

1997 CANMET/ACI

INTERNATIONAL • CONFERENCE • INTERNATIONALE



**DURABILITY
OF
CONCRETE**

**DURABILITÉ
DU
BÉTON**

EDITOR • V.M. MALHOTRA • RÉDACTEUR EN CHEF

Documents
Document Sharing Hub

SP-170 VOL I-ENGL 1997 0662949 0532603 057
Full document details: ACI SP-170-97

Durability of Concrete

Proceedings Fourth CANMET/ACI International Conference Sydney, Australia, 1997

Editor

V. M. Malhotra

Volume 1



SP - 170

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 July 1, 1998. All discussion approved by the Technical Activities Committee along with closing remarks by the authors will be published in the November / December 1998 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 © 1997
AMERICAN CONCRETE INSTITUTE
P.O. Box 9094
Farmington Hills, Michigan 48333

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 Julie Carpenter

Library of Congress catalog card number 97-072250

PREFACE

The Canada Centre for Mineral and Energy Technology (CANMET) of Natural Resources Canada, Ottawa, has played a significant role in Canada for over 33 years in the area of durability of concrete. In August 1991, CANMET in association with the American Concrete Institute, Institute for Research in Construction/National Research Council, Ottawa, sponsored the second CANMET/ACI International Conference on Durability of Concrete. The conference was held August 4-9, 1991, in Montreal, Canada, and was a follow-up of the Katherine 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. The refereed proceedings of the Atlanta and Montreal conferences were published as ACI SP-100 and ACI SP-126, respectively.

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. The proceedings of the of the conference consisting of 65 refereed papers were published as ACI SP-145.

In 1997, CANMET in association with the American Concrete Institute and several other organizations in Australia sponsored the Fourth International Conference on the subject. The conference was held in Sydney, Australia. More than 120 papers from 30 countries were received and peer reviewed in accordance with the policies of the American Concrete Institute; 81 were accepted for publication. The accepted papers deal with all aspects of durability of concrete, including chloride and sulphate attack, freezing and thawing cycling, alkali-aggregate reactions, cathodic protection, and the role of supplementary cementing materials to enhance durability of concrete. A number of papers dealt with the durability of fiber-reinforced concrete and performance of repaired concrete structures. 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.

In addition to the papers which have been published in the refereed proceedings, more than 30 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 20 members of the review panel which met in Casablanca, Morocco in May 1996 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), 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. Brearly for their help in the processing of manuscripts, both for the ACI proceedings and the supplementary volume. The contribution of Helayne Beavers, Managing Editor, ACI, and her staff to publish the proceedings on time is recognized.

As an integral part of the conference, a special dinner to honor Mr. W. G. (Mick) Ryan, Consultant, MacMasters Beach, Australia, for his outstanding contributions over 40 years in the area of concrete technology was held during the conference.

V.M. Malhotra, P.Eng.
Editor
Chairman, CANMET/ACI Fourth International Conference
on Durability of Concrete
August 1997

International Organizing Committee
Fourth CANMET/ACI International Conference
on
Durability of Concrete
Sydney, Australia
1997

V.M. Malhotra
Chairman

H.S. Wilson
Secretary-Treasurer

Members
T.W. Bremner
H.L. Isabelle
Wilbert S. Langley
V.S. Ramachandran

CONTENTS

PREFACE
by V. M. Malhotra iii

LONG-TERM INFLUENCE OF FLY ASH ON CHLORIDE-INDUCED CORROSION
by Peter Schießl and Udo Wiens 1

FIELD EVALUATION OF AN ACRYLIC RUBBER PROTECTIVE COATING SYSTEM FOR REINFORCED
CONCRETE STRUCTURES
by Y. Yamada, T. Oshiro, S. Tanikawa and R. N. Swamy 23

QUANTITATIVE DESCRIPTIONS OF STEEL CORROSION IN CONCRETE USING RESISTIVITY AND
ANODIC POLARISM DATA
by Daksh Baweja, Harold Roper and Vute Sirivivatnanon 65

THE EFFECT OF AIR-ENTRAINMENT ON A PUMPED, HIGH-STRENGTH CONCRETE USED IN A
SEVERE MARINE ENVIRONMENT
by G. C. Hoff and R. Elimov 64

IMPROVED DURABILITY OF HIGH-STRENGTH CONCRETE DUE TO AUTOGENOUS CURING
by S. Weber and H. W. Reinhardt 93

FLY ASH CONCRETES IN SOUTH-EAST ASIA
by Vute Sirivivatnanon and E. U. Kidav 123

EFFECT OF FLY ASH AND CORROSION INHIBITOR ON REINFORCED CONCRETE IN MARINE
ENVIRONMENTS
by Chau Lee and M. G. Lee 141

EFFECT OF SOURCE AND AMOUNT OF FLY ASH ON MECHANICAL AND DURABILITY PROPERTIES
OF CONCRETE
by Tarun R. Naik, Shiw S. Singh and Bruce Ramme 157

DURABILITY OF MORTARS AND CONCRETES CONTAINING GROUND CONVERTER SLAG
by Malolepszy J. Deja 189

EFFECTIVENESS OF MINERAL ADMIXTURES AND CURING REGIMES ON AIR PERMEABILITY OF CONCRETE

by R. N. Swamy and A. A. Darwish 207

INVESTIGATIONS INTO THE DURABILITY OF CORROSION PROTECTION BY EPOXY-COATINGS ON REINFORCEMENT

by J. Moersch, N. Brauer, C. Gehlen and Peter Schießl 231

INTRINSIC PERMEABILITY OF FLY ASH CONCRETE

by C. Y. Lee, M. J. McCarthy and R. K. Dhir 247

ADMIXTURES TO REDUCE THE PERMEABILITY OF CONCRETE

by Salil K. Roy and Derek O. Northwood 267

PERFORMANCE OF REINFORCED BLAST FURNACE SLAG CEMENT CONCRETE SPECIMENS AFTER 10-YEARS' EXPOSURE IN BAHRAIN

by N. H. Olsen and G. R. Summers 285

DURABLE CONCRETE CONTAINING THREE OR FOUR CEMENTITIOUS MATERIALS

by W. Barry Butler 309

INFLUENCE OF BINDER COMPOSITION ON CHLORIDE PENETRATION RESISTANCE OF CONCRETE

by P. F. McGrath and R. D. Hooton 331

CHLORIDE PENETRATION AND WATER ABSORPTION INTO P.C., FLY ASH AND SLAG CONCRETE UNDER DIFFERENT CURING CONDITIONS

by Z. Tian Chang and M. Marosszeky 349

INVESTIGATIONS ON THE THRESHOLD VALUE OF THE CRITICAL CHLORIDE CONTENT

by W. Breit and Peter Schießl 363

PREDICTING THE CORROSION OF STEEL IN CHLORIDE-CONTAMINATED CONCRETE

by Youping Liu and Richard E. Weyers 379

CHLORIDE-INDUCED CORROSION OF EPOXY COATED STEEL IN SATURATED $\text{Ca}(\text{OH})_2$ SOLUTION AND IN CONCRETE

by J. Havdahl, B. B. Hope and C. M. Hansson 397

APPLICATION OF RAPID CHLORIDE PERMEABILITY TEST TO EVALUATE THE CHLORIDE-ION PENETRATION INTO CONCRETE

by K. Torri, T. Sasatani and M. Kawamura 421

PRESTRESSED CONCRETE CYLINDER PIPES EXPOSED INTERNALLY TO AGGRESSIVE WATER

by A. A. Ibrahim, O. A. Abuazza and F. A. Tarrani 437

CHLORIDE THRESHOLD LEVELS, CORROSION RATES AND SERVICE LIFE FOR CRACKED HIGH-PERFORMANCE CONCRETE

by K. Pettersson and P. Sandberg 451

CORRELATIONS BETWEEN RAPID CHLORIDE TEST RESULTS AND ON-SITE CHLORIDE INGRESS

by M. G. Alexander and P. E. Streicher 473

DETERIORATION OF REINFORCED CONCRETE IN THE MARINE-INDUSTRIAL ENVIRONMENT OF THE ARABIAN GULF: A CASE STUDY

by Vladimir Novokshchenov 491

LIMITATION OF THE WATER CONTENT OF CONCRETE AS A REPAIR METHOD FOR REINFORCEMENT CORROSION IN CARBONATED CONCRETE

by Peter Schießl and R. Weydert 519

A CRITICAL REVIEW OF DETERIORATION OF CONCRETE DUE TO CORROSION OF REINFORCING STEEL

by Kimberly E. Kurtis and Kumar Mehta 535

NEW CORROSION PROTECTION SYSTEM FOR CONCRETE STRUCTURES USING NEWLY DEVELOPED ALLOY

by M. Funahashi, W. T. Young, M. R. Tighe, S. F. Daily and C. Firlotte 555

SYNERGY BETWEEN ALKALI-AGGREGATE REACTION AND OTHER DETERIORATION MECHANISMS IN CONCRETE

by M. D. A. Thomas 571

DURABILITY OF IKALINE PORTLAND CEMENT CONCRETE MADE WITH ALKALI-REACTIVE AGGREGATES

by P. K. Krivenko, N. M. Mhitaryan, V. V. Chirkova and E. P. Zgardan 587

ALKALI-AGREGATE RACTION IN THE ROADS AND TRAFFIC AUTHORITY BRIDGES, NSW, AUSTRAILIA

by A. Shayan and H. Morris 597

MICROSTRUCTURE OF CONCRETE FROM PAVEMENT CONTAINING ALKALI-REACTIVE CARBONATE AGGREGATE: AN SEM AND OPTICAL MICROSCOPE STUDY

by E. F. Duke, M. R. Hansen and D. P. Johnston 617

ESTIMATION OF DEPTH OF CONCRETE CARBONATION

by R. H. Zhang, T. Nakazawa and F. Imai 633

USE OF LITHIUM TO CONTROL EXPANSION DUE TO ALKALI-SILICA REACTION IN CONCRETE CONTAINING U. K. AGGREGATES

by B. Q. Blackwell, M. D. A. Thomas and A. Sutherland 649

DURABILITY EVALUATIONS AND PERFORMANCE HISTORIES OF PROJECTS USING POLYOLEFIN FIBER REINFORCED CONCRETE

by V. Ramakrishnan and C. N. MacDonald 665

USE OF HIGH VOLUME FLY ASH IN POLYPROPYLENE FIBER REINFORCED CONCRETE FOR SHOTCRETE APPLICATIONS

by M. H. Zhang, R. L. Chevrier, V. M. Malhotra and J. Mirza 681

SERVICE LIFE PREDICTION OF MARINE STRUCTURES

by Magne Maage, S. Helland and J. E. Carlsen 723

BEHAVIOR OF FIBER-REINFORCED CONCRETE BEAMS IN A HOT, DRY CLIMATE

by S. H. Alsayed and M. A. Al-Shihri 745

SPECIFICATIONS AND TESTING FOR CORROSION DURABILITY OF MARINE CONCRETE: THE AUSTRALIAN PERSPECTIVE

by F. G. Collins and W. R. Grace 757

A RATIONAL MODEL TO PREDICT THE SERVICE LIFE OF RC STRUCTURES IN A MARINE ENVIRONMENT

by K. Yokozeaki, K. Motohashi, K. Okada and T. Tsutsumi 777

SP 170-1

Long-Term Influence of Fly Ash on Chloride-Induced Corrosion

by Peter Schießl and Udo Wiens

Synopsis: The durability of reinforced concrete structures has been acquiring an increasing degree of emphasis in research activities. The development of concrete mixtures with regard to different attacks imposed on concrete structures by climatic influences plays a decisive role in this context. Under certain conditions, the performance of these concretes can be increased by using pozzolanic additions, such as fly ash or blast-furnace slag, as cementitious components. This publication intends to summarise the influence of these cementitious components on important processes contributing to chloride-induced corrosion. Diffusion and corrosion cells were used to examine the diffusion resistance and corrosion rate of mortars and concretes containing up to 60 mass.% of fly ash and up to 75 mass.% of blast-furnace slag in relation to the total content of cementitious binders. The results of pore structure investigations were also employed in order to clarify the influence of these cementitious components on ion transport in the microstructure of the concrete.

Keywords: Blast-furnace slag; chlorides; concrete; corrosion; diffusion; durability; fly ash; porosity.

2 Schießl and Wiens

ACI member Peter Schießl has a Ph. D. in civil engineering from Technical University in Munich and is Director of the Institute for Building Materials Research (Institut für Bauforschung, ibac) of the Aachen University of Technology (RWTH Aachen). Key research topics include concrete technology, utilization of industrial by-products, operational performance and durability of reinforced and prestressed concrete, corrosion, corrosion protection and repair. Professor Schießl chairs or sits in numerous national and international committees.

Udo Wiens has been a Research Engineer at the ibac since 1991. His field of activity includes research work on reaction mechanisms of fly ash and silica fume in concrete and the effect of these additions on chloride-induced corrosion.

INTRODUCTION

The service life of concrete structures exposed to chlorides (see-water, deicing salts, etc.) strongly depends on the quality of concrete cover. Prolonging the time to initiation of the corrosion process and reducing the corrosion rate once the corrosion process has started should be one of the primary aims when designing concrete mixtures for structures exposed to chlorides.

