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Cement composition and sulfate attack
Part I

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Abstract

Four cements were used to address the effect of tricalcium silicate content of cement on external sulfate attack in sodium sulfate solution. The selected cements had similar fineness and Bogue-calculated tricalcium aluminate content but variable tricalcium silicates. Durability was assessed using linear expansion and compressive strength. Phases associated with deterioration were examined using scanning electron microscopy and X-ray diffraction. Mineralogical phase content of the as-received cements was studied by X-ray diffraction using two methods: internal standard and Rietveld analysis.

The results indicate that phase content of cements determined by X-ray mineralogical analysis correlates better with the mortar performance in sulfate environment than Bogue content. Additionally, it was found that in cements containing triclacium aluminate only in the cubic form, the observed deterioration is affected by tricalcium silicate content. Morphological similarities between hydration products of high tricalcium aluminate and high tricalcium silicate cements exposed to sodium sulfate environment were also observed.

Keywords: Durability; Sulfate attack; Ca_3SiO_5; $Ca_3Al_2O_6$; X-ray diffraction

1. Introduction

Sulfate attack occurs in concrete when concrete is in contact with a source of sulfate ions, which can be groundwater, soil, or rainwater. Sulfate attack usually manifests itself by cracking and spalling of concrete accompanied by expansion and/or loss of strength. The resistance of concrete to sulfate attack is determined by several factors, such as water/cement ratio, permeability, and cement characteristics, which include fineness and cement composition. It has long been recognized that controlling cement composition, specifically tricalcium aluminate content, improves concrete resistance to sulfate attack. Both ASTM C150 and AASHTO M85 limit the C_3A content to 8% for Type II cement, which is designated as moderate sulfate resistant cement. AASHTO M85 also limits the maximum C_3S content of this cement to 58%, while ASTM only limits the C_3A. The objective of this research was to verify the effect of cement composition, particularly C_3S content of cements, on durability of cements in a sulfate environment.

Previous research has indicated that durability in a sulfate environment depends on tricalcium aluminate content. By-products of sulfate attack depend on the cation type. In the presence of sodium sulfate source, the main products are ettringite and/or gypsum. Depending on lime availability, calcium hydroxide interacts with sodium sulfate to form secondary gypsum. Consequently, the latter can also participate in secondary ettringite formation. The role of lime in sulfate attack has been addressed by Mehta [1] and others [2] where it is generally indicated that high lime enhances formation of microcrystalline ettringite that is capable of water adsorption and expansion. In addition, it has been shown that lime limits the solubility of aluminates resulting in an expansive topochemical reaction. Finally, high lime availability increases gypsum formation.

Previous work on the effect of C_3S content on sulfate durability of cementitious systems addressed pure alite pastes [3,4] or compared performance of cements with variable chemical composition [5,6]. Studies on the latter relied on

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cement phase composition determined from Bogue calculations. It has long been established that the Bogue calculation provides only approximate values. While compound content determined through Bogue calculations offer good approximation for major cement phases, they do not account for the presence of impurity oxides [7–9]. This would reflect on variances in actual phase content that might introduce ambiguity in data interpretation or hinder observance of specific trends. ASTM introduced methods of determining the aluminate phases in clinker together with periclase using X-ray diffraction. Individual phase analysis is determined with the use of an internal standard and pure phases. This method identifies specific phase content independent of the other existing phases. However, a similar standard does not yet exist for the silicate phases. Another method where the whole generated pattern is fitted, Rietveld analysis, has received attention. Optical microscopy has also been used in the quantification of clinker phases.

In this study, the role of tricalcium silicate on sulfate durability is addressed using four portland cements of similar Bogue calculated tricalcium aluminate content and variable tricalcium silicate content. In the second part of this study, the effect of doping cements with tricalcium silicate will be reported.

2. Methodology

Four cements of similar Bogue calculated tricalcium aluminate content and similar fineness were selected for this study. Mineralogical phase content for the as-received cements was determined using X-ray diffraction. Two methods were used: internal standard and Rietveld refinement. While the former allows individual phase quantification, the latter offers refinement of the whole pattern. The advantage of using the calibrations curves in internal standard method is that it allows for one phase to be quantified without determining the amounts of the other phases present in the sample [10]. In building the calibration curves, it is ideal to use a material that has the exact chemical composition and crystal structure as the material present in the samples to be analyzed. However, this is often difficult when dealing with cement samples due to numerous possible substitutional ions and crystal system polymorphs. Preferred orientation as well as peak overlap is also a concern when using the internal standard method [10]. Care was taken to select peaks free from preferred orientation and with minimal overlap from other phases.

