

Mechanistic Role of Supplementary Cementitious Materials (SCMs) in Alkali-Silica Reaction (ASR) Mitigation

Marie Joshua Tapas¹, Kirk Vessalas¹, Paul Thomas¹, Vute Sirivivatnanon¹, Paul Kidd²

¹University of Technology Sydney

²Cement Concrete Aggregates Australia (CCAA)

Abstract: Alkali-silica reaction (ASR) can cause premature failure of concrete structures and therefore is a major concrete durability issue. The use of commonly available supplementary cementitious materials (SCMs) such as fly ash and slag is generally regarded as the most optimal and economical solution in mitigating ASR. However, the eminent closure of coal fired power stations in favour of greener technologies for producing energy and increasing demand in steel recycling threaten the future supply of SCMs that are currently available. Hence, the need to better understand the ASR mitigation process in order to be able to identify potential alternatives. This experimental study aims to provide a better understanding of ASR mitigation by studying the influence of various SCMs on ASR expansion, portlandite consumption and pore solution alkalinity. Results show that the efficacy of the SCMs in reducing ASR expansion can be correlated to their ability to consume portlandite and bind alkalis. Further, results suggest that any material that has high content of soluble Al_2O_3 and/or SiO_2 is a potential SCM for ASR mitigation.

Keywords: Alkali-silica reaction; supplementary cementitious materials; fly ash; slag

1.0 Introduction

Alkali-silica reaction (ASR), which is a major concrete durability issue, was first identified by Stanton in 1940 following a failure of a concrete pavement in California only 2 years after construction [1]. In Australia, field cases of ASR were identified only in the 1980s. The 1st case of ASR in a bridge structure was reported in 1983 [2].

ASR results when the reactive siliceous components of aggregates react with the alkaline pore solution in concrete. The reaction mechanism for ASR can be summarized as follows: 1) dissolution of silica by hydroxyl attack, breaking the Si-O-Si bonds into silanol (Si-OH) bonds; 2) binding of the sodium ions (Na^+) and potassium ions (K^+) at negatively charged sites on the silicate surface; and 3) reaction of silicate species with calcium ions in solution to form the ASR gel, alkali calcium silicate hydrate (C-(N,K)-S-H) [3]. The ASR gel is porous with a high surface area and bears many hydrophilic groups which increases its adsorption capacity and makes the gel prone to swelling [4]. Localized formation of the gel further aggravated by swelling can induce pressure build up, resulting to expansion, and eventual cracking of the concrete.

Requirements for ASR to occur include use of “reactive” aggregates, high alkali concrete pore solution as well as moisture [2-4]. “Reactive” aggregates contain silica components that are of low crystallinity or amorphous in nature and therefore reacts easily with alkali. Elimination of any of the above factors minimizes the occurrence of deleterious ASR.

The use of a non-reactive aggregate is no doubt the safest mitigation approach to prevent occurrence of ASR. However, due to geographical constraints or local unavailability, the option of using non-reactive aggregates is not always possible. Incorporating supplementary cementitious materials (SCMs) such as fly ash, ground granulated blast furnace slag, metakaolin and silica fume in the concrete mix is therefore widely regarded as the most economical means of preventing ASR. The presence of SCMs allows the use of aggregates that are otherwise not suitable for concrete structures. In Australian context, SCM mitigation means the use of fly ash and slag in concrete mixes with reactive aggregates. The use of more expensive SCMs like metakaolin and silica fume is very limited.

The required dosage for effective mitigation depends on the type of SCM. The SCMs varies widely in composition and it plays a fundamental role in their ability to mitigate ASR. The ternary diagram in Figure 1 shows the typical composition of SCMs with respect to Portland cement. Fly ash, metakaolin and slag contain both silica (SiO_2) and alumina (Al_2O_3). Slag contains them in a much lesser degree

and has much higher CaO content, leading it to behave more like cement. Silica fume is almost entirely composed of amorphous silica and therefore highly pozzolanic.

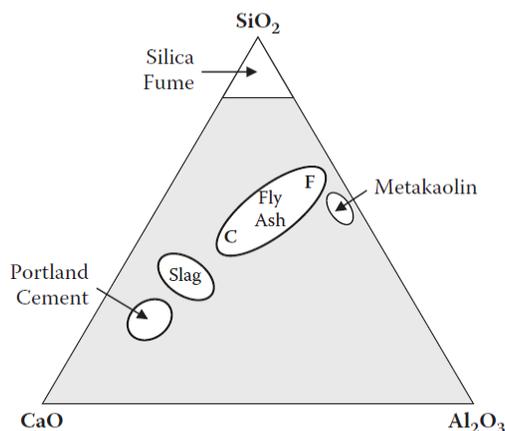


Figure 1 Chemical composition of conventional SCMs [5]

Although SCMs are proven to be effective in preventing ASR, the mechanisms behind mitigation is still a subject of controversy among researchers worldwide. Due to the foreseen scarcity of SCMs, understanding the mechanisms of mitigation is critical in order to develop basis for identifying potential alternatives. This study presents the effect of various SCMs on ASR expansion, pozzolanic behaviour (portlandite consumption) and alkali binding (pore solution alkalinity). The effect of pure Al₂O₃ addition on mortar expansion will also be presented.

