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REVIEW

CONCRETE IN THE MARINE ENVIRONMENT - A REVIEW WITH EMPHASIS ON TROPICAL COASTAL APPLICATIONS

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Abstract: The effect of the marine environment on concrete depends on the climate and the zone of exposure. Degradation of concrete takes place due to a self reinforcing permeation - chemical attack - cracking - permeation cycle. Chemical attack can take place in the concrete or in the steel, if the concrete is reinforced. Cracking can occur due to loading as well as physical and chemical phenomena, either internal or external. Permeation of both water and various harmful ions will depend on the quality of the concrete. This paper reviews field and laboratory investigations on the effects of a variety of environments on various types of concretes. It concludes with a review of specifications for concrete mix design, including water/cement ratio, cement type and content, admixture type and aggregate grading specifications for designing concrete mixes to withstand the marine environment.

Key words: Chloride ingress, Concrete, Marine environment, Mix design, Permeability, Pozzolan, Sulphate attack, Tricalcium aluminate.

THE MARINE ENVIRONMENT AND CONCRETE

Zones of Exposure

The marine environment, because of physical and chemical factors, is perhaps the most severe environment that concrete has been called upon to withstand. Figure 1 gives factors (with examples of each) that have to be taken into account when assessing the performance of concrete in a marine environment. The impact of the marine environment on concrete will vary qualitatively depending on the zone involved. Mehta[1] has classified the marine environment into three zones, namely atmospheric, tidal and submerged, while Fookes *et al.*[2] have used a slightly different terminology, introducing a fourth zone called the splash zone between the atmospheric and tidal zones. Concrete in the tidal and submerged zones is more susceptible to chemical deterioration. However, if the concrete is reinforced, corrosion would be more likely to take place in the atmospheric and tidal zones than in the submerged zone, even though carbonation would be less in the former zones. Where physical deterioration is concerned, concrete is most susceptible in the tidal zone. In addition to freeze-thaw problems in cold climates, the tidal zone will experience wetting and drying, with consequent salt crystallization stresses, in hot climates.

Climatological Considerations

Apart from the zones of exposure, differing climates will have different effects on concrete. A comprehensive table of the occurrence of reinforced concrete deterioration for four different marine climates is given by Fookes *et al.*[2] The above authors also indicate some environmentally related stresses that can be experienced by concrete structures in marine environments, as follows[2]:

Expansion of water due to freezing	200 MPa
Crystallization of salts	2-20 MPa
Hydration of salts	100 MPa
Expansion of clay	2 MPa
Wave impact in existing cracks	100 MPa
Thermal movement in restrained concrete	0.5 MPa/°C.

Unreinforced concrete for coastal applications in the tropics

Apart from being an economical building material, concrete is especially suited for tropical marine environments, where the warmer temperatures may promote corrosion in steel structures and marine borer activity in wooden ones.[3] As freezing and thawing is not present in the tropics, the principal causes of physical deterioration are the wetting and drying cycles and salt crystallization in the evaporation zone. Wick action in the concrete may cause the area affected to be above the actual area of contact with sea water. Shrinkage, which is very high in dry tropical climates, may also result in crack initiation and growth.

Where prestressed or reinforced concrete is concerned, the primary concern regarding the hardened concrete is permeability to chloride ions, for corrosion protection. Unreinforced concrete may not require the same concern regarding permeability, especially because sulphate attack is not very pronounced in sea water. Nevertheless, it is prudent to use low water/cement ratios in concrete production, as this ensures not only good durability, but also high strength and abrasion resistance, that is required for unreinforced concrete to withstand the continuous impact of waves on coastal structures.

