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Differentiating seawater and groundwater sulfate attack in Portland cement mortars

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Abstract

The study reported in this article deals with understanding the physical, chemical and microstructural differences in sulfate attack from seawater and groundwater. Portland cement mortars were completely immersed in solutions of seawater and groundwater. Physical properties such as length, mass, and compressive strength were monitored periodically. Thermal analysis was used to study the relative amounts of phases such as ettringite, gypsum, and calcium hydroxide, and microstructural studies were conducted by scanning electron microscopy. Portland cement mortars performed better in seawater solution compared to groundwater solution. The difference in performance could be attributed to the reduction in the quantity of the expansive attack products (gypsum and ettringite). The high Cl concentration of seawater could have played an important role by binding the C_3A to form chloroaluminate compounds, such as Friedel's salt (detected in the microstructural studies), and also by lowering the expansive potential of ettringite. Furthermore, the thicker layer of brucite forming on the specimens in seawater could have afforded better protection against ingress of the solution than in groundwater.

Keywords: Sulfate attack; Ettringite; Chloride; SEM; Microstructure

1. Introduction

The attack by solutions containing sulfate can have diverse effects on concrete. The nature of the sulfate solution is important, since the influence of other chemicals can affect the mechanism of the reaction. This is especially true in the case of seawater, where the presence of a very high concentration of chlorides can have a bearing on the action of the sulfates. Chlorides have a tendency to bind C_3A in the cement to produce chloroaluminate compounds, such as Friedel's salt, which do not cause any expansion [1]. The lowered availability of C_3A can reduce the damage caused by sulfate attack due to a direct reduction in the quantity of ettringite that can form. Also, ettringite formation in chloride-rich environments is not associated with expansion and cracking [2]. However, although studies on seawater attack are available [3], there are very few studies explaining specifically the process of sulfate attack under these conditions [4].

The sulfates found in groundwater are often a combination of calcium, sodium, and magnesium sulfate. Owing to the low solubility of calcium sulfate (~2 g/l at 20 °C), the highly soluble sulfates (Na_2SO_4, $MgSO_4$, $FeSO_4$) present in soil predominate in the groundwater solution. Sulfate solutions in groundwater possess less chlorides compared to seawater; thus, the mechanism of attack could be very different compared to seawater.

2. Materials and experimental methods

The composition and properties of the ASTM Type I cement used in the study are given in Table 1. The aggregate used for the mortar mixtures was quartz sand (ASTM C-778 [5] graded Ottawa sand) with a specific gravity of 2.65, and an average particle diameter of 0.36 mm.

All the Portland cement mortar mixtures were prepared in accordance with the proportions recommended by ASTM C-109

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Table 1
Composition and properties of Type I cement

Composition/property	
CaO (%)	64.60
SiO_2 (%)	20.63
Al_2O_3 (%)	5.03
Fe_2O_3 (%)	2.80
C_3S (%)	62.00
C_3A (%)	9.00
SO_3 (%)	2.67
Alkalis (%)	0.50
Fineness (cm^2/g)	3600
Specific gravity	3.15

Table 2
Details of the storage solutions

Designation	Solution	Strength	Equivalent SO_3 (ppm)	Equivalent Cl^-/Mg^{2+} (ppm)	Storage temperature (°F)
LW	Limewater	Saturated	–	–	70
SW	Sea water (typical)		2233	19,090/ 1250	70
	NaCl	2.700%			
	$MgCl_2$	0.320%			
	$MgSO_4$	0.220%			
	$CaSO_4$	0.130%			
	$CaCl_2$	0.060%			
GW	Ground water (typical)		2233	1043/950	70
	$MgSO_4$	0.300%			
	$CaSO_4$	0.040%			
	$MgCl_2$	0.140%			

[6], in which the cement:sand:water is 1:2.75:0.485 for non-air-entrained mixtures. Mixing of mortars was done in accordance with ASTM C-305 [7]. After mixing, the mortar was cast into the different categories of molds (presented below) and the specimens were demolded after two days of curing inside a moist room (temperature 25 °C, and RH 100%).

The following types of mortar specimens were prepared:

- 25 mm (1 in.) cubes for compressive strength
- 23 mm diameter × 80 mm height cylinders for mass change and scanning electron microscopy (SEM)
- 4 mm × 14 mm × 60 mm prisms for differential scanning calorimetry (DSC)
- 6 mm × 15 mm × 80 mm prisms with plastic end pieces, which are shown in Fig. 1 (the design of these acrylic pieces has been described by Richards and Helmuth [8] and Kerdegari [9]), for length measurements.

