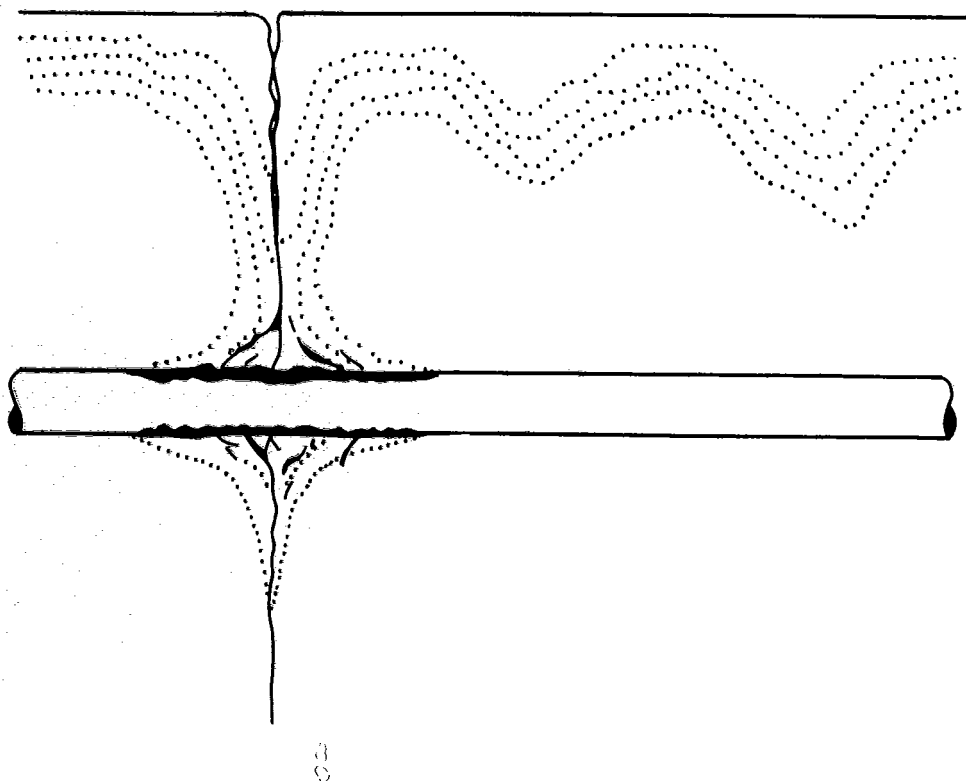


Durability of Concrete

Second International Conference
Montreal, Canada 1991



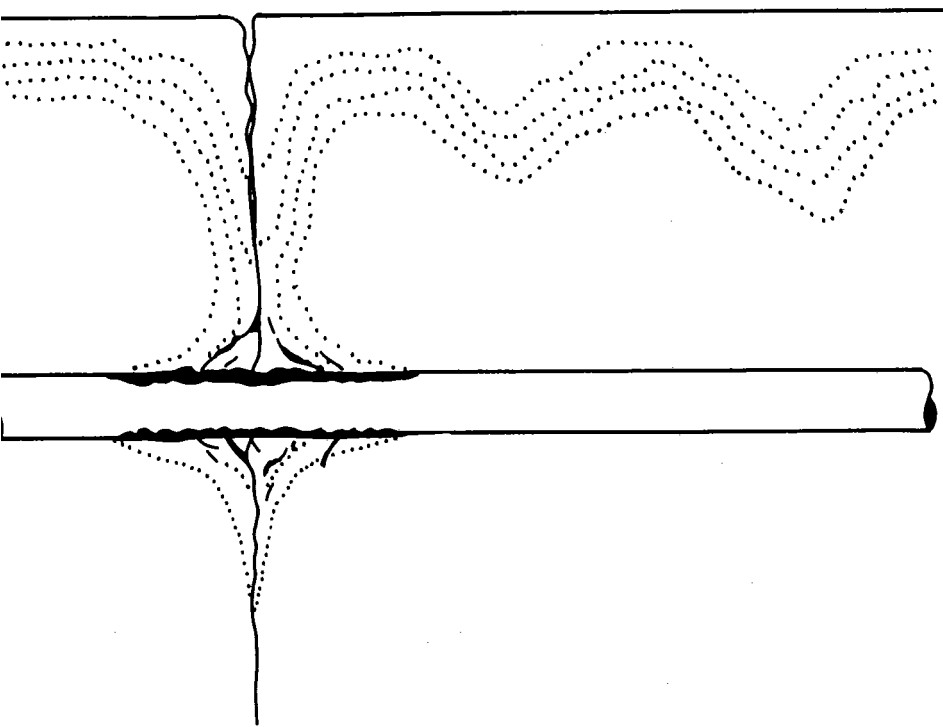
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Durability of Concrete

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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 February 1, 1992. All discussion approved by the Technical Activities Committee along with closing remarks by the authors will be published in the July/August 1992 issue of either ACI Structural Journal or ACI Materials Journal depending on the subject emphasis of the individual paper.

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PREFACE

In August 1991 the Canada Centre for Mineral and Energy Technology (CANMET) in association with the American Concrete Institute; the Institute for Research in Construction/National Research Council, Ottawa; and the Eastern Ontario and Quebec Chapter of the American Concrete Institute 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 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.

More than 100 papers from 20 countries were received and peer reviewed in accordance with the policies of the American Concrete Institute. Seventy were accepted for publication. To all those whose submissions could not be included in the symposium volumes, the Institute and the Conference Organizing Committee extend their appreciation for their interest. The accepted papers are published in two volumes; the first volume contains papers dealing with the freezing and thawing, chloride-ion penetration, corrosion, performance of epoxy-coated reinforcement and the cathodic protection of concrete. The second volume consists of papers dealing with the durability of fibre-reinforced cement composites and concrete, shotcrete, alkali-aggregate reactions, carbonation and sulphate attack. Some papers could have been published in either volume because of the overlapping nature of the subject covered.

In addition to the papers which have been published in these volumes, more than 30 other papers were presented, and published as supplementary papers.

Thanks are extended to eighteen members of the paper review panel which met in Nice, France, in June 11-15, 1990 to review the papers. Without their dedicated effort, it could 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 within the requested deadline. Particular thanks are extended to V. Ramachandran for his assistance in carrying out extensive editing of a number of submissions.

The help and assistance of G.G. Carette, E. Douglas, and Benoit Fournier of CANMET, for acting as members of the slide review panel are gratefully acknowledged. Thanks are also extended to V. Sivasundaram, also of CANMET, for compiling the supplementary papers.

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Second International Conference on
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Dedicated to members of the review panel and others who assisted in the review of the manuscripts.

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SP 126-1

Durability of Concrete— Fifty Years of Progress?

by P.K. Mehta

Synopsis: With special attention to durability of concrete, the author reviewed the proceedings of the cement chemistry congresses as well as other symposia held during the last 50 years by ACI, ASTM, and RILEM. What is presented here is not a comprehensive progress report on the subject of concrete durability but rather a state-of-the-art report from the author's perspective. It seems that, in spite of some important discoveries which are valuable from the standpoint of durability enhancement, today more concrete structures seem to suffer from lack of durability than was the case 50 years ago.

In order of decreasing importance, the major causes of concrete deterioration today are as follows: corrosion of reinforcing steel, frost action in cold climates, and physico-chemical effects in aggressive environments. There is a general agreement that the permeability of concrete, rather than normal variations in the composition of portland cement, is the key to all durability problems. There is also a general agreement that rapid growth of the concrete construction industry after 1940's led to the production and use of wet concrete mixtures, which were able to meet the strength requirement via a change in the composition of portland cement, but were unsatisfactory from the standpoint of corrosion of reinforcing steel, resistance to freezing and thawing cycles, and chemical attacks. A rise in chemical aggressivity of the environment through the increasing use of de-icer salts, and an increase in land, water, and air pollution, has also contributed to concrete durability problems.

Although significant advancements have been made in regard to understanding and control of various physical and chemical phenomena responsible for concrete deterioration, the trend towards less durable concrete structures has yet to be reversed. One of the reasons is that most of the information from tests on durability is in fragmentary form and cannot be easily synthesized into a complete understanding of actual, long-term, effects on field concrete. An over-reliance on test methods and specifications dealing with different aspects of durability has therefore become a part of the problem since accelerated laboratory tests do not correlate well with behavior of concrete structures in practice.

Keywords: Alkali-aggregate reactions; chemical attack; corrosion; deterioration; durability; freeze thaw durability; microcracking; permeability; predictability tests; reinforcing steel.

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INTRODUCTION

The author did not fully realize the immensity of the task when he volunteered to review the major publications of last 50 years on the subject of concrete durability. The Proceedings of the International Conference on Concrete Durability (1), which was held four years ago in Atlanta, Georgia, to honor Katherine and Bryant Mather, contain well over 2000 pages covering more than 100 papers. In addition, the proceedings of symposia sponsored by ASTM (2), ACI (3), and RILEM (4,5), as well as eight international congresses on the chemistry of cement contain a wealth of information on the subject. For instance, at the Eighth International Congress at Rio de Janeiro in 1986, the state-of-the-art report on chemical aspects of durability alone contains a reference to 244 papers (6). Similar reports on the chemical aspects of durability presented at the Seventh Congress at Paris in 1980 (7), at the Fifth Congress at Tokyo in 1968 (8), at the Fourth Symposium at Washington D.C. in 1960 (9), and at the Third Symposium at London in 1952 (10), contain references to 291, 128, 105, and 82 papers, respectively. Interestingly, the proceedings of the Second Symposium at Stockholm in 1938 contain only one paragraph on the subject of chemical resistance, and no other references to concrete durability.

To the above-cited literature on the chemical aspects of concrete durability, if one adds the published literature on deterioration of concrete due to freezing-thawing cycles and corrosion of reinforcing steel, the exercise of doing a comprehensive review simply becomes unmanageable. Under these circumstances, one can at best undertake a review of the previously published reviews. This is exactly what the author has done and reported in this paper. Besides highlighting the major findings from earlier reports (1-10), the author has also attempted to present a synthesis of knowledge accumulated during the last 50 years.

Before proceeding with this review, the author considers it worthwhile to address the question, "how serious is the durability problem with modern concrete structures?" In presenting his summary of the report of the National Materials Advisory Board's committee on concrete durability, Skalny (11) questioned whether we are losing the battle for concrete durability. He made a reference to the epidemic of bridge deck deterioration in the United States. Some 253,000 bridge decks are in varying states of deterioration and approximately 35,000 are being added to this list every year. The cost of bridge deck repair and rehabilitation is \$50 billion, and the overall cost of repairing or replacing all deteriorated concrete structures is estimated to be about \$200 billion. The title of the NMAB Report, "Concrete Durability - A Multi-Billion Dollar Opportunity," seems to provide an answer to Skalny's question.

Concrete durability specialists in Europe seems to confirm the U.S. experience. For instance, O'Brien et al (12) of Arup Research and Development, London, said, "Concrete durability is a growth industry: this is not to say that

there is a great increase in the volume of durable concrete being produced. It is more the increase in the number of people devoted to detailed research together with contracts dedicated to repair, refurbishment or replacement."

Reports from other parts of the world are equally disturbing. For example, Seabrook (13) reported that in 1987-88, on the eastern seaboard of Canada 400 of the ten-year old concrete piles of the Rodney Terminal in St. John, which suffered cracking and spalling from freezing-thawing cycles, had to be repaired by epoxy injection. Gerwick (14), in a paper on future opportunities for concrete structures in the marine environment, said,

"Tremendous strides have been made in the understanding of durability in corrosive environments, yet it still remains the foremost problem facing structural concrete used today. We have only to look at the new Florida keys bridge or at many other recent undersea tunnels to see that we don't yet have foolproof answers. Indeed at one time I thought of titling this talk--*Tunnels in Trouble*. The Kanmon tunnels between Honshu and Kyushu respectively leak so badly that it affects not only the concrete tunnel liners but the rails and the running equipment. The Hong Kong tunnels were designed for a 120 year life and the concrete liners are in major disruption after only 4 to 10 years. The concrete in the Dubai tunnel (built in 1975) leaked so badly that the tunnel had to be completely repaired at a cost twice that of original construction. The Suez tunnel reports similar difficulties... The new dry dock at Abu Dhabi is reportedly also severely damaged."

