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SYDNEY

Balanced alkali limit in cement for alkali-silica reaction risk-free concrete production

by Cibele Sanchez Roboredo

Thesis submitted in fulfilment of the requirements for the degree of

Master of Engineering (Research

under the supervision of Vute Sirivivatnanon and Paul Thomas

University of Technology Sydney
Faculty of Engineering and Information Technology

June 2020

C03017: Master of Engineering (Research)

CRICOS Code: 9468B

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ABSTRACT

The effect of alkali concetration on the alkali-silica reaction (ASR) is presented in the context of balance alkali content in ASR risk assessed concretes. In order to investigate the effect of alkali concetration on ASR, the reactivity of the non-reactive micro-diorite aggregate and reactive greywacke aggregate, classified by the Australian Standard AS 1141.60.2 were investigated. Slurry tests in the presence and absence of calcium hydroxide (CH), dissolution tests to monitor the rate of release of alkali, calcium, silica and aluminium ions into solution and mortar bar and paste tests were carried out as a function of alkali concentration of the immersion solution with and without the addition of the supplementary cementitious material (SCM) fly ash.

Aggregate reactivity in ground aggregate slurry tests as a function of pH and temperature demonstrated that reactivity of ASR increased with temperature, pH and reactivity of the aggregate. The relative reactivity of these aggregates was further confirmed by dissolution tests showing that the rate of dissolution of silica, in particular, increased with aggregate reactivity. The dissolution test for fly ash also showed significant reactivity with respect to the rate of silica dissolution.

Slurry tests in the presence and absence of CH showed that, in the presence of CH, the rate of reaction increased markedly, demonstrating the importance of calcium ions on ASR gel formation. Under the experiment conditions, fly ash happened to consume more calcium which indicates high reactivity. The degree of consumption of CH did not increase with pH. This lack of dependence on the pH was ascribed to diminishing solubility of calcium ions with increased pH and suggests that the composition of the ASR gel formed is dependent on the pH of the solution.

Accelerated mortar bar tests (AMBT, AS 1141.60.1) were carried out as a function of alkali concentration with and without fly ash addition. Expansion rates were observed to increase with aggregate reactivity and with pH. The addition of the Australian fly ash class F significantly reduced expansion suggesting that fly ash acts in mitigation of ASR through competitive reaction inhibiting the progression of the aggregate reaction.

Ground aggregate slurry and mortar bar and paste tests showed increased reaction with pH and reactivity of the silica components present in aggregates. Reduced alkali concentration simply reduced the reaction rate. The continuing reaction even at low alkali concentrations suggests that ASR occurs irrespective of the pH. The potential for deleterious ASR is, however,

dependent on the action of the silica gel formed on the concrete and therefore further work is required into the complete mechanism of ASR to complement the current study.

DEDICATION

I would like to dedicate my work to my parents Delmonte Roboredo and Roseli Sanchez Roboredo, to whom I owe all my achievements. Mom and Dad, I have been tremendously blessed to have you and your unconditional love and support throughout my life. I would not have any achievements in my life without your continuous support. I am also very blessed to have two lovely sisters, Carolina and Catia, who were always on my side even when so far away. Of course I have to thank my beautiful and lovely niece Valentine for the most beautiful smile in my life that always cheers me up. I always had dreams, and with my family, my dreams are becoming achievements!

I also would like to dedicate this dissertation to my forever love Gavin Russell, who supported me in this journey since the very beginning. I would not have concluded my studies without his daily support and love. He always cheers me up and never discourage me. In the most difficult moment of my life, he wiped me tears and lift me up. Thank you for being so patient and caring every day. Now we can enjoy life together!

I feel blessed every day to have the unconditional love of you all!

ACKNOWLEDGMENTS

LIST OF PUBLICATIONS

Roboredo, C., Thomas, P., Vessalas, K. and Sirivivatnanon, V. 'Alkali limit in cement with supplementary cementing materials – A review'. Paper submitted and presented at the 5th International fib Congress, Melbourne, October 2018.

Roboredo, C., Thomas, P., Boyd-Weetman, B., Vessalas, K., Farah, D. and Sirivivatnanon, V. 'Investigation of ASR reactivity through slurry dissolution tests'. Paper submitted to Concrete Institute Australia's Biennial National Conference, Sydney, September 2019.

Roboredo C., Thomas P., Vessalas K. and Sirivivatnanon V. 'Investigation of the role of alkali concentration in mortars incorporating fly ash through AMBT expansion and phase analysis.' Abstract submitted to the 16th International Conference on Alkali Aggregate Reaction in Concrete, ICAAR, in Lisbon, Portugal.

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1   Introduction

Australian manufacturing is continuously growing and according to Cement Concrete & Aggregates Australia (CCAA), more than 30 Mm^3 of concrete was produced in 2017. It is considered one of the most durable materials and cementitious structures typically have a long design life. Structures with poor durability can require substantial repairs, rehabilitation, or replacement, all with costs. Concrete is subjected to a number of changes in the environment such as temperature, moisture, aggressive chemicals and other frequent variations on exposure conditions, which can result in deteriorations and loss of durability. One of the many types of concrete deterioration that can affect durability is the alkali-aggregate reaction (AAR) which is a deleterious chemical reaction that occurs in concrete structures.

AAR was first observed during the 1920s and 1930s in California (USA), where cracking occurred in concrete structures (Stanton 1940). AAR initiates when hydroxyl ions (OH^-) in the pore solution of cementitious materials attack aggregate particles, where a complex reaction produces a gel which absorbs water, causing an expansion and potential cracking of the concrete (Ghanem et al. 2014). AAR is sub-divided by two different minerals; the alkali-silica reaction (ASR), which occurs primarily with aggregates containing reactive silica (SiO_2) and the alkali-carbonate reaction (ACR) with carbonate minerals such as dolomite ($CaMg(CO_3)_2$). ASR was recognized in 1940 when Stanton (1940) categorized one of the causes for cracking in concrete structures as related to a chemical reaction between alkalis from the cement and silica constituents of the aggregate. In 1957, ACR was identified as another type of AAR, where alkalis in the pore solution react with dolomite from the aggregates to form expansive phases which induce cracking (Fournier & Berube 2000).

ASR is the most common form of AAR (Blight & Alexander 2011) and has been identified as the cause of volume expansion and cracking in many concrete structures worldwide. There are different types of cracking that can occur in concrete structures, such as corrosion of steel rebars, drying shrinkage, plastic shrinkage and frost attack. Other causes of cracking are more common than the ASR cracking.(Fournier et al. 2010).

In Australia, AAR damage is addressed according to the guidelines described in the handbook SA HB 79, which recommends methods to reduce the risk of this type of deterioration in concrete structures. The guideline suggests first an assessment of the AAR risk based on the type of structure, the environment conditions and their interaction, followed by

an evaluation of the aggregate for potential reactivity, and lastly the application of relevant precautions to minimise the risk of this deleterious reaction. According to handbook SA HB 79, more than one hundred cases of AAR damage, among dams, bridges and other structures had been reported since 1980.

In Australia, ASR has also been reported to be responsible for the deterioration and cracking of concrete in a range of major infrastructure including dams and bridges (Shayan 1988). Currently there are no reported cases of structural failure or collapse related to ASR cracking as structures showing signs of ASR-induced cracking have been subject to remediation prior to catastrophic damage. In cases of advanced ASR cracking, a few structures have been demolished, such as the Charrest viaduct in Canada, the Alto Ceira dam in Portugal and viaducts in Netherlands and Belgium (Fernandes & Broekmans 2013). Remediation of structures due to ASR damage, therefore, has a significant economic and environmental impact.

The ASR mechanism originates with the dissolution of alkali ions from cement in the pore solution, sulphate being the predominant form as sodium salt in cement. The calcium hydroxide $Ca(OH)_2$ produced by hydration releases hydroxyl ions $(OH)^-$ to maintain the chemical equilibrium through the relative solubilities of sulphate and hydroxide, which increases the alkalinity of the solution (pH > 13) (Newton & Sykes 1987). Elevated pH in the pore solution accelerates the dissolution of reactive silica present in the aggregate. Polymerisation and precipitation of the dissolved silica subsequently results in the formation of the alkali silicate gel (Diamond 1975; Rajabipour et al. 2015). The hydrophilic ASR gel swells on the absorption of moisture and has the potential to generate stresses which can cause cracking. Important factors in ASR are therefore the availability of alkali ions in the pore solution moisture and the presence of a reactive silica (Bérubé et al. 2002). Consequently, the process of inhibiting ASR can be achieved by managing the factors responsible for ASR: elevated alkali content, reactive silica or moisture. Control of these factors greatly reduces the risk of damage due to ASR in concrete structures (Blight & Alexander 2011). Since the control of moisture is difficult to achieve in outdoor concrete structures, this study focuses on the mitigation methods related to the alkali level and the reactivity of the aggregate in the presence of supplementary cementitious materials (SCMSs).

Most reactive aggregates contain reactive forms of crystalline silica such as strained quartz. Microcrystalline silica is a major contributor after which amorphous silicas, cristobalite and tridymite contribute. The amorphous form of silica is more disordered and therefore more reactive, as they are more porous and are more permeable than the crystalline form. The Si-O-

Si bridges of the structure are partially activated and susceptible to hydrolysis, allowing the breakdown of the structure and potential production of alkali-silica gel (Meissner 1941; Savage et al. 1992). One method of inhibiting ASR is by rejecting this type of aggregate, however, a very small quantity of this non-crystalline silica (only 2%) may be enough to produce deleterious damage (Poole 1991).

A risk assessment is an important way of investigating the potential for ASR cracking related to the aggregate reactivity. Aggregates have an enormous range of composition types and a screening process is generally necessary to ascertain the mineral content and the presence of reactive silica. Petrographic analysis can determine the type of aggregate by visual assessment using microscopy, but depending on the composition of the aggregate, further laboratory testing may be required (Wigum 2012). A range of alternative testing methods are available and are used worldwide including the concrete prism test (CPT) at 38°C, the accelerated concrete prism test (ACPT) at 60°C and the accelerated mortar bar test (AMBT) at 80°C (Ideker et al. 2012). The testing period decreases as the temperature of the test increases, as higher temperature accelerates the reaction. For each of these tests the change in length over a specified time period is used to determine the reactivity of the aggregate and the potential for ASR damage (Shayan, Xu & Andrews-Phaedonos 2015).

Another approach to mitigating alkali-silica reaction is to partially replace the cement with supplementary cementitious materials (SCMs), such as fly ash, slag or silica fume in the concrete mix. These materials are industrial by-products and are widely used in concrete construction (Hooton et al. 2013). They are effective in preventing damage due to ASR by reducing the alkalis available, partially replacing the cement and binding the available alkalis from the pore solution (Duchesne & Bérubé 2001). Another advantage of using SCMs is the reduction the materials cost in construction materials. The manufacturing process of low-alkali cement increases the product costs due to higher power consumption (Ernst Worrell 2008) and considering that cement involves about 30% of the total production cost of a concrete batch, the replacement with SCMs significantly reduces the costs for concrete manufactures (Touma, Fowler & Carrasquillo 2001).

In Canada, cement with more than 0.6% Na_2O_e is approved to be used in the presence of other mitigations strategies against ASR, such as replacing cement with a sufficient amount of supplementary cementitious materials. The Canadian standard CSA A23.2-27A permits 1.15% Na_2O_e in cement, used with medium reactive aggregates (Kerenidis & Hooton 2011). A flexible approach to the alkali level is more sustainable and less expensive for the construction

materials industries than a low alkali limit (0.60% Na_2O_e) (Islam 2014; Kerenidis & Hooton 2011).

It is now clear that the acceptable alkali level in the concrete mix to prevent ASR depends on the alkali content in the cement, the aggregate reactivity, types of supplementary cementitious materials used, and also exposure conditions, therefore a comprehensive approach to the alkali content limit is necessary. It is important to perform a holistic evaluation of the alkali limit to then define the most appropriate levels. The balanced alkali content involves a consideration of the aggregate reactivity and identifying the alkali threshold, if possible, which will consequently support the identification of the alkali limits. This matter has to be addressed by understanding more about ASR and by setting the mitigation methods as well the alkali threshold and alkali limits when SCMs are used.

Studies have shown that high alkali cement can be used with a non-reactive aggregate without ASR risk, and a reactive aggregate can possibly be used in cement with an alkali level higher than 0.6% Na_2O_e using supplementary cementitious materials (Nixon, Fournier & Thomas 2016). Establishing a more flexible alkali limit for cementitious materials has already been used in Canada and the United States, where the standards outline different alkali limits according to the aggregate reactivity. Therefore, a balanced alkali limit for cement in Australia should be investigated to allow for an improved flexibility for cement manufacturers.

A more flexible alkali limit in cement has important implications for industry as the cement manufacturing process will become more economic and also reduce the environmental impact (Bérubé et al. 2002). A more relaxed sodium oxide (Na_2O_e) limit in cement will allow for a greater range of natural raw materials to be used in clinker production by allowing for the use of higher alkali content resources. These natural unprocessed materials are analysed in the quarry which may shorten their lifetimes, as one of the requirements for quarry use is alkali content. Also, as locally sourced non-reactive aggregates are depleted, it then becomes a decision based on pros and cons, to use a locally available reactive aggregate over transporting a non-reactive aggregate from some distance.

The approach to mitigating the alkali-silica reaction is to understand the whole system, including the aggregate type being used, the alkali content and the use of SCM, instead of instead of addressing these factors independently. For that reason, it is important to evaluate each particular concrete mix and assess the ASR risk.

The strict control of alkali affects the process of cement production. Many years ago it was easier to control the alkali content in cement (Uwasu, KeishiroHara & HelmutYabar 2014).

The concerns related to the quality of the environment changed cement production and now all alkali remains in the kiln dust (Nakomcic-Smaragdakis et al. 2016).

An understanding of ASR reactions for particular concrete systems is required for a holistic approach to the balance alkali threshold. The amount of alkali necessary for initiating the reaction with different reactive aggregates is unclear, although at the same time, it is essential to have this knowledge to allow for a higher alkali threshold, particularly when supplementary cementing materials are incorporated in the concrete mix. A better understanding of the mechanism and deterioration processes of ASR and also the controlling factors is necessary, so more informed choices can be made to prevent ASR reaction.

The aim of this research is to investigate the influence of alkali content and the role of fly ash (FA) as the SCM on the potential of deleterious ASR expansion caused by slowly reactive and reactive aggregates. The assessment of a balanced alkali content is required to have a flexible alkali approach and still reduce the risk of ASR through the use of available aggregates and the application of mitigation strategies such as in the incorporation of fly ash. Overall, a more flexible approach to alkali limits in concrete mixes and, hence, in the cement, would benefit the society by reducing manufacturing costs and the environmental impact. These aims were carried out by investigating the effect of temperature and alkali concentration on the reactivity of aggregates in alkaline solutions; investigating the release of cations in aqueous and alkali solutions; investigating the reactivity of aggregates and FA in an alkaline environment in the presence of CH as a co-reactant in the precipitation of the ASR gel; and lastly, investigating the effect of alkali concentration on the expansion of mortar bars.

The development of low ASR risk concretes is extremely important to improve the quality and durability of concrete production. The literature review presented in Chapter 2 of this thesis aims to provide the background for a better understanding of cement-concrete systems with respect to the susceptibility of ASR. Firstly, the reaction mechanisms and influencing factors are canvassed. Secondly, the important role of alkalis in ASR are examined. Subsequently, this chapter explores the test methods available to detect the risk of deleterious reactions in concrete and finally presents mitigation methods against ASR. The materials chosen for the investigation into alkali limits and alkali silica reactivity are Australian commercially available materials. Chapter 3 outlines the basis of materials selection and presents the results of characterisation studies carried out prior to experimentation. The following chapter, methodology, describes in detail the different techniques for the preparation of the specimens. The different types of specimens, slurries, cement pastes and mortar bars

allow this research to investigate ASR following a variety of scenarios with focus on investigating the results of different alkali levels. The results collected from the experiments are presented in Chapter 5, with discussions and reflections of each finding related to the risk of deleterious ASR in each specimen design. Finally, conclusions are presented after considering and analysing the results collected with the support of the literature. The elevated costs and increased environmental impact of alkali limits in concrete mixes with low risk for ASR imposes an extreme concern for the cement industry that can be prevented.

2   Literature review

ASR is the reaction between the alkali hydroxide in concrete (i.e. sodium and potassium hydroxide) and the chemically reactive silicates present in some aggregates. The resultant ASR is an expansive alkali-silicate gel (conventionally referred to as ASR gel) that forms inside or on the surface of aggregates and can swell and deteriorate the surrounding concrete upon water imbibition within years to decades. In Australia, the first approach to mitigating ASR is through limiting the alkali content in concrete to less than 2.8 kg/m^3. Mitigation of ASR, however, relies on understanding the relationship between alkali concentration and aggregate reactivity in order to effectively prevent the reaction using a flexible alkali content. Moreover, the study of ASR has a lot of limitations and difficulties since concrete mix design varies tremendously as a function of composition (which in turn is dictated by the aggregate and cement compositions, temperature, and the gel's age and location). In this literature review, the nature of alkali-silica reaction, ASR gel, the mechanism of swelling, aggregate reactivity and the mitigation approach are explained to support the aims and objectives of the research previously described.

2.1   Alkali-silica reaction

Alkali-silica reaction (ASR) is one of the main durability problems of concrete structures and still remains a challenging topic for construction engineers. It is a very complex phenomenon that involves the reaction chemistry which forms the expansive phases and fracture mechanics of the materials with respect to crack propagation. The alkali silica reaction is strictly the chemical reaction, however, the mechanism for ASR induced cracking of concrete is a two-stage process: firstly the formation of the ASR gel and secondly the physical action of the gel expansion on the concrete, resulting in cracking (Vayghan, Rajabipour & Rosenberger 2016).

ASR is a dissolution-precipitation process which is initiated by the dissolution of reactive silica phases present in the aggregate used in the concrete. Once the silica is in solution, it has the potential to polymerise and precipitate into ASR gel. If the ASR gel precipitated is expansive, then expansion may result in cracking of the concrete. The key points of ASR reactions are:

1. That the dissolution of silica through reaction of the reactive silica with the hydroxyl ions is present in the pore water;

2. That polymerisation and precipitation of the silica gel incorporating Ca^{2+} and alkali ions occurs;

3. That expansion of the gel leads to cracking.

2.1.1   Chemistry of the alkali-silica reaction

The alkali-silica reaction occurs in three stages to form the alkali-silica gel. In the concrete mix, the alkali ions (Na^+ and K^+) sourced mainly from cement, do not directly participate in the reaction attacking the silicates. Initially, the pH of the pore solution increases during the initial stage of cement hydration due to the hydroxyl ion released from the C_3S and C_2S dissolution. Concurrently, the dissolution of alkali ions into the pore solution is rapid and pore solution electrolyte is predominately composed of alkali ions within 24 hours of cement hydration (Diamond, Nishibayashi & Kawamura 1989). The hydroxide concentration of the pore solution is controlled by the presence of alkali ions released into the solution by the cement. Increased alkali concentration leads to increased hydroxide ion concentration. The hydroxide ions then react with the reactive silica in the aggregate. Although the pore solution content is predominantly of alkali ions, the proportion of dissolved alkalis may vary from 10% to 60% of the total alkali content of the cement (McCoy & Eshenour 1968), thus alkali ions may be consistently delivered to the pore solution maintaining or further elevating the pH with time.

In the ASR reaction of reactive aggregates with the pore solution, initially surface silanol groups react with hydroxide ions:

$$\equiv Si–OH + OH^- \text{ (aq)} \leftrightarrow \equiv Si–O^- + H_2O \tag{2}$$
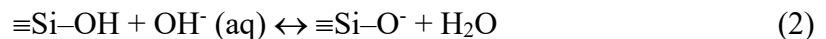
The negatively charged siloxo ions attract positively charged alkali ions (Na^+, K^+) in charge equalisation.

$$\equiv Si–O\text{-} + Na^+ \text{ (aq)} \leftrightarrow \equiv Si–O\text{-}\ldots Na^+ \tag{3}$$
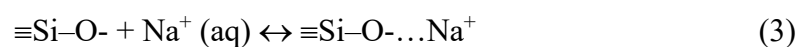
Hydroxide ions then begin to hydrolise the siloxo bridges:

$$\equiv\text{Si–O–Si}\equiv + 2\text{OH}^- \text{ (aq)} \leftrightarrow 2\equiv\text{Si–O}^- + \text{H}_2\text{O} \qquad (4)$$
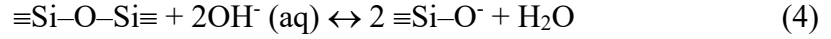
and the process of dissolution is initiated. The overall reaction for dissolution of the silica can be generalised by:

$$\text{SiO}_2 + 4\text{OH}^- \leftrightarrow \text{SiO}_4^{4-} \text{ (aq)} + 2\text{H}_2\text{O} \qquad (5)$$

Equation 5 is a generalised equation for the reaction of silica with the base resulting in complete neutralisation of the orthosilicic acid. At the high pH of the cement pore solution, the dissolution of silica forms species more likely to be SiO(OH)_3^- and $\text{SiO}_2\text{(OH)}_2^{2-}$ (Sjöberg 1996). These species are likely to undergo condensation resulting in oligomer formation (disilicates, trisilicates and cyclic species) which may then precipitate to form the ASR gel.

