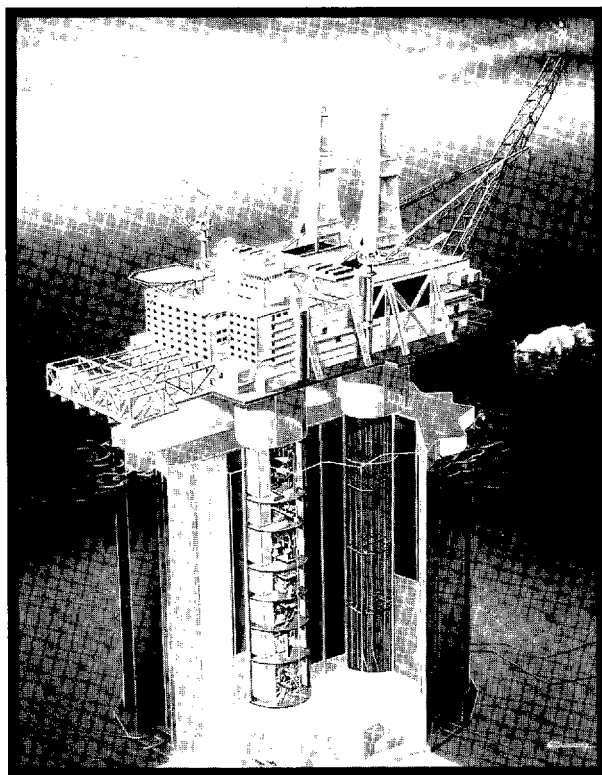


Durability of Concrete

Third International Conference

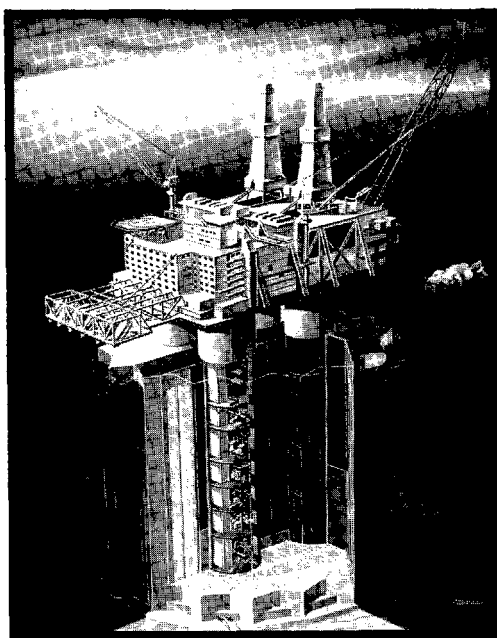
Nice, France 1994



V.M. Malhotra
Editor

Durability of Concrete

Third International Conference
Nice, France 1994



V.M. Malhotra
Editor

aci
SP-145

Cover Sketch — Hibernia Offshore Drilling Platform
Courtesy of Hibernia Management and Development Company Ltd.

DISCUSSION of individual papers in this symposium may be submitted in accordance with general requirements of the ACI Publication Policy to ACI headquarters at the address given below. Closing date for submission of discussion is January 1, 1995. All discussion approved by the Technical Activities Committee along with closing remarks by the authors will be published in the July/August 1995 issue of either ACI Structural Journal or ACI Materials Journal depending on the subject emphasis of the individual paper.

The Institute is not responsible for the statements or opinions expressed in its publications. Institute publications are not able to, nor intended to, supplant individual training, responsibility, or judgment of the user, or the supplier, of the information presented.

The papers in this volume have been reviewed under Institute publication procedures by individuals expert in the subject areas of the papers.

Copyright © 1994
AMERICAN CONCRETE INSTITUTE
P.O. Box 19150, Redford Station
Detroit, Michigan 48219

All rights reserved including rights of reproduction and use in any form or by any means, including the making of copies by any photo process, or by any electronic or mechanical device, printed or written or oral, or recording for sound or visual reproduction or for use in any knowledge or retrieval system or device, unless permission in writing is obtained from the copyright proprietors.

Printed in the United States of America

Editorial production Victoria Wieczorek

Library of Congress catalog card number 94-70306

PREFACE

The Canada Centre for Mineral and Energy Technology (CANMET) of Natural Resources Canada, Ottawa, has played a significant role in Canada for over 30 years in the area of durability of concrete. In August 1991, CANMET, in association with the American Concrete Institute, and the Institute for Research in Construction/National Research Council, Ottawa, sponsored the Second CANMET/ACI International Conference on Durability of Concrete. This conference was held August 4-9, 1991, in Montreal, Canada, and was a follow-up of the Katharine and Bryant Mather International Conference on Concrete Durability held in Atlanta, Georgia, April 27-May 1, 1987. Unlike the first conference, this second conference was not named after any individual or individuals, and the future conferences in this series would follow this precedent.

In 1994, CANMET, in association with the American Concrete Institute and several other organizations in Canada and France, sponsored the Third International Conference on the subject. The conference was held May 22-28, 1994, in Nice, France. More than 90 papers from 25 countries were received and peer reviewed in accordance with the policies of the American Concrete Institute; 65 were accepted for publication. To all those whose submission could not be included in the symposium volume, the Institute and the Conference Organizing Committee extend their appreciation for their efforts and interest. The accepted papers deal with the deicer salt scaling of concrete, freezing and thawing phenomenon, performance of concrete in marine environments, corrosion of steel to chloride-ion attack, alkali-aggregate reactivity, coatings for concretes, carbonation, high-volume fly ash concrete and papers in the general area of durability of concrete.

In addition to the papers which have been published in this volume, more than 40 other papers were presented at the conference. A number of these were published as "supplementary papers," and the authors of these papers are encouraged to publish these in technical journals of their choice.

Thanks are extended to twenty-one members of the review panel which met in Lyon, France, in May 1993, to review the papers. Several other ACI and non-ACI members also assisted in the review process, and their help is gratefully acknowledged. Without the dedicated efforts of the reviewers it would not have been possible to have the proceedings ready for distribution at the conference. The cooperation of the authors in accepting reviewers' suggestions, and in revising their manuscripts accordingly is greatly appreciated. The authors are also to be commended for their prompt return of the revised manuscripts.

The help and assistance of A. Bilodeau (Chairman), and B. Fournier, and R. Chevrier (members) of the slide review panel are gratefully acknowledged. Thanks are also extended to Harry S. Wilson, Maria Venturino, and Gordon D. Brearley for their help in the processing of the manuscripts, both for the ACI proceedings and the supplementary volume.

As an integral part of the conference, a special symposium to honor Dr. P.K. Mehta, Professor Emeritus, Department of Civil Engineering, University of California, Berkeley, CA, was held during the conference. The papers presented at this symposium have been published in a separate volume.

V.M. Malhotra, P. Eng.

Editor

Chairman, CANMET/ACI Third International Conference
on Durability of Concrete

May 1994

Organizing Committee
Third CANMET/ACI International Conference
on
Durability of Concrete
Nice, France
1994

V.M. Malhotra
Chairman

H.S. Wilson
Secretary-Treasurer

Members
T.W. Bremner
G.G. Carette (deceased)
H.L. Isabelle
V.S. Ramachandran

DEDICATION

The Organizing Committee of the Third CANMET/ACI International Conference dedicates this book to the memory of ACI member Georges Carette, P.Eng., Senior Materials Engineer, CANMET, who passed away on August 14, 1993 after a long illness. Georges, after graduating from Laval University, joined CANMET, formerly the Mines Branch, in 1968 as a Concrete Engineer. He rose through the ranks to become a key member of the Concrete Technology Group, and was internationally recognized for his work on fly ash and silica fume.

At the time of his death, he was project manager and project leader of several projects on fly ash and silica fume, and was in charge of monitoring the CANMET specimens at Treat Island Exposure Site in Maine, U.S.A. He was very active on the Canadian Standards Association's Committee on Cement, and in 1992 was elected its chairman. For more than fifteen years, Georges was a key member of the Committee for the Organizing of International Conferences on Concrete Technology, and at the time of his death, he was chairman of the Slide Review Committee for the Third CANMET/ACI International Conference on Durability of Concrete.

Georges, a keen golfer, will be missed by his many friends and colleagues. He is survived by his wife Lise De Moors, and his daughter Anick.



CONTENTS — PART I

Deicer Salt Scaling of Concrete, Freezing and Thawing Phenomenon, Performance of Concrete in Marine Environments, Corrosion of Steel to Chloride-Ion Attack, Other Topics

PREFACE	iii
THE DEICER SALT SCALING DETERIORATION OF CONCRETE—AN OVERVIEW by J. Marchand, E.J. Sellevold, and M. Pigeon	1
SCALING RESISTANCE OF GROUND GRANULATED BLAST FURNACE (GGBF) SLAG CONCRETES by M.D. Luther, W.J. Mikols, A.J. DeMaio, and J.E. Whitlinger	47
INVESTIGATION OF ALTERNATE CONCRETE DEICERS by P.P. Hudec, C. MacInnis, and S.P. McCann	65
W/CM CODE REQUIREMENTS INAPPROPRIATE FOR RESISTANCE TO DEICER SALT SCALING by C.D. Johnston	85
DURABILITY OF CONCRETE STRUCTURES EXPOSED TO CaCl_2 BASED DEICING SALTS by M. Collepardi, L. Coppola, and C. Pistolesi	107
CHLORIDE PERMEABILITY OF HIGH STRENGTH CONCRETE PLATFORMS IN THE NORTH SEA by M. Sandvik, A.K. Haug, and O. Erlien	121
INFLUENCE OF THE CURING METHOD ON THE DURABILITY OF HIGH PERFORMANCE CONCRETES by L. Hasni, J.L. Gallias, and M. Salomon	131
HIGH TEMPERATURE EFFECT ON HIGH PERFORMANCE CONCRETE (70-600 C) STRENGTH AND POROSITY by A.N. Noumowe, P. Clastres, G. Debicki, and M. Bolvin	157
LONG-TERM DURABILITY OF SPECIAL HIGH STRENGTH CONCRETES by P. Nepper-Christensen, B.W. Kristensen, and T.H. Rasmussen	173
DURABILITY PROPERTIES OF HIGH STRENGTH CONCRETE CONTAINING SILICA FUME AND LIGNITE FLY ASH by K.W. Nasser and S. Ghosh	191

CORROSION BEHAVIOURS OF STEEL EMBEDDED IN FLY ASH BLENDED CEMENTS by H.T. Cao, L. Bucea, B. Wortley, and V. Sirivivatnanon	215
THE INFLUENCE OF FLY ASH ON THE RESISTIVITY AND RATE OF CORROSION OF REINFORCED CONCRETE by J.G. Cabrera and P. Ghoddoussi	229
COMPARATIVE EVALUATION OF CORROSION-INHIBITING CHEMICAL ADMIXTURES FOR REINFORCED CONCRETE by C.K. Nmai and P.D. Krauss	245
MINIMIZING CORROSION OF STEEL REINFORCEMENT—IMPLEMENTATION OF RESEARCH INTO PRACTICE by S. Guirguis, H.T. Cao, and D. Baweja	263
DESIGN FOR AVOIDING DAMAGE DUE TO CARBONATION-INDUCED CORROSION by L.J. Parrott	283
USE OF LABORATORY TECHNIQUES TO EVALUATE LONG-TERM DURABILITY OF STEEL REINFORCED CONCRETE EXPOSED TO CHLORIDE INGRESS by N.S. Berke, M.C. Hicks, R.J. Hoopes, and P.G. Tourney	299
LONG-TERM PERFORMANCE OF PORTLAND AND BLENDED CEMENT CONCRETES UNDER MARINE CONDITIONS by H. Roper, V. Sirivivatnanon, and D. Baweja	331
TEN YEAR EXPOSURE TEST OF PRECRACKED REINFORCED CONCRETE IN A MARINE ENVIRONMENT by K. Sakai and S. Sasaki	353
MARINE CONCRETE DURABILITY—CONDITION SURVEY OF CERTAIN TENSILE CRACK EXPOSURE BEAMS AT TREAT ISLAND, MAINE, USA by S.K. Lee, D.V. Reddy, W.H. Hartt, M. Arockiasamy, and E.F. O'Neil	371
SWELLING OF CONCRETE IN DEEP SEAWATER by J. Bijen and G. van der Wegen	389
DURABILITY OF HIGH ALUMINA CEMENT MORTARS FOR THE MARINE ENVIRONMENT by N.C. Baker and P.F.G. Banfill	409
LONG TERM STUDY OF THE INFLUENCE OF THE MINERALOGICAL COMPOSITION OF CEMENTS ON RESISTANCE TO SEAWATER: TESTS IN ARTIFICIAL SEAWATER AND IN THE CHANNEL by A.M. Paillère, M. Raverdy, and J.J. Serrano	423

DURABILITY OF REPAIRED REINFORCED CONCRETE IN MARINE ENVIRONMENT by T. Uomoto, H. Ohga, T. Yonezawa, and H. Ibe	445
THE EFFECT OF NON-LINEAR CHLORIDE BINDING ON THE PREDICTION OF CHLORIDE PENETRATION INTO CONCRETE STRUCTURES by L.O. Nilsson, M. Massat, and L. Tang	469
APPLICATION OF RAPID CHLORIDE PERMEABILITY TEST TO QUALITY CONTROL OF CONCRETE by S. Misra, A. Yamamoto, T. Tsutsumi, and K. Motohashi	487
RESISTANCE TO PENETRATION OF CHLORIDES INTO CONCRETES CONTAINING LATEX, FLY ASH, SLAG, AND SILICA FUME by C. Ozyildirim	503
SIMULATION OF CHLORIDE PENETRATION INTO HARDENED CONCRETE by T. Maruya, S. Tangtermsirikul, and Y. Matsuoka	519
PERFORMANCE OF PLAIN AND BLENDED CEMENTS IN HIGH CHLORIDE ENVIRONMENTS by O.S.B. Al-Amoudi, Rasheeduzzafar, M. Maslehuddin, and S.N. Abduljawad	539
A FIELD STUDY OF THE PENETRATION OF CHLORIDES AND OTHER IONS INTO A HIGH QUALITY CONCRETE MARINE BRIDGE COLUMN by P. Sandberg and L. Tang	557
DURABILITY OF LOADED REINFORCED CONCRETE IN CHLORIDE ENVIRONMENT by R. Francois and G. Arligue	573
EFFECT OF AN ELECTRICAL FIELD ON THE REMOVAL OF CHLORIDE IONS FROM CONCRETE SLABS by L. Tang, L. Berntsson, J. Aavik, and L.O. Nilsson	597
FREEZING AND THAWING DURABILITY OF CONCRETE BLOCK PAVERS by N. Ghafoori and R.P. Mathis	609
FREEZING AND THAWING DURABILITY OF AIR-ENTRAINED WET- AND DRY-MIX SHOTCRETE INCORPORATING SILICA FUME by B. Durand, J. Mirza, and P. Nguyen	623
A STUDY OF FROST RESISTANCE OF CONCRETE USING AN ORGANIC SHRINKAGE-REDUCING AGENT by H. Fujiwara, R. Tomita, and Y. Shimoyama	643

CONTENTS — PART II

Alkali-Aggregate Reactivity, Coatings for Concretes, Carbonation,
High-Volume Fly Ash Concrete, Durability of Concrete