2.0 Materials and Methods

2.1 Raw Materials

Four (4) SCMs; fly ash (FA), slag (SL), metakaolin (MK) and silica fume (SF) were used in the study. Oxide compositions obtained by XRF analysis are listed in Table 1.

Table 1. XRF Analysis of the SCMs

Oxide wt%	Fly Ash	Slag	Metakaolin	SiO ₂ Fume
SiO ₂	59.21	34.12	62.5	91.46
TiO ₂	1.11	0.87	1.02	0.01
Al ₂ O ₃	28.11	14.37	32.39	0.10
Fe ₂ O ₃	3.68	0.3	0.82	0.01
Mn ₃ O 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 ₂ O	0.63	0.35	0.22	0.28
K ₂ O	1.18	0.26	0.28	0.52
P ₂ O 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 ASR Expansion Test

Accelerated mortar bar test (AMBT) using various SCMs (FA, SL, MK and SF) and Al₂O₃ was performed as per AS 1141.60.1. Expansion was measured up to 28 days. Reactive aggregates used are greywacke and dacite. All raw materials are sourced in Australia.

2.3 Characterization of Blended Pastes

Blended pastes containing various SCM types (FA, SL, MK and SF) were prepared by mixing ordinary Portland Cement (OPC), SCMs and water (0.5 water-to-cementitious material ratio) and subjected to the pozzolanicity test and pore solution analysis.

2.3.1 Pozzolanicity

The paste specimens with 0%, 20% and 50% SCM replacement levels were cured for one day in 90%RH and 25°C oven and after which were stored in 1M NaOH 80°C for 28 days. The conditions comparable to AMBT was employed to mimic the environment present during accelerated testing. Pure cement paste (OPC) was also prepared to serve as a reference. Thermogravimetric (TG) data were obtained at 28 days.

2.3.2 Pore Solution Analysis

Blended pastes containing 25% replacement by mass of cement were cured for 28 days and after which were subjected to pore solution extraction. The extracted solution was acidified with nitric acid and subjected to inductively coupled plasma optical emission spectrometry (ICP-OES) to measure concentration of ions in the solution.

3.0. Results and Discussion

3.1 AMBT Expansion Results

AMBT was carried out using both industry replacement levels and at fixed dosages to compare SCM efficacy in ASR mitigation. AMBT expansion results of greywacke aggregate with different SCMs at industry replacement levels in Figure 2 show that 10% SF has comparable capacity to reduce ASR expansion to below 0.10% at 10 days and 0.30% at 21 days as 15% FA, 35% SL and 15% MK.