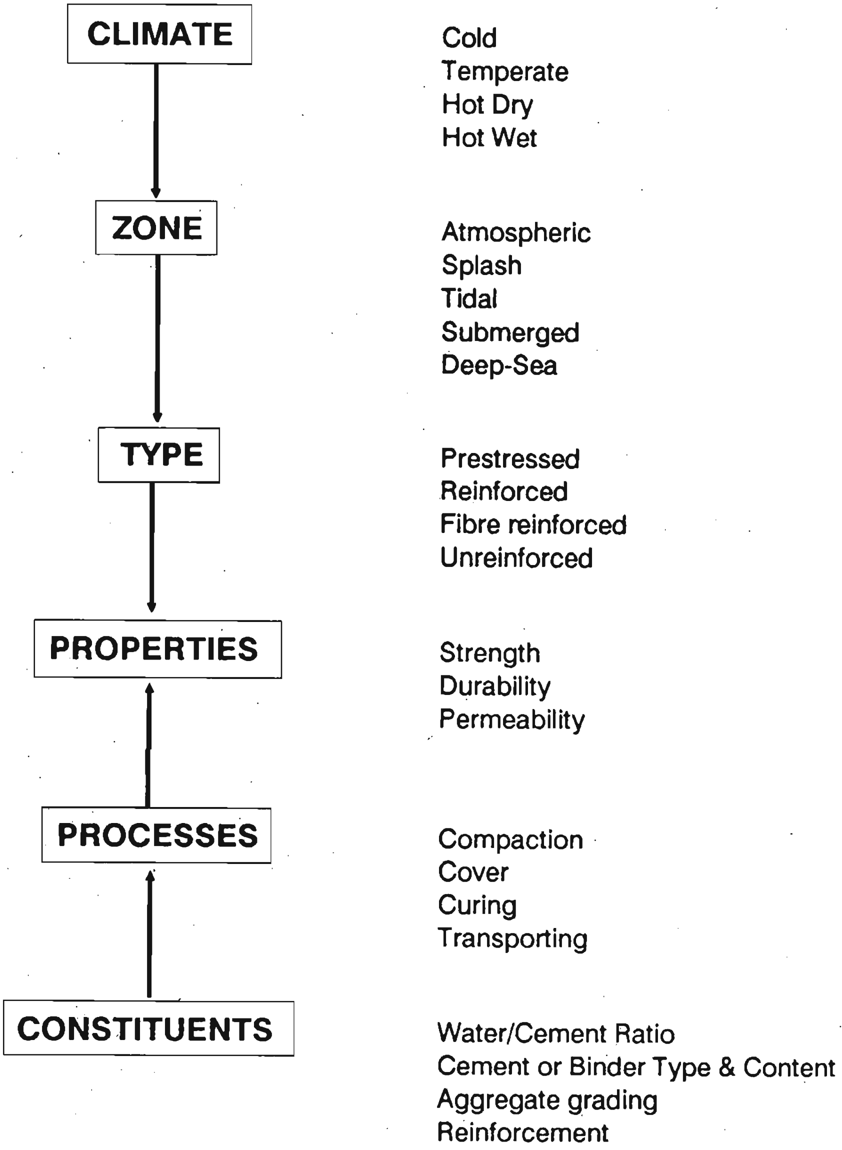

Figure 1: Factors influencing the properties of concrete in the marine environment.

CHEMICAL ATTACK

Chemical composition of concrete and sea water

Hydrated pastes of portland cement contain the following major components[1]:

(i) a microcrystalline calcium silicate having an approximate chemical composition $3CaO.2SiO_2.3H_2O$.

(ii) crystalline calcium hydroxide $Ca(OH)_2$, which may be 24% by weight in completely hydrated pure portland cement pastes. This percentage will be lower in blended cements and blastfurnace slag cements.

(iii) the crystalline monosulphate hydrate, $3CaO.Al_2O_3.CaSO_4.18H_2O$. This hydrate is not present in sulphate resisting cements which contain a minimal amount of tricalcium aluminate, denoted hereafter as C_3A according to cement chemistry conventions.

On the other hand the composition of sea water in grams per litre is as follows[1]:

(i) NaCl	27.0 g/l
(ii) $MgCl_2$	3.2 g/l
(iii) $MgSO_4$	2.2 g/l
(iv) $CaSO_4$	1.3 g/l

The CO_2 concentration in the sea is the highest of all gases, varying between 35 to 60 ml/l, the CO_2 being both dissolved physically and combined chemically in the water[3]. Dissolved oxygen ranges from 5 to 10 ml/l and will affect corrosion as well as biological activity.[3]

The pH of sea water is typically around 8, making it slightly alkaline. Although dissolved carbon dioxide may lower the pH to 7[1], in general the buffering mechanism of the carbon dioxide-carbonate system maintains the pH at around 8[3] - i.e. when CO_2 is dissolved in sea water, although the pH is reduced by the formation of carbonic acid (H_2CO_3), and this reacts with $CaCO_3$ to form HCO_3- ions, which tends to increase the pH once again.

Chemistry of reactions between concrete and sea water

The effect of dissolved CO_2 on concrete are as follows[1]:

$$CO_2 + Ca(OH)_2 \xrightarrow{\qquad\qquad} \underset{\text{(aragonite)}}{CaCO_3} + H_2O \xrightarrow{CO_2} Ca(HCO_3)_2$$

$$CO_2 + [Ca(OH)_2 + 3CaO.Al_2O_3.CaSO_4.18H_2O] \longrightarrow 3CaO.Al_2O_3.CaCO_3.xH_2O + \underset{\text{(gypsum)}}{CaSO_4.2H_2O}$$

$$3CO_2 + 3CaO.2SiO_2.3H_2O \longrightarrow \underset{\text{(aragonite)}}{3CaCO_3} + 2SiO_2.H_2O$$

Both calcium bicarbonate and gypsum are soluble in sea water, causing leaching of material and consequent weakening. The insoluble aragonite ($CaCO_3$) is deposited as a surface layer.