ALKALI-AGGREGATE REACTIVITY (AAR) POTENTIAL OF SELECTED CANADIAN AGGREGATES FOR USE IN OFFSHORE CONCRETE STRUCTURES by B. Fournier, V.M. Malhotra, W.S. Langley, and G.C. Hoff	657
AN ACCELERATED METHOD FOR THE EVALUATION OF ASR RISKS IN ACTUAL CONCRETE COMPOSITIONS by A. Criaud, C. Defossé, and V. Andrei	687
INFLUENCE OF MICROCRACKING ON THE ONSET AND DEVELOPMENT OF THE ALKALI SILICA REACTION by J.S. Guédon and A. Le Roux	713
RESULTS OF A ROUND ROBIN TEST PROGRAM FOR THE VALIDATION OF THE TEST METHODS IN THE FRENCH RECOMMENDATIONS FOR THE PREVENTION OF AAR DAMAGE TO CONCRETE by A. Corneille and B. Bolotte	725
DISTRIBUTION AND SIGNIFICANCE OF ALKALI-AGGREGATE REACTION IN SOUTHERN NORWAY by V. Jensen	741
AN ANALYTICAL STUDY CONCERNING PREDICTION OF CONCRETE EXPANSION DUE TO ALKALI-SILICA REACTION by Y. Furusawa, H. Ohga, and T. Uomoto	757
TEST METHODS FOR ALKALI-AGGREGATE REACTIONS IN NORWEGIAN AGGREGATES: PETROGRAPHIC EXAMINATION AND THE SOUTH AFRICAN NBRI MORTAR-BAR TEST by B.J. Wigum and J. Lindgård	781
INSPECTION AND REPAIR OF A CONCRETE WHARF by M. Maage, S. Helland, J.E. Carlsen, and M. Rønne	797
DURABILITY OF CONCRETE FOR EARLY OPENING OF REPAIRED HIGHWAYS— FIELD EVALUATION by M. Nagi, D. Janssen, and D. Whiting	811

DURABILITY EVALUATION OF REPAIR MATERIALS IN HOT-ARID ENVIRONMENTS by I.A. Basunbul, H.A. Dehwah, and M. Maslehuddin	835
IN-SITU EVALUATION OF A FLEXIBLE SURFACE COATING FOR CONCRETE TO PREVENT CHLORIDE PENETRATION AND STEEL CORROSION by T. Oshiro, R.N. Swamy, and S. Tanikawa	851
THE AGING BEHAVIOUR OF ZINC SPRAY COATING APPLIED FOR CATHODIC PROTECTION OF REINFORCED CONCRETE by P. Delpire, G. Grimaldi, and A. Raharinaivo	871
THE INFLUENCE OF EARLY CURING ON THE SURFACE PERMEABILITY AND ABSORPTION OF SILICA FUME CONCRETE by S.A. Austin, P.J. Robins, and A.S.S. Al-Eesa	883
STUDY OF CONCRETE CONTAINING SILICA FUME AND ACTIVATED AMORPHOUS SILICA by H. Tanaka	901
THE RATE OF CARBONATION IN CONCRETE MADE WITH BLENDED CEMENT by K. Horiguchi, T. Chosokabe, T. Ikabata, and Y. Suzuki	917
MECHANISMS OF CONCRETE DETERIORATION BY SODIUM SULFATE CRYSTALLIZATION by K.J. Folliard and P. Sandberg	933
UNDERWATER FATIGUE PERFORMANCE OF STRUCTURAL LIGHTWEIGHT CONCRETE by V. Ramakrishnan, T.W. Bremner, and V.M. Malhotra	947
MECHANICAL AND DURABILITY PROPERTIES OF HIGH VOLUME FLY ASH CONCRETE by V. Sirivivatnanon, H.T. Cao, and P. Nelson	967
DURABILITY OF CONCRETE USING AIR-CLASSIFIED FLY ASH by M. Ishii, K. Ukita, and K. Kohno	985
DAMAGE DUE TO HYDRATION IN ROLLER COMPACTED CONCRETE: THE CASE OF THE RIOU DAM by J.P. Bournazel and E. Bourdarot	1003
AN EXPERIMENTAL DEVICE TO STUDY CRACKING AND DETERIORATION OF CONCRETE by D. Breyse, B. Gérard, and M. Lasne	1013
SURVEY OF WATER TOWERS, RESERVOIRS, TANKS, AND BASINS: THEIR CONDITIONS AND THE WATERTIGHTNESS OF THE WATERPROOFING by G. Mathieu and J. Sari	1033
THE INFLUENCE OF HEAT TREATMENT ON THE DURABILITY OF CONCRETE by M.S. Akman and H. Gülseren	1051

DURABILITY STUDIES OF CONCRETE CONTAINING LOW CEMENT CONTENT AND FINE PARTICLES OF FOUNDRY SLAG by S.I. Pavlenko and V.S. Bogusevich	1069
DETERIORATION OF CONCRETE DERIVED FROM METABOLITES OF MICROORGANISMS by E.I. Tazawa, T. Morinaga, and K. Kawai	1087
ABRASION RESISTANCE OF HIGH STRENGTH CONCRETE WITH CHEMICAL AND MINERAL ADMIXTURES by I.R. de Almeida	1099
LABORATORY STUDIES AND EVALUATIONS OF CONCRETE CONTAINING DEAD-BURNED DOLOMITE by J.M. Scanlon and J.D. Connolly	1115
CONCRETE DURABILITY SPECIFICATION BY WATER/CEMENT OR COMPRESSIVE STRENGTH FOR EUROPEAN CEMENT TYPES by A.P. Barker and J.D. Matthews	1135
ASSESSMENT OF THE EFFECTIVENESS OF CURING ON THE DURABILITY OF REINFORCED CONCRETE by B.K. Marsh and M.A. Ali	1161
PREDICTING CONCRETE DURABILITY FROM ITS ABSORPTION by R.K. Dhir, M.R. Jones, E.A. Byars, and I.G. Shaaban	1177
DURABILITY OF LOCAL REPAIR MEASURES ON CONCRETE STRUCTURES DAMAGED BY REINFORCEMENT CORROSION by P. Schießl, W. Breit, and M. Raupach	1195
SI (Metric) TABLES	1217
INDEX	1219

SP 145-1

The Deicer Salt Scaling Deterioration of Concrete—An Overview

by J. Marchand, E.J. Sellevold, and M. Pigeon

Synopsis: An overview of the scientific and technical literature published on the subject is presented in this paper. The first part of this report is devoted to the fundamentals of frost action in concrete. The mechanisms of freezing and hypotheses explaining the detrimental effects of deicing salts are discussed. Special attention is paid to the influence of the concrete curing temperature and moisture history on its frost durability. A critical appraisal of three different test procedures designed to assess the deicer salt scaling resistance of concrete is given in the second section. Each test method is evaluated on the basis of reproducibility, variability of test results, operating cost and relationship to field exposure conditions. Finally, the influence of various parameters on the deicer salt scaling resistance of concrete is discussed in the second section. Topics such as mixture composition, air entrainment, casting operations, curing and the use of concrete sealers are reviewed.

Keywords: Chlorides; concretes; curing; deicers; deterioration; freeze thaw durability; popouts; porosity; salts; scaling; tests

2 Marchand, Sellevold, and Pigeon

Jacques Marchand is Assistant-Professor of Civil Engineering at Laval University, Québec City, Canada. He received his doctorate degree from the École Nationale des Ponts et Chaussées in Paris. His research interests are in the areas of durability of concrete and performance of dry concretes.

Erik J. Sellevold is Professor of Concrete Technology at the Division of Concrete Structure of the Norwegian Institute of Technology, Trondheim, Norway. Dr. Sellevold has worked in concrete materials research at Universities, Industry and Research Institutes for more than 25 years. His field of activity includes pore structure-property relationships, condensed silica fume, frost resistance and general durability properties.

ACI fellow **Michel Pigeon** is Professor of Civil Engineering at Laval University, Québec City, Canada. He is a member of ACI Committee 201 on concrete durability and of RILEM Committees TC 115 on high-strength concrete and TC 117 on frost resistance. He received the Wason medal in 1992. He is the author of numerous research papers on various aspects of concrete technology. He was president of the Québec and Eastern Ontario Chapter of ACI in 1986-1987.

INTRODUCTION

In North America and northern Europe, the chloride-induced deterioration of concrete structures has been a matter of major concern for many years. It is well known that the widespread use of deicing salts during winter roadway maintenance operations is one of the major causes of the rapid degradation of concrete roads and bridges [1, 2]. Concrete surfaces subjected to repeated freezing and thawing in presence of deicing salts often suffer from severe scaling. In addition to reducing the serviceability of the structure, surface scaling is known to favour the ingress of deleterious chemicals into the interior of the concrete which consequently increases the risk of deterioration by other phenomena such as alkali-aggregate reactions and corrosion of reinforcing steel. In the United-States, estimates for the costs of rehabilitating deteriorated bridges and roadways range from \$90 billion to \$151 billion [3, 4]. Although inadequate maintenance can account for a large portion of the problem, the deterioration of most northern states bridges is linked, in one way or another, to the use of deicing salts.

Given the increasing importance of the problem, a great deal of research has been specifically dedicated to the study of the deicer salt scaling resistance of concrete. An overview of the scientific and technical literature lately published on the subject is presented in this paper. The first part of this report is devoted to the fundamentals of frost action in concrete. The proposed mechanisms of freezing and hypotheses explaining the detrimental effects of deicing salts are discussed. A critical appraisal of three different test procedures designed to assess the deicer salt scaling resistance of concrete is given in the second section. Each test method is evaluated on the basis of reproducibility, variability of test results, operating cost and relationship to field exposure conditions. Finally, the influence of various parameters on the deicer salt scaling resistance of concrete is discussed in the last section. Topics such as mixture composition, air entrainment, casting operations, curing and the use of concrete sealers are reviewed.

The aim of this report is to provide civil engineers and concrete technologists with a comprehensive summary of the recent research published on the deicer salt scaling of concrete. In the past decades, numerous scientific and technical papers have been published within the scope of this subject. In the course of our work, it appeared

quickly that an enumeration of all these papers would be fastidious and that the main objective of this review would be missed. It was therefore decided to select a certain number of representative publications. Obviously, many valuable contributions had to be set aside in the process.

MECHANISMS OF DEICER SALT SCALING DETERIORATION

In the field of building components, the basic knowledge of a materials properties is of paramount importance. Such a knowledge enables engineers to improve the materials performance and facilitates the development of reliable laboratory test procedures. Over the years, several attempts have been made to explain the deicer salt scaling deterioration of concrete. Unfortunately, as will be seen in the present section, none of the proposed models can account for all the experimental results reported in the literature. The imperfect understanding of mechanisms involved clearly underlines the very complex nature of the problem, and limits our ability to design relevant accelerated test methods.

In many respects, the complexity of the deicer salt scaling phenomenon lies within the heterogeneous nature of concrete. At the microscopic level, the hydrated cement paste is an irregular arrangement of anhydrous phases, various hydration products and residual pore spaces. In concrete, this heterogeneity is exacerbated by the presence of aggregates which affect the porosity of the cement paste at the interfaces. These aggregates have their own pore structures that are significantly different from that of the hydrated cement paste surrounding them. In concrete, pore sizes may range over more than seven orders of magnitude. The diversity of the climatic conditions found in nature adds to the complexity of the problem. Clearly, a global understanding of the deicer salt scaling mechanisms requires a good knowledge of all the parameters involved and of their respective influence on the concrete frost durability.

Despite our imperfect knowledge of the mechanisms involved in the deicer salt scaling deterioration of concrete, significant progress has been made in understanding the freezing phenomena in porous materials with and without deicing chemicals. The systematic application of various experimental techniques, such as low-temperature calorimetry and nuclear magnetic resonance (NMR), has provided useful information on many aspects of frost action. A review of the recent findings made in basic research is presented in this section.

Freezing Phenomena in Porous Materials without Deicing Chemicals

It is well known that the structure of liquid water contained in microporous materials is significantly different than that of bulk water. In a pore, water is subjected to a wide range of surface forces. The extent and the nature of these forces is influenced by the chemical and geometric features of the pore wall and by the distance separating the water molecule from the surface [5, 6]. In the specific case of the hydrated cement paste, various experiments have clearly indicated that water strongly interacts by physisorption and chemisorption with the material [5-10]. In the former case, water molecules are uniformly held to the hydrate surface by Van der Waals forces. Low-energy links of a few kcal/mole are involved and the structure of the water molecule is not modified. In the latter case, water is locally tightly adsorbed to the surface by chemical links, and its molecular structure is modified.

SETZER [9] has proposed a three-category classification of the water held in the hydrated cement paste according to the extent of the surface interaction: the *structured surface water*, the *prestructured condensed water* (also referred to as capillary condensed water) and the *macroscopic bulk water* (see Table 1). The *structured surface water* includes the first layers of water molecules adsorbed to the surface of all pores (whatever their dimension) and the water held in micropores (i.e. with a diameter of less than 2 nm). The *prestructured condensed water* consists of the water held in mesopores (i.e. with a diameter in the 2000 to 50 000 nm range). The *macroscopic bulk water* is contained in the coarser pores (i.e. with a diameter of more than 50 000 nm). The proposed classification of SETZER is given in Table 1.

Measurements of thermodynamic characteristics of pore water in hardened cement paste (see Fig. 1) made by RADJY and SELLEVOLD show continuous decreases in both differential enthalpy and entropy with decreasing relative humidity [10]. Note that high numbers indicate low absolute values of both entropy and enthalpy, as evidenced by the position of the reference lines for bulk water and ice. The comparison with ideal capillary condensate, and measured values in the more *inert* porous Vycor glass, show the strong influence of surface forces in cement hydrates on the state of the pore water. Fig. 1 clearly demonstrates strong depressions of the freezing point of pore water as well as the existence of non-freezable pore water. Estimates based on the entropy data indicate that pore water held in the hydrated cement paste below about 60% relative humidity (R.H.) is not freezable at any temperature. This question will be further discussed in following paragraphs.

The vapor pressure of the prestructured condensed water held in a pore can be calculated with the Kelvin equation (see Fig. 2):

$$\ln \frac{P}{P_0} = - \frac{2 \gamma V}{R_m R T} \quad (1)$$

In this equation P and P_0 stand respectively for the vapor pressures of pore water and bulk water, γ is the surface tension of the liquid, V is the molar volume of water, R_m the curvature of the meniscus, R and T are the gas constant and the temperature in degrees Kelvin. The curvature of the water meniscus is determined by the pore size and the contact angle θ at which the liquid meets the pore wall. In a cylindrical capillary of a radius R_p , the curvature R_m is equal to $R_p/\cos \theta$.

Over the years, the freezing of water in microporous materials has been the subject of many investigations. Nuclear magnetic resonance and low-temperature x-ray diffraction experiments have established that pore water has the same freezing characteristics as bulk water [11, 12]. According to these reports, pore water undergoes upon freezing an 9% expansion to form ordinary Type I_h ice. As shown in Fig. 3, this ice, characterized by its hexagonal structure, has the same density and properties as bulk ice [13, 14]. Due to the surface interaction, the freezing point of the pore water is, however, lowered.

Following the investigations of EVERETT [15] and FELDMAN [16] that had indicated that the capillary condensation and menisci theories can still be applied at subfreezing temperatures, many equations relating the freezing point depression of water to the pore dimension have been proposed [17-21]. All these equations are

more or less refined combinations of the Clausius Clapeyron and Kelvin laws. The following equation has been proposed by SETZER [21]:

$$\ln \frac{T}{T_0} = - \frac{\gamma V_l}{\Delta H R_h} \quad (2)$$

In this equation, T and T_0 are the absolute temperatures, V_l is the molar volume of the liquid water, γ is the surface energy of the ice-liquid interface, H is the freezing enthalpy and R_h is the hydraulic radius which is defined as the ratio of the pore volume to the pore surface.