It is well known that the use of fly ash or blast-furnace slag improves the corrosion resistance of portland cement concretes (1,2). The main beneficial effect of fly ash is related to the refinement of the pore structure by the pozzolanic reaction reducing diffusion rates and electrolytic conductivity of concrete (3). Some authors have reported an increase in the chloride binding capacity when fly ash is added to the portland cement concretes (4,5). Most of the investigations done until now concentrate on the influence of fly ash on chloride binding or chloride transport. In this paper an approach is made to valuate the effects of fly ash on the transport and the physisorptive binding of chloride and the consequences for the corrosion of steel in concrete. Diffusion coefficients were determined on the mortar specimens by means of a rapid-test method. In concrete corrosion cells time-dependent corrosion currents and electrolytic resistances were measured. Additionally, pore structure analysis were carried out to support the explanation of the chloride transport and chloride binding phenomena. Parameters varied in this test series were the fly ash content and the type of cement. The results were compared and correlated with the extensive published data about oxygen diffusion and resistivity measurements (3,6,7).

EXPERIMENTAL

Materials and mixtures

For the mortar and concrete investigations, a portland cement (C1) with low-alkali content and two blast-furnace slag cements containing 46 and 74 mass.% of slag respectively (C2 and C3) in compliance with the requirements of German cement standard DIN 1164 were selected. The chemical composition of the fly ash corresponds to a low-calcium class F fly ash in accordance with ASTM C 618. Table 1 shows the physical and chemical properties of the binding components.

Table 2 summarises the composition of the examined mortars and concretes. The influence of fly ash content was examined by the combination of portland cement (C1) and 0, 20, 40 and 60 mass.% in relation to (c+f) of fly ash. In the case of the blast-furnace slag cement (C2) 20 mass.% of fly ash was used. No fly ash was added to the cement with the high-slag content (C3). Concretes containing this type of cement are known to possess a very high resistance against the penetration of chlorides and sulphates. It is also known that the pozzolanic reaction of the fly ash in conjunction with high-slag blast-furnace cements is only weak which means that the fly ash will not make any substantial contribution to the density of the pore structure (7).

Composition and production of the mortar mixtures were based on EN 196-1, using standard 0.08/2 mm sand. After mixing, prismatic moulds of $70 \times 70 \times 300 \text{ mm}^3$ were filled with mortar, compacted and stored in the vapour chamber (20 °C/95 % R.H.) for 1 day. After demoulding, the storage was continued under water of 20 °C until testing.

The water content of all concretes was kept constant at 180 kg/m^3 . An efficiency factor for the fly ash of $k = 0.5$ was incorporated into the calculated $w/(c+k \cdot f)$ value throughout. In this way, nearly the same compressive strength at 28 days was attained for all the concretes, with the exception of the concrete containing portland cement and 60 mass.% fly ash (see Table 2). Sand and gravel from the River Rhine was used as the aggregate. The grain size distribution of the concrete aggregates corresponded to grading curve A/B 16, in accordance with German standard DIN 1045.

The composition of cementitious components and the water/binder for the mortar and concrete mixtures were identical. The storage of the test specimens and the compressive strength tests were carried out on the concrete in accordance with German standard DIN 1048 (150-mm cubes). The test specimens used to determine time-dependent development of the electrolytic resistance and the

4 Schießl and Wiens

corrosion currents were stored at 20°C/80% R.H. after 2 days in the vapour chamber (20 °C/95% R.H.) and were then connected to a data-acquisition system.

Test procedures

The chloride-diffusion coefficients were determined by means of a rapid-test method developed by Tang and Nilsson, which is described in (8). The experimental set-up (migration cell) is shown in Fig. 1.

Before testing, cylinders of $\varnothing = 50$ and $h = 50$ mm were drilled from the mortar prisms and inserted into the test set-up. A voltage of 30 or 40 V (DC) was applied between anode and cathode, depending on the expected diffusion resistance. No increase in temperature of the solutions or in the measured current was detected during the tests. The chloride concentration in the cathode chamber was $c(\text{NaCl}) = 0.513$ mol/L (in $c(\text{KOH}) = 0.2$ mol/L) in all the tests. After a specified time, depending on the expected diffusion resistance, the cylindric mortar specimens were split along their longitudinal axis and the chloride penetration depths were determined by a colorimetric method described in (9). The calculation of the migration coefficients from the chloride penetration depth (x_d) is presented in (8). The transport coefficient determined with the aid of the migration cell is called D_{CLM} (M = migration).

The experimental set-up to determine the electrolytic resistance is described in (10). In contrast to the description in (10), corrosion cells measuring $200 \times 110 \times 110 \text{ mm}^3$ were used in the course of these tests. One mild steel St-37 (DIN EN 10 025, material No. 1.0037) and one platinised titanium rod (fully coated with $2.5 \text{ }\mu\text{m}$ platinum), measuring length $l = 180$ mm and diameter $\varnothing = 16$ mm served as electrodes (distance of electrodes: 20 mm). In all cases, one mass.% of chloride, related to the cement content, was added to the fresh concrete. A pore size distribution range between 1.8 nm and 150 μm was determined on mortar specimens by mercury intrusion porosimetry.

RESULTS AND DISCUSSION

Diffusion coefficients

The determination of diffusion coefficients for chloride by means of the rapid tests, whereby the chloride ions are driven into the test specimen via an electrical field, is a subject of controversy in the relevant literature (11,12). There is a lack of confirmed knowledge as to the precise processes which occur in such

migration tests. Charge transport in the electric field, for example, is effected not only via chloride ions, but also via other negatively charged ions (e.g. OH⁻ ions). The question as to how chloride binding processes are affected by the electrical field also remains unanswered.

Compared to conventional diffusion tests the rapid-test method has the advantage that the influence of the time-dependent changes in pore structure are eliminated. This is of particular interest with regard to additions, such as fly ash or blast-furnace slag, reacting over a long period. The pore structure of concrete and mortar with these materials changes over a period of years. It is thus often very difficult to specify the time at which a steady state prevails in conventional diffusion cells for determining intrinsic diffusion coefficients. Fig. 2 shows the time-dependent development of D_{CLM} dependent on cement type and fly ash content. Using an efficiency factor of 0.5 for fly ash ($w/(c+0.5 \cdot f) = 0.50$), nearly the same migration coefficients as for the corresponding reference mixtures without fly ash are attained at an age of 28 days, irrespective of the fly ash content. While the migration coefficients for the portland cement (C1) remain virtually unchanged over the test period, the migration coefficients for the mixtures containing fly ash fall markedly as the fly ash content increases. The use of blast-furnace slag is also accompanied by a rise in the diffusion resistance (C2).

The results of these tests together with the migration coefficients published in the relevant literature (5,8) show that the rapid test is highly suitable for characterising the diffusion resistance of concretes containing different additions. It should be taken into account, however, that in the case of slowly reacting additions, such as fly ash or blast-furnace slag, a migration coefficient determined from rapid tests after 28 days or earlier is unsuitable to describe the long-term behavior of these materials, as the pore structure of the concrete is continuously changing over years as a result of the slowly progressing reactions.

Fig. 2 also illustrates that a further reduction of the migration coefficients is possible when combining blast-furnace slag cement (C2) and fly ash. The increase in the diffusion resistance is less for the blast-furnace slag cement (C2) than for the portland cement (C1) at the same fly ash content (20 mass.%), however. This is due to the lower reactivity of the fly ash in the blast-furnace cement mixtures, caused by a lower content of $Ca(OH)_2$, a lower alkalinity of the pore solution and a denser pore structure (7). With the blast-furnace slag cement (C3) migration coefficients of 2.3, 1.7 and $0.3 \cdot 10^{-12} \text{ m}^2/\text{s}$ at 28, 91 and 365 days were measured, respectively. This is in the range of the mixture with blast-furnace slag cement (C2) and 20 mass.% fly ash.

The results of the migration test are essentially confirmed by the conventional diffusion tests (7,13). Fig. 3 shows the intrinsic chloride diffusion coefficients determined via conventional tests in relation to the duration of precuring and the fly ash content (7). It needs to be taken into account that the

test duration of the conventional diffusion test is in the range of several weeks to some month until the steady state is reached, i.e. the measured values for D_{Cl} are mean values over the test period.

When 20 and 40 mass.% portland cement is replaced by the same quantity of fly ash, the diffusion coefficients obtained in conventional tests fall by approximately one or more than one order of magnitude, after a precuring period of 365 days. The reductions measured in the migration test are in the same order of magnitude.

The higher reduction of the migration coefficients caused by the fly ash in the migration tests compared to the diffusion tests are accountable, among other things, to the fact that a fly ash efficiency factor $k = 0.5$ was incorporated into the water-cement ratio for the mixtures used in these tests (Fig. 2), resulting in a lower water/binder-ratio $w/(c+f)$ compared to the mixtures presented in Fig. 3.

The results of these tests together with the migration coefficients published in the relevant literature (8) show that the rapid test is highly suitable for characterising the diffusion resistance of concretes containing different additions.

Influence of pore structure on migration coefficients

Several authors report that the increase in the diffusion resistance of concrete resulting from the addition of fly ash is not accountable solely to the reduction in the capillary pore volume (7,14).

From Fig. 4 it can be derived, that at a given capillary pore volume (defined here as pores with a radius larger than 10 nm), a lower migration coefficient $D_{Cl,M}$ was usually determined as fly ash content increased. Even at relatively high capillary porosities as was measured for the mixture with 60 mass.% fly ash a significant reduction of the migration coefficients could be observed. The migration coefficient as well as the capillary porosity did not change for the reference mortar over the period of testing (28, 91 and 365 days), whereas the capillary porosity is reduced by fly ash on the behalf of the gel pore volume.

This behavior indicates a blocking of the pore channels connecting the capillary pore system due to the CSH-phases which are produced by the pozzolanic reaction. The pore parameter which should best reflect this effect is the threshold radius. This parameter determined by the mercury intrusion porosimetry characterises the pore radius below which a continuous network of pores exists. The smaller this value, the lower will be the continuity of the pore network. The good correlation between the migration coefficient and the threshold radius

confirms the model concept that permeability is reduced primarily through the reduction of this pore entry radius due to pozzolanic reaction of the fly ash (Fig. 5). The pozzolanic reaction of the fly ash distinctly reduces the threshold radius as compared to the reference mixture. The effect becomes more pronounced as fly ash content increases. This influence of fly ash occurs even with blast-furnace slag, but it is less significant with these cements, since the reaction of the slag has already densified the pore structure.

However, the movement of chloride ions in the microstructure of dense concrete is not solely restricted by the blocking of the pore channels. The sorptive binding of chloride in dense concrete is of decisive importance, too. To confirm this assumption the ratio oxygen diffusion coefficient/chloride migration coefficient, $D_{O_2}/D_{Cl,M}$, is plotted against the migration coefficient $D_{Cl,M}$ in Fig. 6. In the range of 9 and $13 \cdot 10^{-12}$ m²/s for $D_{Cl,M}$, the ratio $D_{O_2}/D_{Cl,M}$, nearly remains constant. As the resistance of the mortar to chloride diffusion increases, i.e. as $D_{Cl,M}$ falls below $9 \cdot 10^{-12}$ m²/s, the $D_{O_2}/D_{Cl,M}$ ratio grows disproportionately. Without restrictions by a porous medium, a ratio $D_{O_2,air}/D_{Cl,solution}$ of $\approx 10^4$ is to be expected (15). This is confirmed for migration coefficients of $D_{Cl,M}$ between 9 and $13 \cdot 10^{-12}$ m²/s, e.g. for cement paste of relatively high porosity (see dotted line in Fig. 6). If no interaction took place between the charged chloride ions and the pore walls, the $D_{O_2}/D_{Cl,M}$ ratio would have to remain constant at $\approx 10^4$, even at low chloride migration coefficients, as the oxygen diffusion coefficient would then have to be influenced to an equal degree by the reduction in permeability. Instead, the $D_{O_2}/D_{Cl,M}$ ratio increases substantially.

In view of the densification of the pore structure by supplying additional CSH from the pozzolanic reaction of fly ash, it is to be suspected that chloride transport is very severely inhibited by interactions between the electrostatically charged pore walls and the negatively charged chloride ions. These observations are confirmed by investigations carried out by Ngala et al. (14). For cement paste of low capillary porosity (with or without fly ash), a very substantial difference between oxygen and chloride diffusion coefficients was found (14). A similar result would be obtained, if the diffusion coefficients from Fig. 3 for the graph, instead of $D_{Cl,M}$ were used.

Importance of results for chloride-induced corrosion

Beside the transport of chloride ions the permeability of the pore structure is of decisive importance for processes involved in the corrosion of steel in concrete. One of the most important processes is the charge transport of hydroxide ions between anodic and cathodic steel surfaces, which is determined by the resistance of the electrolyte (in this case the concrete). Fig. 7 shows the time-dependent development of the electrolytic resistance.

8 Schießl and Wiens

For the concretes mixed with fly ash and portland cement, a significant increase in electrolytic resistance is to be observed after approx. 20 days. Studies by Hårdtl (3) and Sybertz and Wiens (16) show that, although a certain quantity of $\text{Ca}(\text{OH})_2$ has been converted into hydration products by this time as a result of the pozzolanic reaction of the fly ash, the absolute quantity of hydration products can hardly be sufficient to reduce the capillary porosity to such an extent as to explain the marked rise in electrolytic resistance as the fly ash content increases. Rather, a thin layer of reaction products on the surface of the fly ash particles would appear sufficient to interfere with the continuity of the pore system. This „pore-blocking effect“ together with the pore wall interactions, described in Fig. 6, are suspected to be the cause for the observed drastic reduction in ion transport through the matrix.

As the age increases, the electrolytic resistance in the mixtures containing 40 and 60 mass.% fly ash exceeds both, of the reference portland cement mixture (C1) and the two mixtures with blast-furnace slag (C2 and C3). After approximately 1 year, the concrete with portland cement (C1) and 20 mass.% fly ash attains the same electrolytic resistance as the concrete with the blast-furnace slag cement (C3). At this age, the electrolytic resistances of the 20, 40 and 60 mass.% containing fly ash mixtures are 7, 19 or 30 times higher compared to the reference portland cement mixture (C1).