It should be emphasized here that around the world there are many 50-90 year old concrete structures still in good condition. On the other hand, numerous cases of deterioration in recently built structure go unreported. Therefore, the above examples of concrete deterioration are not isolated examples. That is why a feeling of uneasiness seems to be growing among the users that concrete as a material of construction is probably not as durable as claimed by its enthusiastic advocates. For instance, in his state-of-the-art report at the 1987 International Symposium on Concrete Durability, Neville (15) said, "This symposium is concerned with concrete durability, and it is tempting to ask why after all these years of research there are still so many problems with the durability of concrete. Possibly, there are even more problems these days than, say, fifty years ago."

Lack of durability manifests in the form of cracking, spalling, loss of strength, or loss of mass. Many physical and chemical causes can be responsible for deterioration, and mechanisms and control of these causes are well-described in concrete textbooks (16-19). A concrete in an advanced state of deterioration is generally found to be suffering from more than one cause, and in the post-mortem it usually becomes very difficult to identify the first cause which might have broken down the ability of concrete to resist attack from a host of other causes. However, failure analysis reports from around the world show that, in order of decreasing importance, the following causes of deterioration need most attention: corrosion of reinforcing steel, frost action in cold climates, chemical effects on hydrated cement paste from external agents (viz., water containing carbon dioxide, sulfates or chlorides), and physical-chemical effects from internal phenomenon, such as alkali-aggregate reaction, and salt weathering. A comprehensive review of the primary causes of concrete deterioration, which is presented next, is therefore not in order of their importance.

CHEMICAL ASPECTS OF CONCRETE DURABILITY

The solid hydration products and the pore fluid in hydrated portland cement paste are alkaline, therefore they readily enter into deleterious chemical reactions with acidic waters. Even fifty years ago, it was well known that natural waters containing carbon dioxide, sulfates, and chlorides eventually weaken the cementing property and must not be permitted to penetrate into cement mortar or concrete. For instance, in 1938, Hedstrom (20) made the following comment at the Second International Symposium on the Chemistry of Cements:

The chemical resistance is, as regards concrete, to a considerable extent dependent on its structure, especially its permeability. Even as regards hardened cement the physical structure must be taken as an essential factor for the resistance. Of importance in this connection are the permeability, the structure of gels remaining after chemical attack which may constitute a protective layer, and the structural changes caused in the surface layer by carbonation in the air.

It is significant that in 600 pages of the Proceeding of the 1938 Symposium on the Chemistry of Cements, the above comment was the only statement on the subject of concrete durability. There were no papers and no discussions on topics such as, corrosion of reinforcing steel, sulfate attack, carbonation, and alkali-silica reaction. Were the cement and concrete researchers of early 1900's ignorant of durability problems, or did they believe that normal variations in the chemistry of portland cement were of no major consequence to durability as long as you pay attention to the first line of defense, i.e., the impermeability of concrete?

The first major paper dealing with chemical aspects of the durability of cement products was presented by Thorvaldson (10) at the Third International Symposium on the Chemistry of Cements, in 1952. This paper contained a detailed account of the history of search for a cement of portland type which would be resistant to the action of sulfate water. Beginning with Ferrari's work in Italy in 1920, and subsequently Fleming's investigations in Canada in 1930's, the development and sulfate resisting properties of modern ASTM Type V cements were described by the author, and a test for evaluation of sulfate resistance using lean (high-porosity) mortar prisms was proposed.

The following remarks by Thorvaldson (10) show that the controversy on the possible mechanisms associated with ettringite formation in sulfate attack is not new:

While the formation of crystals of sulfoaluminate and gypsum in portland cement mortars during disintegration in sulfate solutions is well established, many experimental observations throw doubt on the assumption that physical forces of crystallization are the primary cause of expansion and loss of strength ... Many observations suggest that, (i) volume changes in the mortars are controlled by osmotic forces associated with the swelling and shrinkage of gels, that (ii) the chemical reactions condition the gel systems and destroy cementing substances (while the formation of crystalline material is incidental to these chemical reactions), and that, (iii) the increased resistance to volume changes with increased richness of mix may not be primarily due to decreased permeability

but rather due to the maintenance of condition within the mortar which are unfavorable to the swelling of gels.

Thorvaldson's comment raises the interesting possibility that concrete could expand and crack from internal hydraulic pressures (of the type developed by frost action), which may be caused by swelling of gel-like reaction products formed as a result of chemical attack, such as alkali-silica reaction, sulfate attack, and corrosion of reinforcing steel. Research studies during the 1970's and 1980's seem to support Thorvaldson's hypothesis. For instance, experimental evidence was presented by Mehta and Hu (21) that microcrystalline ettringite goes through considerable swelling on moisture absorption. Figg, and Mehta (22) believe that silica gel produced by the action of a caustic solution (formed on hydration of a high-alkali portland cement) on particles of a reactive-silica aggregate swells in the alkaline environment by water adsorption. The authors also believe that swelling of iron hydroxide gels in an acidic environment (Cl^- , CO_3^{--}) can be one of the possible mechanisms responsible for expansion and cracking of concrete from corrosion of reinforcing steel. Thorvaldson's comments also help to explain why lowering of the alkalinity by pozzolanic additions would improve the resistance of concrete to sulfate-related expansion and alkali-silica expansion, and why too much lowering of the alkalinity from excessive use of pozzolanic additions may be detrimental with regard to expansion associated with corrosion of reinforcing steel.

Thorvaldson (10) also reviewed the effect of minor components of portland cement on durability, such as free CaO , MgO , and alkalis. Hydration of coarsely ground portland cements containing large amounts of free CaO caused expansion and cracking. Better control on the chemical composition, fineness, and homogenization of the raw mix prior to clinker formation solved this problem. In regard to crystalline MgO (periclase), laboratory studies showed that the presence of more than 2-3% crystalline MgO in cement gave large expansion in an autoclave test. The test method (ASTM C 151) and the specification (max. 0.8% expansion in cement paste prisms) are still in use in North America although high- MgO portland cements, which do not meet the ASTM Specification based on the autoclave test, are being safely used in many countries of the world. In a comprehensive report on the subject, this author (23) pointed out that crystalline MgO formed at the temperature of burning of portland cement clinker (1400-1500°C) either does not hydrate under normal environmental temperatures or hydrates too slowly to cause any unsoundness in concrete.

According to Thorvaldson (10), little attention was paid to the effect on durability of small amounts of alkalis usually present in commercial portland cements until Stanton, in 1940, reported that chemical reactions between high-alkali cements and certain California aggregates (opaline chert) caused expansion and cracking. Osmotic imbibition of water by the gels produced by the alkali-silica reaction was reported to be the probable mechanism for expansion, which could be controlled by incorporation of 7-8% voids or by incorporation of suitable pozzolanic admixtures.

The following excerpt from Thorvaldson's report on durability of concrete in seawater shows that there was a recognition of the important role played by the environmental temperature in determining the rate and type of attack on concrete, and also a recognition of the fact that precise analysis or prediction of durability aspects under complex environmental conditions would be hampered by the difficulty to separate the physical effects from the chemical effects:

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There was a general agreement that if seawater penetrated mass concrete, disintegration might follow, and that such action was more pronounced in warmer seas than in northern latitudes where the effect of alternate freezing and thawing and attrition by ice were major factors. It was, however, very difficult to estimate the relative roles of physical and chemical action as each accentuates the effect of the other. A surface layer weakened by chemical action is easily removed by abrasion or may spall due to frost action, presenting a new surface for chemical attack. Physical attrition may thus mask, yet promote, chemical action.

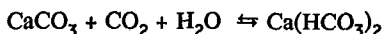
One wonders how would the predictive models and expert systems on durability take into consideration the environmental temperature cycling effect as well as the accentuating, masking, and promotional roles of physical-chemical effects on concrete deterioration, as described by Thorvaldson 40 years ago?

At the Fourth International Symposium on the Chemistry of Cements in 1960, Bredsdorff et al. (9), and van Aardt (24) presented separate papers on internal and external destructive effects, respectively. The former paper and a discussion on the paper dealt almost exclusively with the alkali-aggregate reactivity, and consisted of approximately 60 pages and 150 references. The latter paper, which is discussed here first, described the results of author's experimental investigation on the chemistry of deterioration of different types of hydraulic cements in various aggressive media.

In regard to attack by sulfate and chloride solutions, van Aardt (24) essentially confirmed the already known state-of-the-art; however, the following comments on carbonation, sulfuric acid attack, use of calcareous aggregate, and quality of mortar are noteworthy:

The carbonation of mortars made with portland cement is found to be beneficial, and the substitution of a calcareous aggregate for a siliceous aggregate improves the resistance of cement mortars to sulfuric acid attack. High density and low permeability in mortars reduce their vulnerability to chemical attack, and it is stressed that quality of the mortar is of prime importance in any corrosive environment. Bad practice in this respect can outweigh improvements aimed at by the use of more corrosion-resistant cements.

It should be noted again that impermeability, rather than the cement chemistry, is judged to be more important in determining the durability of concrete to chemical attacks. Also, the above-mentioned reference to the beneficial effect of carbonation is limited to atmospheric carbon dioxide and hard waters. Soft waters containing "aggressive CO_2 " can be very corrosive (16-18). The "aggressive CO_2 " is the amount of free carbon dioxide that is in excess of the quantity required for the stabilization of the carbonate-bicarbonate equilibrium in the reaction:



It is pointed out by van Aardt (24) that the higher the concentration of calcium bicarbonate, the higher will be the quantity of free CO_2 required for stabilizing the equilibrium, and hence for the same amount of free carbon dioxide the lower will be the amount of aggressive carbon dioxide. It should be noted that limited carbonation of hydrated portland cement paste will be impermeability-improving (because the formation of calcium carbonate which is insoluble, plugs up the pores and microcracks) whereas excessive carbonation in the presence of

"aggressive CO_2 " will be impermeability-reducing (because the formation of calcium bicarbonate, which is soluble and can be leached away, widens the existing pores and microcracks).

Following are some of the highlights from Bredsdorff et al's paper (9), based on a review of 20 years of research and investigation around the world, on the problem of concrete deterioration by alkali-aggregate reactions:

1. In concrete, aggregate particles that contain or consist of silica in an amorphous or poorly-crystalline state, are attacked by alkalies, lime, and hydroxyl ions from the liquid phase of the cement paste. The alkali-aggregate reactions produce a silica gel holding alkali and calcium ions in the random-network of silica tetrahedra. By imbibition of water, the gel may either swell almost without limit, or may not swell to any appreciable extent.
2. When condition of "unlimited swelling" are present, a mortar prism or a concrete prism or even a structural member may register expansion, which, depending on the homogeneity of stress effects and conditions of restraint, may or may not accompany cracking. When the reactive aggregate fraction is fine, the stress distribution may be homogeneous and may result in overall expansion without noticeable cracking, especially under restraining conditions.
3. Cracking may reduce the resistance of concrete to freezing and thawing action and facilitate the corrosion of reinforcement and the leaching of the cement paste, which will gradually expose the internal microstructure of concrete to damaging action of ambient air and water. Thus secondary cracking associated with other causes is common in structures afflicted with alkali-aggregate attack.
4. Only 4 percent of the 431 concrete structures in Denmark (mostly less than 25 years old) surveyed in 1954-55 by Idorn, had shown severe deterioration involving alkali-aggregate reactions.
5. A 1914 survey of coastal structures in Denmark, built since 1870, had shown expansion and cracking of concrete associated with white exudations. At that time, the deterioration was attributed to the action of sulfates in seawater. Paulsen in 1910 invented a pozzolanic cement by intergrinding a Danish diatomaceous earth with ordinary portland cement, and on the basis of field and laboratory tests claimed that the use of pozzolanic cement increased the durability of concrete to seawater. Later studies confirmed that the primary cause of deterioration was alkali-aggregate reaction, thus it appears that by inventing the pozzolan cement Paulsen had indeed found in 1910 a corrective measure against alkali-aggregate expansion, though he believed that he was fighting against the action of sulfates in seawater.