As can be seen, there is a great similarity between equation (1) and equation (2). According to these formulae, freezing of the pore water is analogous to desorption and both processes are incremental, i.e. that larger pores freeze or desorb first. This phenomenon is illustrated in Fig. 4. The freezing point depression should be distinguished from supercooling which tends to delay ice formation. The freezing point depression is a reproducible phenomenon that is directly related to the geometric characteristics of the pore. Supercooling is a statistical effect that is dependent on the nucleation process during freezing [21].

It should be emphasized that the validity of equation (2) is strictly limited to the prestructured condensed water. The macroscopic bulk water is not significantly affected by surface forces and freezes near 0°C. Several experimental results have also established that the water layer at the vicinity of the pore surface and in micropores remains unfrozen even at very low temperatures [22-24]. This phenomenon is generally associated with the short-range structuring of water molecules due to surface interaction and to the presence of ions in the solution. Although its viscosity is considerably greater than that of bulk water, the unfrozen interfacial water is supposed to have liquid-like properties. For instance, water molecules in the layer are mobile and can be transported under temperature and concentration gradients [11, 25, 26]. The thickness of the unfrozen layer varies with the pore surface characteristics. For hydrated cement paste, values of approximately 3 BET-equivalent monolayers have been reported [27, 28].

Over the years, the dynamic of ice formation in hydrated cement paste has also been the subject of much attention. An early study by HELMUTH [29] established that ice is growing as an ice front from the nucleation site. In his investigation, HELMUTH observed that, when freezing was not initiated by external means, ice formation usually began at much lower temperatures than that predicted by equation (2). In certain cases, specimens could be supercooled to temperatures as low as -15°C. HELMUTH concluded that:

“there is apparently no feature of the structure of the paste which can serve as nucleation site for ice formation at temperature higher than this”.

In the absence of any initiated seeding, large supercooling was also reported by other investigators [30, 31]. HELMUTH's results indicate that, once nucleation is initiated, ice propagates as a continuous phase through the pore structure of the

hydrated paste. The velocity of the ice front and the stresses consequently induced to the system were found to be directly related to the degree of supercooling [20, 30].

Relationship between the Hydrated Cement Paste Pore Structure and Ice Formation

Following the work of Helmuth, ice formation in hydrated cement paste has been studied extensively by many researchers. In most of these investigations, ice formation measurements were carried out by low-temperature calorimetry. The potential of this technique was first realized in the work of VERBECK and KIEGER [32] who used it to study the relationship between ice formation and the length change of a concrete specimen. Low-temperature calorimetry measurements have been later extensively carried out by many workers to study various aspects of the frost durability of cement-based materials. The technique is based on the fact that ice formation is an exothermal process. While the temperature is lowered, the amount of ice formed can be monitored by measuring the heat flow emanating out of the test specimen. Similarly, the amount of ice melting during heating can be determined by measuring the apparent heat capacity of the specimen. Details on the operating principle and the experimental procedure can be found elsewhere [33].

The systematic application of low-temperature calorimetry to hydrated cement paste systems has provided much information not only on the process of ice formation but also on the pore structure characteristics of these materials. Typical low-temperature calorimetry curves measured for a 0.5 water-cement ratio hydrated cement paste are given in Fig. 5 [31]. In this figure, the apparent heat capacity of the specimen, during cooling and heating, is given as a function of the calorimeter block temperature. As can be seen, there is a marked hysteresis between the cooling and melting curves. Although part of the hysteresis can be attributed to supercooling, most of it is related to the peculiar pore structure characteristics of the cement paste. Scanning electron microscope investigations have clearly established that hydrated cement paste does not have cylindrical pores, but that it is rather characterized by an irregular arrangement of pores of various sizes and shapes [34, 35]. Experiments by AGUIRRE-PUENTE et al [36, 37] have indicated that the propagation of the ice front throughout the system is controlled by the ability of the ice-water interface to penetrate the pore entryway while the melting temperature is determined by the size of the pore itself. In this respect, ice formation during cooling is analogous to mercury intrusion, and the hysteresis between the cooling and heating curves gives information about the continuity of the pore system [38].

In the past decade, low-temperature calorimetry has been extensively used to measure ice formation in various hydrated cement paste systems. As can be seen in Fig. 6, calorimetric results for steam-cured cement paste specimens indicate that the nonfrozen-water content (i.e. the amount of evaporable water not frozen at -55°C) is independent of the water-cement ratio [39]. Similar experiments carried out on paste specimens cured at room temperature showed a slight increase of the nonfrozen-water content with an increase in water-cement ratio [28, 33].

Qualitatively, these data are in relatively good agreement with the findings of POWERS and BROWNYARD [40] who reached the conclusion that the nonfrozen-water content solely depended on the degree of hydration. Quantitatively, calorimetric results indicate, however, that the POWERS and BROWNYARD indirect measurements systematically overestimated the amount of ice formed [39]. They have also established that the amount of ice formed between 0°C and -20°C , which is of particular interest in connection with frost resistance, decreases with the water-cement ratio [39]. These results have been later confirmed by the dynamic modulus

experiments of ZECH and SETZER [41]. This phenomenon was associated with the refinement of the porosity with the reduction of the water-cement ratio.

Low-temperature calorimetry measurements have provided very useful information on the mechanisms of frost damage. For instance, results reported by BAGER and SELLEVOLD [28] showed that the amount of ice formed decreases with the moisture content, and that it is the ice formation at temperatures near 0°C that is first affected. Similar data were later reported by BEDDOE and SETZER [42]. The practical implication of these results is that any hydrated cement paste with a water content lower than that corresponding to a relative vapor pressure of $P/P_0 = 0.9$ can be expected to be frost resistant. Such a conclusion is in good agreement with the findings of MACINNIS and BEAUDOIN [43] who found that non-air-entrained mortars of various water-cement ratios could be frost resistant if their degree of saturation was less than 90%. Calorimetric measurements have also indicated that the type of curing could significantly affect the pore structure of concrete. Results reported by BAGER and SELLEVOLD [39] showed, for instance, that steam curing at 97°C increases the amount of ice formed near 0°C . These data support the conclusions of previous investigations where steam curing was found to coarsen the pore structure of the hydrated cement paste [44-46]. Recent, as yet unpublished, calorimetric data show that the coarsening effect of elevated curing temperature on the pore structure is present also at 45°C and increases continuously to 97°C .

One of the greatest advantages of the low-temperature calorimetry technique is that measurements can be carried out on virgin water saturated specimens. Pore structure alterations caused by drying can therefore be studied without any perturbation from the experimental technique. The influence of the moisture history on ice formation has been extensively studied by SELLEVOLD and BAGER for several hydrated cement paste systems and various drying-resaturation treatments [28, 31, 47, 48]. Their results indicated that even relatively mild drying significantly alters the ice formation pattern. A typical result is given in Fig. 7 where the ice formation pattern of a mortar specimen dried at 50°C and resaturated is compared with that of a virgin specimen. The detrimental effect of a more coarse pore structure (either by elevated temperature curing or by drying-resaturation treatment) on the deicer salt scaling resistance of concrete is very important and is discussed in more detail in the following section.

As can be seen in Fig. 7, the rate of ice formation right after nucleation and the amount of ice formed to -10°C is considerably increased by the drying-resaturation treatment. Similar effects were observed for hydrated cement pastes slowly desorbed and resaturated. A careful analysis of the ice formation results usually indicates that drying increases the amount of large pores and decreases the amount of smaller pores. Such a tendency is in good agreement with previous reports who showed that oven drying tends to increase the freezable water content of cement paste and concrete [49, 50].

Several hypothesis have been developed to explain the effect of drying on the ice formation pattern. Although the drying-resaturation treatment almost certainly induces microcracking in the hydrated cement paste and concrete specimens, many indications tend to demonstrate that the alteration of the freezing can be primarily attributed to a modification of the pore system. Due to the relatively fine pore structure of the hydrated cement paste, high capillary tensions can be induced into the materials during desorption. Such forces originate from the formation curved menisci within the small capillaries and can reach appreciable values under certain circumstances [51]. According to many workers [52-54], under these stresses, the thin walls of hydrates separating some of the relatively small pores present in the

8 Marchand, Sellevold, and Pigeon

structure collapse to create larger pores and increase the continuity of the pore system. Experimental data tend to indicate that the extent of the drying-induced pore structure modifications is a function of the level of desorption and of the period of exposure to the capillary forces.

The effect of drying on ice formation is of particular importance in connection with frost testing. Calorimetric measurements have clearly demonstrated that a dried-resaturated concrete has a different pore structure than one which has constantly been kept saturated. Since in practice most concrete elements are submitted to frequent wetting and drying cycles, any test method designed to predict in the laboratory the frost resistance of concrete should include a drying-resaturation treatment prior to freezing. This is particularly the case for deicer salt scaling since, under field exposure conditions, it is the surface portion of the a concrete structure that is the more likely to be affected by drying.

Freezing Phenomena in Concrete with Deicing Chemicals

It has been long established that saturated concrete exposed to repeated freezing and thawing cycles could be affected by two types of deterioration: surface scaling and internal microcracking. Already in 1945, POWERS [55] underlined the distinction between the two phenomena by writing:

"When concrete specimens are frozen and thawed in water, two distinct types of disintegration have been observed: (1) The specimens may show little change in weight and appearance but large losses in strength and resilience; or (2) they may show progressive loss by crumbling and spalling but relatively little loss in strength and resilience of the remaining material. These are extremes. Specimens falling in neither category will show both crumbling and loss of strength and resilience of the remaining material. These are results that an acceptable hypothesis must explain satisfactorily."

Over the following years, the distinction between the two phenomena has been consistently recognized [56-58]. Laboratory investigations and field experiences have also shown that surface scaling is significantly enhanced by the presence of deicing chemicals. With the introduction in the mid-sixties of the *bare pavement policy* and the systematic application of deicing salts on concrete roadways and bridges, surface scaling rapidly became a major concern. Although, as previously mentioned, the surface scaling mechanisms are not still today fully understood, several studies have helped to clarify the deleterious effects of deicing chemicals.

One of the known effects of the application of deicing salts is that it tends to increase the degree of saturation of concrete at a given relative humidity [59, 60]. This effect originates from the fact that salt solutions have a lower vapor pressure than that of water. Hence, ambient water vapor has a greater tendency to condense into a salt solution than into pure water. A typical example of this effect is given by MACINNIS and WHITING [60]: under 88% relative humidity condition and at equilibrium, the average degree of saturation of various concrete specimens initially saturated with water was 73% while the average degree of saturation for companion specimens initially saturated with a 10% NaCl solution (in mass) was 92%. Such a phenomenon is of particular importance in connection with the deicer salt scaling deterioration of concrete structures in practice. The application of deicing salts is

more likely to maintain them (or at least their surface portion) above the critical degree of saturation. The hygroscopical effect of deicing salts is, however, less critical when concrete is tested in the laboratory since in most test procedures, specimens, after a certain drying period, are resaturated prior to testing.

It is also generally agreed that the detrimental influence of deicing chemicals is mostly physical in nature, and that the chemical reaction of the salts with the cement paste hydration products only plays a secondary role in the deterioration mechanisms. This conclusion was first reached by VERBECK and FLIEGER who investigated the effect of various deicing chemicals, such as sodium chloride and urea, on the surface scaling of concrete [56]. Their test results clearly indicate that, whatever the type of deicer, relatively low deicer concentrations (in the 2% to 5% range) produce more surface scaling than higher concentrations or pure water. Such a phenomenon is illustrated in Fig. 8 for the tests carried out with sodium chloride as a deicer. Their conclusion has been later confirmed by many other reports [61-64].

A critical review of the literature indicates that there is little agreement as to whether it is the salts dissolved in the pore system (i.e. *inside* the concrete) or those present in the solution surrounding the specimen that enhance the deterioration by scaling. This point is of particular interest with regard to testing, and the fact that this question is still debated today clearly emphasizes our imperfect understanding of the mechanisms involved. Reports on the subject are often contradictory. Most deicer salt scaling test results tend to indicate that it is the concentration of the salt solution surrounding the specimen that has a predominant influence on the mechanisms of deterioration [56, 62-64]. For instance, in the study of VERBECK and FLIEGER [56], all specimens had been saturated with pure water, and the concrete surfaces were subsequently covered with a salt solution during the freezing and thawing cycles. Moreover, a recent study by SELLEVOLD and FARSTAD [62] indicates that, for a given concentration of the outer solution, scaling is systematically more severe for the water-saturated specimens than for those that had been impregnated with the salt solution prior to testing.

These results are in apparent contradiction with the results of many basic investigations. Length change isotherms of hydrated cement paste samples impregnated with NaCl solutions at various concentrations (0% to 26%) have been measured by LITVAN [61]. In the same study, ice formation was also monitored by differential thermal analysis (DTA) measurements. Typical results for 1.27 mm thick samples at a cooling rate of approximately 20°C/hour are given in Fig. 9, where it can be seen that maximum residual length changes are obtained for the samples saturated with the 5% and 9% NaCl solutions. The residual length change is believed to be a good indicator of the damage induced to the system. Similar results have been reported by FAGERLUND [64] for mortar specimens and by MACINNIS and WHITING [60] for concrete specimens. In these cases, the greatest residual dilations were also observed for the samples saturated with NaCl solutions at low concentrations (2.5 % and 3% by mass respectively). According to these reports, deterioration mechanisms are enhanced by the presence of low concentrations of salts dissolved in the pore solution.

The influence of the presence of deicing salts on ice formation has been investigated by low-temperature calorimetry [62, 65]. It is well known that, in accordance with Raoult's law, the freezing point of bulk water is depressed by the presence of dissolved ions. In hydrated cement paste and concrete, the freezing point depression due to the dissolved salts seems to be superimposed on the freezing point depression resulting from surface interaction. This effect can be more clearly visualized in Fig.

10. As can be seen, the presence of deicing chemicals (in that particular case NaCl) significantly affects the pattern of ice formation. The primary freezing peak, associated with the formation of ice in the larger pores, is broadened and shifted towards the lower temperatures, and the amount of ice formed between 0°C and -20°C is slightly reduced. According to SETZER [12, 65], these results confirm that the presence of deicing salts not only alter the bulk water properties but also disturb the surface forces acting within the pore system. The author notes that the greatest perturbations are obtained for the salt solutions at low concentration ($\approx 3\%$ by mass), and concludes that it is the salts in the pore solution that are the most detrimental.

More research is certainly needed to clarify the detrimental influence of deicing chemicals on scaling. Additional information on the transport of deicing salts from the outer solution to the pore system would certainly help to understand the mechanisms involved. It is probable that the penetration of the deicing salts into concrete is not diffusion-controlled, and that chlorides are sucked in during the freezing and thawing cycles. Results reported by FAGERLUND [64] indicate that concrete tends to absorb water when subjected to repeated freezing and thawing cycles. His data also show that this absorption is increased when the specimens are immersed in salt solution. According to this process, the penetration rate of deicing salts inside the material could be much quicker than that predicted by the diffusion law.

In order to better understand the behavior of concrete structures in service, more attention should also be paid to the chemical interaction between the deicing salts and the cement paste hydration products. So far, this aspect of the question has been overlooked mainly because early investigations had indicated that the mechanisms of scaling deterioration were mainly physical and that sodium chloride, the deicer most currently used in practice, was much less detrimental than other deicing chemicals [66, 67]. Recent reports clearly show, however, that the long-term exposure to sodium chloride solutions favours the leaching of calcium hydroxide [68, 69, 70]. The chemical reaction is described in (3):



The calcium hydroxide leaching increases the porosity at the vicinity of the exposed surface which is likely to enhance the amount of ice formed near 0°C. According to the following reaction (4), the soluble calcium chloride produced in the process can also react with the aluminate phases in the cement paste to form chloroaluminate crystals:



Although these phenomena are unlikely to affect the deicer salt scaling resistance of concrete during a laboratory test where the exposure time is too short, they may significantly reduce the long-term frost durability of concrete surfaces in service.

