DESIGN FOR CHLORIDE CONTAMINATED HARSH ENVIRONMENTS: CONCRETE PROTECTION - THE KEY TO DURABLE SERVICE LIFE

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الخلاصة :

اتَّضَح من التجارب السابقة خلال السنوات الأربعين أو الخمسين السابقة بأن المواصفات – وإن طبُقت – لا توفر حماية مناسبة للخرسانة من الظروف البيئية القاسية، وأنَّ التصدع السريع للخرسانة ما زال بنسبة عالية وغير مقبولة، وما زال تأكل وصدأ حديد التسليح هو العامل الرئيس لتدهور الخرسانة في الأجواء القاسية المحملة بالأملاح، والرطوبة، والحرارة، والجفاف، وتراكم عوامل وأسباب التدهور يجعلها معقدة ويصعب معرفة تأثيرِ كلِّ سبب على حدة في التدهور الكلي للخرسانة.

في هذا البحث نقدم مقترحاً لتصميم خرسانة على أساس استراتيجية بأقل تكلفة لمبنى مقاوم لعوامل التدهور القاسية، وللعمر الذي صمم من أجله. لقد أظهرت نتائج البحث بأن حماية الخرسانة من أملاح الكلورايد وتأثير الأجواء الحارة الرطبة هي الخطوة الصحيحة لحماية الخرسانة من التدهور المحافظة عليها. ولقد أظهرت النتائج بأنه بالإمكان تصنيع مواد حماية للخرسانة من الماء والأملاح مع خواص ثابتة وجيدة لحماية الخرسانة في المباني وكذلك سدُّ الشقوق الخرسانية.

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ABSTRACT

Experience in the last forty to fifty years shows that current design specifications, even if properly implemented, do not provide for adequate resistance of portland cement concrete to aggressive environments. Premature deterioration of concrete structures is still unacceptably high, and corrosion of reinforcement continues to represent the single largest cause of deterioration of reinforced concrete structures. In chloride contaminated hot/dry/ humid conditions, the time-dependent and interactive effects of exposure and climatic conditions initiate a cumulative deterioration mechanism which becomes an overall synergistic process, and a complex combination of many individual mechanisms, the exact role, effect and contribution of each of which to the totality of damage is not fully known. This paper advances an integrated, holistic approach — a global design/management strategy — which will enable us to design new structures with a specified, cost-effective durable service life when exposed to such aggressive environments. It is shown that in chloride environments, and rapidly drying ambient conditions, protection of the young concrete from external contamination is the first — but not necessarily the only one reliable and positive step, to ensure long-term material stability and structural integrity of concrete structures. Extensive data are presented to show that it is possible to develop concrete surface coatings which can provide long-term durable performance in terms of water-proofing qualities, adequate vapor diffusion, breathability, excellent bond to the concrete substrate, very low permeability to chlorides, moisture and carbonation under extreme exposure conditions, and also maintain the ability to bridge cracks.

Keywords: Design, durability, chlorides, harsh environments, protective coatings, tests.

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INTRODUCTION

Concrete is, in many respects, a wonder material of this century. Of all construction materials, it has the best ecological profile for a given engineering property such as strength or elastic modulus. It is probably the most widely and extensively used building material in the world, due to its relatively low cost, easy availability of constituents, versatility, and adaptability. It is easily prepared and fabricated into many conceivable shapes and structural systems in the realms of infrastructure, transport, and habitation that the material is often identified with a nation's stability and economic progress, and the quality of human life. The most outstanding asset of the material is its inherent alkalinity, providing a passivating mechanism, and a safe, non-corroding environment for the steel reinforcement embedded in it. Long experience and a good understanding of the material have confirmed that concrete is a reliable and durable construction material, when it is exposed to normal or even moderately aggressive environments. It thus seems reasonable to assume that in a rapidly changing world, the concrete industry and technology can offer one of the best ways forward to satisfy the social and human needs and aspirations resulting from the massive movement of peoples from rural areas to urban cities that the latter part of this century has seen, and that will continue well into the twenty first century.

In spite of these intrinsic technical and economic advantages of the material, and in spite of the tremendous scientific advances that have been made in our understanding of its microstructure and engineering, deterioration of concrete has become a major global problem, and there is widespread concern about its lack of durability [1]. In recent times, in many parts of the world, reinforcement corrosion has become the main cause of early and premature deterioration, and sometimes failure, of reinforced concrete structures [2–5]. One of the major factors contributing to this deterioration process is the environment and climatic conditions to which a concrete structure is exposed. Hot/dry and hot/wet salt-laden environments probably provide the most aggressive forces that undermine the stability and durability of concrete structures. When the severity of environments is compounded with poor quality concrete and/or defective design and construction practices, the process of deterioration becomes interactive, cumulative and very rapid, and a cancerous growth that cannot be easily stopped.

This dichotomous situation poses one of the greatest challenges to engineers and concrete material scientists, namely, how do we design and construct structures that will have a long and durable service life, and which will require a minimum of repair and retrofitting? In other words, how do we develop a concrete element which can be designed to give optimum performance for a given set of load conditions and usage in harsh salt-laden environments consistent with the requirements of cost, service life, and durability?

The overall aim of this paper is to show that it is inherent in the nature of concrete as a material, and construction as a technology, that there is no single approach which will ensure long-term concrete material stability and structural integrity when structures are exposed continuously to severely aggressive environments. The paper advocates a **global design strategy** - a spectrum of activities which will involve a judicious integration of material properties and structural design which alone will give a structure its prescribed and specified durable service life. Such a strategy will involve four distinct operations namely,

Development of a Highly Impermeable Concrete Matrix Protection of Concrete Protection of Reinforcement, and Design for Structural Integrity.

In hot/dry/humid salt-laden environments all these distinct design stages would need to be incorporated, and close attention will have to be paid to all these aspects if structures are to function efficiently and satisfactorily.

The focus of this paper is to show that in this design strategy to build structures with a specified durable service life, protection of concrete from external environment and control of the ingress of air-borne and water-borne contaminants is the first and indisputable step in the design process. The paper discusses three distinct parts of this concrete protection technology, namely,

- (*i*) The need to protect concrete
- (ii) The basic requirements of protective surface coatings
- (iii) Material and structural implications of protective coatings.

ARE CURRENT DESIGN SPECIFICATIONS ADEQUATE?

Experience during the last four to five decades shows that corrosion of reinforcement continues to be the major cause of deterioration of concrete structures [1-5], and there is strong evidence to identify that current design codes and specifications lead to structures that do not provide adequate resistance to severe exposure conditions such as those in the Gulf area, and the effects of deicing salts. The inadequacies lie largely in the current approaches to design which are based on "the deemed to satisfy" premise, namely, that if the requirements of concrete grade, cement content, water/cement (w/c) ratio, and concrete cover are met, the structure is, per se, considered durable. These assumptions have been proved to be totally inadequate to ensure "durability" even when the design specifications are correctly implemented [6–7].

Exposure to ambient environment is the one single predominant external factor that is beyond human control, and that can create an alarming degree of degradation in a short time, and critically determine the stability and serviceability of concrete structures [8]. Engineers tend to underestimate the durability effects of aggressive environments on concrete, and the time-dependent and interactive effects of exposure and climatic conditions which ultimately decide the stability and durability of materials and structures [9–12]. Thus current design specifications related to concrete mixes and cover depths grossly underestimate the material and structural implications of exposure to aggressive environments. They will lead to insufficient margins of safely against durable service life, and the number of failures is likely to continue to be unacceptably high.

NEED WE PROTECT CONCRETE?

Concrete is basically a heterogeneous, discontinuous composite material with an intrinsically porous matrix. By its very nature, therefore, concrete has to be, and is, a highly variable material. One of the intriguing and puzzling characteristics of concrete is its dual nature. This paradox of concrete is that whilst being intrinsically protective to steel through its alkalinity, it is also the same material that permits and controls the ingress of water, oxygen, chlorides, sulfates and other deleterious agents that will eventually damage the material and progressively destroy the electrochemical stability of the steel reinforcement embedded in it. Concrete thus needs to be protected, particularly from an aggressive environment, for two major reasons. Firstly the hydration process, and hence, the development of strength and of a highly impermeable pore structure, is itself a time-dependent operation, and further, it requires a favorable wet environment for the chemical interactions to continue. A high resistance to environmental attack, therefore, demands that concrete is protected from adverse environmental conditions, particularly at the early ages, when the material is highly vulnerable to drying as well as diffusion processes arising from external exposure.

Secondly, the degradation process of concrete, apart from also being time-dependent, is not the result of one factor, one process, or one set of aggressive agents. With a complex composite system such as concrete, an aggressive environment becomes a major factor in initiating a progressively cumulative damage activity — indeed, the systematic advancement of deterioration becomes an overall synergistic process, a complex combination of many individual mechanisms, the exact role, effect, and contribution of each of which to be totality of damage is not clearly understood.

In structures exposed to aggressive environments, both these two major processes do not occur in isolation or in idealized surroundings, but are overwhelmingly dominated by the agents of deterioration in the environment, and the highly variable climatic conditions both of which together create a whole range of unknown interactive influences and effects that initiate a cumulative process of deterioration which will eventually destroy the capability of the material and the structural element to fulfil their intended function with adequate margins of safety while maintaining structural integrity. Some of the more important of these influences and effects are briefly discussed below.

THE UBIQUITOUS NATURE OF EXPOSURE

Environmental Considerations

- 1. Adverse geomorphological and climatic conditions such as severe ground contamination, high ambient salinity, high temperature, and high humidity generate the most imperceptible and insidious forces that damage long term ability of concrete to give durable performance.
- 2. Daily and seasonal fluctuations of temperature and relative humidity (RH) can create cyclic thermal and moisture movements. Daily temperature fluctuations in the Gulf area can be as high as 20°-30°C in the hot season, whereas daily and seasonal fluctuations of RH may range between 30% and 100% over a 24 hr period [13]. The RH, on the other hand, can be well above 40 to 50% most of the year in Qatar, for example, the maximum RH can be well

above 85% throughout the year. A highly variable hot moisture - laden environment can create damaging wetting/ drying cycles of exposure.

- 3. The high ambient salinity in a hot/humid environment creates a permanent aggressive atmosphere in which the concrete has to breathe and live. The high salinity of the Gulf water can generate a high rate of sea-salt deposition of the order of 1.5×10^{-3} kg/m²/y. This, in turn, will create high chloride and sulfate contents in the atmospheric air. The chloride content, for example, can be as high as 65×10^{-3} mg/m³ whereas the sulphate content can be of the order of 35×10^{-3} mg/m³. A high ambient temperature will accelerate the rate of corrosion, and the synergistic effects of the simultaneous presence of chlorides, sulphates, and elevated temperature on the long-term properties of concrete and steel corrosion are not fully understood [14–16].
- 4. The presence in the atmosphere of industrial pollutants such as SO_2 gas, CO_2 gas, and carbonaceous particles due to fuel burning can enhance and accelerate the deterioration process of concrete. SO_2 , arising from the burning of coal, oil or gasoline, is probably one of the most corrosive pollutants of the atmosphere [17–19]. A high ambient RH will increase the adsorption of SO_2 on to carbon steel, by a factor of almost 100, as the RH increases from about 60 to 95% [20, 21]. The maximum RH in the Gulf environment which is often well above 85% throughout the year [13] provides just the sort of conditions to accelerate corrosion damage.
- 5. Atmospheric corrosion can be a maximum in the Gulf environment. A combination of high average temperature, high RH, air-entrained sea salt, and industrial pollutants can create the ideal conditions for maximum atmospheric corrosion. The rate of atmospheric corrosion increases rapidly above a critical RH of 50 to 70% RH for steel, copper, zinc, and nickel [20, 22, 23], and in many parts of the Gulf area the RH during most of the year is well above 40 to 50%.
- 6. The synergistic effects of high average temperature, high fluctuations of temperature and RH, air-entrained chlorides and sulfates, and the presence of industrial pollutants are not known and are difficult to predict. There is considerable evidence, to show that a combination of high temperature, and high concentrations of chlorides and sulfates will increase the free chloride ions in the pore solution [14-16, 24].
- 7. Global radiation can be very high, up to between 500 and 800 MWh/cm² over a twelve month period, and this can drastically enhance surface temperatures and thermal gradients in concrete structural elements.