The effect of magnesium salts is shown below[1]:

$$MgCl_2 + Ca(OH)_2 \longrightarrow \underset{\text{(brucite)}}{Mg(OH)_2} + CaCl_2$$

$$MgSO_4 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + \underset{\text{(gypsum)}}{CaSO_4.2H_2O}$$

$$MgSO_4 + [Ca(OH)_2 + 3CaO.Al_2O_3.CaSO_4.18H_2O] \longrightarrow Mg(OH)_2 + \underset{\text{(ettringite)}}{3CaO.Al_2O_3.3CaSO_4.32H_2O}$$

$$MgSO_4 + [Ca(OH)_2 + 3CaO.2SiO_2.3H_2O] \longrightarrow 4MgO.SiO_2.8H_2O + \underset{\text{(gypsum)}}{CaSO_4.2H_2O}$$

Calcium chloride and gypsum, being soluble in water, can cause weakening of the concrete, while the last conversion above is thought to be associated with brittleness and strength loss. The formation of ettringite is accompanied by disruptive expansion.

The chlorides in sea water can react with C_3A in the cement to form the chloroaluminate $C_3A.CaCl_2.11H_2O$. This may occur only when the C_3A content is greater than 8%, as lower percentage of C_3A may be consumed by the gypsum that is present in normal cement.[1] Although the formation of chloroaluminate is expansive, it may not be disruptive, but rather beneficial, because it fills up empty pore space,[4,5] and also has the effect of chloride binding, delaying the ingress of chloride ions to the zone of reinforcement.[1] However, such chloride binding is not stable in sulphate environments (see section on Progress of Chemical attack).

Calcium hydroxide

It is the $Ca(OH)_2$ component in hydrated portland cement that makes it most vulnerable to sea water attack. Not only can it be leached away as calcium bicarbonate and gypsum, causing material weakening, but such leaching also makes the concrete more permeable, leading to the attack of other phases. Hence, the use of blended cements or the addition of partial cement replacement agents, which result in a lower amount of $Ca(OH)_2$ upon hydration, will improve the marine durability of concrete. This has been confirmed by Gjorv,[6] who established that concretes made with calcium aluminate cement, supersulphated cement and blastfurnace slag cements resisted the action of sea water fairly well, and by Smolczyk,[7] whose field and laboratory work revealed that blastfurnace slag cements were more resistant to sea water and sea water salts respectively. The beneficial effect of using pozzolanic partial cement replacement agents such as trass[6] and santorin earth[8] has also been reported. Gjorv[9] reports that the addition of 30% silica fume as a partial cement replacement reduced the pH from over 13 to 12. While this latter figure is not low enough to depassivate the steel (see section on the chemistry of corrosion), the reduction of alkalinity is beneficial for minimizing the risk of alkali-silica reaction. Gjorv also reports that the addition of silica fume increased electrical resistivity but reduced chloride binding.[9]

The level of tricalcium aluminate

The C_3A level in the cement will determine the extent of ettringite formation, which is associated with disruptive expansion. However, the presence of chlorides in sea water is known to inhibit this expansive effect, perhaps as a result of chloroaluminate formation,[8] and also because ettringite is more soluble in solutions containing chlorides as opposed to pure sulphate solutions.[1]

Although it has been suggested that the cubic crystalline form of C_3A will make portland cement more vulnerable to sulphate attack than the orthorhombic or tetragonal forms, there is a lack of consensus in this regard.[1] On the other hand, it has been reported that more $4MgO.SiO_2.8H_2O$ is formed when the crystalline form of C_3A is orthorhombic or tetragonal instead of cubic.[1]

Conjeaud[4] has reported that the morphology of ettringite associated with strength loss in cement mortars exposed to sea water is different to that found in water cured samples. She calls the former "Si-ettringite" as it contains up to about 5% SiO_2 with 0.2% Cl and is not strictly stoichiometric.

In general, however, the level of C_3A in the cement does not seem to have much bearing on the performance of concrete in sea water. Gjorv[6] found that even low C_3A cement contents were affected by sea water when using the rather high water/cement ratios between 0.55 and 0.65. On the other hand, C_3A levels of 12-17% have given excellent long term durability when low water/cement ratios have been used.[1]

The chemistry of corrosion

In a high $(OH)^-$ concentration, the anodic reaction will be as follows[1]:

$$Fe + 3(OH)^- \longrightarrow 1/2Fe_2O_3.3H_20 + 3e^-$$

The ferric oxide is insoluble in an alkaline medium and will act as a protective layer on the steel.

