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Dissolution behaviour of SCMs in alkaline environment and mechanisms behind ASR mitigation

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Abstract

Fly ash and slag are supplementary cementitious materials (SCMs) commonly used to mitigate alkali-silica reaction (ASR). However, future supply of these SCMs is at risk due to a global push to reduce coal-fired energy production and increased steel recycling. Thus, an immediate need to identify alternative SCMs is critical. In order to establish the efficacy of an SCM in its ability to mitigate ASR, an understanding of the chemical processes involved in ASR mitigation is required. This study aims to better understand the mechanisms behind ASR mitigation by comparing the amount of silicon (Si) and aluminium (Al) released by SCMs under AMBT conditions, investigating the interaction of the dissolved SCM species in the system (i.e. formation of reaction products) and how these correlate to explain the differences in SCM dosage requirements for effective mitigation. Results show that the ability of SCMs to release Si is as follows: SF>MK>FA>SL which correlates well with the dosage required to mitigate ASR. This indicates that the efficacy of SCMs in mitigating ASR is primarily due to their ability to release Si in solution. Formation of sodium aluminium silicate hydrate (N-A-S-H) in fly ash and metakaolin and formation of calcium aluminium silicate hydrate (C-A-S-H) in slag post alkali immersion were also observed. This indicates the ability of aluminium to bind silicon and precipate alkali in the process (effectively reducing solution alkali concentration) and highlights its beneficial effect on ASR mitigation. Further, in systems saturated with calcium, Ca is bound instead of Na suggesting the occurence of competitive reactions and subsquent alkali recycling. Calcium, therefore, does not appear to have a beneficial effect on ASR mitigation.

Keywords*: aluminosilicate; fly ash; metakaolin; slag; ASR mitigation*

1. INTRODUCTION

Supplementary cementitious materials (SCMs) are used to mitigate alkali silica reaction (ASR) which is a major concrete durability issue. Traditional SCMs include fly ash, metakaolin, ground granulated blast furnace slag (slag) and silica fume. The required dosage for mitigation varies as a function of aggregate reactivity, pore solution alkalinity and exposure conditions. A quick way to determine the required dosage of SCM for mitigation is through accelerated mortar bar test (AMBT). ASTM C1567 (AMBT), a well-known version of this test, involves storing the samples in 1M NaOH at 80 °C with acceptability criterion of 0.10% expansion at 14 days immersion. Australia, to date, has no dedicated standard to assess SCM efficacy, although the standard method employed to assess aggregate reactivity, AS 1141.60.1, which has comparable test procedure to ASTM C1567 is commonly extended for this purpose [1]. The capacity of an SCM to reduce expansion to acceptable limits varies across different types of SCMs and is an indication of its ability to mitigate ASR.

SCM efficacy in ASR mitigation is reported to be related to its active silica and alumina content [2-6]. The amount of reactive silica is correlated to increased pozzolanic products that has much higher alkali binding capacity. Therefore, it is widely accepted that the higher amount of reactive silica from SCMs, the better the ASR mitigating properties. Several studies have also reported on the beneficial role of aluminium in ASR mitigation [3, 7-13]. The mechanism by which aluminium mitigates ASR however still remains controversial.

This study aims to better understand the role of aluminium by comparing the amount of silicon (Si) and aluminium (Al) released by SCMs under AMBT conditions, investigating the interaction of the dissolved SCM species in the system (i.e. formation of reaction products) and how these correlate to explain the differences in SCM dosage requirements for effective mitigation.

2. MATERIALS AND METHODS

2.1 Raw materials

Four SCMs; fly ash, slag, metakaolin and silica fume were used in the study. Oxide compositions obtained by XRF analysis are listed in Table 2.1. All SCMs used comply with Australian standards.

