

# ALTERNATIVE CEMENTS FOR DURABLE CONCRETE IN OFFSHORE ENVIRONMENTS

Philip S. Zacarias, *ShawCor Ltd.*

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## ABSTRACT

Many specifications for concrete coated offshore pipelines require that the normal weight or heavyweight concrete be manufactured with either ASTM C150 Type II (moderate sulphate resistance) or Type V (high sulphate resistance) Portland cement due to the presence of sulphate in seawater. An important property of cements that determine their resistance to sulphate attack is the tricalcium aluminate ( $C_3A$ ) content and therefore the amount of this mineral phase is limited to 8% and 5% in Type II and Type V cement, respectively. This paper presents a literature review of laboratory and long term field studies which indicate that sulphate attack is not the primary mechanism of deterioration caused by seawater. Furthermore, cement composition does not affect long term performance provided that the concrete has a low water/cement ratio and is impermeable. The available information therefore supports the use of either ASTM C150 Type I (with a maximum  $C_3A$  content of 12%) or Type II Portland cement for the manufacture concrete pipeline coatings. A potential secondary benefit of using Portland cements with  $C_3A$  levels greater than 5% will be their greater capacity to bind chlorides, reducing the apparent diffusion rate of chlorides in concrete. A reduction in the ingress of chlorides will extend the service life of offshore pipelines by delaying the onset of steel reinforcement corrosion.

## INTRODUCTION

Concrete structures exposed to the severe conditions of marine environments can be affected by three types of deterioration mechanisms: 1) physical, such as freezing and thawing, wetting and drying, and abrasion, 2) chemical attack and 3) chloride induced corrosion. Several good reviews have been published on the subject (Mehta 1980, 1988, 1991 and 1996). This paper reviews some of the key literature regarding the mechanisms of chemical attack and factors that affect corrosion of steel reinforced concrete structures in marine environments.

Many commercial specifications for concrete weight coatings for submerged natural gas pipelines typically specify an ASTM C150 Type II Portland cement with a maximum  $C_3A$  (tricalcium aluminate,  $3(CaO)(Al_2O_3)$ ) content of 8%. Ostensibly, the purpose of specifying cements with low  $C_3A$  contents is to prevent or minimize sulphate attack to the concrete weight coating. Sea water contains about 2.71% sulphate ( $SO_4^{--}$ ) (Dickson and Goyet, 1994), which is defined in EN 197 as a "slightly aggressive chemical environment".

Private and national companies which own submerged gas pipelines are frequently forced to provide waivers or exceptions to pipe coating companies when a Type II Portland cement is not available or significantly more expensive. Companies who own submerged gas pipelines need to know the actual risks associated with the use of an ASTM Type I or EN 197 Type CEM I Portland cements having  $C_3A$  content greater than 8%. Literature on the chemistry of

seawater attack of concrete and several long term durability studies clearly indicate that the mechanism of deterioration is not predominantly sulphate attack, and furthermore the physical properties of the concrete are more important for durability of the concrete in marine environments than the actual chemical composition of the cement. The benefits of using supplementary cementitious materials, such as fly ash, ground granulated blastfurnace slag and silica fume are also well established.

## **INTERNATIONAL SPECIFICATIONS FOR MARINE CONCRETE**

ACI 357R-84 (reapproved in 1997), "Guide for the Design and Construction of Fixed Offshore Concrete Structures" states that "The tricalcium aluminate content [of the Portland cement] should not be less than 4% to provide protection to the reinforcement. Based on past experience, the maximum tricalcium aluminate content should generally be 10% to obtain concrete that is resistant to sulphate attack. The above limits apply to all exposure zones." ACI 357R-84 further stipulates that the water/cement ratios of concrete in submerged, splash and atmospheric zones be 0.45, 0.40 and 0.40, respectively. The minimum compressive strength for all zones is 35 MPa (5000 psi). Supplementary cementitious materials conforming to ASTM C618 are permitted provided that their performance can be demonstrated for the specific application.

The British standard for maritime structures BS 6349-1:2000 "Maritime structures. Code of practice for general criteria" specifies Portland cement with a maximum  $C_3A$  content of 10% (page 159). The standard acknowledges that sulphate attack is mitigated by the presence of chlorides in sea water.

