Alternative Cements for Durable Concrete in Offshore Environments

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Outline

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Outline

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- Relationship Between Cement Composition and Resistance to Corrosion
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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% C_3A 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 <u>without</u> 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

- ACI 357-84 (1997) “Guide for Design and Construction of Fixed Offshore Structures”
- BS 6349-1:2000 “Marine structures. Code of practice for general criteria”
- “Offshore Standard DNV-OS-C502, Offshore Concrete Structures” (July 2004)
- USACE EM 1110-2-2000, “Engineering and Design - Standard Practice for Concrete for Civil Works Structures”
- RILEM Technical Committee 32-RCA state-of-the-art report “ Seawater Attack on Concrete and Precautionary Measures” (1985)

International Specifications / Practices

General Summary

- C_3A 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

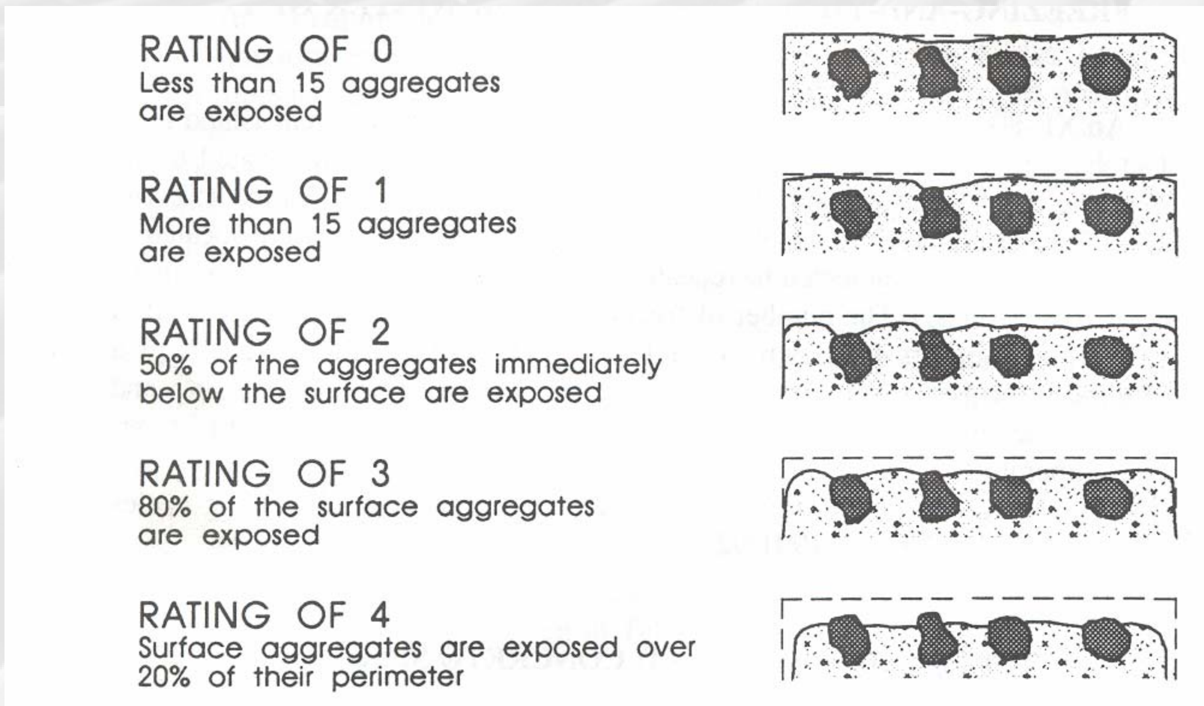
CANMET Long Term Durability Studies

- 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_3A 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_3A 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



(Malhotra and Bremner, 1996)