Geomorphological Considerations

- 1. Generally the top 5 to 6 m of soil in the Gulf area will contain high concentrations of chemicals such as chlorides and sulfates. The hot climate causes high evaporation of water from the upper layers leaving the salts accumulated in the soil. The relatively small changes of tidal movements in the coastal areas can also lead to very little interchange of water between the Gulf and the Arabian sea, and this can also contribute to the accumulation of salts in the soil.
- 2. The soil in the Gulf area is generally alkaline with a pH>7. Mean pH values range between 7.64 and 10.31 in Kuwait, for example, with an average value of 8.19 [25].
- 3. Chloride and sulfate concentrations are very high in both the soil and groundwater. Often, concentrations of organic matter are also found in the soil at depth range of 0-5 m. Nitrate concentration can also occur in the groundwater.
- 4. Chloride salts are generally highly soluble, and chloride concentration therefore increases with the depth of the soil. Sulfate salts, on the other hand, are either negligibly soluble or are only slightly soluble — and the high evaporation rate will ensure that sulfate concentration becomes highest in the top layers of the soil. Where impermeable soil layers exist near the ground surface, high concentrations of both chloride and sulfates may simultaneously occur in the top layers of the soil [25].

Effects on Materials

- 1. The maximum wind speed in the Gulf is well above 40 km/hr throughout the year. Wind-transported air-borne dust and salt will lead to contamination of stored concrete materials, of exposed steel bars and of concrete itself.
- 2. Evaporation rates greatly exceed precipitation and the former can vary from 10 mm to as high as 25 mm in the Summer. High evaporation rates and high levels of solar radiation would increase the water demand, accelerate the hydration of cement and the workability loss of the fresh concrete, and cause premature setting leading to cold joints.

- 3. The high rates of evaporation of the mix and curing water would result in very poor quality cover concrete which can accelerate the transport of chlorides and sulfates into the concrete.
- 4. They can also make chemical attack extremely rapid.

Effects on Concrete

- 1. High ambient temperature and large fluctuations in temperature would lead to plastic and drying shrinkage cracking, and large thermal movements. The latter would also result in cyclic expansion and contraction, and hydration and dehydration.
- 2. The high RH values in combination with the high ambient air temperature and high evaporation rates would lead to settlement cracking.
- 3. Wind-transported air-borne dust and salt in a moist-laden environment can be deposited to work into the cracks in finished structures.
- 4. Direct solar radiation on a typical summer day can raise the temperature of hardened concrete surfaces to as high as 80°C to 90°C, and these will create large undesirable thermal movements.
- 5. Thermal fatigue. Daily variations in ambient air temperature will impose a thermal load (thermal cycling) on the structure as a whole, and particularly on those parts exposed to radiation. Very little is known of thermal fatigue on concrete structures thermal cyclic effects begin to act as soon as a structure is built, well before other loads for which the structure is designed begin to act. Interactions of thermal cyclic effects with other causes of deterioration may have an adverse effect on the life of the structure.

Experience shows that the surface temperature of concrete exposed to solar and other thermal radiation may reach twice that of the ambient temperature, and the upper limit of the thermal cycling may therefore be as high as 100° C, and the thermal range could be as high as 60° C. Temperature distribution through concrete is also highly non-linear. Such thermal cycling combined with internal and external restraints of structures, and the thermal incompatibility between the concrete constituents would lead to very high tensile stresses initiating cracks at the aggregate — matrix interface, and other internal microcracks. Stresses and cracking induced by internal restraints are more complex to evaluate and more difficult to minimize [26–28].

6. The combination of such thermal movements with long-term shortening due to shrinkage and creep can create serious differential movements between the exposed and unexposed areas, and lead to significant long-term serviceability problems of both structural and non-structural elements. For example, a typical 150 m high reinforced concrete column in a high rise structure will shorten by about 200 mm under a sustained service stress of the order of 10 MPa; the thermal movements of the external columns could then be, in addition, as high as 100 mm. These differential movements would create out-of-level floors, cracking of internal partitions and of external cladding elements; and structurally, the floor systems could be subjected to additional shear forces and bending moments arising from differential vertical displacements, leading to cracking and other serviceability problems [29].

Effects on Concrete Durability

A high ambient temperature during placing and setting will naturally be helpful in accelerating the initial rate of hydration, but in this course of action, it can set in motion a series of complex physical and chemical processes that will have significant long-term effects on the engineering properties and microstructure of concrete [30–32]. One of the direct effects of this initial rapid hydration is the significant reduction in the long-term strength of the concrete [33]. Microstructurally, the high temperature results in a much coarser C–S–H morphology and pore structure, which is dramatically reflected in changes in the pore-size distribution, particularly of the large capillary pores greater than $0.10 \,\mu$ m in diameter. A critical implication of this change in the microstructure is a significant increase in the permeability characteristics of the cement matrix [34, 35]. This probably explains, and there is considerable direct evidence for this as shown below, why corrosion of reinforcement through chloride attack still remains the largest cause of structural deterioration on exposure to severe salt environments, even when design code requirements and specifications are properly implemented [1–8].

There is only limited reliable quantitative field data on the penetration of chlorides and sulfates into concrete structures exposed to the Gulf environments [2, 36], but core tests on reinforced concrete structures showing signs of deterioration exhibit a wide range of intrusion of chlorides and sulfates upto 0.40% and 1.85% respectively by weight of concrete [13].

Field studies in similar environments also show that chlorides and sulfates diffuse into concrete at different rates, and that chloride diffusion into concrete exposed to real environments can be as high as ten times that intruding under laboratory conditions [13]. Long-term exposure studies into concrete structural members exposed to similar aggressive salt-laden environments in other parts of the world also show that chlorides penetrate very rapidly into concrete from an early age, and that the amounts and depths of penetration are time-dependent, wide and varied, depending primarily on the exposure conditions [8, 37]. Tests on the KRK bridge in Croatia show chloride ion concentrations of 0.2% to 0.4% by mass of concrete in the cover concrete of columns with a concrete strength of 40 MPa [38]. One of the clear messages of the combined interaction of adverse environmental, geomorphological, and climatic conditions is that their effects are cumulative and concomitant, and that the ultimate result is an unknown factor affecting the microstructure leading to increased permeability and decreased durability.

PORTLAND CEMENTS - NEED FOR CHANGE

The experience that even when specific code requirements for durability in terms of concrete cover and concrete quality are achieved in practice, there is an unacceptably high risk of premature corrosion deterioration in concrete structures exposed to aggressive salt-laden environments, directly points to the fact that portland cement concretes are not totally resistant to chloride ion penetration, even when the water-cement ratio is as low as 0.45 [8, 37, 39]. The strong implication here is that with current design codes, premature deterioration due to corrosion is likely to continue. There is thus a need for a fundamental change in our thinking of concrete and concrete quality made of portland cement concrete [39, 40].

One of the major reasons for this much lower resistance of modern portland cement concrete to chloride ion penetration is the gradual but significant changes that have occurred in the chemical composition of portland cements during the last four to five decades [41]. The two major changes and their implications on engineering and durability properties can be identified as:

- 1. A significant increase in the C_3S/C_2S ratio from about 1.2 to 3.0 resulting in higher strengths at early ages with a lower proportion of strength developed after 28 days. From a design point of view, this implies that structural design strengths can be achieved with lower cement contents and higher w/c ratios.
- 2. A direct result of the change in this chemical composition of portland cement is an increase in the heat of hydration evolved, and more importantly, in the evolution of heat at early ages. It is estimated that the average increase in peak temperature is about 17%, and this peak temperature is reached in less that half the time [41].

The high strength may appear attractive at first sight, but may give misleading ideas of durability. Although strength is clearly the result of the pore-filling capability of the hydration products, there is considerable evidence to show that there is no direct relationship between cement/concrete strength and permeability, and hence, durability, whatever be the nature of the concrete constituents [42]. One of the primary factors leading to this lack of relationship between strength and durability, *per se*, is the internal microcracking and the poor development of hydration products (as discussed earlier) arising from the excessive heat generation due to the increased heat of hydration. In hot climates, the combined effect of ambient temperature and heat of hydration will worsen the situation. Although from an engineering point of view the more rapid development of strength would be beneficial and enable the concrete to resist the thermal stresses better, microstructurally, the effects of changes in portland cement composition and higher ambient temperature will thus be cumulatively adverse.

THE KEY TO CONCRETE DURABILITY

The inadequacies of portland cements (PC) and portland cement concretes in resisting chloride ion penetration in aggressive environments focus attention on the core properties of concrete that are likely to control the overall long-term stability of reinforced concrete. Extensive research over the last two/three decades shows that these two properties have to be (*i*) "impermeability" *i.e.* "pore structure", and (*ii*) "cracking" [1, 43]. One of the great advantages of concrete as a material is that it is possible to select its constituents, and so exploit and optimize the unique properties of each of these components. And there is incontrovertible evidence to show that the most direct, technically sound, economically attractive, and environmentally friendly solution to the problems of reinforced concrete durability lies in the incorporation of finely divided siliceous materials such as fly ash (FA), ground granulated blast furnace slag (GGBFS), and silica fume (SF) as cement replacement materials in concrete [15, 36, 44–48]. The ability of these materials to contribute to strength, stiffness, and durability is chemically-bound within the concrete system, and it is only through *Design* that we can mobilize and extract this unique property of pozzolanic and cementitious materials [46]. If this ability for *Synergic Interaction* can be effectively and fully mobilized, these materials can greatly improve the quality and durability of concrete through control of thermal

gradients, pore refinement, depletion of cement alkalies, and the capability for continued long-term pozzolanic reaction or hydration [46]. In the fresh state, a judicious combination of these materials can enhance flowability and pumping qualities, and reduce segregation, bleeding, and the tendency for plastic shrinkage. In the hardened state, these mineral admixtures can significantly refine the pore structure and thus reduce permeability whilst at the same time improving the resistance of the material to thermal cracking through reduction of the heat of hydration [43, 46]. Thus concrete with mineral admixtures can, through internal microstructural binding, provide a safe haven for many of the durability problems arising from hot/dry, hot/wet salt-laden environments [43, 46].

However, mere incorporation of siliceous admixtures will not, *per se*, produce high performance, or high durability concrete. The "*magic of synergic interaction*" leading to a high degree of impermeability can only be achieved by a clear understanding of the microstructural implications of utilizing these mineral admixtures and through an engineering approach [46], if durable service life is to be assured in very aggressive exposure environments. The major factors that lead to this conclusion are briefly identified below.

