MONTANA STATE UNIVERSITY

The role of phase transformation as a softening mechanism in saline ice
by Ladean Robert McKittrick

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Engineering Applied Mechanics
Montana State University
© Copyright by Ladean Robert McKittrick (1997)

Abstract:
To gain insight into the behavior of saline ice relative to non-saline ice, single crystals of saline and non-saline ice were loaded in compression. Responses from these experiments indicate that single crystals of saline ice are significantly more compliant during the initial load response. Analyses presented in this dissertation indicate that phase transformations in brine cells have the potential to play a significant role in increasing the compliance of saline ice during the initial load response.

Cooling of a sealed brine cell, leading to the precipitation of ice, provides a mechanism for the accumulation of “large” localized stresses. Based on mathematical models, this mechanism has the potential to be a significant source for the nucleation or multiplication of dislocations, and can conceivably make a significant contribution to the greater compliance (softness) of saline ice relative to non-saline ice. These results are consistent with the observation that laboratory grown saline crystals sometimes display extensive differences in mechanical behavior that appears to be due to variations in the growth and storage conditions experienced by the crystals.

The brine cell model presented in this dissertation indicates that there is a transition in deformation modes for brine cell cooling rates on the order of 0.1 °C hr-1. At lower rates, local deformation is dislocation dominated; at higher rates, it is fracture dominated. Whether the pressure build-up in a cooling brine cell is relieved by inelastic deformation or cracking, the change in the internal structure is likely to play a role in the macroscopic behavior of saline ice. In particular, with the proper temperature history, the phase transformation mechanism can significantly increase the density of dislocations, and can therefore make a significant contribution to the macroscopic compliance of saline ice.

THE ROLE OF PHASE TRANSFORMATIONS
AS A SOFTENING MECHANISM IN SALINE ICE

by

Ladean Robert McKittrick

A thesis submitted in partial fulfillment
of the requirements for the degree

of

Doctor of Philosophy

in

Engineering

Applied Mechanics

MONTANA STATE UNIVERSITY-BOZEMAN
Bozeman, Montana

May 1997

D378
M2178

APPROVAL

of a thesis submitted by

Ladean Robert McKittrick

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

Robert Brown   Rh Brown   5/19/97
(Signature)   Date

Approved for the Department of Civil Engineering

Donald Raburn   Donald A. Raburn   5/15/97
(Signature)   Date

Approved for the College of Graduate Studies

Robert Brown   Rh Brown   5/19/97
(Signature)   Date

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a doctoral degree at Montana State University-Bozeman, I agree that the Library shall make it available to borrowers under rules of the Library. I further agree that copying of this thesis is allowable only for scholarly purposes, consistent with "fair use" as prescribed in the U.S. Copyright Law. Requests for extensive copying or reproduction of this thesis should be referred to University Microfilms International, 300 North Zeeb Road, Ann Arbor, Michigan 48106, to whom I have granted "the exclusive right to reproduce and distribute my dissertation for sale in and from microform or electronic format, along with the non-exclusive right to reproduce and distribute my abstract in any format in whole or in part."

Signature Ladean McKittrick

Date 15 MAY 97

TABLE OF CONTENTS

Page

LIST OF TABLES vii

LIST OF FIGURES viii

ABSTRACT ix

1. INTRODUCTION 1

Purpose 1
Overview 2

2. EXPERIMENTAL OBSERVATIONS 5

MSU Test Program 5
    Specimen Preparation 6
    Test Program 8
    Test Results 9
LTS Test Program 12
    Specimen Preparation 12
    Test Program 12
    Test Results 13
Non-saline ice responses 19
Thermal Variations 21

3. PHASE TRANSFORMATION MECHANISM 23

Ice crystallization from brine 23
    Phase changes 24
    Phase densities 25
Volumetric Strain (due to Phase Transformations) 26
    Notation 27
    Brine Transformation-Volume 28
    Differential Changes for the Total Transformation-Volume 29
    Strain Function 31
    Polynomial Approximations 32