Concretes mixed with blast-furnace slag display the typical time-dependent course of resistance, with initially higher values giving way to a slower increase.

Fig. 8 shows the corresponding macrocell currents for concrete mixtures with cement (C1) and 0, 20, 40 and 60 mass.% fly ash. The high overall macrocell currents at the beginning of the measurement are mainly due to the anodic polarisation by the use of a platinised titanium rod as the anode. At the beginning of the measurement, the macrocell current of the fly ash containing mixtures exceeds the values of the reference mixture. At about 10 days the macrocell currents for all mixtures yield roughly the same value. Corresponding to the increase in electrolytic resistance for the fly ash containing mixtures at about 20 days due to the starting of the pozzolanic reaction, a significant drop of the macrocell currents with increasing fly ash content from this date on is observable. From experience it is known that 1 mass.% added chloride is in the range of the critical chloride content for the test conditions given after more than about 365 days. For this reason the polarisation resistances overrule the influence of the electric resistance. Additionally the 1 mass.% chloride are related to the cement content, that means reduced chloride contents related to (c+f) with increasing fly ash content.

As previously explained, ion transport, and in conjunction with this, the corrosion rate of steel in concrete is determined to a decisive degree by the geometric limitations in the pore structure. Fig. 9 shows the interrelationship

between the electrolytic resistance of concrete and the median of the pore size distribution of mortar and cement paste for mixtures with and without fly ash or blast-furnace slag.

The median characterises the radius of a pore size distribution corresponding to a mercury intrusion volume of 50 %, and represents a simple parameter for characterising the pore structure. As the pore structure becomes increasingly finer due to hydration of the cement or the pozzolanic reaction, the median values generally decrease. Especially pore blocking effects cause a significant shift of the median value.

In Fig. 9, the results of these investigations are compared with the results obtained by Hårdtl (3), Raupach (6) and Wiens et al. (10) for normal and high-strength concretes with and without fly ash or blast-furnace slag. Since a decreasing median radius, e.g. caused by the pore blocking effect of fly ash or an increase of the surface of hydration products, resulting in a drastic reduction of ion movement, an exponential interrelationship to the electrolytic resistance is to be expected and confirmed by the graph of Fig. 9.

The lowest median radii and the highest electrolytic resistances for normal strength concretes are observed for the mixture with 60 mass.% fly ash or for mixtures with blast-furnace slag cement.

CONCLUSIONS

Chloride migration coefficients can be determined for concretes mixed with portland cements containing fly ash or blast-furnace slag by means of the migration test developed by Tang and Nilsson (8). When applying this rapid-test method, changes in pore structure over the time of testing do not occur.

The increased resistance to chloride transport in comparison to portland cement concretes which was observed when adding fly ash to concrete is accountable to the densification of the pore structure due to the formation of additional CSH phases. As the pore structure densifies, the interactions between the electrically charged pore walls and the chloride ions acquire a decisive influence, as a result of which chloride transport is inhibited. Another primary reason for the increase in diffusion resistance resulting from the use of fly ash is the effective disruption of the pore system's continuity by reaction products which form on the surfaces or in the vicinity of the fly ash particles. A relatively thin hydrate layer (corresponding to a relatively low level of reaction of the fly ash) appears to be sufficient to effectively seal up the pore channels.

Due to the pozzolanic reaction of the fly ash and the required reduction in the $w/(c+f)$ which is necessary in order to attain the same strength levels, a substantial increase in electrolytic resistance and a subsequent reduction of corrosion rates is attainable. In concretes containing fly ash, a further increase in electrolytic resistance levels is still to be expected beyond the age of 365 days.

ACKNOWLEDGEMENT

The investigations were carried out within a research project at the Institute for Building Materials Research entitled „Influence of Fly Ash on the Chloride-Induced Corrosion of Steel in Concrete“ which is supported by the „Arbeitsgemeinschaft industrieller Forschungsvereinigungen“ (AiF-No. 9523).

REFERENCES

1. Hussain, S.E., Rasheeduzzafar, 'Corrosion Resistance Performance of Fly Ash Blended Cement Concrete, *ACI Materials Journal* **91** (3) (1994), 264-272.
2. Thomas, M.D.A., Matthews, J.D. and Haynes, C.A., 'Chloride Diffusion and Reinforcement Corrosion in Marine Exposed Concretes Containing Pulverized-Fuel Ash'. London: Elsevier, 1990, International Symposium on Corrosion of Reinforcement in Concrete, Wishaw, Warwickshire, UK, edited by Page, C.L., Treadaway, K.W.J. and Bamforth, P.B., (May 21-24, 1990), 198-212.
3. Hårdtl, R., 'The Change of Concrete Structure by the Efficiency of Fly Ash and its Influence on Concrete Properties', Berlin: Beuth, *Schriftenreihe des Deutschen Ausschusses für Stahlbeton* (448) (1995) Ph. D.-Thesis, in German.
4. Li, S., Roy, D.M., 'Investigation of Relations between Porosity, Pore Structure, and Cl-Diffusion of Fly Ash and Blended Cement Pastes', *Cement and Concrete Research* **16** (5) (1986), 749-759.
5. Tang, L. and Nilsson, L.-O., 'Chloride Binding Capacity, Penetration and Pore Structures of Blended Cement Pastes With Slag and Flyash', London: Elsevier Applied Science, 1991, International Conference on Blended Cements in Construction, University of Sheffield, edited by Swamy, R.N. (September 9-12, 1991), 377-388.
6. Raupach, M., 'Chloride-Induced Macro-Cell Corrosion of Steel in Concrete', Berlin: Beuth, *Schriftenreihe des Deutschen Ausschusses für Stahlbeton* (433) (1992), Ph. D.-Thesis, in German.

7. Schießl, P. and Hårdtl, R., Relationship between Durability and Pore Structure Properties of Concretes Containing Fly Ash, Ottawa: CANMET, 1994, Proceedings of the P.K. Mehta Symposium on Durability of Concrete, Nice, France, edited by Khayat, K.H. and Aitcin, P.C. (May 22-28, 1994) 99-118.
8. Tang, L., 'Chloride Transport in Concrete - Measurement and Prediction', Göteborg, Chalmers University of Technology, Ph. D.-Thesis, 1996.
9. Collepardi, M., Marcialis, A. and Turriziani, R., 'La Cinetica di Penetrazione Degli Ioni Cloruro nel Calcestruzzo', *Il Cimento* (4) (1970) 157-164.
10. Wiens, U., Breit, W. and Schießl, P., 'Influence of High Silica Fume and High Fly Ash Contents on Alkalinity of Pore Solution and Protection of Steel against Corrosion', Detroit: American Concrete Institute, ACI SP-153, 1995, Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, edited by Malhotra, V.M. (Vol. 2) (1995) 741-761.
11. Andrade, C., Xu, A. and Chandra, S., 'Calculation of Chloride Diffusion Coefficients in Concrete from Ionic Migration Measurements', *Cement and Concrete Research* 23 (3) (1993) 724-742. Discussion: (Xu, A., Chandra, S.) *Cement and Concrete Research* 24 (2) (1994) 375-379. Reply: (Andrade, C.) 380-384.
12. Andrade, C., Sanjuan, M.A., Recuero, A., Rio, O., Tang, L., Nilsson, L.-O., 'Calculation of Chloride Diffusivity in Concrete from Migration Experiments in Non Steady-State Conditions', *Cement and Concrete Research* 24 (7) (1994) 1214-1228. Discussion: *Cement and Concrete Research* 25 (5) (1995) 1133-1144.
13. Byfors, K., 'Influence of Silica Fume and Flyash on Chloride Diffusion and PH Values in Cement Paste', *Cement and Concrete Research* 17 (1) (1987) 115-130.
14. Ngala, V.T., Page, C.L., Parrott, L.J. and Yu, S.W., 'Diffusion in Cementitious Materials, II: Further Investigations of Chloride and Oxygen Diffusion in Well-Cured OPC and OPC/30% PFA Pastes', *Cement and Concrete Research* 25 (4) (1995) 819-826.
15. Weast, R.C., Astle, M.J. and Beyer, W.H., CRC Handbook of Chemistry and Physics, 69th Edition Boca Raton, CRC Press, 1989.
16. Sybertz, F. and Wiens, U., 'Effect of fly Ash Fineness on Hydration Characteristics and Strength Development', London: Elsevier Applied Science, 1991, International Conference on Blended Cements in Construction, University of Sheffield, edited by Swamy, R.N. (September 9-12, 1991) 152-165.

TABLE 1—CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF THE BINDING MATERIALS

Item	Unit	Cement			Fly Ash
		C1	C2	C3	
<i>Chemical Composition</i>					
SiO ₂	Mass. %	19.3	25.1	30.0	47.1
Al ₂ O ₃		5.05	8.00	9.39	27.3
Fe ₂ O ₃		2.94	1.71	1.23	8.41
CaO		65.6	52.4	46.6	4.72
MgO		0.97	3.60	5.77	2.51
K ₂ O		0.57	0.70	0.54	3.40
Na ₂ O		0.04	0.17	0.14	1.29
free CaO		n.d.	n.d.	n.d.	0.74
SO ₃		2.48	2.13	1.77	1.81
C		0.57	0.56	0.08	0.97
Slag Content		-	46	74	-
Loss on Ignition		2.71	2.86	0.69	1.96
Density	kg/m ³	3130	3030	3000	2290
<i>Fineness</i>					
Surface Area, Blaine	m ² /kg	290	383	415	314
40µm-Residue ¹⁾	Mass. %	28.1	14.5	8.5	16.9
Median Diameter d ₅₀ ²⁾	µm	22.8	15.4	11.4	14.7

n.d.: not determined

1) Air Jet Sieve

2) Particle Size Distribution by Micromeritics Sedigraph 5000 D

TABLE 2—MORTAR AND CONCRETE COMPOSITION IN THE TEST SERIES

Type of Cement	Mortar Composition				Concrete Composition				f _{c,28} ¹⁾
	$\frac{f}{c}$	$\frac{w^2)}{c+k \cdot f}$	$\frac{w}{c+f}$	$\frac{a^3)}{c}$	w	c	f	a ⁴⁾	
-	-				kg/m ³				MPa
C1	0	0.50	0.50	3	180	360	0	1815	48.8
C1	0.25	0.50	0.45	3.2	180	320	80	1770	46.0
C1	0.67	0.50	0.40	3.5	180	240	120	1697	45.8
C1	1.5	0.50	0.35	4.2	180	206	309	1590	37.2
C2	0	0.50	0.50	3	180	360	0	1818	44.5
C2	0.25	0.50	0.45	3.2	180	320	80	1773	45.5
C3	0	0.50	0.50	3	180	360	0	1815	41.4

1) Compressive Strength of Concrete at 28 days (150 mm Cubes)