- 1. Pore refinement, *i.e.* a reduction in pore volume as well as the transformation of the coarse pores, into fine pores is a time-dependent process, and **requires not only adequate internal water content but also a favorable wet environment protected from drying to enable the pozzolanic and hydration reactions to continue. This is illustrated here for concretes with a water/cementitious materials (w/b) ratio of 0.40 and containing 50% cement replacement of GGBFS of three degrees of fineness, namely 453, 786, and 1160 m²/kg. Figure 1 and Table 1 show the role of moist curing on the development of pore volume with time. These data emphasize the following:**
 - (i) Substantial reduction in the total pore volume occurs even with the coarsest slag, but it needs 28 days of moist curing to obtain substantial reductions in pore volume, and at this age, the pore volume of PC concrete is about 70% of that at 3 days, whereas the slag reduces this to about 50% of that at 3 days.
 - (*ii*) Further reduction in pore volume can only occur with adequate internal water to continue the chemical reactions, and a favorable humid environment to prevent drying. At 91 days for example, the total pore volume of slag

Mixture	А	В	С	D	Ε
$\frac{W}{C+S}$	0.40	0.40	0.40	0.30	0.40
Slag fineness m ² /kg	None	453	786	786	1160
Compressive Strength, MPa					
3d	38.6	15.2	17.9	31.3	34.5
7d	48.9	27.7	36.4	64.2	64.8
28d	59.5	58.7	67.8	104.2	101.8
91d	69.3	69.5	90.6	115.8	122.3
Total pore vol. mm ³ /g					
3d	64.9	60.4	68.5	46.1	41.5
7d	57.4	55.9	47.6	38.0	31.6
28d	46.7	30.7	22.8	20.0	16.8
91d	33.5	13.0	12.0	14.5	11.9
Water permeability					
Penetration mm	12.3	8.1	7.1	3.5	2.9
Diff. Coefft. $\times 10^{-2}$ mm ² /s	2.27	0.99	0.76	0.18	0.13

Table 1. Development of Pore Volume and Water Tightness with Slag Concrete.

concrete is less than 20% of that at 3 days, compared to about 50% for the PC concrete, provided the slag concrete is allowed to develop its matured pore structure.

- (*iii*) There is a complex interaction between the fineness of cementitious materials and w/b ratio. The data in Figure 1 and Table 1 imply that perhaps more benefits in terms of pore volume can be derived by moderate increases in slag fineness (and indeed in the fineness of fly ash as well) than by reduction in the w/b ratio.
- 2. The pore refinement arising from the incorporation of cement replacement materials is shown in Table 1. Here the pore refinement is expressed in terms of water tightness *i.e.*, depth of water penetration, and water permeability diffusion coefficient, because these two parameters are a direct reflection of the pore structure of the concrete. Further, these two parameters represent a better measure of the resistance of concrete to steel corrosion, and its resistance to water-borne aggressive agents such as chlorides and sulfates, and chemical reactions such as alkali–silica reactivity. The data shown in Table 1 is for the same concrete mixtures as those in Figure 1 and Table 1. The depth of water penetration was determined from 150 × 300 mm cylinders which were initially cured in water at 20°C for 28 days, followed by air curing at 20°C and 60% RH for 7 days to reach moisture equilibrium, and then subjected to a water pressure of 1.5 MPa for 48 hours. The depth of water penetration can then be related to a diffusion coefficient, and the results are shown in Table 1. These data and those in Figure 1 and Table 1 fully support the earlier arguments that modern portland cements are microstructurally inferior to composite cement concretes, and that dramatic increases in resistance to penetration of water and water-borne aggressive ions can be achieved by a judicious combination of the cementitious materials, their fineness, and the w/b ratio, but above all, by permitting the concrete to fully develop its pore refinement capabilities.

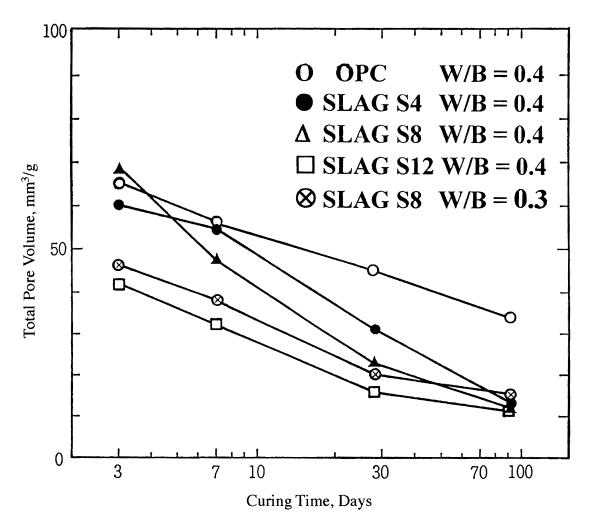


Figure 1. Influence of Age and Moist Curing on Pore Volume.

The pore structure refinement data quantified in Figure 1 and Table 1 are further supported by the chloride concentration profiles shown in Figures 2 and 3, which prove conclusively that the incorporation of FA, slag, and SF in concrete positively reduces the penetration of chloride ions into concrete. The data in Figures 2 and 3 are derived from $1000 \times 500 \times 150$ mm concrete slabs subjected to cyclic wetting and drying with 4% sodium chloride solution. The concrete mixtures used in these tests had a constant w/b ratio of 0.60 (Figure 2) or 0.75 (Figure 3), a constant total cementitious content of 350 kg/m³, and cement replacement levels, mass for mass, of 30% FA, 65% slag, or, 10% SF. The superiority of composite cements over portland cements needs no further proof.

Effect of Environment on Composite Cement Concretes

Thus, although concretes with mineral admixtures can de designed to have a much greater impermeability to the penetration of aggressive ions compared to PC concrete, the question that needs to be asked is whether they are immune to the effects of the hot/dry/humid salt-laden environments, similar to that of the Gulf area, and indeed, whether they can retain their greater impermeability in the long term. The answer to the former has to be in the negative. There is strong evidence to confirm that continual exposure of composite cement concretes to large fluctuations of ambient high temperatures and RH also does lead to adverse effects of wetting and drying, and internal microcracking all of which result in (1) higher total intrusion volume, (2) higher porosity, and (3) a coarsening of the pore structure with transformation to a much higher percentage of coarse pore volume to total pore volume as illustrated in Figures 4 and 5. Such environments also result in higher permeability coefficients [49]. Nevertheless, many studies do also show that although no concrete is immune to the destructive effects of hot/dry/humid salt-laden environments, the benefits of the pore refinement process will be far better retained by composite cement concretes than by PC concrete [50–53], provided the seeds for continuous pozzolanic and hydration reactions exist, and the concrete is allowed to develop its superior microstructure and durability-related properties.

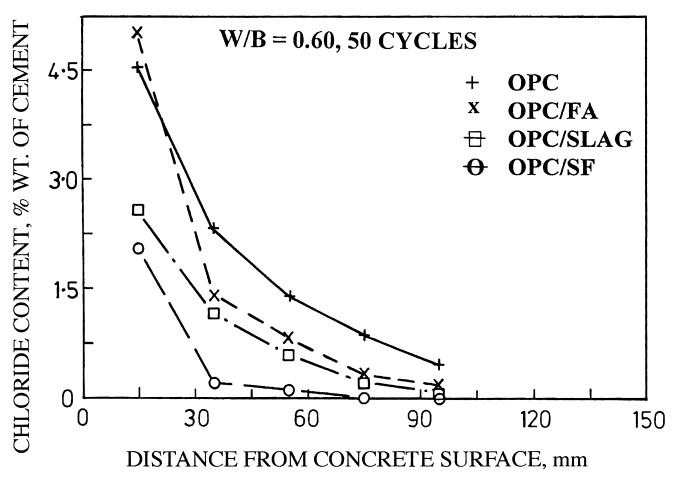


Figure 2. Chloride Concentration Profiles in Concrete with Mineral Admixtures.

CONCRETE PROTECTION: A MUST

All the data and arguments put forward so far in this paper lead to the following conclusions.

- 1. Portland cement concretes are not equipped to provide the same degree of impermeability and resistance to aggressive salt-laden exposure conditions as concrete with mineral admixtures.
- 2. It is possible to design and produce such concretes with a high resistance to stresses arising from ambient thermal and humidity changes, and a high degree of impermeability to external aggressive agents, as evidenced by the low heat evolution, low total pore volume, low total porosity, and a clear-cut refinement of pores as shown by the transformation of the coarser pores into finer parts.
- 3. The high degree of impermeability to aggressive ions can only be achieved provided the concrete is allowed to mature and develop the full potential of chemical bonding and synergic interactions of its constituents through continued hydration and pozzolanic reactions. This is an absolute must if concretes are to retain their refined pore structure in aggressive environments for a long period of time.
- 4. Continuous exposure to high ambient temperature and RH, and large fluctuations of temperature and humidity will lead to high thermal gradients, high thermal stresses, thermal fatigue, cyclic wetting and drying, and the ubiquitous and irreparable internal and external microcracking, to name a few; the effects of all of which are not completely clear, but the cumulative effects of which are a reduction in structural strength and elastic modulus, and microstructural degradation in terms of increased porosity, coarsening of the pore structure, and enhanced permeability.
- 5. Both the processes of microstructural development and material degradation are time-dependent, cumulative, and synergistic. The overriding and overwhelming influence of aggressive ambient environment and exposure conditions on the quality of microstructure, on the one hand, and the totality of damage on the other, is neither fully known nor well-established.

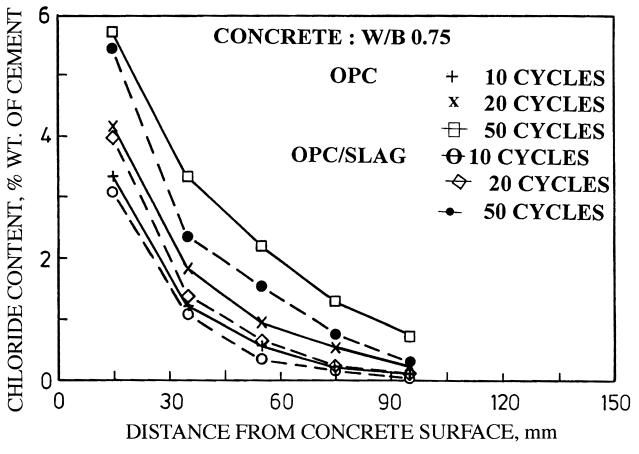


Figure 3. Role of Slag in Chloride Penetration.

In this complex scenario of lack of material stability and structural integrity of concrete structures exposed continuously to aggressive environments, there are still may other unknown factors which make adequate design for durable service life unclear, uncertain and unsure — but they do identify protection from the environment as the only reliable technique to ensure durable service life. Briefly these are:

1. We have no reliable information on the precise interrelationship between strength and durability indicators such as permeability and pore structure. There are inherent difficulties in conducting permeability tests, and in establishing moisture equilibrium before determining air/oxygen or water permeability coefficients [54, 55]. Many studies show that there is no single or unique relationship between strength and permeability coefficients [55, 56]. For example, as shown in Figure 6, concretes of similar compressive strength can exhibit a wide range of oxygen permeability coefficients. Similarly, because of the complexity of the concrete system, variations in test methodologies, and the complicated influence of exposure conditions on microstructure, there are no unique relationships either between permeability coefficients and pore structure. Many studies, however, show the existence of a threshold diameter [57, 58], and although there appears to be some reasonably good relationship between oxygen permeability and threshold diameter as illustrated in Figure 7 for example, a lot more confirmatory data are required before these relationships can be used as a basis for design [42]. The data in Figures 6 and 7 relate to a wide range of concrete mixtures incorporating FA or Slag in combination with SF and exposed to various curing conditions.