    Discussion . . . 34
Elastic Model for Brine Pressure . . . 35
    Notation . . . 36
    Compatibility . . . 36
    Pressure Model . . . 38
    Example . . . 39
    Discussion . . . 40
Elastic Model for Stress Distributions . . . 40
    Example . . . 41
    Discussion . . . 42
Elastic-Anisotropic Finite Element Model . . . 43
    Set Up . . . 44
    Analysis . . . 46
    Discussion . . . 48
Inelastic Model . . . 49
    Rate Compatibility . . . 49
Strain-Displacement Rate Relations . . . 50
    Volumetric Compatibility . . . 51
Equivalent Plastic Strain Rate Model . . . 52
Flow Stress Distribution . . . 53
Differential Equation . . . 56
Volumetric Strain Rate due to Phase Transformations . . . 57
Solution Techniques . . . 59
    Finite Element Solution . . . 60
    Finite Difference Approximation . . . 60
    Flow Approximation . . . 61
    Example . . . 61
        Material Parameters . . . 61
        Transformation Strain . . . 62
        Inelastic Response . . . 63
    Discussion . . . 66
Application of the Inelastic Model . . . 68
    Criteria for Local Crack Formation . . . 68
    Relevance to Sea Ice . . . 70
    Gas Inclusions . . . 71
    Constitutive Assumptions . . . 72
Allowable Cooling Rates . . . 76
Thermal Variations . . . 77
    For Lab Specimens . . . 77
    For Sea Ice (*in situ*) . . . 79
    Diffusivity . . . 81
    Snow on the Surface . . . 83
    Surface Temperatures . . . 84

Application 85
    First Year Sea Ice 85
    Multi-year Sea Ice 89
Migration of Brine Cells 91
Range of Local Deformation 95

4. CONCLUSIONS AND FUTURE RESEARCH 96

Review of New Observations 96
Avenues for Future Research 98

REFERENCES CITED 102

LIST OF TABLES

Table Page

1 Polynomial parameters 34
2 Stress components at the interface 47

LIST OF FIGURES

Figure		Page
1	Stress response for constant strain rate ($\dot{\varepsilon} = 1 \times 10^{-6}$ s^{-1})	3
2	Geometry of experimental test specimens	9
3	Stress response comparison for saline and non-saline ice crystals.	10
4	Peak Stress Comparison	11
5	Variations due to basal plane orientation (45° and 66°).	14
6	Variations with the c-axis oriented at 60° and 90°.	15
7	Strain-rate dependence of the stress response for saline ice crystals.	17
8	Variations with between responses of saline and non-saline crystals.	18
9	Response variations in saline ice under equivalent load conditions.	18
10	Stress response for pre-strained non-saline ice specimens.	20
11	Phase Diagram for $H_2O$and NaCl	25
12	Conceptual (spherical) model for a brine transformations	27
13	Volumetric Transformation Strain (e_T^B)	33
14	Conceptual (spherical) model for a brine cell	36
15	Brine pressure as a function of Temperature.	39
16	Stress Profiles for the brine cell	42
17	Inner section of the finite element model of a spherical ice cell	44
18	Stress contours ($T = -8\,^{\circ}\mathrm{C}$)	47
19	Maxwell Visco-Elastic Model	57
20	Volumetric Strain Rates for Varied Temperature Rates	59
21	Temperature and corresponding volumetric-transformation strain	62
22	Interface responses for the spherical brine cell model	64
23	Equivalent Stress in the Ice at the Interface	66
24	Critical stress as a function of temperature and cooling rate.	77
25	Relative temperature variations in a cylindrical specimen.	79
26	Relative temperature variations through an ice sheet.	81
27	Thermally activated responses for a 50 cm sheet of sea ice.	87
28	Thermally activated responses for a 100 cm sheet of sea ice.	88
29	Thermally activated responses for a 350 cm sheet of sea ice.	90
30	Brine cell migration velocities in the model ice sheets	94

ABSTRACT

To gain insight into the behavior of saline ice relative to non-saline ice, single crystals of saline and non-saline ice were loaded in compression. Responses from these experiments indicate that single crystals of saline ice are significantly more compliant during the initial load response. Analyses presented in this dissertation indicate that phase transformations in brine cells have the potential to play a significant role in increasing the compliance of saline ice during the initial load response.

