

Alternative Test Method for Assessing Alkali-Silica Reaction and the Efficacy of Supplementary Cementitious Materials in ASR Mitigation

Marie Joshua Tapas¹, Lionel Sofia², Kirk Vessalas³, Paul Thomas³, Vute Sirivivatnanon⁴ and Karen Scrivener⁵

¹Research Associate, UTS-Boral Centre for Sustainable Building, University of Technology Sydney

²Research Engineer, École polytechnique fédérale de Lausanne

³Senior Lecturer, University of Technology Sydney

⁴Professor, University of Technology Sydney

⁵Professor, École polytechnique fédérale de Lausanne

Abstract: This paper investigates the efficacy of supplementary cementitious materials (SCMs) in mitigating ASR in conjunction with cement with effective alkali content up to 1% $\text{Na}_2\text{O}_{\text{eq}}$ using the simulated pore solution method. The simulated pore solution method is designed to address the leaching issues in the Concrete Prism Test (CPT) and eliminate the high alkali conditions in the accelerated mortar bar test (AMBT) by making use of the 28 days pore solution alkali concentration as the basis of the storage solutions of the concrete prisms. The concrete prisms were prepared using a dacite aggregate, 2 types of SCMs (fly and slag) and cement with 0.6% $\text{Na}_2\text{O}_{\text{eq}}$ original alkali content that was boosted with alkali to increase effective cement alkali content to 0.8% and 1.0 % $\text{Na}_2\text{O}_{\text{eq}}$. Expansion results for both storage temperatures investigated (38 °C and 60 °C) show negligible expansion in all concretes with SCMs (25% fly ash or 50% slag) regardless of the alkali level in the binder. Extensive amount of cracking and ASR products were observed in concretes without SCMs consistent with the high degree of expansion observed. ASR products were also observed in concretes with SCMs, albeit less. Overall, results suggest that there is a potential to relax alkali limits when cement is used in combination with SCMs (i.e. blended cements) and that the current prescribed replacement levels of SCMs are sufficient to mitigate ASR even when used with cements of higher alkali contents.

Keywords: alkali-silica reaction, fly ash, slag, pore solution, alkalis, mitigation

1. Introduction

Alkali-silica reaction (ASR) which arises from the reaction of the reactive silica from aggregates with the alkalis present in the pore solution of the concrete may lead to expansion and deleterious cracking. To minimize the occurrence of ASR, two primary strategies are employed: 1) limiting the alkali content in the cement (0.6% $\text{Na}_2\text{O}_{\text{eq}}$ for Australian cements) and 2) use of supplementary cementitious materials (SCMs) like fly ash and slag as cement substitute.

The use of SCMs is widely regarded as the most effective and economical way of minimizing the risk for deleterious ASR [1]. The most popular test methods to assess the efficacy of SCMs in mitigating ASR are the accelerated mortar bar test (AMBT) and concrete prism test (CPT). However, despite worldwide popularity, with several countries having their own version of the tests, AMBT and CPT are both in question with respect to their ability to assess the effect of cement alkalinity on ASR expansion [2-4]. The AMBT provides a high alkali storage solution at a fixed concentration (1M NaOH storage solution), making it difficult to detect expansion differences in mortars of varying cement alkali contents [5]. CPT, which is generally accepted as the more reliable test method due to the lower temperature of 38 °C and fixed supply of alkali (cement alkali content is boosted to 1.25% $\text{Na}_2\text{O}_{\text{eq}}$), is prone to alkali leaching. The reported leaching of alkali in concrete prisms for 1 year ranges from 25-35% of the original alkali content [2, 6] and even goes as high as 45% for a 2-year test period [7]. This may result in an underestimation of expansion and consequently may indicate lower dosage of SCMs than required for effective mitigation in the field [8]; hence, the many efforts to prevent leaching and improve reliability of the CPT which, to date, remain unresolved [4, 7, 9]. Field studies, which are considered to be the most reliable, take very long time and require not only commitment but also abundant resources. For this reason, most countries, including Australia, do not have field exposure sites at present.