The "Offshore Standard DNV-OS-C502, Offshore Concrete Structures" (July 2004) states in a guidance note that the  $C_3A$  content of Portland cement "...should preferably not exceed 10%." The standard further recommends a minimum of 5%  $C_3A$  to provide protection to reinforcement. A maximum water/cement ratio of 0.45 is required for most applications, but for the more severe environment of splash zones, a maximum of 0.40 is specified. Provided suitability for use can be demonstrated, blastfurnace slag and pozzolanic cements are permitted for use in the construction of offshore structures.

The U.S. Army Corps of Engineers (USACE) standard EM 1110-2-2000 "Engineering and Design – Standard Practice for Concrete for Civil Works Structures" allows the use of Portland cement with up to 10%  $C_3A$  in concrete structures exposed to seawater, if the water/cement ratio is less than 0.45 and the concrete is submerged at all times. Blended cements conforming to ASTM C595 Type IS or IP, which contain fly ash or natural pozzolan are permitted. In a more recent standard issued by several U.S. government agencies, including USACE and NASA, with the title "Unified Facilities Guide Specifications" Division 03 – Concrete, Section 03 31 29, Marine Concrete (April 2006), a Portland cement with more than 4% and less than 10%  $C_3A$  is specified for marine concrete. The standard permits the use of fly ash (Class C and F), natural pozzolan, granulated blastfurnace slag (Grade 120) and silica fume. The maximum replacement rates for these supplementary cementitious materials are 25%, 50% and 10%, respectively, although higher levels can be used provided that early and late age strengths are met. It should be noted that Class C fly ashes do not enhance the sulphate resistance of concrete (Thomas et al,1999) unless very high substitution levels are used, and the durability of concrete manufactured with Class C fly ash in marine environments has to be established.

The RILEM Technical Committee in a state-of-the-art report (RILEM,1985) recommended concrete exposed to marine environments have a compressive strength greater than 35 MPa (5000 psi), a water/cement ratio less than 0.45, but preferably less than 0.40, and a minimum cement content of 350 kg/m<sup>3</sup>. The maximum recommended  $C_3A$  content for the Portland

cement was 10%. RILEM recognized the particular efficacy of substituting 60% or more of the cement with slag.

## **CANMET LONG TERM DURABILITY STUDIES AT TREAT ISLAND, MAINE, USA**

In 1978 the Canada Centre for Mineral and Energy Technology (CANMET) initiated a research program at the U.S. Army Corps of Engineers' outdoor marine exposure facility on Treat Island, Maine which is located at the entrance to the Bay of Fundy (see Fig. 1). Concrete prisms having dimensions of 305 x 305 x 915 mm, were placed on wooden racks at mid-tide level. The concrete prisms were exposed to daily wetting and drying cycles due to the changes in tide as well as an average of 100 freeze-thaw cycles per year. Various cements, supplementary cementitious materials (SCMs) and aggregates were evaluated over a period extending from 1978 to 1994. Table 1 summarizes the condition of the air entrained concrete prisms in 1995 (Malhotra and Bremner, 1996). The visual rating system used to evaluate the condition of the prisms is given in Fig. 2. In general, it can be seen that concretes with nominal water/cement ratios of 0.4 and 0.5 exhibited only slight deterioration of the surface at ages ranging from 8 to 17 years, regardless of the  $C_3A$  content of the cement. In many cases, concretes having water/cement ratios of 0.6 also performed well. Photographs of prisms from the various phases listed in Table 1 were taken in 2006 by CANMET and obtained by the author for analysis courtesy of CANMET (Bilodeau, 2007). Figures 3, 5 and 5 show concrete prisms that are 28 (Phase I), 27 (Phase II) and 24 (Phase V) years old, respectively. The concretes were prepared with Portland cement having  $C_3A$  contents of 11.4%, 11.8% and 9.3%, respectively; the nominal water/cement ratio for all the concretes was 0.4. In general, the condition of most of the prisms is good to very good considering their age and the severe exposure conditions at Treat Island.

