Alternative Cements for Durable Concrete in Offshore Environments

P. Zacarias, ShawCor Ltd.
Outline

- Introduction
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- CANMET Long Term Durability Studies
- PCA Long Term Durability Studies
- Norwegian Long Term Durability Studies
- Port and Airport Research Institute (Japan) Long Term Durability Studies
- Other Long Term Durability Studies
Outline

- Chemical Attack of Concrete by Seawater
- Relationship Between Cement Composition and Resistance to Corrosion
- Conclusions & Recommendations
Introduction
Introduction
Introduction

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Introduction
Introduction

- Marine structures are affected by several types of deterioration mechanisms:
  - physical: freezing/thawing, wetting/drying, abrasion, etc.
  - chemical attack: cation exchange
  - chloride induced corrosion

- Commercial specifications for concrete weight coating typically specify Portland cements which comply with ASTM C150, Type II requirements:
  - maximum 8% C₃A content to prevent “sulfate attack”
  - sulfate content of sea water ~2.7 (“slightly aggressive chemical environment, EN 197”)
Introduction

- Submerged pipeline owners are sometimes forced to provide waivers or exceptions to allow the use of cements with higher $C_3A$ contents without knowing the associated risk.

- A review of published literature indicates that cement composition does not play a significant role in the durability of concrete in seawater and that physical properties, such as porosity are much more important.
International Specifications/Practices

- “Offshore Standard DNV-OS-C502, Offshore Concrete Structures” (July 2004)
- RILEM Technical Committee 32-RCA state-of-the-art report “Seawater Attack on Concrete and Precautionary Measures” (1985)
International Specifications/Practices

General Summary

- C₃A content: 4/5 – 10% range, or 10% maximum
- Water/cement ratio: 0.40 – 0.45, depending on severity of exposure (tidal vs. submerged)
- Compressive strength: >35 MPa (RILEM)
- Supplementary cementitious materials (SCMs), such as slag, fly ash, natural pozzolan are recognized as beneficial
CANMET Long Term Durability Studies

- Initiated in 1978 at USACE’s Treat Island outdoor marine exposure facility
  - daily exposure to wetting and drying
  - 100 freeze/thaw cycles
- 305 x 305 x 915 mm concrete prisms prepared with cements having C\textsubscript{3}A contents ranging from 8.5 to 12.6\%, with and without various SCMs
- Visually rated until 1995
- After 8 – 17 years of exposure, all concretes with w/c ratios of 0.4 and 0.5 performed well, regardless of C\textsubscript{3}A content
- Concrete mixtures containing SCMs also performed well, but required lower w/c ratios to achieve similar durability
Figure 1. Treat Island, Maine Facility

(Courtesy of USACE)
Figure 2. CANMET Visual Rating System

RATING OF 0
Less than 15 aggregates are exposed

RATING OF 1
More than 15 aggregates are exposed

RATING OF 2
50% of the aggregates immediately below the surface are exposed

RATING OF 3
80% of the surface aggregates are exposed

RATING OF 4
Surface aggregates are exposed over 20% of their perimeter

(Malhotra and Bremner, 1996)
<table>
<thead>
<tr>
<th>Phase</th>
<th>Year Initiated</th>
<th>Age in 1995 Years*</th>
<th>Type I &amp; II Total Cement kg/m3</th>
<th>Type V Total Cement kg/m3</th>
<th>Water/Concrete Ratio</th>
<th>Coarse Aggregate Type</th>
<th>Portland Cement Type, C3A Content</th>
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<td>244</td>
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Notes: all concretes prepared with natural sand

* at the time of inspection in 1995

(Malhotra and Bremner, 1996)
Figure 3. Phase I: 11.4% $C_3A$, 0.4 w/c Ratio

(Courtesy of CANMET)
Figure 4. Phase II: 11.8% C₃A, 0.4 w/c Ratio

(Courtesy of CANMET)
Figure 5. Phase V: 9.3% C3A, 0.4 w/c Ratio

(Courtesy of CANMET)
PCA Long Term Durability Studies

- Initiated in 1959 & 1961 at Los Angeles Harbour
- 152 x 152 x 1220 mm concrete prisms – mean tide level
- ASTM C150 Portland cements:

<table>
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<tr>
<th>ASTM C150 Type</th>
<th>Number Tested</th>
<th>C3A Range %</th>
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<td>11</td>
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<td>II</td>
<td>5</td>
<td>3.7 - 6.6</td>
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<td>III</td>
<td>2</td>
<td>10.4 - 10.8</td>
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<tr>
<td>V</td>
<td>4</td>
<td>3.7 - 6.2</td>
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- Class F fly ash and calcined shale also tested
PCA Long Term Durability Studies

- Cement contents: 223, 307 and 390 kg/m³
- Water/cement ratio: 0.6, 0.4 and 0.3
- Slump 50 – 75 mm; air content: 4 – 7%
- Visually inspected after 32 & 34 years

Results

- Only minor rounding at the edges and slight loss of paste observed at the surface, regardless of cement type or cement content
Figure 6. PCA Long-time Durability Test Site in Los Angeles Habour.

(Courtesy of the PCA)
Norwegian Long Term Durability Studies

- Initiated in 1936 by the Technical University of Norway
- $100 \times 100 \times 750$ mm concrete prisms
- Cement content: $313 \text{ kg/m}^3$, $w/c = 0.6$
- $C_3A$ content ranged between 3 and 13%
- 20 & 40% slag and 60% trass (natural pozzolan)
- Submerged for 30 years in seawater that was $> 1^\circ C$
Norwegian Long Term Durability Studies

Findings

- After 10 years of exposure, the compressive strength of concretes prepared with 6, 9 and 10% C₃A was unaffected by seawater, but those with 11 and 13% exhibited a sharp decline.

- Starting after 15 years of exposure, the flexural strength of all concrete mixtures exhibited a progressive decline, regardless of C₃A content (except for one cement with 11% C₃A).

- Concrete containing slag increased in strength the first 15 years, then 2 slags exhibited declines in compressive strength.
Findings, cont’d

- One cement with 13% $C_3A$ was tested in one series of tests in concrete containing 313 kg/m³ cement and w/c of 0.55, 0.60 & 0.65, and in a second series with 260, 313, 362 and 417 kg/m³ cement ($w/c = 0.5 - 0.6$). After 30 years:
  - loss in compressive strength decreased as w/c decreased and cement content increased

Summary

- Concretes with high w/c do not perform well
- Cements with $C_3A$ contents between 3 and 10% behaved similarly
Japanese Long Term Durability Studies

- 15 year exposure in tidal pool, no freezing
- 150 x 300 mm concrete cylinders
- 9.6% C3A Portland cement, and blended cements which contained 10-70% slag or 10-20% fly ash; w/c = 0.45

Findings

- Compressive strength of PC only and slag mixtures increased in strength
- PC had the highest capacity to bind chloride, but slag blend was least permeable to chloride
Other Long Term Durability Studies

- **Los Angeles Harbour 1905 – 67 year exposure**
  - 1750 x 1750 x 1070 mm blocks, ~10 & 14% cement content
  - 12 and 15% C₃A content
  - slight-moderate increase in compressive strength (from cores)
  - low cement content had soft exterior

- **USACE Treat Island – 30 year exposure**
  - 12.4 and 12.6% C₃A content
  - excellent durability

- **USACE St. Augustine, Florida – 14 year exposure**
  - 150 x 150 x 750 mm prisms
  - w/c = 0.5 (335 – 360 kg/m³ cement content); 50 mm slump
  - 3, 5, 13.5 and 14.3% C₃A
  - 13.5% C₃A + 40% slag
  - no significant decrease in pulse velocity and dynamic Young’s modulus of elasticity for plain and modified concretes
Cement Hydration Chemistry

Cement composition:

- $\text{C}_3\text{S}$ – tricalcium silicate - $3(\text{CaO})(\text{SiO}_2)$
- $\text{C}_2\text{S}$ – dicalcium silicate - $3(\text{CaO})(\text{SiO}_2)$
- $\text{C}_3\text{A}$ – tricalcium aluminate - $3(\text{CaO})(\text{Al}_2\text{O}_3)$
- $\text{C}_4\text{AF}$ – tetracalcium aluminoferrate - $4(\text{CaO})(\text{Al}_2\text{O}_3)(\text{Fe}_2\text{O}_3)$
- $\text{CS}$ - calcium sulfate (gypsum/hemi-hydrate)

Cement hydration:

$$\text{C}_3\text{S}-\text{C}_2\text{S}-\text{C}_3\text{A}-\text{C}_4\text{AF} + \text{H}_2\text{O} \rightarrow \text{C-S-H} + \text{Ca(OH)}_2 + \text{ettringite}$$

*Portland cement*

- $3(\text{CaO}).2(\text{SiO}_2).8\text{H}_2\text{O}$ – C-S-H
- $\text{C}_3\text{A}.3\text{CaSO}_4.32\text{H}_2\text{O}$ – ettringite
Cement Hydration Chemistry

The diagram illustrates the hydration process of cement, showing the amount of different hydration products over time. The x-axis represents the age in minutes, hours, and days, while the y-axis shows the porosity and the amount of hydration products. The hydration products include C-S-H, Ca(OH)$_2$, $C_4(A, F)H_{13}$, ettringite, monosulfate, and ettringite. The graph (Courtesy of the PCA) captures the evolution of these products as cement hydrates.

