

# Reactive Aggregate Fines as Potential Supplementary Cementitious Material for Alkali-Silica Reaction (ASR) Mitigation

Marie Joshua Tapas<sup>1</sup>, Elsie Nsiah-Baafi<sup>2</sup>, Kirk Vessalas<sup>3</sup>, Paul Thomas<sup>3</sup>, Vute Sirivivatnanon<sup>4</sup>

<sup>1</sup>Research Associate, UTS-Boral Centre for Sustainable Building, University of Technology Sydney

<sup>2</sup>PhD Candidate, University of Technology Sydney

<sup>3</sup>Senior Lecturer, University of Technology Sydney

<sup>4</sup>Professor, University of Technology Sydney

**Abstract:** This study investigates the ability of various reactive aggregate fines (greywacke and dacite) to mitigate alkali-silica reaction (ASR). Mortars containing reactive aggregates (greywacke and river sand) and 25% reactive aggregate powder or 25% fly ash (as cement replacement) were subjected to accelerated mortar bar test (AMBT). Blended pastes with 25% substitution levels of the reactive aggregate fines and fly ash were also subjected to thermogravimetric analysis (TG) to assess pozzolanicity as well as pore solution extraction to determine ability to reduce pore solution alkali concentration. AMBT results show that the reactive aggregate fines can mitigate ASR and even self-mitigate when used with the same type of reactive aggregate. However, in comparison with the reactive aggregate fines, fly ash still shows the highest efficacy in ASR mitigation. Microstructural characterization confirms presence of extensive cracking in the mortar with no SCMs, negligible amount of cracks in the mortar with reactive aggregate fines and absence of cracking in the mortar with fly ash. TG results confirm that the reactive aggregate fines are pozzolanic and extracted pore solutions demonstrate the ability of the reactive aggregate fines to reduce pore solution alkali concentration like fly ash. Both properties correlate with their ability to mitigate ASR.

**Keywords:** alkali-silica reaction, mitigation, reactive aggregate, fly ash, pozzolan

## 1. Introduction

Alkali-silica reaction (ASR) is a serious durability issue as it results in premature failure of concrete structures. ASR occurs due to the dissolution of reactive silica minerals in the aggregate and formation of alkali calcium silicate hydrate gel [1]. High alkali concentration of the pore solution of the concrete can facilitate the dissolution of silica. Susceptible silica phases are those with low crystallinity and many defects in the structure.

Supplementary cementitious materials (SCMs) such as fly ash and slag are typically used to mitigate ASR. The SCMs however are industry by-products and are limited in supply. Fly ash is a waste product from coal-fired power stations whereas slag is from iron manufacturing. Closure of coal-fired power stations is projected to drastically reduce the supply of fly ash worldwide. Similarly, slag is also only about 5-10% of total cement production and this amount is not sufficient considering slag is being used at higher replacement levels than fly ash.

Since SCMs are highly limited in supply and face shortage in the future, there is a need for alternative SCMs that are both economically viable and sustainable. Several potential alternative SCMs have been investigated in literature [2-7]. Agricultural by-products like rice husk ash [2, 3] and sugarcane bagasse ash [8] both showed potential for mitigating ASR. Ground glass is also another material of interest due to its impact in reducing glass waste [4-6]. It was reported that an aggregate composed of 100% glass material can be used without any deleterious consequences of ASR, provided sufficient quantity of fine glass powder is used in the mixture [6]. Some studies were also conducted on ground brick where it was found that replacing 25% of cement with ground clay brick (by weight) could significantly decrease the ASR expansion by 67% at the age of 14 days [7].

Recently, there has also been interest in reactive aggregate powders (<150 $\mu$ m particle size). Since the silica in both SCMs and aggregates reacts similarly to alkali, this means that siliceous aggregates present a potential to be used as an alternative SCM. In a study by Cyr et al. [9], it was shown that adding finely ground reactive aggregates led to a reduction in expansion as compared to the control mortar. However, although a few studies have proposed the potential of ground aggregates in ASR mitigation, there is a lack of fundamental work to characterize the mitigation mechanisms. This work aims to investigate the mitigation

mechanisms of reactive aggregate powders and whether these mechanisms are comparable to that of fly ash. AMBT was carried out by replacing a portion of the cement with two reactive aggregate powders (greywacke and dacite) and fly ash. To better understand the efficacy of reactive aggregate powders for ASR mitigation, blended pastes with equivalent replacement levels of reactive aggregate powders as the mortars were characterized for portlandite content and pore solution alkalinity.

