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Durability of Concrete in Marine Environment--A Review

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Synopsis: Case histories of deteriorated portland-cement concretes exposed to sea water, both in mild and cold climates, show that permeability is the most important characteristic determining the durability of concrete. Whether due to improper mix proportions, or poor concreting practice, or cracking of concrete, permeable concretes tend to deteriorate in marine environment. This is because the hydration products of portland cement are chemically unstable to certain aggressive components present in sea water.

In this paper, the chemical reactions between the aggressive components of sea water and the constituents of hydrated portland cement are reviewed. The physical processes of deterioration associated with these chemical reactions are discussed. Also discussed are the fundamental anodic and cathodic reactions involving corrosion of reinforcing steel in concrete exposed to sea water. A summary of recent work on the effectiveness of various admixtures in reducing the permeability of hydrated portland cement is given.

Keywords: admixtures; cathodic protection; climate; concrete durability; corrosion; cracking (fracturing); deterioration; harbor structures; hydration; marine atmospheres; mix proportioning; permeability; portland cements; reinforcing steels; sea water.

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INTRODUCTION

Oceans make up 80 percent of the surface of the earth. This means that the area covered by the oceans is four times larger than the area covered by land. Mans' earliest uses of ocean were for navigation and fishing, however pressures of the growing world population and a corresponding demand for resources is rapidly extending the sphere of a wide variety of human activities to the continental shelves. Already, a fifth of our oil and gas comes from the off-shore facilities. Seabed mining for mineral resources is a distinct possibility in the near future. Manganese nodules present in large quantities in the North and South Pacific can become a major source for supplies of metallic manganese, nickel, copper, and cobalt. In order to relieve the land from pressures of urban congestion and pollution, consideration is being given to the idea of locating cities, airports, nuclear power and waste disposal plants on offshore floating platforms.

Piers, foundations, retaining walls and breakwaters for sea structures are generally made of portland cement concrete. Production and storage facilities on seabeds for exploitation of energy and mineral resources would be made of concrete. Also, if the oil storage tanks in the North Sea are indicative of the trend, most sea structures of the future would continue to be made from portland cement concrete. This is because in the context of the aggressive nature of sea water, concrete is not only the most economic structural material for construction of large structures, but also is the most durable, requiring little or no maintenance during the service life of the structure. Furthermore, in this period of energy consciousness, concrete is expected to replace other structural materials which require much more energy to produce. For instance, for a given load, a prestressed or reinforced concrete member can be made at the expense of 1/4th to 1/6th as much energy as the corresponding steel member.

However, this trend toward more and larger concrete structures, exposed to deeper and rougher sea waters, places an unusual demand on the safety and long-term reliability of structures. Consequently, a fresh look at the subject of durability of concrete in marine environments is needed. Whereas well-made structures of high quality concrete have lasted hundreds of years in sea water, others of inferior workmanship or poor quality concrete are known to have deteriorated. In this paper, case histories of deteriorated concrete exposed to sea water are reviewed in order to arrive at a basic understanding of the various ways in which concrete can deteriorate. The physical processes of concrete deterioration are identified, and the associated chemical reactions between the components of sea water and the constituents of hydrated portland cement are discussed in detail. Also discussed are the anodic and cathodic reactions responsible for corrosion of reinforcing steel in concrete exposed to high concentration of chloride ions present in sea water. In the end, since the permeability of concrete is the most important factor determining long-term durability of concrete sea structures,and since permeability of concrete is greatly influenced by the permeability of cement paste, a brief summary of recent work at the University of California is given on the effect of several admixtures on reducing the permeability of hydrated portland cement.

