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An interim report on the results of the first phase of SHRP project H-205, "Evaluation Procedures for Deicing Chemicals and Improved Sodium Chloride." Includes identification of relevant test procedures for evaluating properties of deicing chemicals, and a list of relevant ASTM standards. The author concludes that chemical deicer test methods require forther experimental development and validation in the following five areas" deicer performance, concrete compatibility, frictional characteristics, concrete reinforcement corrosion, and ecological hazard assessment.

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Strategic Highway Research Program Executive Committee

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Preface

This interim report was prepared by Midwest Research Institute (MRI). The Institute is the contractor for Contract H-205, *Evaluation Procedures for Deicing Chemicals and Improved Sodium Chloride*. Portions of the report were contributed by the subcontractor, the University of Kansas Center for Research Inc. (CRINC). This report presents the findings of the Phase I research that involved a review and assessment of test methods and criteria for evaluating chemicals proposed for use as deicing agents.

The report was prepared under the administrative direction of Dr. William D. Glauz, Director of the Engineering and Materials Sciences Department at MRI. Dr. Cecil C. Chappelow, Senior Advisor for Materials Sciences (MRI), was the principal investigator. Mr. Robert R. Blackburn, head of the Engineering and Statistical Sciences Section (MRI); Dr. A. D. McElroy, Research Associate for Applied Science (MRI); Dr. Carl E. Locke, Professor of Chemical and Petroleum Engineering (CRINC); and Dr. F. Jerry deNoyelles, Professor of Botany and Systematics and Ecology (CRINC), were co-principal investigators. Others who assisted in the research included Mr. Gary R. Cooper, Ms. Rosemary Moran, and Mr. Mark R. Blackburn, all of MRI, and Mr. Paul C. Schwaab of CRINC.

The study under way by Midwest Research Institute will culminate in a manual of recommended procedures, which may differ in detail from the preliminary procedures presented in this report. Prior to implementation of any of the procedures described here, the SHRP office should be contacted for any changes that have occurred. The SHRP staff contact is L. David Minsk, who can be reached at (202) 334-1450.

1.0 INTRODUCTION

This program (SHRP H-205, "Evaluation Procedures for Deicing Chemicals and Improved Sodium Chloride") consists of two phases. The first phase has been directed towards the development of a preliminary set of evaluation procedures based on the thermodynamic and corrosion characteristics of promising categories of potential deicer chemicals. The second phase is directed toward the development and modification of chemical deicer test methods, and the development and evaluation of improved sodium chloride.

This interim report presents the research activities and findings of the Phase I investigations.

1.1 Problem Statement

Current emphasis in the search for an alternative deicing chemical has been on calcium magnesium acetate (CMA), but other chemicals are currently being considered. Furthermore, it is highly probable that industry, realizing the potential for a vast market for an improved deicing chemical, will introduce additional compounds. Experience gained in the evaluation of CMA, which has been the subject of a series of tests over many years, points to the clear need for standard methods of test and evaluation of candidate deicing chemicals which can be used by individual states in the absence of a central testing laboratory. Documenting these methods will also serve to stimulate the search for the introduction of new effective chemicals, since the time from development to market will be reduced. The purpose of this first phase was to prepare a preliminary set of test protocols for chemical deicers, and to develop a technical rationale for improved sodium chloride.

1.2 Research Objectives

The first phase of the program concentrated on the identification, review, and assessment of procedures and methods for the evaluation of candidate deicing chemicals. Phase I had three specific objectives:

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

1.3 Scope of Work

The scope of the Phase I research 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.

The results of the Phase I research study include:

- A report detailing the findings of the review of worldwide laboratory and field testing of deicing chemicals, including identification of the chemicals investigated, the characteristics identified as important, the tests that were applied, and the conclusions reached regarding the validity and adequacy of the tests.
- A guide or handbook for use by materials and maintenance engineers for selecting the critical criteria to be applied to the evaluation of candidate deicing chemicals for the specific use conditions under consideration.
- A series of recommended test procedures for use in evaluating candidate deicing chemicals.
- An interim report, covering the above, and a work plan for Phase II of the program, recommending a "best" combination of research on new or modified test methods, and improved sodium chloride.

1.4 Research Approach

The primary objective of Phase I was the identification and documentation of criteria and procedures for evaluating chemical deicers. The secondary objective was the formulation of technical rationales for the development of improved sodium chloride based deicers.

The Phase I research work was organized into four sequenced tasks. The objectives, activities, and results of each of each of the four tasks are summarized as follows.

1.4.1 Task 1--Review Research on Evaluation and Testing of Deicing Chemicals: The purpose of this task was to conduct a critical review of the scientific, trade, and transportation literature relative to the evaluation and testing of deicing chemicals. The goal of this task was 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.

A Special Report entitled "Evaluation and Testing of Chemical Deicers: Literature Review" was issued on August 5, 1988. The Special Report contains general background information which presents 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 focuses 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 is presented as a basis for structuring a program for the development of improved chemical deicers, including improved sodium chloride.

1.4.2 Task 2--Establish Criteria for Complete Characterization of Chemical Deicers: The purpose of this task 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: (a) fundamental properties, (b) deicer performance, (c) materials compatibility, (d) environmental effects, (e) engineering operations, (f) meteorological and highway parameters, and (g) health and safety practices.

A Special Report entitled "Characterization and Selection of Chemical Deicers: Criteria Document" was issued on October 7, 1988. The Special Report contains general background information which presents the objectives of the criteria document and the methodologies employed in developing the chemical deicer criteria. The major elements of the criteria document are 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.

1.4.3 Task 3--Identification of Relevant Test Procedures for Evaluating Properties of Candidate Deicing Chemicals: The purpose of this task 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 scope of work was organized into three main subtasks: Subtask 3a--Deicer Performance Tests; Subtask 3b--Deicer Corrosion Tests; and Subtask 3c--Deicer Environmental Impact Tests. However, in light of the criteria established in Task 2 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: 42 ASTM standards, 1 OSHA test protocol, 2 nonstandard test procedures requiring documentation, and 7 tentative test procedures requiring further development.

1.4.4 Task 4--Prepare Interim Report and Work Plan for Phase II: The fourth task of Phase I was the preparation of an interim report and the submission of this report for review by SHRP. The interim report includes a detailed presentation of the results of all work performed on Tasks 1, 2, and 3 of Phase I. The report emphasizes the identified methods of testing developed in Task 3. Where possible, the test methods are described in a format similar to the methods published by ASTM or SAE, so that the methods can be used by materials laboratories for evaluating the candidate deicing chemicals and establishing conformance to the criteria identified in Task 2. The preparation of the interim report was accompanied by the preparation of a work plan for Phase II of the research program. The work plan consists of our recommendations for the direction of the remaining research to be conducted under program H-205. The investigations to be performed are specified in detail, along with the allocations of resources to each activity.

Based on an interim evaluation of scope and content of the completed and planned work, a preliminary outline of the interim report and work plan for Phase II was submitted to SHRP on December 1, 1988. An Expert Task Group review of H-205 was held at SHRP headquarters in Washington, D.C., on December 19, 1988. The review included presentations of the completed work on Tasks 1 and 2, which had been documented in two Special Reports, and the ongoing work on Tasks 3 and 4. Recommendations for revisions and additions received during the December review meeting were incorporated and the finalized work plan was submitted to SHRP on January 17, 1989.

Submission of the Phase II work plan document and the materials presented herein, which constitute the Interim Report for Phase I, represent the completion of Tasks 3 and 4 requirements under SHRP Contract No. H-205.

1.5 Organization of Report

The remainder of this interim report is organized as a review of the three primary Phase I research activities. Section 2.0 presents a summary of the review of the literature on the evaluation and testing of chemical deicers. Section 3.0 contains a summary of the criteria for the characterization and selection of chemical deicers. Section 4.0 presents recommended test methods for evaluating chemical deicers. Appendix A presents an organizational summary of the specific test methods selected for evaluation of chemical deicers. Appendix B contains a list of relevant ASTM test methods and standards.

2.0 LITERATURE ON TESTING AND EVALUATION OF CHEMICAL DEICERS

The literature on chemical deicers and deicer-related technology was searched via several computerized literature sources augmented by manual searches. Computerized searches of the following data bases were conducted:

CRREL (Cold Regions Research and Engineering Laboratory)
TRIS (Transportation Research Information Center)
NTIS (National Technical Information Services)
CAS (Chemical Abstracts Search)

Manual searches of the following were conducted:

ASTM Index to Technical Publications and Reports (1961 to 1980)
Better Roads (1980 to 1987)
NACE Corrosion Abstracts (1978 to 1985)
OECD--Organization for Economic Cooperation and Development (1987)
IRF--World Survey of Current Research and Development on Roads and Road Transport (1987 listings)

A general search was conducted for three subject areas:

- State-of-the-art conventional, developmental, and potential deicers
- Chemical deicer composition
- Chemical deicer type

Specific searches for testing procedures were conducted in the following areas:

- Fundamental characteristics
- Deicer performance
- Materials compatibility
- Environmental impacts

The searches yielded well over 1,000 literature citations identified by title and key words or abstracts. Approximately 500 of the citations were procured for review. Approximately 220 were identified as relevant and were cited in the literature review report.

2.1 State-of-the-Art Synopsis

Potential chemical deicers--excluding for the moment two critical factors, cost and significant adverse side effects--consist generally of ionic or nonionic chemicals or mixtures which (a) are highly soluble in water at low temperatures, (b) dissolve in water to yield ions or molecules of reasonably low average molecular weight, and (c) exhibit a eutectic temperature, preferably several degrees lower than the ambient temperature encountered in the ice or snow event of interest.

Accordingly, the inorganic, ionized deicer is usually composed of alkali or alkaline-earth metal chloride salts. Other anions of potential utility include the acetate, formate, phosphate, and organic acid anions which are derived, potentially at low cost, from organic cellulosic matter by chemical or biochemical processing methods. The nitrate, nitrite, and sulfate anions have been proposed as constituents of chemical deicers; the number of acceptable anions is limited, however, by the fact that many of these anions are incompatible with concrete.

Potential nonionic deicers generally are limited to the lower-molecular-weight simple aliphatic alcohols (i.e., methyl alcohol and ethyl alcohol), lower-molecular-weight amines or amides, and polyhydric alcohols (e.g., ethylene glycol and propylene glycol). Water itself is sometimes a key or essential ingredient of a deicing chemical or a deicing formulation.

Although a large number of chemical substances fall within the general framework described above, the number actually used as chemical deicers is relatively small. Their use is described in the following subsections.

Streets and highways: Rock salt is the workhorse chemical deicer for highways and streets. Flake, pellet, and "liquid" calcium chloride (usually 30% to 32% $CaCl_2$ in water) is used, usually in combination with rock salt or abrasives (sand), and particularly at lower temperatures, i.e., less than 20°F. The "liquid" calcium chloride has been found effective for preventive maintenance. It prevents formation of ice films and can be used for treatment or removal of small quantities or depths of snow and ice. A substantive use of liquid calcium chloride consists of treating rock salt in the rock salt stockpile or immediately prior to applying rock salt to highway surfaces. This mode of use of calcium chloride is reported to substantially increase the effectiveness of rock salt at low temperatures and to reduce salt application requirements at low temperatures by 25% to 50%. Both rock salt and calcium chloride (in solid or liquid form) are employed admixed in relatively small proportions with sand or other abrasives. The added chemical provides some melting action and, in addition, serves to fix the abrasive in the snow or ice cover, thereby fixing it within the surface and preventing discharge of the abrasive to the roadside.

Salt brines (e.g., oil field brines) have been used effectively for highway deicers. Salt brines are apparently used significantly and routinely in Europe but less routinely in the United States. High-speed sodium chloride brine jet streams have been successfully field-tested.

Snow and ice control on highways is effected by varying combinations of mechanical measures (plowing, blowing), chemical deicing, and abrasive application. The degree or level of control is furthermore usually varied to correspond with highway type and traffic volumes. Effective use of chemical deicers involves the timely use of the most effective combination of control measures, based as much as possible on accurate anticipation of meteorological conditions--temperatures, precipitation type and amount, wind velocities and directions. Equipment quality, including particularly metering capabilities and deicer-spreading parameters, is cited as being of great importance with respect to optimum cost and material-conserving application of deicers.

Studies have, in fact, indicated that both the costs of ice and snow control and the quantities of deicer usage can be reduced substantially by improvements in equipment, operator training, better or greater use of mechanical measures in combination with chemical deicing, and accurate forecasting of weather conditions.

Ice and snow control on bridges is a special problem, due to some extent to the basic differences between highways and bridges with regard to ice and snow control, but in large measure due to the corrosion of concrete reinforcement that is attributed to chloride-based deicers. Nonchemical approaches such as electric heating have been tested, and noncorrosive or less corrosive chemical deicers have been tested and are used in some parts of the United States. In companion programs to this program, options for controlling/minimizing reinforcement corrosion are under study.

The most substantial and potentially productive advanced deicer activity of the past several years involving calcium magnesium acetate (CMA) has had as a major objective the development of a noncorrosive and environmentally innocuous chemical deicer. The CMA activities encompassed essentially the complete scope of product conceptualization, research and development, including theoretical analyses of optional materials and the selection of potential candidates, formulation and laboratory characterization and testing, process development and cost reduction, hazard and environmental testing, studies of corrosivity and impacts on materials, and limited scale production followed by field testing. Finally, commercial producers or suppliers of deicers are active in the development of corrosion inhibitors for inclusion in relatively minor quantities in chloride-based deicers.

Aircraft and runway deicing: Compatibility with aircraft materials and runways is at a premium in these uses, and the demands for rapid achievement of safe runways are greater than on highways. Urea, formamide, the glycols, water, and inhibitors are the basic ingredients of deicing formulas employed to remove ice from aircraft and to deice runways.

Residential/commercial deicing (sidewalks, parking lots): Rock salt (sodium chloride), potassium chloride, potassium chloride admixed with sodium chloride, calcium chloride, and urea may be variously admixed with small quantities of other materials purported to enhance deicer utility.

Cost, operational reliability, and public safety have been and continue to be the prime considerations in the selection and use of a strategy for snow and ice control. For these reasons rock salt and sand or other available abrasives used in conjunction with the snow plow are generally preferred. A substitute or alternate chemical deicer can easily be 10 times as costly as rock salt, may require higher ratios of application to achieve comparable control of snow and ice, and may in addition be the source of operational difficulties. Nevertheless, in some sections of the United States, the threat to water quality and vegetation has been judged to be severe enough to limit or exclude the use of rock salt.

2.2 Chemical Deicer Fundamentals

Chemical deicing technology is based on well-established chemical and thermodynamic principles, which include the following:

- A theoretically defined potential for chemical ice melting, with limits and capacities defined by low-temperature solubilities in water, molecular or ionic weights of solutes in water, freezing points versus concentration, and eutectic temperature and compositions. Theoretical/fundamental principles and relationships are well established. A substantial body of data is available in the literature and in chemical properties handbooks for a considerable number and variety of chemicals which either have been actively used or tested as deicing materials or might be given consideration. This body of information is largely restricted to single compounds; data on mixtures are generally not available. From a fundamental standpoint, potentially useful deicer chemicals are limited to a relatively small number of compounds, or their mixtures, for the following reasons:

  The higher theoretical melting capacities are associated with low molecular or average ionic weights. Chloride salts of the lower atomic weight alkali and earth metals constitute reference points for evaluating theoretical melting capacities. Sodium chloride, with an average ionic weight of 29.225, is the benchmark reference in this regard for a practical and reasonably priced deicer. Alkali and alkaline earth salts of acetic acid and formic acid generally offer reasonable theoretical melting capacities. Similarly, a relatively small number of water-soluble, lower-molecular-weight organic compounds--alcohols, amides, and amines--possess reasonable theoretical properties; some of these are employed in special-purpose deicers.

  The utility of a deicing candidate material is further constrained by low-temperature solubilities by concentrations in water associated with freezing points and by eutectic temperatures which define the lowest temperature at which a material can melt ice or snow. In this regard, the actual theoretical melting capacity can be determined only by freezing point-concentration measurements, particularly at temperatures substantially lower than the normal freezing point of water. Magnesium chloride and calcium chloride thus have higher theoretical melting capacities per unit weight at temperatures of about 0°F than sodium chloride. Similarly, eutectic temperatures and compositions must be determined experimentally, although it is clear that very low eutectic temperatures are associated with high miscibility or solubility in water, and with a high degree of association between solute and water molecules at lower temperatures. The chloride salts of magnesium, calcium, ferric iron, cupric copper, and zinc thus exhibit low eutectic compositions and freezing point depressions substantially lower than predicted via the freezing point depression constant for water ($K_F = 1.86$).