Table 2.1: XRF Oxide Composition of the SCMs

Oxide wt%	Fly Ash (FA)	Slag (SL)	Metakaolin (MK)	Silica Fume (SF)
SiO_2	59.21	34.12	62.5	91.46
TiO_2	1.11	0.87	1.02	0.01
Al_2O_3	28.11	14.37	32.39	0.10
Fe_2O_3	3.68	0.30	0.82	0.01
Mn_3O_4	0.11	0.36	0.01	0.02
MgO	0.53	5.31	0.67	0.70
CaO	2.48	41.59	0.07	0.24
Na_2O	0.63	0.35	0.22	0.28
K_2O	1.18	0.26	0.28	0.52
P_2O_5	0.41	0.01	0.03	0.14
SO_3	0.16	2.83	0.08	0.07
L.O.I.	1.05	0.35	1.75	5.55

2.2 Accelerated mortar bar test (AMBT)

Accelerated mortar bar test (AMBT) using various SCMs (FA, SL, MK and SF) was carried out based on AS 1141.60.1. The SCMs were used to replace part of the Portland cement (PC) at typical replacement levels used in Australia and at an equivalent replacement of 10% for purposes of comparison. Expansion was measured up to 28 days using a horizontal comparator. Table 2.2 provides the expansion criteria as per AS 1141.60.1.

Table 2.2: AS 1141.60.1 AMBT expansion criteria

Mortar Bar Expansion in 1M NaOH (80 °C) [%]		Reactivity Classification
Day 10 immersion	E < 0.1	Non-reactive
Day 21 immersion	0.1 ≤ E < 0.3	Slowly reactive
	0.3 ≤ E	Non-reactive

2.3 SCM dissolution in alkali environment

SCM slurries were prepared by immersing five grams of each SCM type (FA, SL, MK and SF) in 50 mL of 1M NaOH 80 °C for 28 days. Aliquotes (2 mL) of the supernatant solutions were collected at 7, 14, 21 and 28 days and the concentration of silicon (Si) and aluminium (Al) in solution was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES). The solid residues were filtered and dried at 28 days and were subjected to scanning electron microscope (SEM) imaging and X-ray Diffraction (XRD) analysis to characterize the changes in microsctructure and phases.

3. RESULTS AND DISCUSSION

Figure 3.1 shows the AMBT expansion results of greywacke aggregate with and without different types of SCMs. Figure 3.1a compares the expansion data at recommended SCM dosages for mitigation. Results show that 10%SF, 15%MK, 25%FA and 65%SL are sufficient to mitigate ASR expansion based on the criterion defined in AS 1141.60.1 for non-reactive aggregate screened by the AMBT test. Figure 3.1b shows the expansion of AMBT mortar bar prisms containing an equivalent PC replacement level of 10%. The observed ability of SCMs to reduce expansion is as follows: SF>MK>FA>SL which is consistent with that reported in literature [14]. Australian guide to minimizing damage due to ASR, HB 79:2015 provides recommended levels of SCM replacement to mitigate ASR as follows: SL at 65%, FA at 25%, MK at ≤15% and SF at 10% which is likewise consistent with the reactivity order of SCMs in ASR mitigation as observed in the AMBT expansion results: SF>MK>FA>SL.
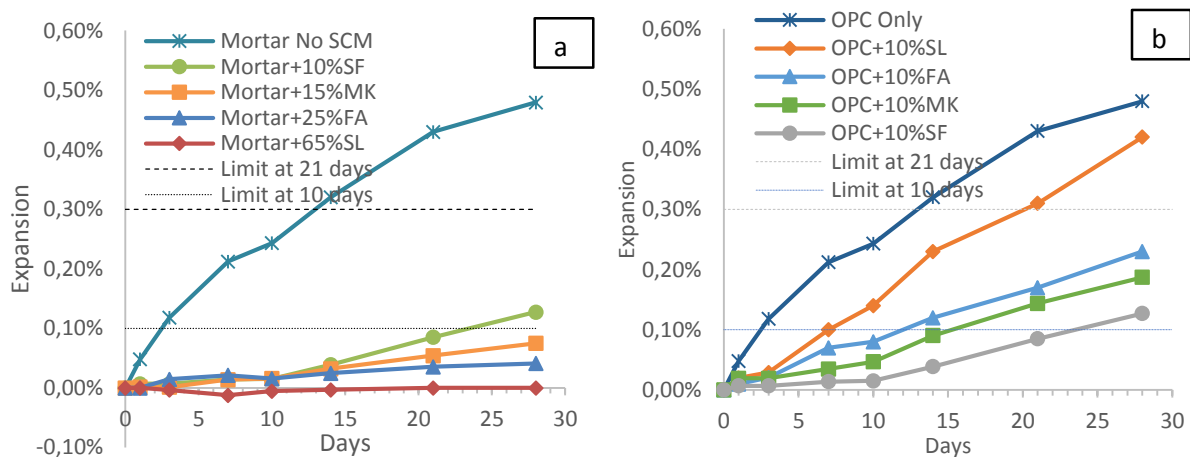