The low alkali limit of 0.6%Na₂O_{eq} imposed for Australian cements renders enormous amount of raw materials to be unsuitable for cement production. Since SCMs are known to mitigate ASR [1], there is then a question as to whether there is a potential to relax the cement alkali limits when SCMs are added into the concrete. Due to the reported limitations of existing ASR test methods for assessing the effect of cement alkalinity, this study uses an alternative method to assess the effect of cement alkalinity on the ability of SCMs to mitigate ASR. The test method, developed by the Laboratory of Construction Materials (LMC) at EPFL [10], makes use of simulated pore solutions to assess the efficacy of SCMs to mitigate ASR addressing the leaching issues in CPT and eliminating aggressive test conditions in AMBT (high temperature and excessive supply of alkalis). By studying the expansion of a highly reactive aggregate in combination with SCMs (fly ash and slag) using the simulated pore solution method, the aim of this study is to determine if the SCMs at recommended dosages will work to mitigate ASR when used in conjunction with cement which has effective equivalent alkali content of 1.0% Na₂O_{eq}. Alkali boosting was carried out to simulate a cement of higher alkali content.

2. Materials and Methods

2.1 Raw Materials

The aggregates were chosen from Stage 2 of the Cement Concrete Aggregates Australia (CCAA) ASR mitigation research. Table 1 lists the X-ray fluorescence (XRF) oxide composition of all the raw materials. Fly ash and slag complies with AS 3582.1 and AS3582.2 respectively. The cement alkali content is 0.6% Na₂O_{eq} and complies with SP43.

Table 1 XRF oxide composition of the raw materials

Oxide wt%	Cement	Fly Ash	Slag	Dacite
SiO ₂	19.67	59.21	34.12	68.38
TiO ₂	0.22	1.11	0.87	0.36
Al ₂ O ₃	4.78	28.11	14.37	13.25
Fe ₂ O ₃	3.10	3.68	0.30	3.32
Mn ₃ O ₄	0.12	0.11	0.36	0.06
MgO	0.91	0.53	5.31	1.30
CaO	64.18	2.48	41.59	2.35
Na ₂ O	0.33	0.63	0.35	2.41
K ₂ O	0.41	1.18	0.26	3.84
P ₂ O ₅	0.06	0.41	0.01	0.08
SO ₃	2.37	0.16	2.83	<0.01
L.O.I.	4.09	1.05	0.35	4.52

2.2 Preparation of the Concrete Prisms

Concrete prisms (70 x 70 x 280 mm) with cement content of 410kg/m³ were cast using Australian reactive aggregates, SCMs and cement. 3 concrete prisms were prepared for each mix using the same type of aggregate for both fine and coarse component keeping the water to cement ratio at 0.46 for all mixes. To simulate a cement with 1.0% Na₂O_{eq} alkali content, the cement with original 0.6% Na₂O_{eq} was boosted with 0.2% and 0.4% extra alkali by adding sodium hydroxide (NaOH) to the mixing water. The alkali was added based on the cement content and not the binder content. The SCMs were used at Australian recommended dosages for effective mitigation, 25% for fly ash and 50% for slag. The concrete prisms were demoulded after 24±2 hours and left to cure for 28 days in a high humidity environment (fog room), at 20±2 °C before being stored in simulated pore solution at 38°C and 60°C. Initial measurements were obtained using a vertical comparator before immersing the concrete prisms in the storage solution (zero hour expansion reference). The ASR expansion measurements were obtained every 28 days thereafter to monitor expansion. For expansion measurements, the concrete prisms were taken out of the climate chamber 1 day prior measurement to cool to room temperature as this ensures that the concretes are in similar conditions and therefore reduce measurement errors.