In spite of Bredsdorff et al's (9) conclusion that the alkali-aggregate reactions by themselves do not present a serious durability problem, and in spite of the fact that a corrective measure against alkali-aggregate expansion was discovered in 1910 (via pozzolanic additions to high-alkali cements), considerable research is still ongoing on the subject. Now, after 50 years since the discovery of alkali-aggregate reaction, a large volume of research effort, and several international conferences on the subject, this is how one of the coauthor's (Idorn) of the Berdsdorff et al. paper recently summed up the state-of-the-art (25):

Experience from many countries shows that in numerous structures with susceptible aggregates used in the concrete, deleterious reactions do not occur, though in some structures with concrete of the same composition damage does develop. In fact, investigations in America, Denmark, England, and elsewhere suggest that in concrete with a potential for alkali-silica reactions, these reactions most often do happen without causing any damage to the concrete at all. This is one reason why none of the many existing test methods for the reactivity of aggregates are individually reliable for evaluation of the behavior of reactive aggregates in concrete structures ...

Map-cracking in unreinforced dolosses of a concrete element may result in loss of structural reliability, especially in hot, marine environments. In contrast, alkali-silica reactions do not usually result in significant decline of structural reliability in reinforced concrete elements as long as cracking does not lead to severe corrosion of the reinforcement.

RESISTANCE TO FREEZING AND THAWING

A highlight of the Fourth International Symposium in 1960 was a 60-page principal report with discussions by Paul Nerenst (26), on the subject of frost action in concrete. In his introductory remarks, the author stated that before the Second World War the factors influencing the resistance of hardened concrete to freezing and thawing were not well known. In spite of this, durable concrete structures existed in areas exposed to numerous freezing and thawing cycles. For instance, a 100-years old coastal fortress near Copenhagen, built with portland cement concrete, was in excellent condition at the time of Nerenst's report in spite of exposure to seawater and numerous freezing-thawing cycles. Commenting that the ideas of making good concrete were much older than 1918, the year when Abrams formulated the relation between water-cement ratio and strength, Nerenst (26) quoted from a book by Henry Reid, published in 1868:

"The due and thorough incorporation of the cement, sand, shingle or gravel, with the least amount of water, is the ABC of the process of concrete making, and unless this is rigorously attended to, much disappointment will be experienced. All ingredients should be well mixed first in a dry state, and when this is thoroughly done a quantity of water is added to render the mixture plastic enough to be placed in moulds or formwork. As a rule, the less quantity of water you can use the better. The concrete should be well rammed in as dry a state as is consistent with the proper requirements of the material, for too small a quantity of water would be as injurious as an excess; again that would be materially influenced by the amount of force applied by the impingement of the rammer. The rammer should be as heavy as should be conveniently used. Sand, where a choice exists, should be as rough and coarse as possible. A rotten or friable aggregate is to be avoided. Where practicable, concrete blocks should be placed for some days or weeks in water. Concrete, when so treated and carefully and thoroughly mixed, will be immensely superior in quality to the ordinary sloppy and roughly-handled mixture commonly called concrete, only in many cases entitled to the name because it contains certain proportions of the necessary ingredients."

Continuing his introductory remarks, Nerenst (26) said:

"In the twenties and thirties of our century the wet concrete mixtures were growing in popularity, foremost in the United States but also in many countries in Europe, and the freezing resistance of concrete was diminishing. The low durability of concrete roads was growing to be a serious problem ..."

Nerenst's analysis of the situation is indeed thought-provoking. By abandoning the common-sense approach to overall concrete quality, as advocated by Reid in 1868, in favor of the practice of designing for strength by using Abram's relationship between water/cement and strength we might have inadvertently entered into an era when many concrete structures are being made with a high-permeability material. This material will have low-durability, because it is easily susceptible to many physical-chemical processes of deterioration, such as carbonation, alkali-aggregate attack, freezing and thawing, and corrosion of reinforcing steel. This author was startled by the thought that researchers 50 years ago did not discuss many of the problems which afflict concrete today, not because they were less knowledgeable but because these problems were virtually nonexistent.

According to Nerenst (26), in 1945 Powers first presented the "hydraulic pressure theory" of expansion of hardened cement pastes subjected to freezing, when the specimen had a certain minimum degree of saturation. A combination of low permeability and high rate of freezing gave rise to a hydraulic pressure gradient, which led to expansion and cracking unless the pressure was relieved by inclusion of closely-spaced air voids. To produce frost resistant concrete, Powers recommended a maximum void spacing factor equal to 0.01 in. (approx. 0.2 mm).

In his principal report on concrete durability at the Fifth International Congress on Chemistry of Cements in 1968, Valenta (8) included frost action as one of the major factors in deterioration of concrete. Confirming the findings of earlier researchers, the author observed:

If air bubbles are to play a role favorable from the standpoint of frost resistance of concrete, they must be connected into the spatial system of capillary channels, be uniformly distributed in the microstructure of cement paste, and have small spacing. The length of and the flow conditions in the channels eventually decide the internal pressure (tension) in concrete and the suitability of the system of pores. The total air content of hardened cement paste, and more so of concrete with aggregates of diverse sizes is, therefore, not an adequate criterion of effective air entrainment.

Valenta also made some interesting comments about the role of voids present at the cement paste-aggregate transition zone on frost damage in concrete. According to him, there are usually large voids caused by entrapped air adhering to rough surface of coarse aggregate. There seems to be close connection between high permeability of concrete and a combination of high water-cement ratio and high specific surface of aggregate. Since the flow of water in concrete follows the path of least resistance, the relatively high permeability of concrete creates conditions leading to strong hydraulic pressures. Further, according to Valenta (8), continuous microcracks sometimes linking into wider cracks originating from the concrete surface, play the greatest role in reducing impermeability. By appreciably facilitating the ingress of water from external sources, they would increase the degree of saturation of concrete, which is a necessary prerequisite for any damage to be caused by frost action.

Valenta (8) presented detailed data on the influence of various factors on the quantity and distribution of pores in air-entrained concrete. In particular, the effects of varying water-cement ratio, admixture type, and vibration time on air content and specific surface of air bubbles were presented. Also given were the effects of cement fineness and grain size of fine aggregate. According to Valenta, several research studies had shown that sand grain sizes, between 0.3 and 0.6 mm, exercised a decisive influence on the air-entraining properties of concrete. The author also cited a research study in France which showed that frost damage in some aggregates followed essentially the same physical-mechanical laws as in saturated cement paste. Higher water absorption in a calcite aggregate with a fine pore structure (capillary pores up to 5 μm diameter) was found to be decisive for the poor performance of concrete on freezing.

In spite of voluminous literature on air entrainment of concrete and durability of adequately air entrained concrete subjected to freezing and thawing cycles (such as ASTM C 666), many reports in the published literature show that concrete structures continue to deteriorate from frost action. Among the reasons for this is the difficulty of maintaining the desired air-void spacing in hardened concrete due to incompatible concrete-making ingredients, high water content of concrete mixtures, overmixing, improper handling of fresh concrete, overvibration during consolidation, etc.

For use in cold climates, there is now evidence in favor of the superior field behavior of low water-cement ratio concrete mixtures without entrained air, compared to high water-cement ratio concrete mixtures with entrained air. Sturup et al (27) presented Ontario Hydro's experience on evaluation and prediction of concrete durability to frost action. The paper is unique in the sense that, in addition to the results from accelerated tests (ASTM C 666), the results from a 28-year outdoor exposure test on companion specimens of both air and non-air entrained concretes are presented. One of the conclusions from this paper is as follows:

In the outdoor exposure tests, equal deterioration is being observed in a low water-cement ratio (0.5 or 0.6) non-air-entrained concrete compared to a higher water-cement ratio (0.7 to 0.8) air-entrained concrete. In contrast, by Procedure A (ASTM C 666 test method) a non-air-entrained concrete with a water/cement ratio of 0.5 has much lower durability than an air entrained concrete with a water-cement ratio of 1.0. While the benefits of entrained air are obvious, Procedure A has overemphasized these benefits with respect to non-air entrained concrete. If acceptable results are obtained by Procedure A, the field performance should be good; but if poor results are obtained the field performance cannot necessarily be predicted.

Sturup et al's work clearly shows that "overmagnification or poor reproduction" of real exposure conditions in laboratory tests can produce misleading results. The authors reported that in field structures such as dams, some of them up to 50 years old, where the maximum water-cement ratio was established (0.5 to 0.6) on the basis of exposure and then rigidly controlled, the non-air-entrained concrete continues to be in good condition.

Interestingly, Sturup et al (27) also reported that a section of the Otto Holden dam, built with non-air-entrained concrete containing fly ash, is in good condition after 33 years of service and is at least comparable in performance to the neighboring non-fly ash concrete. It is well known that the incorporation of mineral admixtures in concrete, such as fly ash and silica fume, generally requires much larger dosages of air entraining admixtures to obtain the

air content and void spacing, needed to satisfy the durability of concrete to frost action, as tested by ASTM Method C 666. The published literature also contains data showing that with high-strength concrete mixtures, made with superplasticizers, it is difficult to maintain the proper air void spacing necessary for satisfactory performance in the ASTM C 666 test. For instance, Malhotra et al (28) found that air-entrained concretes incorporating 10 and 20% silica fume, with 0.35 and 0.30 water-cementitious ratios, showed poor freezing and thawing resistance when tested in accordance with ASTM C 666, Procedure A, in spite of having had more than 4% air in fresh concrete. Non-air-entrained concretes, regardless of the water-cementitious ratio and the silica fume content, showed very low durability in the test. The authors conceded, "whether non-air-entrained concrete will perform satisfactorily if it has greater maturity or the opportunity to dry before being subjected to freezing and thawing is open to question." If the ASTM C 666 test method for freeze-thaw durability is not satisfactory for simulating most field exposure conditions, then why do we really need air entrainment with high-strength concrete mixtures containing fly ash, silica fume, and superplasticizers, especially when the water-cement ratio is held very low and is rigidly controlled? This is a question which must be addressed seriously because 5-6% air entrainment will cause about 25 percent reduction in strength. Recognizing the validity of this issue, it may be noted that the 1986 Japanese Standard Specification for Design and Construction of Concrete Structures has incorporated the following statement into the building code (29):

In regions where the weather is not severely cold comparatively, the use of concretes other than air-entrained concrete may be considered, because the required durability may be assured even without air entrainment, as in the case of high-strength concrete.

CORROSION OF REINFORCING STEEL

The damage to concrete structures resulting from the corrosion of reinforcing steel manifests in the form of expansion, cracking, and spalling of concrete cover. In addition to the cover loss, a reinforced concrete member may suffer structural failure due to loss of bond between concrete and steel. This is why with modern concrete structures, the corrosion of reinforcing steel is considered to be the most serious problem responsible for lack of durability. As described next, there is strong evidence that since about 1960's more concrete structures have suffered from reinforcing steel corrosion than before the 1960's.

In a reference to the general epidemic of bridge deck deterioration in North America, Manning described the experience of the Ontario State's Department of Transportation as follows:

Prior to 1963, the corrosion of reinforcing steel was not the most common cause of deterioration of the portland cement concrete beneath the bituminous concrete overlay (then in use). Beginning 1963, bridge decks with exposed surface were built and a major expansion of the freeway system was undertaken soon afterwards. By the early 1970's it was discovered that the deck slabs were prone to corrosion of the embedded reinforcement due to a combination of factors, such as more frequent application of deicing-chemical (chlorides), lack of adequate cover (min. 25 mm, max. 37 mm), insufficient permeability of concrete (27 MPa 28-d compressive strength), and exposure to large number of cycles of wetting-drying, freezing-thawing, and loading-unloading (fatigue cracking). Clearly, the problems arose because the material

quality and the construction practice (i.e., cover thickness) were not upgraded whereas the environment became more aggressive (i.e., more frequent application of deicers).

As stated earlier, in a 1986 report to the National Materials Advisory Board in 1986, Skalny (11) reported that 253,000 bridge-decks were in varying states of deterioration in the United States; and according to a recent report by Gerwick (14), worldwide many concrete-lined tunnels are leaking as a result of corrosion of reinforcing steel. A survey of collapsed buildings during the 1974-78 period in England showed that the immediate cause of failure of at least eight structures, which were 12-40 years old, was corrosion of reinforcing or prestressing steel (18). According to Litvan and Bickley (31), deterioration of parking garages has become a matter of major concern in Canada. Of the 215 garages resurveyed in Toronto, Ottawa, and Montreal, almost all suffered varying degrees of deterioration due to reinforcement corrosion, which was a result of design and construction practices that fell short of those required by the environment. The authors stated that almost all garages in Canada built until very recently by conventional methods will require rehabilitation at a cost that is likely to exceed \$3 billion.