Figure 3.1: AMBT expansion results for a) SCM replacement of PC at the recommended dosages and b) at equivalent replacement levels of 10%. The expansion limits of 0.1 & 0.3% are based on AS1141.60.1 which is the Australian standard for testing aggregate reactivity typically extended for assessing SCM efficacy [1]

Raw SCMs were exposed to AMBT conditions (1M NaOH 80 °C) to investigate the changes in microstructure, phases as well as the release of Si and Al. Figures 3.2 and 3.3 show the microstructure of the SCMs before and after 28 days exposure to AMBT conditions. All SCMs exhibit a change in microstructure confirming occurrence of a reaction.
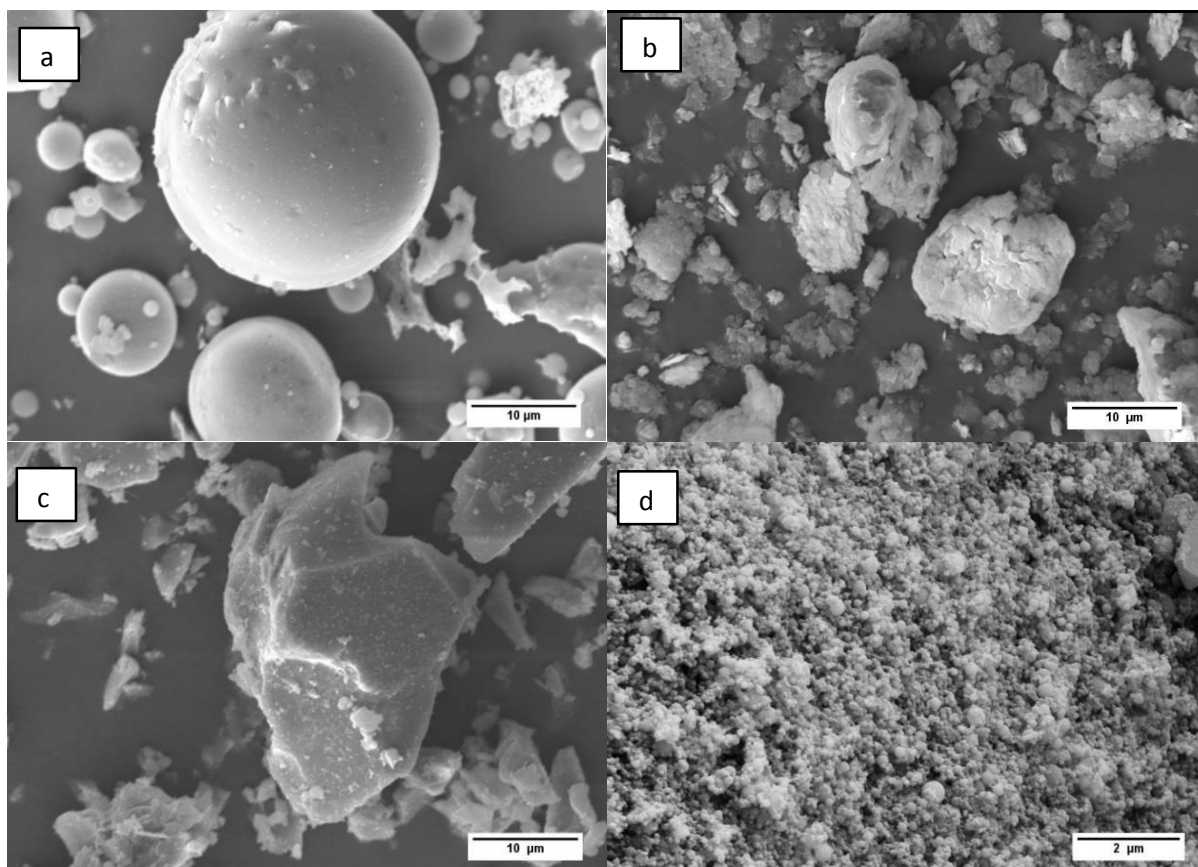