- Fundamental thermodynamic factors: Thermodynamic aspects of ice melting are qualitatively straightforward but are ill defined in quantitative terms. The important factors are (a) the difference between the thermodynamic activity of water in ice and water in the brine or liquid in contact with ice; (b) the energy required to melt ice; (c) the energy of dissolution or dilution of the deicer in water or brines; and (d) the heat capacities and heat transfer coefficients of the ice melting system.

  The energy of melting is fixed and the same for all deicers, and heat capacities and heat transfer coefficients will differ little from deicer to deicer. Energies of deicer dissolution are a deicer property subject to control or variation by selection of deicers and insofar as practical by limiting the exposure of deicer to moisture prior to deicer application. Similarly, the thermodynamic activities of water in ice and in deicer brines are subject to control or variation by deicer selection, by limiting ice melting to temperatures substantially above eutectic temperatures at which activity differences are zero, and by measures which favor or promote rapid dissolution of deicers in brines.

The process of selecting a deicer, and of defining the physical form and mode of deicer application and use, initiates with evaluations and analyses based on the above-enumerated fundamental considerations and associated available data. From a fundamental standpoint, the ideal deicer has a eutectic temperature well below the expected ambient temperature range, dissolves rapidly and exothermically in water and brines, has a low molecular or average ionic weight, and depresses the freezing point of water in high proportions relative to its concentrations in water. The deicer selection process, however, is constrained by other factors: actual performance versus theory; cost and availability; storability, handling, and application properties; and the severity and significance of environmental impacts, materials impacts, and safety in manufacture, handling, and use.

2.3 Chemical Deicer Performance

The fundamental or theoretical properties of deicers define and quantify the limits of ice melting and provide some indication of the probable relationships between these limits and the time-dependent aspects of ice melting. Further, fundamental properties are not rigorously related to the mode of interactions between ice or snow and deicers. In general terms, methods or approaches capable of measuring and quantifying actual versus theoretical performance properties are accordingly needed. One cannot reliably predict, for example, how quickly a given deicer in a specific physical form will interact with ice, and how it will respond with time at varying ambient temperatures.

Further, since snow and ice control with or assisted by deicers seldom involves complete melting of snow or ice, it is difficult to predict or design for the optimum combination of deicer and associated efforts or practices.

The literature review revealed several methods which generally address actual time-dependent deicer performance properties. These are:

2.3.1 An ice-melting rate and capacity test: This test consists of the application of a deicer material to ice, at a specified rate and at a controlled constant temperature, and measurement of volumes of brine melt formed at selected time intervals. Several experimental modifications of this basic method are reported in the literature; numerous application rates have been employed, usually many times greater than normal highway application rates, and never at a highway application rate of the order of about 400 lb/lane mile. Literature results are consistent with regard to general trends and to comparisons between deicer materials but are quite variable from method to method because of variations in methodologies and test conditions.

A preferred ice-melting rate and capacity test has been identified. The method consists of the addition of deicer to a 1/8-in thick layer of ice contained in a Plexiglas dish and decantation and measurement of brine volumes via a syringe at selected intervals of time. The method has been utilized with approximately 15 deicer materials at temperatures of 0°, 5°, 10°, 15°, 20°, and 25°F. Results are satisfactorily reproducible and have served as the basis for comparing deicers and establishing time-temperature relationships.

This method, with some modifications, is being recommended as a standard test method.

2.3.2 Ice-penetration test: The ice-melting rate and capacity test measures the quantity of ice melted without regard to the mode of melting. Ice penetration is a significant performance property in that a major function of a deicer should be disruption of the ice/pavement interface. The time required to penetrate through ice to the pavement and the fraction of the melting capacity available for subsequent melting at the interface generally define the capability of a deicer to assist in ice-removal processes. An ice-penetration test is accordingly designed for measurement of melting in the vertical or downward mode.

Relatively few ice-penetration test methods have been reported in the literature. The methods differ primarily in the configuration of the ice specimen, i.e., in the use of a small slab of free-standing ice or the use of ice formed in a cavity in a material such as Plexiglas. The latter approach has been selected as the basis for a standard ice-penetration test. Tests conducted with approximately 15 deicer materials have yielded satisfactorily reproducible results. Comparison of different deicing materials essentially mirrors comparisons obtained in ice-melting tests. Significant differences between ice melting and ice penetration are observed in many cases. Some deicers have low penetrating capabilities relative to their ice-melting capabilities, and surface melting occurs almost to the exclusion of penetration as eutectic temperatures are approached.

Some modification of ice-penetration method is recommended. These are designed to better represent the surface of ice normally available to deicer particles and to permit the testing of larger deicer particles.

2.3.3 Ice-undercutting test: The ice-undercutting test represents, under controlled laboratory conditions, the combination of ice melting and ice penetration followed by melting at the interface between ice and a substrate material representing highway pavement. The test accordingly provides information and data which relate directly to the ice removal or ice disbondment capabilities of a deicer. The majority of the background data and operational details for the test method are not as yet in the open literature but are available to the reviewers. Ten deicer materials tested at 0°, 5°, 10°, 15°, 20°, and 25°F yielded satisfactorily reproducible results and substantiated comparisons obtained with ice-penetration and ice-melting tests. Relatively minor modifications to the test method are recommended.

2.3.4 Friction tests: The frictional characteristics of pavements under various conditions--wet, dry, snow- or ice-covered with and without abrasives and deicers--have been extensively studied. The frictional property most directly related to deicer selection is the frictional characteristic of pavements wetted with deicer brines or deicer residues. Two ASTM procedures are considered to be suitable for modification or adaptation as standard laboratory methods for measuring this characteristic of deicers.

2.3.5 Chemical deicer characterization: The physicochemical characterization of chemical deicers from a chemical and thermodynamic standpoint potentially requires procedures or methods ranging from procurement of representative samples, through analysis for chemical constituents, to determination of heats of solution and eutectic temperatures. The deicing literature per se is notably devoid of discussion of the appropriate methodologies. These are generally available from sources such as ASTM publications, reference works or standard methods of chemical analysis, and instrument supplier instruction manuals. A few, such as solubility determinations, are described in general terms in chemistry manuals.

A complete characterization of a chemical deicer requires two types of analysis and property determinations. The first consists of identification and quantification of chemical constituents, as follows:

- Principal chemical species identification and quantification.
- Minor chemical species identification and quantification. These potentially include additives and impurities.
- Moisture content including, if appropriate, water of hydration.
- Percent water insolubles.
- Identification of hazardous or toxic constituents.
- pH of aqueous solution.

The second type of measurement or analysis involves the properties which in the aggregate define deicing potential. These are:

- Freezing points and associated deicer concentrations in water.
- Eutectic temperatures and eutectic compositions.
- Solubility, chiefly at temperatures between 0°C and the eutectic temperature.
- Heats of solution in water.
- Viscosities of deicer brines.

2.4 Chemical Deicer Compatibility

A primary driving force in the search for new or improved deicers is the corrosive or materials degrading characteristics of chloride-based deicers. Major costs associated with chemical deicers are costs of maintaining and replacing bridge structures and pavements, and the costs of vehicular corrosion. Substantial costs are also associated with practices employed to minimize corrosion and other materials effects, exemplified by priming and coating metal parts, vehicular design to limit exposure to corrosive chemicals, the use of corrosion-resistant metals or metal surfaces, and the use of air entrained concrete for pavement construction.

The materials compatibility problem is conveniently subdivided into the following principal areas.

- Bare and coated metals, i.e., metals incorporated in bridge structures, highway appurtenances, and vehicles.
- Concrete metal reinforcement corrosion, for which the principal input is degradation of the concrete.
- Concrete or pavement degradation attributable to deicing chemicals.
- Effects on nonmetals such as plastic and rubber.

The types of impacts are well documented, and specific causes of materials degradation are usually well defined and have been related to fundamental processes or mechanisms. While it is quite clear that damage to materials is substantial and costly, the extent and economic significance of damage are the subject of debate and differing opinions or interpretations. Accordingly, emphasis in the literature review was placed primarily on methods employed to measure materials degrading processes and their suitability for use in evaluating chemical deicers.

2.4.1 Compatibility with bare metals: Tests of bare metal corrosion basically consist of exposure of metal to a potentially corrosive environment, accompanied by a variety of electrochemical diagnostic measurements, and followed by posttest measurements designed for determination of the extent and type of corrosion. While the tests are simple in principle, a laboratory-based test may not adequately represent or duplicate exposures encountered in actual use conditions. For this reason, numerous exposure protocols have been employed: total or partial immersion; intermittent immersion; spray; air exposure; wet/dry cycling; and exclusion or inclusion of oxygen. Some tests have been designed to duplicate various types of exposure in vehicular corrosion. Corrosion tests should be sensitive to the type of metal, its geometry in a structural member, and its surface characteristics including surface treatments.

Several standard methods have been accepted by various testing and professional organizations, but standard tests accepted or validated by these organizations for use with deicing chemicals are not available. It has been concluded, however, that a standardized immersion corrosion test is suitable for evaluation of the corrosive properties of deicing chemicals. The test is, however, designed for determination of comparative corrosiveness of deicing chemicals, relative in particular to sodium chloride, under controlled and reproducible conditions. The test in other words is not designed for determination of corrosion under various use conditions.

2.4.2 Compatibility with concrete reinforcement: Concrete reinforcement corrosion has been accorded a high priority for several reasons: the corrosive action of deicing chemicals is economically quite important; mitigation or prevention is difficult; and evaluation procedures are difficult, time consuming, and at present subject to interpretive uncertainties.

Experimental procedures must cope with the slowness and variability of the permeation of deicing chemicals through concrete and with the difficulties inherent in designing and using electrochemical diagnostic systems in concrete/reinforcement matrices.

An ASTM procedure is available for evaluating the corrosive state or condition of concrete metal reinforcement. This method consists of measurement of the potential (EMF) of the metal reinforcement at numerous sites in a specimens, and comparison of data with EMF values associated with passive, corrosive, and questionable or uncertain corrosive conditions. The procedure is intended for use on existing structures, i.e., no protocol is provided for fabricating and exposing test specimens. The procedure is limited in that results do not provide measures of the extent and rate of corrosion.

Research-oriented approaches to studies of concrete reinforcement include techniques for isolating liquids (pore solutions) from concrete matrices, and for investigation of the corrosive properties of simulated pore solutions, including pore solutions modified by deicing chemical constituents.

Test procedures employed to study corrosion of steel in concrete in simulated bridge decks, either indoors or outdoors, have utilized various configurations and various methods for exposing specimens to deicing chemicals.

The effect of deicing chemical, on the reinforcing steel is determined via visual observations, electrochemical potential measurements, macrocell current measurements, and postmortems. These tests can be very useful in determining the effects of deicers on reinforcing steel corrosion. However, with good quality concrete, it can take several years for the deicing chemical to reach the mat.

A laboratory test meeting the requirements specified in this program should provide a response time of a few weeks rather than years, preferably should utilize small test specimens, and should focus on the provision of reliable comparisons of deicer materials rather than on the time- and exposure-dependent parameters of deicer penetration and corrosive action. Such a test is proposed for development in Phase II.

2.4.3 Compatibility with coated metals: Metals are coated primarily to protect the metal against corrosion. Evaluations of the compatibility of chemical deicers with coated metals basically address the effectiveness of the coating in preventing corrosion, but at the same time deal with the integrity or stability of the coating in the chemical environment. Methods available for testing coated meals generally focus on determination of the degree of protection provided by the coating, and of the time that a coating will provide satisfactory protection. Electrical and electrochemical techniques are applicable to coated metals. However, the principal approaches employed for evaluating coated metals essentially consist of the imposition of extreme and accelerating environments, exemplified by salt fog/spray cabinet tests, and qualitative/semiqualitative evaluation procedures. A large body of reference or background data is available for numerous coatings and metals; sodium chloride solutions have been extensively tested in such systems. These methods are accepted and well documented, and are suitable for evaluation of chemical deicers.

2.4.4 Compatibility with concrete: 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 mechanisms of concrete degradation are not as well understood as the mechanisms of corrosion. 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, and air-entrained concrete is considerably less subject to freeze/thaw damage than nonair entrained concrete. Degradation of concrete also occurs under wet/dry exposure to chemical solutions, i.e., in the absence of freeze/thaw cycles.

Tests which have been employed for determination of concrete compatibility are freeze/thaw tests, wet/dry tests, outdoor exposure tests, and penetration/impregnation tests. Diagnostic or evaluation procedures include visual/spectroscopic tests, abrasion tests, mechanical strength tests, and ultrasonic velocity tests.

The rapid freeze/thaw cycle test recommended by the American Society for Testing and Materials (ASTM C 666-84, 1987) is suitable for evaluation of the compatibility of deicing chemicals, and a substantial inventory of reference results obtained with this test is available. This test may, however, require 50 to 100 cycles over a several week test period. In Phase II of this program an accelerated freeze thaw test, with small concrete specimens, will be evaluated. Diagnostic tests to be evaluated are visual methods, abrasion/weight loss, and mechanical strength retention.

2.4.5 Compatibility with nonmetals: The compatibility of chloride based deicing chemicals with plastics and rubber has not been singled out as a significant problem. New or modified deicing chemicals will, however, be suspect in this respect. Standard procedures are available for determining the impacts of deicing chemicals on tensile strength and related properties of this class of materials.

2.5 Chemical Deicer Environmental Effects

The literature contains many publications in which the effects of deicing chemicals are documented, suggested, or implied. Most studies have focused on the effects of sodium chloride and calcium chloride. There is little unanimity in the literature regarding the extent and significance of environmental effects of sodium chloride. Plant growth and crop productivity in the immediate vicinity of highways treated with deicers are known to be affected, and highway deicing is the source of increases in the sodium chloride salinity levels in streams, lakes, and groundwater aquifers. Increased salt concentrations in drinking water supplies pose a human health problem. Definitive studies of long- and short-term effects on aquatic and terrestrial ecosystems have not been conducted.

Evaluation procedures for determining the environmental effects of deicers and of deicer usage are in principle available in the general inventory of methods developed by the Environmental Protection Agency and others. These have primarily addressed materials such as pesticides and require adaptation or modification and testing geared to the effects associated with deicing chemicals and their modes of introduction to and dissemination into the environment.

2.6 Chemical Deicer Engineering Parameters

Several parameters of deicer materials pertain to storage and handling characteristics, suitability for use in materials-handling equipment and deicer-dispensing equipment, and deicer use efficiency in terms of factors such as retention on highway surfaces and the physical and chemical modes of deicer interaction with snow and ice. These parameters include flowability, dusting characteristics, bulk densities, and particle size and size distributions. Methods are available for determination of these properties.

A significant aspect of engineering use parameters is the effect of moisture on the storage and handling characteristics of deicers. Chemical deicers are basically sensitive to moisture, and in the as-received condition may contain varying proportions of water. Calcium chloride deicers are hygroscopic and accordingly require protection from atmospheric moisture. Rock salt absorbs moisture from the air to the extent of about 0.1% by weight at relative humidities less than about 70%, but can be wetted with liquid water at concentrations of 1% to 2%. Water at the higher levels has an impact on materials transfer properties, but more importantly can be the cause of caking or agglomeration. These processes tend to become more severe at low winter temperatures. Wetted rock salt particles also become cemented together when excess moisture is lost by evaporation. Tested and documented procedures are not available for evaluating deicer moisture sensitivities, and the effect of moisture and temperature variations on storage and handling characteristics. Procedures for suitable tests will be proposed for consideration and acceptance in Phase II.

2.7 Chemical Deicer Health and Safety Aspects

Deicer chemicals are subject to the standards and procedures pertaining to the manufacture, transport, and use of chemicals. These essentially require that health and safety hazards or properties of these materials be known and that appropriate protective measures be taken. Present deicing chemicals have been so treated. New or modified chemicals will necessarily be characterized and qualified for use under these regulations and standards.

2.8 Improved Sodium Chloride Based Chemical Deicers

Two basic areas for improvement of sodium chloride have been identified in the scope of work for this program. These are: (a) improvement in the deicing performance of sodium chloride, emphasizing an enhancement of the performance of sodium chloride at or in the vicinity of sodium chloride; and (b) improvement in the materials compatibility and environmental impacts of sodium chloride.

A majority of the deicing literature of the last 25 years relevant to "improved sodium chloride" has focused either on alternates to sodium chloride or on corrosion/materials compatibility mitigation via an additive or inhibitor approach. This literature contains the results of comprehensive compilations and evaluations of chemical deicer alternatives and the conclusion that very few theoretical or practical alternatives to sodium chloride and/or calcium chloride exist. Calcium magnesium acetate and methanol were identified as deicing materials of promise, and CMA in its present status is the principal outgrowth of these studies.

The literature review yielded results in essential agreement with prior literature relative to a substantially different chemical deicer. However, a substantial body of generalized information and some specific data contained in the literature support the conclusion that reasonable approaches are available for improving the deicing performance of sodium chloride. The approaches have been evaluated and conceptually extended by consideration of fundamental factors. Literature support for "improved sodium chloride" is as follows:

- Sodium chloride wetted with calcium chloride solutions or glycols exhibits enhanced ice-melting and ice-penetrating capabilities, with the greatest effect at low temperatures.