Since chlorides are almost always involved in the cases of serious damage to reinforcing steel, it is interesting to review some of the experiences with marine structures as seawater contains about 2% chloride ions. In 1962-64, GjØrv (32) surveyed over seven hundred, 20 to 50 years old, reinforcing concrete wharves of the slender-pillar type along the Norwegian seaboard. The structures were generally in good condition both below the low-tide level and above the high-tide level. Only in the splash zone a significant loss of mass had occurred, and GjØrv attributed this to mainly frost action on non-air-entrained concrete. Reinforcing steel corrosion was noticed only on some of the deck beams. Since seawater had penetrated deeply into the fully submerged parts of the pillars, the absence of corrosion showed that chlorides alone were insufficient to cause the problem.

In 1980, eleven spandrel beams of the San Mateo-Hayward bridge on the San Francisco Bay in California, which were 16 years old, had to be repaired as a result of cracking associated with corrosion of the reinforcing steel (33). The original precast beams were made by the steam curing process, using a high-quality concrete mixture. Interestingly, the same type of concrete had been used to make the remaining eleven beams, which were cast in situ and naturally cured but did not crack after 16 years of service in the same environment. The corrosion and cracking of the steam-cured beams was suspected by the authors to be due to pre-existing microcracks, which probably resulted from thermal stresses on rapid cooling of the massive beams, immediately after the steam curing treatment. Similarly, cracking and spalling of concrete in the Dubai tunnel, which was only 11 years old at the time of repair in 1986, was associated with severely corroded reinforcing steel; however, leaking joints and shrinkage cracks in the outside walls were suspected to be precursors to the reinforcement corrosion (34).

In conclusion, experience with concrete structures in the marine environment shows that generally serious deterioration due to the reinforcement corrosion alone has not been a problem. There is a strong evidence that significant corrosion did not develop unless a concrete was permeable to begin with (e.g., poorly compacted joints, insufficient cover thickness, and the use of high water-cement ratio mixtures), or became permeable in service due to microcracking from the environmental effects (e.g., cycles of heating and cooling, wetting and drying, freezing and thawing, loading and unloading, and expansive chemical reactions). It seems that when concrete quality and cover

thickness are adequate, microcracking need not occur from reinforcement corrosion, rather it precedes corrosion and comes from causes other than corrosion. The significance of this conclusion will become apparent from the following state-of-the-art review of corrosion of steel in concrete.

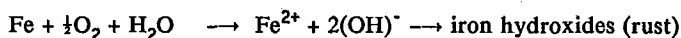
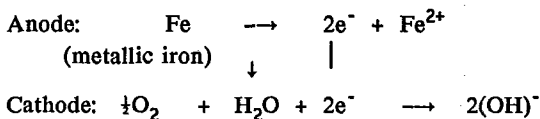
Except for the Eighth International Symposium in 1986, which contains a review paper by Turriziani (35) on electrochemistry of reinforcing steel, the subject has not been covered by the reviewers of concrete durability at the earlier symposia on the chemistry of cements (7-10). Nevertheless, there is a large body of published literature devoted exclusively to the problem of reinforcing steel corrosion. Some of the puzzling questions which need to be answered, are as follows:

- * During the last 20-25 years why has there been an epidemic of concrete deterioration in bridge decks and parking garages from reinforcing steel corrosion?
- * What precisely is the mechanism by which concrete expands and cracks as a result of reinforcement corrosion?
- * By what mechanisms the damage to reinforced concrete is accelerated by chlorides, CO_2 , and sulfates?
- * Can one predict the time to reach a certain level of deterioration of concrete by separating the various rate determining phenomena underlying the corrosion of reinforcing steel?

From a survey of recently published reports (36-42), a review of the fundamental principles governing the corrosion of reinforcing steel in concrete, with special emphasis on the questions raised above, is undertaken next.

Mechanism of Corrosion of Steel in Concrete

Corrosion of steel is an electrochemical phenomenon which involves an anode process and a cathode process:



For transformation of metallic iron to rust, clearly all three of the following conditions must be satisfied.

- (i) For the anode process, iron must be available in a metallic (Fe) state at the surface of reinforcing steel.
- (ii) Oxygen and moisture must be available for the cathode process.
- (iii) The electrical resistivity of concrete must be low to facilitate the electron flow in the metal from anodic to cathodic areas.

In reinforced concrete, with adequate cover of good quality, none of the three conditions listed above may be met during the service life. For instance, let us consider the anode process first. It is well known that there exists an adherent surface film of iron oxides or gamma $\text{FeO}\cdot\text{OH}$ (lepidocrocite), which usually protects (passivates) the underlying metallic iron. This protective film is thermodynamically stable above pH 11 (note that the pH range of hydrated portland cement paste is 12.5 to 13.0). The long-term basicity (alkalinity) of the

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environment is further guaranteed by the deposits of crystalline calcium hydroxide which, due to cement hydration, are plentiful in the immediate vicinity of steel (i.e. the transition zone between steel and concrete). Consequently, the basicity (alkalinity) of the cement paste adjacent to steel must be reduced as well as the protective film of iron oxides or hydroxide must be destroyed before metallic iron becomes available for the anodic reaction.

Similarly, with regard to the cathodic process, a continuous supply of oxygen and water must be available. With normal reinforced concrete members having an adequate cover of good-quality concrete this condition is also not met easily. Because, if concrete is saturated with water, the rate of oxygen diffusion will be very slow. Gaseous diffusion rates are faster in relatively dry concretes, but dry environments are neither suitable for the cathodic reaction nor appropriate for the reduction of electric resistivity, which is the third necessary condition for the corrosion process. The conflicting requirements of humidity with respect to fulfillment of the conditions necessary for corrosion of reinforcing steel in concrete should delay the onset of corrosion in field structures unless, for instance, they are subject to cycles of wetting and drying or freezing and thawing. This is why in marine structures deterioration of concrete from corrosion of steel is more of a problem in the splashing zone (the zone between low and high tides, where the structure is exposed to alternate cycles of wetting and drying) than either in the fully submerged zone or the atmospheric zone.

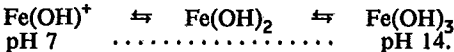
There is a lot of published literature, such as the report by Gjrv and Vennesland (43), on the influence of numerous factors on reinforcing steel corrosion, such as cement type, water-cement ratio, depth of cover and crack-widths, and exposure to CO_2 and chlorides. However, it is difficult to integrate the information for practical use. Tuutti (39) proposed a model (Fig. 1) according to which corrosion damage can be predicted by assuming two distinctly different rate determining periods for the corrosion process, namely the corrosion initiation period and the corrosion propagation (deterioration) period. It is further assumed that the corrosion initiation period and the corrosion/damage period are influenced by different parameters, the former being influenced by the rate of diffusion of CO_2 and chlorides (which cause depassivation of steel), and the latter by the rate of diffusion of oxygen and water (which control the cathodic reaction). In the opinion of this author, such models are no doubt useful for understanding the corrosion process but should not be used for predicting the rate of deterioration of a reinforced concrete structure from steel corrosion. Because, as will be discussed next, it is not possible to separate the microstructural aspects of concrete responsible for the corrosion initiation process from the corrosion damage process.

Let us consider the depassivation of steel. This would require, first, the decomposition and removal of the crystalline calcium hydroxide (in the proximity of the rebar) and, second, the destruction of the protective iron oxide film present on the surface of metallic iron. Aggressive waters containing high concentrations of CO_2 , sulfate, or chlorides will react with calcium hydroxide and form leachable products (such as, calcium bicarbonate, calcium sulfate, and calcium chloride). With portland cement paste, chlorides can form products, such as $\text{C}_3\text{A}\cdot\text{CaCl}_2\cdot\text{H}_2\text{O}$, and $\text{Ca}(\text{OH})_2\cdot\text{CaCl}_2\cdot\text{H}_2\text{O}$. These products will, however, decompose and release the chloride ions in the case of sulfate or CO_2 attack, which does happen with many natural waters. Once the crystalline calcium hydroxide has been removed from the vicinity of reinforcing steel, the pH of the pore solution drops below 11 and the iron oxide film loses its protection. For instance, in the presence of chlorides, a basic iron chloride, $3\text{Fe}(\text{OH})_2\cdot\text{FeCl}_2$, is formed (44) which later decomposes to produce akaganeite (beta $\text{FeO}\cdot\text{OH}$). Incidentally, this explains why the reinforcing steel corrosion

assumed epidemic proportions in bridge decks and parking garages after the use of deicer chlorides was increased.

The loss of the iron oxide protective film by the mechanisms described above, exposes metallic iron from the steel reinforcement. Obviously, increase in the permeability of concrete from cycles of wetting and drying, heating and cooling, freezing and thawing, loading and unloading (including wave action in the case of sea structures) facilitates the ingress of liquids and gases, which not only are capable of depassivating steel but also are essential for the progress of the cathodic reaction. According to Figg (44), this is how the stage is set for the corrosion/durability theater, often a tragedy, sometimes farcical, always expensive and, like the famous Windmill in London, never stops. To explain the deterioration of reinforced concrete structures in the marine environment, Mehta and Gerwick (45) have proposed a cracking-corrosion-cracking model (Fig. 2) according to which a substantial increase in the permeability of concrete through enlargement and interconnection of microcracks must precede before the anodic reaction and the cathodic reaction can make significant progress. Except chloride ions, the permeation of ions and gases by diffusion is an extremely slow process although the presence of chlorides alone is not sufficient to initiate the corrosion of steel.

What is the precise chemical composition of rust and how does rust formation cause expansion in concrete, are among the questions which have not been fully resolved. According to Figg (44), depending on the environmental pH at the anode, ferrous ions may be associated with more or less hydroxyl ions:



Compared to metallic iron, the hydroxides of iron are more voluminous and their formation is accompanied by expansive pressures. Figg (44) as well as this author (46) tend to believe that, similar to expansion of cryptocrystalline ettringite in sulfate attack or expansion of silica gel in alkali-aggregate attack, the gel-like iron hydroxides formed as a result of steel corrosion can imbibe water and swell under certain conditions. Acidic conditions (such as those when hydroxyl ions have been replaced by chloride, sulfate, or bicarbonate) weaken the hardened cement paste, and the paste thus weakened can expand and crack from the development of hydraulic pressure via gel swelling. This explains the field observation that the corrosion of reinforcing steel is usually accelerated not only in the presence of chlorides but also sulfates, and CO₂.

GENERAL OBSERVATIONS

During the last fifty years, a vast amount of new knowledge has been produced on many physical and chemical aspects of concrete durability. The following is a partial list of the most important discoveries: the entrainment of air in concrete as an effective means of reducing the risk of expansion and cracking when exposed to cycles of freezing and thawing, the incorporation of fine particles of mineral admixtures in combination with a superplasticizer to produce highly impermeable concrete mixtures, the use of low-C₃A portland cement to resist sulfate attack, and the use of low-alkali portland cement or pozzolans to combat expansion and cracking associated with alkali-aggregate reactions. However, at the same time, public confidence in concrete as a highly durable material has been shaken due to an increase in the number of structures which contain concrete in serious state of deterioration.

Among the primary reasons for this apparent paradox is the fact that changes in concrete-making materials and construction practice have occurred in an arbitrary manner. When the use of a new material or technology offered a certain advantage, it was incorporated into the concreting practice without a thorough evaluation of all the effects, especially the bad effects. This is particularly true of concrete durability, the evaluation of which by field tests, takes a long time (note that most of the laboratory tests show poor correlation with actual field performance). Examples of how some of the changes in materials and practices might have resulted in general detriment of concrete durability, are given next.