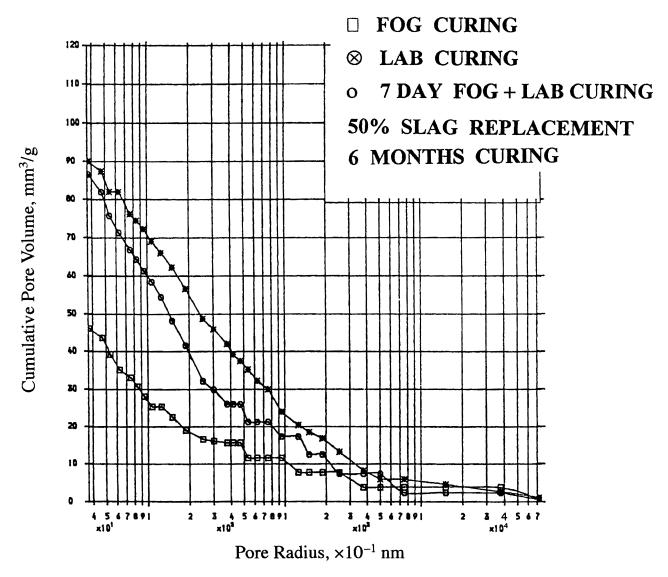


Figure 4. Influence of Air Drying on Pore Structure of Slag Concrete with 50% Cement Replacement.

- 2. There is no clear-cut evidence on chloride threshold levels responsible for the initiation of corrosion-induced deterioration of steel in concrete. Nor is it clear as to whether it is the total chloride content, the free chloride concentration, or the chloride to hydroxyl concentration ratio which can give and represent the best measure of corrosion risk in concrete.
- 3. Concrete exposed to contaminated ground water in the presence of high evaporation rates will lead to salt weathering and salt crystallization. The effects of these on the long term stability of concrete are unknown.
- 4. We have only very limited information on the role of cracking, both internal and external, on the durability of concrete structures [59-60]. All structural concretes are in effect in a cracked state, although the cracks may not be directly visible to the naked eye, since the tensile strain capacity of concrete is only of the order of 150 to 200 microstrains.
- 5. Almost all the published data on durability studies are on small scale test specimens subjected to various exposure conditions in indoor environments. Field studies on large scale structural elements, under load are extremely rare. There are inherent design weaknesses and deficiencies in extrapolating the results of the former to explain the behavior of the latter [9–11].
- 6. Finally, there is now sufficient evidence to show that most concretes used in practice retain enough moisture even after many years of field service, and even after exposure to arid conditions, to be able to initiate microstructural deterioration, if other elements for such deterioration already exist within the body of the concrete [59, 61, 62].

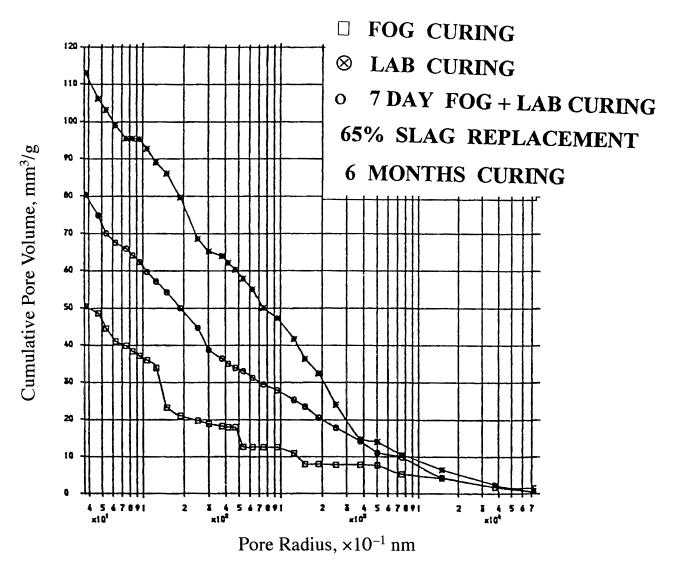


Figure 5. Effect of Curing Regime on Pore Structure of Slag Concrete with 65% Cement Replacement.

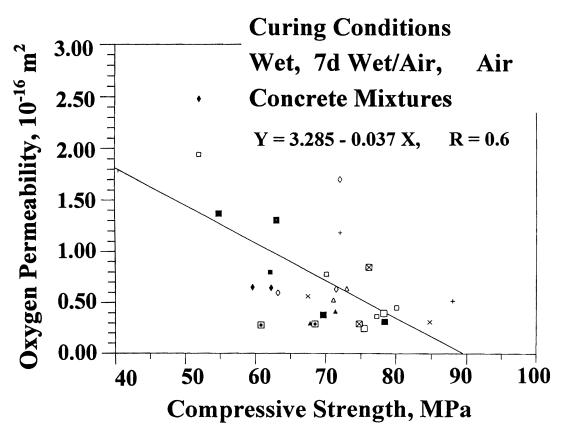


Figure 6. Relation Between Compressive Strength and Oxygen Permeability for a Wide Range of PC/FA/Slag/SF Concrete Mixtures.

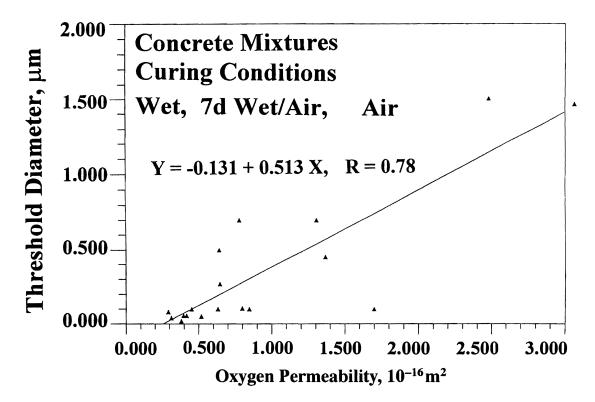


Figure 7. Relation Between Oxygen Permeability and Threshold Pore Diameter for a Wide Range of PC/FA/Slag/SF Concrete Mixtures.

CONCRETE PROTECTION — THE KEY TO DURABLE SERVICE LIFE?

So, where do we go from here? All the previous data emphasize the need for a long maturing period for concretes to develop a dense microstructure, and a high degree of impermeability to ionic diffusion. Since in practice, water curing is almost never effectively carried out, even for a short period of time, protection of the concrete and prevention of its drying, particularly at early ages and especially in aggressive environments, become a paramount necessity. Further, however well-designed and impermeable concrete is, the ubiquitous internal microcracking and external load-induced cracking together with the presence of pockets of flaws, micropores, and microcracks in the outer surface layers of any concrete element will provide paths for the transportation of aggressive ions into the interior of concrete. In aggressive environments, and rapidly drying ambient conditions therefore, protection of the young concrete from external contamination is the first — but not the only one — reliable and positive step in ensuring trouble-free durable service life of concrete structures. The use of controlled permeability formwork will give some degree of densification of the outer layers of a concrete element, but it is unlikely to enhance the overall durability of a structural element, but space will not permit further discussion of this topic here [63].

Why the Mistrust?

Thus of all the possible methods of protecting concrete from aggressive environments, surface coatings alone can offer the most direct, reliable, convenient and relatively inexpensive solution to the durability problems of concrete structures. However, there is considerable mistrust of surface and barrier coatings arising from some of their rather erratic performance in practice. Much of the misgivings and the poor in-situ performance, however, are due to the very different properties and diffusion characteristics of coatings of similar generic types; but the major cause of the present situation is a lack of clear understanding on the part of engineers of the basic engineering properties required of such coatings if they are to give satisfactory and durable performance in real environments. Similar to the gross inadequacies and limitations of current building design code specifications in their lack of ability to ensure durable service life of concrete structures exposed to aggressive salt-laden environments, there are not only no adequate specifications for surface coatings, but those that exist, cater only for short term performance, and do not take into account the engineering and microstructural characteristics required to enable the coatings to resist and retain their protective qualities when exposed continuously to aggressive saltladen environments.

Basic Requirements

Surface coatings must satisfy certain basic requirements which can be broadly classified as follows [64]:

Performance:

Chemical resistance Diffusion resistance Weathering resistance Resistance to expansive forces Resistance to carbonation

Engineering:

Adequate elasticity Fatigue resistance Strain capacity Crack-bridging ability Adhesion strength - coating continuity Abrasion resistance Thermal stability.

Because of space limitations only some of these basic requirements are considered here, and that too, only briefly. Further, cementitious coatings are also not considered here, and all the discussion below relate to polymer-based coatings. Such coatings are easy to apply, either by spraying or brushing; they can be made pleasing to the eye and aesthetic, and above all, they can ensure long service life of the order of 10 to 20 years.

Testing for Durable Performance

A major factor confronting formulators of coatings and engineers is this — what should be the chemistry of the coating and how do we evaluate the qualities of the coating in real aggressive conditions? It is obvious that we can never realistically

simulate field conditions in the laboratory, and therefore, ultimately, the only reliable tests are those where the coatings are exposed to real environments, although laboratory tests can be extremely valuable and provide guidance in formulating the chemistry of the coating.

Another significant factor contributing to the long term stability of the coating is its thickness. Tests show that exposure to solar radiation, ultraviolet rays, ozone, wetting and drying, and structural movements of the substrate concrete all slowly but surely erode many of their chemical and diffusion characteristics. Whilst coating thicknesses of 250 to 500 μ m may show good performance characteristics under laboratory/sheltered conditions, real environments are far more aggressive, and demand thicknesses of the order of 1000 μ m for durable service life [64–66].

Apart from adequate elasticity and strain capacity, coatings should also possess sufficient thermal stability to withstand high ambient temperatures and temperature fluctuations, and still retain their properties of elasticity and elongation. Thermal stability in the range of -50° C to $+70^{\circ}$ C should cover almost all normal and severe exposure conditions, and coatings should be able to preserve both elasticity and strength throughout this range (Figure 8.) [64].

The crack-bridging ability of the surface coating is one of its most important engineering requirements which alone will enable it to maintain its integrity without debonding and rupture, particularly when applied to deteriorating structures, as cracks open and close with variations in the applied load, and changes in exposure conditions. These tests need to be carried out not only over the cracked substrate but also after exposure to aggressive marine environments [65]. In addition, a coating should be able to retain this crack-bridging ability under both static and dynamic conditions. Cyclic tension tests need therefore to be carried out to establish that the coating has the ability to bridge a wide range of crack widths over an adequate temperature change [64, 66]. It is also worth emphasizing that these tests need to be carried our with the coatings acting in tension stretched over cracks. Apart from static and dynamic tests as reported above, the coating should also be able to preserve this property under exposure to both ozone and ultraviolet radiation, at high temperatures, and in the presence of moisture [64–66].

PROTECTIVE QUALITIES

The primary function of surface coatings — whether they be vapor barriers, vapor permeable coatings, surface penetrating sealers, or whatever — is to protect the concrete from the surrounding aggressive agents and prevent the corrosion of the steel embedded in it. In effect, this amounts to having a coating which will have high resistance to the ingress of chlorides, air, water, and other deleterious elements, and maintain this quality for a long time without losing its integrity and suffering damage. Tests show that these properties depend on a host of inter-related and interactive parameters related to their engineering behavior, chemical resistance, weathering resistance, and diffusion characteristics. Unfortunately, there is practically little information to quantify the inter-relationship between these properties and durable performance of the coating. Indeed, we have little understanding of the significance and role of the quantified values of diffusion properties of coatings in the published literature and their resistance, for example, to chloride penetration or to carbonation. This should not be altogether surprising, as we now realize that even with all the knowledge we have of concrete materials, there is still no reliable quantifiable relationship between strength and durability, or between durability indicators such as permeability, diffusion coefficients, and durability.

Thus it is clear that in the present state of our knowledge of surface coatings, the best evidence of the effectiveness, reliability, and dependability of these properties is their performance characteristics when exposed to aggressive environments. Short term tests have little relevance to long term performance, and we ignore at our peril long term test results. In the following sections, a wide range of test results are collated to show that it is possible to design and fabricate a high quality surface coating of excellent resistance to chloride penetration and carbonation whilst maintaining its integrity of bond to the concrete under a variety of aggressive exposure conditions. All the data presented below relate to the acrylic rubber coating developed by the author and his colleagues and described elsewhere in detail [10, 37, 43, 59, 64–66].