The reaction rate is dependent on the reactivity of the silica present and the alkalinity of the solution (Rajabipour et al. 2015). Cement pore solution is likely to be saturated in calcium ions due to the hydration of Portland cement resulting in the precipitation of CSH gel and portlandite (CH) (Nicoleau, Nonat & Perrey 2013). The presence of calcium is important for the formation of ASR gel according to many authors (Hou, Strubleb & Kirkpatrick 2004; Struble & Diamond 1981a; Thomas 2001). The supply of CH is great enough to saturate the pore solution with Ca^{2+} ions resulting in the equilibrium:

$$\text{Ca(OH)}_2 \text{ (s)} \leftrightarrow \text{Ca}^{2+} \text{ (aq)} + 2\text{OH}^- \text{ (aq)} \qquad (6)$$
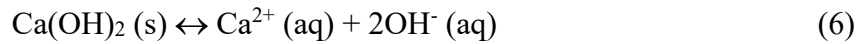
The ASR gel formation requires the presence of portlandite but it can only be generated under high silicate ion concentration as well, which will consume Ca during the reaction (Guo et al. 2019). The calcium ions play an important role in the formation of the ASR gel as they undergo ion exchange with alkali ions and promote precipitation of the silica from the solution to produce the ASR gel (Glasser 1992; Hou et al. 2005; Iler 1979):

$$2((\text{HO})_3\equiv\text{Si–O}^-\ldots\text{Na}^+) \text{ (aq)} + \text{Ca}^{2+} \text{ (aq)} \leftrightarrow$$
$$((\text{HO})_3\equiv\text{Si–O}^-\ldots\text{Ca}^{2+}\ldots^-\text{O–Si}\equiv(\text{OH})_3) \text{ (aq)} + 2\text{Na}^+ \text{ (aq)} \qquad (7)$$

9
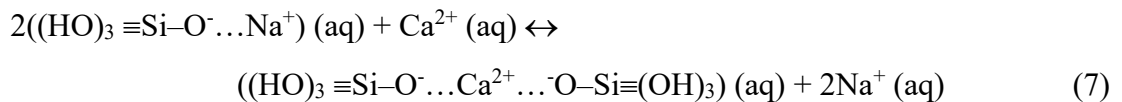
The pH level in the pore solution initially reduces as OH^- reacts with the siloxane bridges (Wang & Gillott 1991). Ion exchange of the alkalis with calcium then occurs in the gel after swelling, recycling the alkalis back into solution after the ASR gel is formed (Hansen 1944; Rajabipour et al. 2015). Ion exchange occurs because the electrostatic energy of the Ca-O bond is much stronger than the alkali bond (Na-O or K-O). Recycling of the alkali ions back into the pore solution results in an increase in the pH and promotes continuous reaction of the reactive siliceous phase (Hou et al. 2005), therefore further development of the ASR gel.

In order for the reaction to occur, the pH needs to be sufficiently high to result in hydrolysis of the Si-O-Si bridges. The pH is raised by the differential solubility of Ca(II) salts, calcium hydroxide ($Ca(OH)_2$) and calcium sulphate ($CaSO_4$). The solubility of each calcium compound can be determined from the solubility product (K_{sp}). K_{sp} is the equilibrium constant for the dissolution of a solid substance in aqueous solution under saturated conditions and is listed for $Ca(OH)_2$ and $CaSO_4$ in Table 2-1 (Masterman 1987; Menéndez & Borge 2014). The reduced solubility of calcium ions in the presence of sulphate ions results in the precipitation of $CaSO_4$ and an increase in the pH of the solution.

Table 2-1: List of solubility products at 25°C, 1 atm and the calculated concentration of calcium ions, $[Ca^{2+}]$, at saturation
(Masterman 1987; Menéndez & Borge 2014)

Salt	K_{sp}	$[Ca^{2+}]$ / M
$Ca(OH)_2$	5.13×10^{-6}	0.0171
$CaSO_4$	4.93×10^{-5}	0.0070

The alkali sulphates from the cement clinker dissolve and this dissolution raises the sulphate concentration in solution. The presence of calcium ions in solution and the lower solubility of calcium sulphate results in the precipitation of calcium sulphate (Sun et al. 2018; Yuan, Wang & Li 2010). The resulting elevated pH promotes the dissolution of reactive silica which subsequently polymerises and precipitates in the presence of Ca^{2+} and alkali (Na^+ and K^+) ions as the C-N-S-H (calcium sodium silica hydrate) ASR gel. This gel is hygroscopic and absorbs moisture from the pore water, inducing volumetric expansion of the concrete and potentially cracking (Thomas 2001).

The calcium ion solubility is supressed by hydroxide ions (OH^-) in solution due to the ionic strength of the solution. Figure 2-1 shows the calcium ion saturation concentration versus hydroxyl ion concentration at 40 °C. The ionic strength of the solution measures the concentration of ions, such as Ca^{2+} and OH^-, and explains that overall concentration of ions in solution will affect the solubility of the salts (Sastre de Vicente 2004).
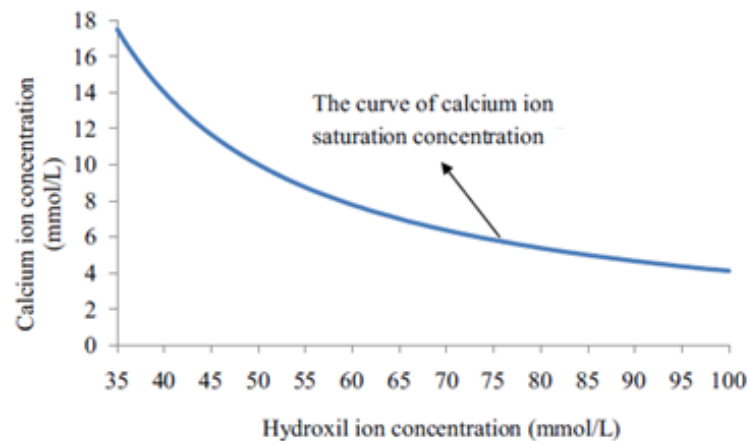
Figure 2-1: Correlation between calcium ion and hydroxyl ion concentration
(Kabay et al. 2015)

The solubility of silica (i.e. its ability to react with hydroxide) increases exponentially above pH 11. As the pore solution even in the absence of alkali ions is pH 13, the solution is unsaturated with respect to silica and so will have the ability to dissolve until equilibrium is reached. The rate of dissolution has also to be considered as the rate increases with increasing pH and is likely to be the most important factor. Some studies (Diamond 1983; Kollek, Varma & Zaris 1986) reported a hydroxyl ion concentration $[OH]^-$ of about 0.3 M which results in pH of 13.48. The data from 7 studies (Diamond 1989) Figure 2-2), show the measurement of OH^- ion concentration of 19 different cements from low-alkali to high-alkali content (0.34 to 1.31 % Na_2O_e) and reveals that even the lowest cement alkali content promotes an alkaline solution with elevated pH.
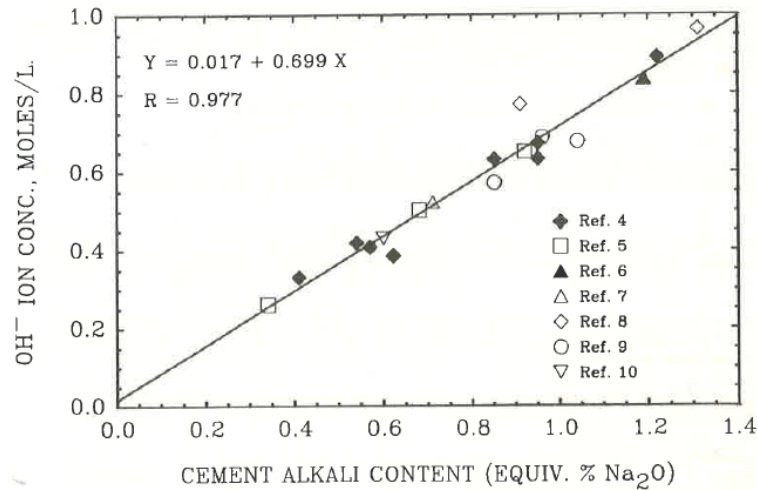
Figure 2-2: Relationship between alkali content in cement with pore solution concentration
(Diamond 1989)

The high levels of alkali and then higher pH pore solution will consequently increase the risk of ASR and potentially cause detrimental cracking. Consequently, there is a clear relationship between the alkali content available in the concrete and expansion. One study (Figure 2-3) tested alkali levels in concrete prism specimens prepared following the CPT standard test method at 38 °C and found that alkali concentration influences rate of reaction and the subsequent expansion associated with the precipitation of the silica gel (Shehata & Thomas 2000).
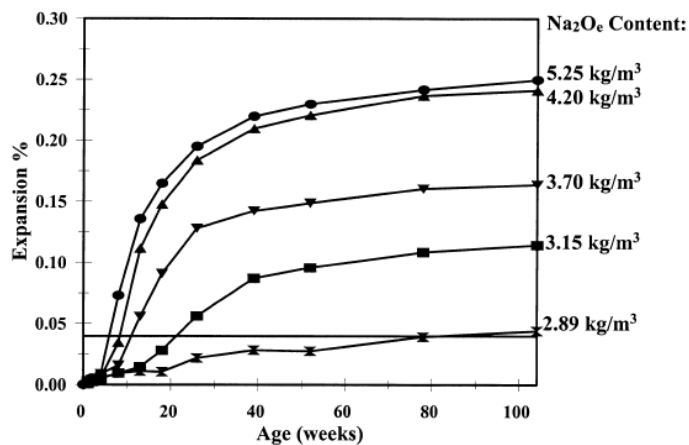
Figure 2-3: Expansion of concrete samples at various alkali contents
(Shehata & Thomas 2000)

The alkali level in the pore solution can be influenced by many factors that will contribute to the occurrence of ASR besides the materials used in the concrete mix, including

the temperature, water/cement ratio, the particle size distribution of aggregates and other exposure conditions (Kamali, Moranville & Leclercq 2008). Higher temperature increases the dissolution of most mineralogical phases found in cement binders and results in an increase in porosity within the concrete matrix. This, in turn, raises the alkalinity of the pore solution since more silica is available to interact with the hydroxyl ions (Kim, Olek & Jeong 2015). The water/cement ratio is very critical since involves the direct dilution of alkalis where a lower water/cement ratio yields a greater pore solution alkalinity. The particle size interfere the dissolution of silica from aggregates where coarse particle size can be more harmful for the reaction instead of small particle sizes. Therefore, the effect of these factors on ASR are mostly related to the participants of the reaction: reactive silica and alkalis, so they also need to be considered when investigating ASR since they can boost or delay the reaction in concrete structures. It is important to mention that these factors are manipulated during the test methods in laboratory with the intention to accelerate the reaction. Structures in the field are also affected by these factors although environmental conditions are not possible to be controlled such as the outdoor temperature and the external water available to the surface of the structure.

2.1.2   Composition of the ASR gel

The hydration of cement primarily produces the calcium silicate hydrate (CSH) which is a binding phase (Richardson 1999). The CSH composition, in particular the Ca/Si ratio, is known to depend on the water to cement ratio (w/c-ratio), the temperature, and also the composition of the cement (Escalante-Garcia & Sharp 1999). The CSH produced by the hydration of cement contain a calcium/silica ratio that can vary from about 0.7 to about 1.45 (Lothenbach & Nonat 2015). The CSH gel formed, on the other side, contains a Ca/Si ratio of 0.15–0.20 (Visser 2018).

A competition between the cations (positively charged ions) occurs to balance the negative electrical charge previously shown (Equation 7). The alkalis (Na^+ and K^+) compete with calcium (Ca^{2+}) to achieve the equilibrium, however the divalent (2+) cation calcium is preferred since it has a stronger electrostatic association (Labbez et al. 2011). The addition of SCMs form pozzolanic reaction where after the hydration of cement, more CSH phases are produced with a much lower calcium content. The composition varies significantly but it is centred on 0.1Ca:0.2Na,K:0.7S on an atom ratio bases (Garcia-Lodeiro et al. 2011).

The swelling behaviour of the ASR gel is directly correlated with the calcium, potassium and sodium content, and many studies have been conducted investigating the relationship between those alkalis and ASR gel (Chatterji 1979; Dent Glasser & Kataoka 1982; Iler 1979). Gel with high calcium levels has a lower propensity to swell (Gholizadeh-Vayghan & Rajabipour 2017), hence, it is possible to form alkali-silica gels which are not deleterious. Divalent calcium ions are capable of cross-linking and behave as network-binding, so high Ca/Si ratios (Ca/Si >0.4) will reduce the gel's potential for swelling as the ratio increases. On the other side, as the alkali concentration increases, the swelling capacity will generally increase, while the presence of calcium reduces the free swelling of the gel (Powers & Steinour 1955).

The ASR products can have different compositions and different expansive behaviour. A study suggested that cation concentration is responsible for gel formation and composition (Visser 2018). The maximum Na/Si and K/Si ratios reported are in the range of 0.3–0.5 (Lothenbach & Nonat 2015).

The concentration of the alkalis in field ASR gels which have been reported are generally is the range of $(Na_2O+K_2O)/Si_2O=0.05\sim0.6$ and $(CaO + MgO)/SiO_2 =0.0\sim0.2$ (molar ratios) (Hou et al. 2005). Hou et. al. performed a study in the field and also in the laboratory where the data collected from gels was used for comparison between both environments, and concluded that aspects like the cement paste composition and the age of the gel may significantly affect the composition of the gels and also the morphology. The swelling properties of the ASR gel are influenced by the composition of the gels (Struble & Diamond 1981b) whereas another study (Kawamura & Iwahori 2004) also found that certain gels were innocuous in terms of swelling. However, they reported that the free swelling capacity could have a high variation of between 0.5% and 81%, including gels with similar compositions.

It has been argued that the presence of calcium is essential for the formation of the gel (Bleszynski & Thomas 1998; Hobbs 2002) since the calcium aids the precipitation process, and in the absence of calcium, the alkali silicate species will remain dissolved in the solution and will not undergo gelation. On the other hand, there is evidence that the presence of calcium present in the gel composition decreases their swelling capacity, and that a calcium-rich gel can be considered as non-swelling gel (Monteiro et al. 1997; Powers & Steinour 1955). Many subjects related to the ASR gels in concrete is not deeply understood, such as the relationship between the composition, behaviour and properties, as due to lack of replication. Consequently,

it does not exist yet a substantial conclusion in regards to the contribution of calcium, sodium and initial moisture content of the gels on the swelling process.

ASR gel has a variable composition and does not contain a simple chemical balance, (Diamond 2000) therefore it becomes difficult to define a unique relationship between ASR gel composition and ASR expansion. It had been reported that gel with moderate amounts of calcium and elevated levels of alkali, i.e., Ca/Si=0.2 and Na/Si≈0.85 possibly cause the highest swelling pressure and consequently the most deleterious gel composition (Vayghan, Rajabipour & Rosenberger 2016).

Calcium ions are important for the precipitation of the gel although they reduce the expansive properties of the gel (Powers & Steinour 1955). Alkali ions on the other hand are hygroscopic, so the adsorption of water increase the volume of the product which causes the gel to expand (Berra et al. 2010). The composition of the gel is a delicate balance between calcium, alkalis and silica content. In order to have expansion the gel cannot have too many calcium ions and instead it requires the hygroscopic alkali ions. Overall the gel is a silica network where silica ions should be the predominant element.

2.1.3 ASR gel expansion

ASR gel is hydrophilic and expands when it absorbs water (McGowan & Vivian 1952) although the complexity related to this reaction leads to a gap of knowledge. The capacity of the formed ASR gel to cause stress on concrete mainly depends on the swelling capacity, which correspond to the composition of the gel, and also the restrained swelling pressure of the gel to exert and maintain the pressure (Gholizadeh-Vayghan & Rajabipour 2017; Morenon et al. 2017).

The swelling pressure created increases with time and once the internal pressure is higher than the tensile strength of the concrete, cracks occur, which damages the concrete structure (Vivian 1951). A concrete structure affected by ASR gel is demonstrated by a combination of small cracks surrounded by large cracks and for this reason this pattern received the name 'map cracking' (Hobbs 1978). The ASR damage occurs in four stages. Firstly, the gel absorbs water and expands, inducing internal stresses; secondly, the induced pressure increases and becomes large enough to cause micro-cracking around the reactive aggregate as shown in Figure 2-4a, but minimal expansion occurs; thirdly, over time, the gel slowly accumulates on the aggregate surface and expands; and finally, the internal pressure is high enough to cause substantial cracks that, with time, will grow and cause severe damage as shown

in Figure 2-4b. Thus, the expansive pressure starts with localized small cracks and slowly it develops and after years the damage becomes greater.

a)   b)
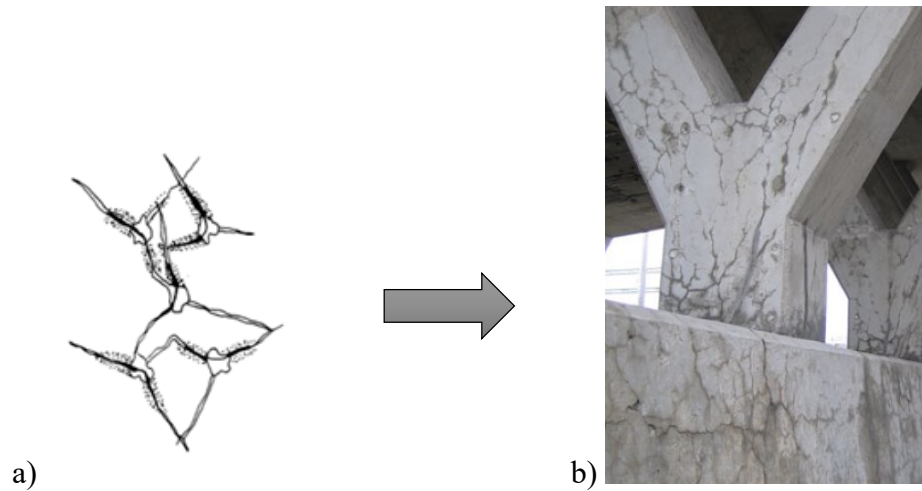
Figure 2-4: a) Observation of micro-cracking; and b) Representation of field cracking (Hobbs 1988) and (Fernandes & Broekmans 2013)

Some studies indicate that ASR gel does not flow into the pores of the cement paste due to a resilient behaviour preventing the gel from flowing and consequently the gel is formed around the aggregate surface (Diamond 1975; Glasser 1979; Ichikawa & Miura 2007). As shown in Figure 2-5, cracking in cement paste can occur without ASR gel flow in the surrounding concrete due to the excess of internal pressure.
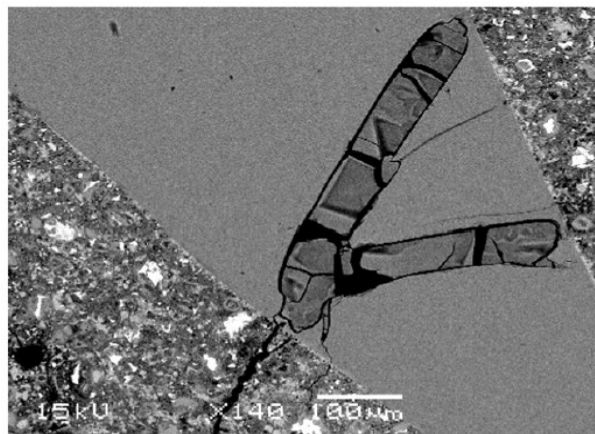
Figure 2-5: Microcracking by ASR gel
(Vayghan, Rajabipour & Rosenberger 2016)

The formation of the gel by itself is not dangerous as previously mentioned, but it is the expansion capacity and swelling pressure of the gel that determines whether the safety of the concrete is compromised. The formation of innocuous sodium-rich gels that can flow enough to diffuse into the pore space or micro-cracks of the cement paste without exerting any significant pressure on their surroundings have been reported (Ramlochan, Thomas & Gruber 2000).

Expansion Mechanism

The mechanism of ASR gel expansion is not completely understood. It is however generally established that an osmotic pressure is generated upon moisture adsorption, which affects the surrounding cement paste and aggregate, resulting in cracks and ultimately expansion of the structure. Currently, three (3) mechanisms are theorized on the expansion of ASR gel. These are described as (a) the Power-Steinour theory (b) the Chatterjee's theory and (c) the Diffuse double layer theory; the most common of the 3 being the Power-Steinour theory. This hypothesis evolves around the availability of calcium. Furthermore, it suggests that for amorphous (porous) silicate aggregates, When Ca^{2+} concentration is low, an increase in the formation of ASR gel within the aggregates occur, resulting in an discharge of gel from the reaction site (Pike 1958)

On the other hand, Chatterji's theory (Chatterji et al. 1986) proposes a supposition stating that, at constant pH and ionic strength, absorption of OH^- ions decreases as the size of the associated hydrated cation (K^+, Na^+, Ca^{2+}) increases. These OH^- absorbed cations will then penetrate into reactive silica to attack the siloxane bonds as discussed earlier. The authors further explain that, this attack removes silica ions from their original sites and thus enables more diffusion of silica from the aggregate grains; a process controlled by the presence of Ca^{2+}. At higher Ca^{2+} ion concentration, the diffusion of SiO_2 is reduced. Ca(OH) thus promotes the penetration of reaction ion molecules (including H_2O) into the reactive grain, and delays diffusion of silicate ions. In this way, when there is a surplus of amount of reaction ions penetrating the reactive silica to the amount of silica leaving the grain, expansion occurs.