According to Wischers (47), to develop high strength at an early age the cement industry during the last 40 to 50 years has made a considerable increase in the $C_3S:C_2S$ ratio of ordinary portland cement. Since concrete mixtures are proportioned on the basis of 28-day compressive strength, this change has gradually resulted in decreasing the cement content and increasing the water-cement ratio of concrete mixtures, with a given consistency. From the United Kingdom typical changes in the cement content and water-cement ratio for a 33 MPa concrete having the same workability during the period 1945 to 1980, are reported as follows:

<u>Period</u>	<u>Minimum Cement Content</u>	<u>Maximum Water-Cement Ratio</u>
1945-47	380 kg/m ³	0.47
1954-58	300	0.60
1975-80	250	0.72

From a review of changes in the composition of British portland cements during 1950 to 1990, Pomeroy (48) has confirmed Wischer's data as shown above. For instance, a 35 MPa concrete mixture (28-day cube, compressive strength) in 1950 was made with 0.50 water-cement ratio, whereas with portland cements made in 1990 a similar strength is attainable with 0.70 water-cement ratio. The implications of this change in cement composition on concrete durability is obvious from the fact that, under normal curing conditions, a concrete mixture with a 0.70 water-cement ratio is unlikely to ever become impermeable.

According to Price (49), in the United States the C_3S content of Type 1 portland cement increased from about 30% in 1950 to 45-50% in 1970's, and during the same period the fineness increased from about 1,000 cm²/g to 4,000 cm²/g. These trends are responsible for the higher early strength of the **normal portland cement** and have enabled more efficient utilization of labor and equipment. However, from the standpoint of durability, the changes in cement composition have brought into the forefront problems that were previously considered minor, e.g. excessive drying shrinkage, excessive heat of hydration, and increased vulnerability to various types of physical and chemical attacks.

The advent of World War II saw a construction boom that continued for at least twenty-five years after the end of the war, during which period the war-time economy was transformed into a peace-time economy. At the same time, a general shortage of steel led to a deepening of interest in concrete as a material of construction and broadened the field of concrete applications, particularly in combination with reinforcing steel and prestressing steel. According to Waddell (50), a greater emphasis on the speed of construction resulted in major changes in concrete handling equipment and consistency of fresh concrete. The use of ready-mixed concrete, transported and mixed in truck mixers, increased tremendously. Also, beginning in the 1950's, placement of concrete by pumping gained increasing popularity. In response to these changes, fueled largely by the speed of construction, the water content of concrete mixtures has to be increased

significantly to meet the workability requirements. As discussed earlier, this did not cause any difficulty in meeting the 28-day concrete strength specifications, because the composition of normal portland cements was altered to obtain higher early strengths. Of course, with the advent of normal water-reducing admixtures in 1950's, a 5-8% reduction in the water content could be achieved but this was probably inadequate to compensate for the larger increase in water demand necessitated by the high consistency requirement. As a net result, the concrete industry did not seem to have paid attention to the permeability and durability of concrete structures.

Imagine the following scenario. To speed up construction, first we created sloppy concrete mixtures. Then to control the problem of drying shrinkage cracking of high water-cement concrete mixtures, we discovered that unreinforced structures had to be reinforced (note that at the end of World War II there was still more plain than reinforced concrete pavement in the U.S.). The use of concrete in more sophisticated structural members made reinforcement and at times prestressing necessary. This would have been all right but for the fact that a combination of factors, such as heavier trucks, increase in traffic, and bare-pavement policy (requiring frequent application of de-icing chemicals) brought on an epidemic of concrete deterioration from reinforcement corrosion. A reduction in the water-cement ratio by increasing the cement content did not necessarily solve this problem if this change was accompanied by either a reduction in cover thickness or an increase in thermal cracking. It is probable that the current practice of proportioning of concrete mixtures by the relationship between strength and water-cement ratio has also contributed to concrete durability problems. It is on account of an over-emphasis on strength alone in concrete mix proportioning, rather than on both strength and long-term soundness (i.e. freedom from cracking during the service life), that a majority of the concrete structures made today suffer from cracking due to excessive heat of hydration, drying shrinkage, creep, and other causes. In mix proportioning, by neglecting an important component of concrete, namely the aggregate type, the seeds were sown for many potential durability problems. It is the aggregate type which controls the dimensional stability of concrete via control of thermal properties, elastic modulus, drying shrinkage, and creep. To be durable, a concrete must remain impermeable or free from microcracking during the intended service life, and this will not be possible until concrete suppliers and users learn to understand and respect the effects on concrete behavior of all the major components of concrete including the aggregate, rather than the water-cement ratio alone.

Another important reason for the paradox why, in spite of an overwhelming body of fundamental knowledge on physical and chemical aspects of durability, a large number of concrete structures (some of them less than ten years old) show evidence of deterioration, is the fact that this knowledge exists mostly in a fragmentary form. Reductionism, that is, the study of one variable at a time, is an easy path to follow in research but the value of data produced from a reductionist approach is rather limited, because the behavior of materials in real life is a result of interactions between many variables acting simultaneously. Sometimes two variables may disproportionately enhance a given effect; at other times they may tend to cancel each other's influence. The following examples from Calleja's principal report in 1980 (7) on chemical aspects of durability of concrete will illustrate this point:

Damages caused by freezing of water and crystallization of de-icing salts have not yet been fully explained, and it is admitted that all of several factors involved must be taken into consideration. In the author's opinion, this is one more of the innumerable cases of durability in which factors, actions, and effects, purely physical

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and purely chemical in nature, cannot be separated from one another as they are linked together in an indissoluble manner, acting either simultaneously or successively. The importance attributed to the one or to the other or to both will depend on conditions and circumstances, and on the evaluation of them in any particular case by an individual researcher ...

Our present knowledge on durability, either in general or in specific aspects of it, such as the alkali-aggregate reactions, is by no means proportional to the efforts made and the number of papers published. A critic (on the alkali-silica problem) has recently stated that the more extensive and deeper the potential knowledge of the problem, the more complex and difficult seems to be its solution. From the list of both solved and yet unsolved questions, the paradoxical conclusion is drawn that the broad knowledge obtained up to date only serves to recognize the enormous complexity and difficulty of the problem, but it hardly aids either the predictability of the alkali-silica expansion or the prevention of it ...

Having reviewed a large number of publications on concrete durability, this author concurs with Calleja's (7) observations that in the field of durability as well as in many other fields of cement and concrete research, most of the research work runs around the same themes, using the same methods, applying the same ideas, and arriving repeatedly almost always at the same partial, and not decisive, conclusions. To solve the durability-related problems, we need to divert more resources toward integration of our present knowledge into a "holistic understanding of the durability issue."

More and more fundamental research on mechanisms, and individual effects of specific phenomena causing deterioration, considered one at a time, have failed to take us near the goal of building durable concrete structures. And, we shall never reach the goal unless we adopt a holistic approach.

Among the few researchers to advocate such a holistic approach is Valenta, and some of the highlights from his 1968 report on concrete durability (which is highly pertinent to our current problems but has almost been forgotten by today's researchers) are as follows. According to Valenta (8), "the durability of concrete cannot be separated from the durability of concrete structures. The durability of concrete structures must be ensured on a complex basis--starting with the choice of building site and suitable system of construction, and ending with the proper design, taking into consideration the nature of the surrounding environment and the technology of concrete with due recognition to the importance of the choice of suitable materials, concrete composition and production, placing, and curing. It is imperative that proper care be accorded to finished structures; this includes protection of concrete and concrete structures against effects of aggressive media, regular checks, and timely maintenance or possible repair."

Some examples, illustrating the significance of factors influencing the durability of concrete structures, mentioned above by Valenta, are given below.

Choice of Building Site: Crystallization pressures associated with mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) formation in large capillary pores of concrete are reported to be responsible for deterioration of garage and kitchen floors in many homes 20-25 years old built at marginal sites in Southern California (51). It is suspected that these sites are in low-lying areas, which formerly served as drainage sumps (stagnant pools) for sulfate-bearing waters from heavily fertilized

agricultural soils. A combination of poor drainage and high-permeability of concrete (with suction of groundwater by capillary action when one surface of concrete is exposed to drying conditions), led to the deterioration of concrete.

Structural Design and Construction: In addition to the pollution of land and water, air pollution is also becoming a major player in durability problems. The fog near urban areas frequently registers 2.5-3 pH and is laden with such pollutants as carbonic acid, sulfurous acid, nitrous acid, and sulfates as well as nitrates of ammonia, lead, copper, nickel, and vanadium. An interesting case of concrete deterioration was documented by the author (52), showing that rain water accumulation, resulting from poor design and construction detailing in an elevated concrete structure in the San Francisco area, was a source of sulfate attack.

Concrete Technology: This author was surprised to find that as far back as 1961, Valenta (53) had warned that the transition zone between aggregates and cement paste is the weakest link in concrete from the standpoint of tensile strength and permeability. Due to the bleeding effect, voids and microcracks usually exist in the vicinity of coarse aggregate (their size being dependent on the water-cement ratio and the specific surface of the aggregate particles). In the beginning, these voids and microcracks may not have much influence on the penetration of aggressive fluids into concrete elements, as they may not be interconnected to form continuous channels of flow. However, after curing, when a concrete is exposed to environmental cycles of heating-cooling, wetting-drying, and freezing-thawing, the local stress effects may exceed the tensile strain capacity of the material. The microcracks thus enhanced would eventually provide the missing links necessary for the high permeability without which concrete does not generally attain a high degree of moisture saturation--a condition necessary for the occurrence of most physical and chemical attacks. With reference to the performance of "finished structures," Valenta obviously meant that the choice of individual concrete-making materials and mix proportions should be such that the permeability of concrete does not increase under the given service conditions.

In the context of Valenta's remarks about the significance of the transition zone to permeability and durability of concrete, two developments are worthy of note. The advent of high range (superplasticizing) water-reducing admixtures in the 1970's has made it possible to produce high-consistency concrete mixtures at very low water content. The resulting product is more homogeneous, free from large pores and microcracks, and essentially impermeable as well as highly resistant to abrasion and erosion damage (18). These benefits are further enhanced by the simultaneous use of fine particles of a mineral admixture, such as condensed silica fume, fly ash, or pulverized slag (18). General use of superplasticizers and some of the mineral admixtures (e.g., condensed silica fume), for the purpose of improving the durability of ordinary concrete is not recommended due to their high cost. Moreover, unless proper attention is paid at the same time to the selection of aggregate type (i.e., compatibility between the aggregate and cement paste regarding the elastic moduli and the coefficients of thermal expansion) even impermeable concretes can become permeable by microcracking under service conditions.

Valenta's (8) comments on tensile cracks should also be noted. He says that while development of such cracks may be favorable from the point of view of stress distribution in the texture of concrete, the situation becomes extremely different when judged from the point of view of concrete's capability to resist aggressive environmental effects. This is particularly important with reinforced concrete structures where the width, depth, and continuity of microcracks play a decisive role in the reinforcement corrosion. Cracks due to settlement, plastic

shrinkage, restrained thermal or drying shrinkage, and accidental overloads may not have any serious effect on the static behavior of a concrete structure, but they do represent a future threat to concrete durability. According to Valenta, since it is impossible to eliminate cracking except in prestressed concrete elements, an important question to be tackled is, "under what conditions is it necessary to properly seal the tensile parts of concrete members and thus exclude the possibility of reinforcement corrosion?"

Valenta (8) was one of the earliest researchers to recognize that microstructural heterogeneities in concrete would be a major source of stress concentration and microcracking, which is detrimental to concrete durability. For instance, seepage of water through microcracked concrete wets the adjacent high-quality concrete, and thus exposes it to chemical dissolution and frost action. The non-homogeneity of concrete also asserts itself adversely by creating conditions conducive to electrolytic corrosion of the reinforcement. Among the causes for non-homogeneities in the concrete microstructure, Valenta lists the following as most important: poor consolidation, high variability of aggregate grading, and improperly proportioned concrete mixtures (e.g., high water-cement ratio).

Protection of Concrete Surface: In regard to strongly aggressive environments, Valenta (8) suggested that protection of the concrete surface must be considered an inseparable part of the solution to the durability problem. Timely protective measures are the most effective and cheapest solution, and can be classified into two groups:

1. **Adjustment of the environment**, such as drainage of the foundation soil, ventilation and withdrawal of aggressive vapors (including prevention of steam condensation on concrete structures), efficient drainage of roofs, prevention of water flow on facades, adequate and regular drainage of de-icer salts from pavements and bridge-decks, and weakening or neutralizing of aggressive solutions before they come into contact with concrete surface.
2. **Treatment of concrete surfaces** to render them completely impermeable to the aggressive medium by impregnating chemical solutions (such as fluorosilicates, which form a dense coating of insoluble calcium fluoride), polymer membranes, asphaltic materials, etc. (This effect may also be achieved by using steel liners or granite panels.)