- Experience with calcium chloride-wetted rock salt in highway deicing indicates that the ice- and snow-melting capability of rock salt is significantly increased.

- Highway deicing with salt brines indicates that control can be achieved with considerably "less salt."

- Laboratory ice melting and ice penetration results with two component deicers (NaCl and KCl; NaCl and urea) show that deicing chemicals are enabled to melt ice below their eutectic temperatures by pairing with a material with a lower eutectic temperature. This observation does not violate theory and justifies the conclusion that the eutectic temperature of sodium chloride can in effect be bypassed by pairing it with appropriate second constituents.

- Theoretical considerations lead to a conclusion that the inherent thermodynamic driving force for ice melting by sodium chloride can be increased by combining sodium chloride with materials which lower freezing temperature limits below the NaCl eutectic temperature (-21.13°C). The increase in the inherent thermodynamic driving force is effected by increasing the magnitude of the difference, at a deicing temperature at or in the vicinity of 0°F (-17.77°C), between the activity (vapor pressure) of water in ice and in concentrated brines.

- Energy-based considerations lead to the conclusion that the actual, time-dependent ice melting capacity of sodium chloride can be improved by incorporating a second constituent which dissolves exothermically in water or brines; this effect can in principle be combined with a freezing point-lowering effect.

- Last, measures which serve to enhance rates of deicer dissolution merit consideration. These include optimization of particle size or shape and chemical or physical modification of the surfaces of rock salt particles.

Recommendations for specific approaches to improving the deicing performance of sodium chloride are presented in the work plan for Phase II.

The literature review also revealed the existence of a considerable activity focused on reduction of the corrosivity of sodium chloride. The deicing literature, at present, is principally company-proprietary in nature. The corrosion literature, however, provides a broad and firm basis for investigation of corrosion mitigation of sodium chloride. Recommended approaches are presented in the work plan for Phase II.

3.0 CRITERIA FOR THE EVALUATION, SELECTION, AND USE OF CHEMICAL DEICERS

The definition of the term "criterion" as it is employed in this study is as follows: a criterion is based on some factor which serves as the basis for evaluating and comparing options or strategies, and which in combination with other criteria is useful for purposes ranging from defining the most promising options for continuing study or development to selection of the ultimately preferred or optimum option. A criterion is useful to the extent that definitive means are available to measure a property or to establish the relative importance of parameters or considerations which do not lend themselves to quantitative or data-based assessments. To the extent possible, the criteria in the aggregate should sum to a quantitated overall measure of performance or utility, upon which the more judgmental criteria can be superimposed to select a preferred option and define its mode of application.

The criteria for evaluation, selection, and use of chemical deicers are organized into six principal criteria categories:

- Fundamental properties
- Deicer performance
- Materials compatibility
- Engineering parameters
- Environmental effects
- Safety and health aspects

Fundamental and deicer performance criteria in the aggregate serve to define whether or not a deicer meets certain requirements for capabilities to melt ice and snow, including capabilities at different temperatures.

Materials compatibility criteria include particularly the corrosive and materials compatibility effects of deicers on highway systems and also encompass the broad spectrum of materials which potentially can be degraded by contact with highway deicers.

Engineering operations criteria generally define the suitability of a material from the standpoint of storability, handleability including compatibility with equipment, and deicing effectiveness as it is governed by properties such as particle size.

Environmental effects criteria generally address the potential effects of deicers on aquatic and terrestrial ecosystems. Safety and health criteria pertain primarily to human health and safety during the manufacture, transport, storage, and application of chemical deicers.

The above six major criteria categories are amenable to evaluation or testing via the methods or procedures which have been identified as appropriate or necessary in the overall process involved in the selection of a chemical deicer and in determining how the material should be used. Thirty-eight methods or procedures have been identified as means to evaluate deicers in terms of various subcriteria.

Two additional criteria classes are important: (a) the meteorological parameters which in large measure define the details of snow and ice control strategies in given storm events and which additionally are the basis for selecting a general strategy for a region or state; and (b) economic criteria. Economic criteria encompass direct costs of snow and ice control; costs of preventing or minimizing adverse impacts or materials and the environment; costs of maintaining or replacing materials to the extent that these are attributable to deicer usage; and numerous benefits which are often difficult to express in monetary units, i.e., the maintenance of levels of service and economic productivity, energy savings, accident prevention, and human injury or death.

A standardized method or procedure for an economic analysis of chemical deicers was not included in the original set of methods proposed for development and/or documentation in this program, principally because such a method will not be a laboratory method. In response to expressions of the need for such a method, in particular for one which is immune to personal bias, the development of a procedure for economic assessment has been included in the work plan for Phase II of this program.

Meteorological criteria have not been addressed as items for a standard procedure or procedures. Instead, the general relationships between meteorological conditions and ice and snow control strategies have been identified, and accurate weather forecasting has been identified as an important and essential part of effective snow and ice control strategies.

The usefulness of criteria is dependent on the extent that reference points or guidelines can be defined for purposes ranging from evaluating the deicing performance of a deicer to predicting the extent or importance of corrosion. In this regard the characteristics of rock salt (sodium chloride) and of calcium chloride comprise the references or guidelines for evaluating alternate chemical deicers for highways. Neither is optimum or ideal in all respects, but they constitute the basis for references or guidelines as follows.

Rock salt is readily available and substantially less costly than other options, and its deicing performance relative to cost and quantity, at 20°F and higher temperatures, is superior to that of competitive materials. Rock salt thus constitutes a cost and performance reference point for deicers designed for use at moderate temperatures.

Rock salt is, however, corrosive. In this sense rock salt serves as the basis for evaluating improvements in corrosivity as well as in general materials compatibility.

The environmental effects of rock salt are minor in the sense that sodium chloride is inherently safe, nontoxic, and universally present in the environment. The environmental effects are, however, significant, albeit variable, and sometimes debatable because highway deicing involves large quantities and localized use of chemicals. An alternate chemical deicer devoid of impacts on roadside vegetation or road-adjacent crops and with a lesser potential to increase sodium chloride contents of groundwater and drinking water supplies would be received favorably in comparison to rock salt.

Calcium chloride serves as a reference or guideline deicer relative to deicing performance at low temperatures. The anhydrous form of calcium chloride has properties: namely, a high exothermic heat of dissolution in water, which is very desirable in a deicer, and a very low eutectic temperature. Calcium chloride accordingly is essentially a model or ideal deicer for low-temperature deicing; its cost is higher than the cost of rock salt, and storage and handling are complicated by its hygroscopic tendencies. Also, materials compatibility characteristics generally resemble those of rock salt.

Calcium magnesium acetate (CMA) tentatively constitutes a deicing material with materials compatibility characteristics superior in several respects to those characteristics of chloride-based deicers. Laboratory and field testing results support a general conclusion that both environmental and materials compatibility impacts may be an improvement relative to rock salt. CMA is comparatively much more expensive, and its deicing properties are the subject of debate and question. Nevertheless, CMA is or represents a deicing material with many of the characteristics desired of an alternate to rock salt.

In summary, criteria for the evaluation, selection, and use of chemical deicers are as follows.

- Deicer fundamental properties, which indicate deicer potential performance.
- Deicer performance properties, which serve as the basis for determining and comparing the actual or probable performance of deicers under field conditions.
- Deicer materials compatibility properties, which define the potential impacts on highway materials and structures.
- Deicer engineering parameters, which define the suitability of a material for use by a highway maintenance organization.
- Deicer environmental effects, which indicate potential impacts on specific environmental components and ecological systems.
- Deicer safety and health practices, which serve on the basis for assessing the safety and health hazards in the manufacturing, transport, storage, and use as a highway deicer.

- Economic factors, which provide direct and indirect cost and cost benefit yardsticks for measuring or assessing alternatives.

- Meteorological parameters, which provide the specific and general regional background considerations required for determining the appropriate ice and snow control practice.

4.0 SELECTED TEST METHODS FOR EVALUATING CHEMICAL DEICERS

In this section 51 specific test methods, which were selected for the complete evaluation of a chemical deicer, are presented and discussed, and the developmental status of each test method is indicated. The selected test methods including ancillary testing references are presented in brief form in Appendix A. A list of 42 ASTM standards that have been selected for inclusion in the set of recommended deicer test methods is presented in Appendix B.

The test methods selected for the complete characterization of chemical deicers have been grouped into eight principal categories as follows:

- Physicochemical Characteristics (4.1)
- Deicing Performance (4.2)
- Compatibility With Bare and Coated Metals (4.3)
- Compatibility With Metals in Concrete (4.4)
- Compatibility With Concrete and Nonmetals (4.5)
- Environmental Effects (4.6)
- Engineering Parameters (4.7)
- Health and Safety Aspects (4.8)

4.1 Physicochemical Characteristics

4.1.1 Sampling: Representative samples should be employed in the numerous tests designed to characterize deicer materials. Samples should be representative with regard to particle size, chemical composition, moisture content, and similar sources of variability within a material.

Protocols for obtaining representative samples generally involve mixing by procedures appropriate to the container or stockpile, randomized sampling from designated segments of the material, and ultimate isolation of one or more samples from combined random samples.

Sampling from liquid containers essentially involves thorough mixing of materials in containers, isolation of small samples from randomly selected containers, and isolation of test size samples from combined random samples.

Several ASTM procedures are available for these purposes, as follows:

Hygroscopic solid deicers	ASTM D 345
Nonhygroscopic solid deicers	
Drums and bags	ASTM D 1568
Trucks	ASTM D 3655
Stockpiles, bins, railcars, barges	ASTM D 75
Liquids	ASTM D 345
Reduction of large (field) samples to testing size or quantity	ASTM C 702
Nonhomogeneous samples, grinding and mixing	ASTM D 2013

4.1.2 Deicer analysis

4.1.2.1 Moisture content: Adsorbed or nonchemically bonded moisture contents of solid deicer materials are determined by drying weighed samples at 110°C to constant weights, as specified in ASTM E 534 for moisture determination in sodium chloride.

Determination of chemically bound water (water of hydration) requires procedures specific to the material, and the exercise of care to ensure that the hydrated material is not partially decomposed. A standardized procedure for determination of bound water accordingly is not presented. Common practice consists of complete analysis of a material, and designation of water content by difference.

4.1.2.2 Water-insoluble content: Deicer materials may contain small percentages of water-insoluble matter. Determination of water-insoluble materials is accomplished by stirring samples in excess water, isolation of undissolved matter on a filter, drying, and weighing as specified in ASTM E 534-86. The water-soluble content of the material is also indicated by this procedure.

4.1.2.3 Chemical analysis of deicers: Procedures for identification of the constituents of chemical deicers and for quantitative measurement are available and described in detail in the analytical chemistry literature. In addition, specific procedures which address the important chemical constituents of products important in certain segments of the chemical use industry are often presented in detail. Standard test methods for the chemical analysis of sodium chloride are presented in ASTM E 534-86; the procedure encompasses moisture-content determination, insolubles determination, and sulfate, magnesium, and calcium analysis, with percent sodium chloride being determined by differences.

A similar procedure for analysis of calcium chloride products is presented in ASTM E 449.

A new product, or one which is not known to be available in a normal range with regard to quality and chemical makeup, will normally be subjected to more specific and detailed chemical analysis. Analytical requirements may include identification and quantitation of potentially hazardous trace constituents.

Applicable ASTM procedure include the following:

ASTM D 3177	Sulfur analysis
ASTM D 3178	Carbon and hydrogen determination
ASTM D 3179	Nitrogen analysis

Metal ions in some cases may be analyzed by wet chemical methods as exemplified by titrimetric determination of calcium and magnesium (ASTM E 449, ASTM E 543). Flame atomic absorption spectrophotometry is employed for the quantitative determination of many metals, and is the only convenient method for direct determination of alkali metals. Atomic absorption methods are described in *Standard Methods for the Examination of Water and Wastewater*, 15th edition, 1980, APHA-AWWA-WPCF (Methods 303 A, 303 B, and 303 C). The 1985 *Annual Book of ASTM Standards, Section 11, Volumes 11.01 and 11.01*, present ASTM methods for atomic absorption spectrometry. Methods for the determination of trace metals in ash from coal or coke are presented in ASTM D 3683.

Inorganic anions can usually be determined by wet chemistry procedures. Methods are described in *Standard Methods of Chemical Analysis*, Volume 1, 6th edition, N. H. Furman, Editor. Ion chromatographic techniques are available for determination of chloride, fluoride, nitrate, nitrite, phosphate, and sulfate ions (EPA report EPA-600-14-84-017, Method 300.0). Ion chromatographic methods for organic acids and acid salts have not been published but are available from the Dionex Corporation, Itasca, Illinois.

4.1.3 Aqueous solubility

4.1.3.1 Test description: The test method is employed for determination of the solubility of deicer materials in water at temperatures from normal ambient temperatures down to eutectic temperatures.

Precise or accurate measurements of solubility essentially involve the careful equilibration of an excess of the material with deionized or distilled water at the temperature of interest, withdrawal of supernatant liquid, and chemical analysis for constituents. This operation is repeated at several temperatures.

Less precise or accurate solubility data may in some cases suffice. For such data, a proximate method is recommended. The proximate method consists of the use of multiple specimens containing varying proportions of deicer and water. These are equilibrated to a succession of temperatures, and proximate solubilities determined by observing points of transition from complete solubility to incomplete solubility.

4.1.3.2 Test objectives: The objective of solubility measurements consists of the determination of whether or not a material is sufficiently soluble at low temperatures to merit consideration as a deicer, and in conjunction with freezing point determinations to define the theoretical limits of a material in terms of ice melting capacities over the temperature range from 0°C to the eutectic temperature.

4.1.3.3 Facilities requirements: Solubility measurements require refrigerated systems capable of maintaining constant temperatures down to the eutectic temperature of the water deicer system. Commercially available constant temperature baths are suitable. A normal complement of laboratory glassware is also required.

Support facilities include equipment needed to analyze and chemically identify the deicer material prior to initiating solubility tests, and to measure the quantities of dissolved materials in saturated aqueous solutions.

4.1.3.4 Data outputs: Primary data consist of the weights of the deicer present in saturated aqueous phases, usually expressed as weight percent of the aqueous phase.

Derived data consists of molecular concentrations of the deicer material. Concentrations may be expressed as the number of molecular weights of the material dissolved in 1,000 g of water; or more appropriately, for mixed materials or materials which yield more than one discrete dissolved species, as the number of equivalent weights of the dissolved species. One mole of $CaCl_2$ thus contains three equivalent weights, and one mole of NaCl two equivalent weights. Molecular or equivalent concentration data may be utilized to estimate freezing points, from the relationship:

$$\Delta T = kC = 1.86C$$

where ΔT is the freezing point depression in °C, k(1.86) is the freezing point depression constant, and C is the deicer concentration (equivalent weight basis) in equivalents per 1,000 g water. This expression is reasonably accurate in relatively dilute solutions, e.g., for freezing point depressions of the order of 5°, and is less reliable at higher concentrations.

4.1.3.5 Sources of error or uncertainty: Solubility measurements and the resulting data are straightforward and subject to no interpretive uncertainties when the material is an essentially pure single material. Deicers will usually not be high in purity, and may contain substances added to improve handling and storage properties, to minimize corrosion, or to improve ice melting; and may contain major proportions of two or more substances (e.g., CMA). Impurities or additives may be readily soluble, sparingly soluble, or essentially insoluble.

Such materials will require care in both the measurement of solubilities and in the interpretation of solubility data. Since the objective of solubility measurements will usually be definition of the probable temperature range and ice melting capacity limits of a material, the impact of impurities or additives on the usefulness of solubility data will be of less concern than it would be if the objective were precise delineation of the phase diagram of a pure material.

Certain preliminary and precautionary steps are nevertheless in order in determination of solubilities of deicer materials. These will vary from material to material, and include:

- Chemical analysis for major and minor constituents, moisture content, and percent water insolubles.
- An obvious excess of the solid phase should be present, to ensure that insoluble materials are not mistaken for an excess of soluble substances.

- Alternatively, concentrated aqueous solutions may be filtered to remove insoluble matter and resulting solutions or recovered soluble solids employed in solubility determinations.
- If soluble impurities--or second and third constituents--are present in greater than minor quantities, the solution phase should be analyzed to determine whether materials are soluble in proportions differing from proportions in the bulk material.
- Data outputs (reported data) should clearly indicate the active (water soluble) ingredients of the deicer materials; the percentage of active ingredients in bulk deicers; and the effective (average) molecular or ionic equivalent weights of dissolved species.

4.1.3.6 Test replication: The number of replicates is user discretionary, and is primarily dependent on use to be made of solubility data. Well-controlled single tests at four to six temperatures will provide data of the extent and quality needed to screen solubilities. Results to be published should be replicated sufficiently to establish data reproducibility and validity.

