

## Microstructure of alkali-activated fly ash and slag concrete exposed to different sulfate resistance testing methodologies

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### INTRODUCTION

Exposure to sulfate rich environments can compromise the durability of concrete. Generally, external sulfate attack is simulated by exposing cement paste, mortar, or concrete samples to a sulfate-containing environment, and correlating changes in the physical/mechanical properties with the susceptibility of the material to sulfate attack. Sulfate attack can be a slow process. One common approach to accelerate the reactions is to increase the concentration of sulfate ions in the test solution. Monitoring length change is the most common approach to evaluate the sulfate resistance. However, sometimes concrete does not experience expansion, but instead experiences mass loss due to scaling [1]. Therefore, monitoring multiple responses should be considered [2].

Most of the existing testing methods have certain weaknesses or drawbacks. In general, short-term testing methods may not simulate the real-world conditions, but are essential for routine quality control tests. On the other hand, long-term testing protocols can provide better estimates regarding the field performance, but are time consuming and expensive to conduct. It is logical to assume that a reliable durability testing method would provide an unfavorable condition to the samples, and at the same time, not offer conditions that could cause improvements in the sample. Exposure to some conditions, such as heat-curing, moist-curing or certain chemicals may be favorable for some materials. This means that the chemistry of the material should to some degree, dictate the selection of the testing methodology. Here, two different testing methodologies were employed. The first test protocol comprised of continuous immersion in a 5% magnesium sulfate solution, while the second test protocol comprised of four drying and wetting cycles followed by continuous immersion in a 5% magnesium sulfate solution. Length and mass changes, overall visual macro-scale damage, and microstructural changes were monitored for up to 2 years. A scanning electron microscope equipped with an X-ray energy dispersive spectrometer (SEM/EDS) was used to perform quantitative mineral standards based chemical analyses on polished thin sections prepared from the tested samples, and to collect back-scattered electron (BSE) images. Two different binders systems were tested, an an alkali activated fly ash (AAF), and an alkali activated slag (AAS).

## EXPERIMENTAL

Mix designs, sample preparation, and curing

The concrete mixes were part of a round-robin testing program run by RILEM Technical Committee 247-DTA Durability Testing of Alkali-Activated Materials, with the slag and fly ash compositions listed in Table 1, and mix designs in Table 2. A 29.4 wt. % SiO<sub>2</sub>, 14.7 wt. % Na<sub>2</sub>O, and 55.9 wt. % H<sub>2</sub>O sodium silicate solution was used, and 99.1 wt. % NaOH purity sodium hydroxide pellets were used to produce the sodium hydroxide solutions.

Table 1: Precursor material compositions

	wt. % oxides											Blaine fine- ness m <sup>2</sup> /kg
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	TiO <sub>2</sub>	LOI	
Fly Ash	48.6	21.7	7.32	8.03	2.11	2.4	1.06	0.64	0.84	0.95	5.26	362
Slag	35.7	11.2	43.9	0.3	0.38	6.5	0.21	0.02	0.44	0.51	0.31	415

Table 2: Mix designs

ID	Constituents (kg/m <sup>3</sup> )							41.7 wt% NaOH sol'n.
	Pre- cursor	Coarse aggr.	Fine aggr.	Water	Sodium silicate	50 wt% NaOH sol'n.		
AAF1	425	1051	696	0	157.1	0	60.1	
AAS1	357	1146	759	140	10.7	21.4	0	

Continuous immersion testing

ASTM C1012 Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution [3] is widely used to evaluate the performance of portland cement and blended cement mortar mixtures against sulfate attack. Immersion in a 50 g/L (33,800 ppm SO<sub>4</sub><sup>2-</sup>) sodium sulfate solution (magnesium sulfate is also permitted) starts when the compressive strength of the mortar cubes reaches 20 MPa. A one-day of heat-curing at 35°C is used to accelerate the strength gain. Depending on the specification regarding the class of exposure, the length changes at certain time intervals are measured up to 18 months. For each measurement, the sulfate solution is refreshed to keep the pH and concentration of the sulfate solution constant. Since 1995, this testing protocol has been used to test the performance of portland cement mortars. This study utilized MgSO<sub>4</sub> solution, and 50×50×285 mm concrete prisms instead of mortar cubes and bars. Furthermore, testing was started after 28 days as opposed to achieving a compressive strength criterion, and testing was extended out to two years.