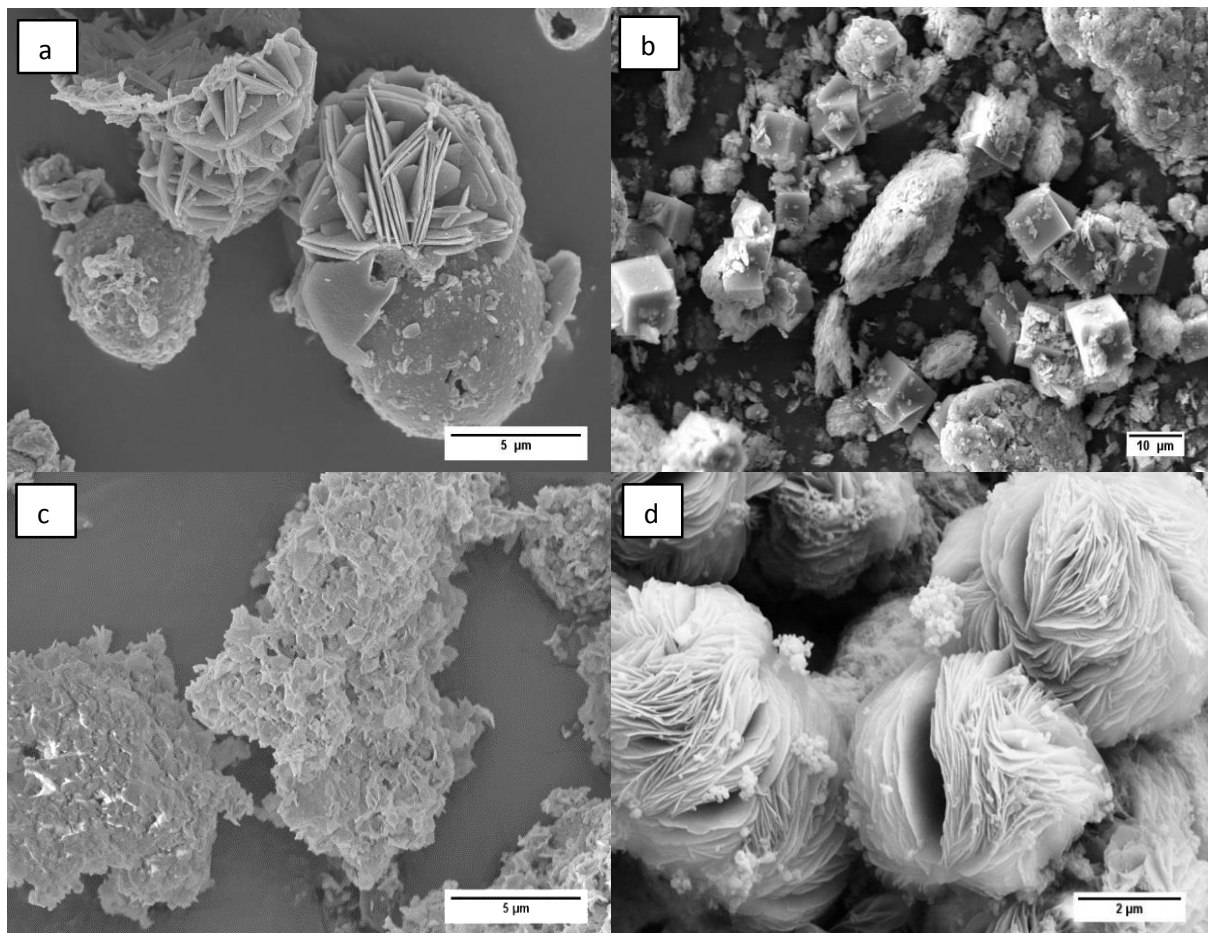Figure 3.2: SEM images of a) fly ash, b) metakaolin, c) slag and d) silica fume before exposure to AMBT conditions (1M NaOH 80 °C)