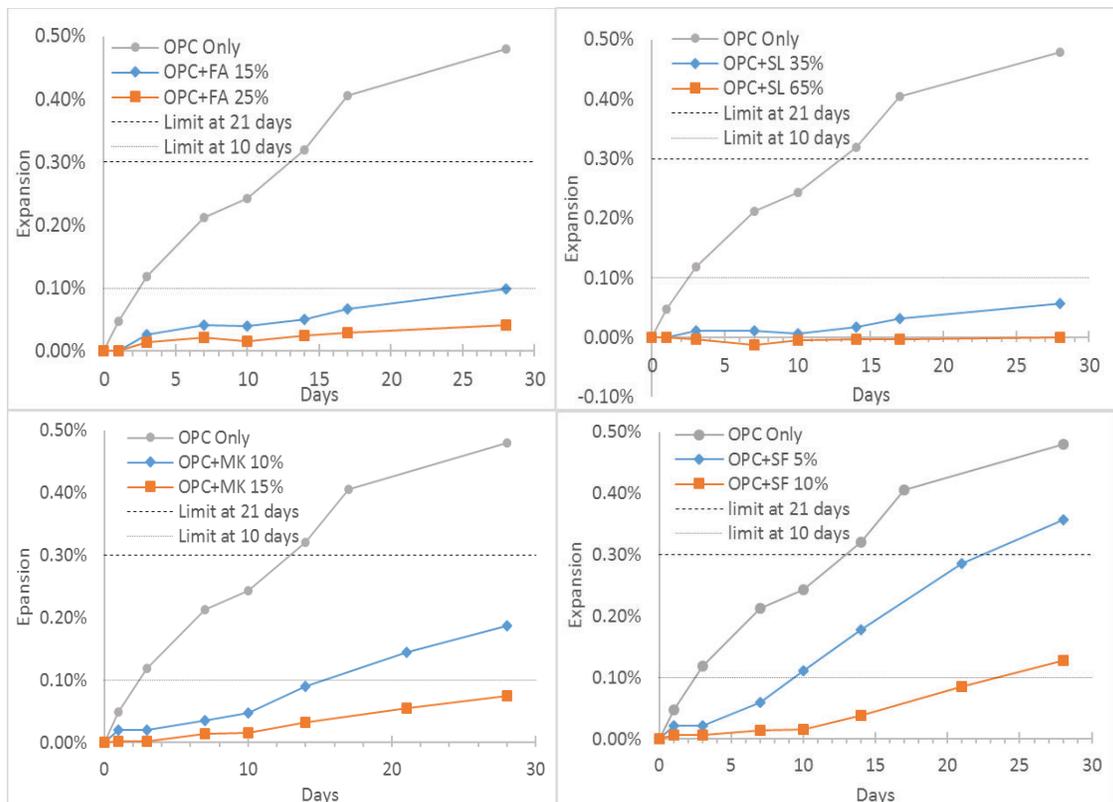


Figure 2. AMBT expansion of greywacke aggregate at industry replacement levels of fly ash (15% and 25%), slag (35% and 65%) metakaolin (10% and 15%) and silica fume (5% and 10%)

Expansion of greywacke mortar specimens in Figure 3 with 10% replacement of each SCM type showed reduction in ASR expansion in the following order: SF>MK>FA>SL. Only the mortar with slag exceeded 0.3% expansion at 21 days.

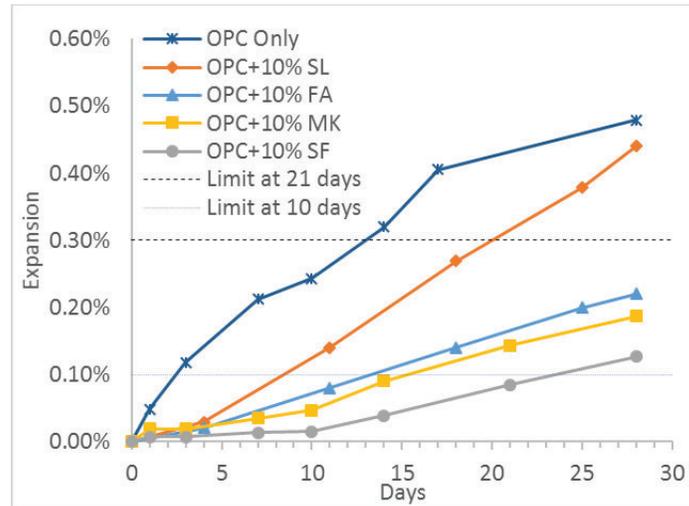


Figure 3. AMBT expansion of greywacke aggregate with 10% SCM replacement level

Observed expansion is consistent with literature where silica fume is widely accepted as the best in reducing expansion due to ASR in terms of dosage requirement, closely followed by metakaolin, Class F fly ash, Class C fly ash and then blast furnace slag [6-8]. In Australia, SA HB 79:2015 provides recommended levels of SCM replacement to mitigate ASR as follows: slag at 65%, fly ash (Class F) at 25%, metakaolin at $\leq 15\%$ and silica fume at 10%.

3.2 Pozzolanicity

Thermogravimetric analysis (TG) was used to estimate the amount of portlandite in the blended pastes. The portlandite amount remaining in the cement-SCM pastes after immersion in 1M NaOH at 80°C for 28 days, plotted as a function of SCM amount in the paste (10%, 20% and 50%) in Figure 4 shows reduced amount of portlandite in all blended systems. Moreover, portlandite further decreases as the amount of SCM replacement increases.

