loss were prepared according to the procedure outlined below:

a. Preweighed metal test specimens were purchased from Metal Samples, Inc., Munford, Alabama. All test specimens had been rinsed with acetone and wiped dry before weighing. The test specimens were packed and shipped and stored in envelopes pretreated with corrosion inhibitor.

b. A nylon string with an ID tag was attached to each test specimen.

c. The tag was labeled with test specimen number and test cell position number and assigned to a test cell.

d. The test specimens were stored in individual envelopes treated with a corrosion inhibitor until placed in the test cell.

1.1.2 Preparation of "Electrode" Test Specimens

a. Each test specimen was degreased by dipping twice in high purity acetone and allowed to dry in laboratory air.

b. A 20-cm insulated wire (22-gauge, single-strand, tin-coated) was attached to the specimen with a brass screw and nut.

c. The connection area of the attached wire was covered with liquid tape.

d. Each "electrode" test specimen was assigned to a test cell.

e. Each electrode test specimen was stored in a desiccator until placement in the test cell.

1.1.3 Preparation of Test Cells

a. The lip of each plastic test cell was notched for 8 test specimens plus 1 electrode test specimen, evenly spaced around the circumference of the cell.

b. A Plexiglas spacer was fitted inside the test cell.

c. The test cell was rinsed with ethanol and allowed to dry in laboratory air.

d. The electrode test specimen was attached to the test cell.

e. The test specimens were hung in the test cell so that the top of the test specimen was just below the bottom of the Plexiglas spacer rim, and the nylon string on the test specimen was secured with tape to the outside of the test cell.

1.2 Preparation of Test Solutions and Initial pH Measurements

The master 3 wt % sodium chloride solution used to prepare all other test solutions and the 25 test solutions, each containing a specified concentration of one of the nine candidate corrosion inhibitors, were prepared as follows:

a. Master solution: 3 wt % NaCl was prepared from Fisher reagent NaCl and deionized water. The pH of the master solution was 6.0. All test solutions containing inhibitors were prepared using the 3 wt % NaCl master solution.

b. First set of inhibited test solutions: Inhibited test solutions were prepared by adding corrosion inhibitor to 3 wt % NaCl master solution. The inhibitor concentrations on a solids basis (weight % of total solids) and the pH of freshly prepared inhibited solutions were:

- PCI, a calcium lignosulfate (Great Salt Lake)

  10 wt % pH = 6.8
  7 wt % pH = 6.8
  4 wt % pH = 6.8

- Na_2MoO_4, sodium molybdate (Aldrich)
  3.5 wt % pH = 7.85
  2.5 wt % pH = 7.85
  1.5 wt % pH = 7.90

- $ZnSO_4$, zinc sulfate, + $Na_5P_3O_{10}$, sodium tripolyphosphate (Fisher)

  7.5 wt % each pH = 5.4
  5.0 wt % each pH = 5.8
  2.5 wt % each pH = 5.7

- Na_2PO_3F, sodium monofluorophosphate (AESAR)

3.5 wt %	pH = 6.25
2.5 wt %	pH = 6.25
1.5 wt %	pH = 6.25

c. First set of control test solutions: All control solutions were prepared at 3 wt % in deionized water. The pH of freshly prepared control solutions were:

- Deionized water: pH = 5.8

- NaCl, sodium chloride (Fisher)

3.0 wt % pH = 6.0

- Rock salt (Morton Safe-T-Salt)

3.0 wt % pH = 9.5

- CMA, calcium and magnesium acetate, (ICE-B-GONE, Chevron)

3.0 wt % pH = 9.9

d. Second set of inhibited test solutions

- $Ca(H_2PO_4)_2$, calcium phosphate (Baker)

3.5 wt %	pH = 3.6
2.5 wt %	pH = 3.75
1.5 wt %	pH = 3.9

- Na_2MoO_4, sodium molybdate (Aldrich) + $Na_5P_3O_{10}$, sodium tripolyphosphate (Fisher)

3.5 wt %	pH = 8.8
2.5 wt %	pH = 8.8
1.5 wt %	pH = 8.8

- Na_2FPO_3, sodium monofluorophosphate (Aesar) + $N[CH_2P(O)(OH)_2]_3$, nitrilotris(methylene)phosphonic acid (Aldrich)

3.5 wt %	pH = 3.0
2.5 wt %	pH = 3.2
1.5 wt %	pH = 3.3

- $ZnCl_2$, zinc chloride + $Na_5P_3O_{10}$, sodium tripolyphosphate (Fisher)

7.5 wt % each	pH = 5.5
5.5 wt % each	pH = 5.9
2.5 wt % each	pH = 6.2

- CMA, calcium and magnesium acetate (Chevron Ice-B-Gone)

10 wt %	pH = 10.2

e. Second set of control solutions: All control solutions were prepared at 3 wt % in deionized water. The pH of freshly prepared control solutions were:

- Deionized water: pH = 5.8
- NaCl, sodium chloride (Fisher), 3 wt %: pH = 5.9

1.3 Start-up Procedure

The following procedure was employed each day for 4 days to start each series of test cells:

a. Test solutions were prepared according to the test schedule.

b. Test specimens were placed in the test cells, and test cells were set in position.

c. Test cells were filled to the 750-mL mark with appropriate test solution.

d. Test cells were covered with a lid through which the aerator tip was attached.

e. Air supply was turned on and the bubble rate was regulated.