The simulated pore solution used to store the concrete prisms was prepared by copying the alkali content (Na and K concentration) of the paste system corresponding to the binder of the concrete at 28 days. Pore solution was extracted from the pastes at 28 days using a compression testing machine and analyzed using ICP-OES. Pastes were cured at similar conditions as the concretes.

2.3 Characterization of the ASR Products

The concrete specimens were sectioned and polished for microstructural analysis. The polished specimens were carbon coated to prevent charging during SEM imaging.

3. Results and Discussion

3.1 Pore Solution Extracted from Blended Pastes

Figures 1 and 2 show the concentration of different elements from the extracted pore solution at 28 days. The results are in agreement with other studies that despite the alkalis being a tiny percentage of the cement, they still dominate the pore solution [1, 11]. Figure 2 shows that the concentration of calcium (Ca), aluminium (Al) and silicon (Si) were less than 0.005mol/L which is significantly lower than the concentration for sodium+potassium (Na+K) which were greater than 0.25mol/L in all binder systems (Figure 1). Adding SCMs (25%fly ash or 50%slag) lowers the pore solution alkali concentration (Na+K). Alkali boosting (by NaOH addition), which was carried out to simulate cements of higher alkali contents, results in the increase in Na concentration with increasing level of boosting (from 0.2% to 0.4%) as may be expected. The concentration of K remains about the same at a fixed level of SCM replacement regardless of alkali boosting.

From Figure 1, it can be observed that a cement with 0.6% $\text{Na}_2\text{O}_{\text{eq}}$ (such as the one used in this study) will have about 0.45mol/L of total alkalis in the pore solution at 28 days. It is also notable that the total alkali content in plain OPC is almost equivalent to that of OPC+25%FA+0.4%alkali and over 20% higher than OPC+50%SL+0.4%alkali. This means that replacing a cement with 1.0% $\text{Na}_2\text{O}_{\text{eq}}$ with 25%FA, results in about similar pore solution alkali concentration as a 0.6% $\text{Na}_2\text{O}_{\text{eq}}$ cement while 50% slag replacement of 1.0% $\text{Na}_2\text{O}_{\text{eq}}$ cement will yield even less alkalis than 0.6% $\text{Na}_2\text{O}_{\text{eq}}$ cement. The observed effect of SCM addition on pore solution alkali concentration is consistent with literature where alkali binding is generally accepted as a fundamental mechanism of ASR mitigation by SCMs [1]. As high alkalinity in the pore solution is a requirement for the dissolution of siliceous phases of the aggregates to occur, reduced pore solution alkalinity inhibits ASR.