### Cyclic wetting/drying + continuous immersion testing

SIA 262/1-Appendix D: Sulfate resistance [4] defines a procedure developed for testing concrete. Six Ø 28×150 mm cores are extracted from a large concrete block and metal plugs are epoxied on the ends of the cores. Similar to the ASTM C1012, a 50 g/L Na<sub>2</sub>SO<sub>4</sub> solution is used, but the solution is not refreshed. The test starts at the age of 28 days with four cycles of drying and immersion as follows: drying at 50 ± 2 °C for 120 ± 2 h; cooling for 1 h at room temperature in a desiccator; immersion in a sulfate solution for 48 ± 1 h; and measurement of length and mass. Next, the samples are immersed in the same sulfate solution and their length and mass measured after 7, 14, 28, 42, and 56 days of immersion [5]. In this study, 50×50×285 mm concrete prisms were used instead of the Ø 28×150 mm concrete cores, MgSO<sub>4</sub> solution was used instead of Na<sub>2</sub>SO<sub>4</sub>, and testing extended out to two years.

### Monitoring changes in paste matrix

After 12 months of exposure, one concrete prism representing each test condition was cut cross-sectionally and used for preparation of fluorescent epoxy impregnated polished thin sections. After carbon coating, the mineral assemblages within the paste matrices, both near the surface and at depth were examined by SEM/EDS under high-vacuum mode. Spot analyses were performed to collect ~50 spectra from the paste matrix within the affected regions near the surface and ~50 spectra from the unaffected paste matrix at depth. Correlations between the Al/Ca atom ratio and S/Ca atom ratio are often used to graphically illustrate the phase assemblages in portland cement based concrete. However, the presence of Mg and its replacement with Ca during magnesium sulfate attack complicates the interpretation of these types of plots. As an alternative, atomic ratios of S/(Ca+Mg) against Al/(Ca+Mg) were plotted here for OPC and AAS concrete samples. Due to the absence of calcium in the AAF concrete samples, a ternary diagram of S, Mg, and Na atomic ratios were used to explain the changes observed in these binders.

## RESULTS

Figure 1 shows length changes observed during the continuous immersion experiment (abbreviated as “imm”) and during the cyclic wetting/drying + continuous immersion experiment (abbreviated as “4cyc+imm”). The AAF concrete showed no signs of damage, and negligible length or mass change, while the AAS concrete exhibited damage (Figure 2) with considerable mass loss in the continuous immersion test, and expansion in the cyclic wetting/drying + immersion test. Figure 3 plots changes in the composition of the AAF paste matrix binders after 1 year of testing, and Figures 4 and 5 plot changes in the composition of the AAS paste matrix after 1 year of testing.

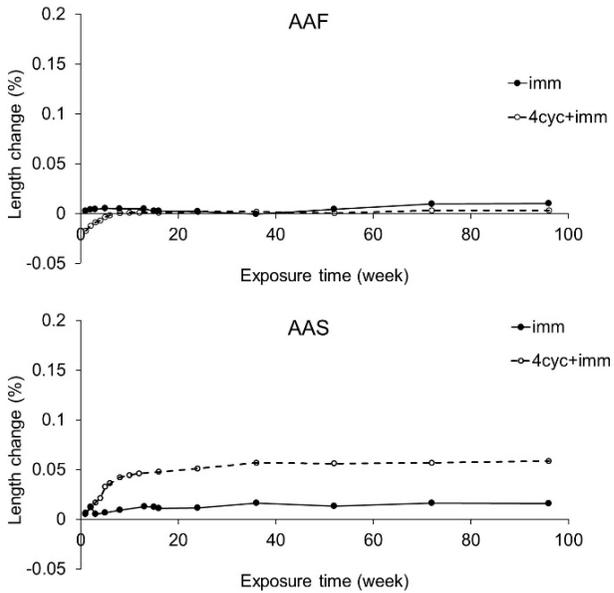


Figure 1: Length change up to 24 months of testing.