CASE HISTORIES OF CONCRETE DETERIORATION IN MARINE ENVIRONMENT

In 1924, Atwood and Johnson (1) published their comprehensive review of the state-of-the-art on the previous 100 years of experience with concrete in sea water. The oldest cementing material cited in the paper consisted of a 60 A.D. lime-pozzolan mortar which, when compared with five recent (1886-1899) mortars, showed that after removal of a part of the original lime present by sea water, the residual lime content in all the six specimens was similar. According to Feld (2), recognition of possible concrete deterioration due to chemical alteration by sea water exposure came as early as 1880, when Professor Prazier of the University of Aberdeen, Scotland, investigated the causes of deterioration of concrete at Aberdeen Harbor. He warned that hydraulic cements used in concrete exposed to sea water would absorb magnesia by ion exchange, resulting in loss of lime and surface disintegration. Further, according to Feld, M. Vicat in France, in his study of disintegration of lime-pozzolan concrete blocks at Marseilles, Rochefort, Algiers, and Cherbourg, arrived at the same conclusions.

From the standpoint of some of the earliest published data on deterioration of portland-cement concrete in sea water, the following three reports cited by Atwood and Johnson (1) are of considerable interest:

(i) A 1920 report by the British Institute of Civil Engineers to the International Navigation Congress on 30 concrete structures, six constructed during 1855-1880 and the remaining 24 during 1880-1912, showed that 17 of the thirty structures were in a state of deterioration. Among the 13 which showed no deterioration, one had a granite facing and four contained pozzolan as admixture in concrete.

(ii) A report of portland cement concrete damage from Port-of-Spain showed that a breakwater was built with 90-day cured concrete which was fully submerged 12 meters below the low-tide line. Within five years,the concrete was found in a state of deterioration. Chemical analysis of cement paste showed considerable loss of lime, and large increases in MgO and CO_2 content.

It can be concluded that fully submerged portland-cement concrete is vulnerable to chemical decomposition by the magnesium salts and CO_2 present in sea water.

(iii) A 1922 report of the San Francisco Bay Marine Piling Committee showed that 457 reinforced concrete cylinders needed repairs from a total of 5198 installed during 1909-1918. In two badly damaged structures, over 25 percent piles showed cracks over the reinforcement above the high-tide line, within ten years of installation.

From this it was concluded that in the case of reinforced concrete, a direct contact between the structure and sea water is not essential for corrosion of steel in concrete and the associated phenomenon of concrete cracking.

Further review of case histories of concrete deterioration in sea water shows that it is desirable to study separately the performance of sea structures in mild climates and cold climates, because in the latter case the effect of freeze-thaw cycles on concrete is often superimposed on the effect of sea water. Tables 1 and 2 contain a summary of some reports on performance of concrete sea structures in mild climates and cold climates, respectively.

CONCRETE EXPOSED TO SEA WATER IN MILD CLIMATES

Regourd (3) studied the effect of 66 years exposure of portland-cement mortars made with different cement contents, 300, 450, and 600 kg/m^3. Lean mortars were severely damaged, however the dense cubes containing 600 kg/m^3 cement, even when made with a 14.9% C_3A cement, remained in good condition. The chemical resistance of cements was found to be significant only in the case of mortars with low cement content which were, therefore, more permeable. In general, portland pozzolan and slag cements which contain less free lime on hydration than pure portland cement, showed better resistance to sea water. Also, irrespective of the type of cement originally used, the deteriorated samples contained the same constituents, namely, calcium carbonate in the form of calcite or aragonite, brucite, and magnesium silicate hydrate. In later work on highly carbonated mortars from the offshore dike in the Cherbourg Port, Regourd et al (4) identified the presence of gypsum, ettringite, and a carbonated form of ettringite, called thaumasite.

Mehta and Haynes (5) reported the results of their investigation on 67 years old unreinforced concrete blocks, made with six different portland cements and three different concrete mixtures, which remained in partially submerged condition in sea water in the Los Angeles harbor. Dense concrete blocks, some made with a 14-15% C_3A portland cement, were still in excellent condition, however, lean concrete showed loss of material and was soft and weak. The cementing constituents originally present, namely CSH and CH, could not be detected in the samples of deteriorated concrete which showed considerable amounts of brucite and gypsum, and small amounts of aragonite, ettringite, and hydrocalumite (carboaluminate hydrate) present. Thus, this investigation confirmed that permeable portland cement paste is inherently unstable to magnesium salts, sulfate ions, and CO_2 present in sea water.