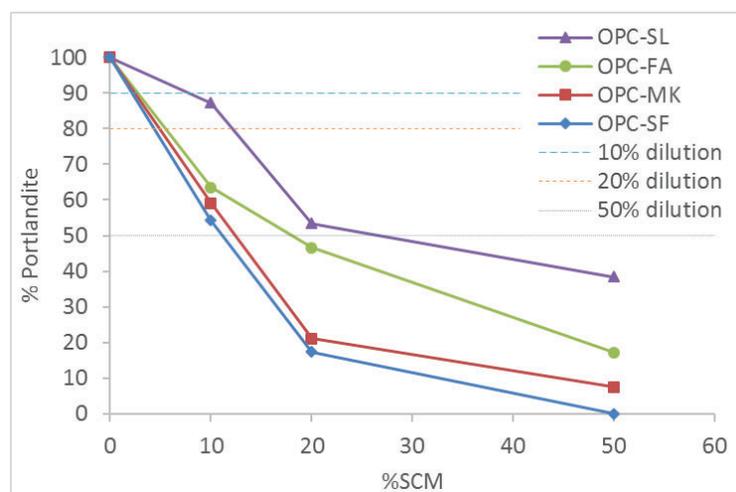


Figure 4. Portlandite content as a function of SCM type and dosage

The reduction in the amount of portlandite is a combination of cement “dilution” and of pozzolanic reactions occurring in the binder system. The observed order of portlandite consumption of the SCMs

is as follows: OPC-SF > OPC-MK > OPC-FA > OPC-SL. Silica fume being the best consumer of portlandite, with OPC-SF 50% having no more portlandite remaining after 28 days.

The pozzolonacity of an SCM is correlated to its alkali binding capacity. Alkali binding, which occurs as a consequence of pozzolanic reactions, is accepted as the main mechanism of ASR mitigation by SCMs [5]. Pozzolanic reactions consume portlandite, a by-product of cement hydration, producing hydrates with much lower Ca/Si ratio and therefore, higher alkali binding capacity. The capacity to bind more alkalis is because of the increase in the amount of acidic silanol (Si-OH) sites in the C-S-H layers that are negatively charged [9, 10]. Hence, they attract alkali cations Na^+ and K^+ from bases such as NaOH and KOH present in concrete. The sorption of alkalis increases as the volume of the silanol sites increases. Both the number and acidity of the sites increase as the Ca/Si ratio of C-S-H decrease [11].

Pozzolanic reactions are dependent on the presence of reactive 'silica' in SCMs. Silica fume, fly ash and metakaolin have high content of reactive 'silica' and thus exhibit high degree of pozzolanicity [5, 7, 12]. Higher amount of "silica" means more reactant available to react with portlandite to produce more negatively charged C-S-H.

Slag was also observed to consume portlandite but it is argued that this is not due to pozzolanic reactions but rather by hydration. Slag normally requires external supply of calcium during hydration to form C-S-H. From C-S-H perspective, slag is calcium deficient. Hence, to form C-S-H, slag in blended cements can get calcium from the dissolution of $\text{Ca}(\text{OH})_2$ [13].

3.3 Reduction in Pore Solution Alkalinity

Extracted solutions of blended pastes with equivalent SCM replacement level (25%) in Figure 5 shows that reduction of pore solution alkalinity as a function of SCM occurs in the following order: OPC-SF25%> OPC-MK25%> OPC-FA25%> OPC-SL25%. Silica fume consuming the most alkali and slag consuming the least. This result is consistent with literature where addition of 20% silica fume was observed to remove almost all the alkali ions in solution [14].