2) k = 0.50

3) Aggregate Mortar: Sand 0.08/2 mm

4) Aggregate Concrete: Sand and Gravel: 0/16 mm

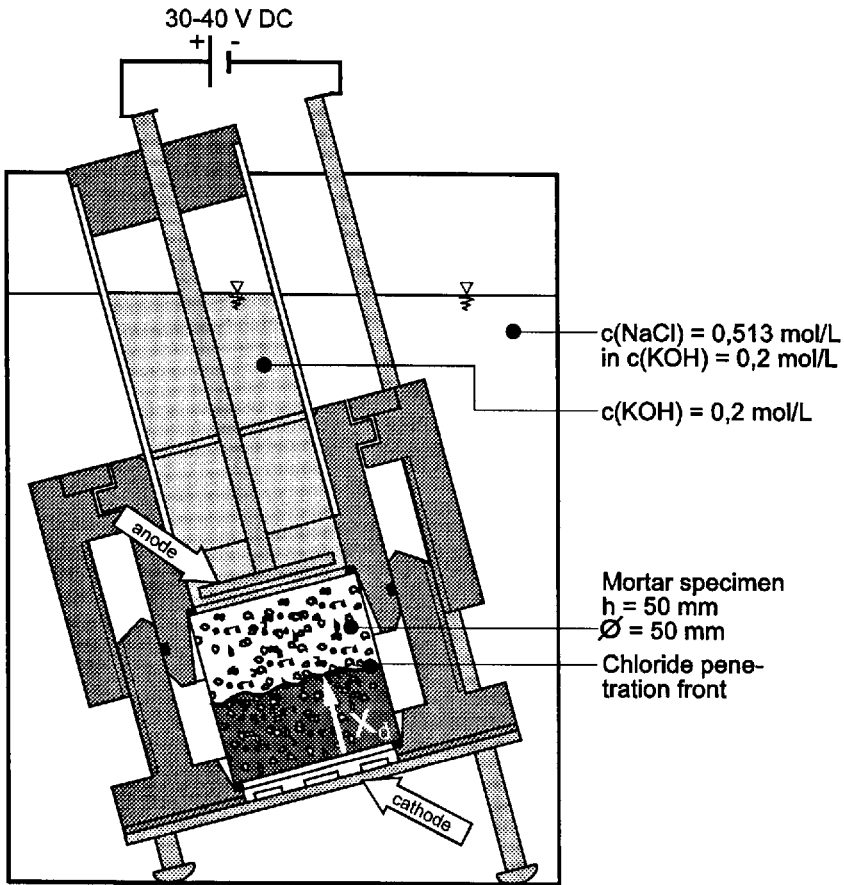


Fig. 1—Test set-up for the determination of chloride migration coefficients

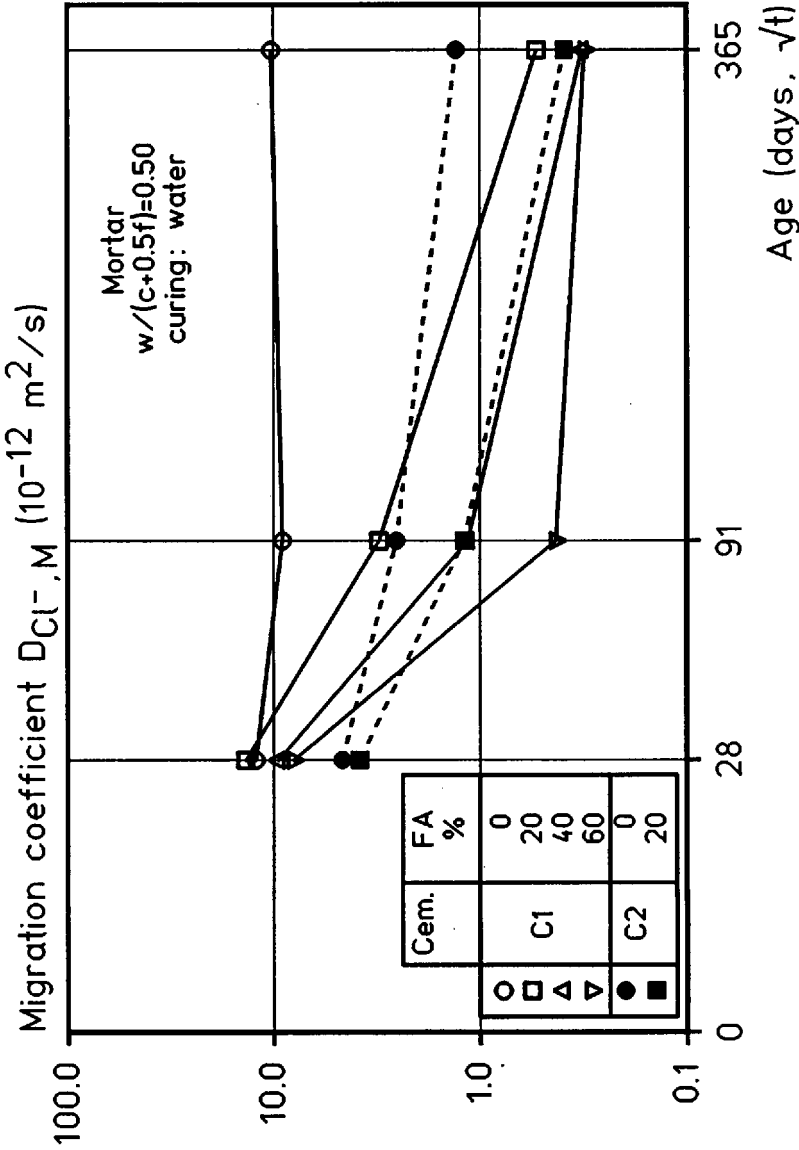


Fig. 2—Time-dependent development of chloride migration coefficients $D_{Cl^-,M}$

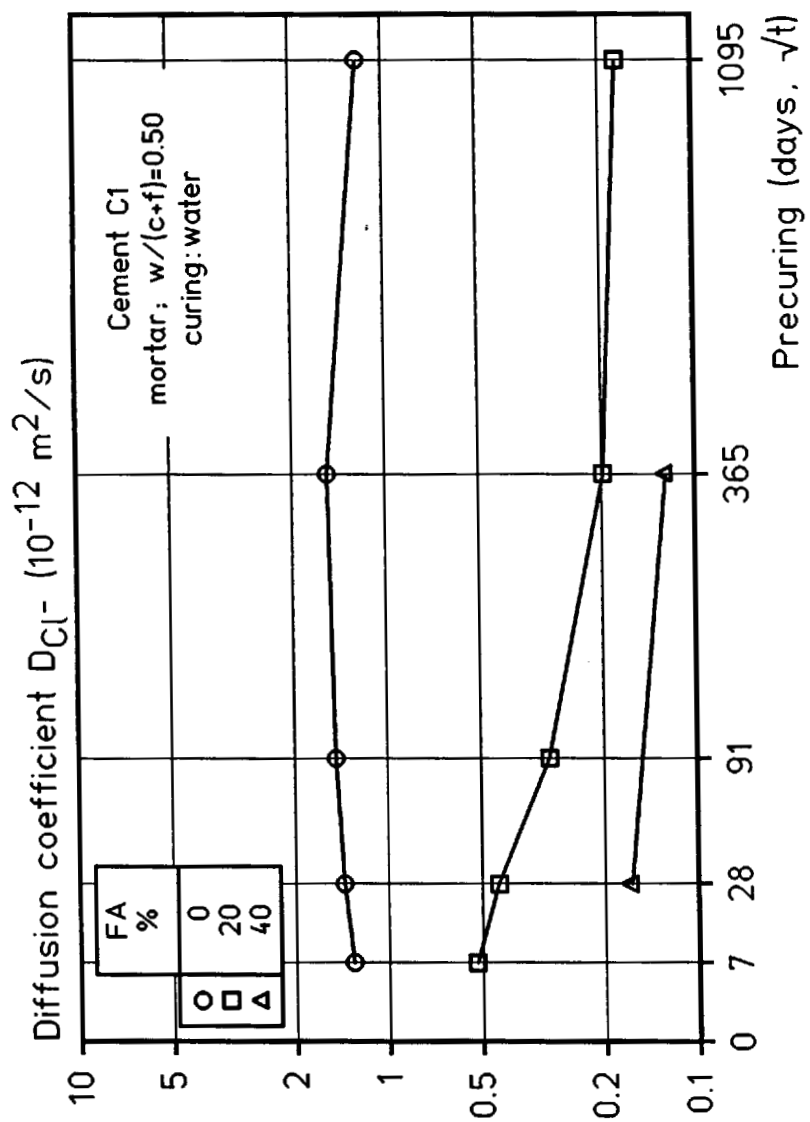


Fig. 3—Diffusion coefficients from a conventional diffusion cell (steady state)
(precuring = age at the beginning of the test); see (7)

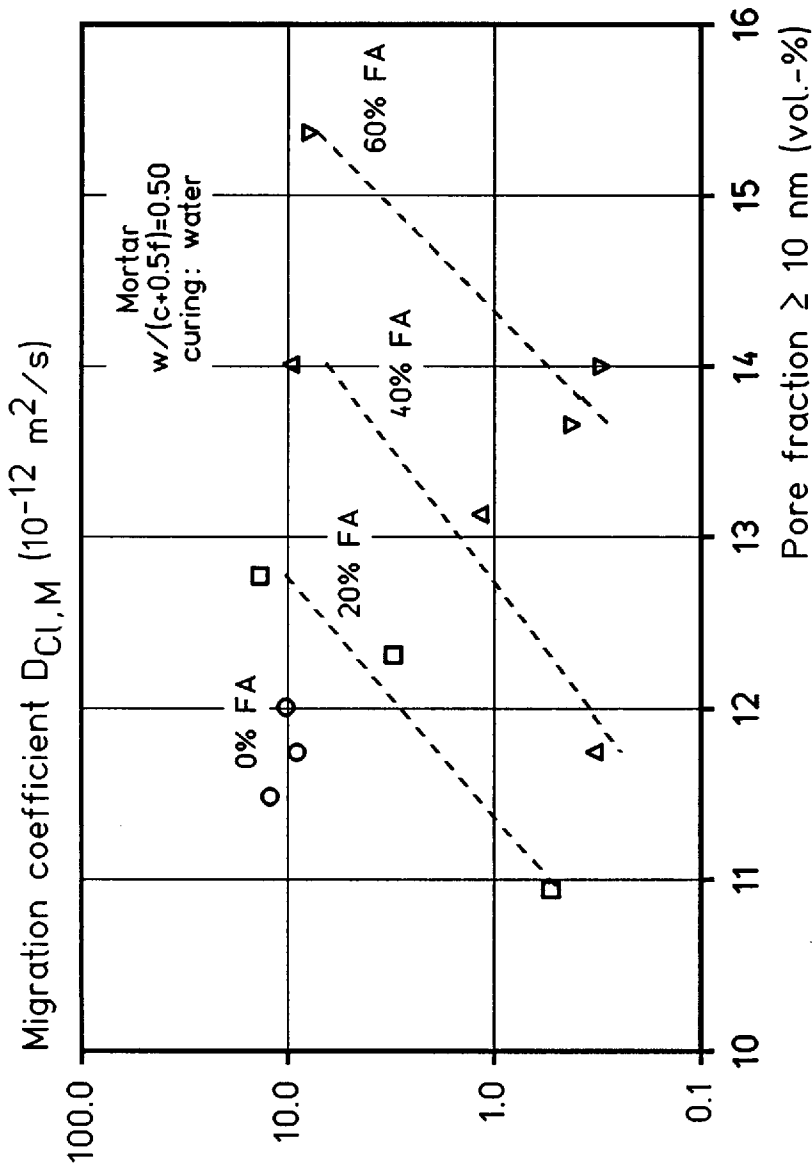


Fig. 4—Migration coefficients $D_{Cl,M}$ vs pore fraction $\geq 10 \text{ nm}$

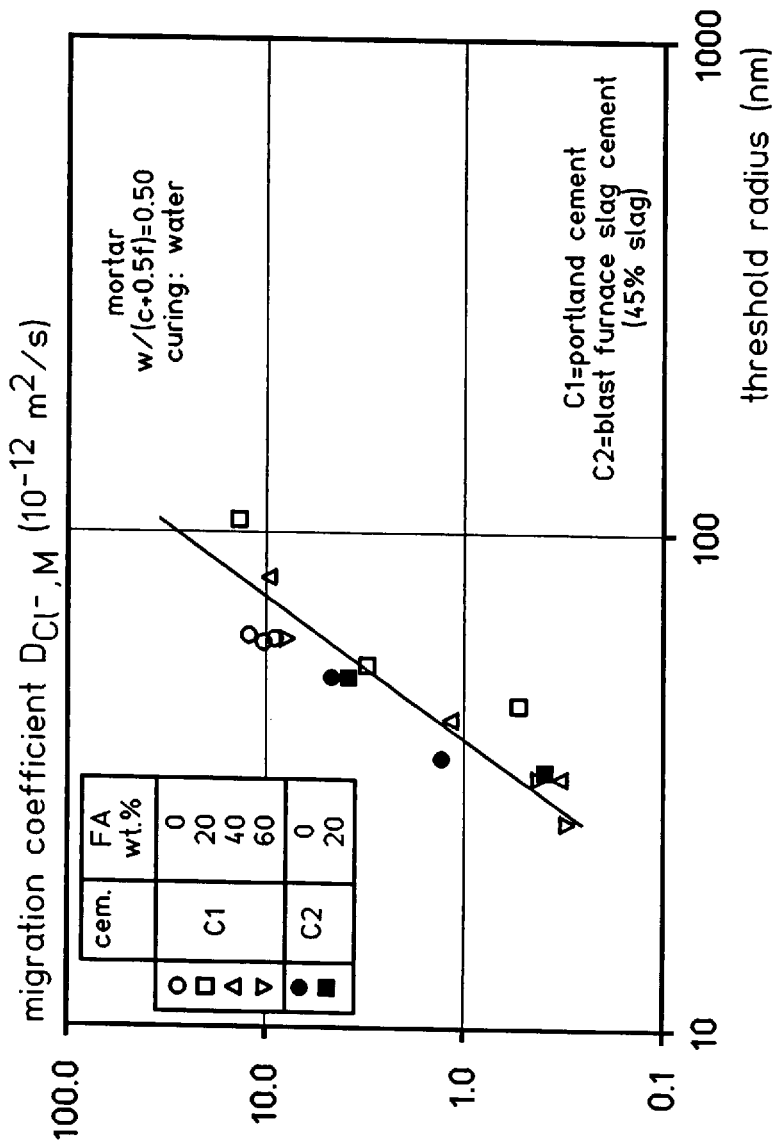


Fig. 5—Migration coefficients $D_{Cl^{-},M}$ vs the threshold radius

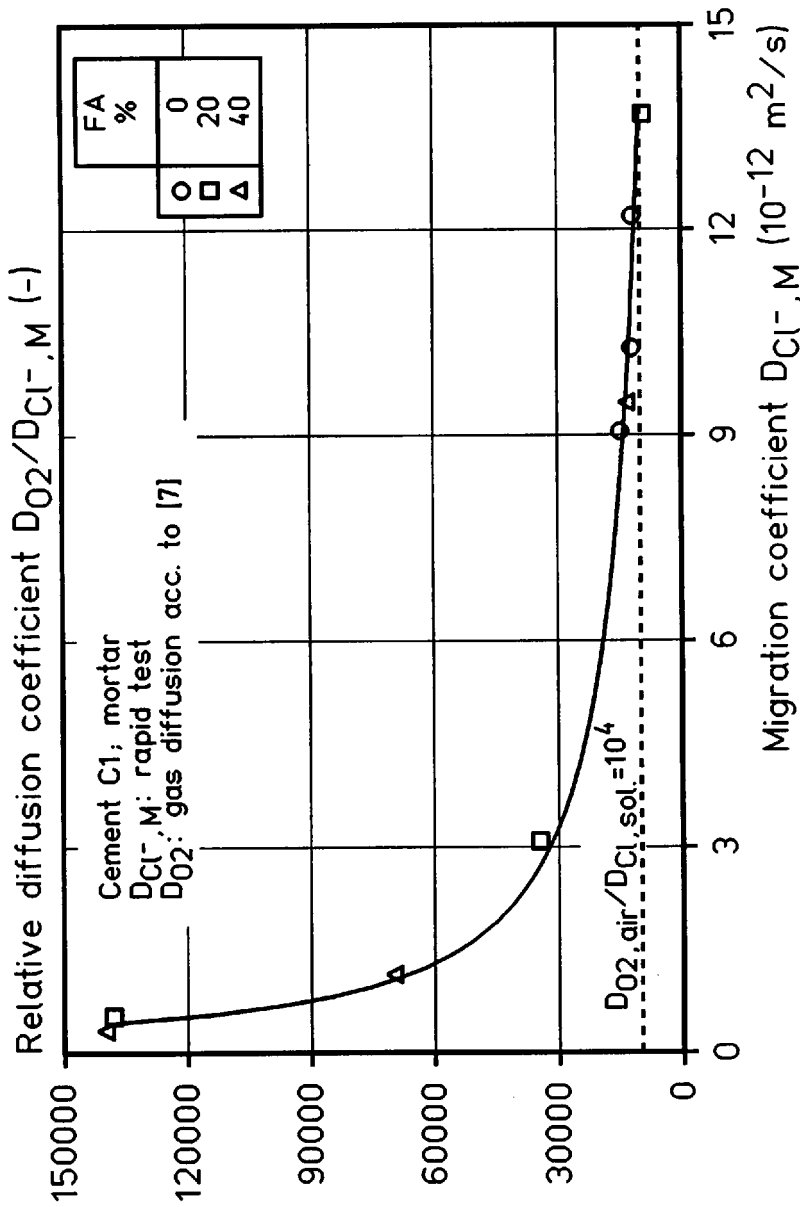


Fig. 6—Relationship between $D_{O_2}/D_{Cl^-,M}$ and the migration coefficient $D_{Cl^-,M}$