## 2. Materials and Methods

### 2.1 Raw Materials

All the raw materials were sourced in Australia. Oxide compositions of cement, SCMs, and aggregates utilized in the study are shown in Table 1. Three types of reactive aggregates were used (greywacke, dacite and reactive river sand).

**Table 1** XRF Analysis of the cement, SCMs and aggregate

Oxide wt%	GP Cement	Fly Ash	Greywacke	Dacite	River sand
SiO <sub>2</sub>	19.67	59.21	66.85	68.4	62.93
TiO <sub>2</sub>	0.22	1.11	0.65	0.4	0.55
Al <sub>2</sub> O <sub>3</sub>	4.78	28.11	14.24	13.3	14.21
Fe <sub>2</sub> O <sub>3</sub>	3.1	3.68	3.8	3.3	4.45
Mn <sub>3</sub> O <sub>4</sub>	0.12	0.11	0.09	0.1	0.09
MgO	0.91	0.53	1.58	1.3	1.43
CaO	64.18	2.48	1.94	2.4	3.46
Na <sub>2</sub> O	0.33	0.63	4.25	2.4	4.31
K <sub>2</sub> O	0.41	1.18	3.11	3.8	1.09
P <sub>2</sub> O <sub>5</sub>	0.06	0.41	0.14	0.1	0.04
SO <sub>3</sub>	2.37	0.16	0.19	<0.01	<0.01
L.O.I.	4.09	1.05	2.29	4.1	7.08

The reactive aggregate powders were prepared by milling the reactive aggregates for 5 minutes. The ground aggregates were further sieved to ensure that all particles are below 150 µm. The particle size distribution was measured using a Mastersizer 2000 and the obtained d(0.5) and d(0.9) for fly ash is 17µm and 63 µm respectively while d(0.5) and d(0.9) for dacite and greywacke powder is both around 50µm and 120µm respectively.

### 2.2 Accelerated Mortar Bar Test

Accelerated mortar bar test (AMBT) was carried out to evaluate the effect of substituting portion of the cement with reactive aggregate powders on ASR mitigation. Mortar bars composed of 1 part of cement to 2.25 parts of graded aggregate by mass (440 g cement per 990 g of aggregate) and water to cement ratio equal to 0.47 by mass were prepared in accordance to AS 1141.60.1. The reactive aggregate powders were used at a replacement level of 25%. Mortar with 25% fly ash was also prepared for comparison.

Total expansion incurred by the aggregate after 10 days and 21 days of NaOH immersion was used to classify its ASR potential when used in the field in accordance to AS 1141.60.1. Since Australia does not have an existing standard for assessing the efficacy of SCMs in ASR mitigation, the same criteria were employed for mixes with SCMs as it is very similar to the widely accepted ASTM C1567. The classification criteria are shown in Table 2.

**Table 2** AMBT expansion criteria (AS 1141.60.1)

Mean mortar bar expansion %		Reactivity classification
Duration of specimens in 1M NaOH 80 °C		
10 days	21 days	
---	$E < 0.10$	Non-reactive
$E < 10$	$0.10 \leq E < 0.30$	Slowly reactive
$E \geq 0.10$	---	Reactive
---	$0.30 \leq$	Reactive

### 2.3 Microstructural Characterization of Mortars Post-AMBT

The mortar specimens were sectioned for microstructural analysis. The scanning electron microscope (SEM) was operated in backscattered electron (BSE) mode, 15 kV accelerating voltage and 12.5mm working distance.