In establishing the calibration curves for the cubic and orthorhombic C_3A, C_4AF and MgO, ASTM C-1356-98 was used. TiO_2 used as an internal standard and the pure phases for the calibration curves were purchased from a commercial lab. The X-ray scans were collected using Phillips X'Pert PW 3040 Diffractometer with Cu Kα radiation. Scanning angles were from 5 to 60° 2θ with a step size of 0.02° per step and counting time of 4 s per step. The tension and current were set at 45 kV and 40 mA. The divergence slit was fixed at 1°, receiving slit had a height of 0.2 mm, and anti-scatter slit was fixed at 1°. The 36.2° 2θ peak of TiO_2 was used in the construction of all calibration curves.

Salicylic acid/methanol extraction (SAM) [9,11] was used in determining the appropriate crystal structure of tricalcium aluminate present in the cements. This extraction procedure dissolves calcium silicates and free lime, thus leaving a residue of aluminates, ferrites and minor phases, such as periclase, carbonates, alkali sulfates, and double alkali sulfates. The software used for phase quantification in the Rietveld refinement method was Philips X'Pert Plus. Only seven crystal structures can be refined at the same time using this software. Due to this limitation, the cement was ignited at 500 °C to transform any bassinite or gypsum present to anhydrite so that this can free the software to analyze additional phases.

In SAM extraction, 20 g of salicylic acid was added to 300 ml of methanol that was mixing on a stirring plate. Then, 5 g of cement and TiO_2 were added and mixed for 2 h in a flask. The amount of TiO_2 was at 10%. The suspension was then vacuum filtered through a Polypro membrane 0.45-µm disc filter. The residue collected on the filter was washed with 100 ml of methanol, and then dried at 100 °C for 30 min.

For expansion and strength measurements, mortar bars and cubes were prepared in accordance to ASTM C-109/C109M-99, ASTM C-1012, ASTM C-490-00a and ASTM C-305. Natural silica sand conforming to ASTM C778-00 was used in preparing mortar cubes and bars. The specimens for strength and expansion measurements were 50-mm cubes and $25 \times 25 \times 285$ mm prisms, respectively. For each cement, six mortar prisms were prepared to monitor expansion. For strength measurements, 6 mortar cubes were used per cement for the compressive strength at seven days. However, beyond the 7 day strength, 3 mortar cubes were used for each testing age. Mortar bars and cubes were prepared using a constant water to cement ratio of 0.485 with one part of cement to 2.75 parts of graded sand. The exposure solution was 5% sodium sulfate which was maintained at room temperature. The solution was changed at

Table 1
Oxide chemical composition of as-received cements

	Cement			
	1	2	3	4
Analyte				
SiO_2	20.78	21.15	20.55	20.52
Al_2O_3	5.47	4.78	4.4	4.92
Fe_2O_3	4.15	3.76	3.61	3.7
CaO	63.14	64.41	64.6	64.31
MgO	0.85	0.95	2.47	1.71
SO_3	2.88	2.58	2.54	2.81
Na_2O	0.26	0.18	0.03	0.01
K_2O	0.6	0.34	0.54	0.41
TiO_2	0.32	0.33	0.22	0.27
P_2O_5	0.18	0.07	0.05	0.03
Mn_2O_3	0.03	0.03	0.05	0.04
SrO	0.05	0.12	0.02	0.04
Cr_2O_3	0.02	<0.01	0.02	<0.01
ZnO	0.02	0.02	0.03	<0.01
L.O.I. (950 °C)	1.3	1.15	0.99	1.08
Total	100.04	99.84	100.12	99.83
Alkalies as Na_2O	0.65	0.4	0.39	0.27
Free CaO	0.44	1.05	2.31	0.92
Blaine fineness (cm^2/g)	3820	3800	3880	3840

Table 2
Bogue mineralogical content

Compound	Cement 1	Cement 2	Cement 3	Cement 4
C_3S (%)	48	57	65	60
C_2S (%)	23	18	10	14
C_3A (%)	7	6	6	7
C_4AF (%)	13	11	11	11
C_3S/C_2S	2.1	3.2	6.5	4.3

each measurement date. The morphology and nature of the hydration phases were studied using scanning electron microscopy and X-ray diffraction.