Cooling of a sealed brine cell, leading to the precipitation of ice, provides a mechanism for the accumulation of "large" localized stresses. Based on mathematical models, this mechanism has the potential to be a significant source for the nucleation or multiplication of dislocations, and can conceivably make a significant contribution to the greater compliance (softness) of saline ice relative to non-saline ice. These results are consistent with the observation that laboratory grown saline crystals sometimes display extensive differences in mechanical behavior that appears to be due to variations in the growth and storage conditions experienced by the crystals.

The brine cell model presented in this dissertation indicates that there is a transition in deformation modes for brine cell cooling rates on the order of 0.1 °C hr^{-1}. At lower rates, local deformation is dislocation dominated; at higher rates, it is fracture dominated. Whether the pressure build-up in a cooling brine cell is relieved by inelastic deformation or cracking, the change in the internal structure is likely to play a role in the macroscopic behavior of saline ice. In particular, with the proper temperature history, the phase transformation mechanism can significantly increase the density of dislocations, and can therefore make a significant contribution to the macroscopic compliance of saline ice.

CHAPTER 1

INTRODUCTION

On the subject of sea ice, there are two classes of problems that are of primary concern to the engineering community. The first class of problems concerns the maximum force that ice can exert on structures. These interaction forces can occur between a moving ice sheet and a stationary structure (e.g., oil drilling platforms) or between a stationary ice sheet and a moving structure (e.g., ice breakers). The second class of problems concerns the safe bearing capacity of ice covers under static or moving loads (e.g., airplanes).

This dissertation presents a set of observed variations in the initial load response of saline ice and a possible explanation for these observed variations. The analyses and observations presented provide evidence that phase transformation mechanisms can significantly increase the initial compliance of saline (NaCl) ice. The relevance of the proposed phase transformation mechanism is then extended, in an approximate sense, to sea ice. An understanding of these initial load response variations is necessary if the ice-structure interaction forces are to be modeled in a knowledgeable fashion.

Purpose

The intent of this dissertation is to present, in some detail, the role that phase transformations might play in the observed variations in the initial compliance of saline ice. Phase transformations are also considered as the mechanism that leads to distinct and somewhat unexpected differences between the initial load responses of saline and non-saline ice crystals. The potential role that phase transformations might play in the structural response is also extended to sea ice.

Overview

Relative to ordinary ice, sea ice has a highly complex internal structure. A large part of this complexity is due to the way that sea ice accommodates brine as a liquid phase. Because of this added complexity, sea ice is poorly understood relative to ordinary ice. To study sea ice, because NaCl is the primary component of salt in sea brine, it is reasonable to first study ice grown from a solution of NaCl brine and then extend that experience base to sea ice.

To gain insight into the differences between saline (NaCl) ice and non-saline ice crystals, quasi-single crystals[1] of saline and non-saline ice were grown from non-saline seed crystals (Kawamura 1986). When these quasi-single crystals were loaded in compression under a constant strain rate, the non-saline crystals displayed a distinct peak stress and then "softened" or displayed decreasing resistance to deformation until eventually approaching a "steady state" stress. To the contrary, the saline crystals often, but not always, lacked the peak stress response displayed by the non-saline crystals. An example of these differences is displayed in Figure 1.

Saline ice crystals typically are conceptualized as a bridged matrix of non-saline ice platelets with a regularly spaced system of brine cavities and possibly air bubbles interspersed throughout. With this conceptual model, one would expect saline ice to display a response similar to that of non-saline ice, though with somewhat lower

---

[1] A *single crystal* may be defined as a specimen that grows solely from one nucleus, so that no part of the specimen is greater than 5 degrees from the mean crystallographic orientation (Winegard 1964, Ch. XII). Using the method developed by Kawamura (1986), a quasi-single is grown from as many as four sintered nuclei or plates with the same orientation. Though we would expect the resulting specimen to behave structurally as a single crystal, it does not meet the definition of a single crystal; therefore, specimens grown by this technique are referred to as *quasi-single crystals*.