Role of maintenance and repair: Valenta (8) placed a great emphasis on the role of regular and timely repair of possible defects caused by uneven settlement of structures, errors in design and construction, inferior quality of concrete-making materials or concrete mixture, problems with placement and consolidation, inadequate curing, etc. By restricting or completely eliminating the defects at an early age, the deterioration of concrete from many physical and chemical causes can be prevented or considerably delayed. It is interesting to point out that twenty years after the publication of Valenta's recommendation regarding maintenance of concrete, Neville (15) expressed the same opinion in his recent state-of-the-art report:

First of all, we must admit to ourselves, as well as to the world outside, that structural concrete does not have an indefinite life. The quality of the concrete, in terms of its composition and not strength measured at 28 days, will determine its life. More than that, maintenance of concrete is needed, and this means regular inspection and occasional repair.

Judging from the increase in concrete durability problems, which started in the 1960's, it is tempting to conclude that if we had paid proper attention to the work of earlier researchers, such as Thorvaldson (10) and Valenta (8,53), we would not have found ourselves in this situation. Nevertheless, the cost of ignorance in terms of repairing or replacing deteriorated concrete structures and wasted research effort is incalculable.

PREDICTING DURABILITY

During the 1970's and 1980's, the use of concrete has been extended to sophisticated structures exposed to severe climates. For example, heavily reinforced and prestressed concrete structures are the major components of more than twenty offshore drilling platforms in the North Sea, where the force of impact of breaking waves against the side of a structure may reach up to 30 t/m^2 (54). In addition to intense wave action, corrosion of reinforcing steel in the chloride-rich environment, and numerous cycles of freezing-thawing in the atmospheric and splashing zones of the structure, create highly demanding conditions in cold climates from the standpoint of durability. On the other hand, structures in areas of hot weather and high salinity such as Saudi Arabia and Gulf States, do not seem to fare any better because a combination of high ambient temperature and salinity greatly accelerate the chemical and electrochemical processes of deterioration. Since many construction projects cost billions of dollars, the owners demand a long service life. For instance, the reinforced concrete lining of the Eurotunnel is designed to last for 120 years, and the estimated lifetime of the concrete for the fixed link across the Great Belt (Storebaelt) is a minimum of 100 years.

The increasing use of concrete in hostile environments is not limited to severe climatic conditions. Concrete is being used, or in other cases under active consideration as a construction material for containment of toxic chemical and radioactive wastes. Some of the radioactive materials have a half-life of several hundred years. Clearly, prediction of durability of concrete in the multi-billion dollar structures and waste containment structures is a very important issue. In this context, in his principal report at the Eighth International Congress in 1986 Oberholtzer (55) summarized the state-of-the-art as follows:

The development of computer-based expert systems, such as DURCON, to assist in making decision on the durability of concrete mixtures, has obvious potential. However, systematic scientific research based on carefully designed experiments, is still required to provide the technical background for the mathematical prediction of service life. In this respect, it is important to define the system (concrete) properly, as well as to establish significance, the extent, and kinds of degradation factors (characterize products of degradation mechanisms, determine a quantitative indicator of degradation, establish how it can be measured, devise an accelerated test to simulate degradation mechanisms and, finally, relate the laboratory test data to field test data and past findings.

The key elements for a reliable method for mathematical prediction of durability appear to be a precise definition of the material (concrete), a precise definition of the environment, and database from accelerated test methods relating laboratory measurements to field behavior. For the following reasons, a quantitative treatment of these key elements for the purpose of mathematical modelling is very difficult, if not impossible.

First, how does one define a material which is constantly changing as a result of interaction with the environment? The pore structure and permeability of concrete are the most important characteristics from the standpoint of durability, and they are always changing as a result of innumerable physical and chemical effects (such as dissolution of cement hydration products, crystallization of new products, and microcracking). How would one model the accentuating, masking, and promotional roles of newly formed products as a result of environmental effects when the types, rates, and amounts of these products cannot be easily predetermined?

Second, how does one accurately define a standard environment or a number of standard environments for the purposes of accelerated laboratory testing, when in the field practice no two environments are exactly the same? For instance, Chandra (56) found that the depth of carbonation increased when a trace of SO_2 (1 ppm) was mixed with CO_2 . In another experiment, more deterioration was found when the specimens were exposed to a mixture of dilute sulfuric and nitric acids (pH 3) compared to a mixture of SO_2 and NO_x gases. Such dilute acid droplets are readily formed as a result of fog condensation in urban areas (increased atmospheric pollution due to heavy increase in traffic and industrial activities since World War II). Service life models take into consideration only the effect of one variable at a time. It should be obvious that in these models, it will be difficult to incorporate the synergetic effects of two or more corrosive elements simultaneously present in the environment, in addition to any temperature and humidity effects, which can be significant.

Third, how does one develop accelerated laboratory tests, which truly simulate the field (service) condition, when after 100 years of research we still do not have test methods and specifications that are considered satisfactory? A brief review of some of the standard test methods and specifications, relevant to concrete durability issues, which is given next, will illustrate this point.

Testing the Sulfate Resistance: A general review of various test methods for evaluation of sulfate resistance of cements, and shortcomings of each of these methods, was given by the author (57). Since then, ASTM has adopted a new test method, ASTM C 1012, which is described by Patzias (58). In this test, length change measurements on standard mortar bars exposed to a mixed solution of sodium and magnesium sulfates, are made until the age of 180 days. A maximum of 0.1% expansion at 180 days is considered appropriate for moderate sulfate resistance, and 0.05% for high sulfate resistance. Although the method is useful in comparing the relative sulfate resistance of high- C_3A and low- C_3A cements, it cannot simulate the service behavior of concrete and will have, therefore, limited value in predicting the field performance. In this regard, the complexities involved in attempting to assess the sulfate attack by seawater, as described by Calleja (7), should be noted:

In regard to sulfate attack, research work (and publications) on the effect of C_3A is copious but not always useful. The effect of mixtures of sulfate salts cannot be foreseen, as they sometimes can be additive and at other times "subtractive." Also, there are several mechanisms involved in sulfate deterioration. (But most test methods and specifications recognize only the one associated with ettringite formation from C_3A and ignore others. Other mechanisms of deterioration are softening as a result of gypsum-formation, spalling as a result of crystallization of mirabilite or $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in pores or cracks, and decomposition of calcium silicate hydrate gel as a result of long-term magnesium ion attack). The physical aspects of the microstructure of concrete (such as capillary porosity and microcracking), rather than the chemical

aspects, are decisive in determining the effects of sulfate attack because the rate of diffusion of sulfate ions in hydrated cement paste is extremely slow.

Even external physical factors such as temperature effects are important in sulfate attack, though this is not always taken into consideration. Temperature may condition the type of hydrated aluminates and sulfoaluminates formed, in addition to changing the nature of compounds once formed as a result of changes in temperature. In spite of a relatively high concentration of magnesium sulfate in sea water, sea-water attack is quite different from that of pure alkali sulfate solutions and generally limited due to surface protection of concrete by brucite and aragonite formations (as a result of CO_2 attack) and by the simultaneous presence of chloride ions (which have an inhibiting effect on ettringite expansion). The very cold temperature of sea water below the surface further ensures that the action of sulfate ions is much less important. The complex situation of sea water attack on concrete clearly illustrates that, when dealing with concrete durability problems, simplifications, generalizations, and extrapolations may be very dangerous.

Testing the Unsoundness of Cement Due to High Free CaO and MgO: Hydration of free CaO and free MgO in hardened concrete can lead to cracking (unsoundness), and a standard autoclave test (ASTM C 151) is used to test the soundness of cements in the United States and Canada. In this test, bars of neat cement paste are normally cured for 24 hours and then subjected to a steam pressure of 2 MPa for 3 hours. A cement is considered unsound if the expansion in the autoclave test exceeds 0.8%. After undertaking a comprehensive review of history of development and status of this test, the author (23) came to the following conclusions:

1. Exaggerated expansion values are obtained in the test because the cohesive forces present in normally cured cement pastes are destroyed by autoclaving.
2. The autoclaving conditions force the crystalline MgO to hydrate and cause expansion, whereas under normal conditions the crystalline MgO in portland cement would remain either unhydrated or hydrate at a rate too slow to be of any consequence.
3. The magnitude of expansion in neat cement bars due to hydration of free CaO or free MgO is high, but in the corresponding concrete specimens it will not be high enough to cause cracking, especially under conditions of global restraint (such as with reinforced concrete members). On the contrary, expansion under restraint is the principle governing modern expansive cements which are so useful in producing crack-free concrete structures for water storage and other purposes (18).
4. No correlation has ever been shown between the autoclave test specification limit (i.e., 0.8% expansion) and the soundness of concrete in service.
5. There is evidence that energy and resource conservation in the cement industry are negatively impacted by complying with the ASTM C151 method and the associated specification limit, which have little relevance to durability of concrete in service.

Testing the Resistance to Freezing and Thawing Cycles: ASTM Method C 666, Procedure A, is the commonly used method of testing the resistance of concrete to freezing and thawing cycles. In this test, concrete prisms normally cured (100% relative humidity, 20°C) for 14 days, are subjected to freezing and thawing cycles in water, and each cycle is completed within 2 to 5 hours. The condition of specimens during the test is monitored by measurement of resonance frequency from which the dynamic modulus of elasticity may be calculated. (The durability factor is the ratio of the dynamic modulus after 300 freezing and thawing cycles to the initial modulus, expressed as a percent.) According to Philleo (59), as early as in 1955 Powers had criticized that the test was too severe to be of practical value. Powers' complaint was two-fold: (1) no drying of specimen is provided in the test whereas under service conditions virtually all concrete undergoes some drying before exposure to freezing and thawing cycles, (2) the rate of freezing in the test is many times that occurring in nature. Note that the rate of freezing is a critical parameter in the expansion and cracking phenomena because it governs the rate at which water would be migrating through the pore structure in the cement paste, thus determining the building up of hydraulic pressures.

In regard to the poor correlation between ASTM C 666 test method and the field performance of concrete, the conclusion from the 28 years of outdoor exposure test carried out by Sturup et al (27), should be noted again:

While the benefits of entrained air are obvious (i.e., demonstrable by the ASTM C 666-Procedure A), Procedure A has overemphasized these benefits with respect to non-air-entrained concrete. If acceptable results are obtained by Procedure A the field performance should be good, but if poor results are obtained the field performance cannot necessarily be predicted.

Like the other ASTM tests, it seems that the practice of using air-entrained concrete mixtures is designed mainly to satisfy the requirements of the standard test methods and specifications. Since the results from ASTM C 666 cannot be used in predicting the resistance of field concrete to cycles of freezing and thawing, more field studies are needed to confirm whether or not air entrainment is really necessary with low-permeability concrete containing mineral admixtures (good quality fly ash, silica fume, or ground granulated blast-furnace slag), in particular with those concrete structures which are not expected to acquire a critical degree of saturation during their service life.

Testing the Alkali-Aggregate Reactivity: A quick method for testing the potential reactivity of aggregates is the ASTM C 289 chemical test. In this test, a sample of crushed aggregate particles is placed in a standard sodium hydroxide solution at 80°C for 24 hours and the filtrate is analyzed for dissolved silica and reduction in alkalinity. This test neither reflects the mechanisms of alkali-aggregate reactions in concrete nor simulates the mechanical effects responsible for distress in real structures. Therefore, it is not surprising that some aggregates failing the ASTM C 289 test continue to give good performance in service, and vice versa. Hobbs (60) gives examples of flint gravels from Thames Valley and from Southern Germany; also, 30% of Japanese aggregates which have a good field performance record in concrete, failed the test. However, some aggregates passed the test, but are known to have an unsatisfactory service record, e.g. Malmesbury hornfels.