### 2.4 Test for Pozzolanic Behaviour of Reactive Aggregate Powders

Paste specimens with 25% replacement levels of reactive aggregate powders were prepared using electronic mixer and cured for one day in a temperature and humidity chamber set at  $23 \pm 2$  °C, 90%RH. After one day curing, the paste specimens were stored in 1M NaOH 80 °C for 28 days. Conditions comparable to AMBT were employed to mimic the environment present during accelerated testing. Plain cement paste (OPC) was also prepared to serve as a reference. Thermogravimetric (TG) data were obtained at 1 day and 28 days.

### 2.5 Pore Solution Analysis

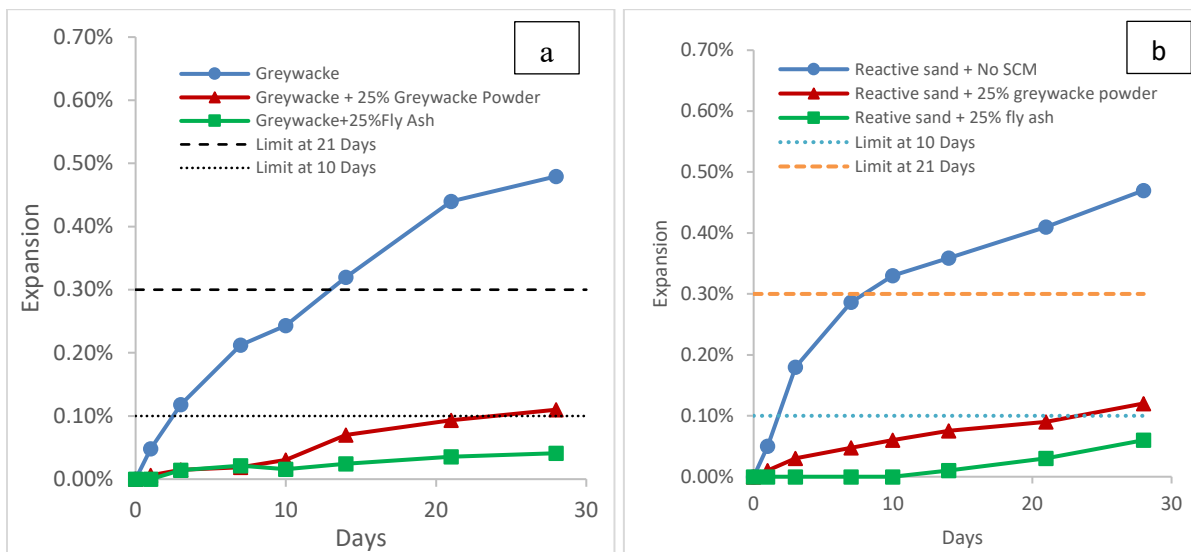
In order to investigate the effect of the reactive aggregate powders and fly ash on the pore solution alkali concentration, blended pastes with 25% replacement levels of the cementitious materials were prepared in sealed containers (200ml) at water to cementitious materials ratio of 0.47. The sealed containers were stored in a temperature and humidity cabinet at  $23 \pm 2$  °C,  $\geq 90\%$  RH. Pore solution extractions were carried out at 28 days using a compression testing machine and a force of 1000kN. All extracted solutions were filtered using a 0.2 µm membrane to remove solids and were analysed using inductively coupled plasma optical emission spectroscopy (ICP-OES).