The CANMET studies have also found that concrete with up to 65% ground pelletized blastfurnace slag or 25% ASTM C618 Class F fly ash as replacements for Portland cement were also very durable provided the water/binder ratio was equal to or less than 0.40 and 0.50, respectively. Silica fume at replacement levels of 10% or less was found to produce durable concrete as well. These findings are consistent with other studies, which have found that as the substitution level of SCM increased, the requirement for low water/binder ratios increased to obtain durable concrete.

## **PORTLAND CEMENT ASSOCIATION LONG TERM DURABILITY STUDIES IN LOS ANGELES HABOUR**

In 1959 and 1961 the Portland Cement Association (PCA) initiated studies on the long term durability of concretes exposed to warm sea water at mean tide level (Stark, 1995). Plain concrete prisms (152 x 152 x 760 mm) were installed under a pier (see Fig. 6) in 1959 and reinforced beams (152 x 152 x 1220 mm) in 1961. Eleven ASTM C150 Type I, five Type II, two Type III and four Type V Portland cements were tested as well as blends with an a Class F fly ash and calcined shale. The  $C_3A$  contents of the Type I, II, III and V cements ranged between 7.5 - 13.2%, 3.7 - 6.6%, 10.4 -10.8% and 3.7 - 6.2%, respectively. Three levels of cement content were evaluated: 223, 307 and 390 kg/m<sup>3</sup>. The w/c ratio ranged between 0.30 and 0.40 for the latter two cement levels, and was 0.6 for the lowest cement content. The air content ranged between 4 and 7%, and slump 50 – 75 mm.

After the first 8 years of exposure the concrete prisms were visually inspected and rated, tested for ultrasonic pulse velocity and dynamic modulus of elasticity and after 32 and 34 years of exposure the concrete prisms were visually inspected and rated only. In general, regardless of cement type or cement content, all plain concrete prisms exhibited only minor rounding at the edges and corners and a slight loss of paste at the surface. Concrete containing fly ash also performed well.

## NORWEGIAN LONG TERM DURABILITY STUDIES

In 1936 researchers at the Technical University of Norway in Trondheim initiated a long term durability study on the durability of concrete in an marine environment (Gjorv, 1971). Concrete prepared with  $313 \text{ kg/m}^3$  of total cementitious materials and a water/cement ratio of 0.60 was cast into prisms having dimensions of  $10 \times 10 \times 75 \text{ cm}$ , cured for 48 hours and then immersed in Trondheim's harbour. Seven different cements with  $C_3A$  contents between 3 and 13% were tested with and without trass (volcanic tuft - a natural pozzolan) and slag; cement was substituted with 60% trass, and 20 and 40% slag. The concrete prisms were exposed to seawater that was never less than  $1^\circ\text{C}$  for 30 years. Gjorv found that the compressive strength of all the mixtures prepared with Portland cements having  $C_3A$  contents of 6, 9 and 10% were unaffected by seawater, but those with 11 and 13%  $C_3A$  exhibited sharp declines after 10 years of exposure. In contrast, all mixtures containing Portland cement (except for the mixture with 11%  $C_3A$ ), exhibited a progressive decline in flexural strength starting from the 15<sup>th</sup> year of exposure, regardless of the  $C_3A$  content. [This appears to indicate an inconsistency between the compressive and flexural specimens, because flexural strength is generally affected more by most forms of deterioration than compressive strength.] All four slag modified cements exhibited increases in compressive strength for the first 15 years; after 30 years of exposure two of the slag mixtures exhibited decreases in compressive and flexural strength. It is interesting to note that the latter slag cements had alumina ( $\text{Al}_2\text{O}_3$ ) contents that were 42% lower than those that did not lose strength.

In two series of tests, concretes with a cement content of  $313 \text{ kg/m}^3$  and water/cement (w/c) ratios of 0.55, 0.60 and 0.65 and concretes with cement contents of 260, 313, 362 and  $417 \text{ kg/m}^3$  (w/c varied between 0.50 to 0.60) were evaluated with a Portland cement having a  $C_3A$  content of 13%. In general, the loss in compressive strength at 30 years of age decreased as the w/c decreased and cement content increased. The best performance was obtained with a cement content of  $417 \text{ kg/m}^3$ . A similar pattern was observed with respect to trends in flexural strength.