4.1.4 Freezing point determination

4.1.4.1 Method description: ASTM D 1177 describes a method to determine the freezing point of engine coolants. ASTM D 1177 can be used to determine the freezing point of aqueous solutions of deicer materials without modification.

Deicer solutions of known concentrations are cooled slowly and with stirring, while recording time and temperature. The freezing temperature is the temperature at which the first ice crystals form.

Near the anticipated freezing point, the deicer solution is "seeded" with frozen crystals of the same deicer solution to prevent supercooling. Cooling of the deicer solution is continued for at least 10 min after the apparent freezing point of the deicer solution. The freezing point is taken as the temperature at the point of intersection of temperature vs. time curves before and after the onset of freezing.

4.1.4.2 Method objective: The objective of ASTM D 1177 is to accurately determine the freezing point of an aqueous solution of deicer material.

4.1.4.3 Facilities and equipment requirements: The equipment requirements described in ASTM D 1177 are: (1) a cooling bath consisting of a 2-L Dewar containing dry ice/methanol or liquid nitrogen; (2) a 200-mL clear Dewar in which the deicer solution is placed; (3) a stainless-steel wire coil stirrer driven by a windshield wiper motor; and (4) accurate thermometers or thermocouples.

4.1.4.4 Data outputs: Data outputs for ASTM D 1177 will be a record of the deicer solution temperature vs. time. The freezing point of the deicer solution is defined as either the temperature at the intersection of the cooling curve and the flat portion of the freezing curve, or the maximum temperature attained immediately after the deicer solution supercools. Freezing points are recorded for several deicer concentrations, and typically are displayed in graphical form.

4.1.4.5 Sources of error or uncertainty: A major source of error arises from supercooling, which can be minimized by stirring and by seeding with ice crystals prepared from test solutions. Freezing point data are also subject to the accuracy of procedures used to establish solution concentrations.

4.1.4.6 Method replication: Tests should be run in duplicate, and individual solutions should be cycled through freezing temperatures until results are in agreement.

4.1.5 Eutectic temperature

4.1.5.1 Method description: An aqueous solution of deicer is cooled slowly and with stirring until further cooling results in a constant temperature which persists until all water is converted to ice and all solutes are converted to solids. The method and equipment utilized in ASTM D 1177 may be employed for eutectic temperature determinations. The eutectic temperatures may be approached by traversing either the freezing point or the solubility curve of a deicer. In the one case, water is gradually separated as ice until the eutectic temperature and eutectic concentration are reached. In the second case, the deicer solute is precipitated gradually until the eutectic composition and temperature are reached.

4.1.5.2 Method objective: The objective of the test is determination of the eutectic temperature of a deicer in water.

4.1.5.3 Equipment: Equipment requirements are specified in Subsection 4.1.4.3 and in ASTM D 1177.

4.1.5.4 Data outputs: The result of interest is the eutectic temperature. The eutectic temperature is associated with a eutectic composition determined via the procedure described in Subsection 4.1.6.

4.1.5.5 Sources of error or uncertainty: A eutectic temperature is an invariant property of a solvent-solute system, and is uniquely associated with a eutectic concentration. Eutectic temperatures and compositions are rigorously associated with single, pure solutes, and can be identified for multiple solutes only in the event that solutes precipitate from the solution phase in proportion to solution concentrations as water is converted to ice. Reliable determination of a eutectic temperature accordingly demands that the solute be either high in purity or that impurities (or other constituents) become essentially insoluble as the eutectic temperature is approached.

Since the eutectic temperature is a property of a pure material, it will usually be determined only for the pure material. Conversely, an apparent eutectic temperature can be identified with a specific compound only to the extent that the purity of the sample is known to be high.

The technique for determination of a eutectic temperature may, however, be employed to locate the lowest temperature at which liquid or brine can coexist with ice, for multisolute or impure materials.

Eutectic temperature determination is straightforward in principle, but may be experimentally difficult if solution phases become highly viscous or exhibit gel-like properties as the eutectic temperature is approached.

4.1.5.6 Method replication: A minimum of two determinations of eutectic temperature is recommended.

4.1.6 Eutectic composition

4.1.6.1 Method description: Eutectic compositions and eutectic temperatures normally will be determined together. The recommended procedure involves equilibration of a deicer/water system to the eutectic temperature, withdrawal of an aliquot of the liquid phase, and determination of the concentration of the solute. Concentrations may be measured by analysis of major constituents, e.g., chloride ion; by recovering, drying, and weighing dissolved solids; or by dilution of withdrawn liquid and measurement of solution conductivity. Eutectic compositions derived in this manner may be verified by determining the freezing characteristics of a solution having the eutectic concentration. In the event that freezing point and low temperature solubility data are available, eutectic compositions may be verified by comparisons with the point of intersection of solubility and freezing point curves.

The method for determining eutectic compositions accordingly consists of analysis of solutes present at the eutectic temperature, as determined via the equipment specified in ASTM D 1177 for freezing point determination.

4.1.6.2 Method objective: Eutectic compositions and temperatures define the lowest theoretically possible temperature at which a deicer can melt ice, and theoretical ice-melting capacities at that temperature.

4.1.6.3 Equipment and facilities: The equipment specified in ASTM D 1177 for freezing point determination is required, plus glassware and instruments needed for chemical analysis of deicer solutions.

4.1.6.4 Data outputs: Eutectic compositions are usually stated as weight percent solute associated with the eutectic temperature. The weight percent of water, obtained by difference, represents the quantity of ice which theoretically can be melted at the eutectic temperature by the weight of deicer corresponding to the eutectic weight percent.

4.1.6.5 Sources of error or uncertainty: Eutectic temperatures and compositions apply rigorously only to pure solutes. Tests with impure solutes or mixed solutes will yield results which should be interpreted with caution, i.e., the results may indicate a lowest achievable temperature which does not constitute a eutectic temperature.

Although eutectic property determinations are simple in principle, experimental difficulties may be encountered if solutions are viscous or gel-like in properties. Isolation of solution free of solids or ice may be difficult, and equilibration of solute concentrations may be sluggish. Substantial excesses of either solids or ice should be avoided, by initiating tests with solute concentrations at or near the eutectic composition.

4.1.7 Heat of solution

4.1.7.1 Test description: Heats of solution are measured via solution calorimeters, which may be purchased or assembled in laboratories. A solution calorimeter consists basically of a Dewar flask system contained in a controlled-temperature chamber and protected from significant inputs or withdrawals of thermal energy from the surrounding environment. The system is instrumented to permit accurate calibration of system heat capacities, and to permit accurate measurement of changes in solution temperatures. The receiving solution, usually water, and the test material are brought to the same temperature, the test material is discharged with stirring into the liquid or solution, and temperature changes are recorded. Recorded temperature changes are customarily translated to energy changes by comparison with quantities of electrical (resistance heating) energy required to produce equivalent temperature changes.

A heat of solution procedure documented in an ASTM format is not presently available; this will be developed in Phase II.

The first approach to obtaining this type of thermodynamic data should involve a search of the thermodynamics literature. Sources of data are chemistry handbooks, the International Critical Tables, NBS Publications, and JANAF Tables of Thermodynamic Data. These sources typically list the heats of formation of solid or crystalline compounds, and of compounds in aqueous phases; the differences between values for solids and solutions is the heat of solution, usually for high dilutions. Experimental determination of heats of solution should seldom be necessary.

4.1.7.2 Test objective: Exothermic dissolution of deicers is preferred, since exothermicity should be associated with a greater degree of spontaneity in the interactions between ice and deicer, and since evolved energy counterbalances, in part the endothermicity of ice melting. Measurement or literature derivation of heats of solution is accordingly of interest relative to the ice-melting characteristics of deicer materials.

4.1.7.3 Data outputs: Heats of solution are customarily expressed as kilcalories per mole of material.

4.1.7.4 Sources of error or uncertainty: Heats of solutions can be readily determined to accuracies needed for evaluation of deicers. Fundamentally-oriented interpretation of heat of solution data demands, however, accurate information on the chemical identities and purities. Particularly important for hydroscopic materials is knowledge of the extent of hydration of a tested material.

4.1.8 Deicer brine viscosity

4.1.8.1 Test description: ASTM D 445-86, standard test method for kinematic viscosity of transparent and opaque liquids (and the calculation of dynamic viscosity) is recommended for determination of the viscosity of deicer brine solutions. In this method, the time is measured in seconds for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled temperature. For deicer brines, viscosities at temperature between 0°C and about -18°C are of interest. Brine concentrations of interest are (a) saturated brines at test temperatures, and (b) freezing point concentrations at test temperatures.

4.1.8.2 Test objective: Deicer brine vicosities are potentially important from the standpoint of highway safety, and fluid or nonviscous deicer brines are preferred from the standpoint of reasonably rapid rates of ice melting and ice penetration.

4.1.8.3 Equipment: Calibrated capillary viscometers, regulated temperature baths or enclosures, accurate thermometers or other available temperature measuring deicers, and timers capable of measuring within about 0.2 sec are required.

4.1.8.4 Data outputs: Measured flow times are multiplied by the calibration constant of the viscometer to derive kinematic vicosities.

4.1.8.5 Sources of error or uncertainty: The method and equipment provides viscosity of the desired precision or accuracy, for deicer brines, without resort to accurate control of temperature or deicer concentrations.

4.1.9 Coefficient of friction

4.1.9.1 Method description: A laboratory method is desired for measuring the frictional characteristics of pavement materials exposed to deicer brines. Two ASTM methods constitute the basis for development of a suitable test: ASTM D 4521 (Coefficient of Static Friction), and ASTM D 2534 (Coefficient of Kinetic Friction). These methods were developed for use with cardboard materials. In Phase II, adaptations of the methods will be investigated. A pavement-like material will be substituted for cardboard, sliding sleds will be constructed of rubber, and operational procedures developed for determining frictional properties which develop when surfaces are exposed to deicing chemical brines.

In ASTM D 4521, static coefficients of friction are determined by increasing the angle of an inclined plane until a sled begins to slide.

In ASTM D 2534, the force required to pull a sled over a substrate is measured, to determine kinetic coefficients of friction.

One or both of these methods will be modified in Phase II and presented as a standard method.

4.1.9.2 Test objective: The objective of frictional property measurement is determination of whether or not deicing chemical brines on pavement surfaces constitute a significant safety hazard.

4.1.10 pH of Deicer Solutions: ASTM E 70 presents a method to measure the pH of aqueous solutions, using a glass electrode. pH measurements can be made on aqueous solutions containing high concentrations of inorganic salts or water-soluble organic compounds, or both. The pH and alkalinity or acidity characteristics of deicer brines are potentially significantly relative to immediate impacts on materials, and relative to long-term impacts on materials and the environment.

4.2 Deicer Performance

4.2.1 Cold temperature facility: Deicer evaluation involves several operations or procedures which require temperatures ranging from about 0°F to a few degrees below the freezing point of water. Temperature control on the order of ±0.5°F or better is desired for three tests--ice-melting rate and capacity, ice penetration, and ice undercutting--recommended for evaluating and comparing chemical deicers. This accuracy of temperature control is recommended because output data from the tests vary 5% to 10% per °F; the reliability of absolute or comparative data is to a considerable extent determined by temperature control.

Several approaches to a cold-temperature facility are possible. However, the overall set of operations involved in tests is such that the recommended facility consists of a walk-in cold room outfitted with a temperature-regulated box or enclosure. The walk-in cold room is set to operate at a temperature a few degrees lower than the temperature desired in the enclosure, and serves three purposes: (a) the withdrawal of heat energy from the enclosure by passive (conduction and convection) or active methods (air circulation); (b) a staging area for the final stages of preparing test specimens; and (c) space for auxiliary facilities for operations such as the controlled freezing of ice on concrete substrates.

A refrigerator-freezer combination is a necessary and convenient adjunct to the cold room facility; it will be used for purposes such as precooling water and concrete specimens to temperatures a few degrees above the freezing point of water and for initial freezing of ice in certain test specimens.

The minimum recommended size for the cold room is 8 x 10 x 8 to 9 ft tall, plus an air lock. The cooling system should be designed for routine achievement of about -5°F to ensure that tests can be conducted at 0°F. An automated defrost system is required. The need for a good defrost system is greatest at low temperatures and in periods of high relative humidity. The defrost system should be designed and programmed so that the defrost cycle does not compromise temperatures in the regulated temperature enclosure. The recommended defrost system involves commercially available dual evaporators or chillers. Hot gases from one evaporator operating in a cooling mode are circulated through the coils of the second evaporator, on an alternating basis, to provide rapid defrost without compromising cold room temperatures.

A regulated temperature enclosure which operates satisfactorily is as follows:

- Box, inside dimensions: 30 in high, 30 in deep, 40 in long, constructed from 3/4-in plywood.

- Insulation: 2-in-thick Styrofoam on bottom, top, ends, and rear side, placed on the outside of walls, ceiling, and floor.

- Plexiglas window, hinged: 30 in long x 18 in wide, hinged at top approximately 2 in from ceiling.

- Two hand ports, with 8-in inside diameter x 4-in plastic pipe sleeves, and the outer opening loosely closed with canvas flaps to permit hand access and restrict airflow when not in use.

- One 15-W fluorescent light, ceiling-mounted.

- One fan, 115 V, 0.2 amp, placed in a convenient location with the air output impinging on a baffle to prevent direct flow of warmed air over test specimens.

- A thermistor temperature sensor attached to an adjustable regulator. The power outlet from the regulator is connected to the fan. The sensitivity of the sensor should be ±0.1°F or better.

- A calibrated thermometer with sensing element placed in the approximate location of test specimens. This thermometer may be used as the sole temperature indicator or alternatively to calibrate other thermometers or temperature-measuring systems affixed directly to test specimens. (Thermometers equipped with highly visible red fluids and with a temperature range of -50° to +70°F are convenient and suitable. Such thermometers also photograph well, in the event that photographic records of tests are necessary or desired.)

- Auxiliary lighting, as required for photography: Lights for this purpose should be on only for a few seconds when pictures are taken. Auxiliary lights may be placed inside or outside the box.

Air temperatures in an enclosure of the type specified above can be changed in about 1 hr from one temperature setting to an adjacent temperature (5° to 10°F change) by lowering or raising cold room temperature, and either opening the window or turning on auxiliary lights. Equilibration of the box (e.g., walls and floors, and test specimens) to a new temperature is basically an overnight process, however. The same consideration applies to test specimens with a substantial mass, such as ice frozen on a concrete block. If such a specimen is prepared at a temperature differing from a test temperature, several hours (preferably overnight) should be allowed for equilibration of specimen temperature to the test temperature.

At the discretion of laboratory personnel, the relatively simple temperature control system may be upgraded to provide a more rapid response to temperature changes or to ensure more uniform temperatures in the enclosure. Potential modifications include continuous air circulation, ducted and controlled circulation of air into and out of the enclosure, and staged inputs of thermal energy. In this regard, temperature control is more difficult for operations which require hand manipulation of specimens, e.g., ice melting capacity tests, than for tests such as ice penetration or ice undercutting.

4.2.2 Ice melting rate and capacity test

4.2.2.1 Test description: A 1/8-in. thick layer of ice is frozen in a flat Plexiglas dish, and the surface leveled by partial melting and refreezing with the dish on a level surface. The test specimen is placed in a temperature regulated enclosure, and allowed to equilibrate to the test temperature. The deicer is broadcast spread over the surface of the ice. At specified time intervals, melted ice or brine is decanted to the edge of the dish, removed, and measured via a syringe, and returned to the test specimen. The normal elapsed time period for the test, 60 min, may be increased or decreased as desired. A minimum of four incremental time intervals is employed to obtain data on rates of ice melting.

4.2.2.2 Test objective: The test has the objective of providing data on the actual or time dependent quantities of ice melted by deicer, so that these quantities can be compared to theoretical or equilibrium quantities of ice and can be employed to estimate quantities melted under field conditions within reasonable lengths of time. The test may be employed to establish useful temperature ranges, to compare generic classes of deicers or to evaluate new or modified deicers, and to ascertain the effects of variables such as particle size or deicer application rates.

4.2.2.3 Facilities requirements: Facilities and equipment requirements are:

- A temperature-regulated, low-temperature enclosure with provisions for handling specimens with operator hands. Temperature requirements include control of temperature to ±0.5°F or better, from 25° to 30°F down to 0°F (see 4.2.1).

- Calibrated temperature indicators; test dishes fabricated from Plexiglas; syringes, timers; balances for weighing to 0.01 g. The recommended dimensions of test dishes will be determined in research to be conducted in Phase II.

4.2.2.4 Data outputs: Data outputs are:

- Recorded data: brine volume, in milliliters, at time and temperature, for a given weight of deicer.

- Data-reporting options:

  * Brine volumes, in milliliters, at time and temperature, for specified deicer weights.

  * Brine volumes per unit weight of deicer in metric or English units.