## 3. Results and Discussion

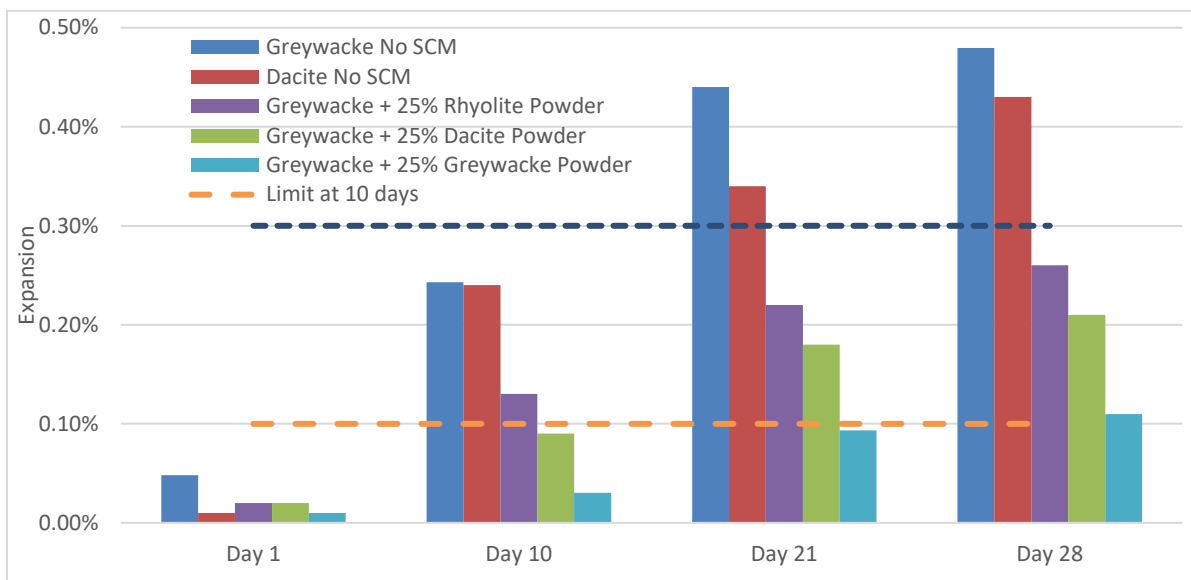
### 3.1 AMBT Expansion Results

Figure 1 shows the ability of reactive greywacke powder to mitigate ASR expansion using two types of reactive aggregate (greywacke and reactive river sand). In both cases the expansion is below 0.10% at 10 days and 0.30% at 21 days which is the non-reactivity criteria based on AS 1141.60.1. Figure 1a shows greywacke powder mitigating ASR when mixed with reactive greywacke aggregate (hence, self-mitigation) and Figure 1b when used with a reactive river sand. In both cases however, it is notable that fly ash reduces the expansion more than the greywacke powder at same level of substitution.

Figure 2 compares the ability of greywacke powder and dacite powder to mitigate ASR. Greywacke is notably better than dacite powder in reducing ASR expansion. Whereas, dacite reduces the expansion considerably, the expansion exceeds the 0.10% expansion limit at 21 days.



**Figure 1** AMBT expansion data for mortars containing Portland cement and blended cements with 25% substitution of either greywacke powders or fly ash; a) Greywacke as the aggregate and b) reactive sand as the aggregate.