The diffuse double layers (DDLs) theory proposed by Rodrigues, Monteiro & Sposito (1999), cited electrostatic repulsion between a DDLs formed, as being responsible for generating expansive forces. Negatively charged cement hydration products react with increasingly highly negative surfaces of amorphous silica in some aggregates, by an exchange of electrical charges (Chatterji & Kawamura 1992). Owed to their combined negatively charged states, resulting in a highly negative gel, cations are attracted and as a consequence an

electrical double layer of positive charge is formed. This layer; also known as the Gouy-Chapman –Stern layer (Oldham 2008), is thin and derived from the ionic strength of the pore solution electrolytes. The DDLs formed is essentially part of a colloidal system composed of dissolved silicate particles surrounded by a diffusion layer of cations with anions dispersed in the pore solution, therefore, the expansion of the gel is determined by the particle-particle interface.

When a concrete structure is exposed in dry condition, the gap between the sol (colloidal) particles is reduced until a maximum attraction energy is achieved such that it overpowers the repulsive electrostatic forces, and a gel is formed. However, at high humidity, layers of water molecules adhere to the particle surfaces thus increasing the distance between the particles and consequently increasing the repulsive electrostatic force over the attractive energy, resulting in the expansion of the gel.

2.1.4   Reactivity of aggregates

Aggregates are complex minerals with a range mineralogical phases including a range of silica phases. Reactive aggregates contain silica formed from strained quartz which is a crystalline silica type (Figure 2-6 a) or amorphous silica forms (Figure 2-6 b). There is a range of different structures in between these two types (Poole 1992). The non-crystalline silica structure (amorphous silica) is classified as the most reactive aggregate type since amorphous silica has a large surface area and is more porous than the crystalline silica form (Poole 1991). The mineral constituents of reactive aggregates are typically opal, chalcedony, cristobalite and tridymite, in order of decreasing reactivity (Hobbs 1988).

Some crystalline silicas such as cryptocrystalline, microcrystalline, or strained quartz may also cause ASR, however the degree of reaction is much slower, taking a longer time to induce damage, and requiring a much greater quantity than amorphous forms of silica (Iler 1979).
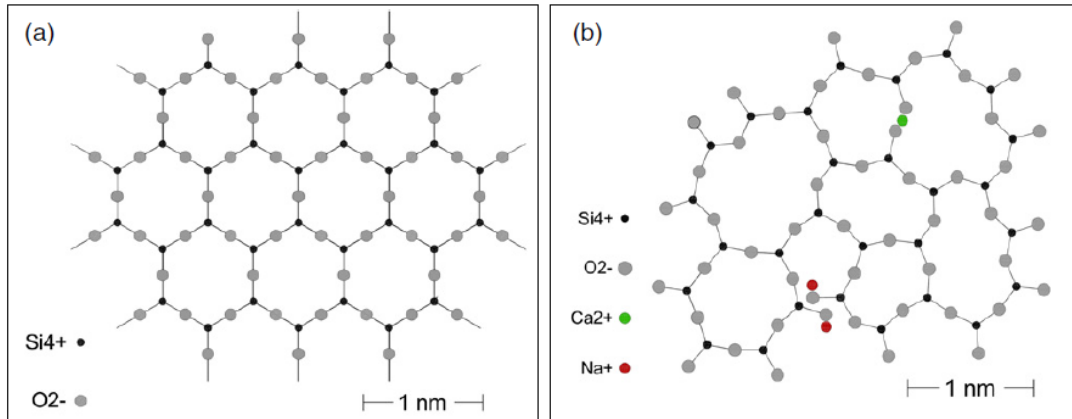
Figure 2-6: silica structure (a) crystalline; (b) non-crystalline
(Rajabipour et al. 2015)

A critical influence of ASR reactivity is the dissolution rate of silica which is effected by the mineral surface area, the temperature and the environment conditions in the pore solution (Bellmann et al. 2015). The amount of reactive siliceous aggregate is critical for ASR expansion since this is going to determine the aggregate reactivity. However, it should be noted that the worst damage will occur at a certain percentage of reactive silica, but beyond that, the expansion will actually decrease, and this is the pessimum effect (West 1996), as shown in Figure 2-7. After exceeding the pessimum level of the aggregate, the expansion proportionally decreases as the percentage of reactive silica increases (Ichikawa 2009).
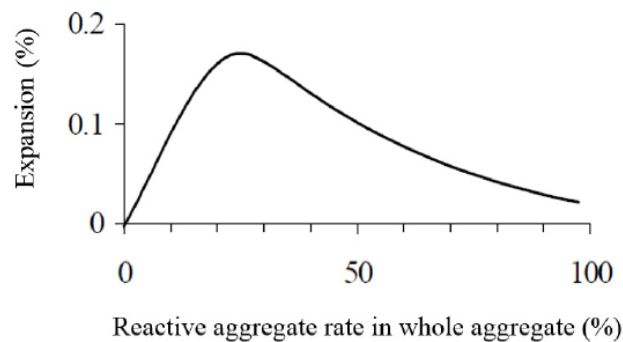
Figure 2-7: Effect of reactive silica content on ASR expansion
(West 1996)

It is important to remember that the critical amount of reactive silica for ASR expansion will be different according to the aggregate type (Binal 2015), since different silica structures result in the different pessimum content. A comparison between opal and chert aggregate in

Figure 2-8 shows that 20% of opal is the pessimum level which causes the highest level of expansion but half of that amount is required for chert.
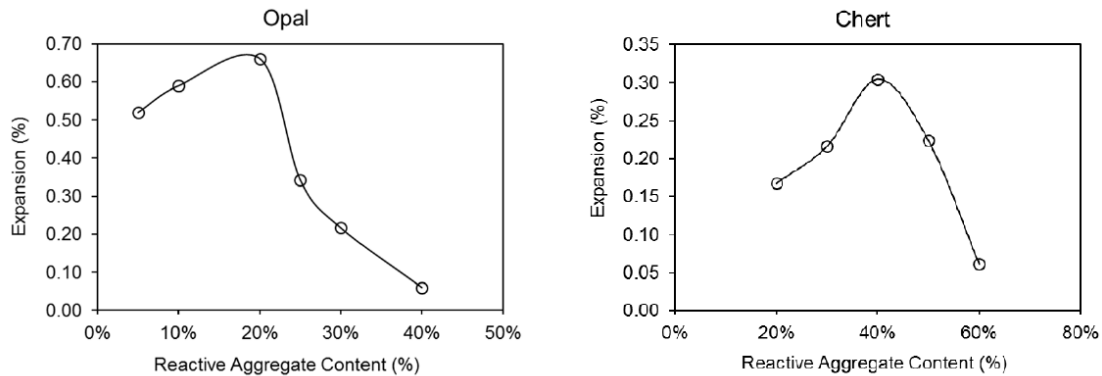
Figure 2-8: Effect of pessimum ratio of opal and chert on expansion (Binal 2015)

Damage caused by ASR expansion is also dependent on the mineral particle size (Diamond & Thaulow 1974; Multon et al. 2010) as the same reactive aggregate may present different ASR expansion depending on the particle size (Dunant & Scrivener 2012). Coarse particles (1.25–3.15 mm) increase the propensity of particular aggregates to form deleterious ASR up to seven times greater than fine aggregates (80–160 μm) (Multon et al. 2007). Specimens prepared with 10% more coarse aggregate following the CPT laboratory method had an significant increase on the expansion up to 50% compared to the standard specimens (Gautam et al. 2017). Accordingly, fine particles have been reported to have a minimal influence on ASR, when below 180 μm (Stanton 1940) and this is probably due to a behave similar to an SCM. In contrast, a study showed that large particle size (5-10 mm) induced less expansion at early ages when compared to fine aggregates (Zhang et al. 1999), but it continuously increases with time. For this reason, the rate of delivery of silica to the solution is important as a high delivery degree will lead to ASR throughout the concrete. At the pessimum, the rate of delivery is commensurate with the rate of formation of deleterious ASR gel which can cause expansion and cracking.

Aggregate size is an essential physical feature, so for this reason it is one of the parameters required for laboratory test methods to evaluate aggregate reactivity and detect potential deleterious reactions. Based on the relative reactivity due to particle size, a deviation of 10% on the grading of reactive coarse aggregate could result in more than a 50% increase in concrete expansion compared to concrete with a standard grading (Gautam et al. 2017), therefore, results obtained in laboratories can be considerably different to those from field tests.

2.1.5 Alkalis sources

Alkalis are one of the fundamental elements necessary for the formation of the ASR gel. Alkalis are naturally present in the raw materials necessary for the production of cement clinker (e.g. mica and clay) and are mostly present as alkali sulphates (Sun et al. 2018), where sodium (Na^+) and potassium (K^+) are the main alkali ions present in the pore solution of concrete materials (Shehata & Thomas 2006).

Since the first report about ASR, it was suggested that limiting the alkali content, specifically in cement, would be effective in preventing cracking since the reaction is inhibited below certain alkali concentration thresholds (Leming & Nguyen 2000). The alkali content in cement and concrete is represented by sodium oxide equivalent (Na_2O_e) which assumes that the behaviour of potassium and sodium ions in solution are equivalent as shown in Equation 1:

$$\text{Sodium equivalent } (\%Na_2O_e) = \% \ Na_2O + 0.658 \ \% \ K_2O \tag{1}$$

The alkali content in cement generally ranges from 0.2 – 1.1% by weight of oxide. Since 1940, the American standard specification for Portland cement (ASTM C150 2017) established an alkali limit in cement of 0.60% Na_2O_e which was initially adopted around the world to prevent alkali-silica reaction. In the Australian context, the alkali limit in concrete, as defined by Standards Australia Handbook HB 79:2015, is 2.8 kg/m^3 Na_2O_e. However there are field studies and laboratory experiments that indicate that limiting alkali content of the concrete mix is not always effective in preventing ASR (Stark 1980) as the authors discuss that besides the alkali content, the aggregate reactivity and exposure conditions are extremely important for the reaction and should not be ignored. In addition to cement, alkalis may also be sourced from aggregates, admixtures, mixing water and external sources such as deicing salts and seawater (Fernandes & Broekmans 2013; Olague, Wenglas & Castro 2003). For this reason, a more recent and common approach to mitigating ASR is the limitation of alkali in the concrete with consideration of the reactivity of the aggregate.

Portland cement is the main source of alkali in concrete that contributes to the dissolution of alkali ions in the pore solution. Due to their solubility, the alkali ions rapidly dissolve in the pore solution during the cement hydration, increasing the pH (Diamond 1989). The alkali in cement comes from the raw materials used to produce the clinker, such as clay, limestone, chalk, and shale. The alkalis are present as alkali sulfates, aluminates, and silicates, with sulfates being the most common form of alkali salts present (Jawed & Skalny 1977).

Aggregates may also be a source of alkalis in the pore water, increasing the total available alkali content in concrete, however, the rate of alkali released and the alkali amount in solution varies according to each type of raw material used in the concrete mix (Leming & Nguyen 2000). Feldspar minerals, for example, can release alkali ions into the pore solution over time, raising the alkali content and the potential for ASR occurrence in concrete in service (Chen, Soles & Malhotra 1993). In this study, alkalis derived from aggregates have not been demonstrated to increase the pH and it was assumed an increase of the pH.

The pH of the pore solution is considered a significant parameter in concrete structures and is usually in the range of 12.5-13.8 when the concrete is Portland cement based (Plusquellec et al. 2017). It has been reported that pH increases proportionally to the equivalent alkali content in cement. In addition, the pH value in the pore solution is related to the water/cement ratio since the availability of water is critical for this system (Li, Nam & Hartt 2005; Vollpracht et al. 2016). Due to the importance of alkali ions to the pore solution alkalinity, many studies investigate this relationship and a correlation among alkali content, hydroxyl ions concentration (pH) and w/c ratio, as shown in Figure 2-9, has been proven to exist.
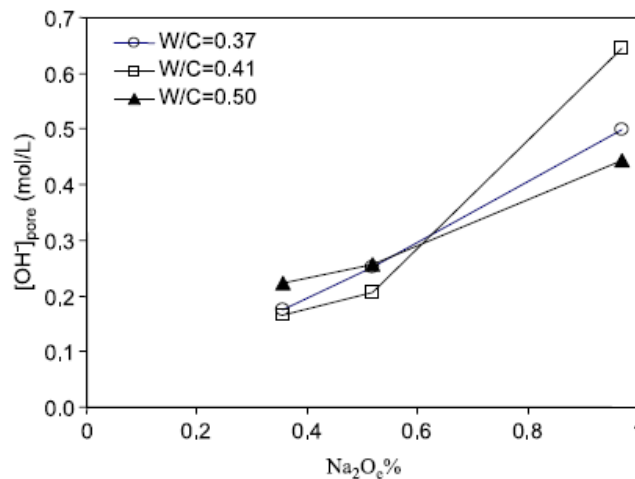
Figure 2-9: Measured pore water [OH⁻] of the various concrete mixes
(Li, Nam & Hartt 2005)

One study (Fournier & Berube 2000) investigated a variety of alkali content in specimens separately using a moderately-reactive aggregate (Sudbury) and a highly-reactive aggregate (Spratt) for one year. The data (Figure 2-10) shows that expansion increased synchronously with increasing alkali content for both aggregates tested although the highly-

reactive aggregate had significant expansion when the alkali content was 4 kg/m^3 Na$_2$O$_e$. Consequently, a high alkali content and the reactivity of the aggregate is going to determine the rate of the reaction and the expansion rate at certain point. Additionally, the results of this study indicate that the alkali threshold is going to be different for each aggregate type and no significant difference of expansion exists below this alkali threshold. For this experiment, very similar expansion occurred at 9 kg/m^3 Na$_2$O$_e$ and above. Therefore, an alkali threshold should be carefully evaluated for each aggregate type.
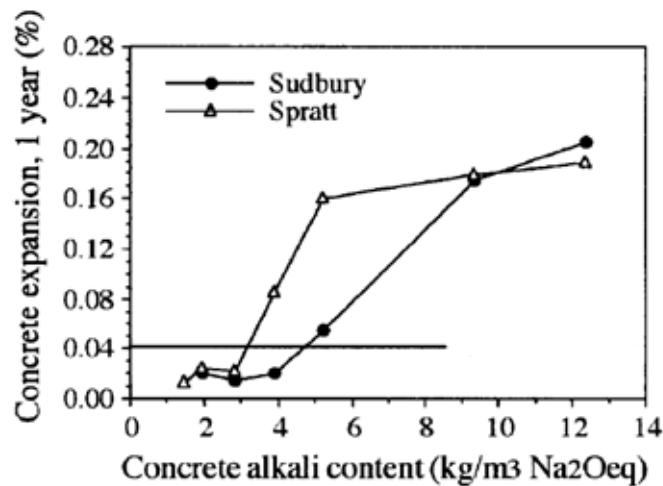
Figure 2-10: Concrete prism expansion and alkali content over 1 year
(Fournier & Berube 2000)

Alkalis released can also originate from the supplementary cementitious materials (SCMs) and sometimes they contain much higher alkali levels than that of Portland cement. These alkalis are known to be released slowly over time and can contribute to the formation of deleterious ASR at a later stage (Shafaatian et al. 2013). There is little free alkali available to ASR due to the presence of alumina ions, where alkalis from SCMs are bond to Al^{+3} (Thomas 2011).

Fly ash may have higher alkali contents than cement, but the alkali content is not significant as it will be bound by the excess of Al in the FA. FA becomes less efficient when the Ca content increases (Chen, Soles & Malhotra 1993). More studies are still required to understand the exact rate of alkali release and releasable amount of alkali in SCMs for ASR in concrete structures before conclusions can be made about the effect of the alkalis available in the pores (Rajabipour et al. 2015).

2.1.6 Reactivity of sodium and potassium ions in solution

The behaviour of the two main alkali ions present in the pore solution of concrete, sodium (Na^+) and potassium (K^+), are approximated to be equivalent (Shehata & Thomas 2006). The relative reactivity of these two alkali ions can be tested by using either sodium hydroxide (NaOH) or potassium hydroxide (KOH) in accelerated tests.

The effect of these two alkalis has been assessed by using NaOH and KOH solution in a concrete system where the products of the NaOH reaction had the presence of more chemically bound water than in KOH (Leemann et al. 2011), although potassium ions have been indicated to be more absorbed by CSH than sodium (Macphee et al. 1989). The relative reactivity of potassium and sodium indicates that it might be erroneous to consider that sodium and potassium have exactly the same behaviour and not consider the differences (Leemann & Lothenbach 2008). Those findings indicate that more investigation have to be done to clarify if there are significant differences between the two alkalis to then consider a change at the international standards, as they all consider sodium and potassium as total alkali content (Na_2O_e). Another studies looked at 17 aggregates at three solutions: NaOH, KOH and pure water (Berube et al. 2002), where 16 of them released more total alkali content ($Na_2O_e\%$) in the alkaline solutions which agrees with these results where a higher release of potassium occurred in the NaOH solution.

In contrast, other studies reveal no significant difference between sodium and potassium in their results (Bentz 2006; Diamond & Penko 1992; Hong & Glasser 1999) and state that ASR expansion is not influenced by individual values of sodium or potassium but the combination of both. Accordingly, studies have specifically investigated the monovalent cations' (K^+ and Na^+) effect on the silica surface where the gel is formed, which did not demonstrate differences in surface charge density (Rodrigues, Monteiro & Sposito 2001) since such information can explain the nature of interface interactions, such as between the reactive aggregate and the pore solution in concrete. No significant variation was found in regards to expansive pressure (Rodrigues, Monteiro & Sposito 1999). Since most of the studies show no difference in sodium and potassium, the sodium equivalent is considered to be an good approximation of the behaviour of alkali ions with respect to the potential of ASR expansion and aggregate reactivity screening in standard test methods (Guo, Dai & Si 2019).

2.2 Supplementary cementitious materials (SCMs)

The use of SCMs has been the focus of many investigations into ASR mitigation (Thomas 2011). SCMs, such as fly ash and silica fume, are siliceous or siliceous and aluminous materials. Typical compositions are listed in Table 2-2. These materials are finely divided and react chemically in the presence of water with calcium hydroxide to form compounds that possess cementitious properties. They are used to partially replace cement in the concrete mix and mitigate ASR expansion by reducing alkali concentration in the pore solution. According to the technical report from CCAA (Cement, Concrete and Aggregate Australia), the SCMs typically used in Australia are fly ash and silica fume.

SCMs generally have excess free silica and alumina available to be released into the pore solution (Lothenbach, Scrivener & Hooton 2011) and they react to form CSH in a similar manner to the ASR which is finely dispersed through the cement matrix and, therefore, does not contribute to expansion (Thomas 2011). Another advantage in applying these materials in concrete is the improvement of the strength and durability of concrete since it is well established that Portland cement–SCM blends develop lower porosity when compared to Portland cement pastes without SCMs (Lothenbach, Scrivener & Hooton 2011).

Table 2-2: Typical SCMs composition
(Thomas 2013)

	Low-calcium fly ash	High-calcium fly ash	Slag	Silica fume
SiO_2	56	32	36	97
Al_2O_3	28	18	10	0.52
Fe_2O_3	6.8	5.2	0.5	0.14
CaO	1.5	30	35	0.58
SO_3	0.1	2.6	3.5	0.01
MgO	0.9	5.2	14	0.13
Na_2O	0.4	1.2	0.35	0.04
K_2O	2.4	0.2	0.48	0.42
LOI	2.8	0.6	1.7	1.5

The pozzolanic reaction slightly changes according to each type of SCM but it basically occurs as shown in Equations (8) and (9).

The pozzolanic activity is a term used that determine how much is the material capable to interact with calcium hydroxide, where two main components are responsible for the reaction: the total amount of calcium hydroxide which combine with the material and secondly is the reaction rate (Massazza 1983). Alkali-silica reaction and pozzolanic reaction are similar although pozzolanic reaction proceed the formation of C-S-H with low Ca/Si ratio (Taylor 1997).

Hydration reaction:	$CaO + SiO_2 + H_2O \rightarrow C\text{-}S\text{-}H + Ca(OH)_2$	(8)
Pozzolanic reaction:	$Ca(OH)_2 + SiO_2 \rightarrow C\text{-}S\text{-}H$	(9)
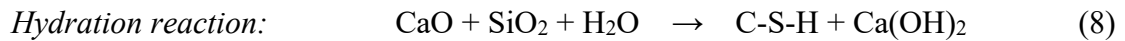
The introduction of a larger amount of silica from the SCMs that replaced cement (low silica content) will react and consume more calcium hydroxide (Duchesne & Bérubé 1994a). When the Ca/Si ratio is low (< 1.5), the charges become primarily negative, promoting the absorption of cations, particularly Na^+ and K^+, therefore decreasing pore solution alkalinity and consequently minimizing the risk of ASR (Glasser & Marr 1985).