3. Results

3.1. Cement characterization

As mentioned above, cements were selected for this study with similar tricalcium aluminate content but variable tricalcium silicate. In addition, the selected cements had similar fineness. Variation in cement fineness affects hydration rate and cement reactivity. Previous work [12,13] showed an increase in expansion with fineness when concrete was exposed to sulfate environment. Based on these considerations, it was decided to eliminate fineness as a variable in this study.

The oxide chemical composition and Blaine fineness of as-received cements used in this study is depicted in Table 1.

Phase content determined through Bogue calculations is shown in Table 2. The results indicate that all cements have similar tricalcium aluminate content and an 18% variation in tricalcium silicate content.

Table 3 presents the amounts of C_3A, C_4AF and MgO determined using XRD-internal standard method. The results indicate that though cements were selected for their similar tricalcium aluminate content, this was not the case. Cement 1 had a C_3A content (6%) approximately double that of the other cements (approximately 3–4%). In addition, all cements showed consistently lower C_3A content than that determined by Bogue calculation. This may indicate that most of this phase is present in an amorphous state for all cements with the exception of Cement 1. In case of this cement, most of tricalcium aluminate is present in crystalline form.

Cements 1, 2 and 3 had similar C_4AF content compared to that determined by Bogue. However, C_4AF content of Cement 4 showed a higher value than the Bogue determination.

Table 3
Phase composition of as-received cements (Internal Standard Method)

Compound	Cement			
	1	2	3	4
C_3S (%)	55	58	63	70
Cubic C_3A (ASTM C 1365) (%)	6	4	3	3
C_4AF (ASTM C 1365) (%)	11	10	11	14
MgO (ASTM C 1365) (%)	0	0	2	1

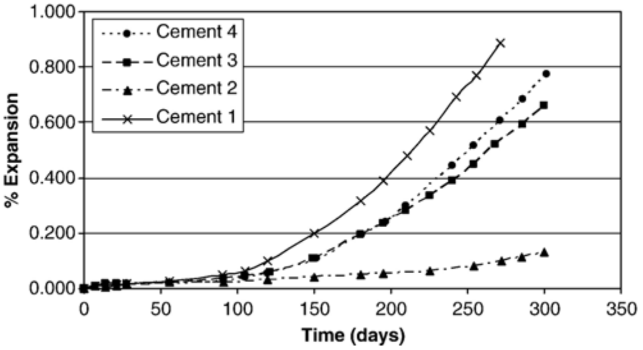

Fig. 1. Length change of mortar prisms prepared with as-received cements.

Rietveld analysis rendered tricalcium aluminate content that is in line with the findings of the internal standard method; however, the former gave numerically higher tricalcium aluminate content for Cement 1. Moreover, both methods indicate that, unlike Bogue calculations, the tricalcium aluminate content of Cements 2, 3 and 4 are similar but approximately half that of Cement 1.

For calcium silicates, Rietveld values for dicalcium silicate were consistently higher than those predicted by Bogue. In addition, tricalcium silicate analysis indicated that Cement 4 had the highest content, followed by 3, 2 and 1. Again, these results are not in agreement with the Bogue findings.

3.2. Durability assessment

In assessing the effects of cement phase content on sulfate durability, compressive strength and length change measurements were conducted. Behavior of mortar or concrete bars in a sulfate solution is generally divided into two stages. The first stage, also referred to as the induction period, is characterized by relatively minor changes in length. In the beginning of the second stage, expansion increases dramatically and the same rate of expansion is maintained until failure [14]. Fig. 1 displays the expansion behavior of the mortar prisms prepared with as-received cements. Cement 1, with tricalcium aluminate content of 8% (Table 4), had the shortest induction period of approximately 105 days. The induction period for Cements 3 and 4 lasted for 120 days, while for Cement 2 it was 270 days. For Cements 2, 3 and 4 of similar crystalline tricalcium aluminate content (Table 4), it can be observed that expansion increased with increasing tricalcium silicate content. However, Cement 1 bars exhibited the highest overall expansion. At 270 days, these bars expanded by 0.89%. Cement 4 prisms had the second highest overall expansion, and the expansion of