  * Via approximate conversion to quantities of ice melted:

    - Weight ice melted per unit weight deicer.
    - Weight ice melted per lane mile or lane kilometer, for a specified deicer application rate.

Conversions to quantities of ice melted are somewhat approximate, due to a general lack of data on densities of brines at test temperatures and to uncertainties about deicer concentrations in collected brines.

4.2.2.5 Principal sources of error or uncertainty: The principal sources of error or uncertainty are as follows.

- Specimen temperature: Brine volumes vary by as much as 10% per °F.

- Low brine volumes at low temperatures.

- Deicer sample integrity: Care should be taken to provide test samples which represent the material and are appropriate to the comparisons to be made.

Comparisons of the melting characteristics of generic classes of deicers should be based on specific sieve fractions.

Comparisons of bulk or as-used materials should utilize samples with bulk proportions of particle sizes. Particularly to be avoided are nonrepresentative proportions of fine particles and large particles.

Deicer materials containing additives, wetted deicers, deicers coated on abrasives, and other modifications will usually pose special problems relative to isolating representative test samples.

4.2.2.6 Test replication: Three replicates are recommended. Standard errors for data reported in the literature vary from about 2 to 10% of the average of three replicates. The larger standard errors, on a percentage basis, are usually associated with small brine volumes, i.e., at short times and at low temperatures.

4.2.2.7 Related procedures:

Ice Penetration (4.2.3)
Ice Undercutting (4.2.4)
Freezing Point Determination (4.1.4)
Eutectic Temperature Measurement (4.1.5)

4.2.3 Ice penetration test

4.2.3.1 Test description: Weighed or size classified individual deicer particles are placed on the surface of an ice specimen and depths of penetration observed and recorded at several time intervals over a minimum period of 60 min. A dye is employed to facilitate observation of the penetration process. Deicer particles may be lightly dusted with a suitable dye, or a dilute aqueous solution of dye may be placed on a spot on the ice surface and frozen prior to emplacing the deicer pellets. After some initial surface melting, the majority of ice melting yields a more or less cylindrical cavity filled with deicer brine. The depths of penetration are recorded at 5 to 15 min intervals over a period of 1 hr or more.

Deicers vary in their ability to adhere to powdered dye materials. Calcium chloride pellets readily absorb dye sufficient to deeply color brines. Sodium chloride pellets do not; particles sufficiently coated dissolve and react at 20° and 25°F, with no apparent inhibition of initial rates. At 5° and 15°F, dusted sodium chloride type deicers are clearly inhibited in initial reaction/dissolution. For this reason, the recommended dye procedure consists of freezing diluted aqueous dye on the surface of penetration cavities. The required quantity of dye is so small that the contribution of dissolved dye to melting or penetration capacities is negligible.

4.2.3.2 Test objective: A principal mechanism for ice control on highways involves the disbondment of ice from pavement resulting from the generation of a thin film of melted ice (brine) between ice and pavement. The penetration test provides a measure of the time required for penetration through a given thickness of ice, and gives a rough approximation of the fraction of melting capacity available for undercutting. The test serves to identify temperatures below which penetration is slight and no undercutting and disbondment can be expected, and to identify deicers having a marked tendency to melt surface ice without significant penetration.

4.2.3.3 Facilities requirements: The facilities requirements are:

- A temperature-regulated enclosure capable of control to ±0.5°F or better. Penetration depths vary about 5 to 10% per degree Fahrenheit. The system described in 4.2.1 is suitable.

- Penetration equipment: The equipment recommended on an interim basis consists of a Plexiglas plate containing 10 to 15 drilled cavities 1/8-in. in diameter, enlarged at the top by countersinking to a diameter of 6 mm (ca. 1/4 in). Deaerated, deionized water is frozen in the cavity, and protruding ice melted to provide a surface level with the top of the cavity. A millimeter grid work is placed behind the plate to permit observation and recording of depths of penetration.

4.2.3.4 <u>Data outputs</u>: Primary data consist of depth of penetration at several time intervals, for each temperature, with particle weights or sizes identified.

Data of particular interest are: (a) the time required for penetration through a selected thickness of ice, such as 1/8 in (3.175 mm), and (b) the depth of penetration in excess of the selected depth after 1 hr on longer. The 1/8 in data indicate time required for penetration to a pavement surface, and the 1 hr penetration data provide an approximate measure of the melting capacity available for undercutting and disbondment.

Recommended data reports are:

- Primary data, the averages of replicates, and standard errors.
- Plots of penetration versus time.
- Time for penetration to a depth of interest.

4.2.3.5 <u>Important factors and sources of uncertainty</u>: Penetration depths are not linearly proportional to particle weights. Comparisons of deicers should accordingly be made with particles with specified weights, and weight tolerances within 8% to 10% of an average weight (e.g., 25 ± 2 mg). The principal uncertainty in interpretation of penetration results arises from the fact that penetration cavities differ in geometric configuration from deicer to deicer. Penetration cavities typically are larger near the surface than at depths of several millimeters; some deicer materials yield penetration tendrils with diameters of 1 to 2 mm; and others yield cavities 3 mm or greater in diameter. The penetration data obtained in tests on which the method is based are averages of two numbers, namely the maximum depth of penetration and the depth at which the diameter of the penetration cavity is 1/8 in (3.175 mm). This method yields data which are approximately the penetration depths expected for penetration cavities equal in diameter for all deicers.

The depth-versus-time curve contains the important information, specifically: times for penetration to certain depths; times required for initiation of measurable penetration, and the general shape of the penetration curve; and penetration depths in excess of the thickness of ice likely to be encountered in highway deicing. Penetration data based on three to five replicated tests provide a good basis for establishing both the ice melting and ice penetration characteristics of a deicer and for comparing deicers. Qualitative aspects of deicer/ice interactions can also be observed and identified more clearly than with other tests; these include rates of deicer particle wetting and of deicer particle dissolution in brine, and identification of tendencies to melt surface ice at the expense of melting with penetration.

The penetration test is a convenient and rapid test for screening deicer materials, for purposes such as monitoring progress in deicer development or modification.

4.2.3.6 Test replication and reproducibility: The minimum number of replicates is three. Since the test lends itself readily to multiple simultaneous tests (10 to 12 in one operation), six or more replicates can be run, and two materials can be compared with five to six replicates of each in one operation. The larger number of replicates is appropriate in situations exemplified by a developmental material with possible particle-to-particle differences in purity or surface properties, or when it is more convenient to test numerous particles than to rigorously control particle weights within a narrow range.

4.2.3.7 Data reproducibility: The minimum readily observable penetration depth is about 2 mm, which can be read to within about ±0.2 mm. Maximum penetration depths, at 60 min and 25°F, are of the order of 20 mm. Potential observation-related errors accordingly range from about 1% to 10% of recorded penetration depths. The other principal source of uncertainty arises from the variability of the penetration cavities, i.e., in top to bottom variations in cavity diameters.

Standard errors calculated from triply replicated tests of pelletized calcium chloride averaged 2% and 5% of average values at 20° and 25°F, and 9% at 5° and 15°F. Triply replicated tests with halite pellets yielded standard errors which averaged 10% of average values, for data obtained at four temperature and six time intervals.

Background data thus indicate standard errors of the following magnitudes.

Penetration Depth, mm	Standard Error Range
20 mm	1-2 mm
10 mm	0.5-1.0 mm
5 mm	0.4-0.5 mm

4.2.3.8 Related procedures:

Ice Melting Capacity Test (4.2.2)
Ice Undercutting Test (4.2.4)

4.2.4 Ice undercutting test:

4.2.4.1 Test description: The ice undercutting test measures the areas of the brine films formed between a layer of ice and a substrate material representing pavement materials. The test utilizes a specified thickness of ice and involves a two-step process. Step 1, penetration through ice to substrate, is followed by the second step in which a fraction of the melting capacity is expended in melting a thin film of ice between ice and substrate.

Various substrates may be employed, but the substrate of choice for deicer evaluation is concrete-based, specifically a mortar mix.

In the recommended test, a 1/8-in-thick layer of ice is frozen slowly and in a bottom-up mode on a concrete block. The substrate is initially at a temperature 3° to 5°F above the freezing point of water, air temperature is maintained at about 35°F, and the substrate is cooled from below. Initially frozen ice in test specimens is partially melted at the surface, refrozen, and placed in a regulated temperature enclosure containing a suitable camera. Accurately weighed deicer pellets are placed on dye spots (prepared by freezing dilute dye emplaced with a felt tip pen), and photographs taken at selected time intervals, for 60 min, to record dye patterns.

Photographic slides are projected in a system which permits measurement of the area of the undercut patterns.

4.2.4.2 Test objective: Ice control on highways is primarily achieved, with deicers, by weakening or eliminating the bond between ice and pavement, or alternatively by interfering with the formation of adhering layers of ice or packed snow.

The ice-undercutting test provides a means to measure the extent and rate of undercutting at various temperatures and with various deicing materials. The recommended test utilizes a controlled and uniform ice/substrate condition, in order to obtain results or data which reproducibly depict the effects of deicer, temperature, and time. The ice-to-pavement bonding utilized in the test limits the undercutting to a fairly symmetrical area, which may be considerably smaller than undercut areas obtained with the less strongly bonded, or less perfect ice formed under natural conditions on highway surfaces.

Undercutting test results are accordingly useful for comparing the undercutting capabilities of deicers over the range of temperatures experienced in highway deicing, for defining temperature limitations and strengths of deicers, and in conjunction with field experience, determining the most suitable deicer and estimating optimum application rates for given conditions.

4.2.4.3 Facilities requirements: The facilities requirements are:

- A regulated temperature enclosure, for use at 0° to 25°F, with temperature regulation to ±0.5°C (see 4.2.1).

- A bottom-chilled insulated cold box, with air temperature maintained at about 35°F, for freezing ice on test specimen substrates.
- Equipment for mixing cement, casting in suitable molds, conditioning surfaces to be contacted with ice, and curing specimens.

The preferred and recommended substrate surface conditions will be developed and tested in Phase II, as will certain operational details of the test method.

4.2.4.4 Data outputs: Primary data consist of undercut areas, in square centimeters, associated with a known deicer particle weight, and with specific temperatures and time intervals.

Derived data may be expressed in a format and in units convenient to the user. Suggested formats are as follows, with time, temperature, and particle weight or size specified:

- cm^2 undercut/g deicer
  typical range: 20 to 100 cm^2/g
- m^2 undercut/kg deicer
  typical range: 2 to 10m^2/kg
- ft^2 undercut/lb deicer
  typical range: 10 to 50 ft^2/lb

4.2.4.5 Important factors and uncertainties: The undercutting test is still under development. The principal proposed modification consists of substitution of a uniformly level, but lightly textured, concrete surface for the broomed concrete surface used in tests to date. The proposed surface should adhere strongly and uniformly to ice, permit greater uniformity in ice thickness within specimens and from specimen to specimen, and result in more symmetrical undercut patterns.

Data deviations and apparent inconsistencies in test data should be diminished with the proposed modifications.

The principal uncertainty associated with undercutting test results arises from the fact that the test procedure does not permit direct observation of the time at which penetration to the pavement surface occurs. Plots of undercutting versus time should indicate no undercutting prior to the time that the penetration cavity or core has contacted the surface, and a rapid increase to the area of the penetration cavity at the time of initial contact. The undercutting test accordingly should be supported with independently conducted penetration tests in which times are determined for penetration through the thickness of ice employed in undercutting tests.

Background tests, obtained with five replicates at each condition, from 0° to 25°F, yielded standard errors which generally were 3 to 10%

of the average undercut areas. The majority of the standard errors fell within 3 to 6% of average values.

4.2.4.6 Related procedures: Related procedures are as follows.

Ice Melting Rates and Capacities (4.2.2)
Ice Penetration (4.2.3)

4.2.5 Ice disbondment test: The literature describes one method, a drop test, for measuring the capability of deicing materials to destroy or disrupt the bond between ice and a pavement substrate. This method is not deemed suitable for a standard test. Related, ongoing studies are addressing the fundamental aspects of ice and substrate interfaces. In unpublished work, a mechanical disbondment apparatus was recently constructed and employed to measure forces and completeness of removal of ice on concrete treated with several chemical deicers. The ice and concrete specimens were prepared so that the ice was uniformly and strongly bonded to concrete, as in the ice-undercutting test. Uniformly-sized deicer particles were placed in symmetrical arrays on the ice, in order to obtain uniform, close to complete undercutting. Under these conditions undercutting was confined to reasonably symmetrical circular patterns, and complete undercutting was achieved only when deicer application rates were sufficient to fill the void spaces between the circular patterns.

Disbondment forces measurements showed clearly that nonundercut areas required vector forces of the order of 40 to 60 lb/in of blade width, and that completely undercut areas required essentially no removal force. The results are informative in that they show that, under idealized conditions for ice and pavement bonding, the effects of individual deicer particles do not extend beyond the areas defined by undercutting, i.e., bonding in adjacent ice is not weakened. The results also confirm data obtained via the undercutting tests.

The undercutting test constitutes a much simpler approach for evaluating the disbondment capabilities of deicers, and the undercutting test should provide the same type of information on less perfectly bonded ice. An ice-disbondment test is accordingly not recommended for development and inclusion in a set of standard test methods. A disbondment test, such as the one based on a laboratory-sized set of loaded wheels, should, however, provide useful and practical information relative to the undercutting and disbondment properties of deicers emplaced on systems subjected to thermal, mechanical, and other types of stress.

4.3 Compatibility With Bare and Coated Metals

4.3.1 Corrosion of bare metal

4.3.1.1 Test method: Bare metal specimens are immersed in corrosion test solutions for specified time intervals. The primary measure of corrosion is weight loss. Instructions are provided for examination of corroded specimens via low power microscopes, by metallographic sectioning, eddy current electromagnetic inspection, and ultrasonic inspection.

Procedures for immersion corrosion testing are provided in the following:

- ASTM G 31-72 (1985), Standard Practice for Laboratory Immersion Corrosion Testing of Metals.
- ASTM G 1-88, Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens.
- ASTM G 46-76 (1986), Recommended Practices for Examination and Evaluation of Pitting Corrosion.

4.3.1.2 Test objective: Immersion corrosion testing of bare metals provide a means to determine the corrosive characteristics of deicer solutions, including evaluations of alternate deicers or of modifications designed to minimize corrosion.

4.3.1.3 Equipment: Minimum equipment needs are glass vessels, analytical balances, micrometers, low power microscopes, and equipment and chemicals for cleaning or preparing test specimens prior to and after tests. Optional equipment for examining corroded specimens is specialized and normally available in a metallographic laboratory.

4.3.1.4 Data outputs: Primary weight loss data are customarily converted to annual corrosion rates, e.g., mils per year. Weight loss data are augmented to the extent possible by observations of pitting or other types of corrosion.

4.3.1.5 Sources of error or uncertainty: Corrosion tests are subject to numerous sources of error; adherence to practices recommended in ASTM G 31 and ASTM G 1 is essential. Duplicate tests, and control tests with water and a reference material such as sodium chloride, are recommended.

4.3.2 Corrosion of coated metal via salt spray

4.3.2.1 Method description: In ASTM B 117-73 coated or bare metal test specimens are exposed to a salt fog (5 wt % sodium chloride) environment at 35°C (95°F). This test, modified by substitution of deicer materials for sodium chloride, is recommended for investigations of candidate deicers.

Associated procedures are as follows:

In ASTM D 1186, a method is presented for nondestructively determining the thickness of nonmagnetic coatings on magnetic substrates. The specification provides for two types of coating thickness gauges: (1) magnetic pull-off type, or (2) magnetic flux type. The thickness of magnetic coatings or coatings on nonmagnetic substrates must be determined using suitable micrometers.

In ASTM D 1654, methods are presented for (a) preparing coated specimens prior to salt fog exposure, (b) cleaning the coated specimens after salt fog exposure, and (c) evaluating the specimens. A scribe mark is made through the coating to the metal substrate. Damaged coatings are removed either with a compressed air blast, or with a dull knife by scraping. A rating system (0 to 10) is specified for evaluation of the specimens after salt fog exposure, by measurement of the average distance of coating failure away from the scribe mark.

In ASTM D 1654, provisions are made for other configurations of scribe marks, including no scribe marks at all. A second rating system, also 0 to 10, is provided in the case of no scribe marks, based on estimation of the percent area of the test specimen with underfilm corrosion or blisters.

In ASTM F 502, a method is presented to determine the effects of cleaning and maintenance materials on painted aircraft surfaces. The effects on the paint are determined by conducting pencil hardness tests on the paint before and after the exposure tests. These procedures should be conducted in conjunction with the salt fog exposure tests to determine impacts on coatings, in addition to the corrosion tests.

4.3.2.2 <u>Methods objective</u>: The objective of these test methods is to determine the corrosive effects of deicer materials on coated metal substrates by salt fog testing, and in addition to determine impacts on coatings or paints.