After demolding, the specimens were transferred to a saturated limewater solution, where they were stored for an additional 12 days (thus the total period of initial curing was 14 days). Following the initial cure, the physical properties (compressive strength, length, and mass) were measured, and the specimens were transferred to containers with various solutions. The details of the solutions used are presented in Table 2. The compositions of the seawater and groundwater solutions were based on data provided by Biczok [10].

Measurement of physical properties (length, mass, and compressive strength) was conducted periodically. The data presented in the figures in this article are the average results for three specimens.

Thermal analysis was performed using Differential Scanning Calorimetry (DSC). The mortar specimens used for DSC measurements were stored in acetone, for at least one day, immediately after removal from the solutions. After removal from acetone, the specimens were ground to a fine powder using a mortar and pestle, and passed through a #200 (75 μm opening) sieve. This material was stored in airtight plastic containers, to be used for DSC experiments within a week from preparation. DSC was conducted at a heating rate of 10 °C per minute up to a maximum of 500 °C. For analysis of the data, calibration standards were prepared using pure samples of ettringite, gypsum, calcium hydroxide and brucite. The peak areas obtained from the DSC scans at different temperatures were then correlated with the standard DSC patterns to determine the amounts of different phases. The detailed procedure for calibration and deconvolution is described elsewhere [11].

The specimens used for scanning electron microscopy (SEM) were dried at 70 °C in an oven for one day, and then embedded in a low-modulus epoxy. The hardened epoxy polymer was then cut with a fine diamond-tipped saw to expose the cross-section of the specimen. This was followed by grinding of the exposed

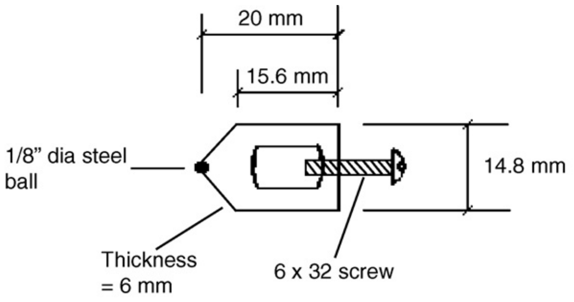

Fig. 1. Plastic end pieces for mortar length change specimens [8].

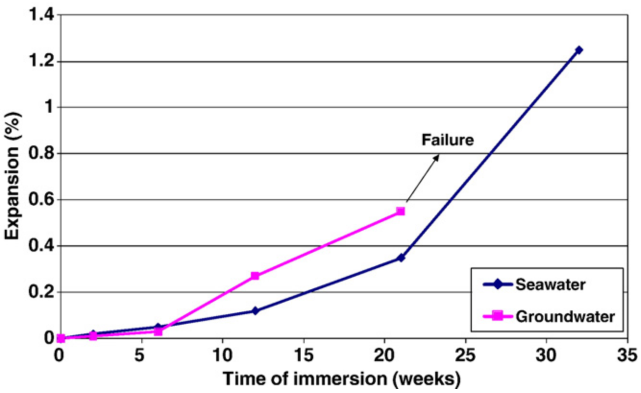

Fig. 2. Expansion of mortars stored in seawater and groundwater solutions.

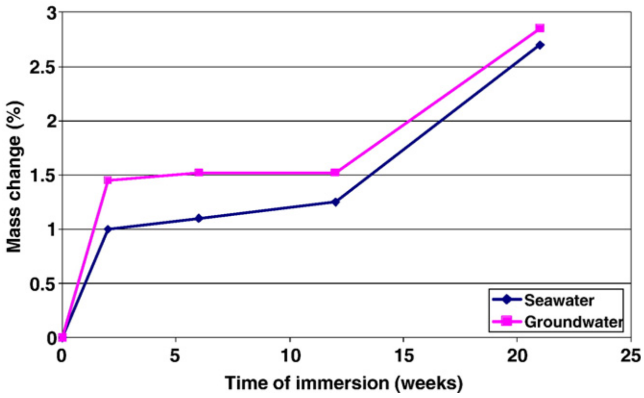

Fig. 3. Mass change for mortars stored in seawater and groundwater solutions.

surface on a series of plates ranging from 45 μm to 15 μm. Fine polishing was then performed using diamond pastes of varying sizes, up to 1 μm. The adequacy of polishing was confirmed after each step using an optical microscope. After polishing, the surface was coated with a layer of gold–palladium. The prepared specimens were then stored in desiccators until testing.