ACCELERATED TESTS

The accelerated salt spray tests quoted here are adapted from ASTM Standard ASTM-B117-54T and the Japanese Standard JIS Z 2371 to evaluate the performance of the coating when subjected to accelerated salt spray in a specially designed chamber [67]. The test specimens were concrete prisms $65 \times 55 \times 150$ mm with one 9 mm dia bar embedded with concrete covers of 20, 25, and 35 mm. The concrete was designed with a high w/c ratio of 0.58 for a 28 day compressive strength of 20 MPa, to ensure that chlorides can penetrate the concrete quickly, and to highlight the effectiveness of the coating when used with a highly permeable concrete. The test specimens were made with NaCl added during mixing at levels of 0%,

0.2%, 0.4%, 0.6%, 0.8%, 1%, 2%, and 5% by weight of mortar (*i.e.* cement and sand). The test methodology consisted of spraying 5% NaCl aqueous solution under an air pressure of 0.1 MPa, at a temperature of 35° C and at a RH of 95-98%. The tests were carried out for two exposure periods of 1000 hrs (42 days) and 5000 hrs (208 days). The rigor of the test is such that an exposure of 150 hrs of accelerated testing is estimated to be equivalent to 1 year of exposure to natural environment for corrosion of metals. The results obtained from these tests are summarized below.

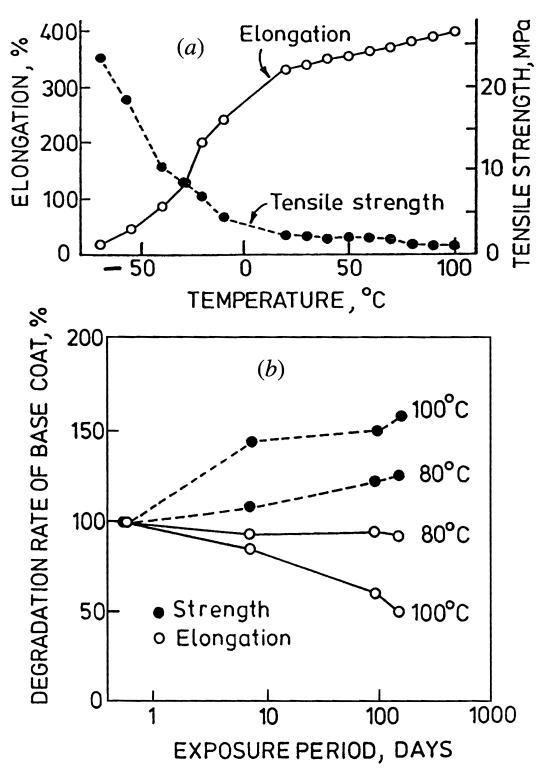


Figure 8. Thermal Stability of Acrylic Rubber Coating in the Temperature Range: (a) -50° C to $+50^{\circ}$ C; (b) 80° C to 100° C.

Chloride Penetration and Steel Corrosion

The penetration of chlorides, expressed as a percentage of soluble chlorides, into the concrete at three different depths from the concrete surface for the two exposure periods are shown in Table 2. These results confirm that the coating totally prevented the penetration of chlorides into concrete in highly favorable situations where substantial amounts of chlorides could penetrate the unprotected concretes.

After the salt and spray tests, all the test specimens were carefully visually inspected, broken open and the steel corroded area and change in bar diameter were individually evaluated. Table 3 presents the corrosion results in terms of corroded area, and Table 4 shows the percentage changes in the diameter of the corroded bars. These results fully support the chloride penetration data given in Table 2. It is interesting to note that even specimens without salt addition showed the presence of considerable corrosion affecting 30-40% of bar surface area. The results in Table 3 also emphasize that no coating can protect concrete already heavily contaminated with salt since the ingredients for corrosion are already within the body of the concrete. On the other hand, a good coating can even then help to moderate and reduce the severity and extent of corrosion by preventing the ingress of air and moisture as shown in the Tables 3 and 4. Examination of the bars extracted from the tests prisms confirmed this.

Casting	Age	Di	Distance from concrete surface		
Coating	(hrs)	0–1 cm	1–2 cm	2–3 cm	
Uncoated	1 000	2.35	2.25	2.11	
	5 000	2.66	2.35	2.22	
Coated	1 000	0.00	0.00	0.00	
	5 000	0.00	0.00	0.00	

 Table 2. Chloride Penetration Under Accelerated Tests (Soluble Chlorides, %).

Coating	Age	e Levels of NaCl							
	(hrs)	0%	0.2%	0.4%	0.6%	0.8%	1.0%	2.0%	5.0%
Uncoated	1 000	30	30	30	30	60	60	80	80
	5 000	40	40	60	60	80	80	95	100
Coated	1 000	0	0	0	0	2	2	5	70
	5 000	0	0	0	0	2	5	60	80

Table 4. Percentage Change in Diameter of Corroded Bars.

Casting	Age								
Coating	(hrs)	0%	0.2%	0.4%	0.6%	0.8%	1.0%	2.0%	5.0%
Uncoated	1 000	3	3	3	3	4	4	4	4
	5 000	4	4	4	4	4	4	6	12
Coated	1 000	0	0	0	0	0	0	1	2
	5 000	0	0	0	0	0	2	2	4

Bond Strength

The bond strength of the surface coating to the concrete substrate was determined by bonding a 50×50 mm steel plate on to the surface of the coating with an epoxy resin and then pulling the plate vertically by a calibrated pull-out test gauge. The control tests on concretes without chlorides and prior to exposure gave a mean bond strength of 1.53 MPa. The results of the tests after exposure are given in Table 5. These results show that although there was some reductions in bond strength after 1000 hrs exposure, the bond appears to have strengthened with further exposure, and after 5000 hrs, the loss in bond strength was only about 10%. The failure after the initial 1000 hrs exposure was at the interface between the top coat and the base coat, whereas after the 5000 hrs test, the breakage occurred within the concrete surface.

The bond between a surface coating and its concrete substrate is influenced by many parameters [64], but the two key factors influencing the integrity of the bond is the moisture state within the concrete body, and the breathability of the coating. Both contribute to substantial reductions in the bond strength, the breathability qualities of the coating being more critical, leading to the trapping of chlorides and moisture at the coating–concrete interface. Here the chemistry of the coating comes into action to prevent this from happening and leading to loss of bond. The data given in Table 5 confirm that the acrylic rubber coating discussed here was able to maintain its bonding characteristics with the concrete substrate in conditions of high temperature, high humidity, and salt spray.

Carbonation Depths

The depth of carbonation was determined in all the tests after the two exposure periods, and the results are shown in Table 6. All the unprotected concretes carbonated to a depth of 1.0 mm after 1000 hrs exposure, and from 2 to 3 mm after 5000 hrs. The coated specimens, on the other hand, showed no carbonation penetration at all throughout the exposure period.

Residual Engineering Properties

Both the tensile strength and elongation of the coating were determined after the salt spray tests. The coating was carefully peeled off the test specimens and tested, and the results are given in Table 7. The virgin unexposed coatings tested at 20°C, had a mean tensile strength of 1.53 MPa and a percentage elongation of 320%. The results in Table 7 confirm that the acrylic rubber coating retained almost all of its original tensile strength and elongation properties after severe exposure tests.

Age	Levels of NaCl										
(hrs)	0%	0.2%	0.4%	0.6%	0.8%	1.0%	2.0%	5.0%			
1 000*	1.46	1.08	1.15	1.28	1.05	1.44	1.21	1.17			
5 000**	1.44	1.26	1.37	1.57	1.32	1.68	1.47	1.41			

Table 5. Bond Strength of Coating After Exposure to Salt Spray (MPa).

* Failure of the interface between top coat and base coat

** Failure in concrete

Gentine	Age	Levels of NaCl							
Coating	(hrs)	0%	0.2%	0.4%	0.6%	0.8%	1.0%	2.0%	5.0%
Uncoated	1 000	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	5 000	2.5	2.5	2.0	2.0	3.0	2.0	2.5	2.5
Coated	1 000	0	0	0	0	0	0	0	0
	5 000	0	0	0	0	0	0	0	0

LABORATORY TESTS

Chloride Penetration

Total resistance to penetration of chlorides is one of the fundamental requirements of surface coatings if they are to protect the embedded steel from corrosion. The accelerated salt spray tests reported above have shown that the acrylic rubber coating discussed here can provide this immunity. Further data on this quality of the acrylic rubber coating are presented here. The chloride penetration tests were carried out on two sizes of reinforced concrete slabs: (1) Slabs S4, S5, and S6, all of $1000 \times 500 \times 150$ mm size, with their entire top cast face protected with the acrylic rubber coating system (Table 8); and (2) Slabs S1, S2, S3 of $1000 \times 1000 \times 150$ mm size, with only half of their top cast face protected by the coating, as shown in Table 8 and Figure 9. The purpose of these half-coated slabs was to simulate real life conditions where the coating may not be properly applied over the entire surface, or where parts of the structure have been missed, or where the coating may have been damaged during service life leaving areas susceptible to chloride penetration.

The test methodology adopted to evaluate the chloride penetration resistance of the coating was cyclic wetting and drying with 4% sodium chloride solution, each cycle consisting of ponding for 7 days followed by air drying for 3 days. Slabs, unlike cores or prisms, make effective tests specimens, as they provide considerably larger surface areas for the chloride to attack. In the tests reported here, the total portland cement content for the concretes in all the slabs was kept constant at 350 kg/m³, with both the aggregate – cement ratio and percentage of sand in the aggregate also kept constant. Three w/c ratios were used (Table 8), but no water reducer or superplasticizer was used. With these mixture proportions, the concretes developed 28 day cube strengths of 30 to 70 MPa as shown in Table 9.

Exposure		Elongation (%)	Tensile strength (MPa)
Initial		320	1.53
Salt	1 000 hrs	310	1.54
Spray	5 000 hrs	300	1.55

Table 7. Residual Properties of Coating After Exposure.

Slab No.	W/C ratio	Slab size (mm)	Area of surface coating
S4	0.45	1000×500×150	Whole-surface
S5	0.60	1000×500×150	Whole-surface
S6	0.75	1000×500×150	Whole-surface
S 1	0.45	1000×1000×150	Half-surface
S2	0.60	1000×1000×150	Half-surface
S3	0.75	1000×1000×150	Half-surface

Table 8. Details of Test Slabs.

Table 9. Slump and Compressive Strength of Concretes.

Slab No. W/C ratio	W/C	1	Comp. st., MPa						
	ratio		7d	28d	128d	242d	556d		
S1, S4	0.45	30	54	72	70	71	81		
S2, S5	0.60	80	32	46	45	46	50		
S3, S6	0.75	165	22	31	33	34	37		

The chloride analysis was carried out after 10, 20, and 50 cycles according to BS1881: Part 124: 1988, and the chloride content is expressed as acid-soluble chlorides by mass of cement. Each chloride concentration shown in the results reported below was obtained from the average of two analyses. The sampling positions were chosen carefully, exactly above the reinforcing bars, as shown in Figure 10. In addition, in the partially coated slabs, the chloride samples were also taken from three locations X1, X2, and X3, as depicted in Figure 10, away from the boundary of the coating in order to assess the effectiveness of the coating when adjacent areas remain uncoated.

The chloride penetration results are summarized in Table 10 for the fully-coated slabs S4, S5, and S6 and in Figures 11 to 13 for the half-coated slabs S1, S2, and S3. The results in Table 10 totally support the results of the accelerated tests, and confirm that no chloride ions entered the protected concretes made with w/c ratios of 0.45, 0.60, and 0.75 even after 50 cycles of wetting with 4% NaCl solution and drying. Figures 11 to 13, on the other hand, confirm that even in partially coated slabs, the acrylic rubber coating acts as an effective and efficient barrier to chlorides. In the data shown in Figures 11 to 13, the chloride penetration is confined to the immediate vicinity of about 70 to 100 mm from the boundary between the coated and uncoated parts. This is quite understandable as the chlorides from the uncoated parts would migrate laterally into the underside of the coated parts, but even then, the coating has a significant effect in reducing both the amount and depth of penetration of chlorides in the vicinity of the coated/uncoated regions.