A commonly used method for testing the deleterious alkali reactivity of a cement-aggregate combination, is the ASTM C 227 mortar-bar expansion test. In this test, the aggregate is crushed and recombined to a prescribed grading, and

mortar bars using an aggregate-cement ratio of 2.25 are made. At 24 hours the bars are demolded, and then stored at 38°C in a humid environment. The specimens are checked periodically for length change. If the observed expansion exceeds 0.10% in 6 months (or 0.05% in 3 months), the cement-aggregate combination is considered potentially reactive. Among the main disadvantages of this test, listed by Hobbs (60), are the unusually high cement content (630 kg/m³), long test period (6 months), questionable environmental conditions (the mortar bars are not in direct contact with water whereas field concretes which crack due to the alkali-silica reaction are usually in direct contact with flowing water or groundwater), and unrepresentative nature of the aggregate size. That the test is unsatisfactory for predicting the field performance of concrete, was known 30 years ago. For instance, expressing a general dissatisfaction with the test, Bredsdorff et al (9) said:

From a practical point of view the most irrelevant requirement in the procedure is the rule that coarse aggregates should be crushed, sieved, and recombined to a linear grading curve. With some aggregates, it is found that there is a marked increase in percentage of reactive particles with rising particle size of aggregates.

Attempts to develop a suitable correlation between the mortar bar test and concrete have largely been unsuccessful. Natural weathering or purely physical effects (wetting and drying, heating and cooling) were found to be an important factor for development of disintegration in experimental specimens.

Interestingly, in their review of published literature on alkali-aggregate reactivity, Bredsdorff et al (9) cited a paper authored by Kennedy and Mather which dealt extensively with fundamental difficulties in transferring laboratory results to field concrete tests, and vice versa. Kennedy and Mather concluded that alkali-aggregate expansion in concrete need not lead to deleterious results. The authors found evidence of beneficial effects of "mild" alkali-aggregate reaction, believed to have been caused by a measurable improvement of bond between slightly reacted chert pebbles in the coarse aggregate and ambient cement paste.

Based on the foregoing review of test methods and specifications, this author has come to the conclusion that, regardless of other purposes served by test methods, such as the ASTM C 289, ASTM C 227, ASTM C 1012, and ASTM C 151, they are not useful for prediction or control of durability of concrete. The author is aware that many experts on concrete durability do not share this view. For example, in a 1975 state-of-the-art report on, "Durability of concrete construction - 50 years of progress," Mather (61) concluded that it was the interest of his paper to suggest that information is now available that will permit the preparation of specifications that, if followed, will preclude the occurrence of concrete deterioration.

CONCLUDING REMARKS

During the last fifty years many major developments have taken place in concrete materials and construction practice. Most of the developments were dictated by needs other than durability. For example, beginning with 1940's a rapid growth of the concrete construction industry resulted in the production and use of wet mixtures with high water content. Obviously, the speed of construction rather than durability was the focus of this development because an

increase in the water content would reduce the durability in general. Cement producers changed the composition of normal portland cement in order to enhance the 28-day strength, at a given water-cement ratio. The purpose of this development was to meet the 28-day strength requirement of concrete mixtures with increasing water content. The strength of concrete, although of value, has now been found to be of secondary importance for safeguarding the durability. The penetrability or water-permeability of concrete turns out to be the only property, which can be directly related to long-term durability. There is an overwhelming evidence that the major durability problems of today, such as the corrosion of steel reinforcement, poor resistance to cycles of freezing and thawing, and cracking from alkali-aggregate reactivity or sulfate attack would be of no consequence with concrete that is impermeable at the time of exposure to the environment, and continues to remain impermeable throughout the intended service life.

Among the durability-enhancing developments that have occurred during the last fifty years are, the use of entrained air to protect concrete against frost action, and the use of low- C_3A or low-alkali portland cements as a protection against expansive cracking due to sulfate attack and alkali-aggregate attack, respectively. A lot of research effort has also gone into the development of laboratory test methods and specifications for evaluation of durability of concrete-making materials and concrete when exposed to various deterioration processes. Since it is not possible to simulate the field service conditions by accelerated laboratory tests, and since the standard specification limits are determined arbitrarily, these test methods and specifications have a limited value for prediction and control of concrete durability.

Actually, it seems to the author that over-dependence on specifications and recommended codes of practice for safeguarding the durability of concrete may have done more harm than good, because it has prevented both the producers and the users of concrete from obtaining a comprehensive understanding of the material as a whole. For example, consider the practice of taking the water-cement ratio as the sole criterion for concrete performance (i.e., strength and durability). In concrete mixtures with high slump and therefore high water content, theoretically, the relationship between strength and water-cement ratio can be satisfied by increasing the cement content. In this way, it is possible to come up with concrete mixtures that are deficient in aggregate content and are, therefore, more prone to drying-shrinkage cracking, which would have the effect of increasing the permeability of concrete and reducing the durability to various deterioration processes. It is suggested that concrete technology in practice today is close to what has just been described. In short, reliance on the water-cement ratio alone as an index of concrete durability, has made the concrete producers and users totally unmindful of the role that aggregate type can play in microcracking of a concrete mixture under service conditions. Hardly any attention is ever paid to the consequences of a mismatch in the elastic moduli or coefficients of thermal expansion between the cement paste and aggregate. To the extent that specifications and codes of recommended practice promote a narrow view of a complex situation, are these not a part of the problem rather than a part of the solution?

In conclusion, as long as we continue to use poorly constituted concrete mixtures, without a broader understanding of the effect of all concrete-making materials on durability, we should not expect the structures to be sound and permanent, especially when they have to be exposed to heavy dosages of de-icer chemicals or to polluted land, water, or air. This is at the heart of the concrete durability problems which, during the last thirty years, have grown to an extent that the reputation of concrete as a sound structural material is being seriously questioned. With the help of a comprehensive understanding of the role of all

the constituents that are an integral part of concrete's microstructure, and by putting into practice the accumulated wisdom left behind by eminent thinkers, such as Thorvaldson and Valenta, we can certainly reverse the situation. Otherwise, the cost for repair and replacement of concrete structures is bound to be staggering and, most importantly, the ecological cost of wasted materials will be unforgiveable. We may not be able to predict the durability of concrete structures, but we are certainly in a position to prolong their service life by making use of the nuggets of useful information that already exist but have become buried with the passage of time.

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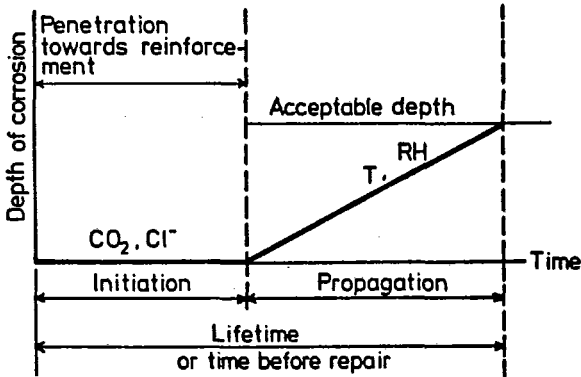


Fig. 1--Schematic sketch of steel corrosion sequence in concrete

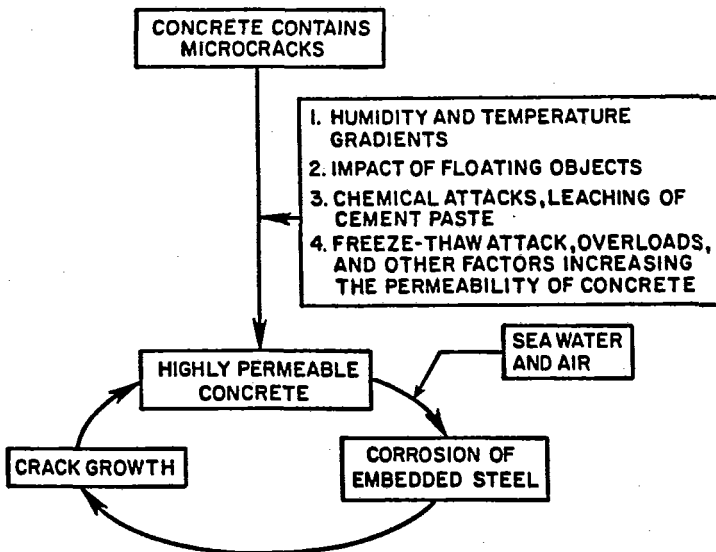


Fig. 2--Diagrammatic representation of the cracking-corrosion-cracking cycle in reinforced concrete

SP 126-2

Durability of Offshore and Marine Concrete Structures

by G.C. Hoff

Synopsis: The durability of concrete is generally regarded as its ability to resist the effects and influences of the environment while performing its desired function. In an offshore or marine environment, the concrete can be subjected to the influences of wetting and drying, freezing and thawing, abrasion by ice and other debris, chemical attack or mineral depletion by water it is in, salt accumulations, and attack by marine organisms. The paper reviews these deteriorating mechanisms and also reviews the recent trends in strength development for concretes made with modern materials. Chloride ion penetration into concrete information from 33-year old Gulf of Mexico offshore concrete platforms is presented. The advantages of supplementary cementing materials in offshore and marine concretes are discussed along with recommendations for producing durable marine concretes.

Keywords: Abrasion resistance; alkali-aggregate reactions; blast furnace slag; carbonation; chloride-ion contamination; corrosion; durability; fly ash; freeze thaw durability; harbor structures; marine atmospheres; marine concretes; portland cement; seawater; silica fume; supplimentary cementing materials.

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INTRODUCTION

Marine concrete structures are generally described as those concrete structures which are located inshore or near-shore. They may also be called maritime concrete structures. In general, these concrete structures are berthing and mooring facilities, container terminals and oil jetties, floating dry docks and graving docks, breakwaters, embankments, light towers, tidal barriers and dams, underwater tunnels and pipelines, foundations and super-structures for transportation structures, and dams. ACI Committee 357 (1) offers a suggestion for a classification of marine concrete structures as shown in Figure 1. Each of these structural types may be designed in several alternatives: cast-in-place, precast, cellular, prestressed, etc.

Offshore concrete structures are generally understood to be those structures exposed to an open-sea environment (2,3). They are designed to remain permanently or semi-permanently fixed to the sea bed by gravity, piles, or anchors, or to remain afloat and moored. They are often associated with the exploration and production of hydrocarbons.

Like most other types of concretes, offshore and marine concretes are usually made with local materials by local labor in conformance to local guidelines or specifications. Thus, they can vary widely in quality. Depending on their particular application, their strengths can vary from 15 to 65 MPa. However, they are all required to be durable. Once a concrete structure is placed in the sea, maintenance becomes very difficult due to the surrounding environment and very expensive. Some offshore concrete platforms have design lives of 50 to 70 years. Seawalls and other wave energy dissipating concrete structures are expected to last much longer than that.

The durability of offshore and marine portland-cement concrete is generally defined as its ability to resist weathering action, chemical attack, abrasion, or any other process of deterioration while retaining its original form, quality, and serviceability when exposed to its environment. This includes resistance to deterioration from freezing and thawing action, chemical attack by the constituents of the seawater, physical abrasion due to wave action, floating or suspended solids and debris, and floating ice, corrosion of steel or other metals imbedded in the concrete, and chemical reactions associated with aggregates in the concrete. When considering all these deteriorating actions collectively as shown in Figure 2 (4), it is easily deduced that the most aggressive exposure a concrete can routinely experience is in a tidal zone in freezing weather.

DESTRUCTIVE MECHANISMS

Freezing and Thawing Process

Philleo (5), in a synthesis on the freezing and thawing resistance of high strength concrete, provides a very straightforward description of the freezing and thawing mechanism in concrete which is paraphrased in the following paragraphs. He notes that with the assumption of the use of durable aggregates, the vulnerability of mature concrete (compressive strength of at least 24 MPa) to freezing is a function of the pore structure of the cement paste and the moisture condition of the concrete when it is exposed to freezing. Lower strength concretes are also vulnerable for the same reasons but may be even more susceptible to damage because of their higher porosities and lower strengths.

There are two types of pores that are generally discussed with respect to a cement matrix: capillary pores and gel pores. Capillary pores are empty spaces between gel particles while gel pores are much smaller and are contained within the gel itself. It is generally agreed by researchers that gel pores are so small that water contained in them will not freeze under normal winter weather conditions, whereas the capillary pores are of such a size that water in them will freeze near, or only a few degrees below, its normal freezing point. Pores are usually distinguished by their origin but may be roughly categorized as shown in Table 1.



The size of the gel pores allows them to imbibe water if any is available in the system. It has been calculated (5) that if no water is provided from the outside, a cement paste with a water-cement ratio of 0.38 by mass will run out of water when only 90 percent of the cement is hydrated. The process of running out of water has been termed self-desiccation and is, in effect, a drying-out of the concrete.