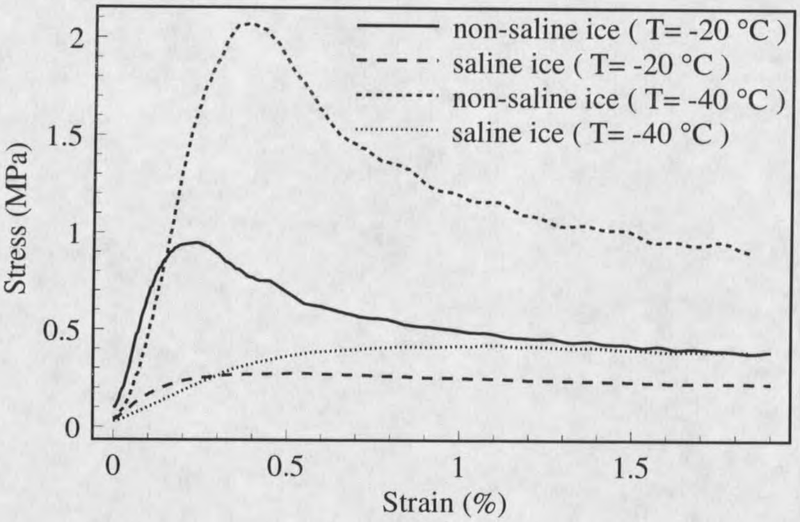


Figure 1. Stress response for constant strain rate ($\dot{\varepsilon} = 1 \times 10^{-6}$ s^{-1})

macroscopic stresses; indeed there are such cases. For an example of such an analogous behavior between saline and non-saline ice, consider the experimental results of Brown & Kawamura (1991).

Typical models for the strength of sea ice (Anderson 1958, Assur 1958, Weeks & Assur 1967, Michel 1978, Weeks & Ackley 1982) connect the reduction in strength of sea ice relative to non-saline ice using a function of brine content with models of the form

$$\sigma^S = c\sigma^N(1 - f(\psi)), \tag{1.2}$$

where σ^S and σ^N are the strength of saline ice and non-saline ice, respectively. ψ is a measure of brine content or porosity of the sea ice and c is a reduction coefficient and is commonly used to include stress concentration factors or other structural characteristics. These models, which use porosity (geometric reduction) to explain the reduced strength of saline ice, indicate that the responses of saline ice and non-saline ice should differ only by a scale factor. As a consequence, these models do not explain the absence of a peaked stress response in saline crystals when such a response is lacking; however, as displayed in Figure 1, it is clear that there are cases where saline ice does not display the peaked stress response or large yield drops that the non-saline ice does such that the initial response differs by more than a porosity scale factor. In this dissertation, the transformation of encapsulated brine to ice will be considered as a means for the alteration of the internal structure of ice such that saline crystals will not display the peaked stress response when subjected to mechanical loads. Saline crystals that have been altered in such a manner are likely to provide much less resistance to deformation and will in essence be much more compliant. As a result, initial forces resulting from structure-ice interactions will be reduced significantly and the increasingly compliant ice will tend to support loads more readily without fracturing in a brittle fashion.

In Chapter 2, a set of experimental observations will be presented concerning the differences between the structural responses of saline and non-saline ice crystals. These observations include variations in the initial responses of saline crystals. Chapter 3 is used to present an analysis of phase transformations as a source of these observed variations. Chapter 4 is used to present a corresponding set of conclusions and a set of related studies that would be helpful in further understanding the mechanisms involved in the structural response of saline ice.

CHAPTER 2

EXPERIMENTAL OBSERVATIONS

This chapter details a set of experimental observations that point to the role that phase transformations may play in the initial compliance of saline ice. Other than these observations, there is very little literature that addresses this issue.

This chapter first presents the results of two experimental programs. One was conducted here at Montana State University (MSU) and the other at the Institute of Low Temperature Science (LTS) in Japan. These programs were conducted to gain insight into the behavior of single crystals of ice. Saline and non-saline ice crystal specimens were loaded with similar restraints so that differences in the structural responses could be observed. The specimens, taken from large quasi-single crystals of both ordinary and saline (NaCl) ice, were tested in compression under constant displacement (strain) rates. The specimens were tested over a range of strain-rates, temperatures, and with varied crystallographic orientations.

The test program initiated here at Montana State University encountered technical difficulties and has not yet been completed; however, the data that was gathered will be reviewed. Similar, tests were run at the Institute of Low Temperature Science by Brown & Kawamura (1991). To provide a more complete overview, a subset of these LTS results will also be reviewed.

MSU Test Program

This section presents a review of the partially completed MSU test program for the structural behavior of saline and non-saline crystals of ice.