Table 4
Rietveld refinement results for cements

Compound	Cement			
	1	2	3	4
C_3S (%)	51	54	61	67
C_2S (%)	28	25	19	15
Cubic C_3A (%)	8	4	3	2
C_4AF (%)	10	13	12	14
MgO (%)	0	0	1.8	0.6
C_3S/C_2S	2.3	2.2	3.2	4.5

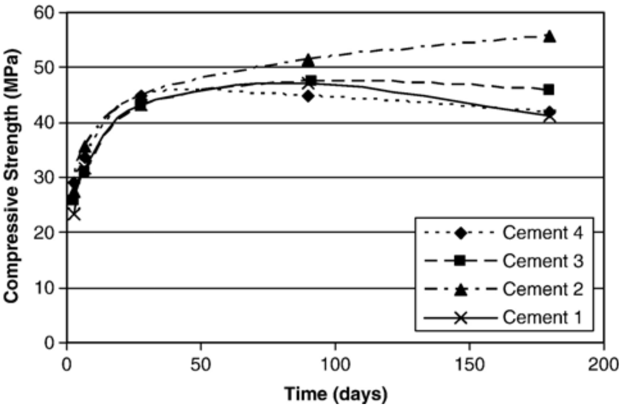

Fig. 2. Compressive strength of mortar in sodium sulfate solution.

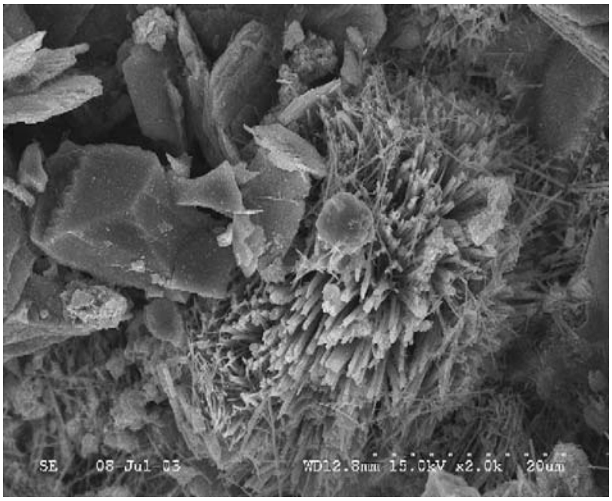

Fig. 3. Ettringite spherulite in Cement 4 cross-section.

Cement 3 prisms was only slightly less. At 270 days, Cement 4 prisms expanded to 0.61%, and expansion of Cement 3 at that age were 0.52%. Cement 2 had the lowest overall expansion of 0.1%.

Fig. 2 illustrates strength variation of mortar cubes prepared with as-received cements and exposed to sodium sulfate solution. In general, compressive strength gain was observed up to 90 days except for Cement 4. Among cements with similar crystalline tricalcium aluminate content; namely, Cements 2, 3 and 4 the latter showed strength reduction of 3 MPa in the 180-day compressive strength compared to its 28-day strength. Although the 180-day compressive strength of Cement 3 was slightly higher than its 28-day strength, it was still experiencing a reduction compared to the 90-day value. At 180 days, Cement 2 showed a strength value that is approximately 11 MPa higher than its 28-day compressive strength. For Cement 1 with highest crystalline tricalcium aluminate content, a strength reduction of 2 MPa was observed at 180 days compared to its 28-day strength value.

3.3. X-ray diffraction analysis of mortar bars

XRD analysis performed on the cross sections of expansion bars showed that for cements with similar C_3A content (Cements 2, 3 and 4) both the amount of ettringite and the amount of gypsum seemed to increase with increasing C_3S content of cement. Table 5 illustrates that Cement 4 bars, which experienced the highest overall expansion and strength reduction, contained the highest amounts of crystalline ettringite and gypsum out of these three cements. While tricalcium silicate hydration products are responsible for gypsum formation, the hydration of tricalcium aluminate is responsible for ettringite formation. However, secondary gypsum formation appears to contribute to secondary ettringite formation.