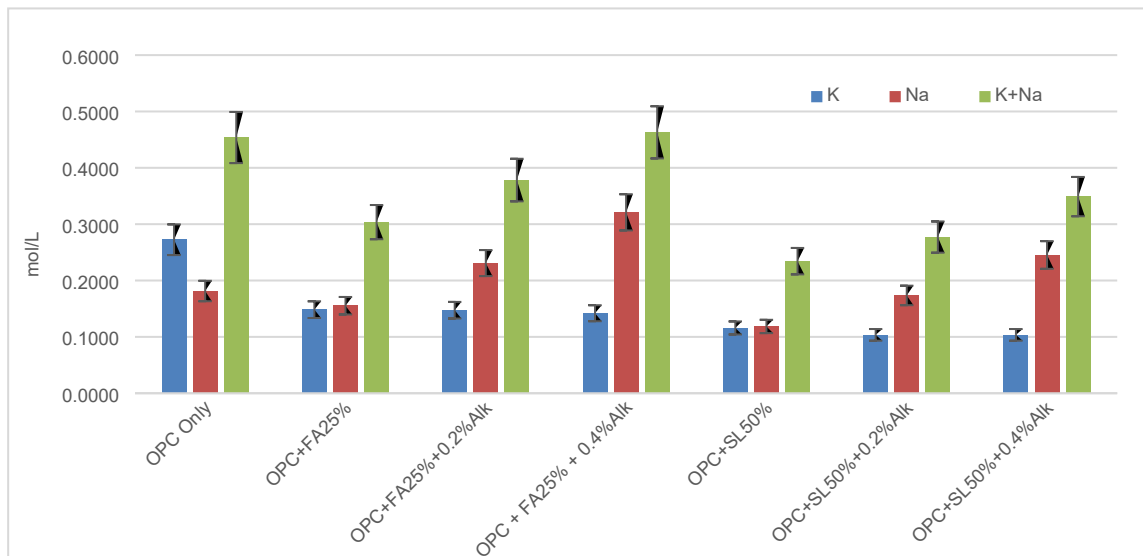


Figure 1 Concentration of alkalis in the extracted pore solution at 28 days

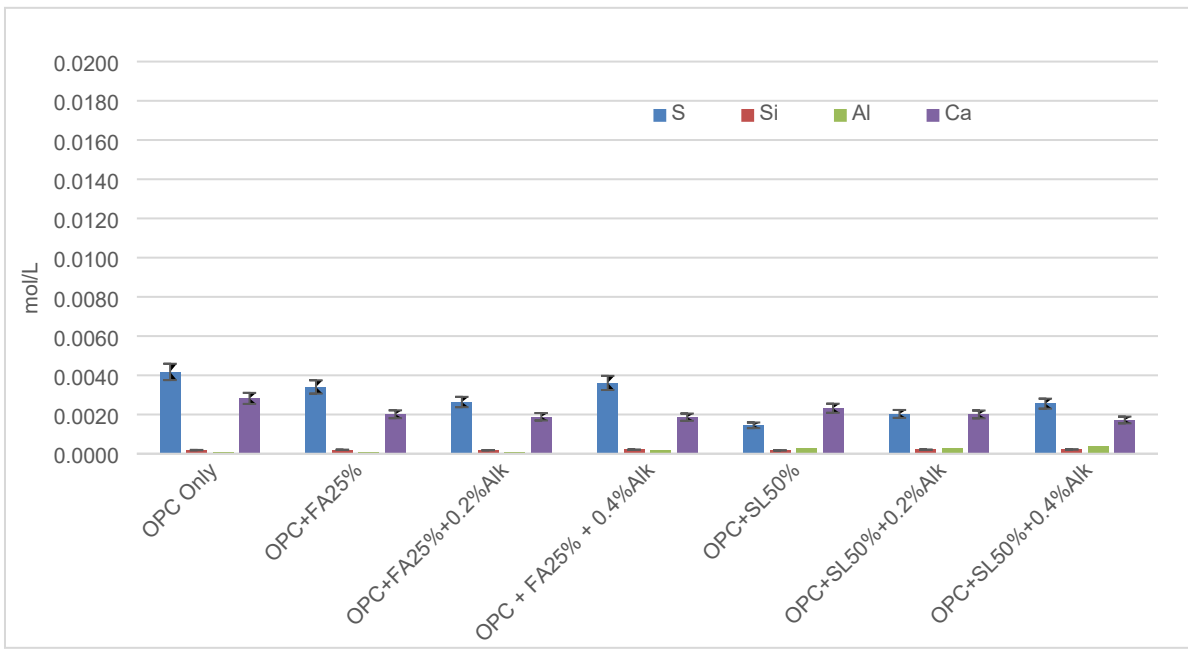


Figure 2 Concentration of calcium, aluminium and silicon in the extracted pore solution at 28 days

3.2 ASR Expansion

Figures 3 and 4 show the ASR expansion of Dacite aggregate up to 1 year for 60 °C storage and almost 2 years for 38 °C storage respectively. For both storage temperatures (38 °C and 60 °C), the concretes with SCMs (25% fly ash or 50% slag) all exhibit negligible expansion even with cement boosted up to 1% Na₂O_{eq}. There is no notable difference in the expansion rates of 0.2% and 0.4% level of cement alkali boosting for concretes with SCMs. Dacite concretes with no SCM, however, show very high expansion. The 6 months expansion at 60 °C is about 0.15% which is equivalent to about 12 months expansion at 38 °C.