Proposed Mechanisms of Deterioration

Over the years, several attempts have been made to explain the damage caused to concrete by freezing with and without deicing chemicals. As previously mentioned, none of the proposed mechanisms can fully account for all the experimental data found in the literature. The theories that have been developed over the years can be divided into two categories: microscopic and macroscopic. The theories from each group will be, hereafter, briefly discussed.

Microscopic mechanisms of deterioration

The most well-known microscopic model of frost action is certainly the *hydraulic pressure theory* proposed by POWERS in 1949 [55, 71]. According to this hypothesis, the destructive internal stresses are due to the flow of water away from the regions where ice is forming. As the temperature decreases below 0°C in saturated cement paste, ice begins to form in the capillary pores. Because the water in these pores contains dissolved chemicals (mostly alkalis) and because of pore size restrictions, ice formation increases gradually with the decrease in temperature. Ice formation is accompanied by a 9% increase in volume that forces water out of the capillaries. This causes a saturated flow towards the escape boundaries in the paste, the air voids. POWERS developed a mathematical formulation of his model:

$$P_{\max} = \frac{\nu}{3} \left(1.09 - \frac{1}{S} \right) \frac{U C}{K} \phi(L) \quad (5)$$

According to equation 5, the pressure (P) developed in the matrix increases with the rate of cooling (C), the rate of ice formation (U) and the maximum distance $\phi(L)$ that water must travel to reach an escape boundary (half the distance between two air void walls), but decreases with the hydrated cement paste permeability (K). In equation 5, ν and S represent respectively the coefficient of viscosity of water and the degree of saturation of the hydrated cement paste. Cracking occurs when the pressure generated by the flow is greater than the tensile strength of the paste.

Since the introduction of the hydraulic pressure theory, several experimental investigations have clearly indicated that this hypothesis cannot account for all the phenomena produced by freezing. For instance, hydrated cement pastes and other porous materials can be significantly damaged by freezing and thawing when they are saturated with organic liquids that do not expand upon freezing [7, 72]. This is illustrated in Fig. 11. HELMUTH has also emphasized that, due to several factors, the occurrence of a saturated flow during freezing is most unlikely [73]. The application of the hydraulic pressure theory, particularly to scaling, should therefore be considered with caution. Nothing in the model can explain the detrimental effect of deicing chemicals, the influence of the length of the freezing period, or that of the minimum temperature reached. The model is also in contradiction with some of the experimental evidence. According to the mathematical formulation of the hydraulic pressure theory, the damage increases with the rate of freezing. This is by no means consistently found to be true in experimental work. For instance, no increase in scaling was found at increased freezing rates by SELLEVOLD and FARSTAD [62]. It is, however, in agreement with the data obtained by PIGEON et al. on the influence of the freezing rate on the internal cracking due to freezing and thawing cycles [74].

In his subsequent investigations of the freezing phenomena in hydrated cement pastes POWERS observed that, after an initial expansion, air-entrained pastes tended to contract upon freezing. After numerous length-change experiments, he concluded that, contrary to the hypothesis of the hydraulic pressure theory, water moved towards the capillaries where ice was forming. In association with HELMUTH, he developed another hypothesis to explain the deterioration of concrete by frost called the *osmotic pressure theory* [75]. As previously discussed, because of surface effects, water in the capillary pores does not necessarily begin to freeze when the temperature drops below 0°C. Ice formation begins first in the larger pores and then, as the temperature decreases, it is possible in the smaller ones. At a given temperature, there is equilibrium in a capillary pore where ice has formed between the amount of ice and the pore water solution. Just enough ice forms so that the unfrozen water contains just enough dissolved chemicals to prevent freezing. This causes a difference in concentration between the solution in smaller pores where ice has not formed (this water is at the original concentration) and the more concentrated solution in larger pores where ice has formed. This difference in chemical potential causes an osmotic pressure because water from the smaller pores migrates to the larger pores where the concentration of the solution is higher, thus building up pressure. According to POWERS and HELMUTH, the osmotic pressure theory explains why an air-entrained paste keeps contracting even when the temperature is kept constant below 0°C (see Fig. 12). Moreover, according to the authors, the osmotic pressure generated during freezing increases with the concentration of the pore water solution, and this explains the deleterious effect of deicer salts.

The osmotic pressure theory was the first model that could explain, at least partially, the detrimental effect of deicing salts. It is also supported by much experimental data. Although there is no mathematical formulation for the model, osmotic pressures are more likely to need time to build up and the extent of the deterioration has to be related, in some way, to the length of the freezing period. This is in good agreement with results published by SELLEVOLD and FARSTAD [62] and STARK [76] where scaling was found to increase with the length of the freezing period. However, in the osmotic pressure theory, it is the chemicals inside the concrete that enhance the deterioration. The model does not explain why, as shown by SELLEVOLD and FARSTAD [62], that scaling is systematically increased when concrete, after a 14-day drying period, is resaturated with water prior to testing.

Recently, it has been suggested by FAGERLUND [77] that the deterioration by scaling could be the result of the combined action of hydraulic and osmotic pressures. As explained by the author, upon cooling, ice formation takes first place in the coarser pores. This generates localized hydraulic pressures and triggers the osmotic process. The total pressure induced to the system is the sum of the pressures generated by both phenomena and it is influenced by the amount of salts dissolved in the pore solution. The higher the salt concentration, the lower the amount of freezable water at a given temperature. The hydraulic pressures should therefore decrease with an increase of the salt concentration since less ice is formed. On the other hand, the osmotic pressures should increase with an increase of the salt concentration. The combination of these two phenomena should yield a pessimum salt concentration as it is schematically illustrated in Fig. 13.

LITVAN has carried out in the last 20 years a large number of experiments to study the behavior of porous materials upon freezing [7, 61, 78, 79, 80]. He found that, during the slow cooling period, a large portion of the evaporable water was lost from the porous samples. He concluded that, because of surface forces, water cannot freeze in situ. Since the vapor or saturation pressure over supercooled water is higher than that over ice, and because ice forms at the surface of the air voids,

water moves to the air voids (or any other escape boundaries such as fine cracks) during freezing to reach equilibrium.

According to LITVAN, the thermodynamic phenomenon causing the movement of water is related to the size of the capillary pores. The difference between the vapor pressure over supercooled water and that over ice increases as the temperature decreases. The relative humidity for the supercooled water in the capillary pores therefore decreases with the temperature since ice forms naturally at all *external* surfaces (including all air void walls). According to Kelvin's equation (see equation 2), the relative humidity required for evaporation decreases with an increase in the curvature of the liquid-vapor interface. Since evaporation of water from a capillary pore or desorption necessarily creates a curved surface, the phenomenon is thus amplified as the temperature decreases. At first, only the larger pores are affected, but, as the temperature decreases, so does the relative humidity and the minimum size of pores affected. When the rate of cooling is high, the amount of what LITVAN calls *unstable* water (the water that must move to re-establish equilibrium) increases more rapidly.

In his publication on the frost action [79], LITVAN attributes the damage of concrete to the following mechanisms:

"If a flaw in the solid is surrounded by sound concrete, any water from the undamaged portion will migrate on cooling, to the crack, filling it completely; on solidifying it causes the fissure to propagate. On the following cooling portion of the freeze-thaw cycle the crack draws more water and freezing results in further damage...Damage also occurs when the required rate of water expulsion usually necessitated by rapid cooling is so high that it cannot be realized in the paste. In such cases some of the passage ways presumably become blocked by ice and internal pressure is generated"

LITVAN also suggests that the presence of deicing salts in the pore solution increases the disequilibrium in the system. According to the author, the fact that more damage is induced in the system at low salt concentrations (see Fig. 9) can be attributed to a combination of many factors [61]:

"...Similar behavior of the NaCl-porous-glass system has been attributed to an increase of the degree of saturation and broadening of the temperature range of freezing. These effects oppose one another and result in the most severe conditions at low (5%) concentrations..."

Since the work of LITVAN, the question of the locus of freezing has been the subject of much attention. Although there are several indications that some part of the non-frozen water tends to migrate upon freezing, LITVAN's assumption that water cannot freeze in situ has been refuted by many experimental investigations. NMR studies by PEARSON and DERBYSHIRE [11] have showed that ice can be formed in small pores. Their findings have been confirmed by the low-temperature x-ray diffraction data reported by SETZER [65] where water was found to freeze in situ. Further evidence that most of the pore water freezes without any previous migration has been provided by FAGERLUND [77]. The theoretical basis of LITVAN's hypothesis that water cannot freeze in situ depends on the assumption that, at a given

temperature, the surface tension throughout the entire adsorbed water layer remains constant. As emphasized by SETZER [9], such an assumption cannot be true since it has been found that surface tension increases when the thickness of the adsorbed film is reduced.

Several other models have been proposed to describe the frost action in hydrated cement systems. SETZER [81], for instance, has developed his own thermodynamic model based on the following differential equation:

$$d\mu = -sdT + V(dP + \frac{\gamma}{R_h^2} dR_h - \frac{d\gamma}{R_h}) \quad (6)$$

In this equation, μ stands for the chemical potential, T for the absolute temperature, P for the pressure, V for the volume, γ for the surface tension, and R_h for the hydraulic radius of the pore. Assumptions that the structured surface water does not freeze until -90°C and that a thermodynamic equilibrium between ice, vapor and the adsorbate within the system is possible are taken into account in the model. Unfortunately, SETZER does not elaborate on the detrimental effects of the deicing chemicals.

The detrimental action of deicing salts has been recently discussed by HUDEC et al. [82]. According to these investigators, the deicer cations present in the pore solution are attracted to the hydrated cement paste surfaces that are negatively charged. The polar water molecules are, in turn, attracted to the cations. Such a process increases the amount of tightly held or *adsorbed* water in the system, the amount of increase being related to various factors such as the concentration of deicer cations, the ionic size to charge ratio, and the clustering geometry of the water-ion system. The increased proportion of adsorbed water could subsequently favour the build-up of osmotic pressures within the material. Although, in this model, the action of deicing salts is extensively described, the detrimental combination of deicing chemicals and freezing remains unclear.

Proposed macroscopic mechanisms of deterioration

Most macroscopic models have been developed on the basis of field observations. These models, however, can only account for a relatively small part of the damage observed on concrete surfaces subjected to freezing in the presence of deicer salts.

RÖSLI and HARNICK [83] have shown that concrete surfaces can be submitted to an important thermal shock when salts are applied to water frozen on concrete surfaces, because heat from the concrete is absorbed by the melting ice. From the temperature profiles recorded after the application of salts on a frozen concrete surface (see Fig. 14), internal stress distributions were calculated (Fig. 15). The results of this analysis revealed that the stresses induced in the surface layers could well surpass the tensile strength of concrete and lead to microcracking. According to the authors, this mechanism does not, of course, apply in all circumstances. For instance, the proposed mechanism can not account for the scaling deterioration observed during most laboratory tests where concrete surfaces are frozen and thawed with a salt solution on top.

BROWNE and CADY [57] have studied the penetration of salts in concrete. Based on deicing salt concentration profiles, they developed the hypothesis that scaling (*the formation of small flat flakes*) is due to hydraulic pressures generated under the surface layer (where ice formation is not possible because the salt concentration is usually too high). Unfortunately, the authors present no data to support this hydraulic pressure hypothesis. Moreover, this hypothesis does not explain why scaling is higher for low salt concentrations [56].

Very often, because salts in the top layers can be washed away, the measured salt concentration profiles in field concretes indicate that the maximum concentration is not located at the surface, but very approximately 10 mm below the surface (see Fig. 16). These observations have led HARNICK et al. [14] to suggest that scaling could be due to the stresses induced by the variable deformations of the different layers when the temperature drops below 0°C. Since ice formation is only possible in the layers where the salt concentration is low, certain layers are subjected to ice formation in the capillary pores, but others are not. This *layer by layer freezing* mechanism, unfortunately, is not compatible with the mechanisms that explain the protection offered by air entrainment. It is also very unlikely that the salt concentration in the capillary pores will be sufficient to completely prevent ice formation.

MOUKWA and ADKINS [84] have observed that, at the end of the afternoon on cold and sunny winter days, a layer of frozen concrete could be trapped between the surface where heat from the sun prevents freezing and the body of the concrete where heat accumulated during the day also prevents freezing. According to the authors, such a phenomenon could induce high pressures just below the surface and cause scaling. Based on these observations, ADKINS [85] even proposed a new test method to assess the deicer salt scaling resistance of concrete. The deterioration mechanism suggested by MOUKWA and ADKINS can probably explain some of the deterioration found in service where concrete surfaces are exposed to wide climatic variations. It does not, however, account for the deterioration of concrete specimens when tested in the laboratory. In most of the laboratory procedures, freezing is uniaxial, and the layer phenomenon described by the authors is unlikely to occur.

LABORATORY TEST PROCEDURES TO ASSESS THE DEICER SALT SCALING RESISTANCE OF CONCRETE

In order to reliably predict the service life of a structure under field exposure conditions, a laboratory test procedure should meet several requirements. As underlined by PETERSSON [86], the method should be realistic, that is the type of failure produced in the laboratory should be similar to that taking place in service. The method should also be reproducible. Finally, the procedure ought to be simple and cheap to operate. Nowadays, civil engineers and concrete technologists have available a large number of test methods to assess the deicer salt scaling resistance of concrete. Originally, the test procedures were designed to reproduce as faithfully as possible the exposure conditions found in service. Over the years, new and more reliable methods have been developed. In the present section, three standardized test procedures are reviewed. Each test procedure is evaluated on the basis of reproducibility, variability and operating costs. The relationship between laboratory test results and field performance is briefly discussed at the end of the section.

ASTM C672 — Ponding Method

Among actual test procedures, the most widely used is certainly the so-called *ponding method*. First adopted in 1971 by American Society for Testing and Materials under the designation C672 [87], this method is now the subject of several national and international standards [88-90]. The procedure does not require any sophisticated equipment, and its operating principle is quite simple. After a drying period of 14 days at 23°C and approximately 50% R.H., the tested surface is covered with a salt solution and the specimen is submitted to a series of 50 daily freezing and thawing cycles. As can be seen in Fig. 17, a dike has to be placed along the perimeter of the specimen in order to maintain a brine pond on the top surface. According to the standard, each daily cycle includes a freezing period of 16 to 18 hours at -18°C ($\pm 2^\circ\text{C}$) and a thawing period of 6 to 8 hours at 18°C ($\pm 2^\circ\text{C}$). No other restrictions concerning the temperature cycle, the salt type and concentration are imposed. At the end of each series of 5 cycles, the surface is flushed and the solution on top is replaced. Specimens are weighed and rated as prescribed by the standard.

Lately, the reliability of this procedure to assess the deicer salt scaling resistance has been increasingly questioned. The fact that the procedure still relies exclusively on a visual examination to assess the degree of deterioration of the tested specimens is viewed by many as a major shortcoming [57]. Despite the detailed guidelines given in the standard, the visual rating is often considered to be highly subjective and closely dependent on the type of surface tested. Nowadays, most laboratories also collect, at regular intervals during the test, the scaled off particles to improve the reliability of the test. Although it is not included in the standard, the mass of scaled off particles is believed to be a much better indicator of the deterioration of concrete surfaces.