Specimen Preparation

To test monocrystal specimens of ice, it is necessary to first grow large crystals from which the specimens can be formed. To grow single crystals of ice in relatively large quantities, it is convenient to first grow a large single crystal of ordinary ice that can be sliced into sections that will serve as a seed for an array of saline and non-saline single crystals of ice. These seed crystals are usually obtained by freezing still water in a large insulated tank. Care must be taken to minimize the number of sites for ice crystal nucleation. To minimize the number of foreign particles that could serve as nuclei, degassed (boiled) and filtered distilled water is used. The water is cooled in a completely filled airtight container to a temperature between 2 and 3 °C. The cooled water is then poured into an insulated tank, that has been prewarmed to prevent ice from nucleating on the sides, and allowed to continue cooling in a quiescent state until an initial ice skim has formed. After an initial skim is established, the size of the crystals forming the skim is evaluated. If there are no crystals of sufficient size the process is repeated.

Once a large single crystal is established, the crystal is allowed to grow until bubbles begin to nucleate below the surface of the ice. This typically occurs after the ice has grown to a thickness of approximately ten centimeters. The orientation of the crystal is then evaluated using an etching technique (Higuchi & Muguruma 1958, Higuchi 1958). Crystals that display a vertical c-axis[2] are suitable as seed crystals, others are discarded. Because ice crystals with a horizontal c-axis have a marked tendency to dominate during growth, particularly in sea ice, it is preferable to construct a seed crystal with horizontal c-axis. Following the technique of Kawamura

---

[2] Ordinary ice has a hexagonal crystalline structure. Based on this crystalline structure, a *c-axis* (also known as the optic axis) is defined parallel to the axis of hexagonal lattice-symmetry. A *basal plane* is then defined as a plane that is perpendicular to the c-axis. Three a-axes (a_1, a_2, a_3) are then defined in the basal plane such that each axis is separated by 120° and is parallel a sector boundary of the hexagon corresponding to the crystalline structure (Hobbs 1974).

(1986), the original crystal is sliced into thin planar sections (~1 cm thick) perpendicular to one of the a-axes. These plates are then rotated 90° so that the c-axes of each plate are aligned. The aligned plates are then sintered back together to form a plate approximately 25 cm square. The resulting quasi-single crystals are then used as "seeds" to grow both saline and non-saline quasi-single ice crystals. Due to the orientation of the seed crystal, the corresponding quasi-single crystals grows with a horizontal c-axis and a vertical a-axis.

To clarify the use of the term quasi-single crystal, it is worthwhile to consider the definition of a single crystal. A *single crystal* may be defined as a specimen that grows solely from one nucleus, so that no part of the specimen is greater than 5 degrees from the mean orientation (Winegard, 1964, Ch.XII). Using Kawamura's (1986) method, when the rotated plates from the original crystal are sintered together, often there is a fine line of small, randomly oriented crystals that develop at the interface between plates. These lines will sometimes extend into a specimen grown from the seed. If carefully applied, this approach yields specimens with crystal orientations within 3 degrees of the mean, except for small ($<$ 1 mm) crystals on the interface planes. The specimens are often seeded from as many as four or five nuclei (plates). Though the resulting specimen would be expected to behave structurally as a single crystal, it does not meet the definition of a single crystal; therefore, specimens grown by this technique are referred to as *quasi-single crystals*.