The pozzolanic reaction forms a CSH product that is finely divided and evenly distributed through the binder matrix. The CSH formed may be involved with pore blocking which may inhibit transport of fluids through the binder matrix. Thus there are two possible mechanisms for mitigation. Competition for alkali ions in the pore solution and restriction of moisture and ion transports in the pore network (Thomas 2011). The degree of reduction of the alkali concentration in the pore solution defines the effective level of SCM replacement required to mitigate ASR, among other factors that must be considered when investigating the most suitable SCM replacement levels.

2.2.1 Fly ash

Fly ash is an amorphous aluminosilicate by-product of the generation of electricity from coal and it is one of the most common pozzolanic materials used for ASR mitigation (Kosmatka, Kerkhoff & Panarese 2002; Wang et al. 2016). According to the American Coal Ash Association, the United States produced 107.4 million tons of coal combustion products in 2016 and less than 14% (14.4 million tons) was recycled in concrete (Adams 2017). The reuse of these materials can reduce costs for cement and concrete industries due to cement

production savings, and the consumption will minimize the amount of waste material deposited in landfills (Siddique & Khan 2011). In Australia, the peak of fly volume was 2.13 Mt^3 in 2011 and has been decreasing since then (CCAA 2017). About 44% of fly ash produced meets the Australian standard requirements and it is recycled in concrete industries (Millington 2019).

Silica is the major chemical element of fly ash composition followed by aluminium or calcium. Due to the highly variable level of calcium content some sources may contain much more calcium than alumina. Considering that chemical composition is extremely important when evaluating the effectiveness of fly ash, the standard ASTM C618 classifies the material as high-calcium class C or low-calcium class F (ASTM C618 2019).

As ASTM C618 indicated, Fly ash is classified as high-calcium when the calcium content is greater than 18% CaO (Class C), low-calcium is Class F with CaO under 18% and the requirement for both F and C is: Silicon dioxide (SiO2) above 50% plus aluminum oxide (Al2O3) plus iron oxide (Fe2O3). Table 2-3 shows the general composition of both classes (Thomas 2013) and also the chemical composition of the most produced fly ash in Australia (Heidrich 2003) fitting in Class F according to the American standard. Low-calcium fly ash is more effective in preventing ASR since it reduces the alkali amount by replacing cement and additionally and increases the content of CSH having a low Ca/Si ratio which has less risk of promoting damage expansion. Majority of the low-Ca fly ash contains an aluminium (Al_2O_3) level higher than high-Ca fly ash (15 – 35%) which promotes the effectiveness of Class F further (Lothenbach, Scrivener & Hooton 2011).

Table 2-3: Principal chemical composition of coal fly ash as percentage including typical Australian fly ash

Class	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	Na₂O	K₂O	SO₃
C	32	18	5.2	30	5.2	1.2	0.2	2.6
F	56	28	6.8	1.5	0.9	0.4	2.4	0.1
AUS F	65	23	5.0	0.2	0.3	0.4	1.8	0.2

Another mechanism related to the effectiveness of FA is the higher alumina content available in the composition (Leemann et al. 2015). The phase CSH formed with a low Ca/Si ratio will bind with the alumina present in those rich-Al SCM and slowly react, forming C-A-S-H which enhances the possibility of binding cations from the pore solution (Chen & Brouwers 2010; Hong & Glasser 2002), as a charge balancing ion (Na^+, K^+) is required to accompany the substitution of silica (Si^{4+}) with aluminium ions (Al^{3+}). The formation of C-A-

S-H phases, therefore, decreases the alkali content as well as the pH in the pore solution, thus suppressing ASR (Lothenbach, Scrivener & Hooton 2011). In contrast, it has been argued that the alumina present in SCMs does not significantly absorb alkalis and consequently does not reduce the alkalinity of the pore solution (Chappex & Scrivener 2012a) even though the presence of high aluminium SCM can reduce ASR expansion and mitigate the reaction. In a following study (Chappex & Scrivener 2012b) it is suggested that aluminium ions interact with the reactive phases of the aggregates and are absorbed on the silica surface. Overall the aluminium participation in ASR is still unclear and further investigation is required to better understand the mechanisms involved.

In Australia, the majority of fly ash available contains a low level of calcium of around 10% or less, however, in New Zealand the chemical composition is more variable as it can be as high as 25% but it is usually below this value (Standards Australia 2016). Since 2011 the amount of fly ash available for cement and concrete industries that meets the requirements has reduced considerably which motivated the importation of fly ash (Chalmers 2016).

2.2.2 Ground granulated blast furnace slag (GGBFS)

Slag is an industrial by-product of the iron and steel-making industries which is quenched, granulated and then ground to be used as ground granulated blast furnace slag, (GGBFS) (Sadek 2014). In Australia, the use of slag for cementitious material increased to almost 1.9Mt in 2016 and 1.1Mt of this was imported, mainly from Japan (CCAA 2018). The higher consumption of slag is probably related to the acceptance of the effectiveness of SCMs and also as a result of the limited availability of fly ash since 2011(Chalmers 2016).

Slag contains the most similar chemical composition to cement compared to the other SCMs currently available. For this reason, the slag reaction is also known as the hydraulic reaction where a mixture of cement and slag hydration form less CH compared to cement hydration (Thomas 2013). Another important difference is that slag hydration is much slower than Portland cement (Kolani et al. 2012) but faster than fly ash in the early stages as shown in Figure 2-11 probably because low calcium fly ash does not undergo hydration as such. Some materials such as Na_2CO_3, natural gypsum ($CaSO_4 \cdot 2H_2O$) and $Ca(OH)_2$ are usually included in activated slag and increase the degree of hydration (Murgier, Zanni & Gouvenot 2004), being that isolated slag hydration will form a silica-rich layer on the mineral preventing the complete hydration (Thomas et al. 2016).

28
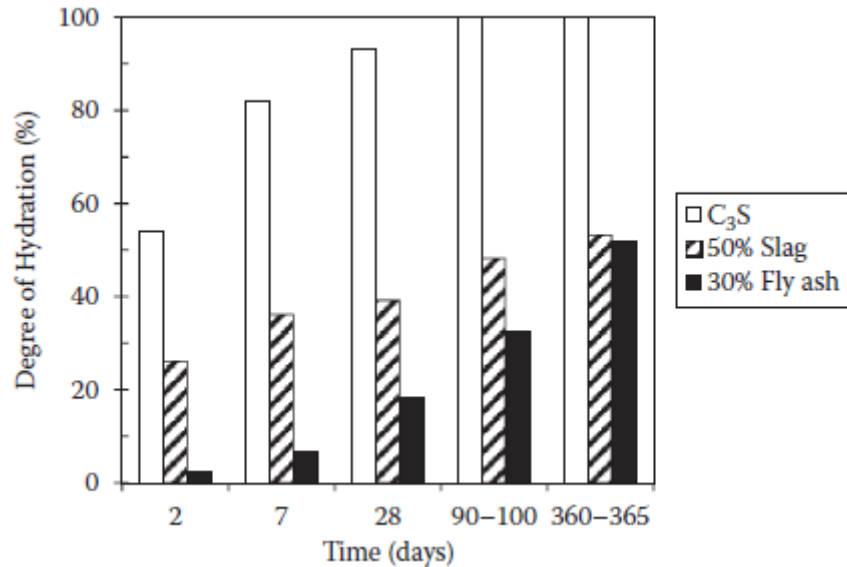
Figure 2-11: Degree of hydration of blended cements
(Locher 2005)

Slag has levels of alumina lower than fly ash but has greater free alumina content than Portland cement, as shown in Table 2-2, as it has been shown to be an effective SCM since the hydration of slag does produce CSH and also CASH phases (Hong & Glasser 2002). It may also reduce water mobility by decreasing the permeability in the cement paste thus suppressing ASR (Canham, Page & Nixon 1987). Three levels of alkali activated slags was investigated by increasing the alkali dosage in mortar specimens where results showed less expansion by the specimens with more alkali content (Shi et al. 2017). This probably is a consequence of the low silica dissolution from the aggregates due to the presence of aluminium, however more research is required to develop a full understanding of the effectiveness of slag.

2.2.3   Silica fume

Silica fume is a by-product of the silicon and ferrosilicon industries. The composition is mostly made of the glassy phase (about 95%) which is responsible for the cementitious properties, although the SiO_2 content can vary extensively between 61% and 98% (Thomas 2013). It has a very small particle size, hence, it is a very reactive material that reacts with the calcium hydroxide released from the cement hydration and forms calcium silicate hydrate

(CSH). Due to formation of more CSH phases, silica fume can enhance good properties in the cementitious mix, such as lowering porosity, lessening the availability of free-lime and increasing the thickness of the transition zone, therefore, improving mechanical properties and giving a longer lifetime to the structure (Siddique & Khan 2011).

Silica fume is the most expensive SCM (Illankoon et al. 2018), however it requires the lowest replacement level to mitigate ASR, and also produces CSH with the lowest Ca/Si ratio which produces a non-deleterious CSH phase (Chappex & Scrivener 2012a). It is used at replacement levels of between 5 and 10% by mass of cementing materials (Kosmatka et al., 2002).

2.3   Test methods for the evaluation of alkali-silica reaction

Identification and classification of aggregates is necessary for evaluating the potential of alkali-silica reactions. According to the Australian guideline SA HB 79, the assessment should start with the evaluation of aggregate field performance history, if possible, followed by the assessment with petrographic analysis and accelerate mortar bar test (AMBT) to confirm. A non-reactive aggregate may be used without extra mitigation depending on the precaution required by the concrete category which is classified according to the acceptability of ASR damage. After that first assessment, if the aggregate receives a classification as slowly-reactive, it should be tested with concrete prism test (CPT) in order to further evaluate aggregate reactivity. Or a mitigation approach should be adopted, as discussed in Chapter 2.4. The Australian recommendation methods for aggregate assessment and quality control of aggregates are presented in the form of a flow chart (Standards Australia 2015).

Field history can be useful as long as the mix design and date of placement is known, the raw materials used must have been characterized, and all of this information must be collected for estimating reactivity although this detailed data is often difficult to source (Kerenidis & Hooton 2011). The history of aggregates in the field helps to know the reactivity level, however exposure conditions and mixtures of different aggregates applied in the same structure leads to uncertain conclusions and a controlled environment might allow for a better evaluation. Standard test methods were developed to investigate the reactivity level of aggregates, such as slowly reactive or reactive, and they are applied to evaluate the risk of expansion due to the alkali-silica reaction, as well as the effectiveness of SCM replacement

(Thomas et al. 2007). Each test method has drawbacks and an ideal test method that is rapid, reliable and reproducible is still not available (Bérubé & Fournier 1993).

The assessment of the relative reactivity of aggregates has generally been carried out with the following American Standards test methods: Concrete Prism Test (CPT) and the Accelerated Mortar Bar Test (AMBT), where different countries have their own standards although with very similar parameters. Test methods are useful for investigating the relative reactivity of aggregates and in classifying aggregates for their potential for ASR, although it is important to correlate previous field performance results with laboratory results since a wide range of aggregates exist and the composition in each country might be different (Hooton et al. 2013).

2.3.1   Accelerated Mortar Bar Test (AMBT)

AMBT is one of the most frequent tests used to detect reactive aggregate during 14 days in North America and many countries in Europe (Alaejos et al. 2014) although Australian method is more conservative and the test is conducted during 21 days. The mortar bars are exposed to 1M NaOH solution at 80°C (ASTM C1260 2014). This test method is a worldwide standard with different names, such as the American Standard ASTM C1260, the Australian Standard AS 1141.60.1 (Standards Australia 2014), the Canadian Standard CSA A23.2-25A , and the European recommendation RILEM AAR-2.1.

Considering the expansion limit of 0.10% at 14 days after immersion of the specimen in the solution, it has been shown to be an effective test method of classifying reactive aggregate, however, there were a few cases where higher expansion limits (0.15 or 0.20%) erroneously classified aggregates as non-reactive, despite the fact that the aggregate caused ASR damage in field structures (Alaejos et al. 2014). The expansion limit overall depends on the age of the experiment, 0.10% is considered the most adequate for 14 days experiment to classifying aggregate reactivity (Ideker et al. 2012) and a limit of 0.30% for 21 days experiment.

The conditions used in the AMBT are often considered to be severe because of the extreme conditions (high temperature and highly alkaline solution), therefore producing false positives for aggregates that have performed well in the field (Thomas & Innis 1999). Due to the potentially misleading results, aggregates that have been found to be reactive using the AMBT aggregates must then be subjected to the more moderate conditions of the CPT to

further assess reactivity (RILEM 2015; Thomas, Hooton & Rogers 1997) where the same recommendation is given in HB 79 for aggregates classified as slowly-reactive aggregate. The effectiveness of AMBT to identify slowly-reactive aggregates was tested using five slowly-reactive Australian aggregates (Shayan 2007) and this study concluded that a limit of 0.10% expansion at 14 days is not accurate in identifying slowly-reactive aggregates, consequently, the Australian standard method measures the specimens at 21 days in order to avoid false conclusions. In table 2-4, the parameters of the Australian AMBT (AS 1140.60.1) and American (ASTM C1260) are given.

After many studies using AMBT to evaluate the effectiveness of SCMs to mitigate ASR (Berube, Duchesne & Chouinard 1995; Shehata & Thomas 2000), another American standard (ASTM C1567) was created, which describes the procedures of preparing the specimens with SCMs regardless of the main experiment conditions being the same (temperature, solution, specimens size, test length, etc.). It is considered the most used test method of evaluating SCM (Thomas 2011) and authors agree that even in those extreme conditions in a short period of time, it is possible to measure the performance of SCM in mitigating ASR (Malvar & Lenke 2006; Thomas et al. 2007).

Table 2-4: Parameters of the accelerated mortar bar tests (AMBT)

Standards	AS 1141.60.1	ASTM C1260
Length	21 days	14 days
Material mass	1430g for 3 specimens (440g cement + 990g aggregate)	1430g for 3 specimens (440g cement + 990g aggregate)
Temperature	80°C	80°C
Sieve Cement	< 4.75mm – same for both	< 4.75mm – same for both
w/c ratio by mass	0.47	0.47
Mortar bar mould	25 x 25 x 280 mm	25 x 25 x 285 mm
Mould period	24 ± 2 h	24 ± 2 h
After de-mould	Immerse in tap water at 23°C and increase temperature to 80°C in 2 hours	Immerse tap water at 23°C and increase temperature to 80°C in 2 hours
Solution storage	1 M NaOH - 80°C	1 M NaOH - 80°C
Length readings	0,1,3,7,10,14 and 21 days	0, (3 intermediate reading),14 days

2.3.2   Concrete Prism Test (CPT)

The concrete prism test (CPT) (AS 1141.60.2) has not been greatly used in Australia, probably due to the long period of experiment before conclusion can be taken. The Australian CPT method was developed based on the American standard concrete prism test (ASTM C1293 2015) and it is used to evaluate the aggregate reactivity in a specific concrete system with an alkali content boosted to 5.25 kg/m^3 (1.25% of Na$_2$O$_e$ by mass of cement). The specimens are prepared according to the standards parameters, as shown in Table 2-5.

Table 2-5: CPT parameters

Parameters	AS 1141.60.2 and ASTM C 1293
Cement	GP cement with no greater than 0.9% Na2Oeq*
Cement content	420 ±10 kg/m3.
Cement Sieve	n.20 – 850µm
Alkali boost	Increase to 1.25% Na2Oeq
w/c ratio	Range of 0.42 to 0.45 by mass
Concrete prism mould	75 x 75 x 285 mm
Storage environment	38°C ± 2 h, high humidity
Length readings	7, 28 days; monthly after demoulding until 12 months

Almost 2 decades ago, inter-laboratory testing was performed and indicated poor repeatability associating field performance and CPT (Shayan 1992). However, after further research, the CPT is now considered the most reliable field performance indicator (Ideker et al. 2010). The procedure consists of increasing the alkali content of the samples up to 1.25% sodium equivalent and the prisms are stored above the water reservoir which provides 100% RH. The high humidity is needed to provide sufficient access to water for the ASR to occur and the coarse aggregate is not crushed, so it is able to identify slowly reactive aggregates (Hooton 1996). According to the concrete prism test in America (ASTM C1293 2015) and the Canadian standard (CSA A23.2-28A) the tests have to be conducted for 24 months (104 weeks) if SCMs are going to be evaluated as mitigating ASR, although the Australian standard is not a requirement (Li, Thomas & Ideker 2018).

The difference between the Australian and American standards for this test method is the expansion limit for aggregate classification, in that the Australian standard classifies the aggregate as 'potentially reactive' if the average expansion of the three concrete specimens is equal to or greater than 0.03% however, the American standard is limited at 0.04%. The aggregate is classified as non-reactive if the expansion is below those limits for both standards. The lower expansion limit in the Australian standard was adopted after the state road authorities' method which considered the field performance of some Australian aggregates and decided to be more conservative (Shayan 2007; Shayan & Morris 2001).

The CPT may also be used to estimate the alkali threshold in the concrete mix, however, due to the drawback of leaching alkalis from the prisms during the course of the test, it provides unreliable conclusions and results that are frequently misleading when compared to field performance (Lindgård et al. 2013). The alkali threshold determined under the laboratory test conditions may, in fact, be much higher than those observed in concrete systems in the field (Lindgård et al. 2012). This issue might be prevented by the use of plastic bags or wrapping each prism (Rogers & Hooton 1991), changing the pre-storage condition to a prolonged pre-storage period at room temperature (18–23°C) (Rivard et al. 2003) or by using an airtight container for each prism (Costa, Mangialardi & Paolini 2017). Those methods demonstrated good results in preventing alkali leaching although the standards have not currently adopted a method of preventing leaching. Nonetheless, the conclusions of the test are still considered more reliable than AMBT (Sirivivatnanon, Mohammadi & South 2016).

A laboratory test method capable of greater reliability is extremely important in the determination of the alkali threshold in concrete systems. The alkali threshold value helps to develop the understanding of the effect of alkali content on reactive aggregates in ASR, so the correct conclusion will allow for a more predictable result, therefore, avoiding ASR damage (Thomas et al. 2006).

2.3.3   Accelerated concrete prism test (ACPT)

In order to obtain results in a shorter period of time, ACPT or CPT60 was developed and proposed after the development of the concrete prism test. It aims to evaluate the reactivity of concrete mix for a period of 3 months by increasing the temperature of the concrete prism test to 60°C, thus increasing the rate of expansion (Ranc & Debray 1992). RILEM recommendations (AAR-4.1) include this accelerated method as one way of enabling a

comprehensive aggregate assessment and many studies have been investigating the reliability of ACPT (Fournier et al. 2004; Ranc & Debray 1992; Touma, Fowler & Carrasquillo 2001).

An extensive study was conducted between five laboratories in the United States and Canada to compare the results of CPT and ACPT and evaluate inconsistencies of the ACPT test (Fournier et al. 2004). The data of the reactive aggregates were compared and demonstrated a good relationship between ACPT and CPT as shown in Figure 2-12. In Australia, a similar study was conducted using 49 aggregates, and the ACPT was effective in detecting reactive aggregates just like CPT and was also effective in detecting slowly reactive aggregates (Shayan, Xu & Morris 2008). For this reason, this test method is under development in Australia (Standards Australia 2015).
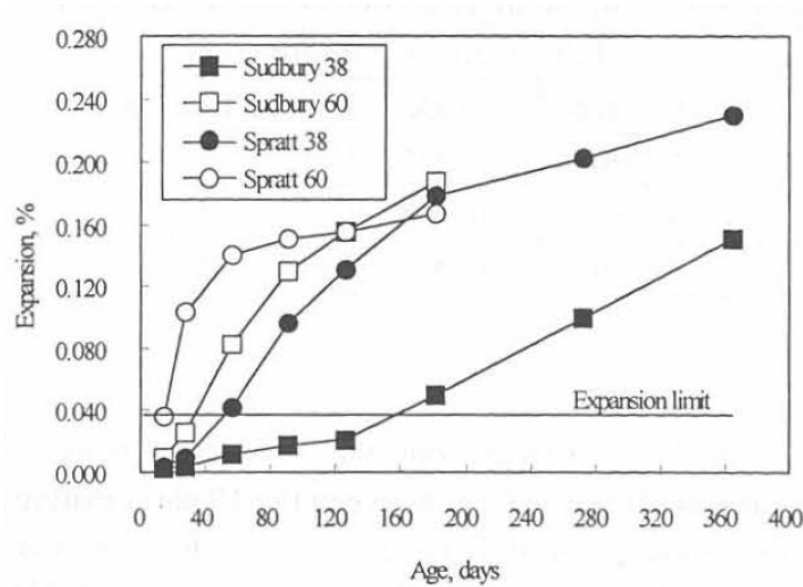
Figure 2-12: Average expansion of the prims at 38 and 60°C
(Fournier et al. 2004)

The accelerated version of the CPT test has great potential of becoming the most significant method for aggregates assessment since ACPT apparently offers realistic results in shorter period of time. However, more research has to be conducted to define the most suitable parameters for pragmatic results.

2.4 Mitigation methods

A range of strategies to minimise the risk of damage due to ASR is proposed internationally with similar parameters. The recommendations in Australia for ASR mitigation techniques are presented in the Standard Australia's Handbook HB 79, where the approach to efficiently prevent the reaction will vary according to the aggregate reactivity, level of precaution required for the concrete structure and alkali content. This section describes the most common approaches to mitigate ASR.