In high Cl^- concentration, where oxygen is present, the anodic and cathodic reactions will be as follows[1]:

Anodic : $Fe + 2Cl^- \longrightarrow FeCl_2 \longrightarrow Fe^{2+} + 2Cl^- + 2e^-$

Cathodic : $1/2O_2 + H_2O + 2e^- \longrightarrow 2(OH)^-$

Since the concentration of dissolved oxygen is less than 10 ml/l in sea water, while being around 210 ml/l in air, it is the atmospheric and tidal zones that are susceptible to corrosion, as opposed to the submerged zone.[1]

Because the presence of Cl^- and $(OH)^-$ ions have opposing effects on the onset of corrosion, it is convenient to define a minimum $Cl^-/(OH)^-$ ratio required to initiate corrosion; this ratio is generally accepted as 0.63.[1] It is suggested by some that a higher ratio may be tolerated because the C_3A in cement can remove some of the Cl^- in the form of the chloroaluminate; this however, may afford only temporary relief.[1]

In this context, the pH of the cement is the controlling factor governing the onset of corrosion. While the pH of hydrated cement paste is between 13 and 14, significant corrosion will take place only if the pH is reduced below 11.5.[1] The pH can be so reduced by carbonation in CO_2 rich sea water or by Mg^{2+} ions which remove $(OH)^-$ from the solution phase by the precipitation of the relatively insoluble $Mg(OH)_2$.

Progress of Chemical Attack

The first phase of attack, on the surface zone itself, is the precipitation of aragonite and the leaching away of this aragonite as the bicarbonate.[1] Aragonite formations have been reported after 7 days of exposure; these gradually form a continuous layer in about 3 months and can increase to around 300 microns thickness after 2 years.[4]

While Mehta[1] reports that second phase attack from Mg^{2+} ions cannot take place until $(OH)^-$ depletion has taken place, Buenfeld and Newman[5] report the formation of brucite, i.e. $Mg(OH)_2$, after only 24 hours of exposing concrete and mortar specimens to sea water. The aragonite layer forms over this layer of brucite, which can be typically 20-50 microns thick.[4] In the third phase, $(SO_4)^{2-}$ ions are removed from sea water by the formation of ettringite and gypsum. Although C_3A, if present in hydrated cement paste, can convert Cl^- into chloroaluminate, this compound is not stable in a sulphate environment and converts to ettringite, releasing the Cl^-.[1] The final phase of attack is the onset of corrosion due to the high Cl^- concentration in the reinforcement zone. The progress of chemical attack is to a large extent dependent on the permeability of the concrete, and this aspect will be considered in the section on permeability, which will also deal with permeability reducing phenomena.

Biological effects

Marine borers are known to attack timber and weak concrete in marine structures. These borers, which depend on the chemical dissolution of calcium carbonate and a mechanism of rasping and wearing or chewing and ingestion, are more likely to be found in warmer climates, in sea water at a pH of 7.5 to 8.5.[3] The accumulation of organisms on structures can increase their weight and the drag forces imposed on them. Such fouling is of particular concern in offshore structures. The specific gravity of the fouling ranges from 1.0 for soft fouling to 1.3-1.4 for hard fouling.[3]

PERMEABILITY

Factors that affect watertightness

The watertightness of a concrete structure can be affected by the following factors[1]:

(i) Cracks in concrete - arising out of transport stresses, deflection due to load, thermal stresses, corrosion of reinforcement, freeze-thaw or wetting and drying cycles, and expansive products of chemical reactions.

(ii) Poor concreting practice - including inadequate compaction, improper placement (e.g. segregation or thick layers of laitence) and poorly formed joints.

(iii) Permeability of the concrete - although poorly graded aggregate may also contribute to this, it is determined mainly by the permeability of the cement paste matrix.

The permeability of the paste is primarily dependent on the water/cement ratio of the mix, a high ratio leading to a greater capillary pore space and causing a permeable paste. The permeability of concrete increases rapidly as the water/cement ratio is increased beyond 0.6.[10] Hence, in order to ensure low permeability, a maximum free water/cement ratio should be specified. Specifications range from 0.4 to 0.5 for concrete in the splash zone,[11] although it would be prudent to adhere to the lower limit. It must be appreciated however, that there will be variations in the localized water/cement ratio within the concrete, due to bleeding[12] and other factors. A paste of nominal water/cement ratio of 0.45 may have local variations ranging from 0.2 to 1.0.[13]

An increase in aggregate size will result in greater areas of high localized water/cement ratios, since aggregates trap the bleed water, causing increases in permeability and micro-cracking.[12] On the other hand, a larger aggregate size will enable lower water/cement ratios to be used because of the reduced water demand for workability. However, in rich mixes, such as those used for marine concretes, the former effect will predominate.[10] The presence of mix particles that are finer than cement particles will inhibit bleeding and also contribute to greater homogeneity.[12] The use of silica fume as a partial cement replacement agent is particularly relevant in this context, as these particles are 50 to 100 times smaller than cement particles.[14]

Sometimes a minimum cement content is specified as well, because this is easier to control than the water/cement ratio. Here again, specifications range from 360 to 400 kg/m^3 for concrete in the splash zone,[11] and in such cases it would be prudent to adhere to the upper limit.