Figure 3.3: SEM images of a) fly ash, b) metakaolin, c) slag and d) silica fume after 28 days exposure to AMBT conditions (1M NaOH 80 °C)

Figure 3.4 show the XRD plots of the SCMs before and after 28 days exposure to AMBT conditions. The aluminium containing SCMs (FA, MK and SL) showed formation of aluminosilicate hydrates after being exposed to AMBT conditions. FA and MK showed formation of N-A-S-H (sodium aluminosilicate hydrate) while slag showed formation of C-A-S-H (calcium aluminosilicate hydrate). The SCMs can be taken as representative of systems rich in Si (SF), rich in Si and Al (FA and MK), rich in Si, Al and Ca (slag). In an alkaline environment, in this case 1M NaOH, the SCMs dissolve and form reaction products. If aluminium is present, it can bind silicon forming aluminosilicates, thus, reducing the free Si in solution [15]. The aluminosilicates are negatively charged in basic environment and therefore attracts a cation to charge balance. Thus, Na^+ and Ca^{2+} compete in the process where Ca^{2+} is more preferentially absorbed. Thus, FA and MK form N-A-S-H (due to the absence of calcium) while slag forms C-A-S-H since it is saturated with calcium. This indicates that in systems with higher calcium contents, less alkalis are bound since calcium competes with the alkali [16].