Results of investigations on over 40 years old reinforced concrete structures exposed to sea water on the west coast of the United States are given by Wakeman et al (6), and a subsequent discussion of this paper by Fluss and Gorman (7). In the Los Angeles harbor, precast reinforced concrete piles were driven in 1912 to support a 800-meters wharf. After 12 years of service, some piles showed longitudinal cracks at the mid-tide level, leading eventually to crumbling and spalling of concrete. The concrete below the low-tide line remained sound. It was postulated by Wakeman et al (6) that corrosion of the reinforcements in concrete by permeation of sea water through fissures probably caused by sulfate attack were responsible for the problem. In 1958, Fluss and Gorman (7) reported on the reinforced concrete cylindrical piles and girders of the San Francisco ferry building constructed in 1912. Good quality concrete containing 658 lbs/yd^3 (395 kg/m^3) of Type I portland cement was used. After 46 years of service, most of the piles were found in good condition in spite of the high (14-17%) C_3A content of the cement. However, one-fourth of the cast-in-place piles and one-third of the transverse girders for Pier Nos. 26 and 28 were found cracked. It was speculated that the presence of micro-cracks in concrete due to excessive deflection under load might have exposed the reinforcing steel to the corrosive action of sea water. Also, poor workmanship was held responsible for differences in permeability of in-place concrete, although the concrete mixture was of satisfactory quality.

Several examples of damage to concrete sea structures are given by Feld (2). After 21 years of use, the concrete piles and caps of the trestle bends of the James River Bridge at Newport News, Virginia, required a $1.4 million repair and replacement job in 1955,when 70 percent of the 2500 concrete piles were found in need of repair. Some 750 precast concrete piles driven in 1932 near Ocean City, New Jersey, had to be repaired in 1957 after 25 years of service. The severity of the loss of material from the piles, caused by higher than normal concentrations of dissolved CO_2 in sea water, can be judged from the fact that the 550 mm dimension of some piles had been reduced to 300 mm. The bridge over the Shrewberry River, New Jersey, built in 1913, had 10 piers, two of which showed signs of failure about a year after they were built. Concrete had been placed by tremie, and alternate layers of concrete and a soft putty containing salt crystals was found on the removal of these piers. Laitance accumulation of 50 to 75 mm in 5 meter depth of concrete placement was common when placing concrete using gravel as aggregate. However, with crushed stone as aggregate, the laitance layer was twice as thick.

Complete removal of such laitance layers should have been done to avoid permeable seams which are first to be subjected to sea water action.

CONCRETE EXPOSED TO SEA WATER IN COLD CLIMATES

Table 2 shows a summary of the results of surveys by Idorn (8), and Gjorv (9) on the performance of mostly 20-50 years old coastal concrete structures in Denmark and Norway, respectively. Pier No. 7 of the Oddesund Bridge in Jutland, Denmark, had to be repaired after 8 years of service. Examination of deteriorated concrete indicated decomposition of the cement and loss of strength below low-tide level, and cracking due to freezing and thawing above high-tide level. Aragonite, ettringite, gypsum, brucite, and alkali-silica gel were detected as the products of cement decomposition. History of structure indicated that caissons were initially cracked due to thermal stresses in concrete, and this could have permitted percolation of sea water into the interior of concrete. The piers of a highway bridge in North Jutland showed severe cracking and spalling at the mean-tide level, producing the typical hour-glass shape, which is characteristic of concrete cylindrical piles exposed for long time to sea water. The failure was caused by poor quality (high water-cement ratio) concrete which was vulnerable to degradation through severe corrosion of reinforcement, freezing and thawing, and alkali-aggregate reaction. Concrete blocks from Groin 71 at the north barrier of the Lim Fiord, Denmark, were found severely deteriorated in 20 years of exposure to sea water. The concrete was very weak as a result of decomposition of the cementitious component. Poor quality of concrete mixture, which contained only 370 lbs/yd^3 (220 kg/m^3) cement, exposure to repeated cycles of wetting - drying, freezing - thawing, and impact of gravel and sand present in the surf were considered responsible for the loss of material.