If it is the water in the capillary pores that will freeze, then any concrete having a cement paste containing capillary pores is potentially a candidate for freezing damage. When water freezes, it undergoes an increase volume of 9 percent. If the water in a capillary pore exceeds 91 percent of the volume of the capillary pore, the expansion of the water cannot be accommodated in the capillary pore. The excess water can be expelled because all of the water does not freeze instantaneously. The low permeability of the cement pastes requires high pressures to move the water very short distances. These pressures can easily disrupt the cement matrix unless receptacles are provided to receive the excess water and are placed close enough together to prohibit the development of high pressures. Intentionally entrained air bubbles provide the receptacles and their size and quantity dictate the spacing of the bubbles. The bubbles must remain at least partially empty of water to function properly. They are the first of any of the voids in the system to empty when drying occurs.

Chemical Attack by Seawater

In general, the salinity and content of various salts within a given sea are fairly stable. However, for different seas, they may vary greatly. In local regions, where the sea receives large amounts of inflow from fresh water rivers or snow and ice melt, the salinity will be greatly reduced compared to other regions of the same sea. It has been reported (6) that the average seawater may be considered a solution of salts of which the highest proportion is attributed to sodium chloride, NaCl (77-79 percent of the salinity expressed in grams per litre), followed by magnesium chloride, MgCl_2 (10.5 to 10.9 percent), magnesium sulfate, MgSO_4 (4.4 to 4.8 percent), calcium sulfate, CaSO_4 (3.4 to 3.6 percent), amounts of carbonates and bicarbonates not exceeding 2.1 percent, plus a number of other minor constituents. The reactivity of seawater is a function of its salt composition and the assumption

that magnesium sulfate and magnesium chloride convert to magnesium hydroxide and that all bicarbonates and equilibrium carbon dioxide, convert to carbonates.

Sulfates in seawater can, in certain circumstances, cause the formation of reaction products which increase the volume of the solid phase within the paste structure of the concrete. This, in turn, leads to cracking and disruption of the concrete.

Magnesium salts in seawater may cause deterioration by exchange of the magnesium ion of seawater sulfates and chlorides with the calcium ion from calcium hydroxide saturated water solution. The resulting magnesium hydroxide is very insoluble and will precipitate, forming a film on the surface of the hardened concrete followed by an accumulation of a white amorphous substance. The more permeable the concrete is and the higher the relative CaO content in the cement, the more amorphous substance will be formed with a corresponding loss in mechanical properties. Small amounts of magnesium hydroxide may be beneficial in reducing the permeability of the concrete as the precipitates fill up the pore space.

The seawater salts can attack both submerged concrete and concrete in both the splash zone and in areas of airborne spray. For submerged concrete, the reactions between the hardened cement and the seawater at the surface of the hardened concrete, cause the seawater that enters the concrete to drastically change its chemical composition. Moskvina, et al (6) proposed a simple model (Figure 3) to show the theoretical zones of destruction in concrete affected by seawater.

The magnesium ion and CO_2 from the water are fixed in the surface layers (Zones 1 and 2).

Most of the gypsum precipitating from oversaturated solutions is also held near the exchange reaction sites. The water penetrating deeper into the concrete becomes enriched with sodium chloride, calcium chloride, calcium sulfate, and insignificant amounts of other salts (nitrates, nitrites, etc.). In Zone 3, the initial attacks by sulfates begin with prevalent formation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Zone 4 sees the formation of calcium⁴ sulphoaluminates (ettringite) with its swelling behavior. Zone 5 is a zone of leaching that is usually active only if there is continual movement

of water through the pore system as might occur from alternate wetting and drying or differential water heads on the concrete.

These zone boundaries are not stable, and, with subsequent degradation, they continuously change, advancing inward. The succession of zones remains essentially the same however.

Not everything in the seawater has an adverse effect on the concrete. Buenfeld and Newman (7) showed that the permeability of seawater exposed concrete reduces significantly with time due to the formation of a discrete layer on the surface of the cement paste, together with a more widespread bulk effect associated with a modification of the pore structure. The surface layer generally consists of a brucite (magnesium hydroxide) layer which becomes evident after only one day. This is overlain by a more slowly developing skin of aragonite (calcium carbonate). After 4 months immersion in North Sea water, the layers on laboratory specimens were typically 30 micrometres and 150 micrometres thick, respectively. These deposits reduced the chloride diffusion rates to 20 percent of their initial values after 5 months.

In the splash zone, the concrete receives salts from the seawater by continually rewetting from wave action and by capillary action. Evaporation of moisture from the upper exposed surfaces accentuates the problem by continuously drawing water up through the mass. Sea water spray also contains the salts and when it continually rewets concrete surfaces, these salts can be deposited in the concrete. Concrete structures some distance from the sea can be affected by this process. This is discussed in more detail later.

Carbonation

Carbonation can occur in all marine structures but is usually not a significant problem. Carbon dioxide occurs both in the air and in the seawater surrounding a marine concrete structure.

In most instances the amount of carbon dioxide in the air is small, being on the order of 0.03 percent by volume of air (8). In normal seawater only small amounts of carbonate and bicarbonate are present, about 10 and 80 parts per million, respectively, along with a small amount of free dissolved carbon dioxide (9). The pH of the seawater varies between

about 7.5 and 8.4 with an average value of 8.2 when the seawater is in equilibrium with the carbon dioxide in the atmosphere. Under these conditions, some carbonation of the hardened cement may occur accompanied by minor leaching of lime from the concrete surface. Exceptional concentrations of carbon dioxide in the air, resulting from internal combustion engines continually running on or adjacent to marine concrete structures, or in the seawater, when high contents of organic matter are present and carbon dioxide is a decay product, can produce a much stronger carbonic acid to attack the concrete. Lea (9), has noted that when the pH of the seawater is above 7.5, there is little likelihood of leaching by carbon dioxide. At a pH of 7, the content of aggressive carbon dioxide may be near the tolerable limit. Below this pH, the content is almost certain to be excessive and will cause damage to the concrete.

Corrosion of Reinforcing Bars

Concrete is damaged by the corrosion of its steel reinforcing bars because the corrosion products that form on the bar are expansive and their formation causes cracking and spalling in the concrete which lead to an easier ingress of seawater into concrete.

In a recent review (10) of the electro-chemical principles associated with the corrosion of reinforcing steel in concrete, it was noted that most researchers agree that chloride ions act as an essential catalyst in the corrosion reaction. The ingress of the chloride ion into the concrete may be aided by carbonation of the concrete. The precise role the chloride ion plays in the reaction, however, is not universally agreed upon. In general, the chloride ions act as part of the corrosion cell by:

1. Lowering the pH of the concrete pore water in contact with the steel, thereby dissolving the passive oxide film on the steel surface, or,
2. Penetrating the film to react with and transport the metallic ion into the electrolyte.

In the latter process, the resulting iron chloride complex ion combines with hydroxyl ions to form ferrous hydroxide in solution and lower the pH. This in turn, thins out the oxide film and speeds penetration of the chloride ions. Eventually, the continuing corrosion results in a pit.

To initiate corrosion, a threshold concentration of chloride is needed in excess of the amount immobilized by reaction with tricalcium aluminate in the cement. The threshold limit is not precisely defined. One investigation of the chloride ion content in the concrete adjacent to corroding reinforcing steel shows the concentration to be 0.59 to 0.83 kg/m³ (10). The Federal Highway Administration in the USA suggests that the threshold is 0.89 to 1.48 kg/m³. Oxygen and moisture are also needed in the process. In most instances, the absence of any of these will not allow corrosion to proceed.

Table 2 shows some actual chloride concentrations obtained from samples of some of the prestressed concrete piles and the pile jackets that form the legs of three offshore concrete platforms. The platforms are located approximately 65 kilometres south of Morgan City, Louisiana, in 12 metres of water in the Gulf of Mexico. The three platforms are similar in configuration, consisting of a number of prestressed concrete pile legs which are individually surrounded by prestressed concrete pile jackets (Fig. 4). The number of legs on the platforms varied at 12, 18 and 21. A structural deck is in place on each array of legs. A more complete description of the platforms and repairs made to them was given by Tate and Core (11).

As shown in Figure 5, the pile and jacket walls are 101 mm thick with a grouted annulus of 127 mm. Eight and 12 ducts were formed in the pile and jacket, respectively, during fabrication of the piles. Each duct had twelve 0.49-mm high strength (1380 MPa) wires threaded through it without the use of sheathing. The wires were post-tensioned to approximately 1.03 MPa. Cover thickness over the wires was approximately 41-mm. Spiral wire reinforcing (6.4 mm) was placed around the outside of the ducts at 152-mm spacing with the intervals shortening to 76-mm near the ends of each section.

As indicated in Table 2, the concrete in both the piles and the jackets is exceptionally strong after more than 30 years in the splash zone. This high strength should be indicative of a very dense concrete, yet the chloride ion measurements indicate that the threshold limit for initiation of corrosion has been exceeded in almost all instances.

The presence of corrosion activity in the piles was substantiated both visually and by the use of

half-cell potential measurements (11). One interesting aspect of the chloride ion observations is that, in general, the chloride ion content was greater near the center of the concrete than it was closer to the exterior surface. This may be due to the fact that the piles were hollow and thus formed an interior surface for evaporation and deposition of salts.

Aggregate Reactivity

The reactivity of some aggregates with the constituents of the cement to cause a general disruption of the concrete which contains it, has been known for almost 50 years.

In general, there are two basic types of alkali-aggregate reactions: alkali-silica, and alkali-carbonate. Alkali-silica reactions (ASR) are the most common and serious. The basic mechanism for the ASR is generally agreed upon by most investigators although various details are still under debate. The reactive form of silica in the aggregate reacts in situ with the highly-alkaline pore solution in the mortar to form alkali-silica gels, which are capable of unlimited swelling as they absorb water. As the water in the pore solution diffuses to the alkali-silica gel, osmotic or swelling pressure exerts stresses which cause disruption of the concrete.

It has been known for some time that the amount of expansion that concrete undergoes due to alkali-silica reactions depends on three factors: the amount of alkali in the mortar fraction of the concrete, the amount and nature of the reactive aggregate, and the amount of available water. In a marine environment, the available water is always substantial. Mixture proportioning may also influence the expansion.

Some concretes made with very low alkali cement have still experienced alkali-silica reactions. This has been attributed to a penetration of alkali from external sources, localized concentration of alkali due to wetting and drying of the concrete, and the release of alkali from aggregates containing small amounts of alkali.

Abrasion Damage

Abrasion damage to marine concrete is generally a surface effect and can occur from the continual

action of water-borne sediments, floating debris (such as timber), ship impacts, and floating ice. The action which causes the loss of concrete surface can vary from simple rubbing or abrading action to the disruption of the concrete surface through microcracking caused by repeated impacts from floating objects, followed by loss of material as the damaged concrete is plucked away by water or floating ice action (12). The abrasion process may be aided by a deterioration of the surface layer of the concrete by any of the other actions as described above.

STRUCTURES NEAR THE SEA

The durability of a concrete structure in close proximity to the sea may be affected by the wind borne spray from the sea. It is well known that in desert environments, the salts from dried salt lakes can be blown many miles by prevailing winds and deposited on structures. Periodic wetting of the structures either by nature or man (lawn sprinkling systems) can cause the salts to penetrate into the concrete and cause problems. Similar behavior is experienced when salt sprays are deposited on nearby structures. Continual rewetting and evaporation allows large buildup of salts to occur which eventually are transported by moisture into the concrete. These salts contribute to the chemical attack and corrosion described previously.

The sea spray may also affect the freeze-thaw resistance of the structure by damaging the surface layer of the concrete when the concrete is immature. This damage allows excess moisture into the concrete which results in frost scaling damage in freezing weather. In a study (13) of frost damage to coastal concrete structures on Hokkaido Island, Japan, it was observed that 70 percent of the structures had scaling damage due to freezing and thawing action within one year of being constructed. These structures were mostly seawalls, breakwaters, wharves and precast concrete armor units. A high percentage of these structures were made with portland-fly ash cement or portland-blast furnace slag cement at water-cement ratios of 0.55 or higher and with air contents of 4.5 percent. The worst scaling was observed in concretes whose compressive strength was less than 25 MPa. Of major significance from this study was the observation of decreasing scaling depth in the concretes as the distance inland from the shoreline increased (Fig. 6).