2.4.1 Aggregate selection

Aggregates play an important role in ASR expansion, and potentially the most significant one. Probably for this reason, the most decisive contributor to defining the mitigation approach according to the Australian guideline HB79, is the reactivity of the aggregate. No mitigation action has to be taken if non-reactive aggregate is going to be used exclusively in the concrete mix design. Therefore, the classification of the aggregate reactivity is critical. Aggregates are natural minerals and, as previously discussed, the option of choosing the aggregate is not always a possibility due to lack of availability or expensive costs for aggregate transportation. Most countries manage the ASR risk by considering the aggregate reactivity and then defining the alkali limit and/or the level of SCM cement replacement. The following two sections are the most applicable methods of preventing ASR in structures that are designed for a long service life and require precautions, usually considering the aggregate reactivity.

2.4.2 Flexible alkali limits

One of the first strategies employed to prevent the ASR formation in concrete is limiting the alkali content from cement (Stanton 1940), especially when reactive aggregates is available (Leming & Nguyen 2000). This approach has been used for decades and has proven to be effective in preventing alkali-silica reaction in many cases, but not all. (Stark 1980). Studies have shown that the low alkali limit of 0.6% Na_2O_e for cement is not necessarily effective in mitigating ASR (Hill 1996; Leming & Nguyen 2000), since it does not restrain the overall alkali content in concrete mix (Hill 1996).

Most cement produced in Australia contains an alkali level of 0.5% – 0.6% Na_2O_{eq} (Standards Australia 2015), which it is considered to be a low alkali level. Limiting alkali content in cement production induces a more restrictive choice of raw materials that can be used. Consequently higher costs and environmental impacts are related to the alkali limit in cement materials (Barker et al. 2009; Fournier et al. 2009). The mitigation of ASR has been successfully achieved by the use of SCMs, which leads to the potential application of higher levels of alkali content in cement. This practice has been used and recommended by places such as Canada and Europe, where higher alkali content doesn't lead to higher risk of ASR.

The aim of a flexible alkali limit for concrete mix is to determine the more appropriate alkali threshold for a known concrete system, been that this threshold is the point at which the ASR process is probably going to initiate. Below the threshold is a safe alkali level where a harmful alkali-silica reaction is unlikely to occur (Berra, Mangialardi & Paolini 1999b). The threshold limit depends on the reactivity of the aggregate in the mix, therefore a precise number is difficult, however, some published work reports an alkali threshold limit for a concrete mix of 5 kg/m^3 Na_2O_e (Sibbick & Page 1992) for slowly reactive aggregates and 3 kg/m^3 Na_2O_e for highly reactive aggregates (Duchesne & Berube 1994b). This approach enables the relaxation of strict single low and conservative alkali limits in cement. Balancing the alkali content of a concrete system using a risk profile approach requires an understanding of the ASR mechanism, the role of SCMs in mitigating ASR and the relative reactivity of the aggregates used to prepare the concrete mix.

The alkali threshold for each concrete mix will vary, but can be determined by testing the combination of aggregate, cement and SCM (if applicable) that initiates ASR before certifying an alkali content limit (Berra, Mangialardi & Paolini 1999b). The alkali level is highly dependent on the aggregate type used since the aggregate is responsible for the amount of reactive silica available to the system. Many authors believe that the reactivity level and the type of aggregate are responsible for the diversity found in the threshold alkali concentration (Fournier et al. 2016; Thomas, Fournier & Folliard 2013).

The optimum mitigation method is to limit the alkali level of concrete which considers the alkali content from other materials, and also the reactivity of the aggregate, thus being more effective in preventing ASR, however, it is difficult to measure the alkali content of all the materials and unpractical for the concrete industry. Therefore the investigation of the threshold alkali content in concrete mix generally only considers the reactivity of the aggregate (Berra,

Mangialardi & Paolini 1999b) and the alkali content in cement to determine this safe limit level in concrete.

Canada and many countries in Europe mitigate alkali-silica reactions using a range of different levels of alkali content of concrete, considering the type of aggregate being used in the system and the precaution level relevant for the construction (Nixon, Fournier & Thomas 2016). RILEM recommended a range of alkali limit according to the mitigation method AAR-7.1-2015 (RILEM 2015), where the alkali content of concrete is limited based on the aggregate reactivity which have to be assessed and determined by the concrete prism test method. This RILEM recommendation is shown below in Table 2-4.

Table 2-6: RILEM recommendation for alkali limit in concrete

Aggregate reactivity	Na_2O_e limit (kg/m^3)
Non-reactive	No limit
Medium reactive	3.0 – 3.5
Highly reactive	2.5 – 3.0

The Canadian standard CSA A23.2-27A has similar preventive measures against alkali-silica reactions that consider the level of precaution necessary according to the desired service life for the structure. It gives flexible alkali limits for the concrete design according to the desired precaution, as shown in Table 2-7, suggesting an alkali limit of 0.7 % Na_2O_e in cement without the addition of SCMs and it may contain alkali level as high as 1.25% Na_2O_e when SCM is also added to the concrete mix (Canadian Standards Association 2014). The structure's required lifetime will indicate the most suitable alkali limit (Berube et al. 2002). Field structures, field tests and concrete prism tests were used to define the protocol for preventing ASR in the Canadian standard CSA A23.2-27A where cement with up to 1.0% Na_2O_e can be used with SCMs (Nixon, Fournier & Thomas 2016).

Table 2-7: Canadian standard CSA A23.2-27A for ASR mitigation

Preventive action	Na$_2$O$_e$ limit (kg/m^3)
Mild	< 3.0
Moderate	< 2.4
Strong	< 1.8
Exceptional	< 1.8 and SCMs

In Australia, the alkali control approach to minimise ASR risk is considered by using concrete mixes with an alkali content of less than 2.8 kg/m^3 Na$_2$O$_{eq}$ (Standards Australia 2015). Despite the fact that other countries have been using the concept of a flexible alkali limit according to the aggregate reactivity to mitigate ASR as discussed previously, this approach still not recommended in this country.

2.4.3   Cement replacement by SCMs

The use of SCMs by partially replacing Portland cement in concrete mixes is a common mitigation strategy. This approach provides the option of relaxing the alkali limits through the risk assessment of the ASR potential in particular cement-SCM-aggregate concrete systems. The Australian guideline published in the handbook HB 79 "Alkali aggregate reaction - Guidelines on minimising the risk of damage to concrete structures in Australia" (Standards Australia 2015) presents the SCMs replacement level recommended to mitigate ASR, as shown in Table 2-6. The percentage of SCM replacement and the total alkali content available in the concrete are two critical components that determine concrete expansion and for this reason an alkali limit for SCMs is usually determined, even though the alkalis available from SCMs are usually bound in secondary hydrates and not effectively in the pore solution (Duchesne & Berube 1994a).

Table 2-8: Australian guidelines for SCM replacement

(Standards Australia 2015)

SCM	Recommended SCM content in binder for ASR mitigation	Maximum SCM alkali level (Na_2O_{eq}) as total alkali
Fly ash (low Ca)	~ 25	3
Silica fume	~ 10	1
Slag (GGBFS)	~ 65	1
Metakaolin	≤ 15	-

However, the alkalis available from SCMs are usually bound in secondary hydrates and not effectively in the pore solution (Duchesne & Berube 1994a).

The most effective SCMs require a low percentage of replacement to mitigate expansion, which usually contain a moderate-low reactive aggregate and/or moderate-low alkali cement and the opposite occurs for less effective SCM (Figure 2-13). The amount of SCM necessary to mitigate ASR depends on reactive silica aggregate, alkali cement levels, SCM composition (Ca/Si ratio and alkali content) and external alkali content (Thomas 2011). This range of conditions can vary widely in each concrete mix, therefore is essential to know the materials' composition.
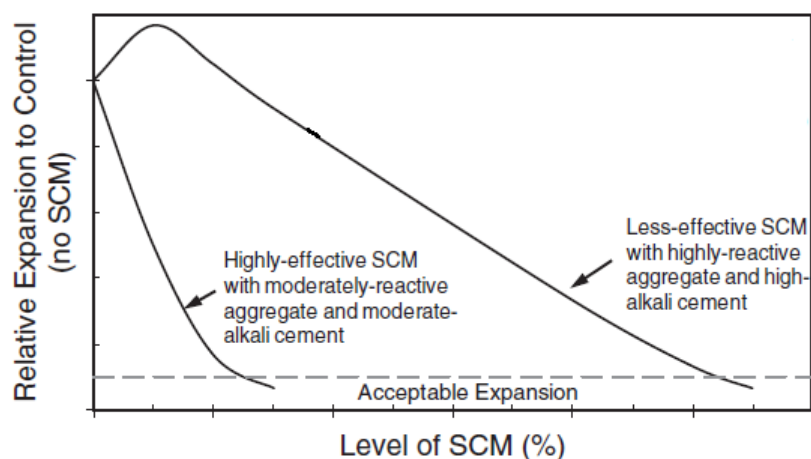
Figure 2-13: Relationship between SCM replacement and expansion
(Thomas 2011)

The mitigation approach using SCMs is also recommended by RILEM however the authors do not consider that it is appropriate to propose specific replacement levels for all SCMs due to the mineral variability. Consequently, the recommendation given is for the application of fly ash and slag only, considering that the effectiveness of these minerals is strongly acknowledged. RILEM proposes a specific recommendation for the replacement of fly ash, due to concerns related to the different possible chemical compositions, as shown in Table 2-9. For the two SCMs, silica fume and metakaolin, it is suggested a replacement of 8% and 15%, respectively, although these SCMs should not be used with reactive aggregates.

Table 2-9: RILEM recommendation for minimum SCM replacement

Aggregate reactivity	% by mass of total cementitious material		
	Low lime fly ash (<8% CaO and <5% Na_2O_{eq}.)	Medium lime fly ash (8-20% CaO and <5% Na_2O_{eq}.)	Ground granulated blastfurnace slag (<1.5% Na_2O_{eq}.)
Low	Any	Any	Any
Medium	25	30	40
High	40	Not recommended	50

Fly ash has the most variable composition among all SCMs, and consequently, the amounts used to replace cement in concrete mix to prevent ASR can be very different. The effectiveness is directly correlated to the level of alkalis and calcium, although other factors such as the nature of the reactive aggregate in the mix and environmental conditions will also have an influence (Shayan, Diggins & Ivanusec 1996). High calcium fly ash has less free silica and less reactive alumina available for the mitigation of ASR (Shehata, Thomas & Bleszynski 1999a), therefore, it is less effective, so it requires a higher level of replacement to mitigate ASR effectively (Malvar & Lenke 2006).

The mitigation and effectiveness of high calcium and low calcium fly ash in preventing ASR was investigated by evaluating 6 fly ashes with distinct levels of calcium and alkali for 2 years (Shehata & Thomas 2000) and the results in Figure 2-14 illustrate that they all reduced the expansion after 2 years when compared with the control specimen, regardless of the fly ash composition. Hence, some SCMs can be more effective in preventing expansion, however they

generally can be efficient in preventing ASR using the sufficient and appropriate replacement level.

The high concentrations of silica released into solution by the fly ash in alkaline solution indicates that fly ash has significant reactivity (Aughenbaugh et al. 2013) and the reactivity of fly ash is consistent with its potential for mitigating ASR. Although this mitigation occurs through the manner in which any silica dissolved from the fly ash will react with the adjacent calcium and produce CSH, which is the pozzolanic reaction, and it will not produce the expensive ASR gels. The alkali ions present in the ASR gel absorbs water and cause expansion of the gel resulting in cracking.

The integration of fly ash into cement in a finely divided form disperses the fly ash uniformly throughout the cement matrix. Any silica gel formed will therefore also be homogenously distributed throughout the concrete matrix reducing the potential of the silica gel to accumulate and expand. In contrast, the ASR gel formed by the dissolution of aggregate silica is localised and has the potential to be disruptive with expansive stresses transferred to the concrete resulting in cracking.
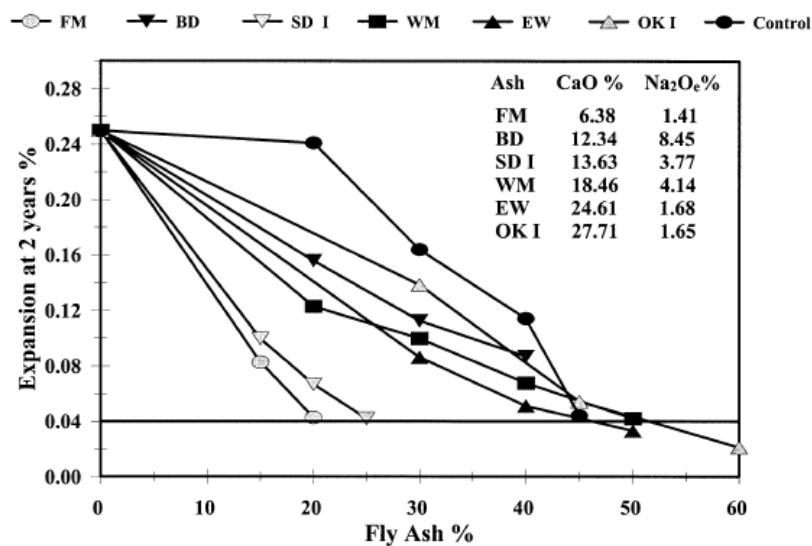
Figure 2-14: Replacement levels of fly ash (Shehata & Thomas 2000)

Some field structures have demonstrated that fly ash can be effective in preventing ASR damage even when they are used with high-alkali content cement ($> 0.6\%$ Na_2O_e), which is the case of Lower Notch Dam in Canada, built in 1969 with highly reactive aggregates, high-alkali cement (1.08% Na_2O_e) and 20% fly ash. No symptoms of deleterious reaction have been

detected (Thomas et al. 2012). Similar results were seen on field exposure tests as well, where large concrete blocks with high-alkali cement and fly ash were built for an outdoor exposure study to support laboratory results. The Building Research Establishment (BRE) which is a centre of building science in the UK, have an exposure site for this type of experiment. One study published in 1996 evaluated the potential of alkali-silica reaction using concrete with high-alkali content (1.15% Na_2O_e) with a reactive flint sand representing 25% of the total aggregate. The results collected after 8 years' exposure shows that high alkali cement can be safely used with 25% low-calcium fly ash replacement without any ASR damage (Nixon 1996).

After this literature review it is evident that ASR expansion in concrete can be mitigated although some mitigation strategies results provide conflicting results in regards to their effectiveness. The effective approach depends upon the degree of aggregate reactivity, the type of SCM and the level of replacement. It is evident that the combination of aggregate classification and SCM is more commonly applicable to ASR mitigation rather than only limiting the alkali content in cement and concrete.

It was also evident that there is an absence of specification for the use of mitigation alternatives in Australia. A combination of aggregate reactivity and SCM replacement would allow a more flexible alkali limit in concrete design and consequently result in a wide range of alternatives of natural sources for concrete mixes.

3   Materials

The investigation into alkali limits and alkali silica reactivity was carried out using commercially available Australian materials and they are described in this section. The materials used in this research included general purpose (GP) cement, slowly-reactive aggregate, reactive aggregate, fly ash, slag, and sodium hydroxide (NaOH) pellets. This section outlines the basis of the materials selection and presents the results of characterisation studies carried out prior to experimentation.

The investigation of balanced alkali content was conducted by analysing the effect of alkali solution concentration on the release of cations from cement, aggregates and SCMs, on aggregate reactivity in slurry and paste tests and in AMBT expansion. The cement in Australia's market contains alkali levels below 0.6% Na_2O_{eq} therefore the study of the effect of alkali content (or concentration) was conducted by using sodium hydroxide solution as the slurry medium, storing mortar specimens in sodium hydroxide solutions or by the addition of sodium hydroxide solution to the mortars. The micro-diorite and greywacke aggregates used in this research were chosen since they have different reactivity classification despite the fact that they have similar composition, and this is discussed in Section 5.1.2. One fly ash and one slag were selected as SCMs.

3.1   Cement

A general purpose cement (type GP) with 7.5% mineral addition was used in this research, which conforms to the Australian Standards AS 3972 General purpose and blended cement. The chemical composition of the cement was determined by XRF and is shown in Table 3-1.

Table 3-1: Chemical composition and compounds of cement as-received

Chemical composition	GP Cement (%)
Calcium oxide (CaO)	62.78
Silicon dioxide (SiO$_2$)	19.66
Aluminium oxide (Al$_2$O$_3$)	5.11
Ferric oxide (Fe$_2$O$_3$)	3.04
Sulfur trioxide (SO$_3$)	2.68
Magnesium oxide (MgO)	1.14
Titanium dioxide (TiO$_2$)	0.26
Potassium oxide (K$_2$O)	0.43
Sodium oxide (Na$_2$O)	0.24
Phosphorus pentoxide (P$_2$O$_5$)	0.12
Manganese oxide (Mn$_2$O$_3$)	0.07
LOI	4.06
Total LOI	99.59

3.2 Sodium hydroxide (NaOH)

Alkaline solutions were used to increase the alkali content or reaction mixtures, pastes and mortars by adding sodium hydroxide solution into the specimens. Sodium hydroxide solutions were prepared using solids in pellets from Sigma-Aldrich with purity ≥ 98% for 1 liter (L) solution and used for specimens stored in alkaline solution and the alkaline water was also used in the ACPT specimens. The 20 L solutions for the storage of the AMBT mortar bars was prepared with NaOH pellets from Rowe Scientific with purity ≥ 97%. All solutions were prepared with deionized water (DI water).

The calculation to prepare the concentration of the required solutions were based on the supplier molecular weight of 40 g/mol, so to prepare 1 L of 1 mol (M), requires 40 g ± 0.05. Solutions of 1 L were prepared to boost the alkali content in the paste specimens and for the slurry test 2 L solutions were used for the immersion of the AMBT specimens.

3.3 Aggregates

For the comparison of the effect of alkali content to different aggregates, two Australian aggregates, a micro-diorite (MD) and a greywacke (GW), were supplied by Cement Concrete and Aggregates Australia (CCAA). The mineralogical composition of the micro-diorite and greywacke was determined by petrographic analysis and the phase composition is listed in Table 3-2. The micro-diorite is classified as igneous rock where on average 52% is feldspar and 6% is free silica with between 0.03 to 0.5 mm quartz particle sizes. The greywacke is classified as a sedimentary rock (a sandstone type) which contains 50% of feldspar and 37% of free silica content, of which 17% is finely divided microcrystalline quartz with particle size < 0.01 mm and 20% coarse quartz.

Table 3-2: Petrographic analysis of aggregates by microscopic analysis

Micro-diorite		Greywacke	
Volume %	Mineral	Volume %	Mineral
52	plagioclase and subordinate K-feldspar	50	finely microcrystalline feldspar and quartz devitrification origin
18	hornblende	13	quartz as silt and sand grains
9	epidote group minerals	8	epidote
7	chlorite	7	feldspar as silt and sand grains
6	quartz	5	lithic clasts of acid volcanic rock (1% finely microcrystalline quartz)
4	calcite	4	lithic clasts of granitic rock (3% quartz)
2	biotite	4	lithic clasts of quartzite
1	Opaque oxide	3	calcite
1	pyroxene	1	lithic clasts of intermediate volcanic rock
<1	sericite	1	sphene
<1	sphene	<1	opaque oxide
trace	apatite	trace	secondary iron oxide

The assessment of the chemical composition analysis using XRF was conducted at the analytical centre at University New South Wales (UNSW), and the results are represented in Table 3-3.

Table 3-3: Aggregates chemical composition

OXIDE WT.%	Micro-diorite	Greywacke
SiO_2	62.29	66.85
TiO_2	0.92	0.65
Al_2O_3	15.55	14.24
Fe_2O_3	5.26	3.80
Mn_3O_4	0.11	0.09
MgO	1.82	1.58
CaO	4.05	1.94
Na_2O	4.81	4.25
K_2O	2.43	3.11
P_2O_5	0.21	0.14
SO_3	0.04	0.19
TOTAL	99.49	99.23

The reactivity investigation of both aggregates was conducted at UTS following the Australian standards AS 1141.60.1 (AMBT) and AS 1141.60.2 (CPT) and a summary of the results are presented in Table 3-4. The expansion results for mortar bars and concrete prisms are shown on the following Figures 3-1 and 3-2.