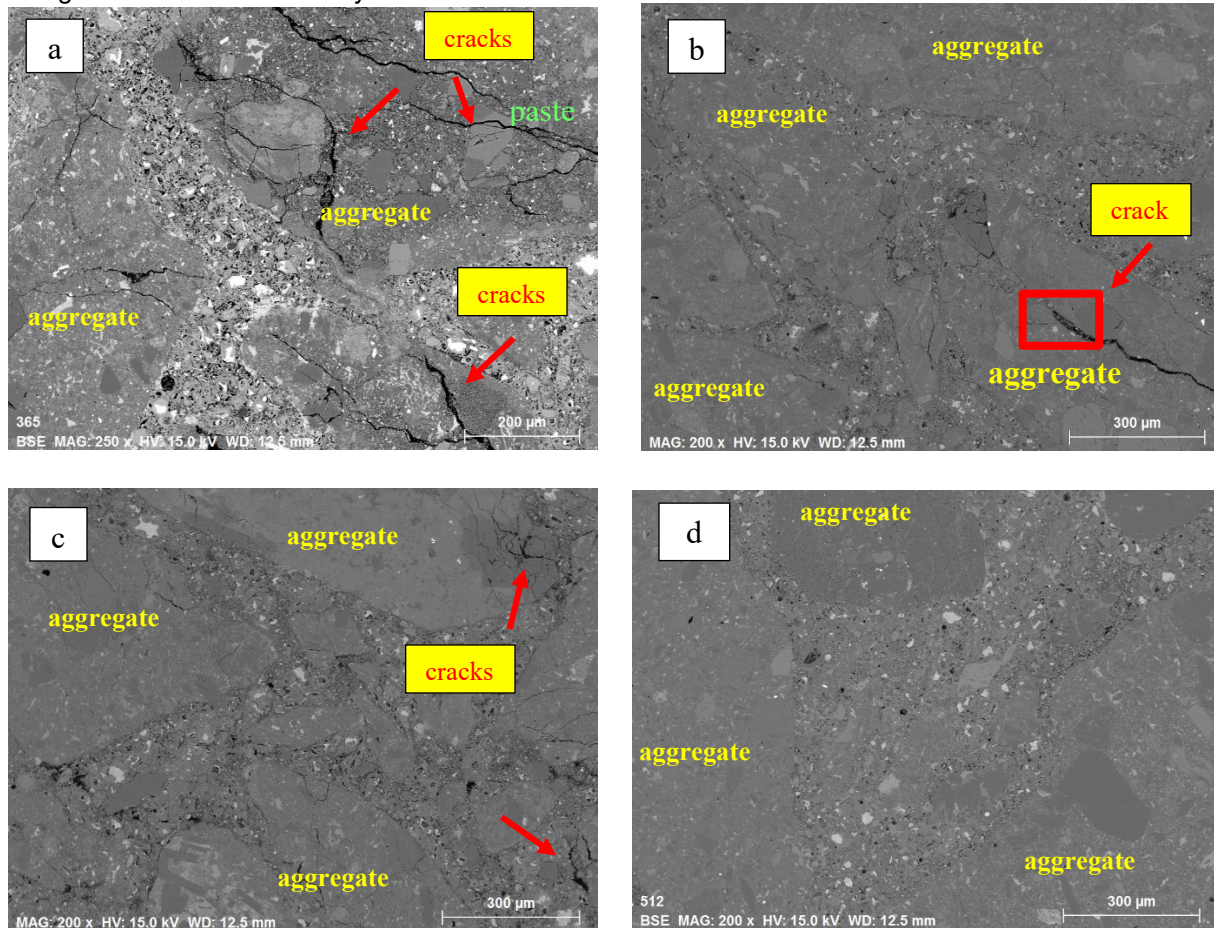
**Figure 2** Efficacy of greywacke powder to mitigate ASR in comparison with dacite powder

### 3.2 Characterization of the mortars post-AMBT

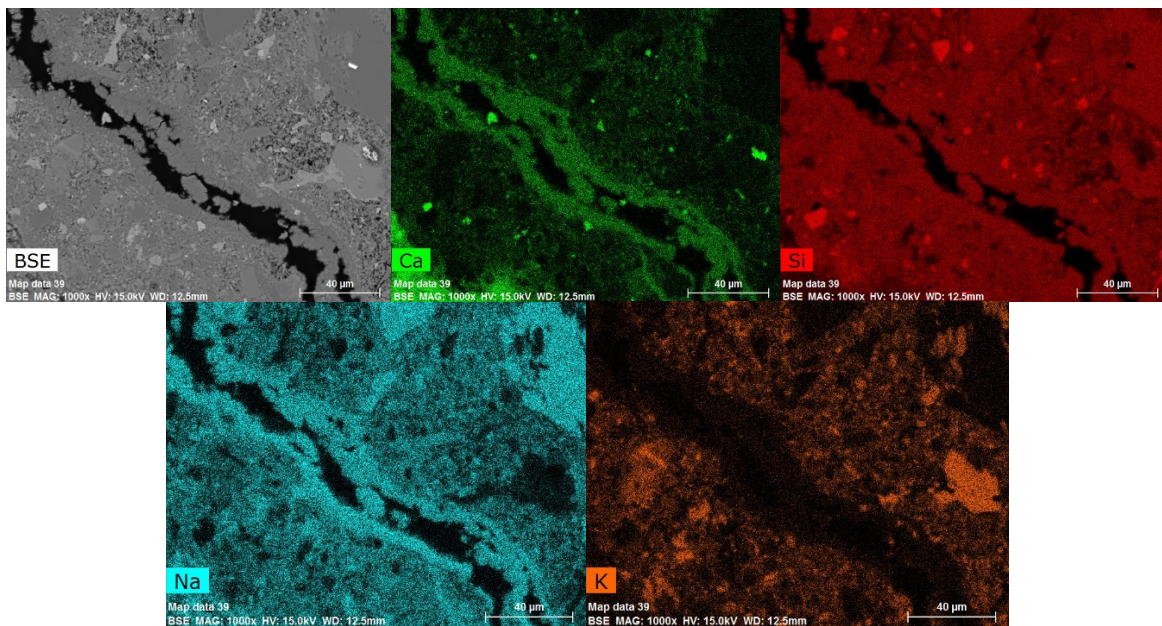
Some of the mortars subjected to AMBT have been sectioned and low magnification SEM images are shown in Figure 3. The plain OPC mortar shows high degree of cracking (Figure 3a). The presence of cracks is also notable in all sectioned mortars with aggregate powders, albeit less. This is consistent with the slight expansion observed in Figure 2a. Only the mortar with fly ash shows no presence of cracks.