In summary, the results reported by Gjorv (1971) demonstrate the concretes with w/c between 0.50 and 0.65 have poor long term resistance to seawater attack, but that cements with  $C_3A$  contents between 3 and 10% behaved similarly. Research by other workers (Malhotra and Bremner, 1996) clearly show the benefits of maintaining w/c below 0.45 or 0.40.

## PORT AND AIRPORT RESEARCH INSTITUTE (JAPAN) LONG TERM STUDY

Mohammed et al (2002) conducted a long term study with Portland cement (PC) containing 9.6%  $C_3A$  and blended cements manufactured with slag (10 - 70%) and fly ash (10 - 20%). The water/cement ratio was 0.45. Cylindrical  $150 \times 300 \text{ mm}$  specimens were placed in a tidal pool after 28 days of moist curing. The concrete cylinders were subjected to two daily wetting and drying cycles (without freezing and thawing) for 15 years. The compressive strength of the PC only and blended cements all increased relative to the initial strength a 28 days, except for the blended cement containing fly ash. It was further established that the ingress of chlorides was retarded in the following order: PC < FA blended cement < slag blended cement. The higher the slag content, the lower the diffusion rate of chloride. Whereas the blended cements were very effective in reducing the permeability of the concrete to chloride, the PC concrete had the highest capacity to bind chlorides. It was further observed that the outer surfaces of the concrete specimens had low porosity due to the deposition of  $\text{Mg}(\text{OH})_2$  (brucite), ettringite and Friedel's salt in the pores.

## OTHER LONG TERM STUDIES

Mehta and Haynes (1978) reported on the condition of concrete blocks (1750 x 1750 x 1070 mm) manufactured with Portland cements having  $C_3A$  contents between 12 and 15% in 1905 and exposed to seawater for a total of 67 years in the Los Angeles Harbour. Six sets of 3 blocks each were prepared with an approximate cement content of 14% and different cements; one set of three blocks were prepared with a cement content of 10% and therefore was more permeable. All the blocks were set on a breakwater that left them partly submerged in Los Angeles Harbour. After 27 years the blocks were cored for compressive strength and then returned to their original locations. In 1972 the blocks were retrieved again (in the intervening years the blocks became submerged because they had been knocked off the breakwater due to storm surges). All of the high cement content mixtures, except one exhibited, either a slight or moderate increase in strength (+0.2 to 39%). Surprisingly, the low cement content concrete exhibited a significant increase in strength, although the exterior surface was soft. X-ray diffraction analysis of concrete cores from the interior showed that only the normal constituents of hydrated cement were present in the high cement content mixtures, but in the low cement content block significant amounts of brucite ( $Mg(OH)_2$ ), gypsum ( $CaSO_4 \cdot 2H_2O$ ), ettringite ( $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ ), aragonite ( $CaCO_3$ ) and hydrocalumnite ( $CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 10H_2O$ ) were detected at moderate depths;  $Ca(OH)_2$  and calcium silicate hydrate (C-S-H) were not detected in the same samples. These results indicated that the latter concrete had suffered attack from magnesium sulphate ( $MgSO_4$ ) and dissolved  $CO_2$  in seawater.

A 30 year study of concrete prisms (unknown dimensions) by the U.S. Army Corps of Engineers (USACE) (Mather 1980) at the Treat Island Maine testing facility found that excellent durability could be achieved with Portland cements having  $C_3A$  contents of 12.4 – 12.6%. Another study by USACE (Buck, 1986) with concrete beams (~150 x 150 x 750 mm) prepared with two low and two high  $C_3A$  Portland cements, a water cement/ratio of 0.50 (cement content was not given, but probably 335 – 360  $kg/m^3$ ), a slump of  $50 \pm 12$  mm and an air content of  $5 \pm 0.5\%$ . The cements had the following respective combinations of total alkali (as  $Na_2O$  equivalents) and  $C_3A$  contents: 0.33%, 3%; 0.94%, 5%; 0.24%, 13.5%, 1.00%, 14.3%. Two sets of beams were also prepared with 40% ground granulated blastfurnace slag and the 13.5%  $C_3A$  cement. The beams were submerged in warm sea water near St. Augustine, Florida and after 14 years of exposure no significant decrease in both pulse velocity and dynamic Young's modulus of elasticity was detected for the plain and slag modified concretes.