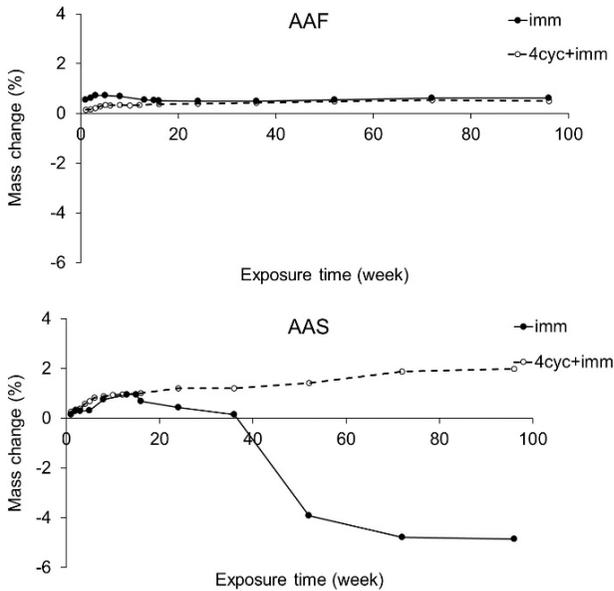
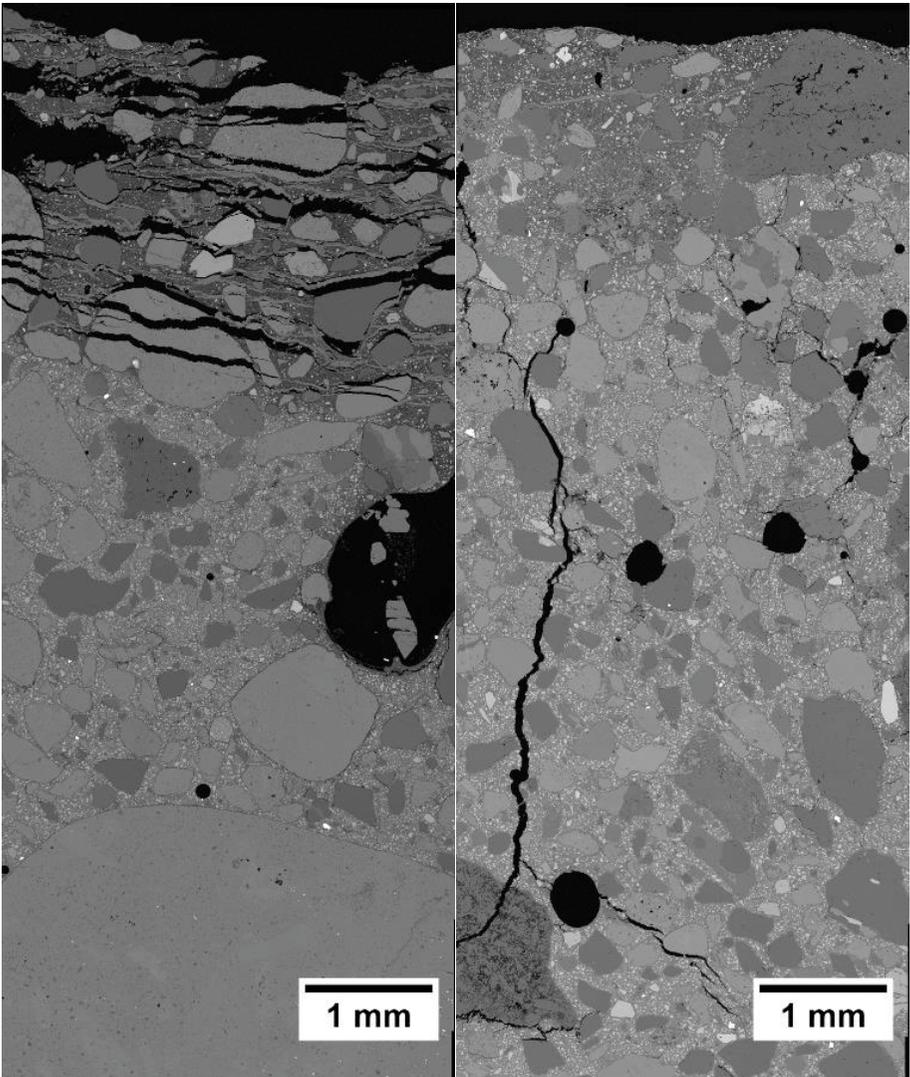


Figure 1: Mass change up to 24 months of testing.