Table 1: Summary of CANMET's Treat Island Studies

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	396-445 320-335 266-282	392 314 272	0.4 0.5 0.6	Gravel	11.4	2 1-2 1-2			2.0	2 2 2
II	1979	16	370-411 297-320 209-233	384 304 225	0.4 0.5 0.6	Gravel	11.8	1-3 2 1-3	5.0	2 1 6	2.3	1 2 4
III	1980	15	480 360 240	480 360 240	0.49 0.61 0.87	Expanded Shale	12.6	2 2 3-4			2.9	2 2 4
IV	1981	14	440 347 262	429 311 244	0.4 0.5 0.6	Dolomitic limestone	8.5	1-2 1 6			2.8	1 1 6
V	1982	13	439 328 259		0.4 0.5 0.6	Dolomitic limestone	9.3	2 1-2 1-3				
VI	1985	10	625 500 375		0.39 0.45 0.63	Expanded Shale			6.1	2 2 1		
VIII	1987	8	346 305		0.39 0.46	Gravel	11.0	2 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

(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% C_3A, 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 Habour
- 152 x 152 x 1220 mm concrete prisms – mean tide level
- ASTM C150 Portland cements:

ASTM C150 Type	Number Tested	C3A Range %
I	11	7.5 - 13.2
II	5	3.7 - 6.6
III	2	10.4 - 10.8
V	4	3.7 - 6.2

- Class F fly ash and calcined shale also tested

PCA Long Term Durability Studies

- Cement contents: 223, 307 and 390 kg/m^3
- 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, <u>regardless</u> 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 x 100 x 750 mm concrete prisms
- Cement content: 313 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 > 1ºC

Norwegian Long Term Durability Studies

Findings

- After 10 years of exposure, the compressive strength of concretes prepared with 6, 9 and 10% C_3A 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 C_3A content (except for one cement with 11% C_3A)
- Concrete containing slag increased in strength the first 15 years, then 2 slags exhibited declines in compressive strength

Norwegian Long Term Durability Studies

Findings, cont'd

- One cement with 13% C_3A was tested in one series of tests in concrete containing 313 kg/m^3 cement and w/c of 0.55, 0.60 & 0.65, and in a second series with 260, 313, 362 and 417 kg/m^3 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% C_3A 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% C_3A 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% C_3A
  - 13.5% C_3A + 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:

- C_3S – tricalcium silicate - $3(CaO)(SiO_2)$
  C_2S – dicalcium silicate - $3(CaO)(SiO_2)$
  C_3A – tricalcium aluminate - $3(CaO)(Al_2O_3)$
  C_4AF – tetracalcium aluminoferrate - $4(CaO)(Al_2O_3)(Fe_2O_3)$
  CS - calcium sulfate (gypsum/hemi-hydrate)