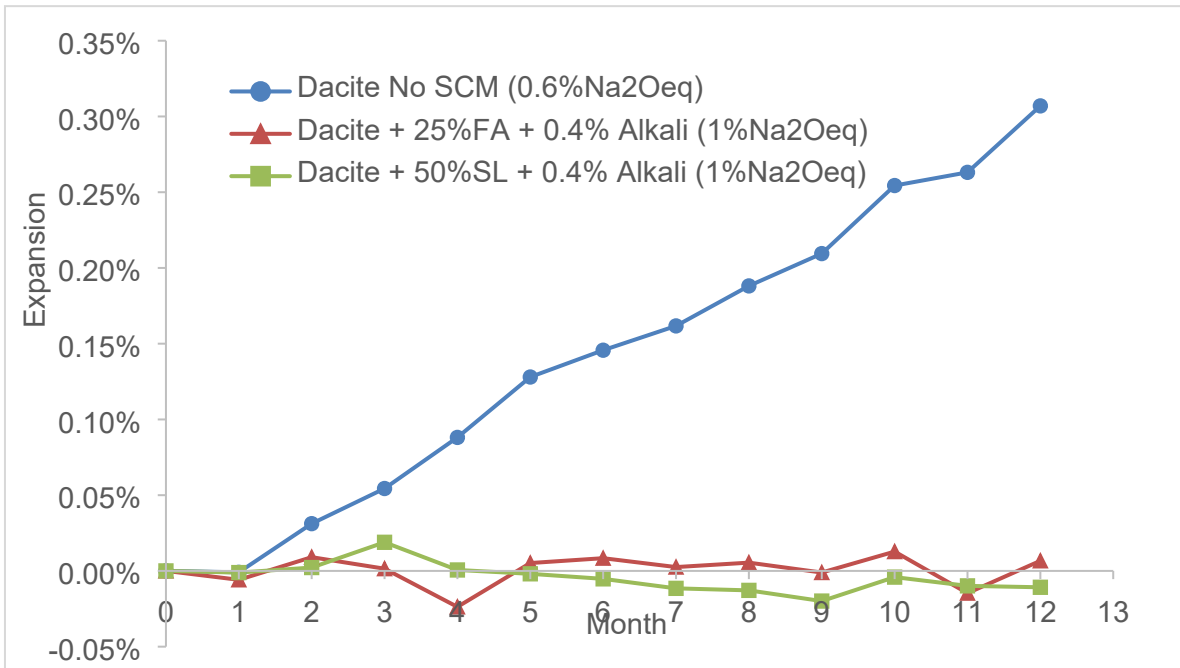


Figure 3 ASR expansion of Dacite concrete at 60 °C

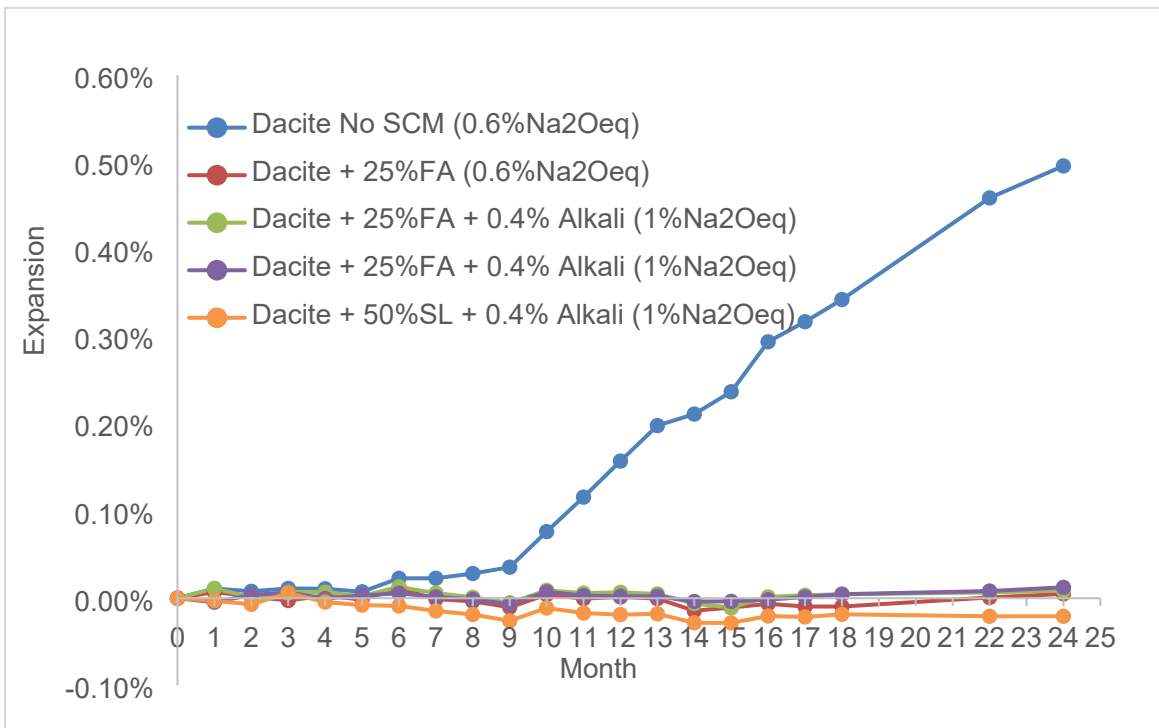


Figure 4 ASR expansion of Dacite concrete at 38 °C

3.3 Composition of the ASR Products

The concrete specimens were sectioned to analyse the ASR products. Extensive amount of ASR products were observed in concrete specimens with no SCMs as can be seen from Figure 5. Figure 6 confirms that the ASR product is mainly composed of calcium, silicon, sodium and potassium. The high concentration of