A few researchers also criticize the procedure for its poor reproducibility. At the end of a round-robin test series, PLÄHN and GOLZ [91] concluded that the ponding method was plagued by a high test result dispersion even when the cumulative mass of scaled off particles was considered. Similar conclusions were drawn by SETZER and SCHRAGE [92] following another comparative test series carried out with concrete paving blocks. Although these authors recognize that concrete is everything but a homogeneous material, they all believe that the significant scattering of test results originates, for the most part, from the procedure itself. In a critical appraisal of various test methods designed to assess the deicer salt scaling durability, SETZER and HARTMANN [93] suggest that the dispersion of the ASTM C672 test results can be mainly attributed to a poor control of the specimen preconditioning and of the temperature regime during the test. The ASTM C672 standard has also been criticized for the absence of any evaporation protection cover on top of the specimen [94]. According to the results of VERBECK and KLIEGER [56] (Fig. 8), small variations of the concentration of the salt solution on top can greatly affect the intensity of scaling.

Swedish Standard SS 13 72 44 — The Borås Method

Essentially, the Swedish Standard SS 13 72 44 [95] can be considered as an improved and more controlled version of the ASTM C672 test method. In the Borås method, the specimen pre-conditioning includes a 7-day drying period (at 20°C and 50% R.H.) and a 3-day water resaturation period. At the end of this period, water is flushed and, as for the ASTM C672, the top surface of the tested specimen is then covered with a brine solution (3% NaCl by mass). The specimen must be subjected

to at least 56 daily cycles of freezing and thawing. After 7, 14, 28, 42, and 56 cycles, the solution on top is flushed, the specimen is weighed and the scaled-off particles are collected.

When compared to that of the ASTM procedure, the requirements of the Swedish standard are, in many aspects, more detailed and more severe. For instance, in order to ensure the development of a uniaxial freezing front, the side and the bottom surfaces of the test specimen have to be thermally isolated. Moreover, during testing, the standard requires the application of a tight evaporation protection film over the solution. Finally, the requirement of the specimen temperature, measured in the salt solution, is well defined throughout the cycle. The better control of the Swedish method is not considered to have any significant effect on the procedure operating cost. Testing can be performed with similar equipment to that used for the ASTM C672.

Due to its recent introduction, there exists actually few data on the reproducibility of the Borås method. In their critical appraisal of existing test methods, SETZER and HARTMANN [93] question the fact that the concrete specimens are resaturated with water prior to testing. According to these authors, such a treatment increases the risk of test result scattering. They suggest that concrete should rather be resaturated with the same salt solution as that used during the test. Results of a round-robin series that included nine different concrete mixtures tested in five different laboratories have recently been reported by SELLEVOLD and FARSTAD [62]. In certain cases, significant variations were noted between the different laboratories. The authors maintain, however, that a large part of the test result scatter can be attributed to the concrete heterogeneity. More research is certainly needed to evaluate the reproducibility of the method.

CSA CAN3 A231.2 M85 — Brine Immersion Test

Well established in Europe for many decades, the concrete paving block industry has experienced significant growth in North America in recent years. Unfortunately, due to the numerous voids resulting from the consolidation operations, these products could hardly be tested in accordance with the ASTM C672. In many cases, the salt solution on top of the sample was found to leak and testing had to be stopped. Moreover, the ASTM standard was not believed to reproduce reliably enough the field exposure conditions where paving blocks are often found to be, more or less totally, immersed in a mixture of brine and melting snow.

For the specific needs of the pre-cast concrete paving block industry, the Canadian Standards Association has recently developed a new deicer salt scaling test [96]. The procedure is very similar to that described by SIEBEL and NECK [97]. Prior to testing, concrete specimens are dried at 110°C until *constant mass* (i.e. until the difference between two measurements made at a two-hour interval is less than 0.2%). Then the specimens are placed in individual plastic containers and resaturated with a salt solution (NaCl - 3% by mass) for 24 hours. At the end of the resaturation period, the specimens are placed in a freezing environment and submitted to a minimum number of 50 daily cycles. As can be seen in Fig. 17, in this procedure, the six faces of the specimen (i.e. not only the top surface) are submitted to the test. For each daily cycle, containers are kept at -15°C ($\pm 2^\circ\text{C}$) for 16 hours. At the end of the freezing period, each container is placed at 23°C ($\pm 3^\circ\text{C}$) for 8 hours. During the saturation and the testing periods, containers are kept sealed in order to avoid any evaporation of the salt solution. At the end of each series of 5 cycles, the solution in each container is replaced. Specimens are weighed and rated

as prescribed by the standard. Finally, scaled off particles are collected, dried and weighed.

One of the great advantages of this method is that specimen preparation is negligible. The fact that each specimen is placed in a sealed container, which prevents any evaporation of the salt solution, certainly reduces the test result scatter. However, the requirements of the standard concerning the temperature cycle should be more precise. Without a good air circulation between the containers, the thawing of the specimens is often incomplete at the end of the cycle. Predrying the specimens at 110°C is also a very harsh treatment totally unrelated to field exposure condition. The effect of drying (aging) will be further discussed in the following section.

Relationship between Laboratory Test Results and Field Performance

There exists very little information in the literature on the relationship between laboratory test procedures and field exposure conditions. Unfortunately, the few available data on the subject appear to be contradictory. In a literature review on the significance of accelerated test procedures, MIELENZ [98] reported that the relative performance of concrete in service generally follows the pattern set in accelerated deicer salt scaling tests. SCHUBERT and LÜHR [99, 100] compared the results obtained from various laboratory test procedures to the performance obtained after five years of exposure to field conditions. They found very little correlation between the two sets of data. Similar conclusions were reached by LITVAN et al. [101] at the end of an investigation on the frost durability of pre-cast concrete elements. The authors concluded that:

"...conventional laboratory tests, under conditions prevailing in the present program, yielded predictions which show little, if any, agreement with actual field performance."

More systematic studies comparing the results obtained by laboratory procedures to field performance are certainly needed. Such an investigation is actually being carried out by the Swedish National Testing and Research Institute [86]. Three field exposure stations have been established and various concrete qualities are being tested. This investigation should provide very interesting information on the reliability of the Borås method.

FACTORS AFFECTING THE DEICER SALT SCALING RESISTANCE OF CONCRETE

In the past decades, several investigations have been specifically devoted to the study of specific aspects of the deicer salt scaling deterioration of concrete. These studies have provided useful information on the influence of various factors. The results of these investigations are reviewed and discussed in the present section.

Materials

The cements that are generally used to make concretes that will be exposed to freezing and thawing cycles in the presence of deicer salts can be divided into two broad categories: portland cements that do not contain any supplementary cementing

material (these are the most commonly used), and blended cements that contain supplementary cementing materials.

The differences between the various types of portland cement that can have a significant effect on the deicer salt scaling resistance of concrete are those that can influence the capillary porosity (and also the tensile strength) of the hardened paste. It has been found, for instance, that the use of finer cements can improve the scaling resistance [102, 103]. This can most probably be related to the reduction in the average size of the capillary pores that is observed when finer cements are used [104]. Although this has not been systematically verified, faster hydration rates probably reduce the risk of early surface damage due to such phenomena as plastic shrinkage, and increase in the water-cement ratio of the surface layers through excessive bleeding. Rapid hydration (particularly by accelerated curing), however, can often result in a coarser microstructure, due to a less homogeneous distribution of the hydration products, and this can of course have a negative effect.

Data available concerning the influence of cement composition (mostly the C_3S , the C_3A , and the alkali content) are scarce. Laboratory test results reported by FAGERLUND indicate that the use of low alkali/low C_3A cements reduces the amount of scaling and the spread between individual specimens [103]. This conclusion is in good agreement with the data recently reported by MALMSTRÖM [105]. FAGERLUND attributes the detrimental influence of high alkali/high C_3A cements to their effect on the mechanisms of air entrainment. It has been shown that a reduction of the alkali content of the pore water facilitates the production of low spacing factors [106]. It is, however, unlikely that the detrimental effect of high alkali/high C_3A cements can solely be explained by their influence on air entrainment. In his survey of the field performance of non-air-entrained concrete pavements, JACKSON [107] also reported that scaling increases with the C_3A and alkali contents. Moreover, if high alkali contents are known to reduce the efficiency of the air-entraining agent, it has been recently demonstrated that they also tend to increase the stability of the air-void system in fresh concrete [108]. Clearly, further research is needed to clarify the influence of cement composition on the deicer salt scaling resistance of concrete.

The three most commonly used supplementary cementing materials in concrete are silica fume, fly ash, and slag. There are slightly conflicting laboratory and field reports on the salt scaling durability of normal strength air-entrained concretes containing silica fume. Several studies indicate that, when it is tested in the laboratory according to standard procedures, this type of concrete is slightly more susceptible to scaling than ordinary portland cement concretes [109-110]. Laboratory data reported by other workers [62, 112], however, show that silica fume can improve the scaling resistance of concrete. In all cases, there is, however, little difference between the durability of the two types of concrete. Probably in good part because the use of silica fume reduces the surface permeability of concrete through the refinement of the capillary pore structure, properly air-entrained normal strength silica fume concretes have been observed to have an excellent scaling durability under severe field conditions [112, 113], as long as the amount of silica fume that is used as partial replacement for portland cement is not too high (10% is normally considered the upper limit). Although they are not recommended for use under very severe exposure conditions, non-air-entrained normal strength silica fume concretes have been found to have a scaling resistance that is much better than that of similarly non-air-entrained ordinary portland cement concretes. Again, this can be related to the reduction of the average capillary pore size. The effect of silica fume on the deicer salt scaling resistance of concrete will be further discussed in the following section devoted to aging effects.

The published data concerning the salt scaling resistance of concretes containing fly ash and slag are often contradictory. Many laboratory studies have shown that the use of fly ash in properly air-entrained concretes reduces significantly the scaling durability [114-117]. Other studies, however, have shown that good scaling resistance is possible in concretes made with up to 30% fly ash (as partial replacement for portland cement) [118], and the field performance of so-called high volume fly ash concretes have also indicated that they can have a good scaling resistance [119]. A good part of these contradictions is mainly due to the variable nature of fly ashes. Their negative influence can certainly be related, in almost all cases, to their relatively slow rate of hydration, and to the increased brittleness of the cement paste matrix resulting from the reduced calcium hydroxide content of the hardened paste. On the other hand, the refinement in the capillary pore structure that the use of some fly ashes yields certainly has a positive effect, both on the total amount of freezable water and on the reduction of the surface permeability. The proper use of fly ash depends on a good knowledge of its physical and chemical characteristics and on their influence on the concrete properties. Special care should be taken with fly ashes containing a significant amount of organic particles. Studies have shown that the presence of these particles can reduce significantly the air-entraining agent efficiency and compromise the stability of the air-void system [120-122]. In most cases, the amount of fly ash should be limited to 30% of the total mass of binder.

Reports on the deicer salt scaling resistance of granulated blast furnace slag cement concretes appear to point in both directions. In many cases, the replacement of cement by slag has been found to reduce the deicer salt scaling resistance of concrete [118, 123, 124]. Carbonation has been found to increase the average capillary pore size of concretes containing slag [125], and this could further explain, in some cases, the observed reduction in scaling resistance [124]. However, a field study conducted by VIRTANEN [112] has indicated that the surface layers of 7-year old test sections made of slag cement concrete were less carbonated. Field observations and laboratory tests carried out on cored specimens also indicated that slag concretes had a better salt scaling resistance. These conflicting results clearly emphasize the need of more research to clarify the influence of slag on the deicer salt scaling resistance of concrete. The use of slag cement in the production of concrete elements exposed to deicing salts should also be considered with caution.

Mixture Characteristics

The most fundamental characteristic of any concrete mixture is of course the water-cementitious material ratio. This ratio influences the porosity of the paste (both in the bulk and at the aggregate-paste interface), and thus all concrete properties, most notably the strength related properties and the durability related properties. As could be expected, most field and laboratory data show that, for normal strength concrete, the deicer salt scaling resistance increases as the water-cementitious material ratio decreases [103, 111, 126, 127].

High performance concretes (sometimes referred to as high strength concretes) generally have water-cementitious material ratios in the 0.35 to 0.25 range. Since, as this ratio decreases, so does the freezable water content, it can be expected that there exists, for a given type of cement, a value such that air entrainment will not be required as a protection against freezing in the presence of deicer salts when the ratio is lower than this *critical* value. When silica fume is used as partial replacement for portland cement, it has been found that air entrainment is generally not required for scaling resistance when the water-cementitious material ratio is equal to or lower

than 0.30 (even if air entrainment is still required to obtain an adequate resistance to internal cracking due to frost) [111, 128, 129]. For concretes made with portland cement without silica fume, the critical value is of the order of 0.25 [111, 128-130], and, for concretes containing significant amounts of supplementary cementitious material, it seems to be lower than 0.25 (but there is unfortunately very little published data on this subject).

For all concrete mixtures, slump is an important property, since it determines the ease with which they can be properly placed and consolidated. The very few test results reported on the topic indicate that normal strength concretes with very high slumps tend to have a reduced scaling resistance [103]. In such concretes, bleeding tend to increase permeability, cause segregation, increase the water-cement ratio in the surface layers, and also cause water lenses to form under the aggregate particles that are close to the surface. Very high slumps can also destabilize in certain cases the air-void system. Very low slump values can probably also be deleterious, because proper consolidation and surface finishing operations will be hampered.

Unsound aggregate particles can cause the formation of surface craters known as *pop-outs*. Many sound aggregate particles do not break during freezing, but nevertheless create disruptive pressures at the aggregate-paste interface, because they expel water. This often results in the loss of the mortar cover on the aggregate particles that are close to the surface. Again, not all authors consider this to be a scaling problem, but it is clear that only the use of low porosity aggregates can prevent this phenomenon.

Cement content is not, per se, an important parameter as regards scaling resistance. There are, however, clear indications that the best concretes (with respect to mechanical properties) are always those with the lowest paste content (so long as they have an adequate water-cementitious material ratio and that their workability is sufficient to allow proper consolidation). It can thus be assumed that the same rule applies to durability-related properties. A lower paste content means an overall lower concrete porosity.

Certain concretes, often known as dry concretes, have a very reduced paste content, and thus require the use of special placing techniques. This is the case, for instance, for roller-compacted concrete, and for concrete paving blocks. In these materials, adequate air-entrainment and proper dispersion of the mixing water can only be obtained with the combined use of high-energy mixers and high dosages of air-entraining agents [131-133]. It has also been found that the use of supplementary cementing materials in these concretes can improve the cement paste homogeneity and helps to reach higher mechanical strengths [132, 133]. The results of the deicer salt scaling tests that have been published in recent years indicate that roller compacted concrete pavements and concrete paving blocks can have a good scaling resistance without air entrainment [134-136]. Data from another test series demonstrate that no-slump concrete elements, such as the pre-cast New-Jersey safety barrier, can also be frost resistant without air entrainment [133]. In all cases, however, the production of spherical air bubbles significantly increases the concrete scaling resistance. More research will be necessary to fully investigate this question. Shotcrete has also been investigated recently in this respect, and fundamental studies are also warranted in this area.

It should be clearly emphasized that for most concretes, air entrainment is always required for good resistance to freezing in the presence of deicer salts. In addition to the theoretical considerations which have previously been discussed, there is an absolutely overwhelming amount of laboratory and field data that proves the positive

influence of air entrainment [137-139]. The beneficial effect of air entrainment can be visualized in Fig. 18 where the results of a condition survey of concrete structures built in the Québec City area are plotted. Unfortunately, however, air entrainment is not the only important requirement for good scaling resistance, and field problems still occur relatively frequently in properly air-entrained concretes, often because of poor mixture proportions and bad curing techniques. Test results have shown that there is no critical value of the air void spacing factor for scaling resistance, as it exists for the resistance to internal cracking due to freezing and thawing cycles [109]. Generally, the deterioration due to scaling simply increases with an increase of the spacing factor. An important consequence of this is that inadequate air entrainment is much better than no air entrainment. Certain tests have also indicated that excessive air entrainment can reduce the scaling resistance, probably because of the reduction of the tensile strength of the paste and of the easier saturation of the surface layers [140].