Another way of reducing the permeability of the paste matrix is to reduce the amount of end-product $Ca(OH)_2$, which is susceptible to being leached away. Reduction in paste porosity has been obtained by the use of rice husk ash[1] and santorin earth[8] as partial cement replacement pozzolans. Mehta[1] points out, however, that the reactivity of the pozzolan is an important consideration, as slow reacting ones like pulverized fuel ash (pfa) may take around three months to cause a decrease in porosity. One of the fastest reacting pozzolans currently available is silica fume.[14] The conversion of the crystalline $Ca(OH)_2$ to the poorly crystalline calcium silicate hydrates by the above pozzolans will make the paste structure more uniform and also reduce the potential for micro-cracking, since the interfaces between the crystalline $Ca(OH)_2$ and the poorly crystalline hydrates in hydrated cement paste are considered to be points of crack initiation.[12] Permeability is related to the degree of interconnection of capillary pores and microcracks.[12] Hence the reduction of permeability should be attempted by measures that reduce both the capillary porosity and the potential for micro-cracking.

Ingress of ions

Conjeaud[4] found that the penetration of Cl^- was much greater than that of SO_4^{2-} into mortar bar specimens. Gjorv and Vennesland[15] found that Cl^- can penetrate to a depth of 30 mm in two years even in a mortar specimen with a water/cement ratio as low as 0.4. Hence, they conclude that it is only a matter of time until Cl^- reaches the reinforcement zone even through good quality concrete. The same investigators also found that the paste water/cement ratio (varied from 0.4 to 0.6) had a significant effect on Cl^- penetration in the first 10 mm from the surface but no effect beyond 20 mm from the surface.[15]

In the latter region, the cement composition seemed to have an effect on Cl^- penetration, pure OPC pastes being more susceptible than blended cements.[15] They infer from this that ion exchange is important for Cl^- penetration in this zone, as pure OPC pastes have more $(OH)^-$ than blended cement pastes. They also found that an OPC paste with as much as 8.6% C_3A did not slow down the Cl^- penetration by chloride binding. This is explained by suggesting that either greater percentages of C_3A are required or that chloride binding is more a physical adsorption process than a chemical reaction.

Permeability reducing phenomena

Buenfeld and Newman[5,16] found that the electrical resistance of concrete and mortar exposed to sea water increased gradually. They attribute this to a loss of permeability due to both surface and bulk effects. This was deduced from their observations that the resistance dropped significantly, but not to the original value, when a 1 mm layer was ground off the surface after 18 weeks' exposure.[16]

The surface effect is caused by the formation of brucite and aragonite layers. These layers were observed using the scanning electron microscope by the above researchers as well as by Conjeaud,[4] who reported that they slowed down Cl^- and $(SO_4)^{2-}$ diffusion into mortar specimens; the latter also found a deceleration in the rates of calcium chloroaluminate and ettringite formation, calcium hydroxide consumption and compressive strength loss. The brucite layer has been detected after only 24 hours of exposure[5] and its thickness quoted as being typically 20-50 microns.[4] Conjeaud[4] says that the thickness of this layer does not increase beyond two days, although its crystallization improves; Buenfeld and Newman, however, report an increase in thickness.[5]

The aragonite layer has been detected after 4 days in some cases but only after 28 days in others.[5] It has been found to form a continuous layer over the brucite deposit after 3 months[4] and increase in thickness up to around 300 microns after exposure of 6 months[5] to 2 years.[4] There is, however, supposed to be great variability in this thickness.[4,5] Conjeaud[4] has tried to relate the development of these layers to exposure times of between 1 and 3 months, after which deceleration was obtained for various phenomena, as described beforehand.

Surface water absorption tests performed after pre-drying to 105^0C showed that sea water exposed beams absorb less water than those cured in lime water; this was used to suggest that wetting and drying in the tidal zone may not have an adverse effect on the protective layers.[16] However it is not clear whether alternate wetting and drying by sea water would be sufficient to produce these layers in the first place or whether a large number of such cycles would in fact lead to their deterioration.

Where this surface phenomenon is concerned, Buenfeld and Newman[5] point out that it is very sensitive to the level of Mg^{2+} in sea water, not only for the formation of brucite, but also because Mg^{2+} stimulates the formation of aragonite in preference to calcite. Hence, they emphasize that sea water used in laboratory experiments be renewed regularly (e.g. every month) in order to prevent depletion of Mg^{2+}, which is present only in concentrations of 1.2 g/l. This may explain why this surface phenomenon is not reported by some investigators.

The bulk reduction in permeability reported by Buenfeld and Newman is associated with the reduction in volume of larger pores.[5] Mercury intrusion porosimetry was used to show that all mortars which showed a bulk increase in resistance had a smaller volume of pores greater than 100 nm and a larger volume of smaller pores. This effect was less in a zero C_3A mix, where the chloroaluminate would not have been formed. Hence, the formation of chloroaluminate which can expand into the pore space[4] is suggested as a cause for the decrease in bulk permeability.[5] It should be noted that a pfa mix showed a bulk reduction in resistance, accompanied by an increase in the volume of pores greater than 100 nm.