The results of the expansion according to the procedure outlined in the Australian standard AS1141.60.1 accelerated mortar bar test (AMBT) for 10, 14 and 21 days are shown in Figure 3-1. This test method classifies the aggregate reactivity as slowly reactive when the expansion is between 0.10 and 0.30% in 21 days, and reactive when the expansion is ≥ 0.30.
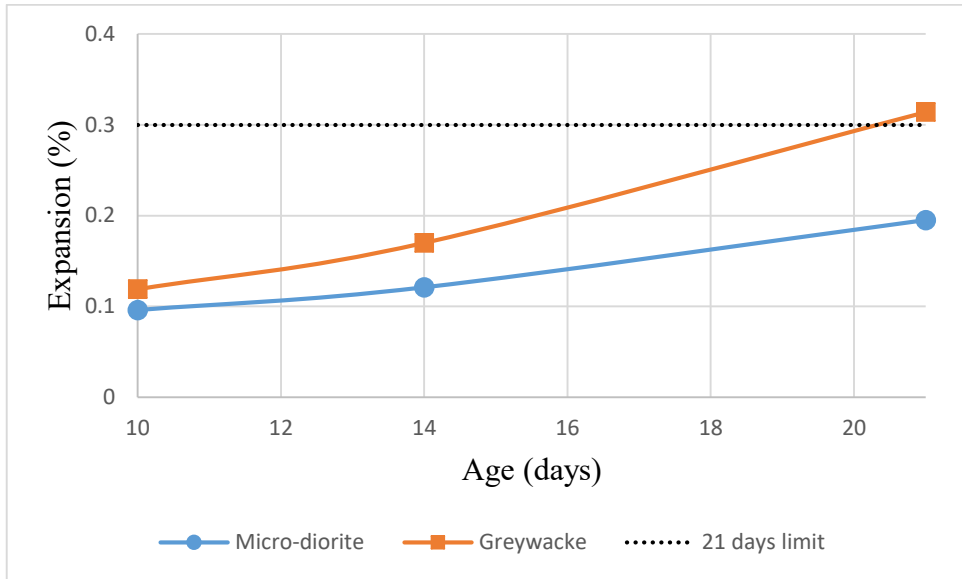
Figure 3-1: AMBT expansion of the aggregates at UTS.
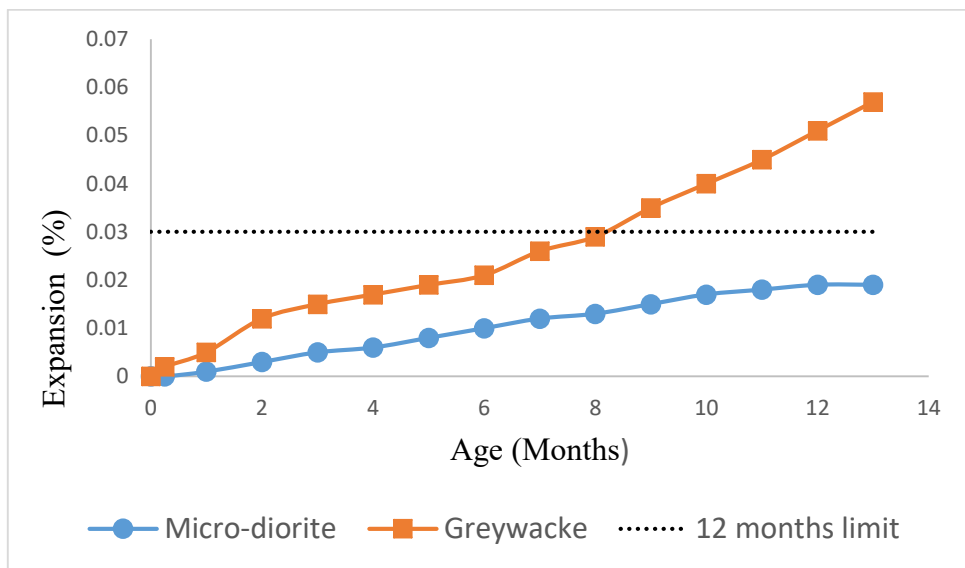
Figure 3-2: CPT expansion of the aggregates at UTS

Table 3-4: Aggregates reactivity according to CCAA results using AMBT and CPT

Aggregate	AS1141.60.1 (AMBT)	AS1141.60.2 (CPT)
Micro-diorite	Slowly reactive	Non-reactive
Greywacke	Reactive	Reactive

3.4 Fly ash and slag

CCAA provided fly ash and slag. A classified fly ash was used throughout out this study which complies with AS 3582.1 "Supplementary cementitious materials for use with Portland and blended cement Part 1: Fly ash". Fly ash was the primary SCM investigated in this research considering high acceptance in the market. Fly ash was used for the investigation of alkali release and for the evaluation of mitigation efficacy in mortar bars by cement replacement.

A single source of slag was used to investigate the release of chemical compounds to the pore solution for the purpose of comparison between these two SCMs and consequently understand their mitigation method. The chemical analysis of both SCMs, based on XRF analysis, is shown in Table 3-5.

Table 3-5: Oxide chemical composition of the SCMs: fly ash and slag

Oxide wt.%	Fly ash	Slag
SiO_2	62.71	34.12
TiO_2	1.00	0.87
Al_2O_3	24.98	14.37
Fe_2O_3	2.72	0.30
Mn_3O_4	0.08	0.36
MgO	0.49	5.31
CaO	2.25	41.59
Na_2O	0.87	0.35
K_2O	1.49	0.26
P_2O_5	0.23	0.01
SO_3	0.13	2.83

4 Methodology

The experimental work was conducted by preparing different types of specimens: slurries, fine aggregate mortars and mortar bars. Three chemical analyses were used to characterise the samples. This section describes each of them. The different methods for the preparation of specimens allow the investigation of ASR following a variety of scenarios with focus on investigating the consequences of varying alkali content.

4.1 Samples preparation

4.1.1 Slurry of the raw materials

Slurry was carried out to evaluate the alkali released from the materials into solution and also to measure the reactivity of aggregates in sodium hydroxide solutions. The investigation of the raw materials cement, micro-diorite aggregate, greywacke aggregate, fly ash and slag had the purpose of looking at the behaviour of each material in various solutions at different temperatures. The aggregates were ring mill ground to a fine particle size (< 150μm) and the other materials were tested as received. Each specimen was prepared by mixing 1.00 ± 0.01 g of the material with 10 mL of the following solutions:

- Deionized water (DI water),
- 0.33 M NaOH,
- 0.66 M NaOH,
- 1.00 M NaOH and
- 1.33 M NaOH.

The material was mixed into solution in an HDPE (High-density polyethylene) tube, closed tightly and shaken to produce homogenous slurries. Each mix was placed for 28 days in ovens at 80°C.

After 28 days the samples were filtered using 20 micron filter paper, and the solid material retained was kept in a vacuum drying oven at 40 °C for 48 hours and then placed in new HDPE tubes until required for analysis.

4.1.2 Sample preparation for MP-AES analysis (Microwave plasma atomic emission spectroscopy)

The slurry specimens prepared with DI water and 1 M NaOH solution and stored at 80°C and had 1.0 mL of the supernatant collected on days 1, 7, 14, 21 and 28. A solution of 1% nitric acid solution (HNO_3) was prepared from a 69% concentrated solution supplied by Choice Analytical containing trace impurities of <10 ppt. The collected sample was diluted in 20 ml of 1% HNO_3 and then filtered with 0.45 µm membrane filter and syringe, then stored in a new HDPE tube at room temperature for MP-AES analysis.

4.1.3 Slurry of aggregates with calcium hydroxide

The reactivity of the silica phase was investigated with the addition of calcium hydroxide ($Ca(OH)_2$) in order to simulate pore water solution environment. The silica phase from the aggregates and from the fly ash was investigated by mixing the aggregates, or the fly ash, with calcium hydroxide and using four different solutions: 0.6 M, 0.8 M, 1.0 M and 1.25 M NaOH solution. This slurry test was carried out by mixing each material as shown in Table 4-1 with 10 ml of sodium hydroxide solution, the 1:1 ratio makes a reproducible mix and the CH is in excess resulting in a saturated solution with respect to Ca ions. The tubes were closed tightly and. The tubes were then placed in a 38°C oven and after 28 days the samples were filtered with 20 micron filter paper and the retained material was dried in a vacuum oven at 40 °C for 48 hours and then stored in a double-sealed bag until required for analysis.

Table 4-1: Mix design of slurry specimens of aggregates, fly ash and calcium hydroxide

Sample ID	10 mL NaOH (M)	Micro-diorite (g)	Greywacke (g)	Fly ash (g)	Ca(OH)$_2$ (g)
MD 0.6	0.6	1	-	-	-
MD 0.8	0.8	1	-	-	-
MD 1.0	1.0	1	-	-	-
MD 1.25	1.25	1	-	-	-
MD-CH 0.6	0.6	1	-	-	1
MD-CH 0.8	0.8	1	-	-	1
MD-CH 1.0	1.0	1	-	-	1
MD-CH 1.25	1.25	1	-	-	1
GW 0.6	0.6	-	1	-	-
GW 0.8	0.8	-	1	-	-
GW 1.0	1.0	-	1	-	-
GW 1.25	1.25	-	1	-	-
GW-CH 0.6	0.6	-	1	-	1
GW-CH 0.8	0.8	-	1	-	1
GW-CH 1.0	1.0	-	1	-	1
GW-CH 1.25	1.25	-	1	-	1
FA 0.6	0.6	-	-	1	-
FA 0.8	0.8	-	-	1	-
FA 1.0	1.0	-	-	1	-
FA 1.25	1.25	-	-	1	-
FA-CH 0.6	0.6	-	-	1	1
FA-CH 0.8	0.8	-	-	1	1
FA-CH 1.0	1.0	-	-	1	1
FA-CH 1.25	1.25	-	-	1	1

4.1.4 Fine aggregates mortar bars with aggregates and fly ash at 60 °C

The cement paste specimens were prepared mixing cement and fine aggregates with and without fly ash. The alkali content in cement was considered for the calculation of the sodium hydroxide solution. The aim was to boost the alkali concentration to the desired total alkali content (Na$_2$O$_{eq}$) and the mix design is described in Table 4-2 below. It followed a water/binder ratio of 0.5 where the aggregates were crushed down to particle size of below 150 µm. The fine aggregates mortars were placed in HDPE centrifuge tubes, closed tightly and

stored in a 60 °C oven. Over 4 months at the age of 1, 7, 14, 21, 28, 56,84 and 112 days, one sample of each mix was taken out of the oven and ground for characterisation analysis.

Table 4-2: Mix design of mortars specimens stored at 60 °C

| Sample number | Sample ID | Alkali boosted (%) Na_2O_{eq} | Aggregate (g) | Cement composition (g) | |
			Micro-diorite	GP cement	Fly ash
1	MD 0.6	0.6	24	24	-
2	MD 0.8	0.8	24	24	-
3	MD 1.0	1	24	24	-
4	MD 1.25	1.25	24	24	-
5	MD-F 0.6	0.6	24	18	6
6	MD-F 0.8	0.8	24	18	6
7	MD-F 1.0	1	24	18	6
8	MD-F 1.25	1.25	24	18	6
Sample number	Sample ID	Alkali boosted (%) Na_2O_{eq}	*Greywacke*	GP cement	Fly ash
9	GW 0.6	0.6	24	24	-
10	GW 0.8	0.8	24	24	-
11	GW 1.0	1	24	24	-
12	GW 1.25	1.25	24	24	-
13	GW-F 0.6	0.6	24	18	6
14	GW-F 0.8	0.8	24	18	6
15	GW-F 1.0	1	24	18	6
16	GW-F 1.25	1.25	24	18	6

4.1.5 Mortar bars preparation for AMBT experiment

The effect of different alkali levels to potentially induce ASR was investigated by analysing mortar bars' expansion and chemical analysis of small mortar specimens for 56 days, and 28 days respectively. The standard AS 1140.60.1:2014 – AMBT requires a storage solution of 1M sodium hydroxide and in this experiment the same mortar mixes were also stored at 0.7 M and 1.3 M NaOH solutions besides the standard solution.

The cement and fly ash were used as received. The coarse aggregates were crushed, sieved, and remixed to provide based on the particle size distribution required by AS 1140.60.1 shown in Table 4-3.

Table 4-3: Particle size distribution of aggregates for mortar bars

| Sieve size | | Mass (%) |
Passing (mm)	Retained on (mm)	
5	2.5	10
2.5	1.25	25
1.25	0.63	25
0.63	0.315	25
0.315	0.150	15

The proportion of dry materials for every mix was 1 part of GP cement to 2.25 parts of graded aggregate (by mass) as outlined in AS 1141.60.1 accelerated mortar bar test. The water-cement ratio was 0.47 and each batch had enough mix to prepare three bars (2.50x2.50x250cm) and the extra material of the batch was used to prepare small specimens on ice cube trays (about 3x3x3cm). The mix design of the mortar specimens is in Table 4-4.

Table 4-4: Mortar bar mix design

Specimen #	Sample ID	Aggregate	Cement proportion (%)		Stored solution
			Cement	*Fly ash*	NaOH (M)
1	MD 0.7	Micro-diorite	100	0	0.7
2	MD 1.0				1.0
3	MD 1.3				1.3
4	MD-F 0.7		75	25	0.7
5	MD-F 1.0				1.0
6	MD-F 1.3				1.3
7	GW 0.7	Greywacke	100	0	0.7
8	GW 1.0				1.0
9	GW 1.3				1.3
10	GW-F 0.7		75	25	0.7
11	GW-F 1.0				1.0
12	GW-F 1.3				1.3

The preparation of the mixes followed the procedure described in the standard, where the water is first poured in the mixing bowl and cement is added to the water. A Hobart mixer was used to mix the batches, starting at slow speed for 30 seconds. In the first 10 seconds the

desired aggregate was added to the bowl, combined with fly ash if required, and then the speed was increased to medium for another 30 seconds. Then, the mixer was stopped and the mortar collected on the sides was scraped into the bowl for 20 seconds, after which the mixer was turned on for another 60 seconds at medium speed.

After the mixing was concluded, each batch was placed in a mould and stored in a humidity chamber (Thermoline Scientific) set at 24°C with a humidity ≥ 90 % for 24 hours. The mortar bars were then de-moulded and submerged in a tank with room temperature water. The tank was placed in an oven where the temperature of the water was increased to 80°C in less than 2 hours. After 24 hours, the specimen lengths were measured and the specimens were transferred a tank containing sodium hydroxide solution at 80°C for the rest of the experiment.

The length measurement of each sample was taken after the mortar was taken out of the batch and within 15 seconds it was dried and measured where the room temperature was set at 23°C ± 2°C. This was done to ensure that ambient temperatures did not affect the expansion readings. The same digital length comparator and reference bar was used during the entire experiment to secure accuracy. The same procedure was conducted with the mini specimens placed in the ice cube tray.

4.2 Specimens analysis

4.2.1 Microwave plasma atomic emission spectroscopy (MP-AES)

Elemental analysis can be carried out by MP-AES which is an atomic emission technique where the microwave plasma is fuelled with nitrogen which reaches 4700°C and at this high temperature the atomic emission is strong and produces excellent detection limits (Vudagandla et al. 2017). A nebulizer and a spray chamber converts the liquid sample to aerosol and introduces it into the centre of the hot plasma where atomisation occurs and each component is excited (Figure 4-1). Once an atom of a specific element is excited, it emits light, an emission spectrum, in a characteristic pattern of wavelengths, as it returns to the lowest energy state and an atomic emission detector measures the results. MP-AES quantifies the concentration of elements in a sample by comparing the emission obtained from the sample with a plotted calibration curve prepared using solutions with a known amount of each element. The final result is the concentration of the elements in the sample.

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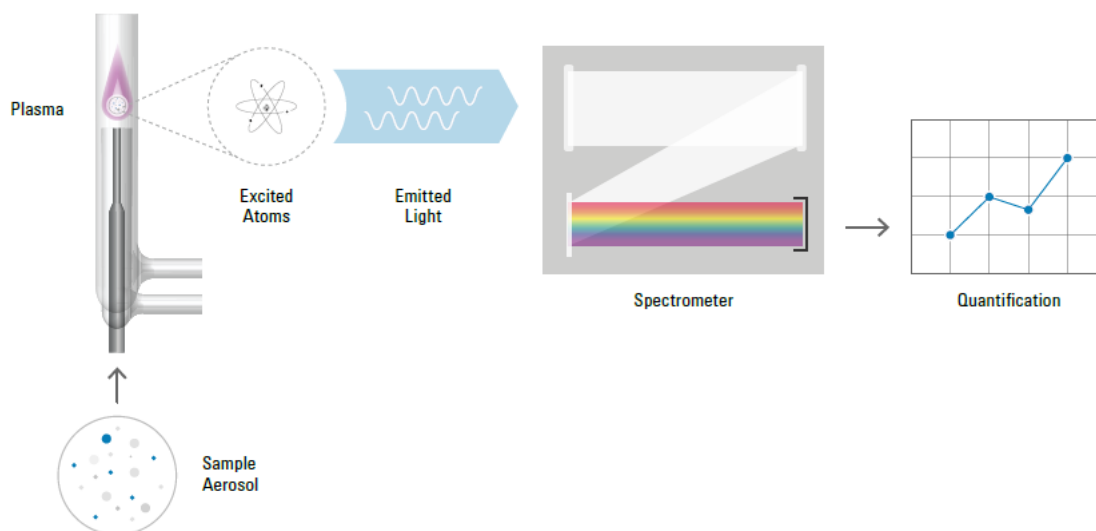
Figure 4-1: Diagram of microwave plasma atomic emission spectrometer
(Agilent 2018)

The analysis was carried out using a 4210 MP-AES Agilent. The instrument was equipped with a nebulizer and a double pass spray chamber. Every analysis consisted of a 45 second rinsing with acid solution (0.5% nitric acid + 0.5% hydrochloric acid) followed by 55 seconds of sample uptake (pump speed 80 rpm) and then 15 seconds of stabilization time before the readings (with pump speeds at 15 rpm). The nebulizer flow was 0.95 L/min for every wavelength with 3 replicate readings.

The wavelengths were carefully chosen from the options pre-existing in the instrument based on the most sensitive with the lowest spectral interference. After some experiments, the wavelengths were selected and are given in Table 4-5 with the corresponding selected elements. The automatic background correction mode available in the software and the autosampler Agilent SPS-4 were used during the analysis.

The calibration solutions were prepared from a multi-element solution by Merck containing 1000 ppm of Ca, Na, K and Al. Additionally, the silica was introduced to the calibration solutions from a single element solution of 1000ppm by Merck. The standard solutions were diluted for calibration of the MP-AES in the range 0.05 to 10 ppm with 1% HNO_3. The calibration curve was linear with a correlation coefficient >0.997. The calibration solutions were analysed in the beginning and after every 20 samples.

Table 4-5: Wavelengths for MP-AES analysis

Elements	Wavelength (nm)
Sodium	589.592
Potassium	766.491
Calcium	396.847
Silica	251.611
Aluminium	396.152

4.2.2 Thermogravimetric analysis (TG)

The degree of hydration of the specimens were carried out by thermogravimetric analysis (TG) which measure the mass loss at particular temperatures allowing a semi-quantitative determination of certain phases present in the specimen (Monteagudo et al. 2014). The mass loss data was collected using a Netzsch thermogravimetric analyser. The samples were dried in an oven at 40°C for three days and then ground using a ring mill grinder for 2 minutes. Each sample as then mixed after homogenises for a representative sample, and a fine sample was weighed (20 ± 0.5 mg) in an alumina crucible and placed into the instrument. After the introduction of the sample the instrument stabilised at 40°C for 10 min prior to heating at a rate of 10°C/min to 1000°C in a helium purge with a flow rate of 60 mL/min.

The collected data files were converted to csv files and analysed in Microsoft Excel. The TG curve show the mass loss of the specimen over a period of time as the temperature increase, as shown in Figure 4-2. The mass difference method can cause a significant error, mainly because the samples were not free from carbonation. In addition, CSH does not decompose only from 150~400°C as It loses water in the very wide range of temperature from 100 ~900°C. This means that 400~480°C is not only for $Ca(OH)_2$ decomposition but also has CSH decomposition. Thus, if one can only rely on the mass loss between the temperature, it may overestimate the results. You may want to see the paper (Kim T. and Olek J., 2012).
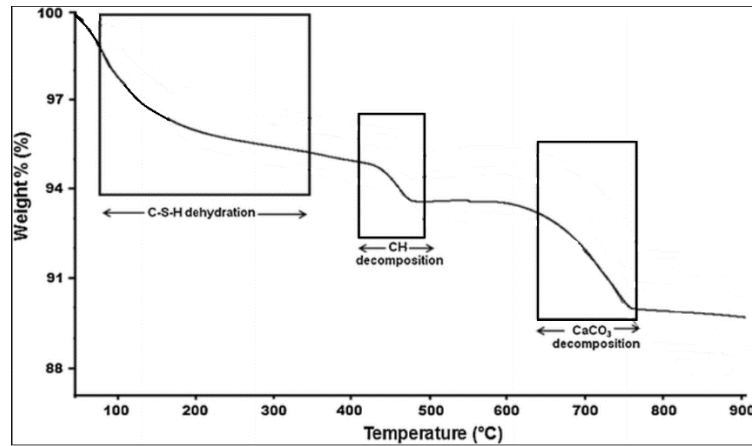
Figure 4-2: General TG curve of cement mortar
(Singh et al. 2015)

The issue identified in this experiment is that as cement hydrate, more CSH is formed, more bound-water content in the specimen, even though the cement was dried for extended period of time. Ideally, the final mass is determined but there is no absolute mass measure but only relative mass. Therefore, there is an error related to the determination of degree of hydration, on the CSH and CH content. The temperature chosen to calculate the mass loss in each phase can significantly change from one study to another, especially for the mass loss of the CSH dehydration phase (Monteagudo et al. 2014). Table 4-6 give the temperature range to measure each chemical phase. These parameters of measurement to estimate the degree of dehydration and rate of reaction are general and could be slightly modified to other experiments since it is based on the chemically bound water of mineral additives blended cement (Deboucha et al. 2017).