Figure 4 shows the EDS map of the ASR gel found in the mortar with 25% greywacke powder. This area corresponds to the region boxed in red in Figure 3b. The ASR gel is dominated by sodium (Na), silicon (Si) and calcium (Ca). Negligible amount of potassium (K) can be detected which indicates that the pore solution is dominated by Na due to the 1M NaOH storage solution consistent with what has been reported in other

AMBT studies [10-12]. The high concentration of calcium (Ca) observed is consistent with the ASR gel being alkali-calcium-silicate hydrate.



**Figure 3** SEM images greywacke mortars containing a) no SCM, b) 25% greywacke powder, c) 25% dacite powder and d) 25% fly ash powder

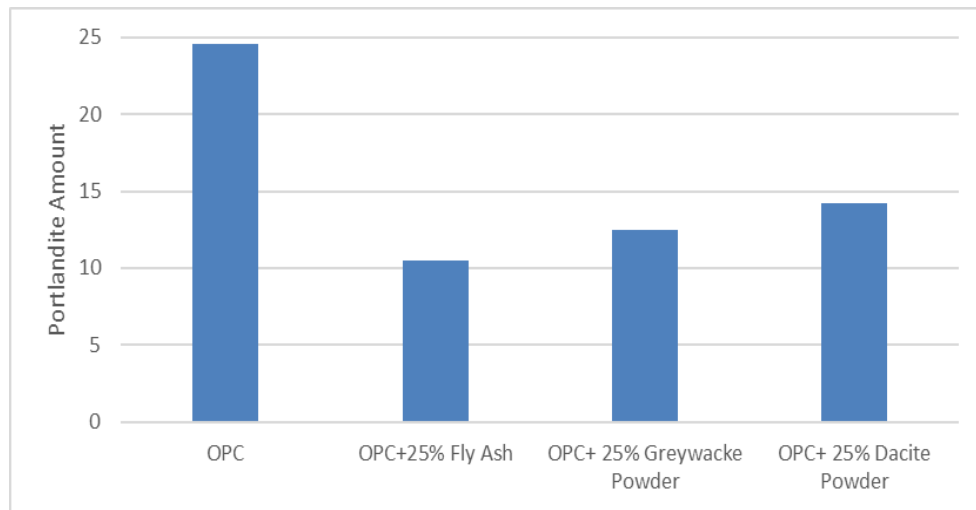


**Figure 4** EDS map of sectioned mortar+25% greywacke powder showing the elemental composition of the ASR gel (boxed region in Figure 3b)

### 3.4 Pozzolanic Behaviour of the Reactive Aggregate Powders and Fly ash

Pozzolanicity refers to the ability of an SCM to react with portlandite (a by-product of cement hydration) and produce secondary calcium silicate hydrate (C-S-H). Pozzolanic reactions which result in the depletion of portlandite in the binder (i.e. the higher the amount of consumed portlandite, the more pozzolanic), is related to the ability of SCMs to release silica into the pore solution. Figure 5 shows the amount of portlandite remaining in the pastes obtained from thermogravimetric analysis. All pastes with 25% reactive aggregate powder or fly ash replacement showed much lower amount of portlandite than reference OPC. Fly ash has the least amount of portlandite remaining followed by greywacke and then dacite.