The characteristics of the air-void system that are important for scaling resistance are obviously those in the surface layers, and not those in the bulk of the concrete. Normally, when the surface of the concrete is not significantly disturbed during the finishing operations (i.e. when the surface is simply lightly troweled with a wooden instrument), a clear relationship exists between the scaling resistance and the air-void characteristics in the bulk of the concrete. It seems that there are generally fewer large voids in the surface layers, but that the number of small voids is approximately the same as in the bulk of the concrete. Overworking of the surface, however, as well as excessive vibration, can reduce the number of small air voids, and thus increase the spacing factor and the possibility of surface damage during freezing.

Accelerators, retarders, and the other type of admixtures that are used for making concrete can all influence the resistance to deicer salt scaling. These admixtures can affect the durability of concrete in both direct (modification of the concrete pore structure) and indirect manners. In the former case, little work has been published. Available data on the subject seem to indicate that the use of these admixtures do not result in any marked change in the capillary pore structure of ordinary concrete [31]. The use of retarders, however, can increase bleeding, and thus affect the porosity in the surface layers. The most significant influence that any admixture can have is probably on the value of the air void spacing factor, since many admixtures have been found to influence air entrainment [103, 141, 142]. This is particularly the case for superplasticizers, when they are used to increase workability in normal mixtures (and not, of course when they are used to make low water-cementitious material ratio concretes). Depending on the mixture composition, the type of air entraining agent and the type of superplasticizer, the air void spacing factor in superplasticized concrete can be equal to, or much higher than, the spacing factor in similar non-superplasticized mixtures [143-145].

Casting and Curing Procedures

Curing, primarily because of its influence on the capillary porosity of the hardened paste, is obviously very important as regards durability [103, 124, 146]. This, of course, is particularly true for deicer salt scaling resistance, since curing mostly affects the surface layers of concrete. Furthermore, in many cases, if curing procedures are delayed, plastic shrinkage cracking can occur, and surface durability can thus be significantly reduced.

Although the reasons for this are not always well understood, the type of curing can have a very significant influence on the scaling resistance. Many authors have reported in recent years that concretes cured with a membrane forming curing compound have a better scaling resistance than similar water cured concretes. This has been found to be true in laboratory [118], as well as field experiments [135, 136]. A possible explanation for this could be that, contrary to membrane curing, water curing promotes the formation of denser concrete in the surface layers (due to better hydration). This could hamper water movements from the concrete to the surface during freezing, and thus increase the possibility of surface damage. Early curing at high temperatures (such as is commonly used in prefabrication plants) has been found to be very detrimental to the scaling resistance of certain types of concretes [146, 147]. As previously discussed, this seems to be related to the fact that curing at elevated temperatures results in a coarser pore structure, and consequently more ice formation in the 0°C to -20°C range [39, 44-46]. Microstructural damage due to the different coefficient of thermal expansion of water, cement and aggregates is also possible. It is interesting to note that silica fume concretes appear to be less affected by curing at high temperatures [146, 147].

Surface finishing operations, as previously mentioned, can influence the properties of the surface layers, and thus the scaling resistance. Overworking, in particular, can increase the value of the air void spacing factor. Moulded surfaces, as opposed to troweled surfaces, are also often exposed to freezing in the presence of deicer salts. This is the case, for instance, for New-Jersey type highway barriers. Are such surfaces more susceptible to scaling damage? Again there is very little published information on this question. The wall effect is probably more important in this case, and the properties of moulded surfaces can be expected to vary with the type of mould and the type and amount of oil used on the inner surface of the mould. It can also probably depends on the orientation of the surface relative to the bleeding direction. What the available information suggests is that certain types of concrete can be more susceptible to scaling if the exposed surface has been moulded rather than troweled. In a published series of tests results, concretes containing silica fume were found to have a lower scaling resistance than that of similar concretes containing no silica fume [148]. The type of mould, however, wood or steel, was found to have little influence. At the present time, the information that is available is insufficient to understand clearly the phenomena involved, or to determine in which cases there will be a significant difference between the resistance to scaling of a moulded surface and a troweled surface.

Use of Sealers

Sealers are generally used to prevent the ingress of chloride ions and reduce the risk of reinforcement corrosion. Unless the concrete has no access to moisture, those which form an impervious coating on the surface of concrete (such as the epoxy or acrylic based types), because they completely prevent moisture movements, generally tend to debond with time. As shown by FAGERLUND [149], moisture generally accumulates in the concrete just underneath the coating, and subsequent freezing completely disrupts the bond.

Silane and siloxane-based sealers penetrate into the surface layers of concrete, and an impervious layer is formed which prevents the ingress of both chloride ions and moisture. This layer, however, does not form a vapor barrier, and drying is possible. Many laboratory deicer salt scaling tests have nevertheless shown that these sealers, although they offer some protection against scaling to non-air-entrained concretes, tend to increase the deicer salt scaling damage to air-entrained

concretes [150, 151]. It seems that, largely because the surface of the concrete is always covered with a deicer salt solution during the tests, water accumulates under the sealed layer in concrete. After a sufficient number of cycles, microcracking just below this sealed layer disrupts the concrete, and this layer then relatively rapidly becomes completely debonded from the bulk of the concrete. Under field conditions, the influence of sealers will thus depend on the position of the surface in the structure. Vertical surfaces will normally be less affected by the use of sealers than horizontal surfaces which can, in certain cases, be covered with water for long periods of time [152].

Aging Effects

In service, concrete structures are exposed to various exposure conditions that can affect, in one way or another, the properties of the surface layers. For instance, after a certain period of exposure, the first few millimeters of concrete under the surface are usually highly carbonated. Except for blended slag cement concrete, carbonation usually reduces the concrete porosity which subsequently increases the resistance to scaling [124].

Concrete surfaces are also subjected to frequent wetting and drying cycles. As was previously discussed, low-temperature calorimetry measurements have clearly indicated that drying tends to coarsen the hydrated cement paste pore structure. According to these data, drying should therefore reduce the scaling resistance of concrete. Unfortunately, existing reports on the subject point in both directions. Early results reported by VERBECK and KLIEGER [56] indicate that a short and relatively mild predrying can enhance the deicer salt scaling resistance of concrete. These conclusions have been recently confirmed by many other studies [103, 153, 154]. Other data, however, demonstrate that prolonged predrying or predrying at higher temperatures (40 to 50°C) lead to an increased scaling [62, 99, 100, 155]. The effect of predrying at 50°C is illustrated in Fig. 19.

More research is certainly needed to clarify the effect of drying on the scaling resistance of concrete. Predrying at 40°C is certainly not unrealistic relative to natural exposure conditions, and its effect on the deicer salt scaling resistance should probably be taken into account in the laboratory testing of concrete. Moreover, the effect of supplementary cementitious materials such as silica fume and fly ash has to be investigated more fully. Some studies have indicated that the deicer salt scaling resistance of concretes containing silica fume is much less affected by drying [62, 155].

CONCLUDING REMARKS

In the past decades, significant progress has been made in understanding freezing phenomena in porous materials. Despite the great deal of research specifically dedicated to the subject, the mechanisms of the deicer salt scaling deterioration of concrete are not yet fully understood. More research is particularly needed to clarify the detrimental influence of deicing chemicals.

It is well known that the characteristics of the surface layer tend to differ significantly from that of the bulk concrete. More research is needed, however, to evaluate how the surface layer properties are affected by parameters such as the finishing operations, the chemical interaction with chlorides and the aging effects.

More information is also required to better understand to what extent the alteration of the surface layer pore structure affect the deicer salt scaling resistance of concrete.

The deicer salt scaling resistance of concrete can be significantly improve by air entrainment, appropriate curing and good concreting practices. Unfortunately, even when all these conditions are met concrete surfaces can nevertheless suffer from scaling.

Civil engineers and concrete technologists have numerous test methods available to assess the deicer salt scaling resistance of concrete. More information is needed on the reliability of these procedures. More research is also required to understand how these methods relate to field exposure conditions.

ACKNOWLEDGEMENTS

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada and the Fonds FCAR of the Government of the Province of Québec for their financial support for this project. The authors also thankfully acknowledge Mr. Jean Parent for his fine work in reproducing the figures.

REFERENCES

- [1] CARLES-GIBERGUES, A. and PIGEON, P. (1993), *La durabilité des bétons en ambiance hivernale rigoureuse*, in *La Durabilité des Bétons*, Presses de l'Ecole Nationale des Ponts et Chaussées, Paris, pp. 227-284, (in French).
- [2] MEHTA, P.K., SCHIESSL, P. and RAUPACH, M. (1992), *Performance and durability of concrete systems*, Proceedings of the Ninth International Congress on the Chemistry of Cement, New Delhi, India, Vol. 1, Theme IV, pp. 571-659.
- [3] DUNKER, K.F. and RABBAT, B.G. (1993), *Why America's bridges are crumbling*, Scientific American, Volume 268, N° 3, pp. 66-72.
- [4] STIX, G. (1993), *Concrete solutions*, Scientific American, Volume 268, N° 4, pp. 102-112.
- [5] POWERS, T.C. and BROWNYWARD, T.L. (1946), *Studies of the physical properties of hardened portland cement paste — Part 2: Studies of water fixation*, Journal of the American Concrete Institute, Vol. 18, N° 3, pp. 249-336.
- [6] RADJY, F. and SELLEVOLD, E.J. (1973), *Internal friction peaks due to adsorbed and capillary water in microporous substances*, Nature Physical Science, Vol. 241, N° 111, pp. 133-135.
- [7] LITVAN, G.G. (1978), *Adsorption systems at temperature below the freezing point of the adsorptive*, Advances in Colloid and Interfaces Science, Vol. 9, pp. 253-302.
- [8] REGOURD, M. (1982), *L'eau*, in "Le Béton Hydraulique", Presses de l'Ecole Nationale des Ponts et Chaussées, Paris, pp. 59-68, (in French).

- [9] SETZER, M.J. (1990), *Interaction of water with hardened cement paste*, in Advances in Cementitious Materials, American Ceramic Society Transactions, Vol. 16, pp. 415-439.
- [10] RADJY, F. and SELLEVOLD, E.J. (1976), *Thermodynamic parameters of pore water in hardened cement paste and porous Vycor glass*, Unpublished results, Building Materials Laboratory, The Technical University of Denmark.
- [11] PEARSON, R.T. and DERBYSHIRE, W. (1974), *NMR studies of adsorbed water on a number of silica surfaces*, Journal of Colloid and Interface Science, Vol. 46, N° 2, pp. 232-248.
- [12] SETZER, M.J. (1988), *Abnormal freezing of water in concrete — Influence of pore structure and deicing chemicals*, Paper presented at the International Workshop on Low Temperature Effects on Concrete, Sapporo, Japan, 20 p.
- [13] DROST-HANSEN, W. (1967), *The water-ice interface as seen from the liquid side*, Journal of Colloid and Interface Science, Vol. 25, N° 1, pp. 131-160.
- [14] HARNIK, A.B., MEIER, U. and RÖSLI, A. (1980), *Combined influence of freezing and deicing salt on concrete — Physical aspects*, ASTM Special Technical Publication STP-691, Edited by P.J. Sereda and G.G. Litvan, pp. 474-484.
- [15] EVERETT, D.H. (1961), *The thermodynamics of frost damage to porous solids*, Transactions of the Faraday Society, Vol. 57, pp. 1541-1551.
- [16] FELDMAN, R.F. (1970), *Length change-adsorption relations for the water-porous glass system to -40°C*, Canadian Journal of Chemistry, Vol. 42, N° 2, pp. 287-297.
- [17] DEFAY, R., PRIGOGINE, I., BELLEMANS, A. and EVERETT, D.H. (1966), *Surface tension and adsorption*, Longmans, London, pp. 243-255.
- [18] BLACHERE, J.R. and YOUNG, J.E. (1972), *The freezing point of water in porous glass*, Journal of the American Ceramic Society, Vol. 55, N° 6, pp. 306-308.
- [19] BRUN, M., L'ALLEMAND, A., QUINSON, J.F. and EYRAUD, C. (1977), *A new method for the simultaneous determination of the size and shape of pores — The thermoporometry*, Thermochimica Acta, Vol. 21, pp. 59-88.
- [20] FAGERLUND, G. (1973), *Determination of pore size distribution from freezing-point depression*, Materials and Structures/Matériaux et Construction, Vol. 6, N° 33, pp. 215-225.
- [21] SETZER, M.J. (1992), *Basic phenomena of frost action*, Proceedings of RILEM TC-117 Research Seminar, Lund, Sweden, Edited by G. Fagerlund and M. Setzer. pp. 5-17.
- [22] ANTONIOU, A.A. (1964), *Phase transformations of water in porous glass*, Journal of Physical Chemistry, Volume 68, N° 10, pp. 2754-2764.

- [23] ANDERSON, D.M. (1967), *The interface between ice and silicate surfaces*, Journal of Colloid and Interface Science, Vol. 25, N° 1, pp. 174-191.
- [24] SELLEVOLD, E.J. and RADJY, F. (1976), *Low dynamic mechanical response of porous Vycor glass as a function of moisture content — Part I: The capillary transition*, Journal of Materials Science, Vol. 11, pp. 1927-1938.
- [25] HOEKSTRA, P. and MILLER, R.D. (1967), *On the mobility of water molecules in the transition layer between ice and a solid surface*, Journal of Colloid and Interface Science, Vol. 25, N° 1, pp. 166-173.
- [26] BELFORT, G., SHERFIG, J. and SEEVERS, D.O. (1974), *Nuclear magnetic resonance relaxation studies of adsorbed water on porous glass of varying pore size*, Journal of Colloid and Interface Science, Vol. 47, N° 1, pp. 106-116.
- [27] RADJY, F. (1975), *Thermodynamic parameters for sorption of water by hardened cement*, Paper N° 6 presented at the Seventy-Seventh Annual Meeting of the American Ceramic Society, Cements Division, Washington, D.C., USA, 10 p.
- [28] BAGER, D.H. and SELLEVOLD, E.J. (1986), *Ice formation in hardened cement paste - Part I: Room temperature cured paste with variable moisture contents*, Cement and Concrete Research, Vol. 16, N° 5, pp. 709-720.
- [29] HELMUTH, R.A. (1960), *Capillary size restrictions on ice formation in hardened cement paste*, Proceedings of the Fourth International Congress on the Chemistry of Cement, Washington, D.C., USA, Monograph 43, Vol. II, Session VI, Paper VI-S2, pp. 855-869.
- [30] GRÜBL, P. and STOKIN, A. (1980), *Rapid ice formation in hardened cement paste, mortar and concrete due to supercooling*, Cement and Concrete Research, Vol. 10, N° 3, pp. 333-345.
- [31] SELLEVOLD, E.J. and BAGER, D.H. (1985), *Some implications of calorimetric ice formation results for frost resistance testing of cement products*, Technical Report 86/80, The Technical University of Denmark, Building Materials Laboratory, 28 p.
- [32] VERBECK, G. and KLIEGER, P. (1958), *Calorimeter-strain apparatus for study of freezing and thawing concrete*, Highway Research Board Bulletin, N° 176, pp. 9-22.
- [33] LE SAGE DE FONTENAY, C. and SELLEVOLD, E.J. (1980), *Ice formation in hardened cement paste—Part I: Mature water-saturated systems*, Durability of Building Materials and Components, ASTM Special Technical Publication STP-691, Edited by P.J. Sereda and G.G. Litvan, pp. 425-438.
- [34] DIAMOND, S. (1976), *Cement paste microstructure: An overview at several levels*, Proceedings of the Conference on Hydraulic Cement Paste — Their Structure and Properties, Sheffield, England, British Cement and Concrete Association, pp. 2-30.