Table 5
Mortar properties after exposure to sodium sulfate

Mortar properties	Cement		
	4	3	2
Strength Change (180-day strength–28-day strength), MPa	−3.1	+2.8	+11.1
Expansion (%)	0.981	0.660	0.209
Ettringite intensity ratio (cross-section)	0.44	0.32	0.20
Gypsum intensity ratio (cross-section)	0.40	0.27	0.21
C_3S (% Rietveld)	67	61	54
C_3A (% Rietveld)	2	3	4
C_3A (% internal standard)	3	3	4
C_3S/C_2S	4.5	3.2	2.2

3.4. SEM

Scanning electron microscopy observations of mortar bars exposed to sodium sulfate solution for a year revealed that spherulites were present in the cross-sections of all the bars that experienced high expansion, namely Cements 1, 3 and 4. It is not clear whether these ettringite formations are responsible for high expansions of these cements or just a product of ettringite recrystallization in existing voids.

As it can be seen in Fig. 3, the pores of Cement 4 bars were populated with large clusters of ettringite spherulites of rather

Fig. 4. Ettringite spherulite in Cement 3 cross-section.

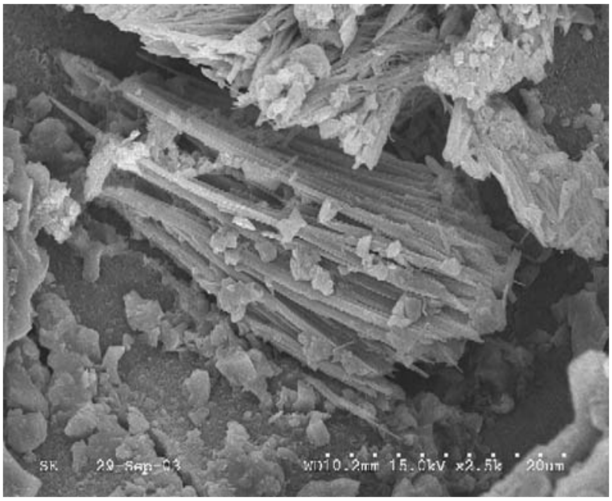

Fig. 5. Needle-like ettringite crystals in Cement 2 mortar.

significant size. They were very similar in size and number to those observed in Cement 1, but much larger in diameter and much more numerous than the spherulites in Cement 3 bars shown in Fig. 4. In fact, the diameter of the spherulites in Cement 1 and 4 bars was 2 to 4 times larger than their diameter in Cement 3. Cement 2 bars generally had prismatic crystals as illustrated in Fig. 5. In general, ettringite crystals in all of these bars were forming disjointed local clusters.

4. Discussion

While it is customary to use Bogue compound determination in addressing the behavior of cementitious materials, the current study indicates that it might not explain accurately experimental data. Bogue compound determination revealed similar tricalcium aluminate content for cements; however, X-ray analysis indicated differences in tricalcium silicate and crystalline tricalcium aluminate content of the as-received cements. While total tricalcium aluminate content is relevant to external sulfate attack, crystalline tricalcium aluminate content is of significance. The highest expansion in this study was experienced by Cement 1. Cement 1 had the highest crystalline tricalcium aluminate content. It therefore appears that calcium aluminates present in amorphous form are less susceptible to external sulfate attack. This is rather expected as the reactivity of both forms is different with the crystalline form being more reactive. The significance of crystalline tricalcium aluminate content of cements of similar tricalcium silicate is clear when comparing the expansion behavior of Cements 1 and 2. Though both cements had similar tricalcium silicate content as indicated in Table 4, Cement 1 had higher expansion than Cement 2. This is not surprising as the amount of crystalline tricalcium aluminate determined for Cement 1 is twice that of Cement 2. It is also noted that Cement 1 is the only cement in this study that exceeded the (C_4AF+2C_3A) limit set in ASTM C-150-02 at 25%.

Additionally, for cements with similar tricalcium aluminate content (in form and amount), durability assessed by expansion appears to be dependent on tricalcium silicate content. Again, the C_3S was quantified using X-ray diffraction methods. Table 5 shows such relationship. Increasing tricalcium silicate content or C_3S/C_2S ratio in cement generates more calcium hydroxide on hydration. This has possibly two effects. First, high lime solutions limit the solubility of aluminates. Second, lime availability increases formation of secondary gypsum. While expansion accompanying gypsum formation has been debated in the literature, its participation in secondary ettringite formation is generally of no question.