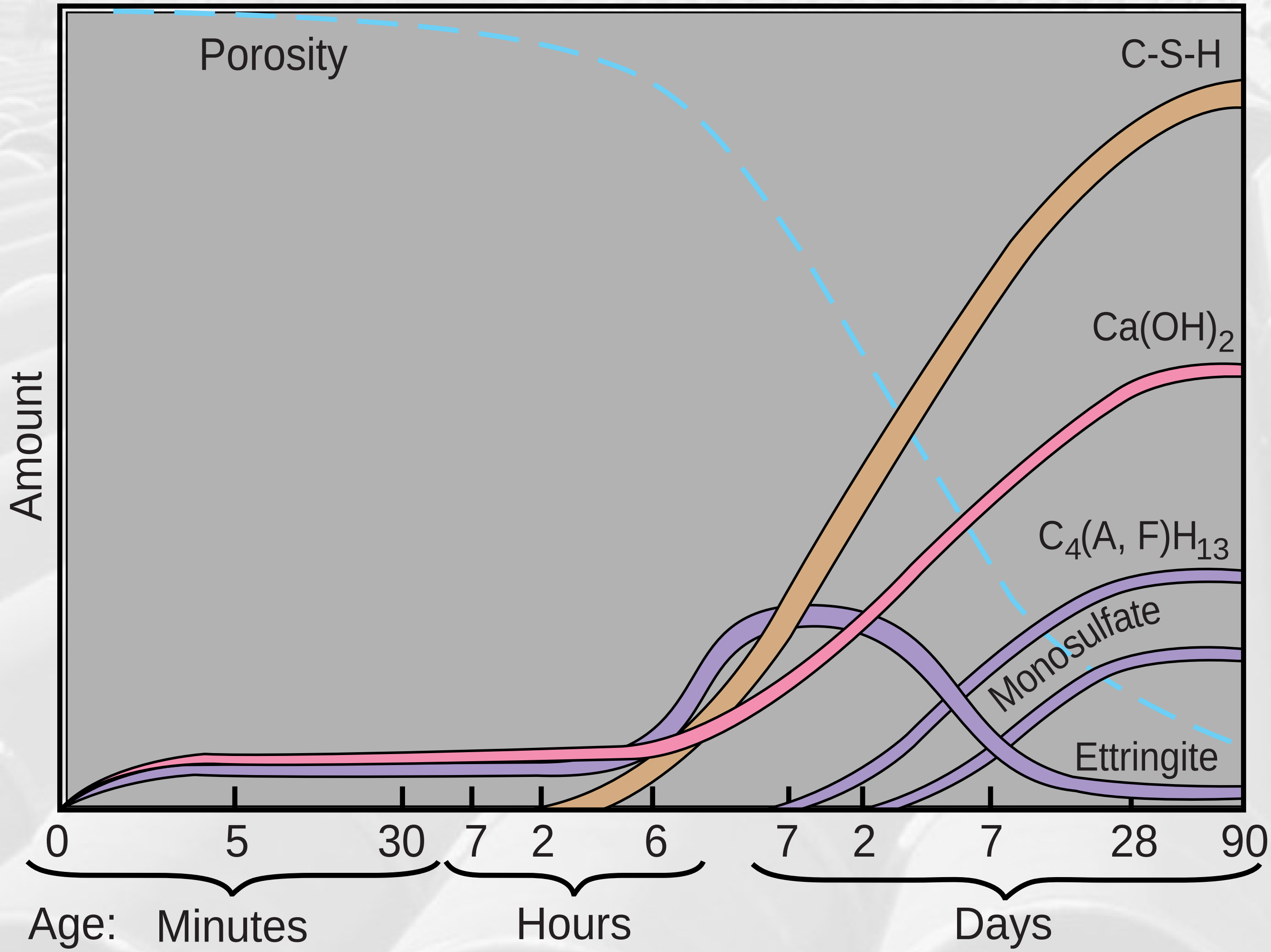
Cement hydration:

$$\underbrace{C_3S\text{-}C_2S\text{-}C_3A\text{-}C_4AF}_{\textit{Portland cement}} + H_2O \rightarrow C\text{-}S\text{-}H + Ca(OH)_2 + \text{ettringite}$$