4.3.2.3 <u>Facilities and equipment requirements</u>: The basic equipment consists of a salt fog cabinet, as specified in ASTM B 117, augmented by scribing tools, thickness gauges or micrometers, compressed air nozzles, and scraping tools.

4.3.2.4 <u>Data outputs</u>: The primary data output of these ASTM methods will be a rating (0 to 10) of the corrosive effects of the deicer material on coated metal substrates. The rating of corrosive effects will be determined by either:

- Measuring the average distance of coating failure away from a scribe mark.
- Estimating the percent of specimen area with corrosion effects (rust and blisters) for specimens with no scribe marks.

Secondary data outputs will be:

- Visual observations of the specimens for color changes, swelling, and chalking.
- Pencil hardness of paints before and after salt fog exposure.

4.3.2.5 Sources of error or uncertainty: Preparation of the coated test specimens is the most critical step of salt fog testing. The ASTM methods do not specify methods for coating metals. (ASTM F 502 describes the application of an aluminum conversion coating/epoxy primer/polyurethane topcoat system to aircraft aluminum test specimens, which may be of little interest to highway maintenance laboratories.) The coated test specimens for salt fog testing should be prepared according to either (1) state highway department specifications, or (2) the coating manufacturer's recommendations.

4.3.2.6 Method replication: A recommended number of replicates is not specified in ASTM B 117. However, three to five test specimens for each coating system and each substrate type are considered appropriate. If the deicer material causes considerable corrosion or coating degradation, test specimens for each coating system and each substrate type should be withdrawn and examined at one-fourth, one-half, and three-fourths of the anticipated salt fog test period of 500 hr or longer. Test protocols should include reference tests with sodium chloride salt fogs.

4.4 Compatibility With Metals in Concrete

A simplified and accelerated test method will be evaluated and developed in Phase II. A standard method for determining half-cell potentials of steel in concrete is available as ASTM C 876-87. This method is described in 4.4.1.

4.4.1 Half-cell potential measurement for steel in concrete

4.4.1.1 Test description: The half-cell potential of steel in concrete, relative to a standard electrode such as copper-copper sulfate, is measured via a system consisting of the reference electrode bridged to the concrete surface, a voltmeter, and an electrical connection to an exposed portion of the embedded steel. Profiles of electrode potentials are obtained by moving the reference electrode over the concrete surface.

4.4.1.2 Test objective: Half-cell potentials are indicative of the corrosive state of steel in concrete. Data obtained from the test permit the estimation of the probability that the steel is in a passive state, a highly corrosive state, or an intermediate or questionable state relative to corrosion.

4.4.1.3 Equipment requirements: Equipment consists of a standard half cell, an electrical junction device to provide a liquid bridge between the electrode and the concrete surface, a battery-operated voltmeter with ±3% end-of-scale accuracy and an input impedance no less than 10^6 ohms when operated at 100 mV, and electrical lead wires of specified resistivity.

4.4.1.4 Data outputs: Half-cell potentials are recorded to the nearest 0.01 V for several positions which represent the configuration of the specimen being tested. Potentials are located on a plan view of the concrete member and equal potential contours constructed. Potentials are further analyzed by statistical techniques, and a plot of half-cell potential versus cumulative frequency constructed. Results, for as many areas as appropriate, are interpreted as follows:

Potential vs. Copper Sulfate	Corrosive Potential
< -0.20 V	90% probability of no corrosion
-0.20 to -0.35 V	Corrosion uncertain
> -0.35 V	90% probability of corrosion

4.4.1.5 Sources of error or uncertainty: The method is limited by electrical circuitry and is sensitive to the moisture content of concrete. The test provides information on the existing corrosive state, but not on the extent of corrosion or on a corrosion rate; and test results are subject to interpretive uncertainties, particularly if neither a clearly passive nor a clearly corrosive state is indicated.

4.4.1.6 Replication: Successive measurements at a given location (measure, disconnect, remeasure) with one electrode should not yield voltages differing by more than 10 mV. The number of measurements required for a specimen is determined by the variability of voltage readings and specimen dimensions.

4.5 Compatibility With Concrete and Nonmetals

4.5.1 Scaling resistance of concrete (ASTM C 672)

4.5.1.1 Test description: Concrete specimens 3 in thick, with a surface area of about 72 in^2, are prepared and cured in accordance with specified procedures or alternatively taken from concrete structures. Deicing brine is ponded on the surface via a mortar or other suitable dike, and the specimens subjected to freeze-thaw cycles as follows: 16 to 18 hr at 0° ± 5°F, 6 to 8 hr at 73° ± 3°F, for 50 or more cycles. At intervals of five cycles, specimens are flushed, visually examined, and results recorded in accordance with instructions for a 0 to 5 visual rating. (Note: A simplified, shortened time concrete compatibility test will be evaluated in Phase II.)

4.5.1.2 Test objective: The test provides a measure of the resistance of concrete to scaling when exposed to chemicals in freeze-thaw cycles. The test may be employed to compare the effects of different chemicals at varying concentrations, as well as to evaluate the scaling resistance of different types of concrete, including concrete taken from existing structures.

4.5.1.3 Equipment and facilities

- Concrete mixing equipment, scales, molds for casting specimens, tamping rods, and small tools for finishing concrete.

- A freezer set to operate at 0°F.

- Provisions for monitoring and controlling humidity and temperature.

- Slump cone (ASTM C 143)

- Air meter (ASTM C 173)

4.5.1.4 Data outputs: Data outputs consist of visual ratings of scaling on a scale of 0 to 5, at intervals of five freeze-thaw cycles, combined with identification of type or history of the concrete specimen and the composition of deicing brines. Photographs and descriptions of surfaces should be included.

4.5.1.5 Sources of error or uncertainty: Tests are evaluated visually in qualitative terms. Ratings are subject to operator bias or interpretation, and may not be appropriately subjected to statistical analysis for error or deviation.

4.5.1.6 Method replication: Specifications for replication are not stated. Multiple tests will normally be required.

4.5.2 Abrasion resistance

4.5.2.1 Test description: The test is described in ASTM C 944-80, Abrasion Resistance of Concrete or Mortar Surfaces by the Rotating-Cutter Method. Cored or fabricated concrete or mortar specimens are abraded in a rotating, abrading cutter; weight loss and depth of wear are measured.

4.5.2.2 Test objective: The test gives an indication of the relative wear resistance of concrete and mortar. Relative to chemical deicer selection and use, the method constitutes an option for determining the wear resistance of concrete specimens subjected to freeze-thaw tests or for evaluating wear resistance of pavement surfaces exposed to deicing chemicals.

4.5.2.3 Equipment requirements: The basic piece of equipment consists of a rotating cutter drill press, as described in ASTM C 944-80. Auxiliary equipment includes molds and associated equipment for fabricating specimens or equipment for obtaining core samples, balances for weighing samples prior to and after tests, and instruments for measuring depth of wear.

4.5.2.4 Data outputs: Data reports include average weight loss in grams, or depth of wear in millimeters; documentation of sample size, finish, compaction, age, and strength; and documentation of test conditions.

4.5.2.5 Precision and accuracy: For normal test conditions: single-operator coefficient of variation of 21%; two tests by one operator should not differ by more than 59% of the average. For severe test conditions: single-operator coefficient of variation of 12.6%; two tests by one operator should not differ by more than 36% of the average.

4.5.2.6 Related procedures and documents

ASTM Standards

- C 192-81, Making and Curing Concrete Test Specimens in the Laboratory
- C 31, Method of Making and Curing Concrete Test Specimens in the Field
- C 33, Specification for Concrete Aggregates
- C 70, Test Method for Surface Moisture in Fine Aggregate
- C 125, Definitions of Terms Relating to Concrete and Concrete Aggregates
- C 127, Test Method for Specific Gravity and Absorption of Coarse Aggregate
- C 128, Test Method for Specific Gravity and Absorption of Fine Aggregate
- C 138, Test Method for Unit Weight, Yield, and Air Content (Gravimetric) of Concrete
- C 143, Test Method for Slump of Portland Cement Concrete
- C 172, Method of Sampling Freshly Mixed Concrete
- C 173, Test Method for Air Content of Freshly Mixed Concrete by the Volumetric Method
- C 231, Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method
- C 330, Specification for Lightweight Aggregates for Structural Concrete
- C 470, Specification for Molds for Forming Concrete Test Cylinders Vertically
- C 511, Specification for Moist Cabinets, Moist Rooms, and Water Storage Tanks Used in the Testing of Hydraulic Cements and Concretes
- C 566, Test Method for Total Moisture Content of Aggregate by Drying
- C 567, Test Method for Unit Weight of Structural Lightweight Concrete
- C 617, Practice for Capping Cylindrical Concrete Specimens
- D 448, Specification for Standard Sizes of Coarse Aggregate for Highway Construction

National Bureau of Standards

Handbook 44 Specifications, Tolerances, and Other Technical Requirements for Commercial Weighing and Measuring Devices

4.5.3 Concrete mechanical strength retention

4.5.3.1 Test description: A compressive axial load is applied to molded cylinders or cores of concrete at a rate within a prescribed range until failure occurs. The compressive strength of the specimen is calculated by dividing the maximum load during the test by the cross-sectional area of the specimen.

The method is described in ASTM C 39-86, Standard Test Method for Compressive Strength Determination of Cylindrical Concrete Specimens.

4.5.3.2 Test objective: The objective of this test is determination of the compressive strength of molded or cored concrete specimens. The method is generally applicable for investigations of the effects of chemical deicers on compressive strengths.

4.5.3.3 Equipment requirements: The principal equipment is a screw-driven or hydraulically-operated test machine capable of applying loads at specified loading rates, continuously and without shock.

Auxiliary equipment includes concrete-mixing equipment, molds and finishing tools, or coring equipment.

4.5.3.4 Data outputs: The primary data output is compressive strength, calculated by dividing maximum load by average cross-sectional area. Supporting data or information include specimen history, specimen dimensions, maximum load, type of fracture, and defects in specimens or cap.

4.5.3.5 Sources of error or uncertainty: Values obtained depend on specimen size and shape, batching and mixing procedures, fabrication methods, and age, temperature, and moisture conditions. Reproducibility of results for fabricated specimens requires adherence to uniform procedures for fabricating and conditioning specimens and conducting strength tests.

4.5.3.6 Test replication and precision or bias: Precision and bias have not been determined. Multiple tests are generally indicated as being necessary.

4.5.3.7 Applicable documents and procedures

"Manual of Aggregate and Concrete Testing," *Annual Book of ASTM Standards*, Vol. 04.02

ASTM Standards

C 31, Method of Making and Curing Concrete Test Specimens in the Field
C 42, Method of Obtaining and Testing Drilled Cores and Sawed Beams of Concrete
C 192, Method of Making and Curing Concrete Test Specimens in the Laboratory

4.5.4 Effects on nonmetals

4.5.4.1 Test description: ASTM procedures are available for measuring the tensile properties of plastics (ASTM D 638) and rubber (ASTM D 412). In order to determine the effects of deicers on nonmetals, these two tests are recommended in conjunction with materials exposure either via a modified salt fog test (ASTM B 117 with deicer substituted for sodium chloride), or by immersion in deicer solutions as a immersion corrosion tests (ASTM G 31 procedure).

In ASTM D 638 and ASTM D 412, the following properties may be measured or calculated:

- Tensile strength at yield
- Tensile strength at break
- Elongation via an extension measuring device
- Elastic modulus (calculated)

4.5.4.2 Methods objective: The objective of these test methods is to determine the effects of exposure of test specimens to aqueous solutions of deicers on mechanical properties of nonmetals.

4.5.4.3 Facilities and equipment requirements: The equipment requirements are either a salt fog chamber (ASTM B 117), or immersion systems (ASTM G 31); and equipment requirements for ASTM D 638 and D 412, including a testing machine capable of constant crosshead motion, grips to hold the specimen, load indicator (load recording device recommended), micrometers, calipers, cutting die or machine to cut test specimens, conditioning chamber at 23° ± 2°C and 50% ± 5% relative humidity, compression set apparatus (optional), and extension measuring device, (optional).

4.5.4.4 Data outputs: The data outputs will depend on the equipment used to determine the tensile properties. At a minimum, the data outputs will be:

- Visual observation for changes in the test specimen appearance.
- Maximum load applied to the test specimen.
- Average specimen width in the test area.
- Average specimen thickness in the test area.

The elongation of the specimen can be determined if a suitable extension indicating device is used.

The elastic modulus can be calculated if the applied load is recorded. A suitable recording device records the load on one axis and either time, extension, or strain on another axis.

4.5.4.5 Sources of error or uncertainty: Tensile properties of plastic and rubber materials are dependent on several factors including method of loading, rate of load application, temperature, humidity, and previous history. Test protocols should include control specimens.

4.5.4.6 Method replication: A minimum of five test specimens is required for determining the tensile properties of plastic materials.

4.6 Environmental Effects

Numerous relevant test procedures are available for the ecological risk assessment of chemicals, such as pesticides and industrial effluents which may be introduced into the environment. These tests are employed in the framework of a generalized protocol, with specific tests being selected on the basis of their suitability and responsiveness to the type or magnitude of the impact posed by a material, including the characteristics of potentially affected environmental systems. Such tests have not been applied in a systematized evaluation of the impacts of chemical deicer usage. As a consequence, a set of tests specifically designed for use with chemical deicers is not presently available; these will be developed and documented in Phase II of this program. In the following subsections a set of generic tests are presented in summary fashion together with an environmental assessment protocol or framework within which the tests will be employed.

4.6.1 Environmental test protocol

4.6.1.1 Protocol description: An environmental test protocol consists of a system for preliminary identification of the characteristics of a deicer in relation to potential environmental effects, determining the mode of dissemination into the environment and quantifying quantities or concentrations in environmental receptor systems, selection of appropriate tests, and designation of test sequences, together with guidelines for determining when environmental questions have been adequately addressed.

The elements of the protocol are as follows:

- Chemical analysis and identification of chemical species, both major and minor.
- Preliminary hazard analysis, environmental risk identification, and definition of significant systems at risk, together with probable or potential types of impacts.
- Estimation of probable environmental concentrations in receptor systems and of the magnitude or size of affected systems.
- Identification of species at risk and of appropriate test species.
- Identification of appropriate tests and test sequences with specified checkpoints.
- Guidelines for determining when environmental questions have been satisfactorily resolved.

4.6.1.2 Protocol objective: The objective of the protocol is provision of an operating framework for conducting environmental evaluations and tests in a systematized manner, with test procedures or methods to the extent possible suitable for use in highway maintenance laboratories.

4.6.2 Method for estimating environmental concentration

4.6.2.1 Method description: Details of a method will be developed in Phase II.

The method will consist of the following basic elements:

- An enumeration of data requirements and data sources, or alternatively of estimating techniques for deriving needed data.
- Submodels or estimating procedures for describing and quantifying the dissemination of deicer chemicals into and through the environment.
- Overall models for predicting the concentration of deicer materials in environmental receptor systems, i.e., aquatic and terrestrial systems, and additionally for estimating ultimate fate or persistence.
- Guidelines or procedures for relating estimated environmental concentrations to environmental risk potential, for defining species or systems at risk, and for identifying appropriate test procedures.

4.6.2.2 Method objective: The objective of the use of this method is provision of information and data on the expected fate of deicer materials in potentially impacted environmental systems, to ensure the effective utilization of environmental test methods.

4.6.3 Environmental test methods

4.6.3.1 Test description: Environmental test methods potentially encompass a range of tests designed to establish acute and chronic toxicities of materials with appropriate single species in aquatic and terrestrial habitats, through the determination of long-term effects on balanced, multispecies systems. Tests suitable for use in a highway maintenance laboratory will likely be single species tests. Basic procedures for such tests are described in the literature, but adaptations for use with deicer materials are needed; these will be developed in Phase II.

Protocols for various types of tests are described in the following publications:

Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms, EPA/600/4-85/013

Short Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, EPA/600/4-85/014

Standard Practice for Conducting Acute Toxicity Tests With Fishes, Macroinvertebrates, and Amphibians, ASTM E 729-780

Test Methods for Assessing the Effects of Chemicals on Plants, EPA/560/5-75/008

Protocols for tests in laboratory systems of mixed assemblages of species are given in the following:

Community Toxicity Testing, ASTM STP 920
Standardized Aquatic Microcosm Protocol, EPA 223-802352

The potentially applicable tests involve the exposure of aquatic or terrestrial species to chemicals at specific levels or concentrations under controlled conditions and for specific time periods, and the documentation of mortality rates or quantitative/qualitative evidence of chronic effects. Exposure levels range from those required to cause mortality to levels in the vicinity of estimated environmental concentrations.

4.6.3.2 Test objectives: The overall objective of environmental testing consists of the determination of whether or not the environmental effects of a deicer material pose a significant risk, and the provision of a basis for determining whether identified risks are sufficient to either preclude use of the material or to prescribe limitations for its use.