In 1962-64, Gjorv (9) surveyed 716 concrete structures along the Norwegian seabord. At the time of the survey, about two-thirds of the structures were 20-50 years old. He found that, in general, concrete pillars were in good condition both above the high-tide line and below the low-tide line. In the tidal zone, about 50 percent of the surveyed pillars were in good condition while others showed signs of damage. Fourteen percent pillars had more than 30 percent reduction in area of cross section, and twenty-four percent had 10-30 percent reduction. This deterioration was ascribed mainly due to the effect of frost action for which the concrete was not designed. Among the numerous other examples of cracking and disintegration of reinforced concrete sea structures in cold climates is Pier No. 2 of a concrete wharf in Halifax, Nova Scotia, which according to Tibbetts (10) needed extensive repairs. The concrete in the tidal zone was protected with timber jackets but it cracked above the high-tide line, probably due to the combined effect of freeze-thaw cycles and corrosion of the reinforcement.

LESSONS FROM CASE HISTORIES OF DETERIORATED CONCRETES

The first lesson from the case histories of concrete damage in sea water is that portland-cement concretes invariably contain seeds of potential deterioration. These seeds are present in the form of the hydration products of portland cement, especially calcium hydroxide, which being basic in nature, are vulnerable to chemical decomposition as a result of chemical interaction with certain components of sea water, namely $MgCl_2$, $MgSO_4$, and CO_2.

Whether these seeds turn into deleterious products depends mainly on the ability of a concrete to keep water from penetrating into the interior. Thus, the second lesson from the above case histories of concrete failures is that permeability of concrete is the most important property determining long-term durability. Again, from the case histories of deteriorated concretes, the following causes for lack of water-tightness can be identified:

(i) Improper mix design: Permeability of concrete is derived mainly from the permeability of cement paste. Low cement content and high water-cement ratio produce a readily permeable product on hydration. Poorly graded aggregate can also be a source of lack of water-tightness.

(ii) Poor Concreting Practice: Even a high quality concrete mixture can yield a permeable concrete if the concrete is not properly compacted. Poorly constructed joints can also permit percolation of water. Carelessness in placement, such as segregation of concrete mixture and formation of thick layers of laitance at joints, or dilution of concrete mixture with additional water, has frequently been identified as a source of concrete permeability.

(iii) Cracks in Concrete: Despite good quality of concrete and proper workmanship, concrete structures may yet be permeable to sea water if they develop cracks during the course of their service life. Among the common sources of cracking are excessive deflection due to load, carelessness in transporting precast members and driving precast piles, thermal stresses due to temperature gradient in thick concrete structures, freeze-thaw cycles on non-air-entrained concrete, corrosion of reinforcing steel and expansive chemical reactions such as these involving formation of ettringite and alkali-silica gel.

Another lesson from the case histories of concrete deterioration in sea water is that, depending on the tidal lines, the individual processes of deterioration tend to limit themselves to different parts of a structure. From this standpoint a structure can be divided into three zones which are illustrated by Fig. 1. The uppermost part, which is above the high-tide line, is not directly exposed to sea water. However, it is exposed to atmospheric air, winds carrying sea salts, and frost action. Consequently, cracking due to corrosion of reinforcement in concrete and/or freezing and thawing of concrete are the predominant deleterious phenomena in this zone. The structure in the tidal zone, which is between high-tide and low-tide mark, is not only vulnerable to cracking and spalling of concrete due to wetting and drying, frost action, and corrosion of reinforcement, but also to loss of material due to chemical decomposition of hydration products of cement, and impact of waves containing floating ice, sand, and gravel. The lower part of the strucutre, which is always submerged in sea water is vulnerable to strength retrogression and loss of material as a result of the chemical reactions between sea water and hydration products of cement. Due to the absence of frost action and due to lack of oxygen, cracking of concrete due to freeze-thaw cycles and corrosion of the reinforcing steel is seldom a problem here.