(Courtesy of the PCA)
Cement Hydration Chemistry

Degree of hydration, %
Relative volume, %

(Courtesy of the PCA)

The GLOBAL LEADER in Pipe Coating Solutions
Chemical Attack of Concrete

Chemical attack in seawater:

\[ \text{Ca(OH)}_2 + \text{MgSO}_4 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{Mg(OH)}_2 \]

\[ \text{C-S-H} + \text{MgSO}_4 + x\text{H}_2\text{O} \rightarrow \]
\[ \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{Mg(OH)}_2 + y\text{SiO}_2 \cdot \text{H}_2\text{O} \]

\[ 4\text{Mg(OH)}_2 + \text{SiO}_2 \cdot \text{H}_2\text{O} \rightarrow \text{M-S-H} + \text{H}_2\text{O} \]

- \text{Ca(OH)}_2: calcium hydroxide (portlandite)
- \text{MgSO}_4: magnesium sulphate
- \text{CaSO}_4 \cdot 2\text{H}_2\text{O}: calcium dihydrate (gypsum)
- \text{Mg(OH)}_2: magnesium hydroxide (brucite)
- \text{SiO}_2 \cdot \text{H}_2\text{O}: hydrosilicate (silica gel)
Chemical Attack of Concrete

- Cation exchange reaction & barrier formation
  - calcium is substituted by magnesium (similar atomic radii)
  - magnesium silicate hydrate has no binding properties
  - Mg(OH)_2 (brucite) is very insoluble; equilibrium pH is 10.5
  - brucite forms a stable and impermeable barrier (only when w/c is low)

- Ettringite
  - stable when pH >10.5, and potentially expansive
  - no significant expansion occurs in seawater
  - low w/c concrete is less permeable, less susceptible to attack
  - with time converts to monosulfate (C_3A.CaSO_4.12H_2O)
Monosulfate reacts with chloride ion to form calcium chloroaluminate hydrate \( (\text{C}_3\text{A}.\text{CaCl}_2.10\text{H}_2\text{O}) \)
- cements which generate more monosulfate will be able to bind more chloride and reduce its concentration in the pore water
- implications for corrosion of reinforcing steel
Cement Composition and Corrosion

- The time to start of rebar corrosion in marine concrete is determined by the porosity of the concrete and the composition of the cement.

- The rate of chloride diffusion in concrete is low when w/c < 0.45 due to low porosity.

- C₃A reacts with chloride to form chloroaluminate hydrate, Friedel’s salt, which removes chloride from solution.

- A minimum amount of C₃A required to bind chloride: 4 – 5%.
Summary

- Seawater attacks concrete via a cation exchange process
  - Ca\(^{++}\) in calcium silicate hydrate is replaced by Mg\(^{++}\)
  - magnesium silicate hydrate has no binding capacity

- Sulfate attack does not occur despite the presence of moderate amounts of sulfate in seawater
  - pH of the pore solution is too low
  - chloride ion suppresses the formation of expansive ettringite

- **Porosity** is the most important determinant of concrete durability
  - as the water/cement ratio decreases, porosity decreases
  - concrete with w/c < 0.45 has no connected pores and is very impermeable
Conclusions

- A layer of impervious magnesium hydroxide (Mg(OH)$_2$) is formed on the surface of concrete, which prevents the ingress of additional magnesium ions.

- Several international long-term exposure studies have demonstrated the durability of low w/c concrete to marine environments, irrespective of cement chemical composition. Concrete containing supplementary cementitious materials also perform well and are recommended.
Recommendations

- Specifications for concrete weight coating should be revised based on existing specifications for marine concrete and results of the long term durability studies.
- The minimum $C_3A$ content of Portland cement should be 4-5%, and maximum 10 to 12%.
- $w/c < 0.45$, preferably 0.4.