Figures 3.5 and 3.6 show the amount of Si and Al the SCMs released in solution under AMBT conditions. The measured concentrations of Si and Al in solution represent instantaneous concentrations of these species on extraction of the aliquot of supernatant fluid. From Figure 3.5, the highest concentration of dissolved Si is observed for silica fume, followed metakaolin, fly ash and then slag consistent with that reported in another study [17]. The amount of Si in solution for fly ash, metakaolin and silica fume increases significantly with respect to time. Slag on the other hand, has very little (almost none) free Si available in solution. The absence of Si in solution for slag implies that all available silicon is bound in the products. SCMs with high proportion of reactive SiO_2 content such as SF, MK and FA therefore have significant potential in mitigating ASR. Indeed, silica fume which is almost entirely amorphous silica generally requires lowest replacement level among the SCMs at 5-10%, while slag which is both silica poor and calcium rich requires highest dosage to mitigate.
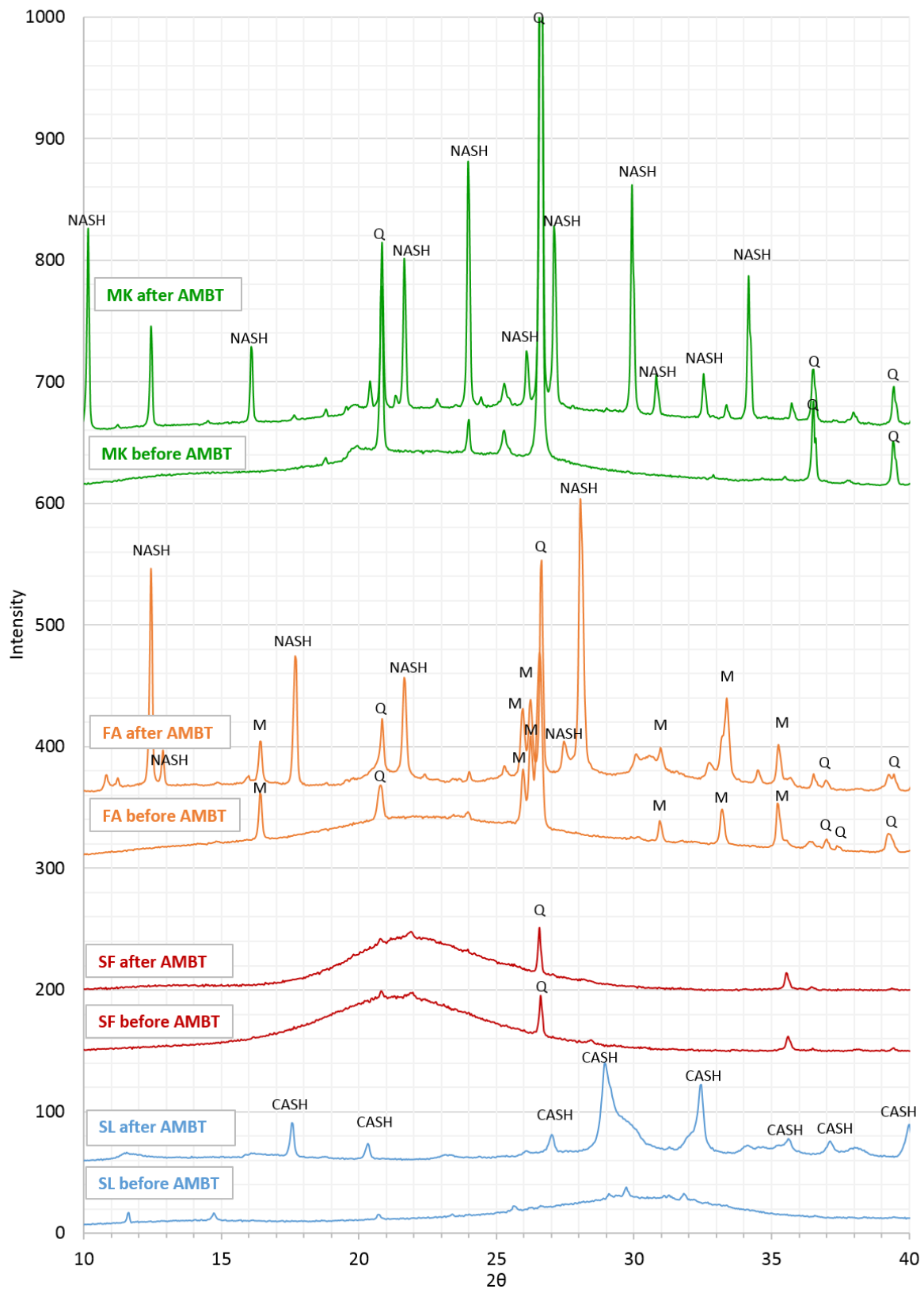
Figure 3.4: XRD patterns of the SCMs before and after exposure to AMBT conditions (1M NaOH 80 °C). Formation of N-A-S-H was observed in FA and MK and C-A-S-H in SL.