CHEMISTRY OF REACTIONS BETWEEN SEA WATER AND HYDRATION PRODUCTS OF PORTLAND CEMENT

The chemistry of reactions responsible for the decomposing action of sea water on the constituents of hydrated portland cements is summarized in Table 3. Before a discussion on the subject, it is desirable to briefly review the relevant features of sea water composition, and microstructure of hydrated portland cement paste.

Typically, sea water contains about 3.5 percent soluble salts by weight. The relative ionic concentrations in grams per liter are 18 gpl Cl^-, 12 gpl Na^+, 2.6 gpl $(SO_4)^{2-}$, 1.4 gpl Mg^{2+}, and 0.5 gpl Ca^{2+}. In terms of chemical salts, the composition of sea salt can be expressed as 2.7 gpl NaCl, 0.32 gpl $MgCl_2$, 0.22 gpl $MgSO_4$, and 0.13 gpl $CaSO_4$. Whereas the presence of chloride ions in sea water has considerable influence on corrosion of steel in concrete, it is the magnesium salts present which exercise the most harmful effect on the hydration products of portland cement. Carbon dioxide dissolved in sea water can also become instrumental in decomposing a hardened cement paste. Normally, the pH of sea water is about 8 and only very small amounts of dissolved CO_2 are present. However at times, due to presence of decaying organic matter, highly carbonated sea waters show pH values of 7 or less, and they can be quite deleterious to the hydration products of portland cement.

Well-hydrated pastes of ASTM Type I/II portland cement consist mainly of a microcrystalline calcium silicate hydrate, having an approximate chemical composition, $3\,CaO \cdot 2\,SiO_2 \cdot 3\,H_2O$, and two hydrates which are well crystalline, namely calcium hydroxide and the monosulfate hydrate, $3\,CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 18H_2O$. The latter is responsible for the expansive reaction involving formation of ettringite when hardened pastes of Type I/II portland cement are exposed to sulfated water. The monosulfate is not present in the hydration products of Type V portland cement.

Completely hydrated pastes of pure portland cement contain about 24 percent $Ca(OH)_2$ by weight, and this is the most vulnerable constituent of cement paste from the standpoint of ease of attack by the aggressive components of sea water, such as CO_2, $MgCl_2$, and $MgSO_4$. As discussed in Table 3, some of the products of chemical interaction between $Ca(OH)_2$ and the aggressive components of sea water being soluble in sea water, lead to removal of $Ca(OH)_2$ from the hardened cement paste - a phenomenon associated with weakening of the material and loss in its strength. Increased permeability caused by lime leaching exposes the other constituents of cement paste to carbonation attack. Thus, eventually, even the principal cementitious phase, $3\ CaO \cdot 2SiO_2 \cdot 3H_2O$, can be destroyed, as shown in Table 3.

Several investigators have shown that cements which contain little or no $Ca(OH)_2$ on hydration are more durable to chemical attack of the type discussed above. In a study involving 30 years of immersion in sea water of 2500 concrete specimens, made with 18 different kinds of cements and mixtures having 0.55 to 0.65 water-cement ratio, Gjorv (11) established that concretes made with calcium aluminate cement, supersulfated cement and blastfurnace slag cements resisted the action of sea water fairly well, even when the specimens were not cured prior to immersion in sea water. However, even the low C_3A portland cements were affected. Addition of trass, a pozzolan, greatly improved the durability of the cement.