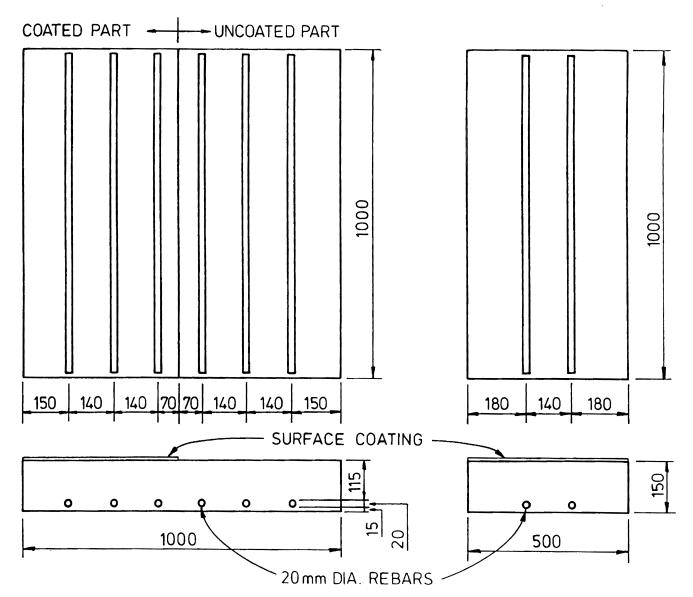


Figure 9. Coating and Reinforcement Arrangement of Slabs S1, S2, and S3.

R.N. Swamy

Slab	W/C	Exposure		Depth from concrete surface, mm						
No.	ratio	cycles	5-25	25-45	45-65	65-85	85-105			
		10	0.00	0.00	0.00	0.00	0.00			
S4 0.45	0.45	20	0.00	0.00	0.00	0.00	0.00			
		50	0.00	0.00	0.00	0.00	0.00			
		10	0.00	0.00	0.00	0.00	0.00			
S5	0.60	20	0.00	0.00	0.00	0.00	0.00			
		50	0.00	0.00	0.00	0.00	0.00			
		10	0.00	0.00	0.00	0.00	0.00			
S6	0.75	20	0.00	0.00	0.00	0.00	0.00			
		50	0.00	0.00	0.00	0.00	0.00			

Table 10. Chloride Concentration Data in Fully Coated Slabs (mm).

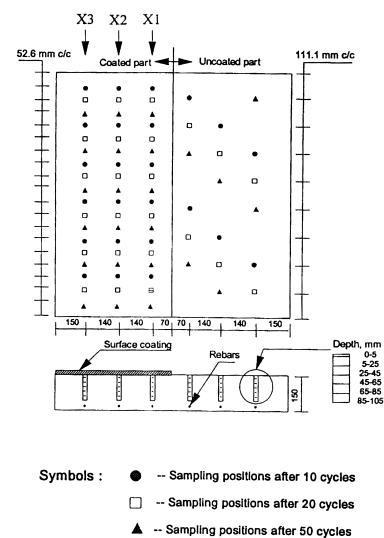


Figure 10. Sampling Positions and Depths for Chloride Analysis.

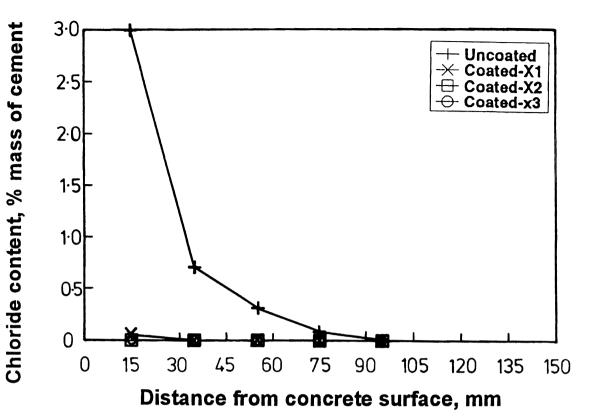


Figure 11. Chloride Profiles for Slab S1 (w/c = 0.45) After 50 Cycles of Exposure.

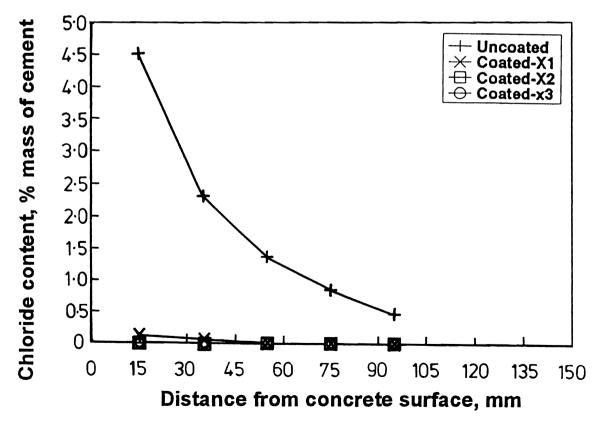


Figure 12. Chloride Profiles in Slab S2 (w/c = 0.60) After 50 Cycles of Exposure.

Bond Strength Characteristics

The bond strength of the coating to the concrete substrate determined after 20 and 50 cycles of cyclic exposure to chlorides is shown in Table 11 for the fully-coated slabs S4, S5, and S6, and in Table 12 for the partially coated slabs S1, S2, and S3. These data are remarkable, especially those in Table 12, as they emphasize the ability of this particular acrylic rubber coating to withstand the damaging effects of repeated wetting and drying in salt solution. These data also provide indirect evidence of the structural integrity of the coating–concrete interface and in preventing the chlorides from the uncoated parts infiltrating into the interface. The results also emphasize some weakening of the bond strength where the parent concrete has a high water content of the order of 0.75, identifying the significance of the moisture state of the concrete in influencing the bond between the coating and the concrete substrate. The fact that these results derived from long-term chloride penetration tests fully corroborate the data from short-term and small scale tests [64] is a measure and reflection of the validity of the test methods used in these studies, and the reliability of the acrylic rubber coating for long-term durable performance.

Table 11. Bond Strength of Surface Coating, MPa, After Cyclic Exposure to Chlorides — Fully-Coated Slabs.

Slab No.	W/C	Exposure			-	Test position	s		
	ratio	cycles	1	2	3	4	5	6	Ave
S4	0.45	20	1.45	1.50	1.25	1.30	1.35	1.40	1.38
S4	0.45	50	1.45	1.60	1.45	1.55	1.60	1.50	1.53
S5	0.60	20	1.50	1.35	1.30	1.40	1.35	1.40	1.38
S5	0.60	50	1.30	1.60	1.35	1.55	1.50	1.35	1.44
S6	0.75	20	0.80*	0.75*	1.40	1.20	1.35	1.20	1.12
S 6	0.75	50	0.70*	0.90*	1.25	1.20	1.30	1.10	1.08

*Failure at concrete/primer interface.

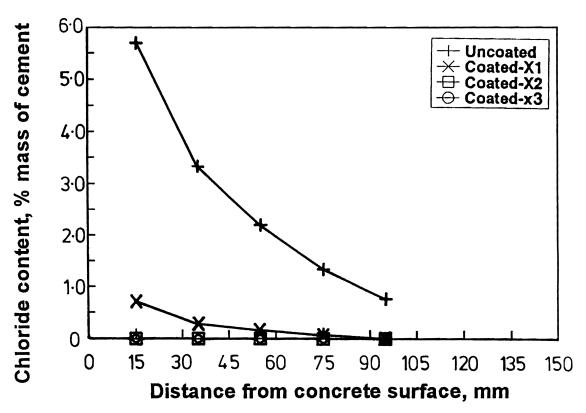


Figure 13. Chloride Profiles in Slab S3 (w/c = 0.75) After 50 Cycles of Exposure.

FIELD EXPOSURE TESTS

There is, unfortunately, only very limited data on the long term performance of surface coatings in real environments. This situation is compounded by the fact that our own understanding of the diffusion mechanisms by which coatings control the transport of liquids and gases is far from clear. In addition, there is again only very limited data to give us any idea of the interrelationship between quantified values of diffusion characteristics and durable performance in salt-laden, harsh environments. There are, however, very clear indications that the chemistry of the coating, its make-up and total thickness, as well as its bond capabilities with the substrate concrete have an overriding influence on their performance in aggressive environments. In the present state of development of surface coatings for concrete, it is clear that the ultimate proof of their effectiveness, efficiency, reliability, and stability has to be based on their real life performance in very unfavorable environments [10, 37, 66, 68]. In the following sections, some field data on acrylic rubber coatings are presented to provide further proof that it is not impossible to develop such coatings for the protection of concrete structures.

Concrete Prism Tests

These tests were carried out on reinforced concrete prisms, $200 \times 200 \times 300$ mm in size, and reinforced with 12–16 mm dia bars, and 2–9 mm dia links. The main reinforcement had covers of 20 mm and 30 mm. The concrete was made with a water-cement ratio of 0.58. NaCl was added to the concrete during mixing at six levels: 0%, 0.2%, 0.4%, 0.6%, 0.8%, and 1.0% by weight of mortar. Coated and uncoated specimens were then partially immersed in sea water and left in this condition for 8 years. Some of the major results arising from those studies are discussed below.

Slab	W/C	Exposure	Location]	Fest positions	5		
No.	ratio	cycles	line	1	2	3	4	5	6	Ave
			X 1	1.28	1.45	1.25	1.30	1.25	1.40	1.32
		20	X2	1.30	1.24	1.32	1.45	1.35	1.55	1.37
S 1	0.45		X3	1.34	1.42	1.48	1.30	1.35	1.45	1.39
31	0.45		X 1	1.42	1.36	1.34	1.28	1.35	1.46	1.37
		50	X2	1.40	1.46	1.38	1.28	1.32	1.41	1.38
			X3	1.50	1.44	1.38	1.45	1.52	1.34	1.44
		20	X 1	1.35	1.20	1.26	1.24	1.45	1.40	1.32
			X2	1.35	1.42	1.28	1.30	1.25	1.45	1.34
S2	0.60		X3	1.40	1.28	1.52	1.44	1.28	1.42	1.39
52	0.00	50	X 1	1.28	1.32	1.26	1.24	1.32	1.46	1.31
			X2	1.26	1.38	1.47	1.42	1.43	1.35	1.39
			X3	1.44	1.30	1.47	1.52	1.38	1.42	1.42
			X 1	1.02	0.85*	0.88*	0.92*	1.10	1.15	0.99
		20	X2	0.90*	1.24	1.10	0.92*	1.01	1.32	1.08
62	0.75		X3	1.35	0.87*	0.87*	0.87* 0.95* 1	1.30	1.34	1.10
S 3	0.75	50	X 1	0.75*	0.85*	1.20	1.10	1.24	0.92*	1.01
			X2	0.95*	1.20	1.32	1.18	0.84*	1.28	1.13
			X3	0.88*	0.95*	1.34	1.28	1.22	1.26	1.17

Table 12. Bond Strength of Surface Coating,	MPa. After Cyclic Exposure	to Chlorides — Partially Coated Slabs.

*Failure at concrete/primer interface

Chloride Penetration

The chloride concentration profiles relating the water-soluble chloride content with penetrated depth are summarized in Figure 14 after 8 years' exposure. The uncoated prisms show substantial intrusion of chlorides, and give evidence of considerable movement and transportation of water and chlorides between the sea water and the body of the concrete. The net result is a highly variable distribution of chlorides within the concrete, and there is some indication of a tendency for chlorides to accumulate in the vicinity of the rebars.