Fluss and Gorman (1958) reported on the condition of 46 year old reinforced concrete piles and girders in a San Francisco ferry building which was constructed with a Portland cement containing 14 – 17%  $C_3A$  and a cement content of 400  $kg/m^3$ . Most of the piles were found in good condition, but suffered from corrosion due to microcracking induced at the time of construction.

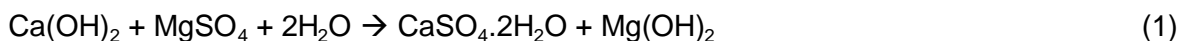
Long term tests by Regourd (1975) in France demonstrated that mortars prepared with 600  $kg/m^3$  of Portland cement which had a 14.9%  $C_3A$  content were in good condition after 67 years of exposure to sea water. In contrast, mortars prepared with the same cement but with a cement factor of 300  $kg/m^3$  were destroyed.

## CHEMICAL ATTACK OF CONCRETE BY SEAWATER

The predominant mineral phases in Portland cements, in approximate descending order of mass, are tricalcium silicate ( $3CaO \cdot SiO_2$  or  $C_3S$ ), dicalcium silicate ( $2CaO \cdot SiO_2$  or  $C_2S$ ), tricalcium aluminate ( $3CaO \cdot Al_2O_3$  or  $C_3A$ ), tetracalciumaluminoferrate ( $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ , or  $C_4AF$ ), calcium sulphate hemi- and dihydrate ( $CaSO_4 \cdot 0.5H_2O$ ,  $CaSO_4 \cdot 2H_2O$ ), periclase ( $MgO$ ) and calcium oxide ( $CaO$ ) (Taylor 1997). Approximately 3 – 6% gypsum is typically added to control the hydration rate of the most reactive phase,  $C_3A$ . The earliest phases

formed when Portland cement hydrates are calcium hydroxide (from the residual CaO in the clinker) and ettringite ( $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ ). Since a less than stoichiometric amount of sulphate is added for reaction with  $C_3A$ , a second phase, monosulfate ( $C_3A \cdot CaSO_4 \cdot 12H_2O$ ) starts to form after several days, followed by a concomitant decline in ettringite content. The rate of these reactions depend on the amount of sulphate and the reactivity of the  $C_3A$ ; the cubic form of  $C_3A$  is more reactive than the orthorhombic (Regourd, 1980).  $C_3S$  and  $C_2S$  reacts with water to form calcium silicate hydrate (C-S-H), which is amorphous and of variable composition;  $C_3S$  is significantly more reactive than  $C_2S$  and generates a by-product, calcium hydroxide, which at later ages may comprise between 20 to 30% of the mass of the hydrated Portland cement paste. All of the aforementioned reactions and hydrates have implications for the durability of hydrated Portland cement in seawater.

Al-Amoundi (2002a) and Cohen & Bentur (1988) describe the sequence of attack by magnesium sulphate in seawater as follows (the equations are simplified, and therefore non-stoichiometric):



$Ca(OH)_2$	calcium hydroxide (portlandite)
$MgSO_4$	magnesium sulphate
$CaSO_4 \cdot 2H_2O$	calcium dehydrate (gypsum)
$Mg(OH)_2$	magnesium hydroxide (brucite)
$SiO_2 \cdot H_2O$	hydrosilicate (silica gel)
C-S-H	calcium silicate hydrate ( $\sim 3(CaO) \cdot 2(SiO_2) \cdot 8H_2O$ )
M-S-H	magnesium silicate hydrate ( $4(MgO) \cdot SiO_2 \cdot 8.5H_2O$ )