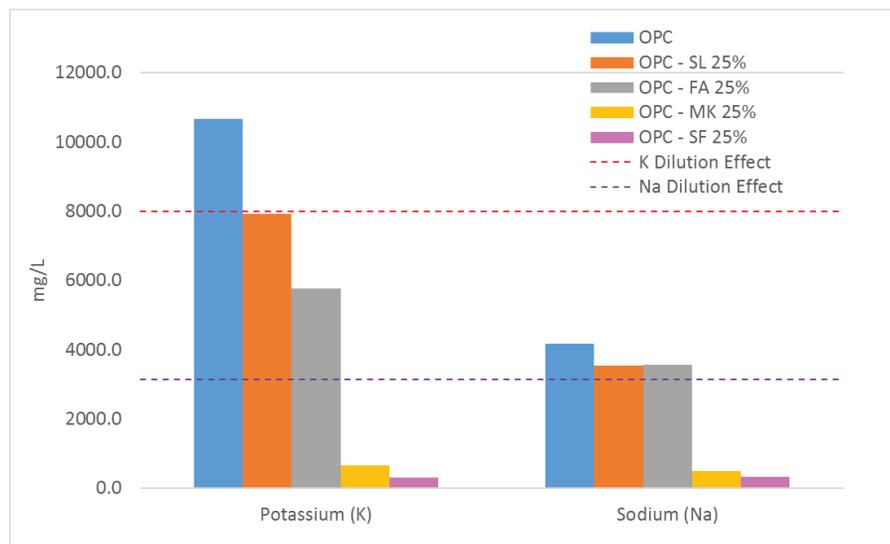


Figure 5. Effect of SCM type on pore solution alkali concentration

The effect of SCM type on the pore solution hydroxyl ion concentration correlates with pozzolanic behaviour and with the recommended SCM replacement levels for effective ASR mitigation. The higher the degree of pozzolanicity of the SCM, the higher the ability to reduce pore solution alkalinity, the lower the dosage requirement for effective ASR mitigation. High calcium fly ash and slag are the least effective SCMs for lowering pore solution alkalinity while silica fume and metakaolin are the most effective. Hence, silica fume and metakaolin generally requires lowest replacement level among the SCMs to mitigate ASR.

3.4 Role of Aluminium in ASR Mitigation

Although, the role of silicon in ASR mitigation is fairly well understood, the role of aluminium remains controversial. Figure 6 shows that replacing part of cement with 25% Al_2O_3 can actually result in significant reduction in mortar expansion. This result agrees with recent reports where the use of Al_2O_3 , $\text{Al}(\text{OH})_3$, and even aluminium pieces and powder as cement substitute can successfully mitigate ASR [15-17]. This is attributed to the dissolution control of amorphous silica through integration of $[\text{Al}(\text{OH})_4]^-$ into the silica framework which results to the formation of negatively charged aluminosilicate surface sites, repelling OH^- ions and thus limiting their attack on the silica structure [4, 18]. It has also been reported that aluminium in the SCMs can be further incorporated into the pozzolanic reactions to form C–A–S–H (also known as Al-modified C–S–H) which has enhanced alkali binding capacity [11, 19]. The incorporated aluminium in the silanol layer leads to a free negative valence, resulting in the compensation of this charge by the positive alkali ions Na^+ and K^+ .

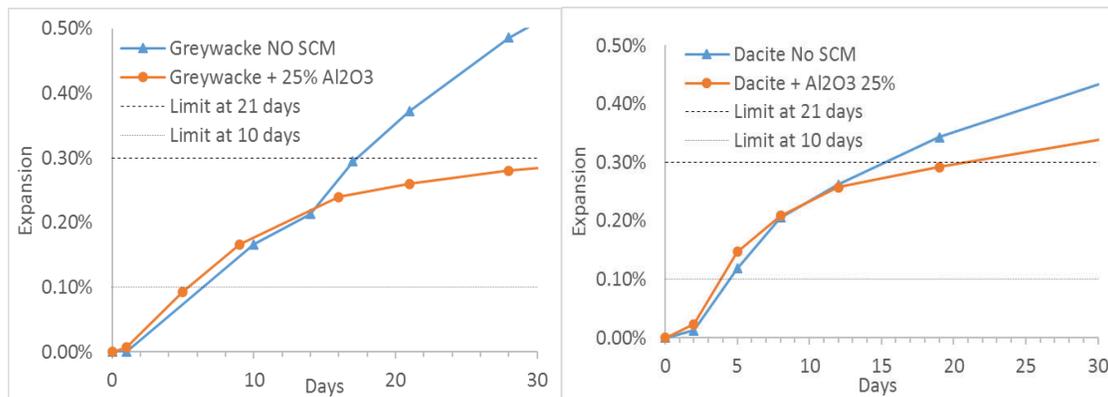


Figure 6. Effect of 25% Al_2O_3 cement substitution on ASR expansion of greywacke and dacite aggregates

4.0 Conclusions

The efficacy of the SCMs in reducing expansion due to ASR can be correlated to their pozzolanic behaviour and alkali binding capacity. SCMs rich in soluble silica are pozzolanic and higher pozzolanic activity results in the formation of more hydrates with lower Ca/Si ratio that has higher alkali binding capacity [9-11]. Thus, silica fume being the most pozzolanic demonstrates highest alkali binding capacity among the SCMs and therefore requires the lowest dosage to mitigate ASR. Slag being the least requires the most to mitigate.

A material rich in soluble aluminium also presents the potential to mitigate ASR. The ability of aluminium to mitigate is related to its ability to prevent dissolution of siliceous components of the aggregates [4, 18] and to enhance the alkali binding capacity of the C-S-H [11, 19].

The results of the experimental investigation therefore suggests that any material that has high content of amorphous (soluble) Al_2O_3 and/or SiO_2 is a potential SCM for ASR mitigation.

Acknowledgement

This paper is a part of the alkali-silica reaction research funded through Australian Research Council Research Hub for Nanoscience Based Construction Materials Manufacturing (NANOCOMM) with the support of the Cement Concrete and Aggregates Australia (CCAA).

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