3. Results

3.1. Physical properties

The results from expansion measurements shown in Fig. 2 indicate that the mortar in groundwater solution expands more than the mortar in seawater solution. The specimens stored in groundwater solution failed before the 32-week measurements could be made.

The mass change patterns, shown in Fig. 3, are similar for the two solutions. After an initial mass increase (at 2 weeks), there is a period (until 12 weeks) where the mass change is not significant. After 12 weeks of immersion, a sudden increase in mass is observed for specimens in both solutions.

Until 12 weeks of immersion, the drop in compressive strength of mortars (shown in Fig. 4) in both types of solutions is similar. However, when the storage period is extended to 32 weeks, the mortar specimens in groundwater solution exhibit higher loss in compressive strength compared to the specimens in seawater solution.

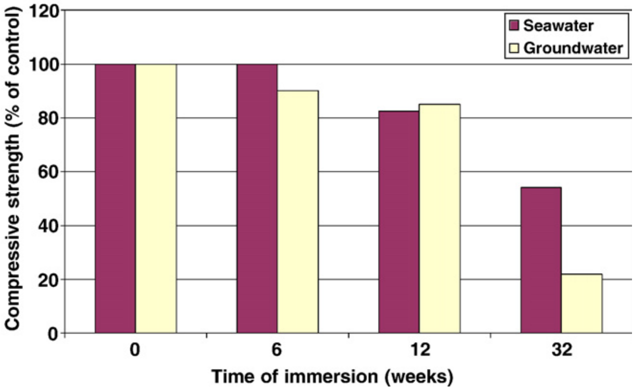

Fig. 4. Compressive strength for mortars stored in seawater and groundwater solutions.

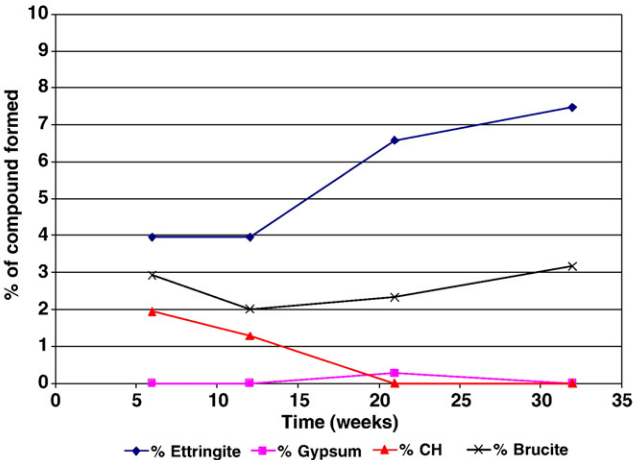

Fig. 5. DSC results for PC mortar stored in seawater solution.

Overall, it may be said that the performance of Portland cement mortars in seawater solution is better than in groundwater solution.

3.2. Thermal analysis by DSC

Thermal analysis results for mortars stored in the two solutions are presented in Figs. 5 and 6. The mortar in seawater solution undergoes a major increase in the quantity of ettringite after 12 weeks of immersion, as shown in Fig. 5. This increase in ettringite is matched by the sudden increase in expansion and mass change as seen from Figs. 2 and 3. The quantity of brucite fluctuates between 2 and 3%, while the amount of CH decreases steadily. Gypsum can only be found in very small quantities (<0.5% at 21 weeks).

The DSC observations for the mortar in groundwater solution, presented in Fig. 6, are similar to those for seawater solution. There

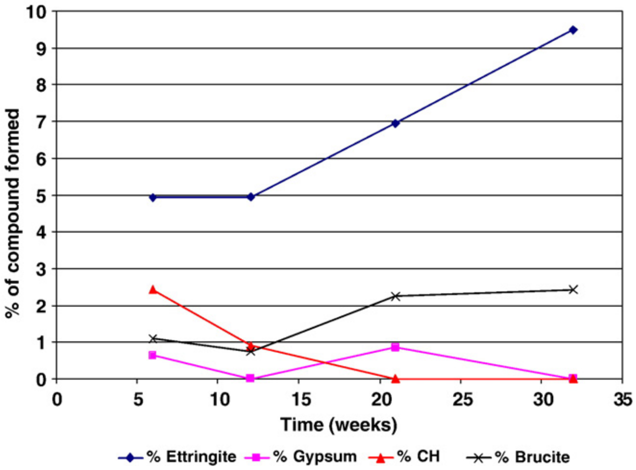

Fig. 6. DSC results for PC mortar stored in groundwater solution.