New technologies for protection

The use of polymers in concrete can improve watertightness. Polymers can be applied in 4 ways - i.e. polymer coatings, polymer impregnation, the use of polymer modified cement and the exclusive use of polymers as the binder.[17] Because of the cost involved, polymer concrete may have applications primarily in repair work. However, both laboratory[18] and full scale[19] exposure tests have confirmed the superior performance of the first two techniques over conventional concrete. Epoxy coated reinforcing bars are another option for protection, in this case, directly of the reinforcement.[20]

DEGRADATION

General

In general, the degradation of concrete in the marine environment is associated with the presence of water, and with various expansion phenomena.[21] Examples of these are the sulphate attack of concrete and the corrosion of reinforcement. Mehta[12] has drawn attention to the importance of micro-cracking and crack growth in concrete for the progress of deterioration, as permeation of harmful ions via such cracks would be quicker than by diffusion through sound concrete. It should be noted that the permeation - chemical attack (of either concrete or steel) - cracking - permeation cycle (Figure 2) is a self-reinforcing one.

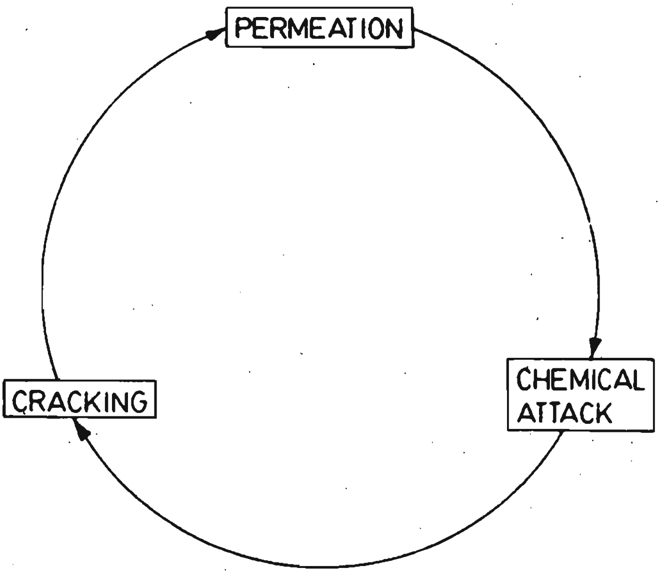

Figure 2: Cycle of degradation

Cracking or crack growth can occur as a result of internal chemical reactions as well, e.g. alkali-silica reaction, where the alkalis are found in the cement and the reactive silica in the aggregate. Here too, external moisture is probably required to initiate or promote the reaction. Another cause of cracking may be physical e.g. shrinkage, freeze-thaw cycles or salt crystallization. Salt crystallization is more relevant for tropical climates than is freeze-thaw degradation. The crystallization of salt in the evaporation zone causes expansive strains resulting in spalling, as in freeze-thaw damage. This similarity in mechanism is the reason that salt crystallization techniques are used for determining frost susceptibility of aggregates.[21]

Field observations

When the cement content in concrete has been greater than around 400 kg/m^3, concrete has performed well in marine environments up to 50 years and longer, even though the C_3A contents of the cements were as high as 14-17%; furthermore, cement contents as high as 600 kg/m^3 were not found to be detrimental in mortar cubes.[1] On the other hand concrete with a low cement content (e.g. 220 kg/m^3) had to be repaired after 20 years' service.[1] In general, cements which contained pozzolan and slag have resulted in concretes that are more durable in coastal and marine works.[1,7] Poor concreting practice and cracks induced in concrete have also shortened the life of concrete structures exposed to marine conditions.[1] Concrete that has deteriorated due to sea water attack shows loss of material, especially at edges, and is soft and weak; it may also be cracked severely.[1,7] Concrete cubes stored in the spray (i.e. atmospheric and splash), tidal and submerged zones under U.K. exposure conditions indicated that strength development was best in the spray zone, while susceptibility to freeze-thaw cycles was greatest in the tidal zone; carbonation in the splash zone was also found to be minimal, because of the wet, humid conditions.[22] Salt crystallization has been found to be essentially a surface phenomenon, producing flaking and spalling in successive layers, without an overall swelling effect, sometimes resulting in patchy erosion and at other times producing Liesegang ring "onion skin" spalling.[21]

Laboratory immersion tests

Some of the properties that have been measured after immersing concrete in sea water are compressive strength,[4,6,8,23] flexural strength,[6] dynamic modulus of elasticity[23] and length change.[23] Where strength is concerned, it initially increases, since hydration continues to take place. Hence, initially any strength loss is relative - i.e. with respect to the strength of water cured specimens - and may be expressed as the ratio of the former to the latter.[4] It may take 6 months or longer, depending on the concrete type, for absolute strength properties to show a declining trend.[6,23] Gjorv[6] found that flexural strength started decreasing after around 5-10 years whereas compressive strength remained unaffected for 30 years.