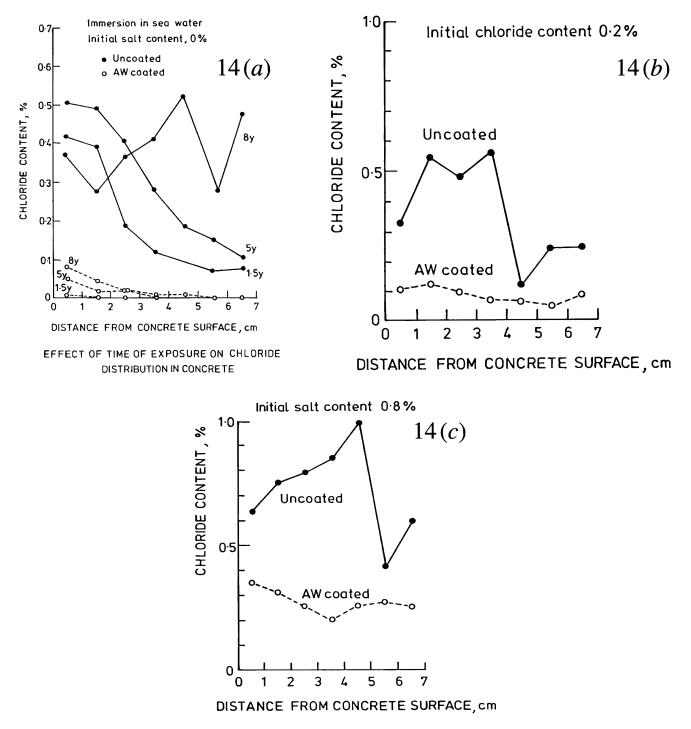


Figure 14. Chloride Concentration Profiles in Uncoated and Coated Prisms: (a) with no added salt; (b) with 0.2% added salt; and (c) with 0.8% added salt after 8 years of Exposure.

The coating on the other hand, is seen to be very effective in acting as a barrier to external water and chlorides, whilst at the same time permitting sufficient mobility of chlorides inside to achieve a more uniform distribution, without peak concentration at rebar levels.

The results in Figure 14 highlight the basic requirements of diffusion and breathability characteristics of concrete surface coatings. The acrylic rubber coating discussed here has not only resisted the ingress of water and chloride from the outside, but it has also permitted sufficient vapor diffusion from inside resulting in a more uniform distribution of the trapped chlorides already present in concrete.

Corrosion of Embedded Steel

After the 8 years of exposure, the state of corrosion of the embedded bars in the prisms was evaluated. The extent of corrosion was evaluated visually and by measuring their loss in weight. The results are shown in Figure 15. These data depict widespread corrosion in the uncoated prisms — in concretes without and with added salt, as well as in the dry and immersed parts. It is clear that without protection of the concrete and/or steel, concrete structures containing chlorides and exposed to a salt environment will have little chance of survival. The surface coating on the other hand shows absolutely no corrosion in concrete without added salt, and was able to prevent completely the ingress of water-borne chlorides, and protect the embedded steel. Even in chloride contaminated concrete, the coating can effectively and significantly reduce the damaging effects of the salt and sea water. This particular coating has thus the important dual capability of protecting steel both in uncontaminated concrete exposed to sea water as well as in salt-contaminated concrete exposed to marine environment.

Adhesion Strength

The coatings were tested for their bond strength after 8 years of exposure, and the results are shown in Table 13. These results show that the presence of chloride within the concrete affects the bond strength of the coating whether it is immersed in sea water or not. The highest bond strength was maintained in the upper part above the water line, and it varied from 2.7 MPa for the concrete without the salt to 1.7 to 1.8 MPa at very high chloride contents of 0.8 to 1.0%. In the continuously immersed section, the bond strength was less ranging from 1.7 MPa in the salt-free concrete to 1.2 to 1.3 MPa at salt contents of 0.8 to 1.0%. In spite of this loss, the coating is able to maintain excellent adhesion and continuity to concrete without and with added chlorides.

The data in Table 13 highlight and emphasize some of the basic requirements of coating to maintain their integrity, continuity, and protective ability when exposed to highly varying and aggressive exposure conditions. It is clear and logical

Initial salt, %		()	0	.2	0	.8	1	.0	
Conc	Concrete cover, mm		20	30	20	30	20	30	20	30
AW coated.	Appearanc	ln sir e sea water								
	Corroded	P	0	0	5	0	25	10	30	15
	Area(X)	Links	0	0	60	20	70	40	80	50
N on coated	Appearanc	In air sea	批	1	世		——]]			НЦ
		water	ייק	1.	די	TT'	חי	T	חי	
	Corroded		100	80	100	80	100	90	100	100
	Area(%)	Links	100	100	100	85	100	70	100	100

Figure 15. Corrosion of Steel in Chloride Contaminated Concrete Without and With Surface Protection.

that there will be a weakening of the adhesion contact zone/interface due to the presence of moisture [64]. This implies that surface coatings should have a low water permeability and a high water vapor diffusion capacity [64]. Only then will a coating remain strong, retain its adhesion continuity and maintain its protective qualities when continuously exposed to varying exposure conditions.

Carbonation Depth

Both the coated and uncoated specimens were tested for carbonation depth after 8 years' exposure by spraying with 1% phenolphthalein ethanol solution containing 10% water. Table 14 summarizes the range of minimum and maximum carbonation depths as well as the mean values measured in both the upper part exposed to salt weathering in air, and the lower immersed part. These results confirm the very high diffusion resistance of the acrylic rubber coating to carbon dioxide, reiterating similar previous data under accelerated and laboratory tests.

IN-SITU TESTS

The data presented in this section are derived from long-term exposure studies of a reinforced concrete structure especially designed and constructed to monitor the time-dependent performance characteristics of the acrylic rubber coating in preventing

Salt content	Adhesion stre	Adhesion strength, MPa					
%	Top section (above sea water)	Bottom section (in sea water)					
0.0	2.70	1.67					
0.2	2.55	1.77					
0.8	1.67	1.18					
1.0	1.81	1.29					

Table 13. Bond Strength of Acrylic Rubber CoatingAfter 8 Years' Marine Exposure.

Salt*	Location**	Coated	d	Uncoated		
%		Min–Max	Mean	Min–Max	Mean	
0	Dry	0-0.5	0.2	1-8	6.3	
	Water	0-1.0	0.3	1-6	3.6	
0.2	Dry	0-0.5	0.3	3-8	7.2	
	Water	0-1.0	0.3	1–12	5.8	
0.8	Dry	0-1.0	0.3	5-14	7.9	
	Water	0-1.0	0.3	2-4	3.6	
1.02	Dry	0-1.0	0.3	2-6	4.5	
	Water	0-1.0	0.3	5-12	6.6	

* Sodium chloride, % of mortar

** Dry - above sea water

Water - in sea water

chloride penetration and protection of the embedded steel. The structure was built in 1984, and is located in a marine environment exposed to sub-tropical weather conditions of high temperature and humidity, and further, exposed on three sides to salt-laden breeze, sea water spray, and splash during high winds. The test building was constructed with two types of concrete mixtures, both identical in their mix proportions, except that the second mix contained salt. The concrete was made with portland cement, and a w/c ratio of 0.63, giving a cylinder compressive strength of 21 MPa at 28 days. The concrete mixture with salt contained 0.5% sodium chloride by weight of concrete added at the mixing stage. Figure 16 gives details of the structural layout of the test building, and identifies the structural elements made without and with salt in the concrete. The structural elements were designed according to the appropriate ACI Building Code.

The structure is being continuously monitored for visual external deterioration processes, cracking, chloride penetration, and steel corrosion. The structures are cored at regular intervals, and the water-soluble chloride content determined. A potential difference titration method using a chloride selective electrode is used to quantify the chloride content which is then expressed as a percentage by weight of concrete.

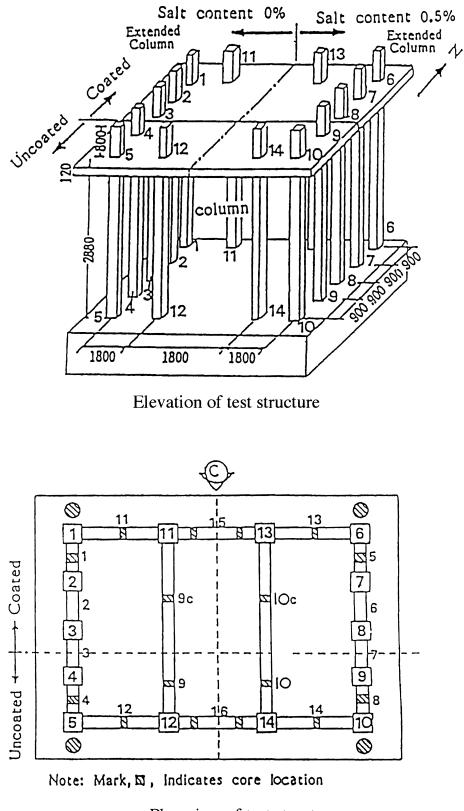
In this paper chloride penetration data, after 9 to 10 years of exposure to the aggressive marine environment described earlier, are presented. These data relate to typical reinforced concrete beams, slabs and columns, and are shown in Figures 17 to 21. These results provide further incontrovertible proof that surface coatings can provide an almost total barrier to water and chloride ions, and prevent the peaking of chloride concentrations in the vicinity of the reinforcing bars. The results also confirm the ability of the acrylic rubber coating to protect concrete already contaminated by chlorides, and maintain this property for several years even where the structure is exposed to an environment that favors and causes rapid permeation and transportation of chlorides into concrete.

RESISTANCE TO CARBONATION

Data on the ability of the acrylic rubber coating to resist carbonation has been demonstrated earlier in this paper. Further proof is provided from core tests carried out on four structures in Japan which had deteriorated, and were repaired subsequently with the acrylic coating. Details of the structures are given in Table 15 together with their history of construction, repair, and of testing for carbonation. All these structures are located in aggressive environments with two of them within about 0.5 km from the sea, and another at about 10 km from the sea. One of the structures was made with concrete containing sea sand. Cores extracted from these buildings were tested for carbonation prior to and after repair. The results are summarized in Table 15. These data again confirm that the acrylic rubber coating can effectively act as a barrier to the penetration of CO_2 . Indeed, these results emphasize two important properties of the acrylic rubber coating described here. First, it has prevented the penetration of water and CO_2 , and secondly, it has also reduced the depth of carbonation in the coated parts. In other words, this particular coating possesses the unique property of *realkalization* by permitting further hydration of the concrete. This property is a direct result of the high water vapor diffusion capability of the coating [64] described earlier in connection with the bond strength data given in Table 13. It is also this property that is responsible for the uniform redistribution of chlorides trapped in coated concretes as illustrated in Figure 14.

Structure		History		Carbonat	on depth, mm			
	Construction	Repair	Investigation	Before Repair	After Repair			
	Construction			Uncoated	Uncoated	AR Coated		
Building	1968	1979	1987	12.5	16.4	7.1		
Building	1973	1981	1987	9.8	13.0	8.0		
Building	1961	1983	1987	27.6	30.0	0.0		
Building	1958	1981	1987	22.3	25.0	1.0		

Table 15. Details of Structures Repaired with Acrylic Surface Coating and its Carbonation Resistance.



Plan view of test structure

Figure 16. Structural Details of Test Building for Long-Term Exposure Studies.