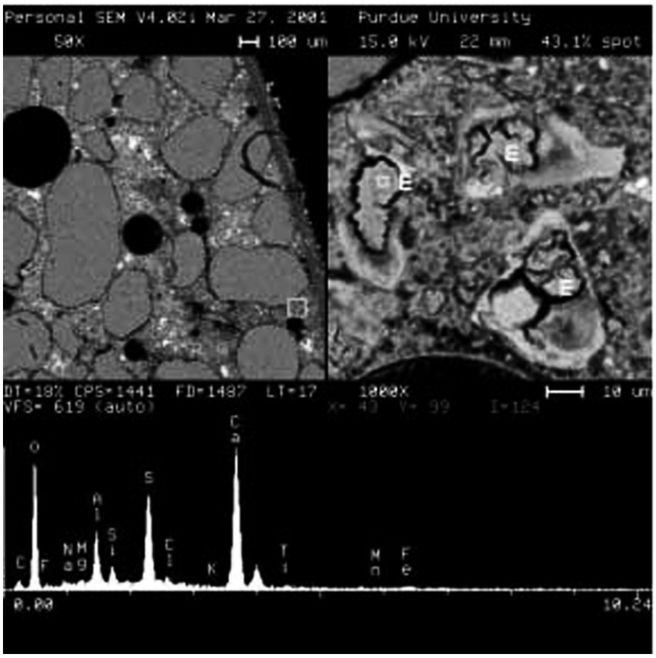

Fig. 7. PC mortar stored in seawater solution showing the formation of ettringite (E).

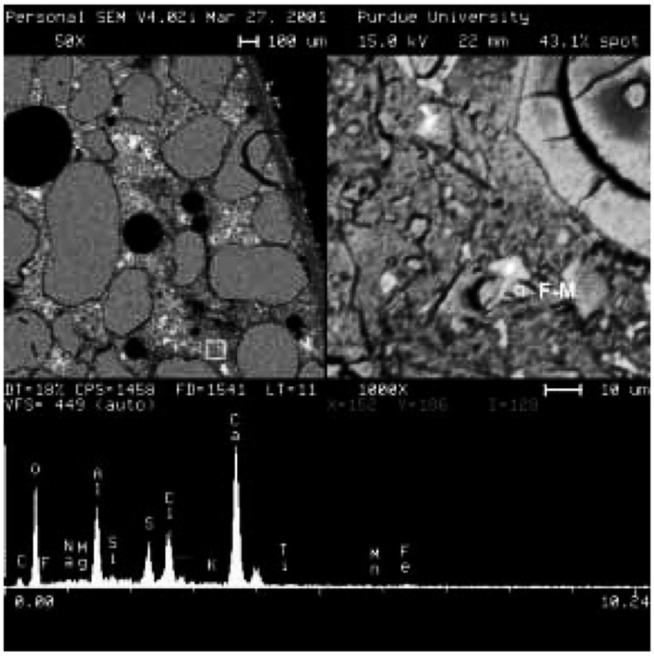

Fig. 9. PC mortar stored in seawater solution showing a deposit of a mixture of chloroaluminate and sulfoaluminate.

is a sudden increase in the amount of ettringite after 12 weeks. Once again this trend is matched by the increase in expansion and mass change. CH is completely consumed by 21 weeks of immersion. The amount of brucite increases between 12 and 21 weeks, and remains constant thereafter.

In comparison to the mortar in seawater solution, the mortar in groundwater solution shows a higher amount of gypsum and ettringite formation. On the other hand, the quantity of brucite forming in the seawater solution is higher.

In both solutions, the quantity of ettringite remains stable between 6 and 12 weeks of immersion. It is possible that the formation of a surface brucite layer could have suppressed the formation of new ettringite between 6 and 12 weeks of immersion. However, at 12 weeks, the quantity of brucite is seen to decrease,