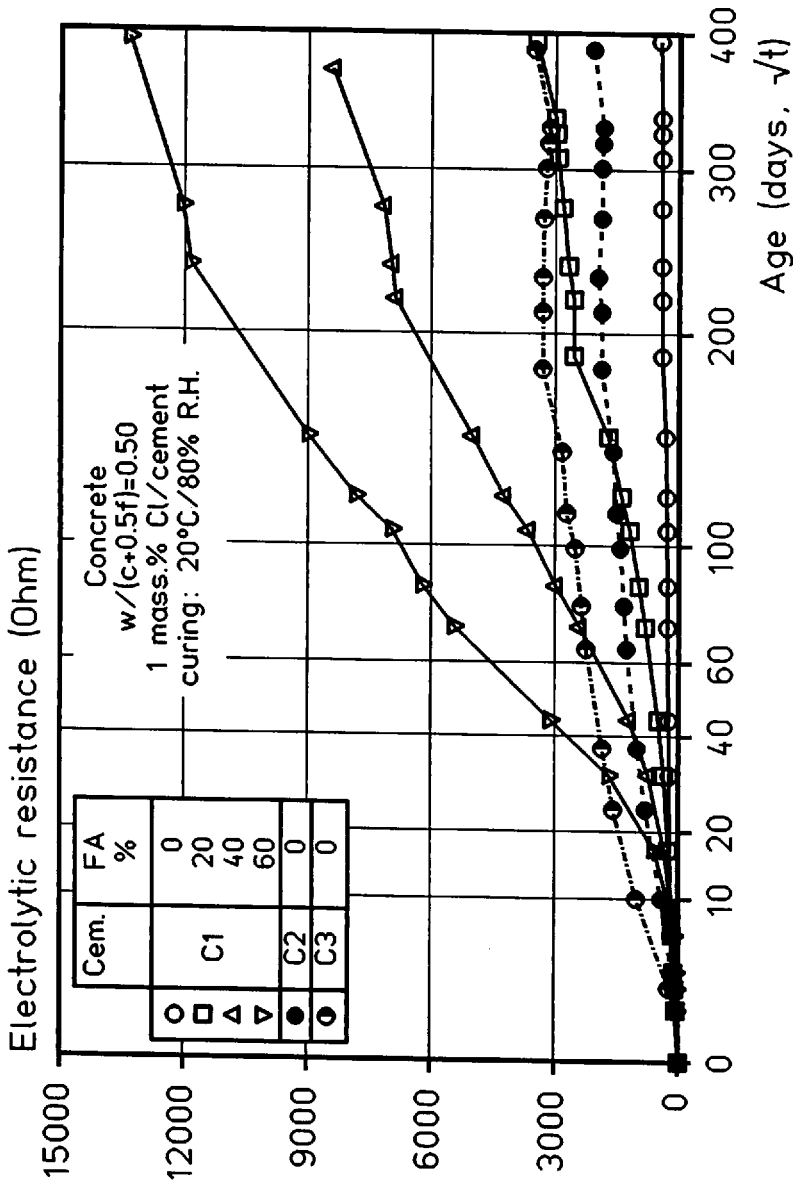


Fig. 7—Electrolytic resistance vs time

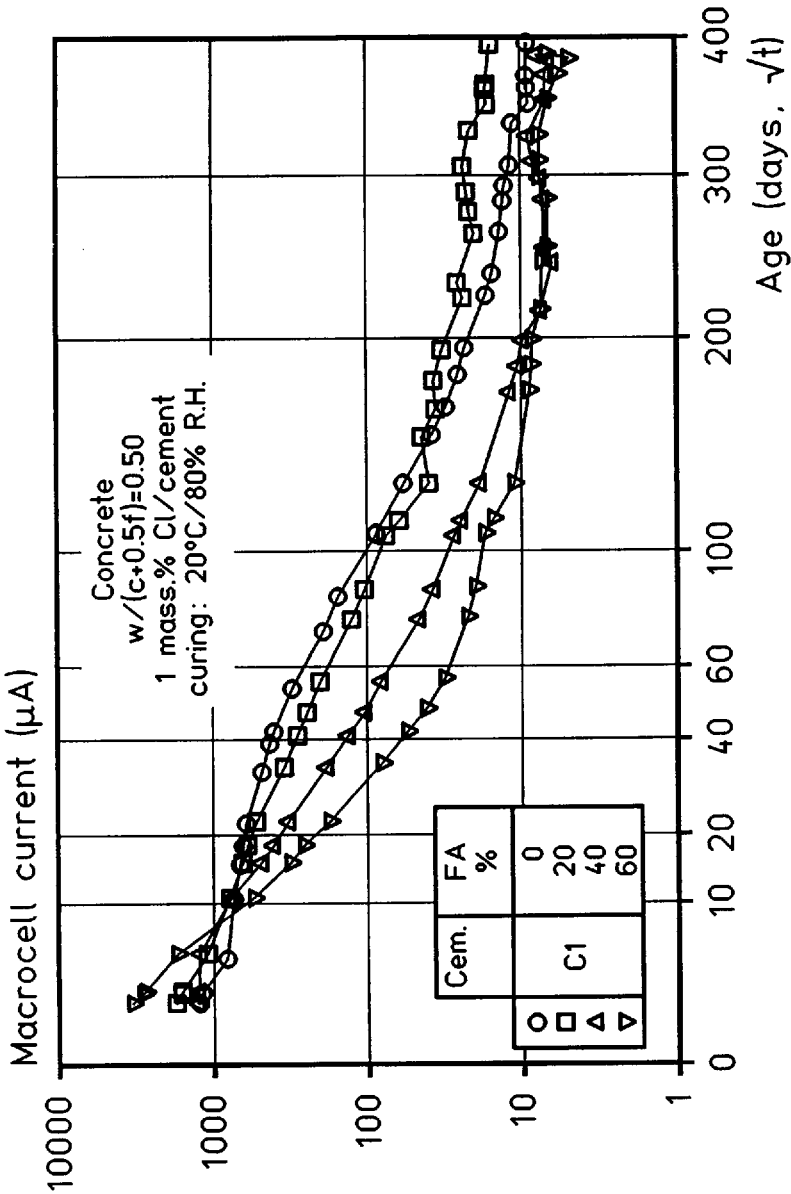


Fig. 8—Macrocell current vs time

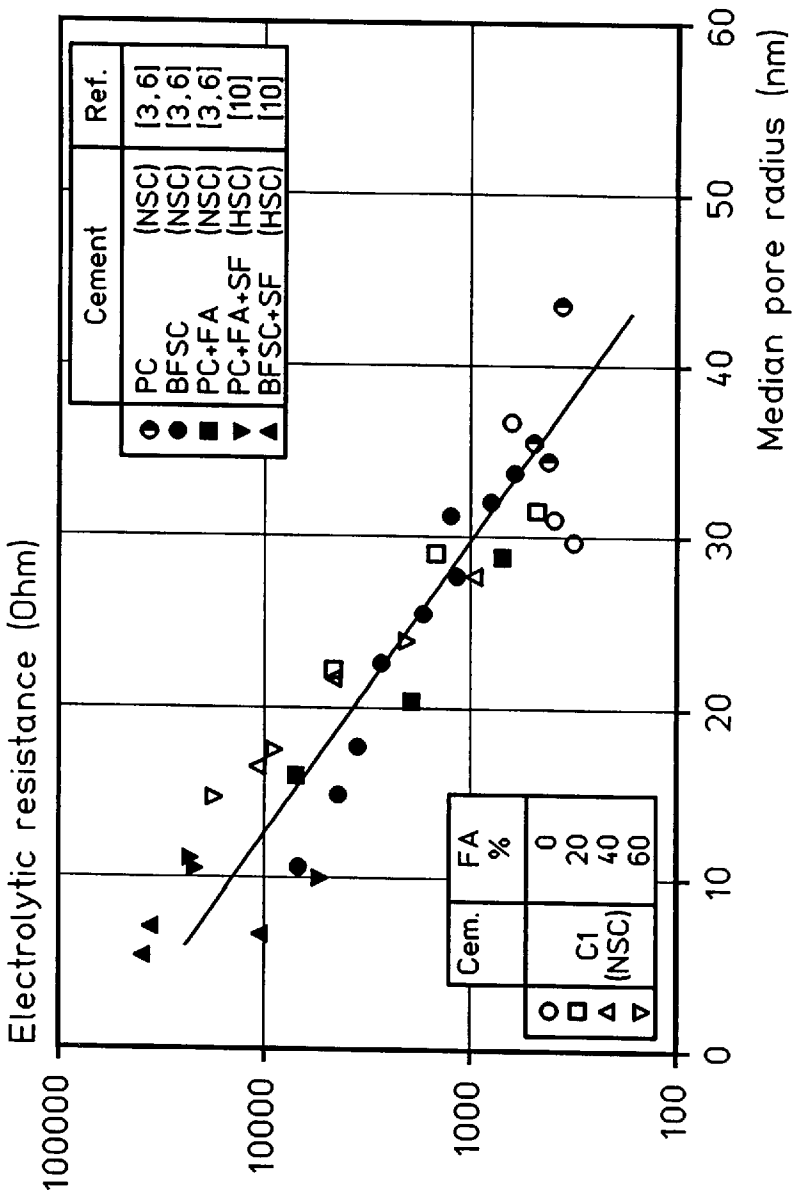


Fig. 9—Electrolytic resistance of concrete vs median pore radius of mortar or cement past: PC - Portland cement; BFSC = blast-furnace slag cement; FA = fly ash; SF - silica fume; NSC = normal strength concrete ; HSC = high strength concrete (28 day-cube-compressive strength: $\approx$ Mpa); age of specimens: 28, 91 and 365 days

Field Evaluation of an Acrylic Rubber Protective Coating System for Reinforced Concrete Structures

by Y. Yamada, T. Oshiro, S. Tanikawa and R. N. Swamy

Synopsis : This paper presents extensive long-term data on chloride penetration into unprotected and protected members of a reinforced concrete structure exposed to an aggressive salt-laden environment. The test results up to 11 years of exposure show that chlorides penetrate very rapidly into the concrete from an early stage, and this penetration increases with time. There was a visible peaking of chloride concentration in the vicinity of the location of the reinforcing bars. Structural members protected with the acrylic rubber coating showed an almost total absence of penetration of chlorides throughout the exposure period, and the coating maintains long-term durability of RC structures under marine environment. The accumulated chloride ions in concrete become important for the durability of reinforced concrete and these have been calculated from the distributions of chlorides in relation to the exposure period. Analytical evaluation shows that the accumulated chlorides are expressed by a model represented by an equation with coefficients, where the coefficients are closely related to environmental conditions and characteristics of concrete.

Keywords: Chlorides; durability; environments; impurities; protective coatings; tests.

INTRODUCTION

Yoshitomo Yamada is a Research Associate, Dept. of Civil Engineering and Architecture, University of the Ryukyus, Okinawa, Japan. He received his MS in 1989 from Osaka University, Osaka, Japan and has since been active in research on the durability of reinforced concrete structures. He is a member of JCI.

Takeshi Oshiro is a Professor, Dept. of Civil Engineering and Architecture, University of the Ryukyus, Okinawa, Japan. He received his PhD in 1970 from University of Delaware, Delaware, U.S.A., and has since been active in research on the durability of reinforced concrete structures. He is a member of ACI and JCI.

Shin Tanikawa is a Project Engineer at Toagosei Co. Ltd. He received his MS in 1975 from Nagoya Institute of Technology, Aichi, Japan and has carried out extensive research on surface coatings for concrete. He is a member of ACI and JCI.

R. Narayan Swamy is a Professor of the Structural Integrity Research Institute and Concrete at the University of Sheffield, England. He is Editor of Cement and Concrete Composites and the Book Series on Concrete Technology and Design. He recently received the CANMET/ACI Award for contributions to Durability of Concrete.