4.7 Engineering Parameters

4.7.1 Particle size distribution

4.7.1.1 Method description: The method and procedures are based on ASTM C 136-84a, Sieve Analysis of Fine and Coarse Aggregates. Representative samples of solid deicers are separated into several size fractions via a succession of standard mesh-size screens.

4.7.1.2 Method objective: Particle size analyses are employed to determine whether a commercial deicer conforms to specifications (e.g., ASTM D 632 for rock salt), or to determine particle sizes of alternate or developmental deicers in order to obtain information related to deicer handling and application properties.

4.7.1.3 Equipment requirements: Five to six standard mesh screens are required. Mesh sizes correspond to sizes designated for material specifications, or alternatively are selected to provide isolated samples which represent the size distribution of the material. Auxiliary equipment includes balances or scales capable of weighing 100 g to the nearest 0.1 g and an oven for drying certain materials at 110°C. A mechanical sieve shaker is optional. Hygroscopic materials may require dry boxes for sieving and other handling operations.

4.7.1.4 Data outputs: Results are normally expressed as percent passing each screen employed in the sieve analysis. Other options are percentages retained on individual screens, and percentages passing a screen and retained by the next smallest screen.

4.7.1.5 Sources of error or uncertainty: The principal source of error is the representativeness of the sample employed in the sieve analysis.

4.7.1.6 Replication: One carefully conducted test will usually suffice for a given sample. Tests with multiple samples may be required to determine sample to sample variations or to characterize bulk materials.

4.7.2 Deicer particle shape: Deicer particle shape is generally considered to be significant relative to the mode of ice melting, and possibly relative to ice-melting rates. The deicer materials presently in use or available for use range from irregularly shaped flakes (flake calcium chloride) through spherical particles (pellet calcium chloride, urea, and one manufactured form of CMA). Rock salt particles are generally not spherical. The rock salt particles include fine grains and small platelets; square particles with a height dimension of perhaps 50% of a length dimension; flat, generally rectangular particles with sharp corners or edges; and variously shaped chunks having several flat or curved faces. The large particles and the fine particles tend to be uniform in shape; intermediate-size particles are more variable in shape.

The literature review did not reveal the existence of a relatively simple method for determining particle shape. Approaches to quantifying or describing particle shape have been described. A two-dimensional approach involves measurement of the perimeter of a particle and comparing the perimeter to the perimeter of a circle of equal area. A second two-dimensional approach consists of dividing length by width. Three-dimensional approaches for irregular particles define shapes in terms of the diameter of a sphere having the same surface area or the diameter of a sphere having the same volume or mass. The three-dimensional approaches primarily define size in terms of equivalent spheres, however.

Techniques for measuring particle dimensions for a two-dimensional approach are simple in principle. For a material such as rock salt, the measurement process will be laborious and time-consuming, however. Given the current lack of documented relationships between deicer performance properties and deicer shape, a standard method for determination of particle shape, based on particle-by-particle dimension measurement, is not recommended.

4.7.3 Flow characteristics

4.7.3.1 Test description: A test method prescribed for measurement of apparent densities and pourability of plastic materials (ASTM D 1895-69) is recommended.

Apparent or bulk densities are determined by collecting and weighing a specified volume of material discharged into a container through a funnel, with a drop height of 3.8 cm.

Pourability tests will usually be conducted at temperatures in the region of ambient temperatures anticipated during deicer use. Supporting information includes moisture contents of tested deicer materials, in order to establish the effect of moisture and storage at low ambient temperatures on deicer flow properties.

4.7.3.2 Test objective: The objective of pourability tests is determination of the flowability of deicer materials, and particularly the determination of whether flow properties are affected by storage under a range of temperatures and by changes in moisture contents.

4.7.3.3 Equipment: Equipment requirements include funnels of specified dimensions, volume calibrated collection vessels, timers, balances, and thermometers.

4.7.3.4 Data outputs: Control or reference pourability data are obtained with appropriate reference materials, e.g., moisture-free rock salt with a normal particle size distribution. The pourability of test samples taken from incoming supplies or from stockpiles is compared to that of the reference material. Test results include observations of bridging, caking particle agglomeration, and similar impediments to flow.

4.7.3.5 Sources of error or uncertainty: The flow characteristics of test samples will be affected by mechanical disturbances of the material when samples are taken from stockpiles or containers. Surface samples can be expected to have flow properties different from flow properties of samples taken from the interior of a stockpile. Uniform, consistent materials-handling procedures are accordingly important, as are records of the origin and history of test samples.

4.7.4 Storage characteristics: Bulk storage of deicers is preferred for reasons of economy and convenience. A storage facility should protect deicers from precipitation to prevent losses of materials, as well as dissemination into the environment by dissolution in rainfall or snowmelt. Exposure to precipitation will also normally result in substantial changes in handling properties which become more severe at low winter temperatures. Changes include caking and apparent freezing because of moisture-activated interparticle interactions which tend to cement particles together.

Some deicer materials, most notably calcium chloride products, have an affinity for atmospheric moisture sufficient to mandate storage in airtight, moisture-proof containers.

Standard tests for evaluating storage characteristics and for determining the moisture sensitivity of deicer materials are not available. Potentially required tests include determination of the existence and identity of solid hydrates and associated temperature-water vapor pressure conditions; determination of temperature and humidity conditions associated with deliquescence for essentially nonhygroscopic materials; determination of the uptake of moisture from ambient air at appropriate temperatures and relative humidities; and determination of whether or not adsorbed or chemically bound moisture causes caking or agglomeration of particles into larger particles or into mechanically intractable masses.

Procedures or methods for obtaining qualitative or quantitative information on moisture sensitivity are as follows.

4.7.4.1 For pure compounds present in a deicer as major or minor constituents: The following types of literature data or calculations based on literature data can be used to assess moisture consistivity.

- The vapor pressures of water in saturated solutions of pure compounds are generally available. Alternately, relative humidities of saturated solutions are reported at various temperatures. Such data translate directly to the temperature and humidity conditions associated with deliquescence, i.e., the absorption of moisture vapor from the atmosphere followed by eventual liquefaction. Deliquescence can be expected when the vapor tension of moisture in air slightly exceeds the vapor pressure of water over a saturated solution of the chemical.

- Solid hydrates of numerous chemical compounds are reported in the literature, usually in combination with water vapor tensions associated with given temperatures and specified hydrates.

- Moisture contents of commercial products are usually reported. Such data are indicative of the moisture adsorbing and retention capacities of materials under normal conditions of handling and storage.

4.7.4.2 Experimental methods for determining moisture uptake: Desired information will normally address moisture sensitivity at normal storage or use temperatures and associated relative humidities.

A basic procedure suitable for this purpose consists of drying a weighed sample at 110°C, reweighing to determine the as-received moisture content, exposing the dry material at a fixed relative humidity and temperature, and weighing at selected time intervals until moisture uptake ceases or until evidence has been obtained for deliquescence or the formation of solid hydrates.

Constant relative humidities, ranging from about 40% to 98% over a temperature range from 0° to 70°C, can be provided with glycerin-water solutions. Instructions for preparation and use of the solutions are given in ASTM E 104, Maintaining Constant Relative Humidity by Aqueous Solutions. A reservoir of the appropriate solution is placed in an airtight enclosure, such as a glass desiccator, and open samples of test materials placed in the enclosure. Data of the required accuracy and completeness will usually be obtained with tests conducted at normal laboratory temperature and at perhaps two temperatures in a refrigerator.

Data obtainable from such tests include:

- Rates of moisture uptake.

- Moisture adsorption capacity, i.e., adsorbed but not chemically bound water.

- Solid hydrate formation. Identification of specific hydrates and of associated water vapor tensions will, however, require carefully controlled conditions and a greater number of tests.
- Conditions for deliquescence.

4.7.4.3 Determination of storability characteristics: Laboratory representation of the range of temperature, moisture contents and humidities, and materials packing conditions encountered in bulk storage is clearly not possible. Nevertheless, certain simple tests can be conducted to obtain evidence of changes in deicer materials properties accompanying temperature variations. A recommended test protocol follows:

- Determine the particle size distribution of as-received or candidate deicer materials.
- Characterize the material by chemical analysis and moisture determination.
- Prepare 50- to 100-lb batches of material with a range of moisture contents, packaged in a container designed to retain moisture.
- Cycle the materials between a normal ambient temperature and a specified low temperature for time periods of 5 to 7 days at each temperature.
- After each part of the cycle, examine and test the material to ascertain mechanical properties, i.e., resistance to flow, hand scoopability and spreadability, the presence and size of clumps, fracturability under stresses exemplified by dropping a bag or barrel, and sieving to determine changes in particle size and particle size distribution. Flow characteristics (pourability) can be established via procedures presented in 4.7.3.

The test cycle should include return to warm ambient temperature conditions, in order to determine whether changes reverse on warming.

Adaptations of the test procedure may be employed to evaluate other aspects of storability. Some examples follow:

- An as-received material may contain higher than normal moisture contents. Evaporative losses may be accompanied by the cementing together of particles.
- Exposure of stored materials at high relative humidities may result in significant moisture uptake and in the onset of deliquescence, followed by evaporative losses at low relative humidities and by particle agglomeration.

- Additives introduced for purposes such as corrosion inhibition may significantly affect storage characteristics. Tests of moisture absorbancy characteristics, followed by temperature and moisture content cycling, will define storage characteristics.

4.7.5 Dusting Susceptibility

4.7.5.1 Test description: In ASTM D 4331-84 a sample of granular solid material is placed in a vertical fluidizing tube equipped with a vibrator, a controlled air supply, flowmeters, dust filters, and a dust sampling pump. Air is passed through the sample, and suspended dusts collected, weighed, and analyzed as appropriate.

4.7.5.2 Test objective: The objective of the test is determination of deicer dusting tendencies relative to deicer materials loading or transfer and application to highways.

4.7.5.3 Equipment

Vertical-fluidizing tube on ring-stand assembly, as specified in ASTM D 4331-84, with accessories
Timers
Analytical balances

4.7.5.4 Data reports: Weights of collected dust are reported, together with a complete description of the sample and test conditions.

4.7.5.5 Sources of error or uncertainty: Dusting susceptibilities are significantly affected by sample moisture contents and humidity levels in air used to entrain dusts. Precision and bias are unknown.

4.7.5.6 Test replication: A minimum of five replicates as specified.

4.7.6 Specific gravity of liquids: ASTM D 1122 describes a method to determine the specific gravity of engine coolants, i.e., antifreeze. The method is appreciable for determining the specific gravity of liquid deicer materials. The procedure involves cooling the sample to 15.5°C (60°F) in a transparent cylinder, and measuring specific gravities with a hydrometer.

4.8 Health and Safety Aspects

4.8.1 OSHA protocol: The manufacture, import, and use of chemicals are subject to federal regulation via the Hazard Communication Standard (HCS) of the Occupational Safety and Health Administration (OSHA). The HCS covers all employers with employees exposed to hazardous chemicals in the workplace. The protocols and requirements of the HCS are presented in an abbreviated format in this section.

4.8.1.1 Elements of the HCS: Five areas are specified in the HCS. These are:

- Hazard Evaluation.
- Labels/Forms of Warning.
- Materials Safety Data Sheets.
- Employee Training.
- Written Hazard Communication Program.

Activities in the above area are organized to ensure that all hazards are identified and characterized relative to specific hazards; that procedures are placed in operation to ensure that potentially exposed workers are made aware of hazards; that operational procedures for protecting workplaces and ensuring worker safety are developed and emplaced in an operating plan; that workers are informed and trained: and that an ongoing hazard communication system is instituted and maintained.

4.8.1.2 Hazard evaluation: Hazard evaluation initiates with an inventory of chemicals, developed in accordance with a specified definition of chemicals. Any substance that presents a physical or health hazard, as defined by OSHA, is considered regulated under the HCS. Four lists, totaling about 1,200 chemicals, comprise the floor of regulated chemicals.

Hazard evaluation is based on currently available information on health hazards and on information or data which define the physical hazards of a chemical. Compilations of information and lists of chemicals are available in the following sources:

Hazardous Chemicals

- 29 CFR, Part 1910, Subpart 2, Toxic and Hazardous Substances

- *Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment*, American Conference of Industrial Hygienists (ACGIH), latest edition

Carcinogenic Chemicals

- 29 CFR, Part 1910, Subpart Z, Toxic and Hazardous Substances

- *National Toxicology Program (NTP) Annual Report on Carcinogens*, latest edition

- *International Agency for Research on Cancer (IARC) Monographs*, latest editions

4.8.1.3 Labels/forms of warning: The purpose of labels is to warn about potential danger of significant risk of chemicals that are shipped or used in the workplace. Information on labels includes the identity of the chemical, the types of risk or hazard, and optional identification of protective measures.

4.8.1.4 Materials safety data sheets (MSDS): Materials safety data sheets constitute the basic vehicle for organizing and presenting the identity and concentration of chemicals, together with a variety of data and information which define physical and health hazards and indicate appropriate protective measures. The MSDS is the principal means of transferring information from manufacturers to users.

Information in the MSDS includes the following:

- Chemical identity, including constituents which are a health hazard and are present in concentrations of 1% or more, and carcinogens present at 0.1% or more.
- Physical and chemical characteristics such as vapor pressures, flash points, explosivity, and reactivity.
- Physical hazards and health hazards.
- Permissible exposure levels.
- Safe handling and use precautions such as eye or skin protection.
- Recommended engineering controls.
- Emergency procedures.

4.8.1.5 Employee training program: The purpose of the employee training program is to reduce chemically related illness or injury by informing workers of hazards and providing training relative to safe practices. A written training program is required, which encompasses designated responsibilities and schedules, as well as the specific procedures to be employed in communicating hazards to workers and providing training in safe work practices.

4.8.1.6 Written hazard communication program: The written hazard communication program consists of a written record of all the elements which must be complied with in the HCS. The program involves the implementation and updating of a system for recording hazard evaluation/identification and following through with MSDS, labeling/warning, and employee training.

5.0 CONCLUSIONS AND RECOMMENDATIONS

The Phase I investigation provided a sound basis for assessing the adequacy of available test methodologies for the characterization of chemical deicers, and for developing technical rationales for the improvement of sodium chloride as a deicing chemical. Based on these findings, the following major conclusions and recommendations are offered.

- Chemical deicer test methods require further experimental development and validation in the following five areas: deicer performance, concrete compatibility, frictional characteristics, concrete reinforcement corrosion, and ecological hazard assessment.
- Recommended experimental approaches for the development and/or modification of specific test methods in the five identified chemical deicer evaluation areas are presented in the Phase II work plan.
- Sound technical rationales exist for improvement of the utility and acceptability of sodium chloride as a chemical deicer in the two following major areas: deicing performance and materials compatibility.
- Recommended exploratory development approaches for improvement of the deicing performance and enhancement of the materials compatibility of sodium chloride-based deicer formulations are presented in the Phase II work plan.

The conclusions derived from the Phase I studies provide the basis for structuring the Phase II work plan and the resultant recommended approaches constitute the major thrust of the proposed Phase II investigation.

APPENDIX A

SELECTED TEST METHODS FOR EVALUATING CHEMICAL DEICERS

I. INTRODUCTION

The test methods selected for evaluation of chemical deicers are presented in this appendix.

Test methods in five areas of chemical deicer evaluation are scheduled for study in Phase II. The developmental studies or research will range from relatively minor modification of a procedure through major adaptation or extension of existing technology in order to develop a procedure which yields definitive results in a reasonably short time period.

Some methods have not at this point been documented or described in an ASTM-type format. The entire set of test methods will be documented and described in an ASTM-type format in Phase II. The material in this appendix accordingly constitutes a preliminary version of the test methods. Methods subject to modification, documentation in the ASTM format, or substantial developmental efforts in Phase II are presented in an abbreviated or summary format, including designation of the type of effort required to finalize and document procedures.

Forty-two ASTM procedures are referenced in this appendix. These are found together in alphanumerical order in Appendix B. The majority of the ASTM procedures are either directly applicable to deicers or deal specifically with deicers. Others fall in one of two classes: (a) the basic procedure is applicable to deicers, but operational modifications are required and planned; or (b) the procedure is considered to be of value or interest as a reference procedure and likely will be presented in this light in a finalized set of procedures.

II. SYNOPSES OF TEST METHODS

The synopses of test methods are presented in six general categories as follows: physicochemical characterization, deicer performance, materials compatibility, environmental effects, engineering parameters, and health and safety aspects.

A. Physicochemical Characterization

1. Sampling: Representative samples of deicers are a requirement for use in tests such as chemical analysis, fundamental property measurement, materials compatibility tests, and others. The following ASTM procedures address sampling procedures for a variety of sources. The methods are suitable without modification.