The products of magnesium sulphate attack are gypsum, brucite and a magnesium silicate hydrate. The latter hydrate has no binding properties. Brucite is considerably less soluble than portlandite (0.01 and 1.37 g/l, respectively) and a saturated solution has a pH of 10.5 compared to 12.4 for portlandite. The lower pH is not conducive to the formation of expansive ettringite, which requires a pH greater than 10.5. The lower pH causes C-S-H to release lime in order to maintain equilibrium with the pore solution, the result of which leads to a progressive decalcification of the paste. Furthermore, magnesium and calcium are both divalent and have similar atomic radii and it is relatively easy for magnesium to substitute for calcium in C-S-H. With time the concentration of gypsum and brucite increases in sea water, but in contrast to sulphate attack by sodium sulphate solution, the gypsum formed does not lead to the formation of expansive 'secondary' ettringite. If the water/cement ratio of the paste is high (e.g., > 0.45), there is the potential for the chemical attack to continue until all the C-S-H has been decalcified; if the w/c is low (e.g., < 0.45), the chemical attack is surficial and brucite forms an impermeable layer.

Calcium chloroaluminate hydrate ( $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$ ), also known as Friedel's salt, is an important phase formed during the exposure of concrete to seawater (Mehta 1981). It appears to be formed predominately by the reaction of chloride ion with monosulfate, which typically appears only after several days of hydration. The solubility constants of ettringite, monosulfate and Friedel's salt are  $1 \times 10^{-40}$ ,  $1.7 \times 10^{-28}$  and  $1.0 \times 10^{-30}$  according to Zhang et al (1980). Ettringite has the lowest solubility product (Ksp) and therefore it is formed preferentially relative to Friedel's salt, but monosulfate is not stable in the presence of chloride. Chloride binding will occur when monosulfate is present and therefore cements which generate large amounts of monosulfate at later ages (i.e., cements that have  $C_3A$  contents greater than 8% (Mehta, 1981)) will have a greater chloride binding capacity.

Although ettringite and gypsum have been found in concrete exposed to seawater (Mehta and Haynes), the excessive expansion and cracking typically associated with sulphate attack (e.g., by  $\text{Na}_2\text{SO}_4$ ) is not observed. Mehta (1991) has proposed that the presence of chloride in the pore water suppresses the expansion of concrete because ettringite requires an alkaline environment to swell.

## **RELATIONSHIP BETWEEN CEMENT COMPOSITION AND RESISTANCE TO CORROSION**

Reductions in the permeability of concrete can be achieved through the use of higher cement contents (which inherently have lower w/c ratios), high range water reducing admixtures to reduce the w/c ratio further, and supplementary cementitious materials, such as fly ash, slag and silica fume, which reduce porosity through the formation of additional C-S-H from pozzolanic reactions. Nevertheless, the reduction the porosity of the concrete and the concomitant reduction in chloride diffusion rates is not the only important factor which can reduce the potential for corrosion of steel reinforcement in marine structures. There is considerable evidence that concretes manufactured with Portland cements with higher levels of  $\text{C}_3\text{A}$  are more resistant to corrosion than those with sulphate resisting cements.

Rasheeduzzafar et al (1992) found that as the  $\text{C}_3\text{A}$  content of the Portland cement used to prepare the concrete increased, the time to initiation of corrosion increased linearly. Concrete prisms (100 x 62.5 x 300 mm) were prepared with a single 12.5 mm rebar and after 28 days of moist curing were subjected to accelerated testing by immersing in 5% NaCl for up to 600 days. The half-cell potentials (relative to a saturated calomel electrode) were monitored via a data acquisition system. The threshold potential for corrosion was assumed to be 270 mv. The time to reach to the threshold potential of 270 mv was 93, 163, 180 and 228 days for cements having  $\text{C}_3\text{A}$  contents of 2.04, 9.1, 11.02 and 14.0%, respectively. The increased time to initiation of corrosion was attributed to the increased binding capacity of concretes with high  $\text{C}_3\text{A}$  via the compound chloroaluminate hydrate, or Friedel's salt ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$ ). As the  $\text{C}_3\text{A}$  content of the Portland cement increased, the concentration of chloride in the pore solution decreased; Friedel's salt was detected in the high  $\text{C}_3\text{A}$  concretes. Importantly, the substitution of 10% high  $\text{C}_3\text{A}$  cements with silica fume increased the time to corrosion 7 fold relative to the non modified concrete.