EXPERIMENTAL DETAILS

Examination of the behaviour of many concrete structures over a period of time shows that concrete can be a highly durable construction material, and can give trouble-free service life for many years, provided inspection and maintenance are carried out regularly. However, experience also shows that in practice, the realities of construction and exposure conditions are such that deteriorating processes of some form or other set in when structures are built in aggressive environments. Whatever be the source of deterioration and the mechanism of its development, corrosion of steel reinforcement is recognized as the major world-wide problem, and the most expensive, affecting the durability and structural integrity of concrete structures.

It is also known that the seeds for much of the potential for damage and deterioration are sown during the early life of a concrete structure, and that many of the corrosion inducing agents are water-born and permeate the concrete in a

liquid phase through a combination of physical and chemical interactions. It, therefore, stands to reason that the most promising and cost-effective protection of concrete and its embedded steel is probably through a barrier surface coating on the concrete that will effectively, and for a specific period of time, prevent the intrusion of agents such as water, chlorides and sulphates until the concrete can mature and develop an impermeable interior. A coating that can be applied immediately after construction, and which can also be applied on cracked and chloride contaminated surfaces can provide a valuable technique of structural retrofitting and rehabilitation. This paper presents extensive long-term site evaluation of the ability of an acrylic rubber coating to protect concrete structures exposed to severe marine environment from deterioration.

The test specimens reported in this study are the structural members of a reinforced concrete building specially designed and constructed to investigate the role and effectiveness of the acrylic rubber coating in preventing chloride penetration, and protecting the concrete and the embedded steel. Built in 1984, the performance of the uncoated and coated members has been monitored over a period of 11 years, and the measurements presented here represent the rate of penetration with time of chlorides in aggressive environmental and climatic conditions. The structure is located in a marine environment in sub-tropical weather conditions of high temperature and humidity, and is openly exposed on three sides to salt-laden breeze, sea-water spray and splash during heavy winds. The structural layout of the test building is shown in Figs. 1 and 2.

Two types of concrete mixtures, both identical in their mixture proportions except for the presence of NaCl in one of them, were used to construct the test building. The concrete mixture was made from ASTM Type 1 portland cement, with a water-cement ratio of 0.63. The concrete had a slump of 180 mm and 28-day cylinder compressive strength of 21 MPa. The mixture with salt contained 0.5% sodium chloride by weight of concrete added at the mixing stage. Figs. 1 and 2 identify the structural elements made with and without salt in concrete.

To evaluate the effectiveness of the acrylic rubber coating in preventing chloride penetration and in affecting the performance characteristics of the coating when exposed to an aggressive environment, one half of the building facing the sea was

left exposed for four months (Sept. to Dec., 1984) and then subsequently coated with the acrylic rubber coating, while the other half was left uncoated, and the concrete left exposed to the surroundings. Figs. 1 and 2 also identify the uncoated and coated structural elements in the test structure. The beams and columns in the structure had a concrete cover of 40 mm for the reinforcement, and 30mm for the slabs.

The acrylic rubber surface coating used in the structure is one that has been subjected to extensive laboratory and field testing, and is reported in the literature (1-6). The total thickness of the coating is about 1.1 mm, and it is designed to provide effective long-term performance in terms of water-proofing qualities, adequate vapor diffusion, breathability, good bond to the substrate, very low permeability to chlorides and moisture under service conditions and temperature extremes, and also maintain ability to bridge cracks.

Test for Chlorides

The test building has been monitored through close visual observation at regular intervals as well as by a variety of measurements. In particular, all external deterioration processes such as cracking have been regularly evaluated. The water-soluble chloride content of the concrete was determined from cored samples taken from the various structural elements. A potential difference titration method using a chloride selective electrode was used to quantify the chloride content, in terms of NaCl, as a percentage by weight of concrete. Typical data obtained over a period of 11 years are presented here.

TEST RESULTS AND DISCUSSION

The test structure has provided extensive data on the process of chloride penetration into reinforced concrete structures exposed to an aggressive, salt-laden environment, which can only be described as the most favourable for the transport of chloride ions into the concrete. The nature of the concrete used in the building is also such that it provides much less resistance to chloride penetration (w/c , 0.63). If the coating is able to act as a barrier to the penetration of chloride ions in such circumstances, the coating will have been subjected to the most rigorous test in real life conditions. The focus of this paper is to establish the process of chloride intrusion with time into reinforced concrete made with concrete of high water-cement ratio,

without and with salt added during mixing and to quantify the capability of the acrylic rubber coating to control chloride diffusion into such concrete. It is also worth reporting that the period during which the data were collected also includes six months with strong winds in winter (Dec 1992-May 1993) .

Beams and Columns

In order to provide representative data, information is presented on the measured chloride contents in several beams and columns in Figs. 3, 4, 5. Figs. 3A and 3B refer to uncoated and coated beams respectively made with concrete without any added salt at the mixing stage. Figs. 4A and 4B show similar uncoated and coated beams but with 0.5% salt added to the concrete during construction. Figs. 5A and 5B relate to uncoated and coated columns respectively made with concrete without salt. Where appropriate, chloride penetration data into small scale 150 x 150 x 600 mm prism at 6 months are also provided in these figures. The prisms were made with the same quality of concrete as those in the test structure.

All the uncoated beams with and without salt as well as the uncoated columns show a progressive and steady permeation of chlorides into these structural members. In all cases there is also a visible concentration of salts in the vicinity of the reinforcing bars. The results are shown in Figs. 3B, 4B and 5B. It can be readily seen that not insignificant amounts of chloride had penetrated into the concrete during this early period. However, subsequent coating had stabilized the distribution of chlorides within the body of the concrete and even after 6 to 10 years of exposure to very favorable chloride penetration conditions, there was neither any increase in the chloride content, nor was there any concentration of chlorides in the vicinity of the reinforcing bars. These data thus confirm the almost total impermeability of the acrylic coating to chloride penetration from outside.

Slab

Figs. 6A and 6B show the chloride contents in the uncoated and coated slabs made with concrete without salt, and exposed for a period of ten years. Similar data for uncoated and coated slabs made with 0.5% added salt at the construction stage are shown in Figs. 7A and 7B, respectively. The results again show how rapidly chlorides penetrate into unprotected concrete, while the acrylic rubber coating provides almost a total barrier to chloride penetration. In the uncoated slabs, both the top and the bottom faces of the slabs were left exposed, and there are different amounts of salt concentrations in the two faces due primarily to washing out by

rain and movement of chloride ions within the body of the concrete.

The data shown in Figs. 3 - 7 provide the strongest and visible proof of the ability of the acrylic rubber coating to give long and durable protection to concrete from the surrounding salt-laden environment. The engineering properties of the coating such as extensibility, temperature stability and crack-bridging ability all play a very significant part in imparting to the coating this ability to stop the transportation of chloride ions into the concrete.

Air-laden Chlorides

Air-laden chlorides have been collected by using a collector originally designed by Civil Engineering Research Center, Ministry of Construction, G.O.P., and set on the slab of the test building. The collector is able to collect air laden chlorides through a $100 \times 100\text{mm}$ (dm^2) stainless steel plate and store these with rain water in a plastic tank. This chloride solution is collected monthly and tested by a potential difference titration method to quantify the salt content and is expressed in terms of mg/dm^2 per day.

Fig.8 shows the average values of chlorides collected every month over a period of one year (1994) , and Table1 gives the total chloride contents collected through the year with respect to the four directions. It should be noted that the sea shore at this location is formed by reefs yielding break-water, and a great amount of chlorides is transported by winds. These data show that air-laden chlorides become large during winter from December to March due to strong seasonal winds from the north, and the average daily amount of chlorides collected during this time is $10\text{mg}/\text{dm}^2$ per day. The period from June to July generally yields the smallest chlorides of $0.59\text{mg}/\text{dm}^2$ per day. During the typhoon season, the amount becomes large, and the maximum value of $27\text{mg}/\text{dm}^2$ per day was recorded in October, 1994.

Chloride Accumulation

The chloride distributions in concrete shown in Figs.3 - 7 give clear evidence that the amount of chlorides has increased with the exposure period. However, the rate of this increase seems to be different. During the first period, the rate of increase becomes large compared to that after seven years. To investigate this process of chloride accumulation, new approach has been introduced here, that is, calculation of the total amounts of chloride ions accumulated in concrete core samples. Referring to the chloride distributions, Figs.3A and 3B, the total amounts of chloride ions

accumulated in four concrete core samples from coated and uncoated north side and south side have been calculated by a numerical integration, adding cumulatively the chloride contents at different locations from surface to center of the cores. The results are shown in Fig.9A in relation to the exposure period. Similar calculation was performed with referring to Figs.6A and 6B for slab, and the numerical results are shown in Fig.9B. Also, the exactly same process was followed for beam at east and west side, and the results are shown in Fig.9C.

Evaluating the plotted data, the amounts of chlorides can be represented by the following equation ;

$$Q = \frac{I_0}{b} (1 - e^{-bT}) \quad (1)$$

where,

Q : chloride ions accumulated during the total exposure period per unit area (g/cm²)

I₀ : initial flux of penetrated chloride ions (g/year · cm²)

b : factor representing attenuation of accumulated chloride ions

T : exposure period (year)

The flux is defined as the amount of chloride ions penetrated per unit year and unit surface area (g/year · cm²), and the initial value is determined as the initial flux, I₀. This initial flux is closely related to the amount of air-laden chlorides and material characteristics, that is, the concrete surface with a high air-laden chlorides and lower concrete quality yields larger value. The factor b represents the characteristic related to the attenuation of flux and corresponds qualitatively to environmental conditions and material property such as pore structure and moisture content of the concrete. Large value of b yields large attenuation of chloride ions during the exposure period. Chloride ions accumulated in each concrete sample converge to the value of I₀/b after a long period, which can be derived from Eq. (1).

The values I₀ in Table2 show that the largest value is obtained from the core taken from the north side whose surfaces have been exposed to the most severe saline environment. The core at the south side gives the smallest value corresponding to the least air-laden chlorides. The relation between the factor b and carbonation depth becomes clear from the numerical evaluation shown in Table.2. The larger values of b are obtained at the top and bottom parts of slab cores, and also at the

north side of beam core. The carbonation depths at these locations are relatively small compared to the values at other locations. This relation seems to be true except at the south side of beam, where the factor becomes large even though the carbonation depth is large. The reason for b being large is considered to be due to the location of the beam, where strong sunshine of the subtropical weather dries the concrete, thus affecting its moisture content.

By differentiating the above equation, Eq. (1), with time, one obtains the following equation representing the flux of chlorides ;

$$I = I_0 \cdot e^{-bt} \quad (2)$$

This equation shows that the flux through the core decreases exponentially with time, where the coefficients, I_0 and b mentioned above are closely related to the characteristic of the flux.

CONCLUSIONS

The results presented in this paper show that chlorides permeate from a very early age into unprotected concrete exposed to a salt-laden environment, and this salt penetration increases progressively with time. The chloride content data showed clear evidence of chloride ions concentrating in the vicinity of the reinforcing bars. The coating provides an almost total barrier to water and chloride ions and prevents any peaking of the chloride concentration in the vicinity of the reinforcing bars. The results also confirm the ability of the coating to protect concrete already contaminated by chlorides and maintain this property for several years even where the structure is exposed to an environment that favors the rapid transport of chloride ions into concrete.

The accumulation of chloride ions in concrete has been calculated from the chloride distributions with the exposure period and expressed by an empirical model. The coefficients in the equation are closely related to the environmental condition and material properties.

REFERENCES

1. Oshiro, T. and Tanikawa, S., "A Field Study on Durability of RC Building Exposed to a Marine Environment", *Protection of Concrete* Edited by R.K.Dhir and J.W.Green, E&F.N. Spon, 1990, pp469-482.
2. Swamy, R.N., and Tanikawa, S., "Control of Steel Corrosion in Chloride Contaminated Concrete through Aron Wall Surface Coating", *Durability of Concrete* Edited by V.M.Malhotra, ACI SP-126, Vol. 1, 1991, pp371-391.
3. Oshiro, T., Tanikawa, S., and Goto, N., "Study on Durability of Structures Exposed to Marine Environment", *Evaluation and Rehabilitation of Concrete Structures and Innovations in Design* Edited by V.M.Malhotra, ACI SP-128, 1991, pp433-447.
4. Swamy, R.N., and Tanikawa, S., "An External Surface Coating to Protect Concrete and Steel from Aggressive Environments", *Materials and Structures*, Vol. 26, No. 162, Oct. 1993, pp465-478.
5. Oshiro, T., Swamy, R.N., and Tanikawa, S., "In-Situ Evaluation of a Flexible Surface Coating for Concrete to Prevent Chloride Penetration and Steel Corrosion", *Durability of Concrete* Edited by V.M.Malhotra, ACI SP-145, 1994, pp851-870.
6. Tanikawa, S. and Swamy, R.N., "Unprotected and Protected Concrete, On-site Chloride Penetration with Time in an Aggressive Environment", *Corrosion and Corrosion Protection of Steel in Concrete* Edited by R.N.Swamy, Sheffield Academic Press, Vol. 2, 1994, pp1069-1080.
7. Tuutti, K., "Effect of Cement Type and Different Additions on Service Life", *Concrete 2000* Edited by Ravindra K.Dhir and M.Roderick, Jones, 1993, pp1285-1295.
8. Saeki, T., Ohga, H. and Nagataki, S., "Mechanism of Carbonation and Prediction of Carbonation Process of Concrete", *Proceedings of JSCE*, No.414/V-12, 1990, pp99-108.
9. Saeki, T., Ohga, H. and Nagataki, S., "Change in Micro-Structure of Concrete Due to Carbonation", *Proceedings of JSCE*, No. 420/V-13, 1990, pp33-42.