As will be discussed later, in reinforced and prestressed concrete, some reserve basicity provided by the presence of free lime in hydrated cement paste is considered useful for protection of steel from corrosion. However, for protection of both steel and concrete from attack by sea water, it is desirable to remove a part of the potential free lime by pozzolan addition to concrete. Simple calculations show that addition of 15 percent of a good-quality pozzolan (by weight of cement) to a portland-cement concrete mixture will be able to remove only one-half of the potential free lime from well-hydrated cement paste. Similarly, in response to a discussion of her paper, Regourd (3) pointed out that portland cements containing belite as the principal silicate phase, rather than alite, will be more resistant to sea water because hydration of belite liberates less lime.

There is considerable confusion in published literature regarding the role of C_3A in portland cement on sulfate resistance of concrete exposed to sea water. Several investigators, including Regourd (3), Mehta and Haynes (5), and Fluss and Gorman (7) found excellent long-term durability of relatively rich (low water-cement ratio) concretes made with portland cements of 12-17 percent C_3A content. Although, ettringite in minor quantities was detected in deteriorated concrete, ettringite has seldom been conclusively demonstrated to be the sole cause of cracking of an off-shore concrete structure exposed to sea water. This is because the presence of chlorides, as in sea water, inhibits the expansive phenomenon associated with ettringite. Lea (12) states that, according to Batta, the reactions involving formation of ettringite and gypsum are not accompanied by swelling to the same degree in sea water as in pure solutions of sodium or magnesium sulfate because both ettringite and gypsum are more soluble in solutions containing chlorides.

Attention has been drawn to the possibility that different crystalline forms of C_3A may show different degrees of resistance to sulfates in sea water. Regourd (3) studied the hydration characteristics of both synthetic and industrial cements containing cubic,orthorhombic or tetragonal C_3A. The pastes containing orthorhombic or tetragonal C_3A, made with 0.5 water-cement ratio and allowed to hydrate in sea water, showed at 90 days more chloroalmuninate hydrate than ettringite. The reverse was observed when the C_3A phase in cement was in the cubic form. This implies that the presence of cubic C_3A, instead of orthorhombic or tetragonal C_3A, will make a portland cement more vulnerable to sulfate attack associated with ettringite. Recent unpublished work by this author did not confirm this.

Cole (13) identified the presence of a magnesium silicate hydrate, $4MgO \cdot SiO_2 \cdot 8H_2O$, in samples of old concrete subjected to prolonged sea water exposure. Regourd (3) observed that the presence of magnesium silicate hydrate made the specimens friable and weak. In Table 3, the chemical reaction is shown by which magnesium sulfate of sea water converts the principal cementing products in portland cements, namely the calcium silicate hydrate and lime, to the magnesium silicate hydrate and gypsum. In the synthetic cements of Regourd (3), it was reported that more magnesium silicate hydrate was formed when the cement contained tetragonal or orthorhombic C_3A rather than cubic C_3A.

POSSIBLE PATTERN OF CHEMICAL DECOMPOSITION OF CEMENT PASTE IN SEA WATER

Biczok (14) cites a possible pattern, proposed by Moskvin, on the progress of chemical reactions into the interior of a hardened portland-cement paste exposed to sea water. Concrete surface can be considered as the first zone of sea water attack. As a result of Ca^{++} and OH^- ions moving out to the concrete surface, aragonite is generally precipitated at the surface. In highly carbonized sea water, aragonite is converted to bicarbonate, and being soluble it is leached away. The action of CO_2 present in sea water is thus limited to the concrete surface. The second zone is the zone of Mg^{++} ion attack. Dense precipitates of $Mg(OH)_2$ (brucite) are generally found here, while SO_4^{--} and Cl^- ions continue to move further into the interior of the cement paste where, in the third zone, the chloroaluminate hydrate and sulfoaluminate hydrate (ettringite) are formed.

According to Kalousek and Benton (15), the Mg^{++} cannot penetrate into the paste so long as supply of OH^- to the paste surface-solution interface is maintained. When OH^- ion concentration is depleted at an advanced state of deterioration, Mg^{++} ion penetration into paste can occur, thus exposing the calcium silicate hydrate to Mg^{++} ion attack.