Mortar strength data accumulated for 180 days in sulfate solution indicates that for a given aluminate content, cements with higher lime content experience higher strength loss. The significance of lime content is that it appears to affect expansion in addition to strength loss. The hydration products for higher tricalcium silicate content or high tricalcium aluminate content cements appear to be very similar. Higher lime content in cements retards tricalcium aluminate hydration. In the presence of an external source of sodium sulfate, which is being continuously replenished, secondary gypsum participates in the formation of secondary ettringite. Such formation is accompanied by expansion and strength loss. Similar results were obtained with increasing crystalline tricalcium aluminate content of cement.

X-ray diffraction of mortar bars at the exposure time of 360 days indicates the abundance of crystalline ettringite and gypsum. The quantities of both phases seem to increase with lime content of as-received cements. Morphological distinction between cements with high and low lime appears to be in the clusters of the formed ettringite and their sizes. The morphology of high lime cement was observed to be similar to that of high crystalline tricalcium aluminate cement.

5. Conclusions

Phase quantification of as-received cements based on Bogue calculations, though important, appears to limit observation of important phase-related durability issues. The role of crystalline phases, particularly tricalcium aluminate and tricalcium silicate, in external sulfate attack can be better addressed with appropriate quantification methods. Currently, ASTM has established techniques for quantifying aluminates; however, no such procedures are available for calcium silicate compounds.

The role of tricalcium silicate in external sulfate attack is of significance; as such, limits on its content for external sulfate attack need to be addressed.

References

[1] P.K. Mehta, Mechanism of sulfate attack on portland cement concrete—another look, Cem. Concr. Res. 13 (3) (1983) 401–406.

[2] Rasheeduzzafar, O. Al-Amoudi, S. Abdulfauwad, M. Maslehuddin, Magnesium–sodium sulfate attack in plain and blended cements, J. Mater. Civ. Eng. 6 (2) (1994) 201–222.

[3] P.K. Mehta, Mechanism of expansion associated with ettringite formation, Cem. Concr. Res. 3 (1) (1973) 1–6.

[4] B. Tian, M.D. Cohen, Does gypsum formation during sulfate attack on concrete lead to expansion? Cem. Concr. Res. 30 (1) (2000) 117–123.

[5] P.J. Monteiro, K.E. Kurtis, Time to failure for concrete exposed to severe sulfate attack, Cem. Concr. Res. 33 (7) (2003) 987–993.
[6] H.T. Cao, L. Bucea, A. Ray, S. Yozghatlian, The effect of cement composition and pH of environment on sulfate resistance of portland cements and blended cements, Cem. Concr. Compos. 19 (2) (1997) 161–171.
[7] H.F.W. Taylor, Cement Chemistry, 2nd ed.Thomas Telford Publishing, London, UK, 1997.
[8] P.C. Hewlett (Ed.), Lea's Chemistry of Cement and Concrete, 4th ed., John Wiley and Sons, Inc., New York, 1998.
[9] P.E. Stutzman, Guide for X-ray powder diffraction analysis of Portland cement and clinker, National Institute of Standards and Technology, Internal Report, 1996.
[10] R. Jenkins, R.L. Snyder, Introduction to X-ray Powder Diffraction, John Wiley and Sons, Inc., New York, 1996.
[11] W.A. Gutteridge, On the dissolution of the interstitial phases in portland cement, Cem. Concr. Res. 9 (3) (1979) 319–324.
[12] I. Odler, Expansive reactions in concrete, in: J. Skanly (Ed.), Materials Science of Concrete, vol. 2, American Ceramic Society, Westville, OH, 1991, pp. 221–247.
[13] G.A. Arenes-Oliva, Influence of the Variation of Cement Source on Fresh and Hardened Concrete Properties, Master's Thesis, University of South Florida, 2002.
[14] M. Santhanam, M.D. Cohen, J. Olek, Mechanism of sulfate attack: a fresh look: Part 1: Summary of experimental results, Cem. Concr. Res. 32 (6) (2002) 915–921.