Table 4-6: Temperature ranges for phases identification

Temperature (°C)	De-hydration phase
40 – 150	Free water
150 – 400	CSH phase
400 – 480	dihydroxylation of $Ca(OH)_2$
480 – 900	decarbonation of $CaCO_3$

4.2.3 X-ray diffraction (XRD)

This X-ray diffraction (XRD) was used for investigation of the chemical phases in the specimens. This technique allows us to investigate the crystalline phases of samples and obtain

phase quantification with quick and reliable results. In this research the XRD data were collected using a Bruker Discovery D8 XRD using Cu Kα radiation with a wavelength of 1.5148 Å. The powder samples were evenly packed into the sample plates and diffraction patterns were collected in the range 3° to 75° with a step increment of 0.04 °2θ at 0.630 s for each point. DIFFRAC.SUITE software was used for data acquisition and evaluation. Phase identification was carried out using the International Centre for Diffraction Data (ICDD) ICDD Products - PDF-4+ database.

4.2.4 Fourier transform infrared spectroscopy (FTIR)

FT-IR spectroscopy is a useful and convenient method to study the cementitious materials. This technique provides the characterization of the chemical compounds in each sample allowing the investigation of reaction and modifications. The analyses were carried out on a Nicolet iS10 fitted with a Smart iTX (diamond) by Thermo Scientific ATR accessory. Circa 10 mg of powdered sample was placed on the ATR crystal and spectra were collected using a resolution of 4 cm-1 averaged over 64 scans.

4.2.5 Mortar bar length measurement

The length of the mortar bars was measured periodically using the same horizontal comparator and reference bar for every reading during the entire experiment. The expansion of each specimens was calculated according to the formula:

$$E_{n=} \left(\frac{\ln -l_z}{lg} \right) x100$$

Where:

$E_n =$ Expansion of each specimen after a period of *n* days since the zero reading

$l_n =$ specimen length after a period of *n* days since the zero reading

$\quad l_z =$ specimen length at zero reading

$\quad l_g =$ the effective gauge length of the specimen

The overall expansion of each mix for each time period was calculated with the average expansion of the three specimens. This physical investigation allows us to evaluate the effect of each alkali solution concentration into each aggregate with and without fly ash.

Due to water evaporation, a liquid sample (± 50 ml) was taken from each bath once a week to measure changes in the concentration by titration and then water was added to adjust the solution to the desired solution concentration.

5   Results and discussion

The experiment program of this research was developed to investigate the potential of an alkali threshold in concrete systems and the opportunity to propose a balanced alkali limit to mitigate ASR. One of the important factors for ASR is alkalinity which is influenced by alkali ion content of the pore solution; reactive silica present in the aggregates and water for hydration of the hygroscopic alkali ions in the formed ASR gel causing expansion and potential cracking. A series of experiments were carried out to investigate the role of alkali concentration in the ASR reaction in the context of the potential for threshold determination in a balance alkali approach to concrete mix design. The reason for the investigation of the alkali concentration and reactivity was to initiate the process of ASR. In order to understand threshold, firstly it is required to understand the chemical part of the reaction involved in ASR.

An initial assessment of the aggregates was carried out to evaluate their relative reactivity to alkali by investigating the influence of temperatures and alkali concentration on slurries of finely ground aggregate. After a better understanding of the relationship between reactivity and alkali content, the investigation of aggregates dissolution and SCMs was carried out by monitoring the Ca, Si, Al, Na and K in aqueous and alkaline slurry tests. The fundamental evaluation on each material support the research for an understanding of the important factors related with ASR, aggregate reactivity and cations. Subsequently, slurry tests in the presence and absence of calcium hydroxide (CH) with aggregates and fly ash were prepared to investigate the reactivity using TG (CH) and XRD (CH and quartz). Lastly, the physical reaction of ASR was investigated by AMBT expansion studies incorporating fly ash at a range of alkali concentrations combined with phase analysis.

5.1   Effect of temperature and alkali concentration in aggregates reactivity

The aggregate reactivity and the rate of alkali-silica reaction can vary according to the environment of the concrete structure. High alkali availability in the pore solution can cause more deleterious reactions. Figure 2-2 of the literature review showed that higher alkali content provides higher pH solution. Therefore, a range of alkali concentrations at a range of temperatures should provide a relationship between alkali concentration reactivity and rate in the context of accelerated reactions. Thus, the reactivity of micro-diorite (MD) and greywacke (GW) was investigated by determining the influence of four temperatures and five alkali

concentrations on the dehydration of the specimens. The N-S-H phase content was investigated using thermogravimetric analysis (TG) to determine the degree of reaction by measuring the water loss in the temperature range 40 to 100°C.

$$\text{Aggregate Reactive Silica (SiO}_2) + \text{Solution Alkali (NaOH)} \longrightarrow \text{N-S-H gel}$$
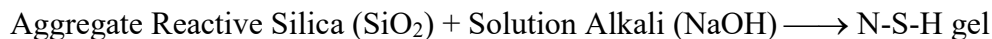
The results in Figure 5-1 shows that increased reaction occurred at higher temperatures and higher alkali concentrations for both aggregates studied. At low temperature, 23 °C and 38 °C, minimal reaction was observed over the reaction time frame for all alkali concentrations studied. The mass loss of water increased as the concentration of NaOH solution increased at 60 and 80 °C for greywacke, demonstrating it to be more reactive than micro-diorite. Consequently, this result provides a good correlation with AMBT and CPT expansion.

Minimal reaction was observed at ambient temperature. The ASR in concrete occurs after a period of time and so it correlates that ambient and 40 °C show minimal reaction for both aggregates over the short period of time (28 days). The results demonstrate that under laboratory conditions accelerated aging is required for aggregate screening. i.e. acceleration is at elevated temperature or the study must be conducted over longer periods of time. At elevated temperature, even for a slurry test, it is possible to evaluate the relative reactivity of the aggregates suggesting that this is a possible screening test method.

The increase of alkali levels at 60 °C impacted the reactive aggregate and the highest temperature (80 °C) had the greatest reactivity. This indicates that the relative reactivity of the aggregates is not significantly affected by the increase in alkali content in lower temperatures. Considering the experimental error, it appears that there is no threshold and simply the degree of reaction increases with increasing concentration of alkali at high temperatures (≥60 °C). This is not given in room temperature or 38 °C as the reaction is too slow for the time frame studied within the experimental sensitivity of the test. More extensive experiments might be necessary since this is a slow reaction that can take years or even decades to occur in a real outdoor concrete structure. In extreme environments such as elevated temperatures, the reaction occurs at a much faster rate and indicates that an increase in the pH pore solution will potentially cause ASR.
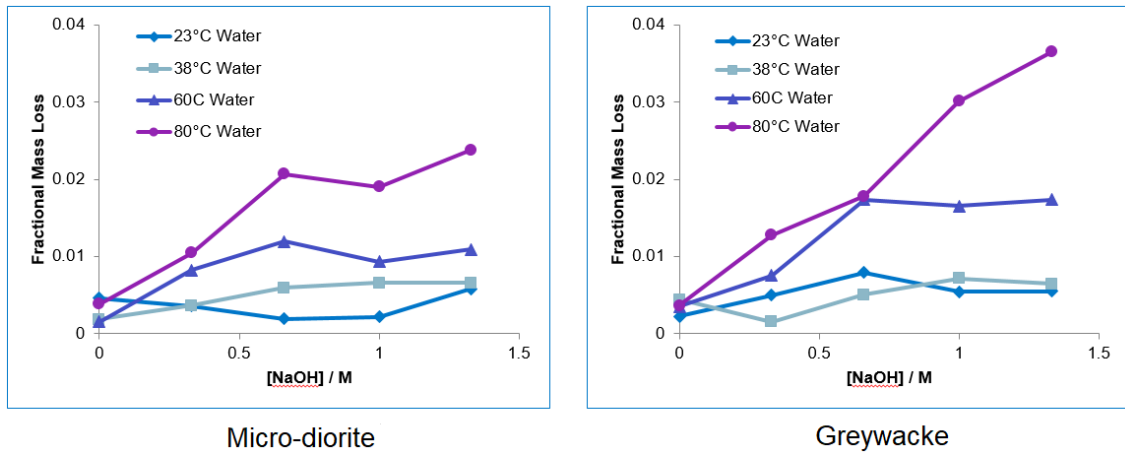
Figure 5-1: Water loss of the specimens versus NaOH concentrations

5.2 Release of cations from slurries submerged in water and alkali solutions

An investigation of the rate of release of alkali, calcium, aluminium and silicon ions into solution was carried out for each raw material in neutral and alkaline media. The collected supernatant samples were analysed using MP-AES to investigate the quantity of cations released from cement, micro-diorite, greywacke aggregate, fly ash and slag. The elements released measured were: sodium (Na), potassium (K), calcium (Ca), silica (Si) and aluminium (Al). These chemical elements are essential for understanding alkali-silica reaction. The slurry specimens prepared in this study are listed in Table 5-1.

Table 5-1: Specimens identification

Sample ID	Solution	Material
H2O CE	Water	Cement
H2O MD	Water	Micro-diorite
H2O GW	Water	Greywacke
H2O FA	Water	Fly ash
H2O SL	Water	Slag
NaOH CE	1 M NaOH	Cement
NaOH MD	1 M NaOH	Micro-diorite
NaOH GW	1 M NaOH	Greywacke
NaOH FA	1 M NaOH	Fly ash
NaOH SL	1 M NaOH	Slag

Sodium

The availability of alkalis to the pore solution was investigated by this qualitative experiment which can provide an indication of the relative degree of alkalis released based on the concentrations measured in the tests. In water, cement releases a significant amount of alkalis (Na^+) while the other materials do not. The alkali in cement comes from the raw materials such as clay, limestone, chalk, and shale mostly present in the form of alkali salts (Jawed & Skalny 1977). The sodium concentration measured among those four materials is indicative that the primary source of sodium ions originates from the hydration of the cement.

As shown in Figure 5-2, sodium released appears to take longer than 1 day for cement, but is high from 7 days onward. Among the aggregates, micro-diorite and greywacke released similar amounts of sodium where both aggregates show much less release than cement as might be expected according to the literature review (Berra, Mangialardi & Paolini 2018). Therefore, the aggregates can release a small amount of alkali to the pore solution and may contribute to the overall alkali content. The supplementary cementitious material had the lowest amount of sodium released. The concentration values reported in this section are the concentrations in the real solutions after correcting the dilution and due to the very small amount of sample for analysis and high water cement ratio, the values found are very low.

It is evident that cement is the principal supplier of sodium to the solution, followed by the aggregates and then lastly fly ash. These alkalis released by cement are available to the pore solution, since firstly, the cement hydration does not bind alkalis in the hydration product CSH (Wang et al. 2008). The alkali-silica reaction is likely to occur in an environment with a high alkali content, and these results show us that even in a lower amount in comparison to cement, aggregates and SCMs can also supply sodium to the system. Accordingly, with these results, the release of alkalis by other materials in the concrete mix besides the cement, have been found. Nonetheless, it is important to evaluate the total alkali content of the overall concrete system instead of measuring the alkali content of cement only since the alkali content can be significantly increase and consequently causing deleterious ASR.
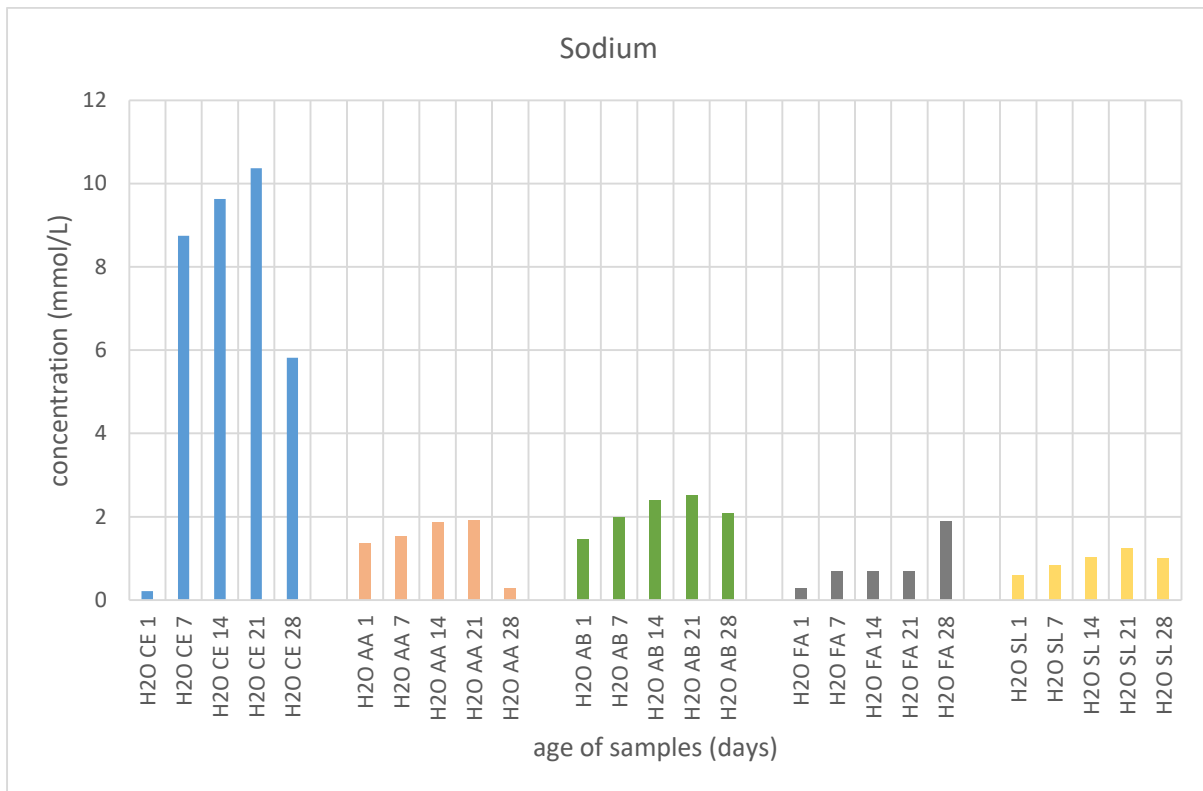
Figure 5-2: Sodium ions (mmol/L) release over 28 days period at 80°C

Alkali ions in the pore solution elevate the pH as many researchers acknowledge that the presence of monovalent cations (Na+, K+) influence the pH by increasing the alkalinity of the pore solution (Plusquellec et al. 2017). At elevated pH the other materials can release alkalis which is critical in the alkali cycling as the ASR-gel is formed. Investigating dissolution of the alkalis from the other materials in alkaline solution is therefore of value as it may contribute to the continued reaction.

Potassium

In Figure 5-3 the potassium ion concentrations in the pore solution are shown. GP cement released significant amount of the ions in water and NaOH systems, indicating that cement is again the primary source of dissolved alkalis, which is consistent with the sodium ion concentration data.

Micro-diorite and greywacke released potassium cations to the solution in the alkaline solution only due to the elevated solubility of the constituent silica phases present in 1 M NaOH. Fly ash and slag release potassium in a much lower extent under the same conditions.

The higher release of potassium in sodium solution have been previously reported, as discussed in Section 2-1-6, in accordance with these results. The released alkali emphasises the importance of many practical ASR problems where the higher alkali concentration, the greater the concrete expansion due to ASR. These results confirm that other materials besides cement can supply alkali to the pore solution.

This indicates that at higher pH, aggregates as well as SCMS may be an additional source of alkali ions in solution. In addition to cement, aggregates and SCMs may contribute to the pore solution alkali content increasing the potential risk of ASR (Drolet, Duchesne & Fournier 2017a). The elevated potassium ion concentrations for elevated pH dissolution suggest that this may be an issue where further release of alkali ions from the aggregates and/or SCMs may replenish the alkali ion concentration in the pore solution.
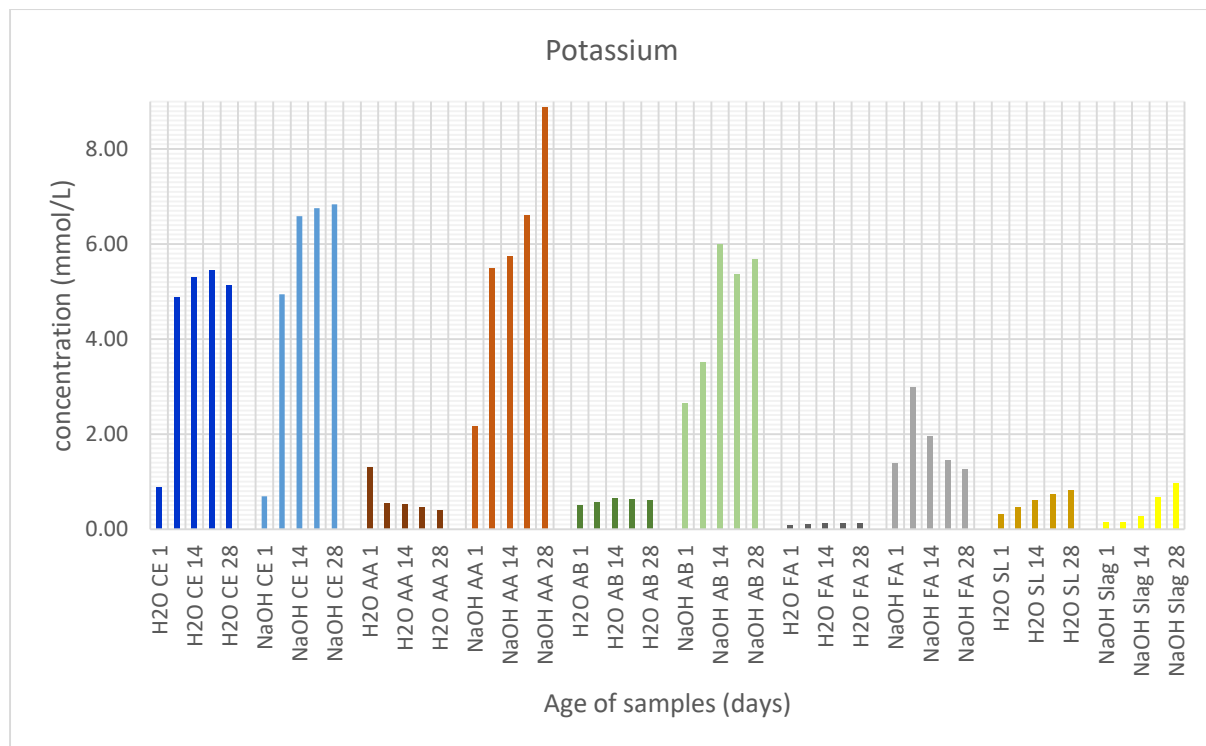
Figure 5-3: Potassium ions (mmol/L) released over 28 days period at 80°C

Calcium

In Figure 5-4, calcium availability was higher in water solutions for all the materials, as expected, since hydroxide ions suppress calcium ion solubility in saturate CH solution, due to the common ion effect (Wang & Gillott 1991) so a lower concentration of calcium was measured in alkaline solution. It is important to always evaluate the calcium dissolution (Ca^{2+})

since it is abundant in Portland cement and increases the rate of precipitation of the silica gel (Leemann et al. 2011).

The dissolution of calcium ions into the solution occurred in significant quantities for cement as the aggregates and FA are relatively low in CaO content (Table 5-5). The calcium ion concentration in the NaOH solution is significantly suppressed as the solubility of calcium ions decreases significantly as the pH increases (Moragues, Macias & Andrade 1987).