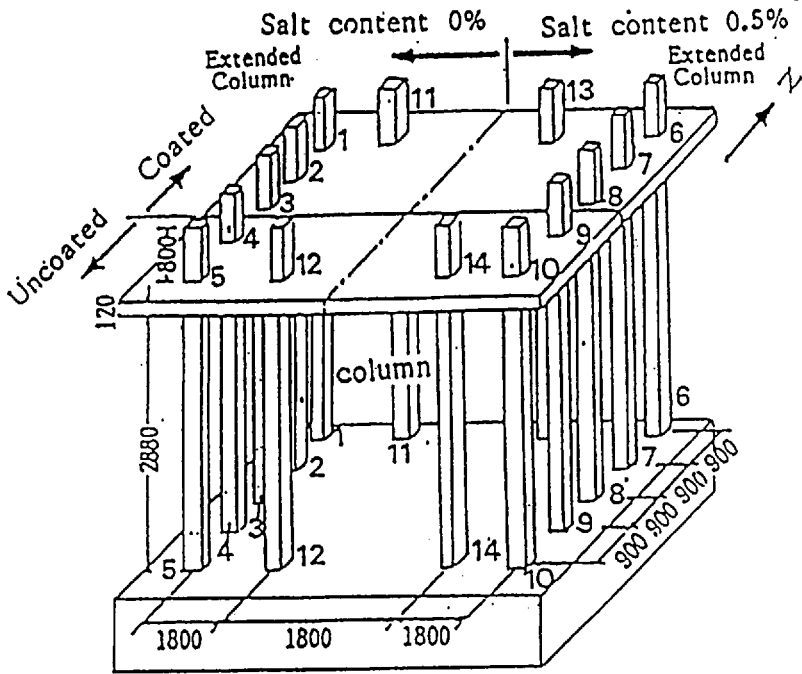
TABLE 1—AMOUNT OF ANNUAL CHLORIDES

Bise Exposure Site (Unit : mg/dm ² per year)			
North	East	South	West
4925.9	2110.2	1103.9	1279.2

Measured Period : 1993.12~1994.12

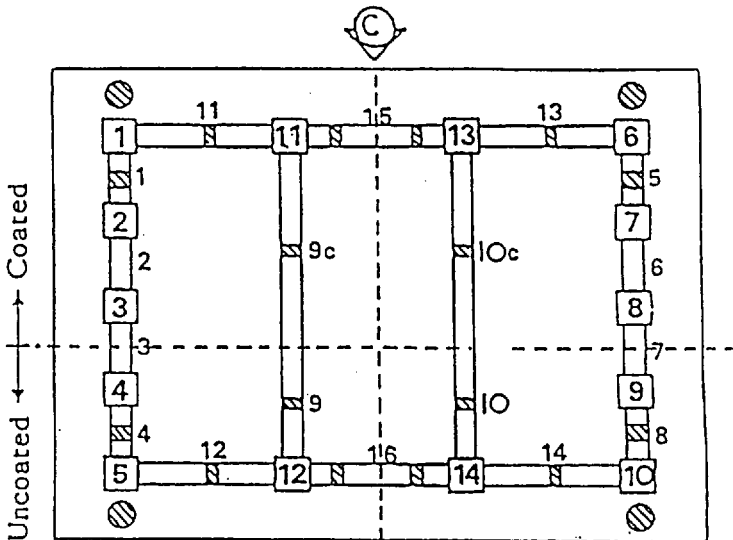
TABLE 2—VALUES OF COEFFICIENTS

	Location	I_0	b	I_0/b	Carbona- tion Depth (mm)	Order of Carbona- tion
Beam	North	1.604	0.108	14.852	11.0	4
	East	0.955	0.065	14.615	15.9	1
	South	0.627	0.166	3.777	14.0	2
	West	0.716	0.068	10.529	13.0	3
Slab	Upper	1.111	0.301	3.691	3.5	6
	Lower	0.674	0.175	3.851	9.8	5



Elevation (mm)