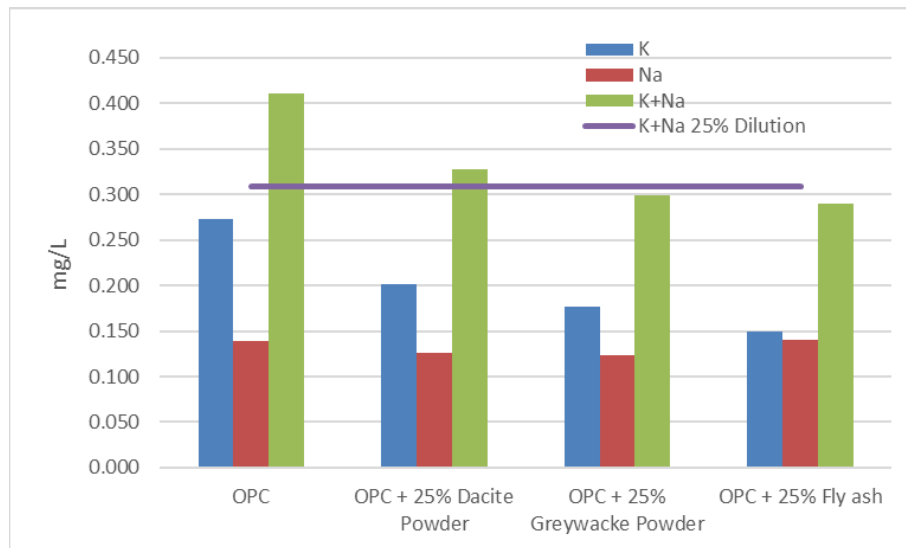
The ability of the reactive aggregate powders/fly ash to consume portlandite follows similar trend as their ability to reduce expansion. Results therefore suggest that pozzolanic materials are potential SCMs for ASR mitigation and the higher the degree of pozzolanicity, the higher the efficacy in ASR mitigation.



**Figure 5** Portlandite (CH) remaining in cement and blended cement pastes after 28 days immersion in 1M NaOH 80°C

### 3. 5 Reduction in Pore Solution Alkali Concentration

It is generally accepted that alkali binding is the primary mechanism by which SCMs mitigate ASR. Figure 6 shows the effect of reactive aggregate powders on alkali concentration (Na and K). All blended pastes with reactive aggregate powder show lower total alkali content than reference OPC after 28 days which is an expected effect of dilution. Fly ash however, demonstrates slightly better efficacy to reduce alkali in the pore solution than the reactive aggregate powders. The trend in the reduction of alkali at 28 days occurs in the following order: OPC+25%fly ash > OPC+25%greywacke> OPC+25%dacite. This order is consistent with the ability of fly ash and reactive aggregate powders to consume portlandite and reduce ASR expansion although longer-term monitoring of alkali binding is expected to provide more information.



**Figure 6** Effect of the reactive aggregate powders and fly ash on pore solution alkali concentration at 28 days

#### 4. Conclusions

This study aims to determine the ability of reactive aggregate powders to mitigate ASR and compare the mitigation mechanisms with that of fly ash. Below summarizes the important findings from this study.