Page (1968) found that the diffusion rate of chloride was similar in cement pastes prepared with Portland cements having  $\text{C}_3\text{A}$  contents ranging between 7.7 and 14.3, but pastes with 1.3  $\text{C}_3\text{A}$  exhibited higher diffusion rates.

Mehta (1981) concluded from laboratory tests and theoretical calculations that concrete in marine environments require Portland cement containing at least 8%  $\text{C}_3\text{A}$  in order to bind and remove chloride ion from solution. Verbeck (1968) found that the rate of cracking associated with corrosion of beams in seawater decreased as the  $\text{C}_3\text{A}$  content increased. For  $\text{C}_3\text{A}$  contents of 2 – 5%, 5 – 8%, 8 – 11%, the amount of linear cracking per specimen was 11, 9.1 and 4 meters, respectively. The results indicated that the  $\text{C}_3\text{A}$  content should be greater than 8% to obtain good protection of the reinforcing steel.

## **CONCLUSIONS**

Sea water attacks concrete by a cation exchange process whereby the calcium in calcium silicate hydrates is replaced by magnesium to form magnesium silicate hydrates, which have no binding capabilities.

The porosity (pore size distribution) of concrete is an important factor determining the durability of the concrete in a marine environment. A layer of impervious magnesium

hydroxide is formed on the outer surfaces of the concrete with low water/cement ratios, which prevents the further ingress of magnesium ions.

Several well conducted long term studies have clearly demonstrated that concretes with low water/cement ratios are very durable, irrespective of the composition of the Portland cement used to manufacture the concrete. Concretes with cement partly substituted with fly ash, slag and silica fume are also very durable provided that low water/binder ratios are maintained.

## RECOMMENDATION

It is recommended that specifications for concrete weight coating be revised in light of the information presented in this paper. Many specifications for marine concrete specify Portland cements with  $C_3A$  contents greater than 4-5% and less than 10%, provided that the water/cement ratio is less than 0.45. Concrete weight coatings applied to gas pipe lines by either the impingement or wrap process typically have water/cement ratios much less than 0.45, and therefore standard specifications for marine concrete should be introduced for concrete weight coated pipe.

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# APPENDIX

Figure 1. Treat Island, Maine Facility (Courtesy of USACE)

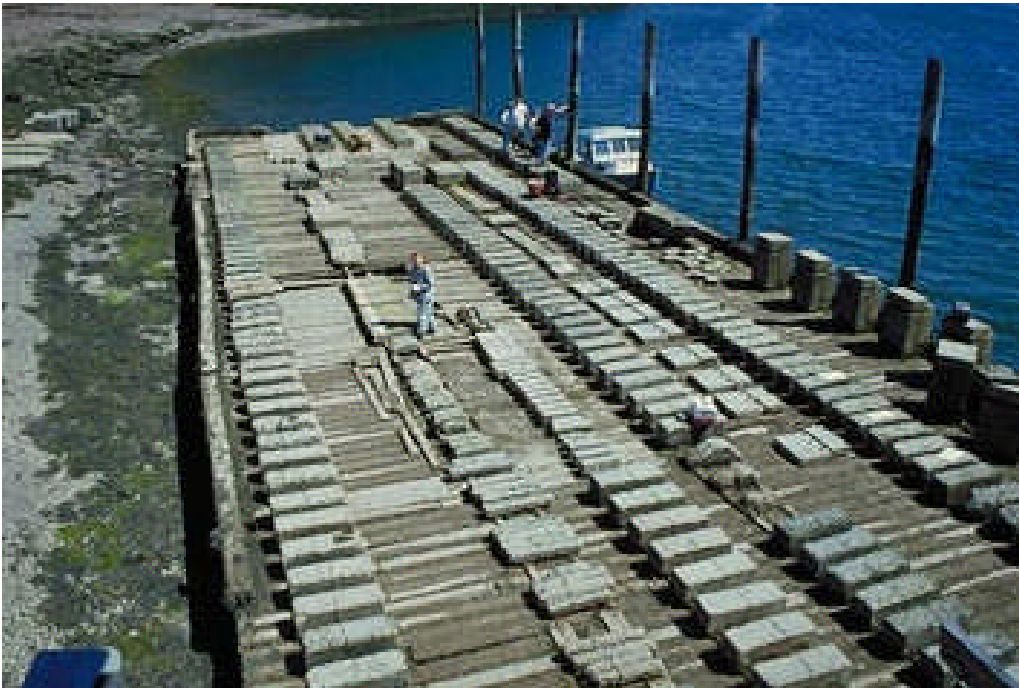


Figure 2. CANMET rating system (Malhotra and Bremner, 1996)