Drums and bags, hygroscopic solids	ASTM D 345-80
Drums and bags, nonhygroscopic solids	ASTM D 1568-63
Stockpiles, barges, railcars	ASTM D 75-82

Trucks	ASTM D 3665-82
Liquid containers	ASTM D 345-80
Field samples	ASTM C 702-80
Nonhomogeneous solids: size reduction and mixing	ASTM D 2013-86

2. Deicer analysis: Accurate data on deicer chemical identities and compositions are necessary for characterization of chemical deicers. Minor as well as major constituents are potentially important. Methods applicable to chemical analysis range from colorimetric titrations through instrumental chromatographic and spectroscopic methods.

Selected methods are as follows:

Moisture content	ASTM E 534-75
Water-soluble/water-insoluble	ASTM E 534-75
Inorganic constituents	ASTM E 534-75, ASTM E 449-84
Inorganic anions via ion chromatography	EPA Method 300.0
Carbon and hydrogen	ASTM D 3178-84
Sulfur	ASTM D 3177-84
Nitrogen	ASTM D 3179-84
Metals via atomic absorption spectrophotometry	Method 303A, Standard Methods for the Examination of Water and Wastewater, 15th Edition, 1980

The above methods are described, in detail, in the appropriate format. They are suitable for use in laboratories equipped with the necessary equipment and staffed with experienced analytical chemists.

3. Deicer property measurements: Several physical-chemical properties are related to chemical-deicer performance potential. The properties and associated methods are as follows.

a. Aqueous solubility: The solubility of a deicing chemical in water at low temperatures is related to a theoretical ice-melting capacity. Temperatures of interest range from about 0°C to the eutectic temperature of a deicer-water system. Solubility measurements basically involve the equilibration of an excess of solute with water at a constant temperature, followed by chemical analyses of supernatant liquids. The measurements must be accompanied by analysis of the deicer for purity, moisture content, and water insolubles.

The method for solubility determination will be documented in an ASTM-type format in Phase II.

b. Freezing-point determination: Freezing-point determination involves the establishment of the concentration of the deicing chemical in water associated with various freezing points, from slightly less than 0°C to near the eutectic temperature.

ASTM D 1177-82 is the selected method for determination of freezing points. Aqueous solutions at several selected concentrations are cooled slowly with stirring, from a temperature above the freezing point to a temperature a few degrees below the onset of freezing. The intersection of cooling curves (time vs. temperature) represents the freezing point of a solution.

c. Eutectic temperature determination: The equipment and general procedures employed for freezing point determination in ASTM D 1177-82 are employed for eutectic temperature determination. A solution, initially at a concentration preferred to be either at, slightly lower, or slightly higher than the eutectic composition, is cooled slowly until a constant temperature is reached. The temperature remains constant until no liquid is present.

ASTM D 1177-82, modified as above, accordingly constitutes the method for determining eutectic temperatures.

d. Eutectic composition: The equipment and general procedures of ASTM D 1177-82 are employed for determination of eutectic compositions via the following modification. Aliquots of the solution phase in equilibrium, with ice and solid deicer at the eutectic temperature identified by the method for eutectic temperature determination, are withdrawn and analyzed chemically.

ASTM D 1177-82, modified as above, accordingly constitutes the method for determining eutectic compositions.

e. Heat of solution: Experimental measurement of heats of solution of deicers in water should seldom be required. Compilation of data on heats of formation of solid or crystalline materials and of aqueous solutions usually will obviate the need for experimental determinations. Literature sources also will suffice for calculation of the heats of solution of mixed solutes. In the event that experimental determinations are judged to be necessary (e.g., for a material for which literature data are not available), solution calorimeters are available from several commercial sources. A solution calorimeter consists basically of a dewar-type flask in which water and solute are mixed and temperature changes measured via set procedures. The calorimetric equipment includes instrumentation needed for calibration so that temperature changes due to solute dissolution can be distinguished from the effects of calorimeter system heat capacities.

Procedures for experimental determination of heats of solution and for calculation from literature data will be incorporated in ASTM format in Phase II.

f. Deicer brine viscosity: Brine viscosity, particularly at ice and snow temperatures, is of interest for two reasons--viscous or nonfree-flowing brines will likely be associated with low ice-deicer interaction rates and can be anticipated to be objectionable from the standpoint of brine-pavement frictional characteristics.

ASTM D 445-86 has been selected as the method for measurement of brine viscosities.

g. Brine-pavement frictional characteristics: The frictional characteristics of pavement surfaces exposed to deicer brines are of concern from a safety standpoint. Two laboratory-oriented methods have been selected for modification to permit determination of either static coefficients of friction (ASTM D 3248-73) or kinetic coefficients of friction (ASTM D 2534-73). The two ASTM procedures are included in this appendix with the understanding that they constitute reference rather than final procedures.

h. Brine pH: Deicer brine pH, together with brine capacities to contribute to the alkalinity or acidity of the receiving environment, is potentially important relative to corrosion or materials degradation and relative to impacts on soils or receiving bodies of water. pH measurements are described in ASTM E 70-77. A method for measuring alkalinity is presented in ASTM E 449-84.

B. Deicer Performance

1. Ice-melting rate and capacity test: This test involves the fabrication of ice with a specified thickness (1/8 in) in a flat Plexiglas dish; equilibration to within 0.5°F of a specified temperature; broadcast addition of deicer; and at specified time intervals, collection of brine via decantation, measurement of brine volume, and reintroduction of brine to the system for time periods of 1 hr or more.

In Phase II, experimental tests will be conducted at lower deicer application rates corresponding to highway application rates, with equipment expanded in size if necessary.

The finally adopted apparatus and procedure will be documented in an ASTM-type format in Phase II.

2. Ice-penetration test: In this test, deicer particles of uniform weights are placed on the surface of ice, and depths of penetration measured over a period of 1 hr or more. A small quantity of water-soluble dye is placed on the ice surface to render the brine cavities highly visible. In the reference method the ice specimen is frozen in small cavities drilled in Plexiglas with a countersink surface.

Modifications to the apparatus will be tested in Phase II. The modified test will be documented in Phase II.

3. Ice undercutting: In this test a 1/8-in-thick layer of ice is frozen on a concrete surface, a dye emplaced on isolated spots on the surface, and weighed deicer pellets placed on the dye spots. Penetration through the

ice to the concrete surface is followed by melting at the ice-substrate interface in approximately circular undercutting patterns. Photographs taken at selected time intervals are employed to measure undercut areas, which are converted to undercut area per unit weight of deicer.

A broomed concrete surface was employed in the reference method. In Phase II a smooth, textured surface will be investigated, together with procedural changes designed to eliminate certain inherent problems. The modified test will be documented in Phase II.

C. Materials Compatibility

1. Bare metal corrosion: The recommended test method is ASTM G 31-72, an immersion/weight loss method.

Related procedures are:

- ASTM G 188, cleaning procedure for corroded metal specimens.
- ASTM G 46-76, pit depth analysis.

2. Corrosion of coated metal: ASTM B 117-73, a salt spray test, is recommended.

Related or supporting methods are:

- ASTM D 1186-81, coating thickness.
- ASTM D 1654-79a, specimen evaluation.
- ASTM F 502-82, effects on painted aircraft surfaces.

3. Corrosion of metals in concrete: ASTM C 876-80 is available for evaluating the corrosive state of metals embedded in concrete.

Simplified and accelerated methods for evaluating the effects of deicing chemicals on concrete reinforcement corrosion will be investigated in Phase II. These will be documented in Phase II.

4. Concrete scaling resistance: The reference method for determining the effects of deicing chemicals on concrete is ASTM C 672-84, freeze/thaw cycling.

Related or support methods are:

- ASTM C 944-80, a modified drill press method for evaluating abrasion resistance.

- ASTM C 39-84, a method for evaluating mechanical strength retention.

- ASTM C 192-81, procedures for preparing laboratory concrete test specimens.

A simplified and accelerated method for evaluating the effects of deicing chemicals will be investigated in Phase II. If results are favorable, the method will be recommended as an alternate to or substitute for the time-consuming freeze/thaw procedure of ASTM C 672-84.

5. Compatibility with nonmetals: Procedures selected for evaluation of compatibility with nonmetals are:

- ASTM B 117-73, salt spray test.
- ASTM G 31-72, modified immersion corrosion test.
- ASTM D 638-84, plastic tensile strength.
- ASTM D 412-83, rubber tensile strength.

D. Environmental Effects

The environmental literature provides an authoritative, generalized protocol for evaluating the environmental effects of chemical deicers and numerous specific experimental procedures. These are not, at present, specifically adapted for use with deicers. This task will be undertaken in Phase II and the appropriate tests presented in standard procedure format.

Reference procedures and reference documents are as follows:

- ASTM E 943-88, terms and definitions

- ASTM E 729-80, acute toxicity: fish, macroinvertebrates, and amphibians

- ASTM E 1197-87, soil core: terrestrial environmental effects

- EPA/600/4-85/013, Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms

- EPA/600/4-85/014, Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms

- EPA/560/5-75/008, Test Methods for Assessing the Effects of Chemicals on Plants

- ASTM STP 920, Community Toxicity Testing

- EPA 223-802352, Standardized Aquatic Microcosm Protocol

E. Engineering Parameters

1. Particle size distribution: Selected methods are:

- ASTM D 632-84, for sodium chloride and nonhygroscopic deicers.
- ASTM D 345-80, for hygroscopic materials.

2. Particle shape: No test is available or recommended.

3. Flow properties: The selected method is:

- ASTM D 1895-85, a pourability test.

4. Dusting tendencies: The selected method is:

- ASTM D 4331-84, equipment and procedures for collecting and measuring air-entrained particulate matter.

5. Density: Selected methods are:

- ASTM D 1895-69, bulk or apparent density measurement of solids.
- ASTM D 1122-84, liquid density measurement.

6. Moisture sensitivity: Applicable procedures are as follows:

- ASTM E 534-75, moisture content of nonhygroscopic materials.

- ASTM E 104-51, methods for achieving constant relative humidities and exposing materials to constant moisture vapor tensions.

- ASTM D 3201-86, a reference method which details procedures for evaluating moisture uptake by wood products.

These procedures, with appropriate modifications or additions to be provided in Phase II, are applicable for determining moisture adsorbing capacities, conditions for deliquescence, and hygroscopic moisture uptake.

7. Moisture-related storage characteristics: Standard procedures for evaluating the effects of moisture on deicer storage properties are not available. Of particular interest are low-temperature storage properties.

A relatively simple temperature-cycling procedure involving selected moisture levels in deicers will be documented in a standard procedure format in Phase II.

F. Health and Safety Aspects

The health and safety aspects of deicer manufacture, transport, and use are regulated via OSHA (Occupational Safety and Health Administration) protocols, as outlined in detail in the Hazard Communication Standard (HCS).

APPENDIX B

LIST OF RELEVANT ASTM STANDARDS

RELEVANT ASTM STANDARDS

ASTM B 117-85, Standard Method of Salt Spray (Fog) Testing, Section 6, Vol. 06.01, 1989.

ASTM C 39-86, Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens, Section 4, Vol. 04.02, 1989.

ASTM C 192-88, Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory, Section 4, Vol. 04.02, 1989.

ASTM C 418-81, Standard Test Method for Abrasion Resistance of Concrete By Sandblasting, Section 4, Vol. 04.02, 1989.

ASTM C 672-84, Standard Test Method for Scaling Resistance of Concrete Surfaces Exposed To Deicing Chemicals, Section 4, Vol. 04.02, 1989.

ASTM C 702-87, Standard Practice for Reducing Field Samples of Aggregate To Testing Size, Section 4, Vol. 04.02, 1989.

ASTM C 876-87, Standard Test Method for Half-Cell Potentials of Uncoated Reinforcing Steel in Concrete, Section 4, Vol. 04.02, 1989.

ASTM C 944-80 (1985), Standard Test Method for Abrasion Resistance of Concrete or Mortar Surfaces by the Rotating-Cutter Method, Section 4, Vol. 04.02, 1989.

ASTM D 75-87, Standard Practice for Sampling Aggregates, Section 4, Vol. 04.02, 1989.

ANSI/ASTM D 345-80 (1986), Standard Methods of Sampling and Testing Calcium Chloride for Roads and Structural Applications, Section 4, Vol. 04.02, 1989.

ASTM D 412-87, Standard Test Methods for Rubber Properties in Tension, Section 8, Vol. 08.01, 1989.

ASTM D 445-86, Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (And the Calculation of Dynamic Viscosity), Section 5, Vol. 05.01, 1989.

ASTM D 638-87, Standard Test Method for Tensile Properties of Plastics, Section 8, Vol. 08.01, 1989.

ASTM D 1122-84, Standard Test Method for Specific Gravity of Engine Coolants by the Hydrometer, Section 15, Vol. 15.05, 1989.

ASTM D 1177-82, Standard Test Method for Freezing Point of Aqueous Engine Coolant Solution, Section 15, Vol. 15.05, 1989.

ASTM D 1186-87, Standard Test Methods for Nondestructive Measurement of Dry Film Thickness of Nonmagnetic Coatings Applied to a Ferrous Base, Section 6, Vol. 06.01, 1989.

ASTM D 1568-63, Standard Methods for Sampling and Chemical Analysis of Alkylbenzene Sulfonates, Section 15, Vol. 15.04, 1989.

ASTM D 1654-79 (1984), Standard Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments, Section 6, Vol. 06.01, 1989.

ASTM D 1895-69 (1979), Standard Test Methods for Apparent Density, Bulk Factor, and Pourability of Plastic Materials, Section 8, Vol. 08.02, 1989.

ASTM D 2013-86, Standard Method of Preparing Coal Samples for Analysis, Section 5, Vol. 05.05, 1989.

ANSI/ASTM D 2534-73, Standard Test Method for Coefficient of Kinetic Friction for Way Coatings, Section 5, Vol. 05.02, 1989.

ASTM D 3177-84, Standard Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke, Section 5, Vol. 05.05, 1989.

ASTM D 3178-84, Standard Test Methods for Carbon and Hydrogen in the Analysis Sample of Coal and Coke, Section 5, Vol. 05.05, 1989.

ASTM D 3179-84, Standard Test Methods for Nitrogen in the Analysis Sample of Coal and Coke, Section 5, Vol. 05.05, 1989.

ASTM D 3201-86, Standard Test Method for Hygroscopic Properties of Fire-Retardant Wood and Wood-Base Products, Section 4, Vol. 04.09, 1989.

ASTM D 4521-85, Standard Method of Test for Coefficient of Static Friction of Corrugated and Solid Fiberboard (Inclined Plane Method), Section 15, Vol. 15.09, 1989.

ASTM D 3665-82 (1987), Standard Practice for Random Sampling of Construction Materials, Section 4, Vol. 04.01, 1989.

ASTM D 3682-87, Standard Test Method for Major and Minor Elements in Coal and Coke Ash by Atomic Absorption, Section 5, Vol. 05.05, 1989.

ANSI/ASTM D 3683-78 (1983), Standard Test Method for Trace Elements in Coal and Coke Ash by Atomic Absorption, Section 5, Vol. 05.05, 1989.

ANSI/ASTM D 3684-78 (1988), Standard Test Method for Total Mercury in Coal by the Oxygen Bomb Combustion/Atomic Absorption Method, Section 5, Vol. 05.05, 1989.

ASTM D 4331-84, Test Method for Effectiveness of Dedusting Agents for Powdered Chemicals, Section 11, Vol. 11.03, 1985.

ASTM E 70-77 (1986), Standard Test Method for pH of Aqueous Solutions with the Glass Electrode, Section 15, Vol. 15.05, 1989.

ASTM E 104-85, Standard Practice of Maintaining Constant Relative Humidity by Means of Aqueous Solutions, Section 8, Vol. 08.03, 1989.

ASTM E 534-86, Standard Test Methods for Chemical Analysis of Sodium Chloride, Section 15, Vol. 15.05, 1989.

ASTM E 729-88a, Standard Practice for Conducting Acute Toxicity Tests with Fishes, Macroinvertebrates, and Amphibians, Section 11, Vol. 11.04, 1989.

ASTM E 943-88, Standard Definitions of Terms Relating to Biological Effects and Environmental Fate, Section 11, Vol. 11.04, 1989.

ASTM E 978-84, Standard Practice for Evaluating Environmental Fate Models of Chemicals, Section 11, Vol. 11.04, 1989.

ASTM E 1197-87, Standard Guide for Conducting a Terrestrial Soil-Core Microcosm Test, Section 11, Vol. 11.04, 1989.

ASTM F 502-83, Standard Test Method for Effects of Cleaning and Chemical Maintenance Materials on Painted Aircraft Surfaces, Section 15, Vol. 15.03, 1989.

ASTM G 1-88, Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens, Section 3, Vol. 03.02, 1989.

ASTM G 31-72, (1985), Standard Practice for Laboratory Immersion Corrosion Testing of Metals, Section 3, Vol. 03.02, 1989.

ASTM G 46-76, (1986), Standard Practice for Examination and Evaluation of Pitting Corrosion, Section 3, Vol. 03-02, 1989.