- [35] ALFORD, N. McN and RAHMAN, A.A. (1981), *An assessment of porosity and pore sizes in hardened cement pastes*, Journal of Materials Science, Vol. 16, N° 11, pp. 3105-3114.
- [36] AGUIRRE-PUENTE, J. and DUPAS, A. (1972), *Vitesse critique du front de congélation dans des milieux poreux fins*, Bulletin de Liaison du Laboratoire des Ponts et Chaussées, Vol. 61, Septembre-Octobre, pp. 145-154, (in French).
- [37] BUIL, M. and AGUIRRE-PUENTE, J. (1981), *Thermodynamic and experimental study of the crystal growth of ice*, Proceedings of the American Society of Mechanical Engineers Winter Annual Meeting, Washington, D.C., USA, 7 p.
- [38] SELLEVOLD, E.J. and BAGER, D.H. (1980), *Low temperature calorimetry as a pore structure probe*, Proceedings of the Seventh International Congress on the Chemistry of Cement, Paris, France, Vol. 4, pp. 394-399.
- [39] BAGER, D. and SELLEVOLD, E.J. (1980), *Ice formation in hardened cement paste—Part II: Steam-cured pastes with variable moisture contents*, *Durability of Building Materials and Components*, ASTM Special Technical Publication STP-691, Edited by P.J. Sereda and G.G. Litvan, pp. 439-454.
- [40] POWERS, T.C. and BROWNYWARD, T.L. (1946), *Studies of the physical properties of hardened portland cement paste — Part 8: The freezing of water in hardened portland cement paste*, Journal of the American Concrete Institute, Vol. 18, N° 8, pp. 934-969.
- [41] ZECH, B. and SETZER, M.J. (1989), *The dynamic modulus of hardened cement paste — Part 2: Ice formation, drying and pore size distribution*, Materials and Structures/Matériaux et Constructions, Vol. 22, pp. 125-132.
- [42] BEDDOE, R.E. and SETZER, M.J. (1990), *Phase transformations of water in hardened cement paste — A low temperature DSC investigation*, Cement and Concrete Research, Vol. 20, N° 2, pp. 236-242.
- [43] MACINNIS, C. and BEAUDOIN, J.J. (1968), *Effect of the degree of saturation on the frost resistance of mortar mixes*, Journal of the American Concrete Institute, Vol. 68, N° 3, pp. 203-207.
- [44] RADJY, F. and RICHARDS, C. (1973), *Effect of curing and heat treatment history on the dynamic mechanical response and the pore structure of hardened cement paste*, Cement and Concrete Research, Vol. 3, N° 1, pp. 7-21.
- [45] BRAY, W.H. and SELLEVOLD, E.J. (1973), *Water sorption properties of hardened cement paste cured and stored at elevated temperatures*, Cement and Concrete Research, Vol. 3, N° 6, pp. 723-728.
- [46] SELLEVOLD, E.J. (1974), *Mercury porosimetry of hardened cement paste cured or stored at 97°C*, Cement and Concrete Research, Vol. 4, N° 3, pp. 399-404.

- [47] BAGER, D.H. and SELLEVOLD, E.J. (1986), *Ice formation in hardened cement paste - Part II: Drying and resaturation of room temperature cured paste*, Cement and Concrete Research, Vol. 16, N° 6, pp. 835-844.
- [48] BAGER, D.H. and SELLEVOLD, E.J. (1986), *Ice formation in hardened cement paste — Part III: Slow resaturation of room temperature cured paste*, Cement and Concrete Research, Vol. 17, N° 1, pp. 1-11.
- [49] VUORINEN, J. (1970), *On the use of the dilation factor and degree of saturation in testing concrete for frost resistance*, Nordisk Betong, Vol. 1, pp. 37-64.
- [50] SELLEVOLD, E.J. and RADJY, F. (1976), *Drying and resaturation effects on internal friction in hardened cement pastes*, Journal of the American Ceramic Society, Vol. 59, N° 5-6, pp. 256-258.
- [51] YOUNG, J.F. (1986), *Physical mechanisms and their mathematical description*, Proceedings of the Fourth RILEM International Symposium on Creep and Shrinkage of Concrete — Mathematical Modeling, Edited by Z.P. Bazant, pp. 43-78.
- [52] PARROTT, L.J., HANSEN, W. and BERGER, R.L. (1980), *Effect of first drying upon the pore structure of hydrated alite paste*, Cement and Concrete Research, Vol. 10, N° 5, pp. 647-656.
- [53] PARROTT, L.J. (1981), *Effect of drying history upon the exchange of pore water with methanol and upon subsequent sorption behaviour in hydrated alite paste*, Cement and Concrete Research, Vol. 11, pp. 651-658.
- [54] FELDMAN, R.F. (1988), *Effect of pre-drying on rate of water replacement from cement paste by propan-2-ol*, Il Cemento, N° 3, pp. 193-201.
- [55] POWERS, T.C. (1945), *A working hypothesis for further studies of frost resistance of concrete*, Journal of the American Concrete Institute, Vol. 16, N° 4, pp. 245-272.
- [56] VERBECK, G. and KLIEGER, P. (1957), *Studies of "salt" scaling of concrete*, Highway Research Board Bulletin, N° 150, pp. 1-17.
- [57] BROWNE, F.P. and CADY, P.D. (1975), *Deicer scaling mechanisms in concrete*, American Concrete Institute Special Publication SP-47, pp. 101-119.
- [58] PIGEON, M., PLEAU, R. and AITCIN, P.C. (1986), *Freeze-thaw durability of concrete with and without silica fume in ASTM C666 (Procedure A) test method: Internal cracking versus scaling*, Cement, Concrete and Aggregates, Vol. 8, N° 2, pp. 76-85.
- [59] GARRECHT, H., HILSDORF, H.K. and KROPP, J. (1990), *Hygroscopic salts — Influence on the moisture behaviour of structural elements*, Proceedings of the Fifth International Conference on the Durability of Building Materials and Components, Brighton, Edited by J.M. Baker, P.J. Nixon, A.J. Madjumdar and H. Davies, E. & F.N. Spon, pp. 313-324.

30 Marchand, Sellevold, and Pigeon

- [60] MACINNIS, C. and WHITING, J.D. (1979), *The frost resistance of concrete subjected to a deicing agent*, Cement and Concrete Research, Vol. 9, N° 3, pp. 325-336.
- [61] LITVAN, G.G. (1975), *Phase transitions of adorbates — Part VI: Effect of deicing agents on the freezing of cement paste*, Journal of the American Ceramic Society, Vol. 58, N° 1-2, pp. 26-30.
- [62] SELLEVOLD, E.J. and FARSTAD, T. (1991), *Frost/salt testing of concrete: Effect of test parameters and concrete moisture history*, Nordic Concrete Research, Vol. 10, pp.121-138.
- [63] PETERSSON, P.E. (1986), *The influence of silica fume on the salt frost resistance of concrete*, Technical Report SP-RAPP 1986:32, Swedish National Testing Institute, Division of Building Technology, 18 p.
- [64] FAGERLUND, G. (1992), *Studies of the scaling, the water uptake and the dilation of mortar specimens exposed to freezing and thawing in NaCl solutions*, Proceedings of RILEM TC-117 Research Seminar, Lund, Sweden, Edited by G. Fagerlund and M.J. Setzer. pp. 36-66.
- [65] BEDDOE, R.E and SETZER, M.J. (1988), *A low-temperature DSC investigation of hardened cement paste subjected to chloride action*, Cement and Concrete Research, Vol. 18, N° 2, pp. 249-256.
- [66] SMOLCZYK, H.G. (1968), *Chemical reaction of strong chloride solutions with concrete*, Proceedings of the Fifth International Congress on the Chemistry of Cement, Tokyo, Japan, Vol. III, Paper 31, pp. 274-280.
- [67] CHATTERJI, S. (1978), *Mechanisms of the CaCl₂ attack on portland cement concrete*, Cement and Concrete Research, Vol. 8, N° 4, pp. 461-468.
- [68] HOFFMANN, D.W. (1984), *Changes in structure and chemistry of cement mortars stressed by a sodium chloride solution*, Cement and Concrete Research, Vol. 14, N° 1, pp. 49-56.
- [69] GÉGOUT, P., REVERTÉGAT, E. and MOINE, G. (1992), *Action of chloride ions in cement pastes: Influence of the cement type and long time effect of the concentration of chlorides*, Cement and Concrete Research, Vol. 22, N° 2-3, pp. 451-457.
- [70] GAGNÉ, R., PIGEON, M., REVERTÉGAT, E. and AITCIN, P.C. (1992), *Chloride-ion attack on low water-cement ratio pastes containing silica fume*, American Concrete Institute Special Publication SP-132, Edited by V.M. Malhotra, pp. 1471-1490.
- [71] POWERS, T.C. (1949), *The Air Requirement of Frost Resistant Concrete*, Proceedings of the Highway Research Board, Vol. 29, pp. 184-211.
- [72] BEAUDOIN, J.J. and MACINNIS, C. (1974), *The mechanism of frost damage in hardened cement paste*, Cement and Concrete Research, Vol. 4, N° 2, pp. 139-147.

- [73] HELMUTH, R.A. (1960), *Discussion of Paper VI-2 "Frost action in concrete"*, Proceedings of the Fourth International Congress on the Chemistry of Cement, Washington, D.C., USA, Vol. 2, Theme VI, pp. 829-833.
- [74] PIGEON, M, PRÉVOST, J. and SIMARD, J.M. (1986), *Freeze-thaw durability vs freezing rate*, Journal of the American Concrete Institute, Vol. 82, N° 5, pp. 684-692.
- [75] POWERS, T.C. and HELMUTH, R.A. (1953), *Theory of Volume Changes in Hardened Cement Paste During Freezing*, Proceedings of the Highway Research Board, Vol. 32, pp. 285-297.
- [76] STARK, D. (1989), *Effect of length of freezing period on durability of concrete*, Portland Cement Association, Research and Development Bulletin RD096, 9 p.
- [77] FAGERLUND, G. (1975), *Studies of the destruction mechanisms at freezing of porous materials*, Proceedings of the Sixth International Congress on the Problems Raised by Frost Action, Le Havre, France, Fondation Française d'Etudes Nordiques, pp. 166-196.
- [78] LITVAN, G.G. (1972), *Phase Transitions of Adsorbates: IV, Mechanism of Frost Action in Hardened Cement Paste*, Journal of the American Ceramic Society, Vol. 55, N°. 1, pp. 38-42.
- [79] LITVAN, G.G. (1973), *Frost action in cement paste*, Materials and Structures/Matériaux et Constructions, Vol. 34, pp. 3-8.
- [80] LITVAN, G.G. (1980), *Freeze-Thaw Durability of Porous Building Materials*, Durability of Building Materials and Components, Durability of Building Materials and Components, ASTM Special Technical Publication STP-691, Edited by P.J. Sereda and G.G. Litvan, pp. 455-463.
- [81] SETZER, M.J. (1976), *A new approach to describe frost action in hardened cement paste and concrete*, Proceedings of the Conference on Hydraulic Cement Paste — Their Structure and Properties, Sheffield, England, British Cement and Concrete Association, pp.313-325.
- [82] HUDEC, P.P., MACINNIS, C. and ACHAMPONG, F. (1992), *Evaluation of various concrete deicers*, Proceedings of the Ninth International Congress on the Chemistry of Cement, New Delhi, India, Vol. 5, Theme IV-C, pp. 289-295.
- [83] RÖSLI, A. and HARNIK, A.B. (1980), *Improving the durability of concrete to freezing and deicing salts*, Durability of Building Materials and Components, Durability of Building Materials and Components, ASTM Special Technical Publication STP-691, Edited by P.J. Sereda and G.G. Litvan, pp. 464-473.
- [84] MOUKWA, M. and ADKINS, D.F. (1988), *New Approach for a Concrete Scaling Test Based on Field Conditions*, Cement, Concrete and Aggregates, Vol. 10, N° 2, pp. 103-108.

- [85] ADKINS, D.F. (1986), *Laboratory duplication of surface scaling*, Concrete International, Vol. 2, February, pp. 35-39.
- [86] PETERSSON, P.E. (1991), *Scaling resistance of concrete: Testing according to SS 13 72 44*, Proceedings of RILEM TC-117 Research Seminar, Lund, Sweden, Edited by G. Fagerlund and M.J. Setzer, pp. 103-116.
- [87] AMERICAN SOCIETY FOR TESTING AND MATERIALS (1984), *Standard Test Method for scaling resistance of concrete surfaces exposed to deicing chemicals*, American Society for Testing and Materials, ASTM Standard C672, Annual Book of ASTM Standards, Vol. 4.
- [88] O-NORM (1982), *Prüfung der Frost-Tausalz-Beständigkeit von vorgefertigten Betonner-zeugnissen.*, O-NORM B 3306, pp. 24-25.
- [89] ISO/DIS 4846, *Concrete: Determination of scaling resistance of surfaces exposed to de-icing chemicals*.
- [90] CANADIAN STANDARD ASSOCIATION (1990), *Scaling resistance of concrete surfaces exposed to deicing chemicals*, Canadian Standard Association, CAN3 A23.2-16C.
- [91] PLAHN, J. and GOLZ, W. (1984), *Vergleichsuntersuchungen an vier Prüfverfahren für den Frost-Tausalz-Widerstand von Beton*, Straße und Autobahn, Vol. 35, pp. 14-21 (in German).
- [92] SETZER, M.J. and SCHRAGE, I. (1991), *Testing for frost de-icing salt resistance of concrete paving blocks*, Concrete Precast Plant and Technology, Vol. 57, N° 6, pp. 58-69.
- [93] SETZER, M.J. and HARTMANN, V. (1991), *Improved frost/de-icing salt resistance testing*, Concrete Precast Plant and Technology, Vol. 57, N° 9, pp. 73-82.
- [94] PETERSSON, P.E. (1984), *The salt-frost resistance of concrete: A comparison of three test methods*, Technical Report SP-RAPP 1986:07E ISSN 0280-2503, Swedish National Testing Institute, Division of Building Technology, 51 p.
- [95] SIS (1992), *Concrete testing - Hardened concrete - Frost resistance*, Standardiserings-kommissionen i Sverige, Swedish Standard SS 13 72 44.
- [96] CANADIAN STANDARD ASSOCIATION (1985), *Precast Concrete Paving Blocks*, Canadian Standard Association, CAN3 A231.2 M85.
- [97] SIEBEL, E. and NECK, U. (1990), *Durability of paving setts and flagstones*, Concrete Precasting Plant and Technology, Vol. 56, N° 8, pp. 34-38.
- [98] MIELENZ, R.C. (1968), *Significance of accelerated durability tests of concrete*, Proceedings of the U.S.-Japan Joint Seminar on Research on Basic Properties of Concrete, Tokyo, Japan, pp. 17-34.
- [99] SCHUBERT, P. and LÜHR, H.P. (1976), *Zur Prüfung von Betonwaren für den Straßenbau auf Frost und Tausalzwiderstand (Part I)*, Concrete Precast Plant and Technology, Vol. 42, N° 11, pp. 546-550.