Aluminium concentration in solution as reported in Figure 3.6 is in the following order: MK>FA>SL>SF. That is, metakaolin with highest amount of aluminium in solution followed by fly ash and slag with almost equivalent amounts. No presence of aluminium in solution was detected for silica fume. Moreover, it is notable that the aluminium concentration in solution decreases as a function of time suggesting that they precipitate in solution to form other phases.
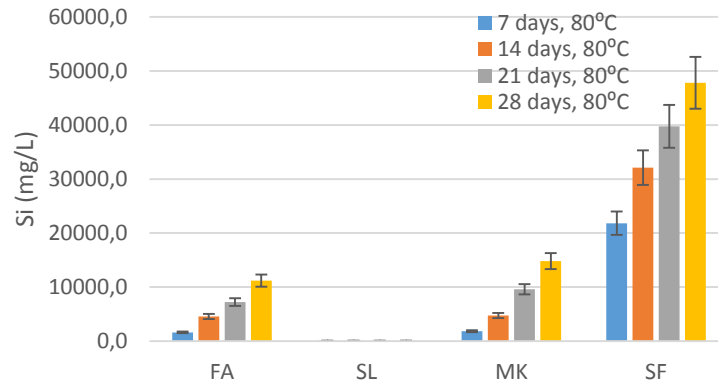

Figure 3.5: Measured concentration of silicon (Si) after 7, 14, 21 and 28 days in 1M NaOH at 80 °C
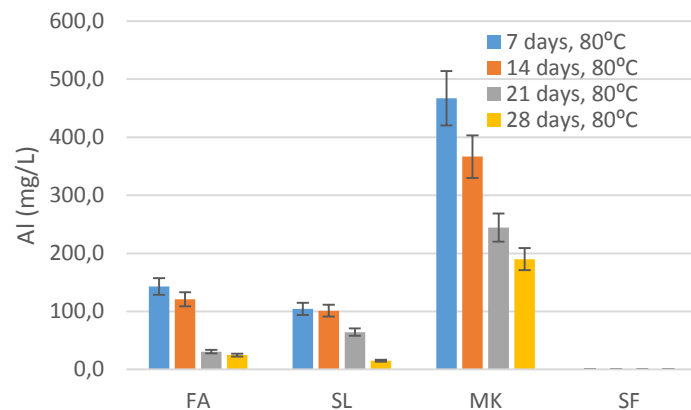

Figure 3.6: Measured concentration of aluminium (Al) after 7, 14, 21 and 28 days in 1M NaOH 80 °C

4. CONCLUSIONS

The AMBT expansion results show that the ability of SCMs to reduce expansion is as follows: SF>MK>FA>SL. That is, silica fume requiring least dosage to mitigate and slag the most.

SCMs (FA, SL, MK and SF) were immersed in 1M NaOH 80 °C for 28 days to determine concentration of soluble silicon and aluminium from the SCMs. The ability of SCMs to release Si is as follows: SF>MK>FA>SL which correlates well with the dosage required to reduce ASR expansion confirming that the release of Si from SCMs is the primary source of its efficacy in ASR mitigation.

The solid residues post SCM dissolution test were characterized. Microstructure and phase studies confirm formation of aluminosilicate hydrates in all SCMs with the exception of silica fume. This indicates that the presence of aluminium can precipitate silicon. The lack of development of a crystalline phase in silica fume was attributed to the lack of calcium or aluminate ions in solution to promote the precipitation of a crystalline aluminosilicate hydrate. Fly ash and metakaolin both formed sodium aluminosilicates (N-A-S-H) whereas, slag formed calcium aluminosilicates (C-A-S-H). This shows competitive reaction between Na^+ and Ca^{2+}, where the latter is always preferentially adsorbed. The dissolution of the SCMs and observed formation of reaction products can also be taken as a representative of systems that are: 1) rich in silicon without aluminium and calcium (silica fume), 2) rich in both silicon and aluminium (fly ash and metakaolin) and 3) rich in silicon, aluminium and calcium (slag) similar to actual hydrated cement or concrete. Under these conditions, as observed, if aluminium is

present, it will bind silicon and take either alkali cations (Na^+ or K^+) or divalent cation Ca^{2+} as a form of charge compensation. The binding of alkalis is expected to reduce the solution alkali concentration. However, if solution is saturated with calcium, Ca^{2+} is preferentially bound instead of alkali. Therefore, presence of calcium lowers the amount of bound alkali and does not appear to have a beneficial effect on ASR mitigation.