Portland cement

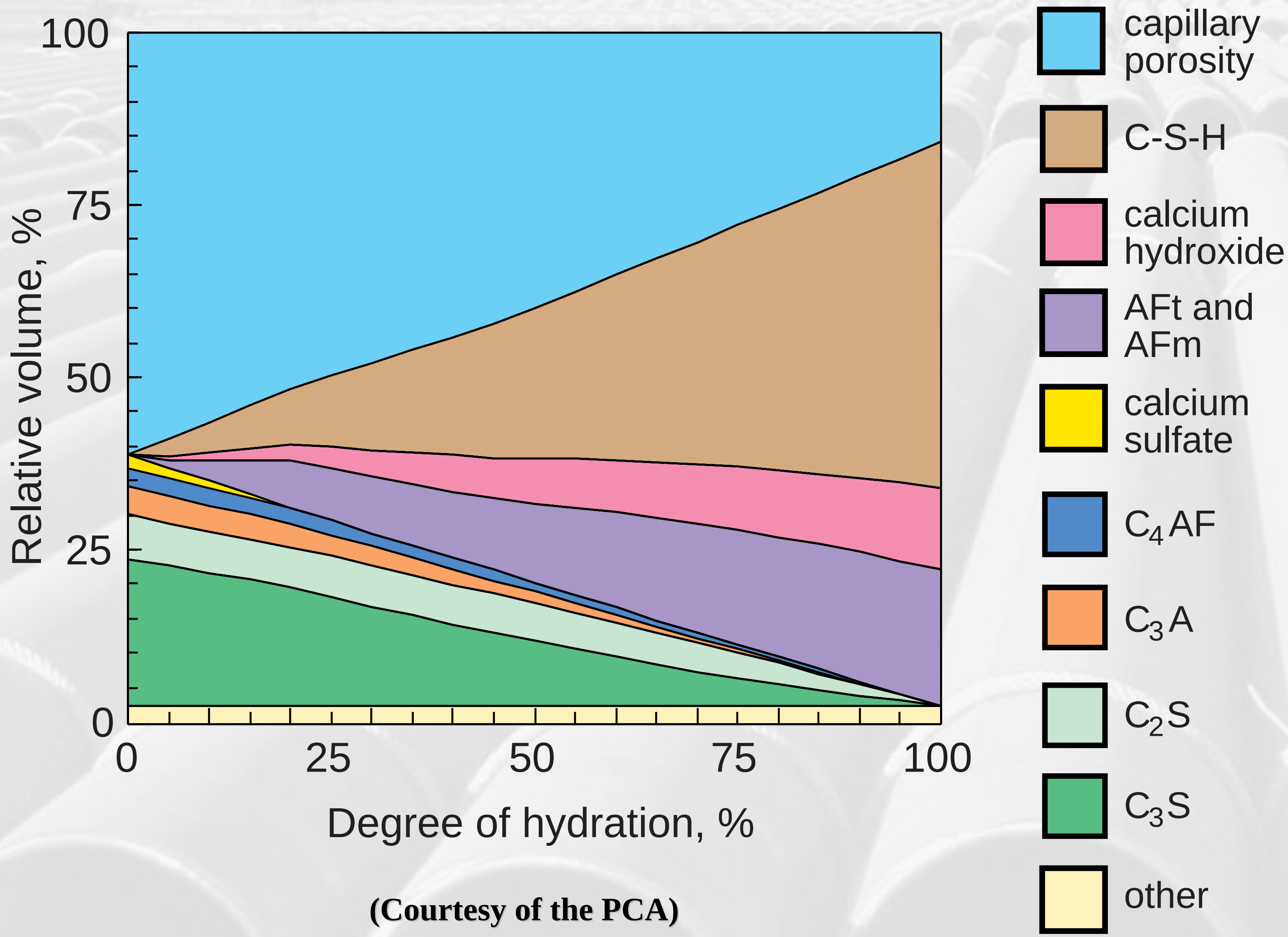
$3(CaO).2(SiO_2).8H_2O)$	C-S-H
$C_3A.3CaSO_4.32H_2O$	ettringite

Cement Hydration Chemistry



(Courtesy of the PCA)

Cement Hydration Chemistry



(Courtesy of the PCA)

Chemical Attack of Concrete

Chemical attack in seawater:

$Ca(OH)_2 + MgSO_4 + 2H_2O \rightarrow CaSO_4.2H_2O + Mg(OH)_2$

$C\text{-}S\text{-}H + MgSO_4 + xH_2O \rightarrow$

$CaSO_4.2H_2O + Mg(OH)_2 + ySiO_2.H_2O$

$4Mg(OH)_2 + SiO_2.H_2O \rightarrow M\text{-}S\text{-}H + H_2O$

$Ca(OH)_2$	calcium hydroxide (portlandite)
$MgSO_4$	magnesium sulphate
$CaSO_4.2H_2O$	calcium dihydrate (gypsum)
$Mg(OH)_2$	magnesium hydroxide (brucite)
$SiO_2. H_2O$	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 ($C_3A.CaSO_4.12H_20$)

Chemical Attack of Concrete

- Monosulfate reacts with chloride ion to form calcium chloroaluminate hydrate ($C_3A.CaCl_2.10H_20$)
  - 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
- C_3A reacts with chloride to form chloroaluminate hydrate, Friedel's salt, which removes chloride from solution
- A minimum amount of C_3A 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
- <u>Porosity</u> 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