*Figure 2: BSE images of AAS concrete after continuous immersion test, exhibiting gypsum filled cracks concentrated near the surface (left) and cracking at depth for the cyclic wetting/drying + immersion test (right).  $MgSO_4$  solution exposed surface at top in both images.*

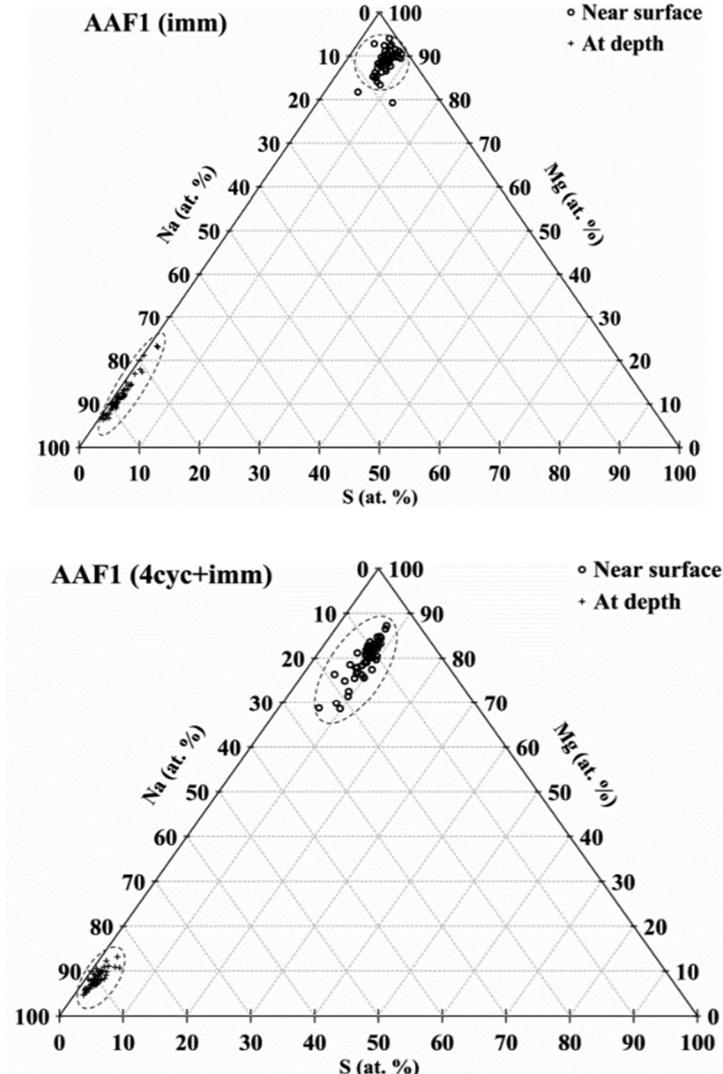


Figure 3: AAF paste composition at the surface and at depth after one year testing.

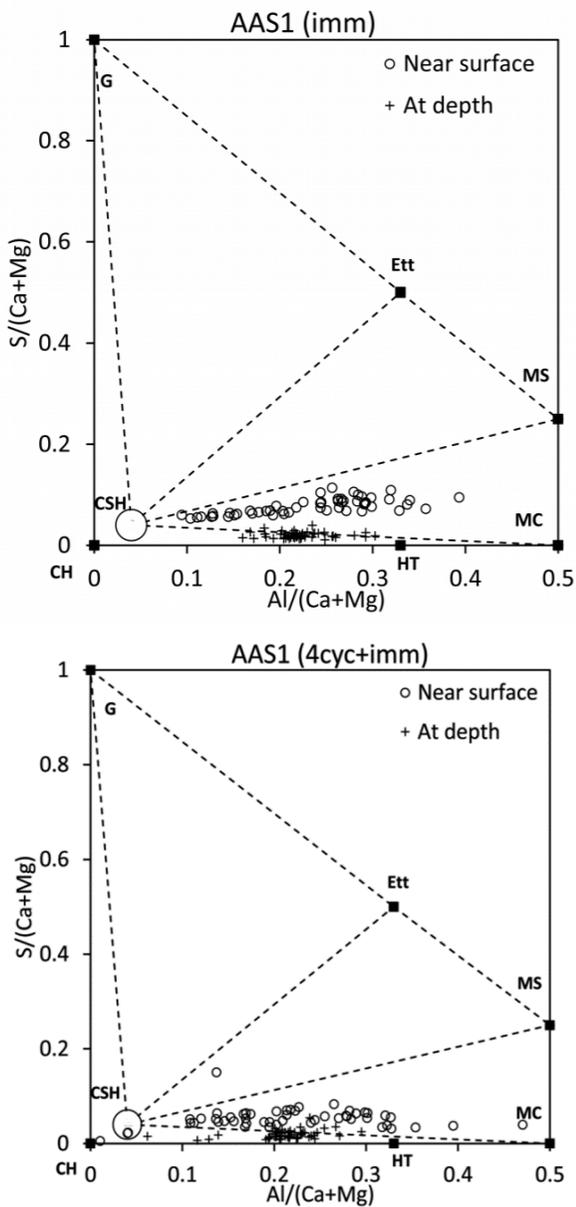


Figure 4: AAS paste compositions at the surface and at depth after one year testing.