Fig. 1—Evaluation of test structure



Note: Mark, ■, Indicates core location

Plan

Fig. 2—Plan view of test structure

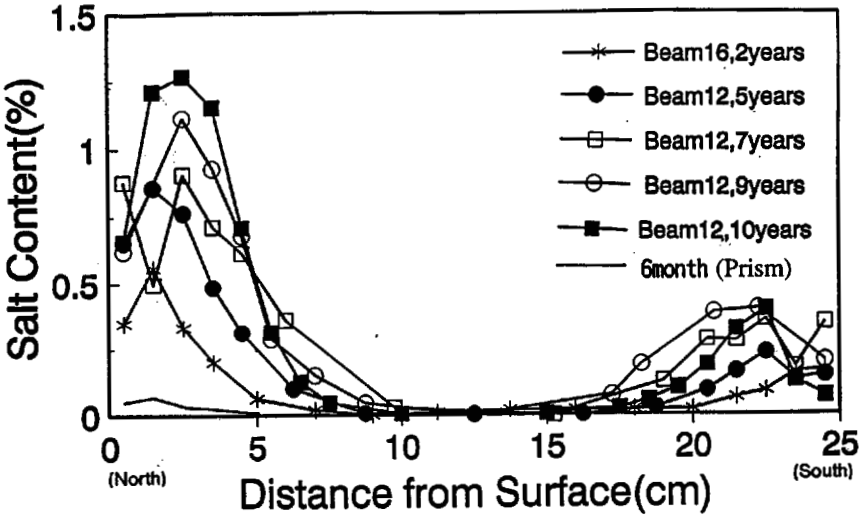


Fig. 3A—Chloride distributions in uncoated beams without salt

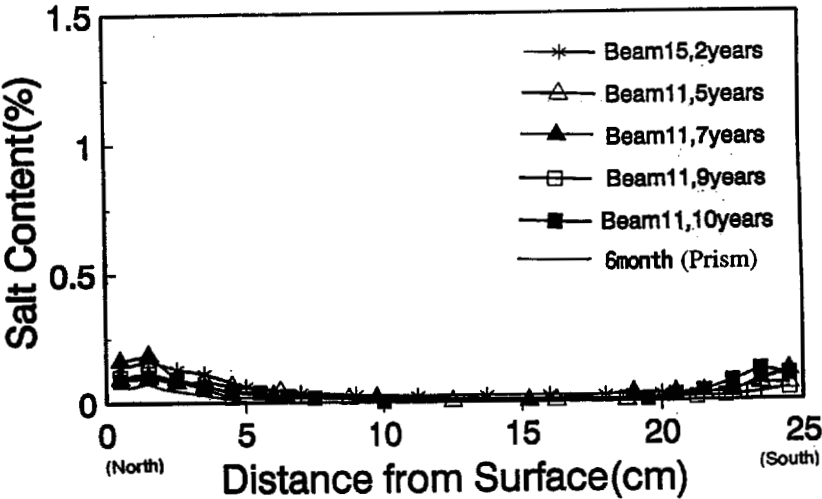


Fig. 3B—Chloride distributions in coated beams without salt

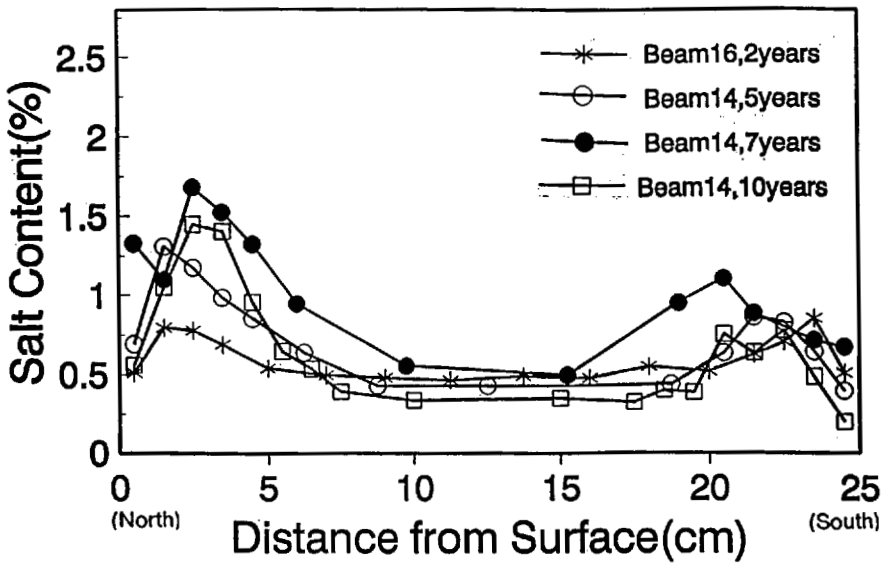


Fig. 4A—Chloride distributions in uncoated beams with 0.5% salt

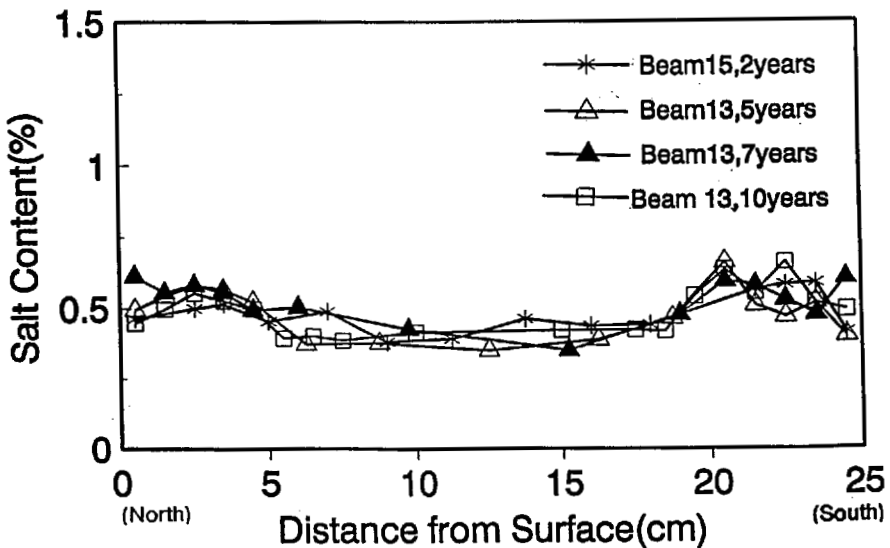


Fig. 4B—Chloride distributions in coated beams with 0.5% salt

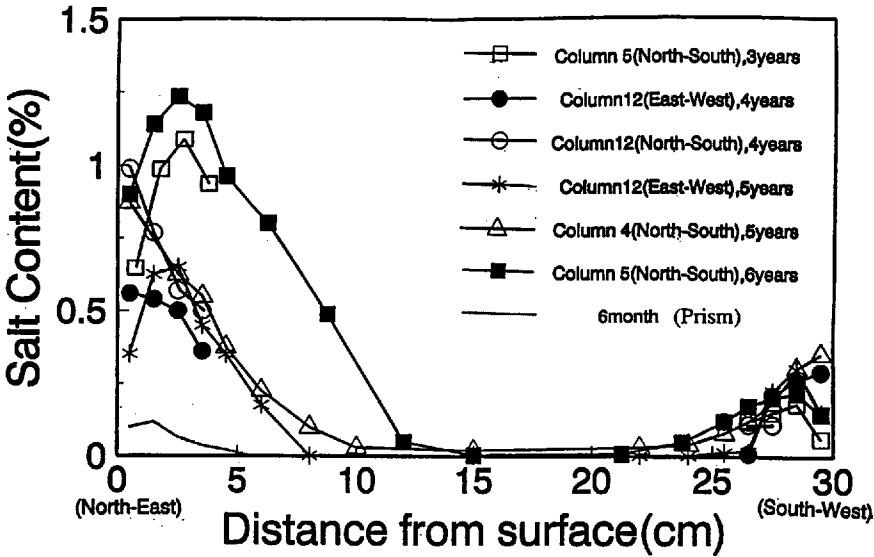


Fig. 5A—Chloride distributions in uncoated columns without salt

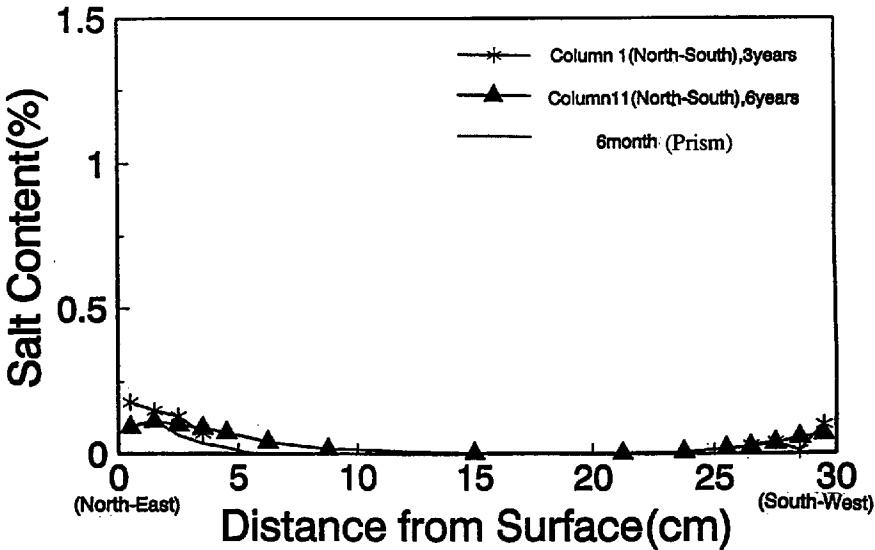


Fig. 5B—Chloride distributions in coated columns without salt

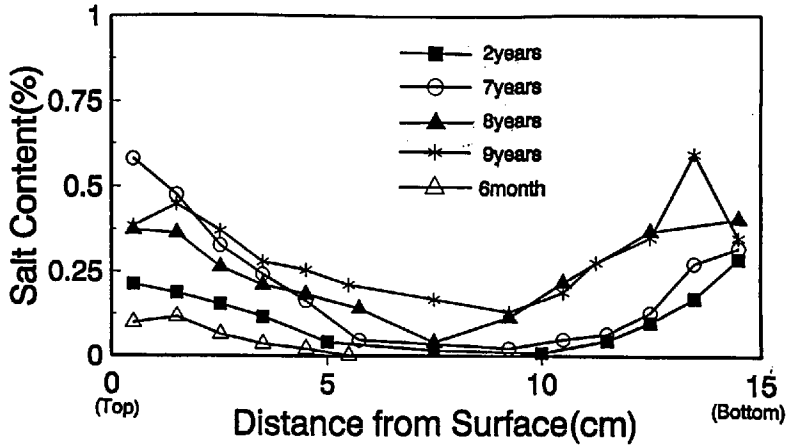


Fig. 6A—Chloride distributions in uncoated slab without salt

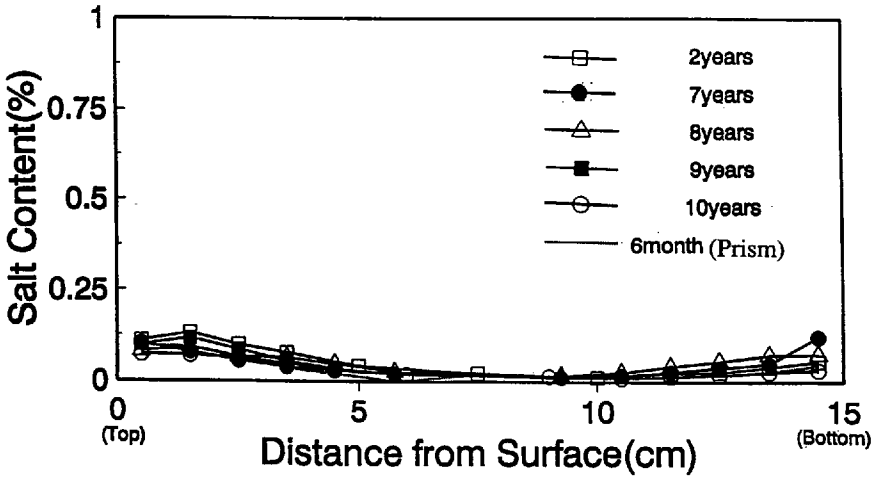


Fig. 6B—Chloride distributions in coated slab without salt

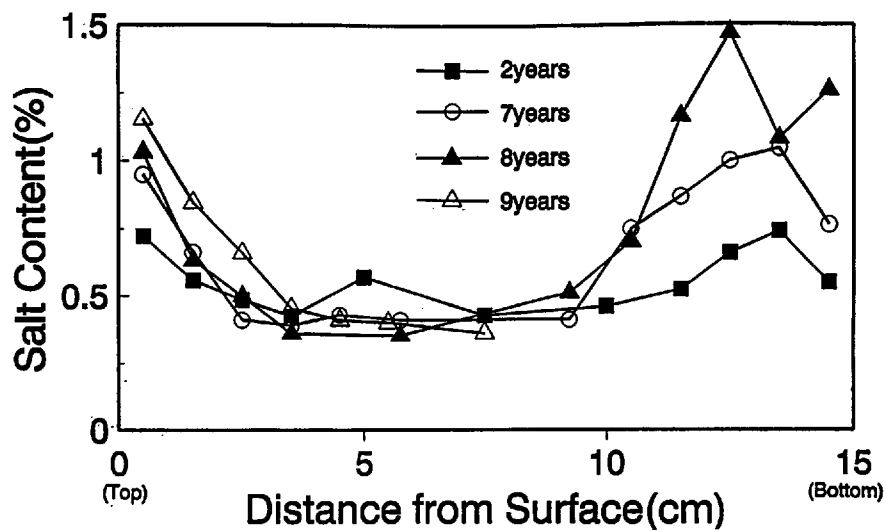


Fig. 7A—Chloride distributions in uncoated slab with 0.5% salt

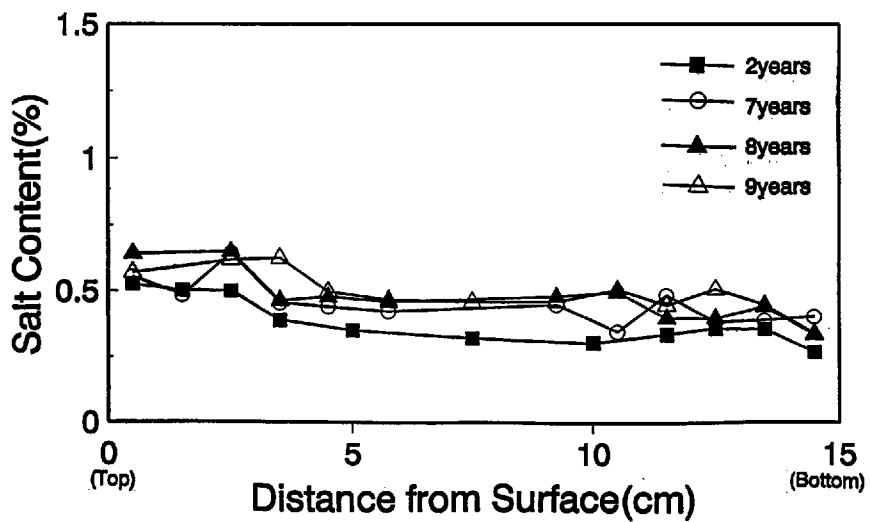


Fig. 7B—Chloride distributions in coated slab with 0.5% salt

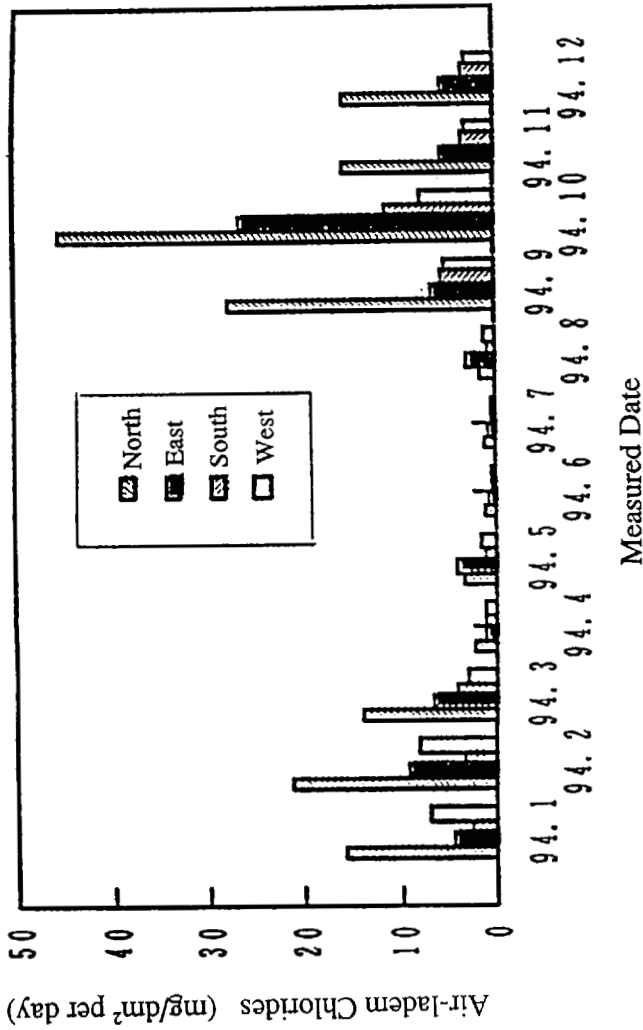


Fig. 8—Amounts of daily chlorides

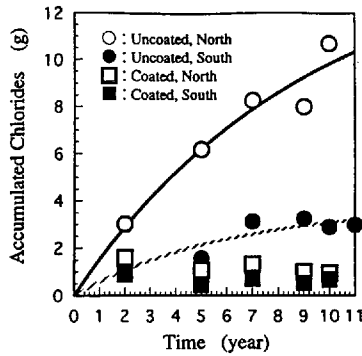


Fig. 9A—Relation between accumulated chlorides and exposure time, beam (north and south sides)

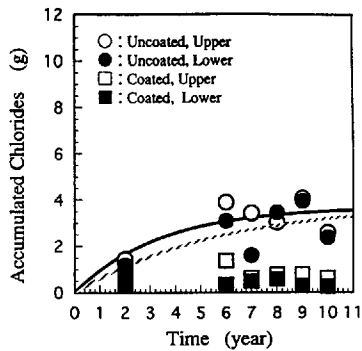


Fig. 9B—Relation between accumulated chlorides and exposure time, slab

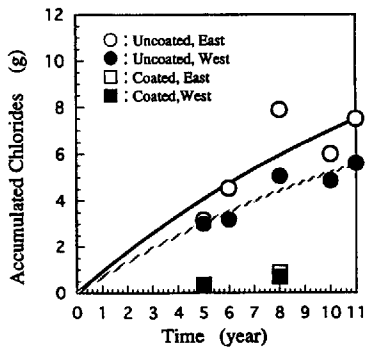


Fig. 9C—Relation between accumulated chlorides and exposure time, beam (east and west sides)

SP 170-3

Quantitative Descriptions of Steel Corrosion in Concrete Using Resistivity and Anodic Polarism Data

by Daksh Baweja, Harold Roper and Vute Sirivivatnanon

Synopsis: This paper presents results from a major long-term study on chloride induced steel corrosion in concrete. Specifically, data on concrete resistivity and estimated corrosion rates of steel in concrete have been measured and compared. The performance of 50 reinforced concrete slabs made with a range of portland and blended cement binders was evaluated. A high C₃A cement, a low C₃A cement, a blended fly ash cement and a blended blast furnace slag cement were used. All reinforced concrete slabs were exposed to high chloride conditions by partial immersion in simulated sea water conditions. Reinforcement was cleaned and weighed prior to embedment into the concrete slabs. Periodic non-destructive measurements of concrete performance included half cell potential monitoring, concrete resistivity and electrochemical measurements of rates of corrosion of steel in concrete using potentiodynamic anodic procedures. In addition, individual slabs were broken for reinforcement recovery at predetermined times during the study and measurements made of the area of corrosion and the weight loss of steel through corrosion.

As opposed to the initiation-propagation model frequently cited in the literature, three distinct segments were apparent when the estimated corrosion current data were plotted against the concrete resistivity over a period of five years for reinforced concrete slabs considered in this study. The first stage was described as the Quiescent Stage, during which it was found that resistivity increased with time and estimated corrosion current values were low. Upon reaching a maximum resistivity value, a second stage of corrosion took place. This stage was described as the Active Stage, during which resistivity values decreased and estimated corrosion current values increased. After this, a third or Breakaway Stage of corrosion was reached, during which resistivity values decreased at a lower rate while estimated corrosion currents increased significantly. The findings for each of the above stages were consistent with the exposure conditions applied to the slab, in that, after chlorides had reached the steel and caused depassivation, the concrete resistivity decreased while the steel corrosion rate increased. Using the above information, it was found that the time taken to reach the maximum resistivity value could be used as a criterion for corrosion onset as, after this time, steel corrosion rates in concrete could be expected to increase.

Keywords: Chlorides; corrosion; data acquisition; steels.

Daksh Baweja is Technical Manager - Marketing for CSR Construction Materials in Sydney, Australia. He has a Doctorate and a Masters from the University of Sydney covering the fields of Corrosion of Steel in Concrete, Concrete Durability, Use of Mineral Additives in Concrete and High Performance Concretes. He has carried out research in Australia, UK and USA and is currently involved with technical marketing and technology transfer activities relating to High Performance Concretes.

Harold Roper has recently retired as Associate Professor in the School of Civil and Mining Engineering, The University of Sydney and is Research Associate of that School. He is now Principal of Harold Roper and Associates. He has teaching, research and consulting interests in the field of materials for use in reinforced and prestressed concrete structures. He has thirty years experience in cement and concrete technology and is the author of over seventy research papers on the properties of aggregates, cements and concretes.

Vute Sirivivatnanon is Principal Research Scientist with the CSIRO Division of Building, Construction and Engineering in North Ryde, Australia. He is Project Leader of a research team working in the area of Cement and Concrete Technology. His research interests cover the use of mineral additives for High Performance Concrete, supplementary cementitious materials for use in concrete and quality assurance of concrete cover. He has industrial experience in the specification and QC of durable concrete structures.

INTRODUCTION

One of the key environments where reinforcement corrosion is likely to take place in concrete structural elements is under marine conditions. Researchers and practitioners currently use a variety of approaches to describe the factors influencing reinforced concrete performance in marine environments. Examples of some of these can be found in the literature (1,2,3). The approaches taken to address issues of concrete durability and corrosion of steel reinforcement generally differ significantly from one to another. Such differences can be also observed in specifications for concrete in marine environments.

The current Australian Standard 3600 for concrete structures (4) classifies concretes into a series of classes depending on the severity of exposure. Increases in concrete strength and cover to reinforcement are recommended for increasingly aggressive service conditions. For marine (splash zone) conditions, the concrete specification is based on having a minimum characteristic compressive strength (f'_c) of 50 MPa and a minimum cover to reinforcement of 50 mm. In this Standard, limits are also placed on the types of cement and cement blends that can be used for structural concretes. Although this Standard covers minimum recommendations for concrete in marine environments, significantly different approaches have been taken on concrete specifications for key infrastructure developments that have recently been constructed in Australia (5). Such developments and specifications include:-