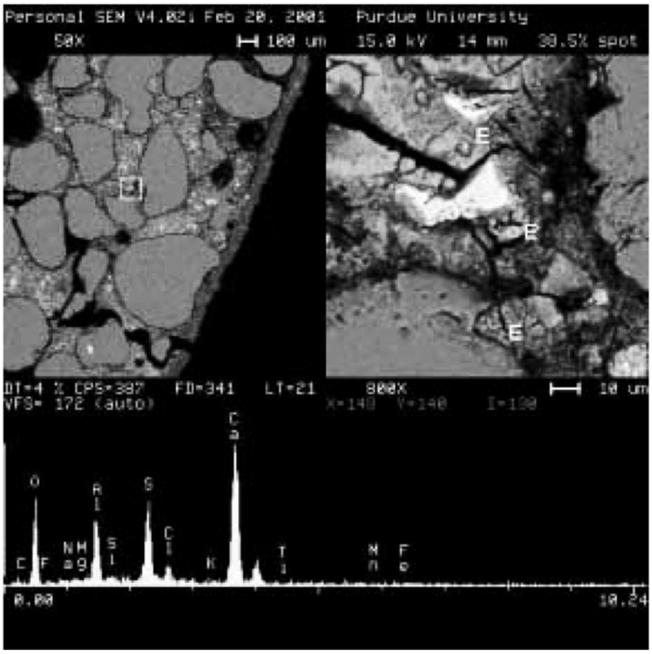

Fig. 8. PC mortar stored in seawater solution showing deposits of ettringite (E) almost 500 μm inside the mortar.

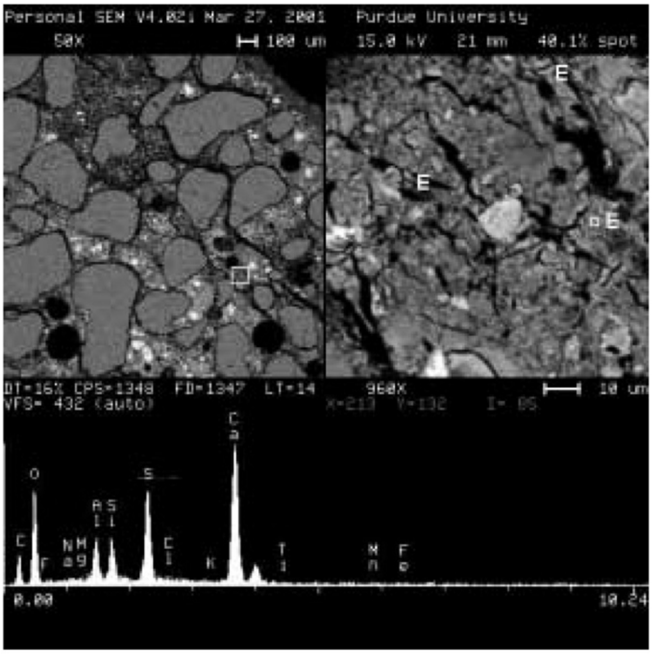

Fig. 10. PC mortar stored in groundwater solution showing deposits of ettringite (E).

indicating possible damage to this layer, which might have caused increased ingress of the solutions, and thus resulted in formation of increased amounts of ettringite in the subsequent storage periods.

3.3. Microstructural investigations by SEM

3.1. Seawater

The micrographs for the mortar stored for 32 weeks in seawater are presented in Figs. 7, 8 and 9. The image in Fig. 7 shows a region close to the surface of the mortar where deposits of ettringite are observed. Such deposits are numerous close to the surface. No gypsum is seen, and this fact is consistent with the absence of gypsum in the DSC tests. Some cracking was observed in the unattacked interior regions of the mortar. Also, a brucite layer almost 100 μm thick can be seen. The cracking is not extensive. Another region of the mortar is shown in Fig. 8, where deposits of ettringite almost 500 μm into the mortar can be observed (confirmed by the energy dispersive X-ray analysis pattern). A small deposit of a mixture of chloroaluminate (possibly Friedel's salt) and sulfoaluminate can also be seen (Fig. 9). Such deposits were also found elsewhere in the mortar. The observation of these mixtures is consistent with the results of the studies by Brown and Badger [12] and Brown and Doerr [13].

3.2. Groundwater

Cracking in the mortar stored for 32 weeks in groundwater is more extensive compared to that stored in seawater; however, this cracking is restricted to the surface zones, as seen from Fig. 10. The deterioration is evident from the highly cracked appearance of the paste in this figure. The paste in the regions close to the surface has numerous ettringite deposits. The brucite layer forming in groundwater is less than 50 μm thick, according to the low magnification image in the same figure. Fig. 11 shows a region at the surface of the mortar. The paste under the surface layer of brucite appears disintegrated. Ettringite deposits are fairly common close to the surface.