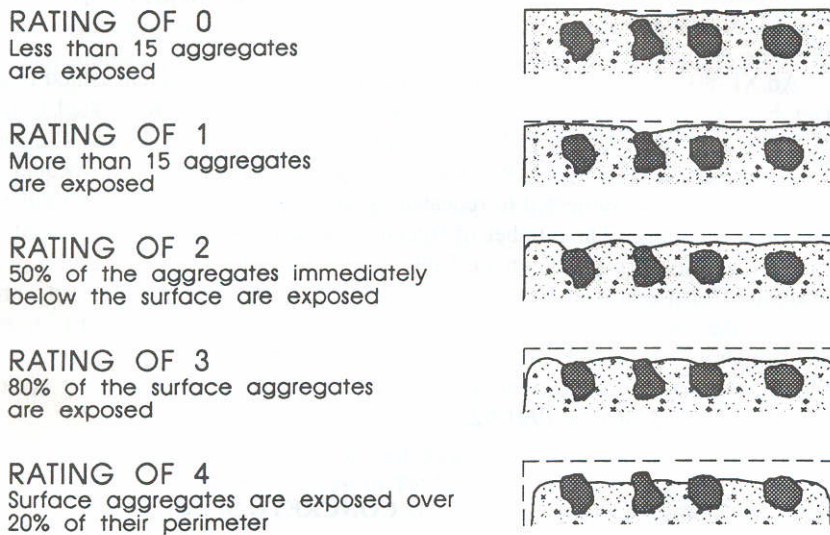


Figure 3. Phase I: 11.4% C<sub>3</sub>A, 0.4 water/cement ratio (Courtesy of CANMET)



Figure 4. Phase II: 11.8% C<sub>3</sub>A, 0.4 water/cement ratio (Courtesy of CANMET)



Figure 5. Phase V: : 9.3% C<sub>3</sub>A, 0.4 water/cement ratio (Courtesy of CANMET)



Figure 6. PCA Long-time Durability Test Site in Los Angeles Harbour. (Courtesy of the Portland Cement Association)



**Table 1: Summary of CANMET's Treat Island Studies (Malhotra and Bremner, 1996)**

Phase	Year Initiated	Age in 1995 Years*	Type I & II Total Cement kg/m3	Type V Total Cement kg/m3	Water/Cement Ratio	Coarse Aggregate Type	Portland Cement Type, C3A Content						
							Type I	Visual Rating	Type II	Visual Rating	Type V	Visual Rating	
I	1978	17	396-445	392	0.4	Gravel	11.4	2			2.0	2	
			320-335	314	0.5			1-2				2	
			266-282	272	0.6			1-2				2	
II	1979	16	370-411	384	0.4	Gravel	11.8	1-3	5.0		2.3	1	
			297-320	304	0.5			2				2	
			209-233	225	0.6			1-3				6	4
III	1980	15	480	480	0.49	Expanded Shale	12.6	2			2.9	2	
			360	360	0.61			2				2	
			240	240	0.87			3-4				4	
IV	1981	14	440	429	0.4	Dolomitic limestone	8.5	1-2			2.8	1	
			347	311	0.5			1				1	
			262	244	0.6			6				6	
V	1982	13	439		0.4	Dolomitic limestone	9.3	2					
			328		0.5			1-2					
			259		0.6			1-3					
VI	1985	10	625		0.39	Expanded Shale			6.1			2	
			500		0.45							2	
			375		0.63							1	
VIII	1987	8	346		0.39	Gravel	11.0	2					
			305		0.46			2					
IX	1987	8	334		0.5	Gravel	12.0	1-2					

Notes: all concretes prepared with natural sand

\* at the time of inspection in 1995