1.4 Daily Experimental Operations

a. Unexposed test specimens for cleaning control were:

   (1) Removed from protective envelopes.

   (2) Initial weights recorded on daily data sheet.

b. Lids and air source were removed from all test cells to be tested.

c. pH of test solutions was measured at 1, 2, 4, and 6 weeks. The electrical potential of the electrode specimens in the test solutions was measured after 1, 2, 4, and 6 weeks.

d. All test specimens for the day were removed and suspended in beakers of deionized water, steel, and aluminum specimens in separate beakers. Lids and air supply were reattached to the test cells.

e. The test specimens were cleaned according to ASTM G1-81.

f. The cleaned test specimens were weighed and their weights recorded.

g. Visual inspection of test specimens for pitting was conducted.

h. Inspected test specimens were stored in plastic bags in a desiccator.

i. All test cell solution levels were adjusted to the 750-mL mark with deionized water, and air bubble rate was regulated.

1.5 Corroded Test Specimen Cleaning Procedure

One steel and one aluminum unexposed test specimen were cleaned along with the exposed test specimens each day.

a. Nylon brushing under running tap water (cold): nylon toothbrush (one for steel, one for aluminum).

- Test specimens were placed in holder and scrub-brushed 20 to 30 times on each side. All test specimens on any given day were given the same number of strokes.
- Then, each test specimen was (a) rinsed with deionized water from a squeeze bottle; (b) rinsed with acetone from a squeeze bottle; and (c) placed on a paper towel to dry.
- Note: During brushing/rinsing operations, all test specimens were handled by the attached nylon string.

b. Acid bath: Test specimens were handled with vinyl gloves; fresh acid was used each day.

- Nylon string with ID tag was cut off test specimens.
- Test specimens were strung onto a Teflon band with Teflon spacers between to prevent contact. Steel and aluminum were placed on separate bands. Bands were closed with tape.
- Test specimens were immersed in appropriate acid bath.

c. Steel test specimens:

- Cleaning solution: 50 g stannous chloride + 20 g antimony trioxide + 1,000 mL concentrated hydrochloric acid: 120 mL in a 150-mL beaker, stirred with an ultrasonic bath.
- 10-sec immersion time at 77°F (25°C).

d. Aluminum test specimens:

- Cleaning solution: 20 g chromic oxide + 50 mL concentrated phosphoric acid, diluted to 1 L with deionized water: 120 mL in 150-mL beaker, heated on a steam bath.
- 2-min immersion time at 144° to 212°F (90° to 100°C).

e. Rinsing and drying: Test specimens were handled with vinyl gloves and Teflon forceps.

- Deionized water rinse: Immersed twice, clean water each time.
- Acetone rinse: Dipped twice in acetone, clean each time.
- Test specimens were hung to dry.

f. Fiberglass brushing: Test specimens were handled with vinyl gloves and Teflon forceps.

- Test specimens were removed from the Teflon band.
- Specimens were brushed 20 to 30 strokes on each side and once around edges. All test specimens of the same metal on any given day were brushed the same number of strokes. Steel test specimens were scrub-brushed. Aluminum test specimens were brushed by stroking in one direction.
- Test specimens were wiped with paper towels.
- Test specimens were dipped in acetone and put on a paper towel to dry.
- Note: Some variance in the abrasiveness of the fiberglass brush refill was noted from day to day.

1.6 Test Specimen Weighing Procedure

a. Test specimens were handled with Teflon forceps.

b. Test specimens were weighed in random order to avoid bias.

c. The balance was rezeroed before each weighing.

d. Steel and aluminum test specimens were stored in separate bags in desiccators after weighing.

e. Test specimens were weighed to 0.1 mg.

1.7 Equipment and Materials Specifications

- Nylon toothbrush, adult, Revco Med. No. 1953.
- Fishing line: Omni Flex 6-lb test (Shakespeare), monofilament.
- Sample ID tags: Dennison metal-rim 0 tags, No. 14-312-1.
- Fiberglass brushes: "Eraser Co.," Syracuse, NY 13221
  Fiberglass: Super Fybrglass Eraser Model AB0001; brush refills AB0009, Vigor No. 703, local.
- Electrodes:
  - (1) For mV measurements: Fisher Calomel Reference Electrode No. 13-620-259, gel-filled.
  - (2) For pH measurements: Fisher Calomel Reference Electrode No. 13-620-104.
- Test cell electrode attachment coating: "Liquid tape," GC Electronics, No. 10-1762.
- Air system filter: Balston No. A915A, Lexington, MA.
- Air system pressure indicator: Balston Type 41-070, Lexington, MA.
- Test cell beakers: 1,000-mL polyethylene plastic (~ 11.5-cm inside diameter top, 10-cm inside diameter bottom, 14.5-cm height).
- Plexiglas spacers: ~ 9-cm inside diameter, 1-cm height (inserted so bottom edge of spacer is about 7 cm from top of cell).
- Test cell lids: Polystyrene (1-cm hole in center for air inlet).
- Metal test specimens: Steel (C1018) and aluminum (A7075) were obtained from Metal Samples, P.O. Box 8, Munford, Alabama 36268. Specimens were preweighed

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