sodium and potassium however notably terminates as the ASR product reaches the cement paste. The change in composition occurs because there is abundant calcium in the pore solution. As the ASR product gets closer to the cement paste, calcium replaces the alkali in the ASR product, resulting in an ASR product with much higher calcium and lower alkali [12].

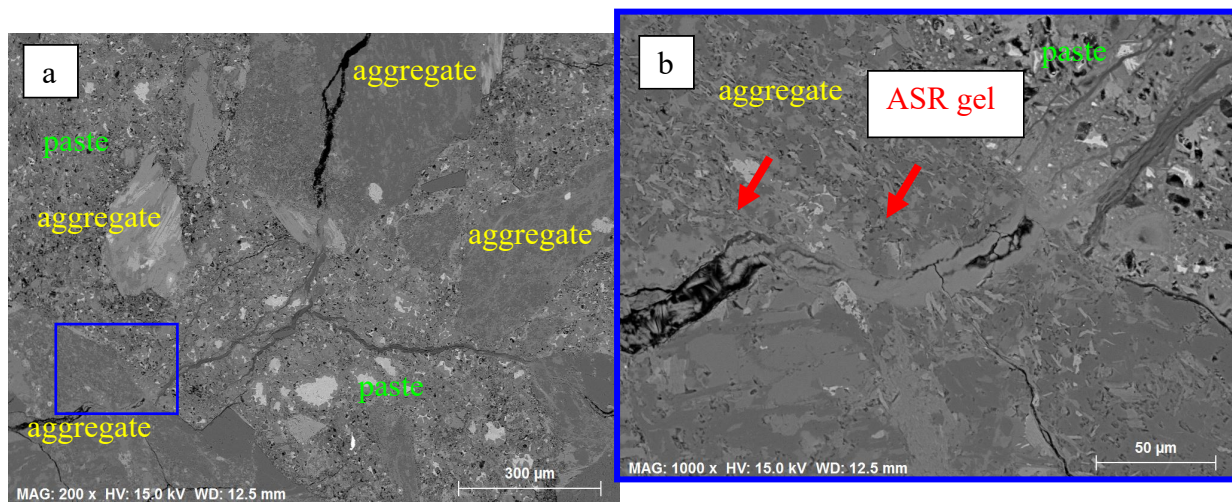


Figure 5 ASR gel found in Dacite concrete without SCM at 6 months a) taken at 200x magnification and b) at higher magnification of 1000x