Lower water/cement ratios were seen to have a significant effect on the resistance to sea water, i.e. ratios of 0.4 compared to 0.6[23] and 0.55 compared to 0.65.[6]

Blended cements such as blastfurnace slag cements were found to produce concrete with better sea water resistance,[6,23] while the addition of pozzolans such as trass[6] and santorin earth[8] generally produced marked improvements. Gjorv[6] found that high C_3A cement concrete performed badly, although it should be noted that his lowest water/cement ratio was 0.5 and highest cement content 417 kg/m^3. Although Gjorv[6] did not find any difference in durability between concretes where fresh water and sea water had been used as mixing water, Nishibayashi *et al.*[23] found that using sea water as mixing water affected the durability of OPC concrete, especially at the higher water/cement ratio of 0.6. Nishibayashi *et al.* also found that precuring (i.e. immersion in sea water after 28 days of presumably air or moist curing) had no beneficial effect and in some cases a detrimental effect, again in OPC concrete having the higher water/cement ratio of 0.6 and where sea water had been used for mixing.[23] They attribute this to the possibility that the ettringite formation in concretes exposed directly (i.e. after 3 days) to sea water is less disruptive than in precured concretes, because the degree of cement hydration in the former is less, thus causing less restraint to the ettringite expansion. Although there may be some evidence in support of this deduction in Gjorv's results - whose precuring, however, was for 6 weeks in fresh water and 6 weeks in air - some of his concretes did actually show improved durability after precuring.[6]

It should be noted that no connection has been highlighted between permeability reducing phenomena and compressive strength changes, except by Conjeaud.[4]

Laboratory accelerated tests

Some investigators have used alternate wetting and drying tests[23,24] as accelerated methods of investigating the effect of sea water on concrete. Their methods consist of repeated cycles of immersion followed by oven drying to temperatures between 50 and 80^{0}C. The upper temperature may be a little too high, as thermal shock could be introduced.[24] Each phase (i.e. wetting or drying) was of the order of 6-24 h duration. Dynamic modulus of elasticity and length change have been used to monitor the degradation of concrete, in addition to compressive strength. The results of such investigations are broadly in keeping with the results of immersion testing, with respect to the effect of various parameters. For example, higher water/cement ratios and higher salt concentrations were found to result in greater deterioration, and blended cements such as blastfurnace slag cement produced concretes with better durability properties.[23,24]

Nishibayashi *et al.*[23] have developed sea water resistance factors, in order to evaluate the performance of different concretes. These are based on the number of cycles required to reduce the dynamic modulus to 60% of its original value, and the length change after 200 cycles. Nishibayashi *et al.*[23] have also tried to correlate their accelerated test results with the long term immersion test results of Gjorv[6], and conclude that one of their cycles (24 h wetting and 24 h drying at 60-80^{0}C) corresponds to about 50-60 days immersion in sea water.

It should be noted however, that where the concrete in the tidal zone is concerned, the wetting and drying tests may represent real time scale phenomena, as opposed to accelerated phenomena. This is especially so with regard to the question as to whether permeability reducing phenomena will be experienced in the tidal zone.[5]

Freeze-thaw degradation

Where freeze-thaw conditions are anticipated, air entrainment of the concrete is recommended. These discrete bubbles of air (of magnitude around 0.05 mm) relieve the pressure caused by water expansion during freezing and also limit the growth of ice particles.[10] For air entrainment to be effective, the spacing between the bubbles should not exceed 0.2 mm[10], and the FIP recommendation is that 4-7% of air be entrained.[25]

Laboratory investigations on freeze-thaw durability have yielded the following general conclusions[26] :

(i) Non air entrained concretes perform poorly, regardless of the water/cement ratio employed.

(ii) Air entrained concretes perform well, but the performance drops when the water/cement ratio exceeds 0.7.

(iii) Even though the bubble spacing for superplasticized concretes is greater than 0.2 mm, these concretes perform well.

(iv) Silica fume concretes incorporating high percentages of silica fume (10-20% or more) perform poorly, even with over 4% air entrainment, due to unsatisfactory bubble spacing.

Freeze-thaw tests have been carried out at natural weathering sites as well. However, attempts to correlate results from such trials with laboratory results have not been very successful[26], due to significant differences in the nature of the exposure.