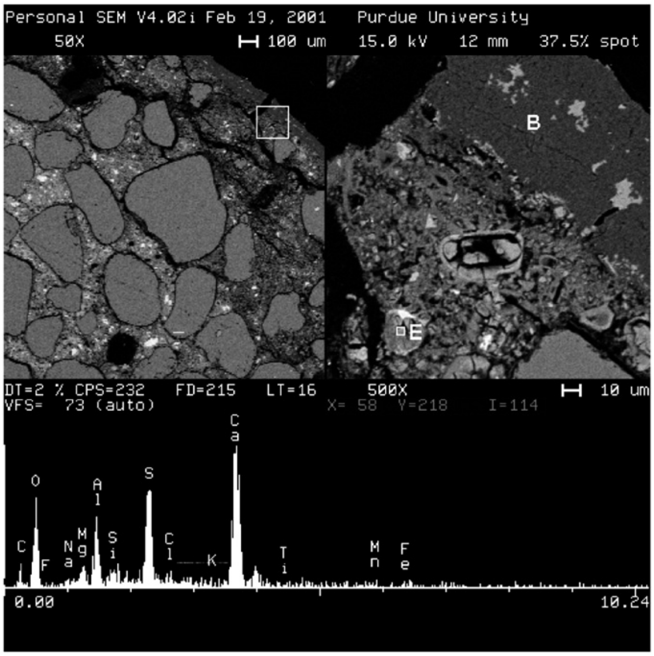

Fig. 11. Deposition of ettringite (E) near the surface, and brucite (B) layer on the surface for the mortar stored in groundwater solution.

4. Discussion

The seawater and groundwater solutions used in this study had the same concentration of SO_3 (2233 ppm). However, the Cl ion concentration of seawater was 19,090 ppm compared to only 1043 ppm for groundwater. A comparison of the data from expansion, mass change and thermal analysis measurements between 6 and 21 weeks of storage in the respective solutions can be used to show the differences in the performance of mortars stored in seawater and groundwater solutions.

In the case of the groundwater solution, while the expansion increases steadily between 6 and 21 weeks (from 0.03% to 0.55%), the mass does not change significantly. Thermal analysis results show that the quantity of ettringite remains stable between 6 and 12 weeks (at 5%), and then increases steadily from 12 weeks onwards. This indicates that over the 6 to 12-week period, ettringite formed previously (by 6 weeks) exhibited expansion (mechanisms are discussed in [14]), while beyond 12 weeks, the continued generation of ettringite (and precipitation of gypsum) contributed to the expansion.

The behaviour in seawater solution shows some differences. The increase in expansion between 6 and 12 weeks (the period when quantity of ettringite remained stable) was less compared to groundwater (seawater −0.05 to 0.12%; groundwater −0.03 to 0.27%). This indicates that the expansive nature of ettringite in the seawater solution may have been suppressed. It has been reported previously that ettringite forming in conditions of high Cl concentration has a reduced tendency to expand [15].

Two other differences contributed to the different performance in the two solutions. One was the presence of chloroaluminate compounds (possibly Friedel's salt) in the mortar in seawater solution. This indicates that there was some binding of aluminate phases by the chlorides [3,13]. Indeed, thermal analysis results showed that the quantity of ettringite forming in seawater was lower than in the groundwater solution.

The other difference was that the quantity of brucite forming in seawater was greater than in groundwater (as seen from thermal analysis and SEM). The presence of a thicker layer of brucite in the seawater solution could have resulted in a better protection against the further ingress of the solution. The expansion specimens in seawater (despite showing expansions as high as 1.25%) did not crumble at the end of 32 weeks of immersion, possibly due to the rigid skin offered by the thick brucite layer.

5. Conclusions

- More deterioration was observed for Portland cement mortars stored in the groundwater solution compared to the seawater solution.

- While the mass change for mortars in the two solutions was similar, the expansion and strength loss for the specimens in the groundwater solution were higher than for the seawater solution.
- In comparison to the mortars in groundwater solution, the mortars in seawater solution were found to contain smaller quantities of ettringite and gypsum. In any case, substantial ettringite formation was observed for the mortars in seawater solution. The high Cl concentration of this solution could have reduced the expansive nature of the ettringite formed.
- Mortars in seawater solution also showed evidence of chloroaluminate compounds, such as Friedel's salt, indicating the possibility of binding of aluminates.
- The thickness of the brucite layer for the mortars in seawater solution was significantly higher than in groundwater solution, and may have acted as a barrier slowing down the attack.

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