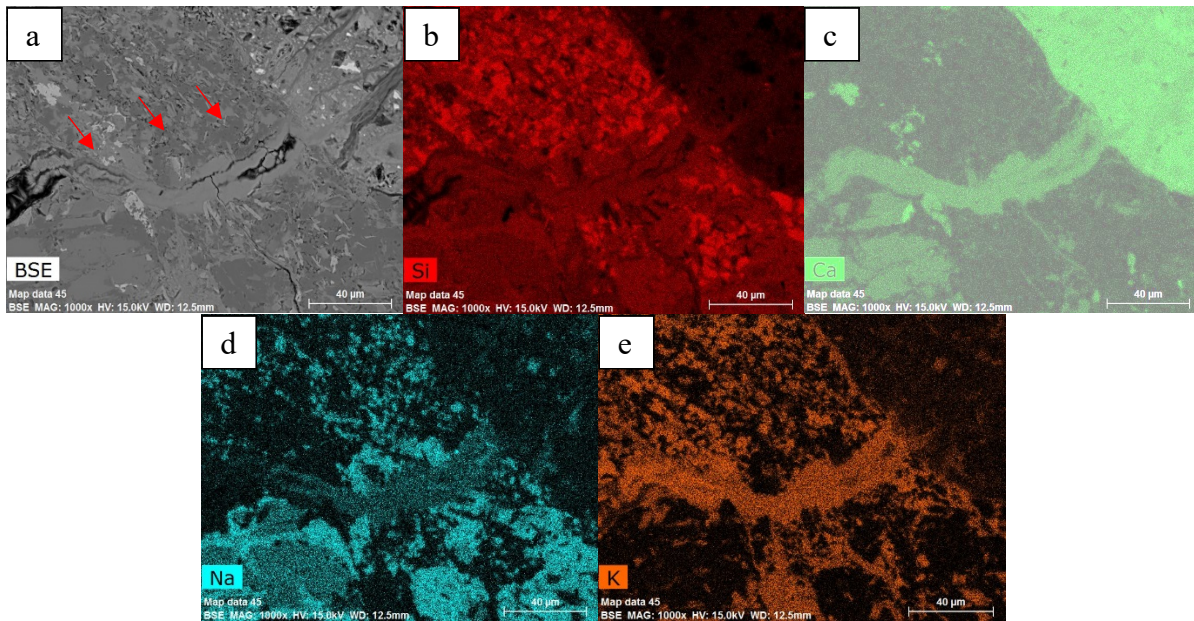


Figure 6 EDS map of the a) ASR product within an aggregate in Dacite concrete without SCM at 6 months confirming presence of b) silicon (Si), c) calcium (Ca), d) sodium (Na) and e) potassium (K)

ASR products were also observed in concrete with SCMs despite negligible expansion, albeit less. Figure 7 shows a representative SEM image of ASR product in the concrete with 50% slag. The ASR product is however notably thinner (~5 microns) in comparison to the ASR products observed in the concrete without SCM (~20 microns).