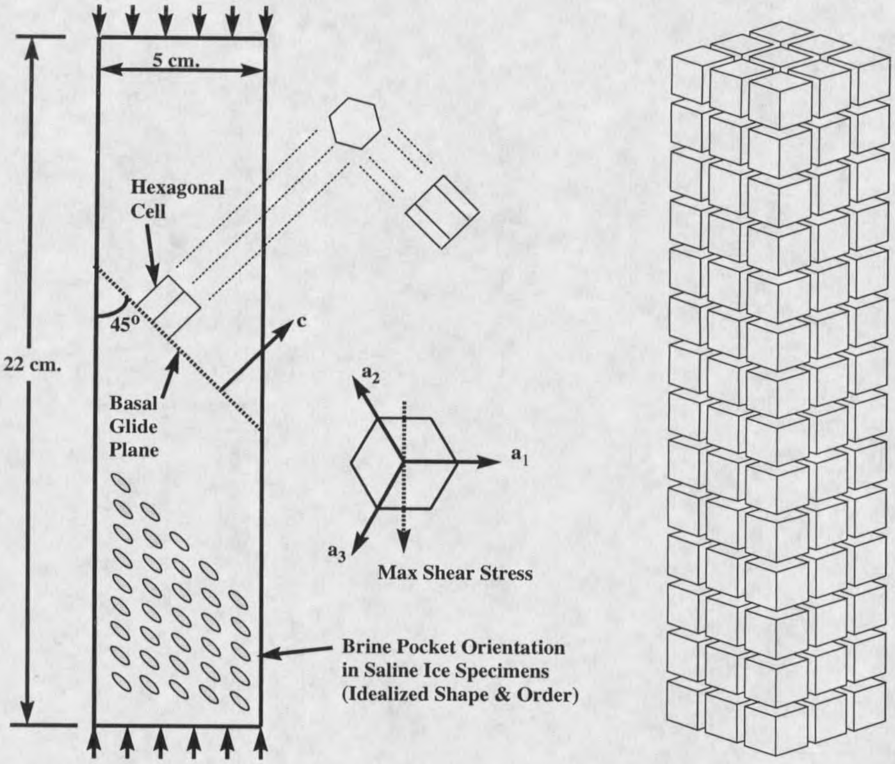
After using the previous method to establish an array of seed crystals, large quasi-single non-saline ice crystals were grown from distilled and degassed water. As a result, the test specimens had a very low bubble content and most were completely bubble free.

From the same array of seed crystals, large quasi-single crystals of saline ice were grown from a brine solution of distilled water and table salt (NaCl) that had a salinity of 0.0035 at a slow and reasonably controlled rate of approximately 1 cm per day. The slow rate was maintained to minimize the nucleation of bubbles. Once the crystals grew to a depth exceeding 20 cm, they were removed from the growth tank and the saline crystals were allowed to drain for more than a week. The saline crystals were drained for an extended period of time so that they would have approximately the same "drained" brine content at the time of testing. After draining, the crystals were cut into sheets perpendicular to the growth direction. Thin sheets, approximately 1 cm thick were taken from the top, middle, and bottom of the crystal. These thin sheets were used to evaluate crystal quality throughout the presumed quasi-single crystal, using cross polarized light to determine the existence of large spurious inclusions. The remaining thicker sheets were cut into specimens 5 centimeters square and 22 centimeters long where the c-axis was oriented at 45 degrees relative to the long axis of the specimen (see Figure 2). Spurious inclusions were avoided if at all possible, though small (~1 cm diameter) inclusions remained in the end sections of a small subset of the specimens.

After the lab specimens were trimmed to the prescribed dimensions (5 cm × 5 cm × 22 cm ± 2 mm), the ends were squared and flattened to provide an accurate match with the load platens. However, some of the specimens still demonstrated initial load responses indicative of an imperfect match.

Test Program

As displayed in Figure 2, all specimens tested at Montana State University were oriented with the c-axis at a 45° angle to the long axis of the specimen with an a-axis exiting one of the lateral surfaces at a 90° angle. All specimens were compressed under a constant displacement rate that correlated with a constant strain rate of 10^{-6} s^{-1}. During each test, the temperature was held constant ($\pm 0.5\,^{\circ}C$). Test temperatures


5 cm.
Hexagonal
Cell
45°
c
22 cm.
Basal
Glide
Plane
a_2
a_1
a_3
Max Shear Stress
Brine Pocket Orientation
in Saline Ice Specimens
(Idealized Shape & Order)

(a) Sketch of Experimental Specimen (b) Specimen Geometry

Figure 2. Geometry of experimental test specimens

were varied from −10 to −45 °C.

Test Results

The saline ice crystals had bulk salinities that were grouped around 0.006, though they ranged from 0.0045 to 0.0075; two specimens had salinities outside this range. The densities for the saline and non-saline specimens were closely grouped around 913 and 916 kg m^{-3}, respectively, as measured at a temperature of −10 °C. The range of salinities and densities presumably reflect variations in specimens taken from different vertical ranges of the original crystals. Overall, approximately 40 quasi-single crystal specimens were tested. Typically, two non-saline and three saline specimens were tested at each temperature.