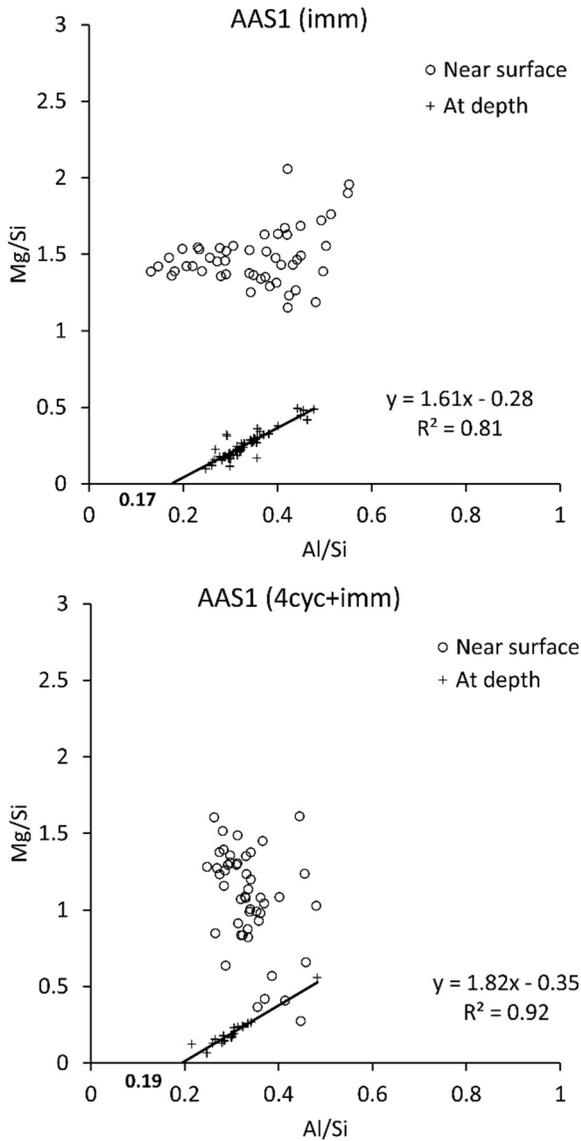


Figure 5: AAS paste compositions at the surface and at depth after one year testing.

#### DISCUSSION AND CONCLUSIONS

The AAF concrete performed well under both test regimes, but the two test methodologies caused different physical and microstructural damage in the AAS concrete. The AAS concrete experienced severe gypsum surface scaling during the

continuous immersion test, while the cyclic wetting/drying + immersion test caused only minor damage to the corners of the concrete prisms. On the other hand, the cyclic wetting/drying + immersion test exhibited overall expansion for the AAS concrete. SEM/EDS spot analyses show similar uptake of magnesium by the paste at the surface under both test regimes for the AAF concrete. Similarly, for the AAS concrete, the paste matrix shows Mg enrichment near the surface. In the case of the continuous immersion experiment, Mg enrichment came at the expense of Ca in C-S-H, resulting in precipitation of gypsum. While the same Mg enrichment was observed in the cyclic wetting/drying + continuous immersion experiment, the elevated temperatures experienced during the initial cycling period may have accelerated curing, densifying the pore structure of the paste matrix, leaving it less susceptible to Ca ion exchange, thereby avoiding severe gypsum surface scaling. However, the same cyclic wetting/drying may have initiated the cracks that penetrate deep into the prism (Figure 2), acting as conduits for solution ingress that helped to drive the long term expansion. At depth, the linear correlation between the atomic ratios of Mg/Si and Al/Si (Figure 5) suggest the presence of hydrotalcite phases, with the positive x-axis intercept interpreted as the level of Al in the binder [6], and the slope interpreted as the average Mg/Al atomic ratio in the hydrotalcite phase [7]. The scatter in Figure 5 for the near surface analyses suggest the absence of hydrotalcite. The contrasting results for the AAS concrete when subjected to the two different tests emphasizes the importance role of the testing methodology itself, as well as the parameters monitored, when assessing the performance of concrete.

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