1. All reactive aggregate powders investigated demonstrate the ability to reduce ASR expansion. Hence, reactive aggregates in finely ground form can behave as an SCM. Fly ash (class F and high in SiO<sub>2</sub> like the one used in this study), however, still showed better efficacy to mitigate ASR than the reactive aggregate powders. The difference in efficacy in mitigation may be due to the larger average size of the reactive aggregate powders in comparison to fly ash. This, however, remains to be further investigated.
2. Microstructure investigation confirms presence of extensive cracking in the mortar without reactive aggregate powders or fly ash. Less cracks were noted in the mortar with reactive aggregate powders and no cracks were observed in the mortar with fly ash.
3. The ASR gel observed is primarily composed of sodium, calcium and silicon. The absence of potassium indicates that in AMBT, the 1M NaOH dominates the pore solution.
4. Thermogravimetric analysis confirm that all reactive aggregate powders are pozzolanic like fly ash. The order of pozzolanicity is as follows: fly ash > greywacke > dacite. Pore solution analysis shows similar trend as the pozzolanic behaviour. Thus, the higher the pozzolanicity, the higher the alkali binding capacity, the better the efficacy for ASR mitigation. Long term monitoring of the pore solution alkali concentration is however, expected to provide more information, in particular, to the alkali release from aggregates.
5. The mechanisms by which the reactive aggregate powders mitigate ASR appear to be comparable to that of the fly ash. Moreover, the more reactive the aggregate, the more effective it is when used as an alternative SCM for ASR mitigation (i.e. greywacke is more reactive and hence more effective in mitigating ASR than dacite).

## 4. Acknowledgements

This study is a part of University of Technology Sydney research funded through Australian Research Council Research Hub for Nanoscience Based Construction Materials Manufacturing (NANOCOMM) with the support of Cement Concrete and Aggregates Australia (CCAA). This work would also not have been possible without laboratory equipment provided by Laboratory of Construction Materials at EPFL Switzerland courtesy of Professor Karen Scrivener.

## 5. References

- [1] L.D. Glasser, N. Kataoka, The Chemistry of Alkali-Aggregate Reaction, *Cem. Concr. Res.*, 11 (1981) 1-9.
- [2] S. Abbas, S.M.S. Kazmi, M.J. Munir, Potential of rice husk ash for mitigating the alkali-silica reaction in mortar bars incorporating reactive aggregates, *Construction and Building Materials* 132 (2017) 61–70.
- [3] R. Zerbino, G. Giaccio, O.R. Batic, G.C. Isaia, Alkali-silica reaction in mortars and concretes incorporating natural rice husk ash, *Construction and Building Materials*, 36 (2012) 796–806.
- [4] K. Zheng, Pozzolanic reaction of glass powder and its role in controlling alkali silica reaction, *Cem. Concr. Compos.*, 67 (2016) 30-38.
- [5] C. Shi, Y. Wu, C. Riefler, H. Wang, Characteristics and Pozzolanic Reactivity of Glass Powders, *Cem. Concr. Res.*, 35 (2005) 987-993.
- [6] K. Afshinnia, P.R. Rangaraju, Influence of fineness of ground recycled glass on mitigation of alkali-silica reaction in mortars, *Construction and Building Materials* 81 (2015) 257–267.
- [7] K. Afshinnia, A. Poursaee, The potential of ground clay brick to mitigate Alkali-Silica Reaction in mortar prepared with highly reactive aggregate, *Construction and Building Materials*, 95 (2015) 164–170.
- [8] S.M.S. Kazmia, M.J. Munira, I. Patnaikuni, Y.-F. Wua, Pozzolanic reaction of sugarcane bagasse ash and its role in controlling alkali silica reaction, *Construction and Building Materials* 148 (2017) 231–240.
- [9] M. Cyr, P. Rivard, F. Labrecque, Reduction of ASR-expansion using powders ground from various sources of reactive aggregates, *Cement & Concrete Composites*, 31 (2009) 438–446.
- [10] E. Gavrilenko, D.G.d. Amo, B.C. Perez, E.G. Garcia, Comparison of ASR-gels in concretes against accelerated mortar bar test samples, *Mag. Concr. Res.*, 59 (2007) 483–494.
- [11] S.M.H. Shafaatian, A. Akhavan, H. Maraghechi, F. Rajabipour, How does fly ash mitigate alkali-silica reaction (ASR) in accelerated mortar bar test (ASTM C1567)?, *Cem. Concr. Compos.*, 37 (2013) 143–153.
- [12] M.J. Tapas, K. Vessalas, P. Thomas, V. Sirivivatnanon, Influence of Limestone Mineral Addition in Cements on the Efficacy of SCMs in Mitigating Alkali-Silica Reaction Assessed by Accelerated Mortar Bar Test, *J. Mater. Civ. Eng.*, (2021).