- [100] SCHUBERT, P. and LÜHR, H.P. (1976), *Zur Prüfung von Betonwaren für den Straßenbau auf Frost und Tausalz widerstand (Part II)*, Concrete Precast Plant and Technology, Vol. 42, N° 12, pp. 604-608.
- [101] LITVAN, G.G., MACINNIS, C. and GRATTAN-BELLEW, P.E. (1980), *Cooperative test programme for precast concrete paving elements*, Durability of Building Materials and Components, ASTM Special Technical Publication STP-691, Edited by P.J. Sereda and G.G. Litvan, pp. 560-573.
- [102] ROSE, K., HOPE, B.B. and IP, A.K.C. (1989), *Statistical analysis of strength and durability of concrete made with different cements*, Cement and Concrete Research, Vol. 19, N° 3, pp. 476-486.
- [103] FAGERLUND, G. (1986), *Effect of air-entraining and other admixtures on the salt-scaling resistance of concrete*, Paper presented at the International Seminar on "Some Aspects of Admixtures and Industrial By-Products on the Durability of Concrete", Göteborg, Sweden, 33 p.
- [104] SARKAR, S.L. (1990), *Effect of Blaine fineness reversal on strength and hydration of cement*, Cement Concrete Research, Vol. 20, N° 3, pp. 398-406.
- [105] MALMSTRÖM, K. (1990), *The importance of cement composition on the salt-frost resistance of concrete*, Technical Report SP-RAPP 1990:07, Swedish National Testing Institute, Division of Building Technology, (in Swedish with abstract in English).
- [106] PISTILLI, M.F. (1983), *Air-void parameters developed by air-entraining admixtures as influenced by soluble alkalies from fly ash and portland cement*, Journal of the American Concrete Institute, Vol. 80, N° 3, pp. 217-222.
- [107] JACKSON, F.H. (1958), *Long-time study of cement performance in concrete — Chapter 11: Report on the condition of three test pavements after 15 years of service*, Journal of the American Concrete Institute, Vol. 29, N° 12, pp. 1017-1032.
- [108] PIGEON, M., PLANTE, P., PLEAU, R. and BANTHIA, N. (1992), *Influence of soluble alkalies on the production and stability of the air-void system in superplasticized and nonsuperplasticized concrete*, Journal of the American Concrete Institute, Vol. 89, N° 1, pp. 24-31.
- [109] PIGEON, M., PERRATON, D. and PLEAU, R. (1987), *Scaling test of silica fume concrete and the critical spacing factor concept*, ACI Special Publication SP-100, Edited by J. Scanlon, pp. 1155-1182.
- [110] BILODEAU, A. and CARRETTE, G.G. (1989), *Resistance of condensed silica fume concrete to the combined action of freezing and thawing cycling and deicing salts*, ACI Special Publication SP-114, Edited by V.M. Malhotra, pp. 945-969.
- [111] HAMMER, T.A. and SELLEVOLD, E.J. (1990), *Frost Resistance of High-Strength Concrete*, Proceedings of the Second International Symposium on the Utilization of High-Strength Concrete, ACI Special Publication SP-121, Edited by W. T. Hester, pp. 457-487.

- [112] VIRTANEN, J. (1990), *Field study on the effects of additions on the salt scaling resistance of concrete*, Nordic Concrete Research, Vol. 9, pp. 197-212.
- [113] AITCIN, P.C. and PIGEON, M. (1986), *Performance of condensed silica fume concrete used in pavements and sidewalks*, Durability of Building Materials, Vol. 4, N° 3, pp. 353-368.
- [114] GEBLER, S.H. and KIEGER, P. (1986), *Effect of fly ash on the durability of air-entrained concrete*, ACI Special Publication SP-91, Edited by V.M. Malhotra, pp. 483-519.
- [115] KIEGER, P. and GEBLER, S.H. (1987), *Fly ash and concrete durability*, ACI Special Publication SP-100, Edited by J. Scanlon, pp. 1043-1069.
- [116] WHITING, D. (1989), *Deicer salt scaling resistance of lean concrete containing fly ash*, ACI Special Publication SP-114, Edited by V.M. Malhotra, pp. 349-372.
- [117] BILODEAU, A. and MALHOTRA, V.M. (1992), *Concretes incorporating high volumes of ASTM Class F fly ashes: Mechanical properties and resistance to deicing salt scaling and to chloride penetration*, ACI Special Publication SP-132, Edited by V.M. Malhotra, pp. 319-349.
- [118] BILODEAU, A., CARETTE, G.G., MALHOTRA, V.M. and LANGLEY, W.S. (1991), *Influence of curing and drying on the salt scaling resistance of fly ash concrete*, ACI Special Publication SP-126, Edited by V.M. Malhotra, pp. 201-228.
- [119] MALHOTRA, V.M. (1993), Personal communication.
- [120] GEBLER, S.H. and KIEGER, P. (1983), *Effect of fly ash on the air-void stability of concrete*, ACI Special Publication SP-79, Edited by V.M. Malhotra, pp. 103-142.
- [121] STURRUP, V.L., HOOTON, R.D. and CLENNDENNING, T.G. (1983), *Durability of fly ash concrete*, ACI Special Publication SP-79, Edited by V.M. Malhotra, pp. 71-86.
- [122] UCHIKAWA, H., UCHIDA, S. and OGAWA, K. (1982), *Characteristics of fly ash and adsorption properties of several organic additives*, C.A.J. Review of the Thirty-Sixth General Meeting, Technical Session, pp. 38-40.
- [123] FAGERLUND, G. (1989), *Effect of industrial by-products on the frost resistance of concrete*, Proceedings of the Second International Seminar on the Durability of Concrete — Aspects of admixtures and Industrial By-Products, Swedish Council for Building Research, Document D9:1989, pp. 33-52.
- [124] GUNTER, M., BIER, T. and HILSDORF, H. (1987), *Effect of curing and type of cement on the resistance of concrete to freezing in deicing salt solutions*, ACI Special Publication SP-100, Edited by J. Scanlon, pp. 877-899.

- [125] LITVAN, G.G. and MEYER, A. (1986), *Carbonation of granulated blast furnace slag cement concrete during twenty years of field exposure*, ACI Special Publication SP-91, Edited by V.M. Malhotra, pp. 1445-1462.
- [126] JOHNSTON, C. (1987), *Effects of microsilica and class C fly ash on resistance of concrete to rapid freezing and thawing and scaling in the presence of deicing agents*, ACI Special Publication SP-100, Edited by J. Scanlon, pp. 1183-1204.
- [127] WHITING, D. and SCHMITT, J. (1989), *A model for deicer scaling resistance of field concrete containing high-range water reducers*, ACI Special Publication SP-119, Edited by V.M. Malhotra, pp. 343-359.
- [128] GAGNÉ, R., PIGEON, M. and AITCIN, P.C. (1990), *Deicer salt scaling resistance of high-performance concrete*, ACI Special Publication SP-122, Edited by D. Whiting, pp. 29-44.
- [129] GAGNÉ, R., PIGEON, M. and AITCIN, P.C. (1991), *Deicer salt scaling resistance of high-strength concretes made with different cements*, ACI Special Publication SP-126, Edited by V.M. Malhotra, pp. 185-199.
- [130] FOY, C., PIGEON, M. and BANTHIA, N. (1988), *Freeze-thaw durability and deicer salt scaling resistance of a 0.25 water-cement ratio concrete*, Cement and Concrete Research, Vol. 18, N° 4, pp. 604-614.
- [131] PIGEON, M. and MARCHAND, J. (1993), *The frost durability of dry concrete*, Report GCS-93-06, Department of Civil Engineering, Laval University, 196 p.
- [132] MARCHAND, J., HORNAIN, H., PIGEON, M., GUIRAUD, H. and MADI, R. (1993), *The microstructure of dry concrete products*, Third Canadian Symposium on Cement and Concrete, August 3-4, Ottawa, Canada, pp. 177-195.
- [133] JACOBSEN, S., FARSTAD, T., GRAN, H.C. and SELLEVOLD, E.J. (1992), *Frost/salt scaling of no-slump concrete: Effect of strength, air entraining agent and condensed silica fume*, Nordic Concrete Research, Vol. 11, 15 p.
- [134] BOISVERT, J., MARCHAND, J., PIGEON, M. and ISABELLE, H.L. (1992), *Durabilité au gel-dégel et résistance à l'écaillage des pavés de béton*, Canadian Journal of Civil Engineering, Vol. 19, pp. 1017-1024, (in French).
- [135] MARCHAND, J., BOISVERT, J., PIGEON, M. and ISABELLE, H.L. (1991), *Deicer salt scaling resistance of roller-compacted concrete pavements*, ACI Special Publication SP-126, Edited by V.M. Malhotra, pp. 131-153.
- [136] MARCHAND, J., PIGEON, M., BOISVERT, J., ISABELLE, H.L., and HOUDUSSE, O. (1992), *Deicer salt scaling resistance of roller-compacted concrete pavements containing fly ash and silica fume*, ACI Special Publication SP-132, Edited by V.M. Malhotra, pp. 151-178.
- [137] KLIEGER, P. (1980), *Durability studies at the Portland Cement Association*, *Durability of Building Materials and Components*, ASTM Special Technical Publication STP-691, Edited by P.J. Sereda and G.G. Litvan, pp. 282-300.

- [138] MATHER, B. (1990), *How to make concrete that will be immune to the effects of freezing and thawing*, ACI Special Publication SP-122, Edited by D. Whiting, pp. 1-18.
- [139] FOURNIER, B., BÉRUBÉ, M.A. and VÉZINA, D. (1987), *Condition survey of concrete structures built with potentially alkali-reactive limestones aggregates from the Québec City area (Québec, Canada)*, ACI Special Publication SP-100, Edited by J. Scanlon, pp. 1343-1361.
- [140] GAGNÉ, R. (1992), *Frost durability of high-performance concrete*, Ph. D. Thesis, Department of Civil Engineering, Laval University, 434 p. (in French).
- [141] WHITING, D. (1983), *Control of air content in concrete: State of the art report*, Appendum to NCHRP Report 258, National Cooperative Highway Research Program, 263 p.
- [142] PLANTE, P., PIGEON, M. and FOY, C. (1989), *Influence of water-reducers on the production and stability of the air void system in concrete*, Cement and Concrete Research, Vol. 19, pp. 621-633.
- [143] PETERSSON, P.E. (1989), *The use of air-entraining and plasticizing admixtures for producing concrete with good salt-frost resistance*, Technical Report SP-RAPP 1989:37, Swedish National Testing Institute, Division of Building Technology, 15 p.
- [144] SIEBEL, E. (1989), *Air-void characteristics and freezing and thawing resistance of superplasticized air-entrained concrete with high workability*, ACI Special Publication SP-119, Edited by V.M. Malhotra, pp. 297-319.
- [145] PLANTE, P., PIGEON, M. and SAUCIER, F. (1989), *Air-void stability — Part II: Influence of superplasticizers and cement*, Journal of the American Concrete Institute, Vol. 86, N° 6, pp. 581-589.
- [146] LANGLOIS, M., BEAUPRÉ, D., PIGEON, M. and FOY, C. (1989), *The influence of curing on the salt scaling resistance of concrete with and without silica fume*, ACI Special Publication SP-114, Edited by V.M. Malhotra, pp. 971-990.
- [147] JACOBSEN, S. and SELLEVOLD, E.J. (1992), *Frost/salt scaling of concrete: Effect of curing temperature and condensed silica fume on normal and high-strength concrete*, Fourth ACI/CANMET International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Supplementary Papers, pp. 369-384.
- [148] VÉZINA, D., BEAUPRÉ, D. and PIGEON, M. (1991), *Influence de l'âge au démoulage et du type de moule sur la résistance à l'écaillage de bétons contenant de la fumée de silice*, Canadian Journal of Civil Engineering, Vol. 18, pp. 575-580, (in French).
- [149] FAGERLUND, G. (1971), *Le degré critique de saturation — Un outil pour l'estimation de la résistance au gel des matériaux de construction*, Materials and Structures/Matériaux et Constructions, Vol. 4, N° 23, pp. 271-285, (in French).

- [150] PERENCHIO, W.F. (1988), *Durability of concrete treated with silanes*, Concrete International, November, pp. 34-40.
- [151] SEDRAN, T., PIGEON, M. and HAZRATI, K. (1993), *The influence of penetrating sealers on the deicer salt scaling resistance of concrete*, Accepted for publication in the Proceedings of the Sixth International Conference on Durability of Building Materials and Components, Omiya, Japan, 10 p.
- [152] KLIEGER, P. and PERENCHIO, W. (1963), *Silicone influence on the concrete resistance to freeze-thaw and de-icer damage*, Highway Research Record, N° 18, pp. 33-47.
- [153] WONG, A.Y.C., ANDERSON, C.L. and HILSDORF, H.K. (1973), *The effect of drying on the freeze-thaw durability of concrete*, Engineering Experiment Station Bulletin 506, University of Illinois, 41 p.
- [154] PETERSSON, P.E. (1992), *Scaling resistance of concrete — Influence of curing conditions*, Meeting of RILEM TC 117 Task Group, Dübendorf, October.
- [155] SORENSEN, E.G. (1983), *Freezing and thawing resistance of condensed silica fume (microsilica) concrete exposed to deicing chemicals*, ACI Special Publication SP-79, Edited by V.M. Malhotra, pp. 709-718.

TABLE 1 — PROPOSED CLASSIFICATION OF PORE SIZES (ACCORDING TO REF. 9)

Name	Upper radius	Type of pore water
Macro capillaries	2 mm	Macroscopic bulk water
Meso capillaries	50 μm	
Micro capillaries	2 μm	
Mesopores	50 nm	Condensed water
Micropores	2 nm	Structured surface water

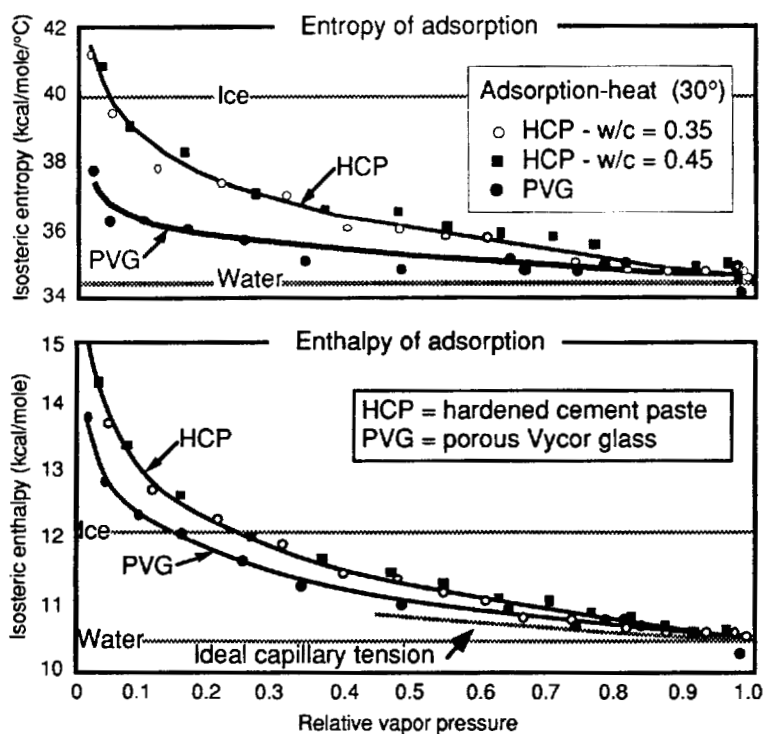


Fig. 1—Differential entropy and enthalpy of pore water in hydrated cement paste (HCP) and porous Vycor glass (from Ref. 10)

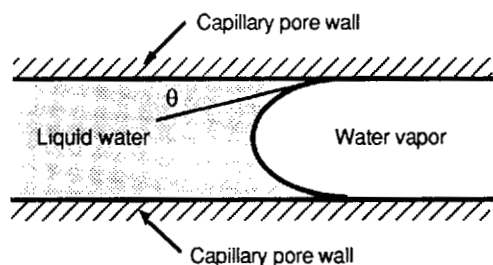


Fig. 2—Curved liquid water-water vapor interface in a capillary pore partially filled with water