Reinforcement corrosion

Reinforcement corrosion is a very significant contributory factor towards degradation, not only because of the attack on the reinforcement, but also because the products of corrosion are around 2 to 4 times as bulky as the original steel,[27] and hence cause cracking or spalling of concrete. In general, steel embedded in good quality concrete has been known to exhibit very little corrosion, even after 35 years of immersion in sea water.[28] However, reinforced or prestressed concrete in the tidal and atmospheric zones is probably more susceptible to corrosion. The electrochemical corrosion of steel embedded in concrete depends on a number of factors, including chloride penetration, oxygen availability and the ratio of cathodic to anodic areas.[27,28] Low quality (i.e. very porous) concrete will particularly enhance corrosion, because parts of the steel surface will be separated from the protective concrete by voids.[28] Where cracked concrete is concerned, cracks parallel to the steel are of greater concern than those transverse to the steel; there is also some evidence of crack healing in sea water.[28]

Cyclic loading tests

Apart from the material degradation that takes place as described above, both offshore and coastal structures will be subjected to cyclic stresses. Cyclic loading tests performed on beams have indicated that fatigue life is reduced in seawater compared to that in air, particularly at high water/cement ratios.[29,30] Other factors that have to be considered are the pumping action of water trapped in flexural cracks,[30] salt build up in the cracks[29] and reinforcement corrosion.[29] Impact testing on concrete armour units has indicated that the addition of steel fibres to the mix increases the stabilizing stress, perhaps as a result of a softer impact surface; however, the effect of fibres was less pronounced in bulky armour units, when compared to slender elements such as beams.[31]

SPECIFICATIONS

Concrete Mix

The main concern for marine concrete is permeability, which is determined by the water/cement ratio. Various codes and standards allow a range of permissible water/cement ratios.[11] It may be reasonable to allow a maximum water/cement ratio of 0.4 for the splash or tidal zones and relax this to 0.45 for the atmospheric and submerged zones.[25] These low water/cement ratios will also ensure the achievement of high strength, which may also be important, especially if the concrete is not reinforced.

Another way of ensuring a sufficiently low water/cement ratio is to specify a minimum cement content.[11] The most recent FIP recommendations[25] suggest 400 kg/m^3 for concrete in the splash zone and 320 kg/m^3 or 360 kg/m^3 elsewhere, depending on whether the maximum aggregate size is 40 mm or 20 mm. They also suggest that cement contents in excess of 500 kg/m^3 may give rise to drying shrinkage cracking in thin sections or thermal stresses in thick sections.

One way of increasing the binder content, without the ill effects of shrinkage and heat of hydration, is to use a cement replacement agent, such as pfa or rice husk ash.[1] Typical values for a mix may be 330 kg/m^3 OPC plus 130 kg/m^3 pfa.[32] As stated before the addition of such pozzolanic material can be beneficial, because it reacts with the $Ca(OH)_2$ component. In addition, the ability to use more fine material in the mix may improve the workability properties.[10] In general, blended cements, such as the pozzolan mixes above or blastfurnace slag cements, have better resistance to sea water than ordinary portland cement.

Although American practice requires that the C_3A content of OPC be greater than 4% (to ensure some chloride binding) and less than 10% (to prevent sulphate attack), laboratory studies have shown that it is only a matter of time before Cl^- ions reach the reinforcement[15] and that the level of C_3A in OPC has little bearing on its performance in sea water.[6]

A poorly graded aggregate may also contribute towards lack of watertightness.[1] It is better, therefore, to use mixes based on well graded aggregate as opposed to gap graded ones. A limitation on the maximum aggregate size to be used may also be desirable, although no guidance is given in American or FIP codes.[12] There is also evidence to indicate that mixes with a greater number of fines produce stronger concretes.[33]

In order to achieve good workability, a sufficient amount of fine particles - i.e. those under 150 and 75 microns - should be present in the mix[10]. Another technique is of course to use water-reducing admixtures, but care should be taken about ensuring the durability of such concretes.[34]

If freeze-thaw conditions are expected, 4 to 7% of air (by volume) should be entrained.[25]

Given that marine exposure is particularly conducive to corrosion, one way of reinforcing precast concrete armour units is to use polypropylene fibres in the mix. It has been shown that volume percentages over 1% are not economical,[35] and a typical value is 0.6% by volume of 75mm fibres.[36] There seems to be a tendency in more recent times however, to move away from fibre reinforcement to conventional steel reinforcement, which may be able to restrict the spread of local damage better and allow repair more easily.[37]

Other Factors

If the concrete is reinforced or prestressed, the provision of sufficient cover is of great importance. Here too, there is a range of values permitted by various codes and standards,[11] e.g. 40 to 75 mm for reinforced concrete and 45 to 100 mm for prestressed concrete, depending on the exposure zone. Curing also should be carried out properly, in order to ensure a cover zone of high quality, especially if reinforced or prestressed concrete is being used.

Since the water/cement ratio employed in these mixes will be low, the greatest care must be taken in compacting the concrete, which may be of stiff consistency. Consideration should be given to improving the workability of the mix, as described earlier. The proper formation of joints, if any, is crucial for obtaining low permeability concrete.

The restriction of crack width is also very important in reinforced concrete structures. Static cracks and dynamic cracks may be different in nature.[11]

Concrete units or structures should be designed for all stresses experienced in service as well as transport. Dynamic loading will be especially significant and similarity methods of testing may need to be performed.[29,31] Transport stresses will be particularly important for unreinforced precast concrete units, such as armour units.

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