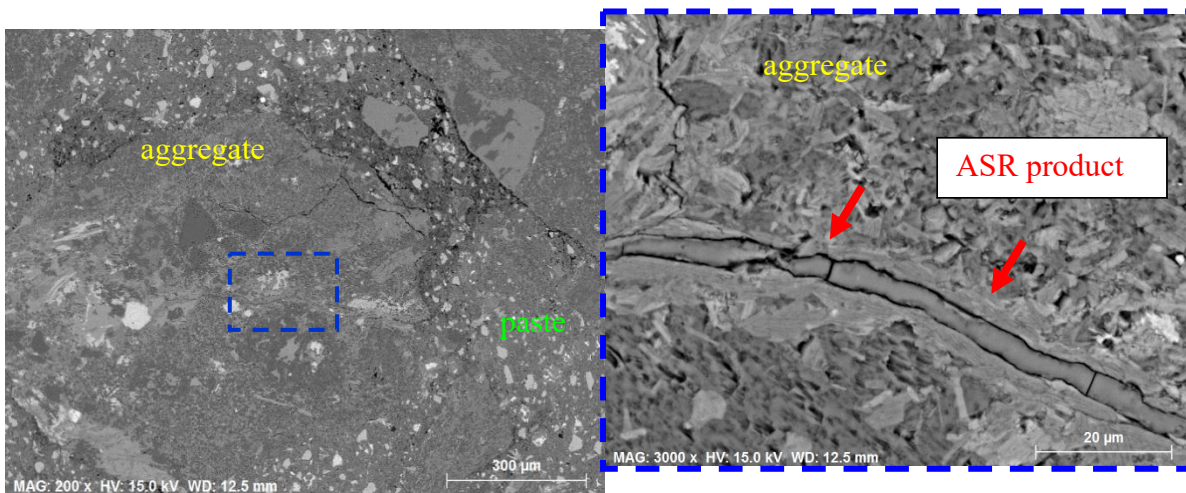


Figure 7 ASR products observed in Dacite concrete with 50% SL and 0.4% Alkali at 6 months

4. Discussion and Conclusions

This study investigated the ability of Australian SCMs to mitigate ASR when the effective cement alkali content was raised up to 1.0% $\text{Na}_2\text{O}_{\text{eq}}$ from original alkali content of 0.6% $\text{Na}_2\text{O}_{\text{eq}}$. To avoid high alkali concentration associated with AMBT, and leaching in CPT, simulated pore solution prepared based on the pore solution alkali concentration at 28 days was used as storage solution. Below summarizes the important findings from this study:

1. The measured concentrations of the 28 days extracted pore solutions demonstrate that SCMs drastically reduce the pore solution alkali concentration. Results show that a 1% $\text{Na}_2\text{O}_{\text{eq}}$ cement

with 25% fly ash replacement will have equivalent pore solution alkali concentration as 0.6%Na₂O_{eq} cement. This suggests that there may be a potential to relax alkali limits in cements used in combination with SCMs.

2. The expansion results show that, whereas, the concretes with no SCM have significant expansion after 1 year at 60 °C, the concrete mixes with SCMs (either 25% fly ash or 50% slag) has no expansion up to 1 year. These results are in agreement with the 2-year expansion results at 38 °C. Results therefore suggest that the SCM dosages currently in use are sufficient to mitigate ASR even when used with cement of higher alkali contents (up to 1%Na₂O_{eq}).
3. Results of the microstructural investigation show extensive cracking in the concrete without SCMs consistent with the high degree of expansion. ASR products were also observed in extensive quantity. The concretes with SCMs, although did not manifest expansion, also showed the presence of ASR products, albeit less.
4. Overall, results demonstrate that the pore solution method is a viable test method to assess different binder systems and may also be an effective test method for assessing cement and concrete alkali limits. Longer term monitoring as well as comparative study with field data are however necessary in order to establish the test limits for the proposed test method. Aggregates with existing field expansion data may be subjected to the pore solution method in order to derive correlation. Moreover, as the cement alkali content in this study was artificially boosted, it may be worth assessing inherently high alkali cements (>0.6%Na₂O_{eq}) in combination with SCMs to determine whether natural alkali and artificially raised alkali will have similar effect on ASR expansion and on the efficacy of SCMs in ASR mitigation.

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