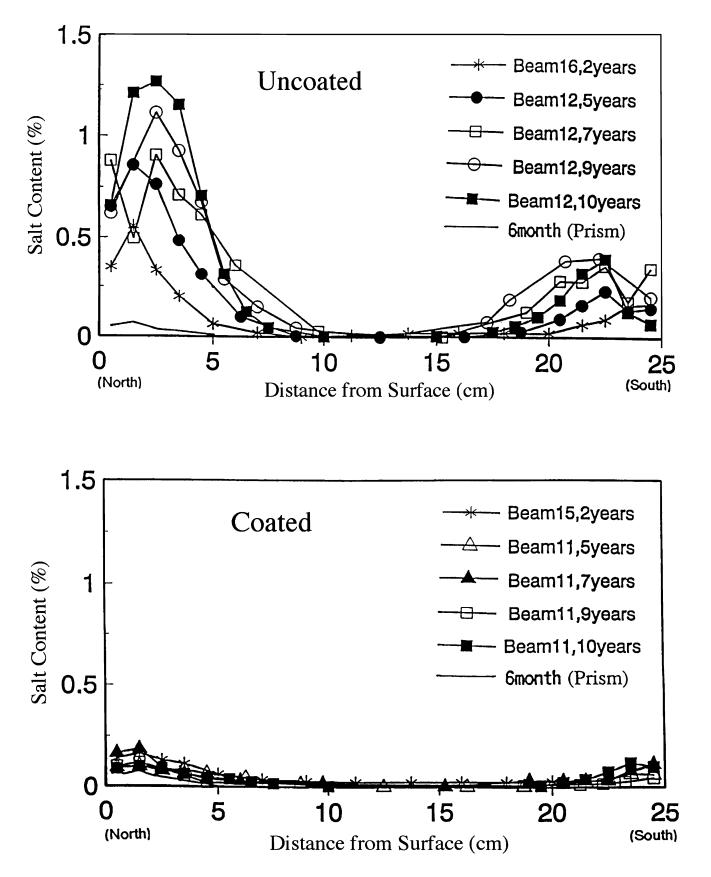


Figure 17. Chloride Penetration into Uncoated and Coated Beams Without Salt – 10 Year Exposure Data.

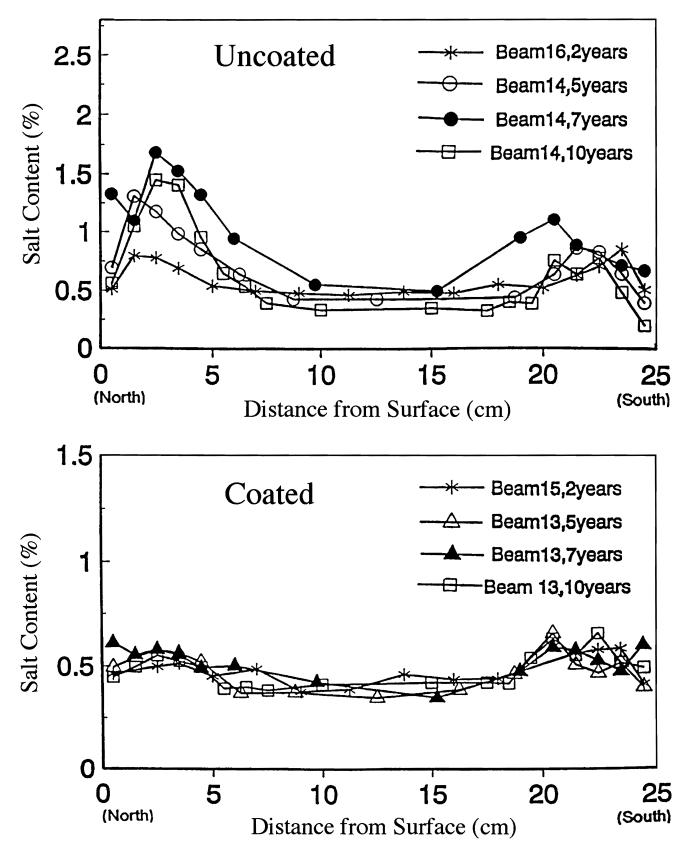
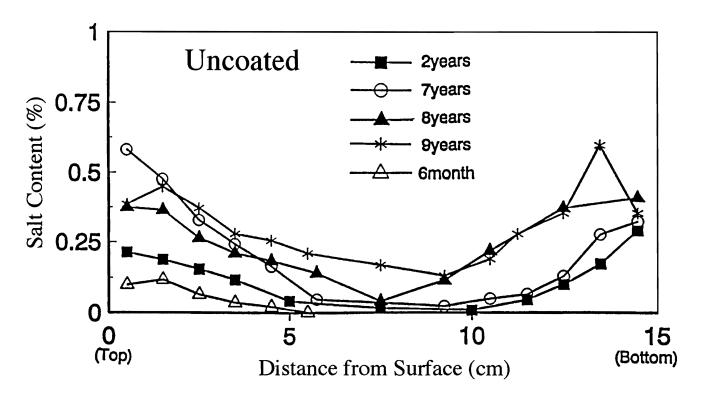


Figure 18. Chloride Concentration Profiles in Uncoated and Coated Beams Made With 0.5% NaCl and Exposed to Harsh Marine Environment.



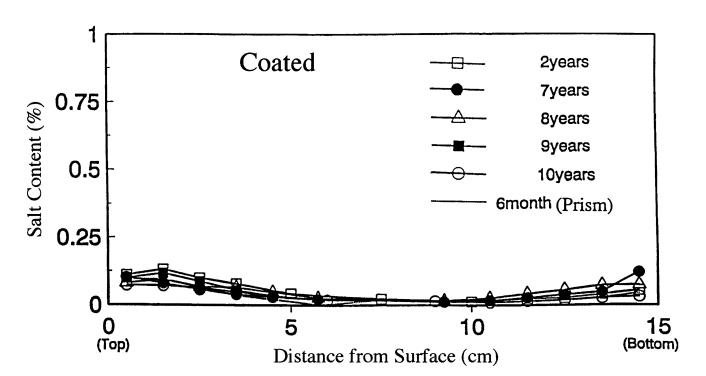
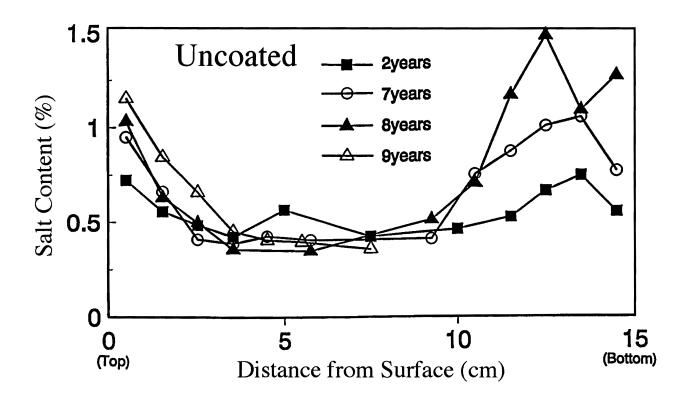


Figure 19. Chloride Intrusion into Uncoated and Coated Slabs Without Salt During 10 Years' of Marine Exposure.



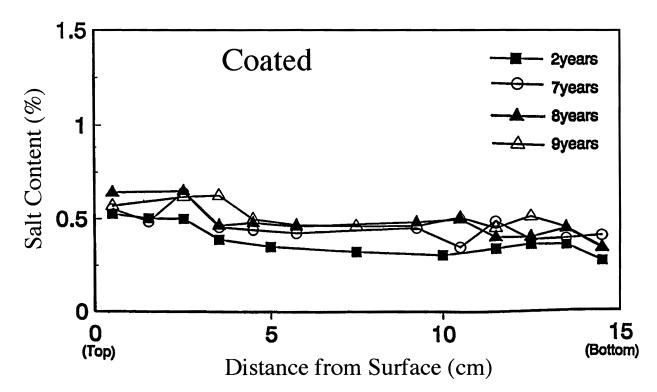


Figure 20. Chloride Profiles in Uncoated and Coated Slabs Made With 0.5% NaCl and Exposed to Marine Environment.

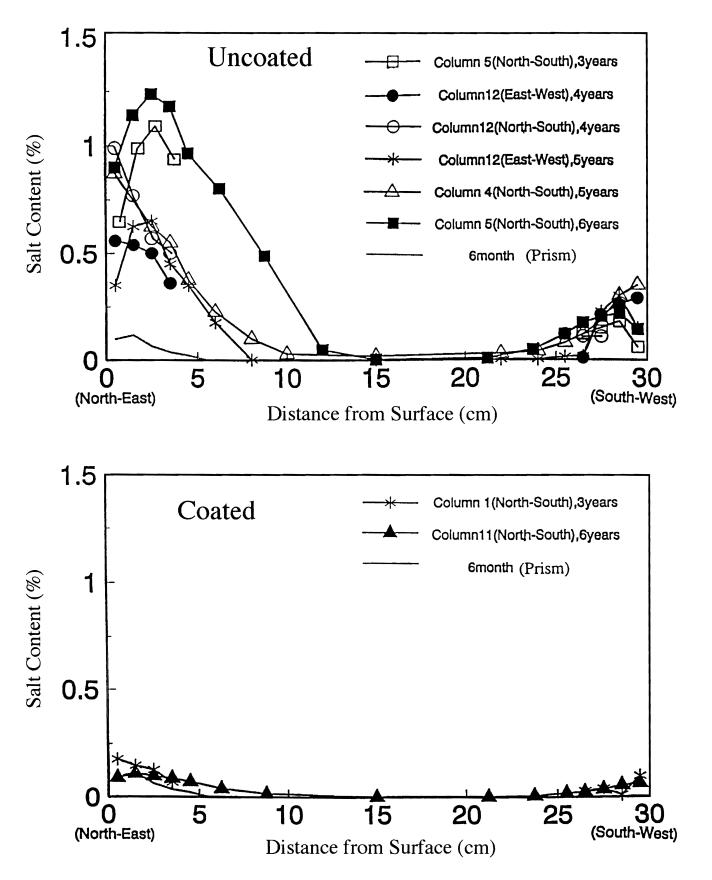


Figure 21. Chloride Distribution in Uncoated and Coated Columns Without Salt During 10 Year's Marine Exposure.

CONCLUDING REMARKS

The overall aim of this paper is to show that protection of concrete is the first key step to ensure long-term durable service life of concrete structures exposed continuously to harsh, salt-laden environments. It is shown that current design specifications and modern portland cement concretes are totally inadequate to provide adequate resistance to chloride penetration and carbonation. Further, the combined interaction of adverse environmental, geomorphological, and climatic conditions is such that their damaging effects are cumulative and concomitant, the ultimate result of which is an unknown factor leading to microstructural degradation, increased permeability, and decreased durability. There is incontrovertible evidence to prove that the most direct, technically sound, economically efficient, and environmentally friendly solution to the problems of reinforced concrete durability in such circumstances lies in the incorporation of finely divided siliceous materials such as fly ash, slag, and silica fume. However, a high degree of impermeability to aggressive ions can only be achieved if the concrete is allowed to mature and develop the full potential of chemical bonding and synergic interactions of its constituents through continued hydration and pozzolanic reactions. This implies that in addition to using a concrete and prevention of its drying, particularly at early ages and especially in aggressive environments, become a paramount necessity.

It is then shown that of all possible methods of protecting concrete from harsh salt-laden environments, surface coatings alone offer the most direct, reliable, convenient, and relatively inexpensive solution. Surface coatings must, however, possess rigorous requirements in terms of their chemistry, overall thickness and durable performance in chloride contaminated hot/dry/humid climatic conditions. Extensive test data, and in particular, long-term field performance extending over ten years are presented to show that it is possible to develop surface coatings that can protect concrete and the steel embedded in it from corrosion with confidence, reliability, and cost-effectiveness.

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