5. ACKNOWLEDGEMENTS

6. REFERENCES

[1]   V. Sirivivatnanon, D. Hocking, K. Cheney, P. Rocker, Reliability of extending AS1141.60.1 and 60.2 test methods to determine ASR mitigation, Concrete 2019, Concrete in Practice-Progress through Knowledge Sydney, Australia, 2019.

[2]   M.D.A. Thomas, Supplementary Cementing Materials in Concrete, Taylor & Francis Group, LLC, Boca Raton, Florida, 2013.

[3]   T. Chappex, K. Scrivener, The influence of aluminium on the dissolution of amorphous silica and its relation to alkali silica reaction, Cem. Concr. Res., 42 (2012) 1645–1649.

[4]   Y. Scholz, C. Hübert, K.-J. Hünger, The Influence of Supplementary Cementing Materials on the Dissolution of Aggregates in Alkaline Solutions 15th International Conference on Alkali-Aggregate Reaction (ICAAR 2016) Brazil, 2016.

[5]   M.H. Shehata, M.D.A. Thomas, The effect of fly ash composition on the expansion of concrete due to alkali-silica reaction, Cem. Concr. Res., 30 (2000) 1063-1072.

[6]   R. Snellings, K.L. Scrivener, Rapid screening tests for supplementary cementitious materials: past and future, Mater. Struct., 49 (2016) 3265–3279.

[7]   S.-Y. Hong, F.P. Glasser, Alkali sorption by C-S-H and C-A-S-H gels Part II. Role of alumina, Cem. Concr. Res., 32 (2002) 1101–1111.

[8]   M.A. Berube, J. Duchesne, Does silica fume merely postpone expansion due to alkali-aggregate reactivity?, Construction and Building Materials 7(1993) 137-143.

[9]   T. Chappex, K. Scrivener, The Effect of Aluminum in Solution on the Dissolution of Amorphous Silica and its Relation to Cementitious Systems, J. Am. Ceram. Soc., 96 (2013) 592-597.

[10]   B.R. Bickmore, K.L. Nagy, A.K. Gray, A.R. Brinkerhoff, The effect of Al(OH)4- on the dissolution rate of quartz, Geochim. Cosmochim. Acta, 70 (2006) 290–305.

[11]   R. Hay, C.P. Ostertag, On utilization and mechanisms of waste aluminium in mitigating alkali-silica reaction (ASR) in concrete, Journal of Cleaner Production 212 (2019) 864-879.

[12]   X. Feng, Y. Jia, C. Hu, Effect of Admixtures Rich in Aluminium on Expansion due to Alkali-Silica Reaction, Applied Mechanics and Materials 268-270 (2013) 806-810.

[13]   A. Brykov, A. Anisimova, Efficacy of Aluminum Hydroxides as Inhibitors of Alkali-Silica Reactions, Materials Sciences and Applications, 4 (2013) 1-6.

[14]   M. Thomas, The effect of supplementary cementing materials on alkali-silica reaction: A review, Cem. Concr. Res., 41 (2011) 1224–1231.

[15]   K.-J. Hünger, The contribution of quartz and the role of aluminum for understanding the AAR with greywacke, Cem. Concr. Res., 37 (2007) 1193–1205.

[16]   E. L'Hôpital, B. Lothenbach, K. Scrivener, D.A.Kulik, Alkali uptake in calcium alumina silicate hydrate (C-A-S-H), Cem. Concr. Res., 85 (2016) 122–136.

[17]   C. Panagiotopoulou, E. Kontori, T. Perraki, G. Kakali, Dissolution of aluminosilicate minerals and by-products in alkaline media, Journal of Material Science, 42 (2007) 2967–2973.