The high level of free silica (SiO_2) and low levels of calcium (CaO) available in fly ash composition supports the efficacy of mitigating ASR, remembering that cement is very high in calcium and low in silica. The Ca dissolved from the slag hydrates to form CSH where in the high pH condition, calcium released from the solid can easily combine with silica and produce CSH and it may be the reason for the almost negligible amount of calcium in the system. And this also explains the low Ca present in FA, due to the formation of CSH which limits the availability of Ca to the solution (Thomas 1995).
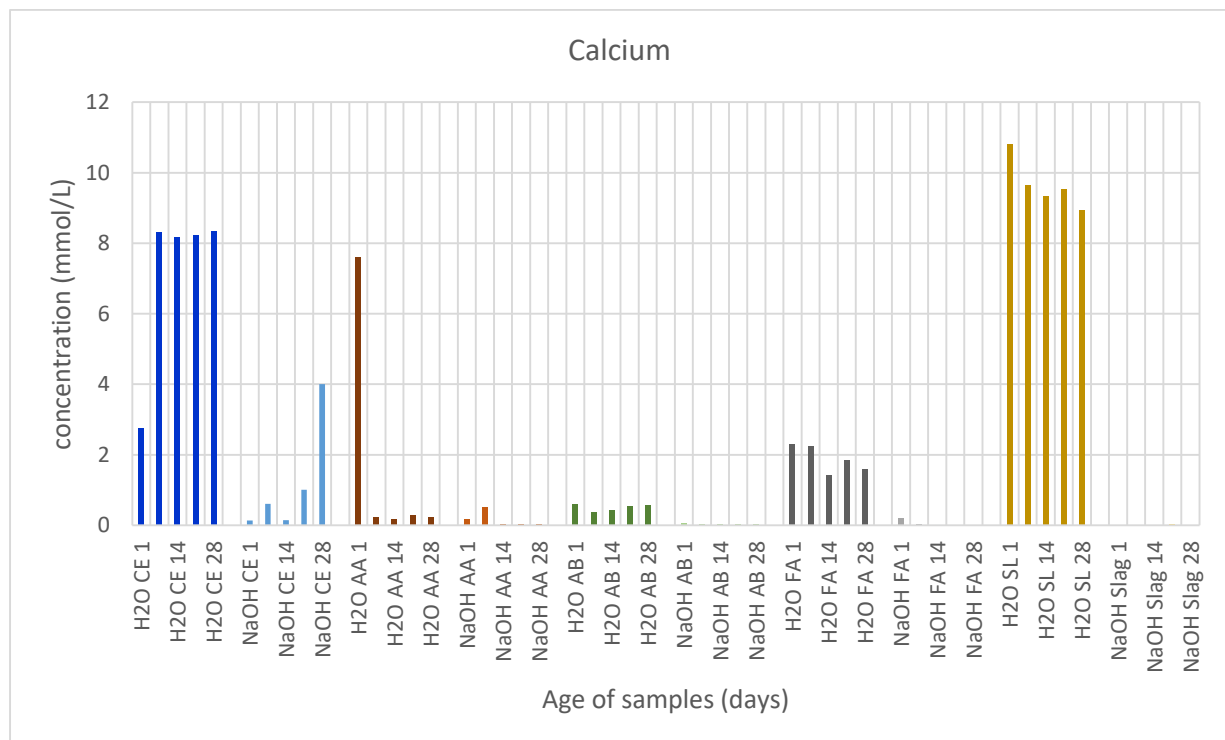

Figure 5-4: Calcium ions (mmol/L) released over 28 days period at 80°C

Silica

The solubility limit of silica relies on the pH of the pore solution (Kim, Olek & Jeong 2015) where at water solution (low pH) the hydrolysis (dissolution) is low and increases as the

alkali concentration increases (Maraghechi et al. 2016). Thus, the solubility of silica in alkaline solution increases with pH. In Figure 5-5 it is possible to visualize the silica dissolution in alkaline solutions and also the availability or lack of silica in high calcium content materials in the specimens.

The release of silica is dependent upon the amount of free silica, the reactivity of the available silica and the calcium available to react with silica. The silica released in the water solution was very little (< 0.5 mmol/L). Amorphous silica has a solubility of circa 10^{-3} mmol/L at pH 7 and therefore strained quartz, or more reactive silica phases such as opal, do not be release silica into the solution (Iler 1979).

The absence or negligibly low amount of silica in the system may be due to the CSH formation. CSH can reach the equilibrium condition in the system with a very low concentration. Whenever Ca is available in the system, released silica from the solid source readily react with Ca and precipitated as silica. Calcium silicates, C_3S and C_2S, are sufficiently soluble and react with water fast. Consequently, this effect obviously affects the absence of Si in cement, fly ash, and slag system..

Micro-diorite had a much lower level of silica when compared to greywacke, which demonstrated that the greywacke aggregate is more reactive, therefore increases the reactivity of ASR. Among the SCMs, the fly ash had a much higher level of silica than slag, which shows that fly ash is potentially more effective in preventing ASR, since the silica from SCMs is going to bind with more alkalis from the pore solution and consequently reduce the alkalinity of the system and mitigate ASR. The fact that micro-diorite did not release significant concentrations of silica into the solution is consistent with its classification as slowly reactive in AMBT and non-reactive by CPT.

The FA is also observed to release significant concentrations of silica into the solution at concentration at levels similar to the behaviour exhibited by greywacke. This release of silica is a key factor in ASR mitigation. From the context of the concrete pore solution, the release of silica ions into the solution from the FA provides solution silica for precipitation throughout the binder matrix. This precipitation is a competing reaction to the ASR reaction associated with aggregate silica. These processes are similar in that reactive aggregates release silica into the solution in an equivalent manner to FA. The elevated concentration of silica in solution results in polymerisation of the silica and precipitation of silica gel; however, for the reactive aggregate this precipitation process is a localised process where the silica gel can accumulate and expand to exert hydrostatic stresses, which may cause cracking of the concrete. In contrast,

the silica gel precipitated by the dissolution of silica from the FA is widely dispersed and non-localised. This dispersed accumulation of the silica gel formed is likely to be non-deleterious.
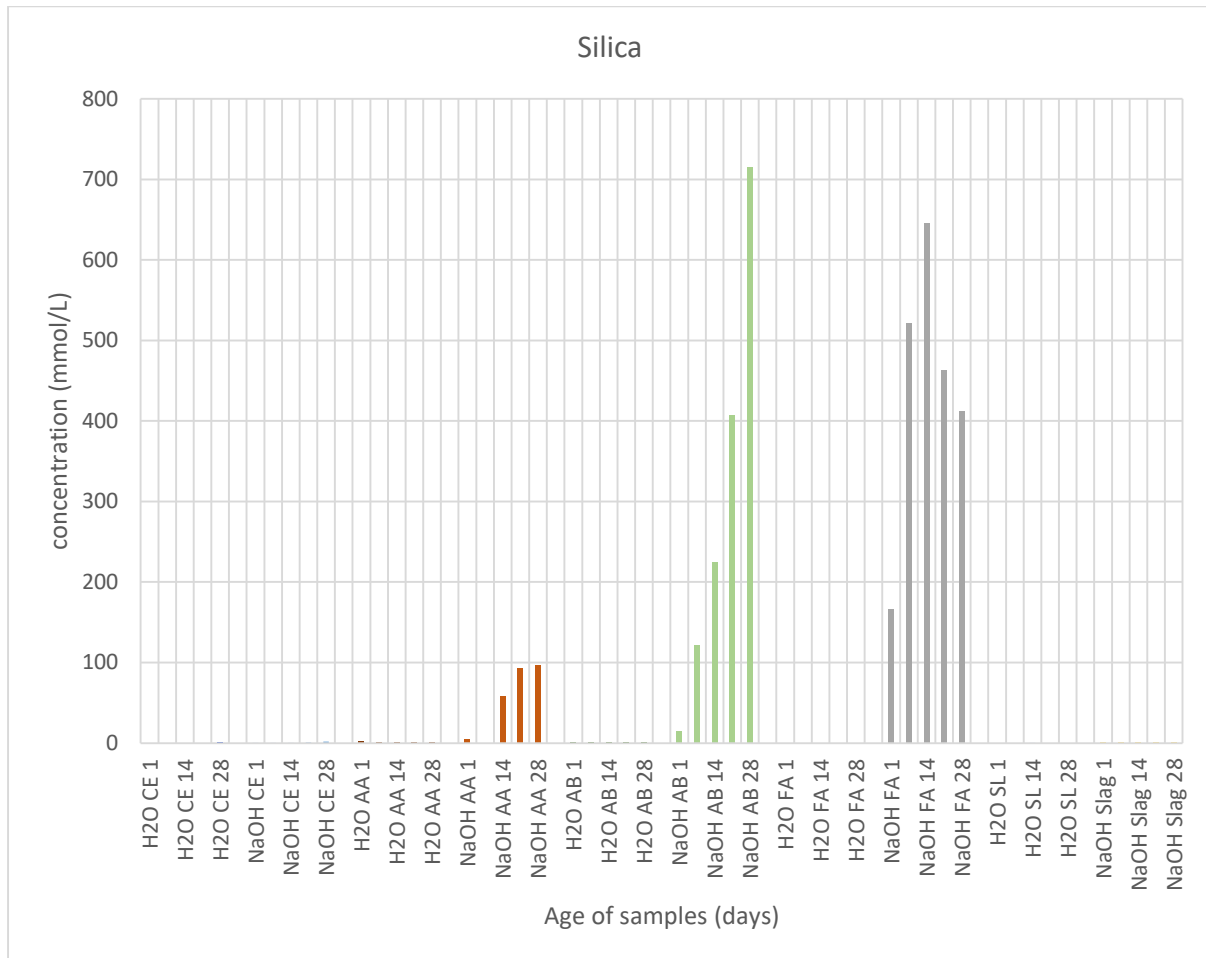
Figure 5-5: Silica ions (mmol/L) released over 28 days period at 80°C

Aluminium

Aluminium (Al) is released into solution at high pH hence very low levels were measured in water solution. For cement this is associated with the decomposition of the mineral ettringite $[(Ca_3Al(OH)_6.12(H_2O)_2.2H_2O]$. For the other materials, Al^{3+} is quickly released into the pore solution and soon after it is adsorbed into the silica surface hence the alumina concentration decreases with time (Chappex & Scrivener 2012b; Hay & Ostertag 2019).

The levels were higher in the alkaline solutions of day 1 in fly ash, MD and GW, which decreased during the 28 days analysis (Figure 5-6). Conversely, the Al^{3+} levels increased in the cement and slag samples in the alkaline solution. It had been shown that the aluminium content influences the alkali bound during the formation of CSH gel, depending also on the Ca/Si ratio

(Drolet, Duchesne & Fournier 2017b). This result agrees with other studies that show that the greywacke (Aggregate B) releases aluminium and silica where an interaction between them occurs (Hünger 2007).
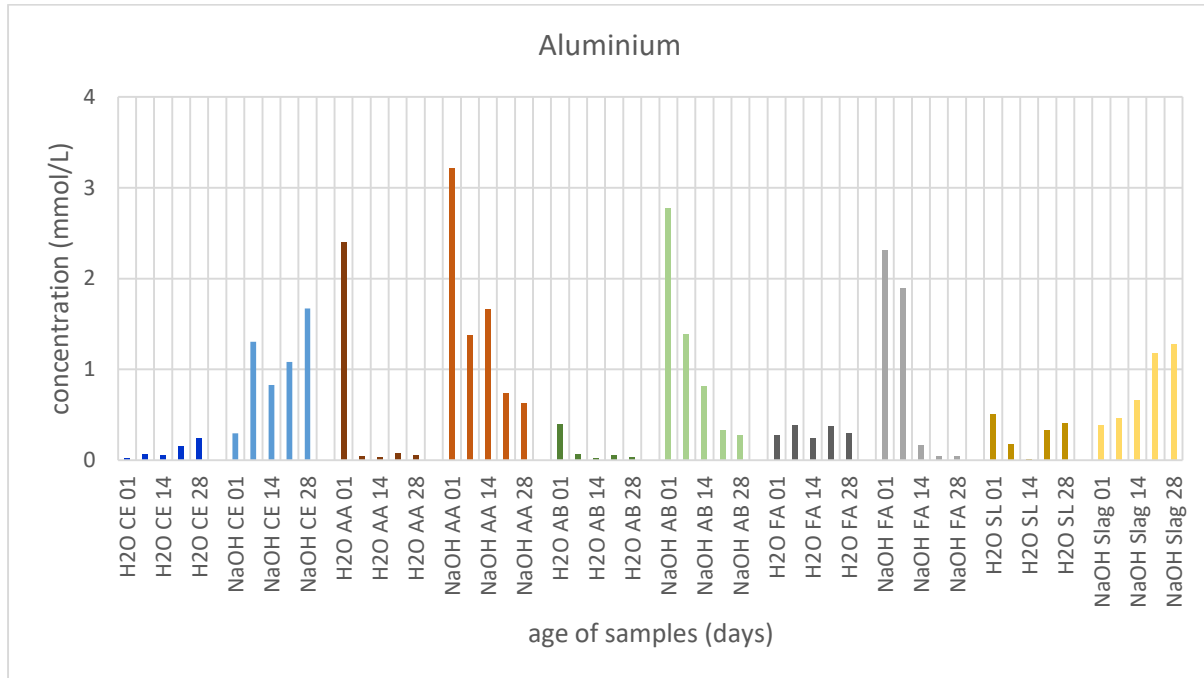
Figure 5-6: Aluminium ions (mmol/L) released over 28 days period at 80°C

5.3   Effect of (Ca(OH)₂ solution on the reactive silica phase of aggregates

The reactivity of the micro-diorite and greywacke aggregates were also investigated with the addition of calcium hydroxide (Ca(OH)₂, CH). The hydration of the cementing phases (C_3S and C_2S) produces the CSH cementing phases, but also produces CH as a by-product. The CH has two roles; releasing hydroxide ions to the pore solution through differential solubility and through the incorporation of Ca^{2+} ions in the ASR gel. Calcium ions act a s a co-reactant and help to precipitate the ASR gel. Without calcium ions incorporated into the process the precipitation of the ASR gel would be slow or may not occur and silica would be simply released to solution without precipitation (Diamond 1989). This section, therefore investigates the ASR reaction in the presence of CH through the addition of CH to the alkaline slurry mixes containing aggregates and FA.

Slurry tests were carried out by mixing 1g of aggregate and 10 mL of 1M NaOH or 1g of aggregate with 1 g of CH and 10 mL of 1M NaOH and storing the specimens for 28 days at

80°C. After 28 days the slurry specimens were filtered and dried in a vacuum oven at 40 °C for 48 hours then kept in a double sealed bag until analysis (mix designs are listed in Table 4-1). The investigation of the reaction was conducted by thermogravimetric (TG) analysis and X-ray diffraction (XRD). The nomenclature of the specimens is described in Table 5-2.

Table 5-2: Specimens nomenclature

Sample ID	Material	Additional
M	Micro-diorite	No
M-CH	Micro-diorite	Calcium hydroxide
G	Greywacke	No
G-CH	Greywacke	Calcium hydroxide
FA	Fly ash	No
FA-CH	Fly ash	Calcium hydroxide

From the TG data, the mass loss in the range 150 and 400 °C corresponds to the dehydration reaction of the CSH phase and between 400 and 480 °C corresponds to the decomposition of the CH phase. The graph in Figure 5-7 shows the correlation between the mass loss of the CSH region of each specimen and the alkali concentration of the solution where the specimens were stored. Although the CH decomposition is predominantly CH, there is some underlying CSH and carbonate decomposition in this range as well which is not accounted for in the method used. Higher fractional mass loss of CSH indicates lower degree of reaction. CSH region mass loss was observed to be negligible without CH as expected, while slurries containing CH showed mass loss which correlated to reactivity of the silica present.

The specimens with additional 1 gr. of CH showed reaction among all three materials, with increasing degree of reaction at the higher alkali concentrations. The reactivity for the aggregates and fly ash for all pH slurries followed the predicted reactivity: micro-diorite the least reactive followed by greywacke with fly ash being the most reactive. The reactivity of the aggregates in the presence of CH is consistent with the categorisation of the aggregate reactivity based on standard expansion tests.

The results suggest that the reactivity of the material is apparently more significant for the reaction than the alkali content where the degree of reaction increases up to 1 M then the increase is less pronounced. Although both are important and should always be considered, especially at high alkali levels with reactive materials. According to these results fly ash produced more CSH than the aggregates, and this agrees with previous studies discussed in Section 2.2.1. Fly ash is more reactive than the reactive aggregate greywacke since it contains more amorphous silica which will react with the CH to produce more CSH.
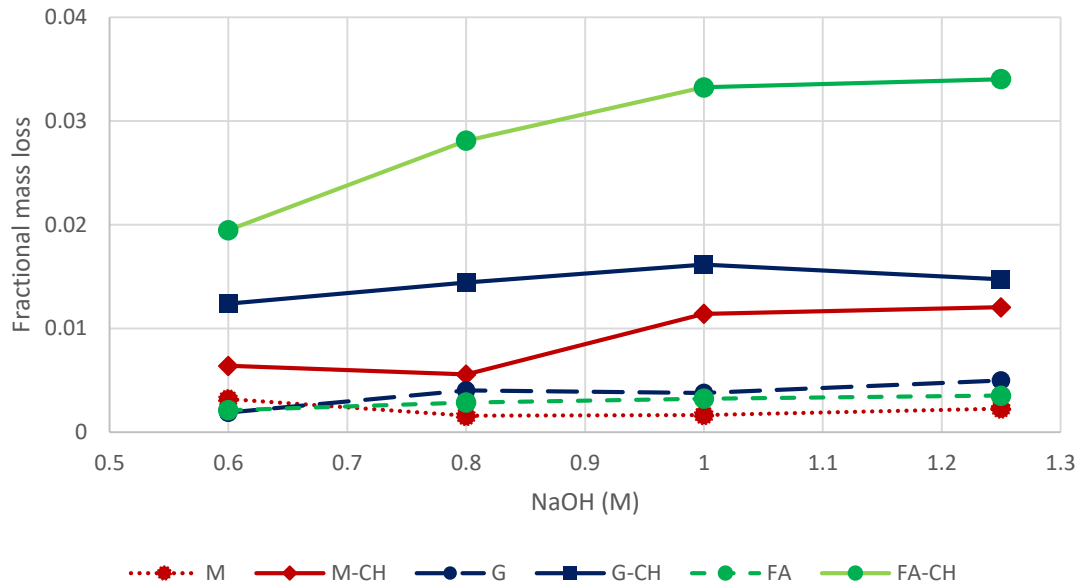
Figure 5-7: Fractional mass loss of CSH phase as a function of NaOH concentration.

The fractional mass loss of the calcium hydroxide (CH) determined from TG analyses is plotted in Figure 5-8. The specimens without the addition of CH were not included in this graph since CH was not present. The mass loss of each material is on average the same in all four solutions indicating that the increase of alkali concentration does not affect the consumption of CH. The figures together indicate that the presence of CH is an important indicative of reactivity, but it does not represent the formation of ASR and neither pozzolanic reaction. The CSH gel formation indicates without certainty that the amount of CH is consumed, but the lack of dependence on pH suggests that CH consumed is a balance between concentration in solution and rate of reaction. Higher pH means more reaction and more gel produced, but as there is less Ca ions in solution, it might be expected that less Ca is incorporated in the gel. The lack of a dependency on pH suggests that the depression of the solution concentration of Ca ions by increasing the pH gel is compensated by the relative rate of precipitation of CSH gel. i.e. The amount of CH consumed will depend on the reactivity of the silica phases present in the aggregate (Taehwan et. al 2019).

The higher consumption of CH in Figure 5-8 indicates greater formation of CSH and consequently more reaction. In this analysis, the reactivity indicated according to the consumption of CH follows the order FA>G>M. Possible origin of the different reactivity between the aggregates is the access to reactive silica which is limited by particle size. It should

be noted that deleterious expansive ASR gel should be formed in the later stages of the reaction during the hardened state where expansion can cause cracking therefore the relative reactivity should be based on later stage consumption of CH, being that these samples were analysed after only 28 days in solution. Most likely the fly ash is the most reactive materials as it consumes the most CH.
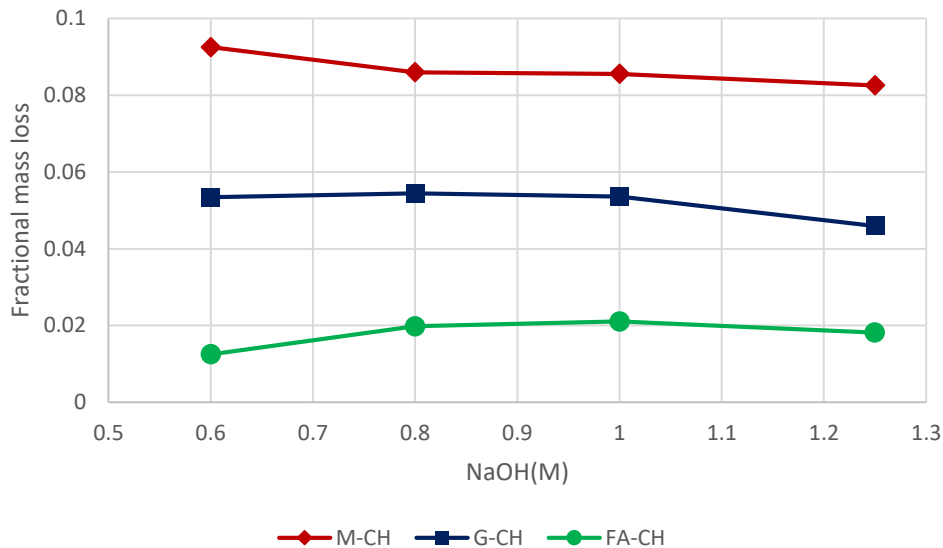
Figure 5-8: Fractional mass loss of CH as a function of NaOH concentration

The reactivity of the two aggregates and fly ash was additionally investigated by measuring the quartz peak with XRD. The results easily differentiate the reactive and non-reactive aggregate by following the relative intensities of the diffraction peak at $26.64°2\theta$ (Cu Kα). Figure 5-9 shows the normalised peak intensity of the aggregates and fly ash as a function of NaOH concentration.

The results show that micro-diorite aggregate had higher quartz peak for the specimens stored in every solution. The reactive aggregate greywacke had similar results to fly ash where lower quartz peak was measured for these two materials although the FA is predominantly amorphous, the quartz present shows similar reactivity to the GW on a normalised basis. The reduction of quartz by increasing the alkali concentration indicates that the higher alkali concentration (higher pH) increases quartz dissolution.

Aggregate micro-diorite classified as non-reactive by CPT shows a minor change even at elevated NaOH concentration and temperature (38°C) in which the reaction has occurred. The reduction of the quartz intensity peak shows that less of the mineral was present in the

solid sample and consequently, more of the silica ion was available in the pore solution. The relative degree of dissolution corresponds to the reactivity level of the aggregate. Greywacke aggregate has been classified as reactive and correspondingly, the quartz peak is observed to decrease significantly.

These results show that greywacke contains more silica available for reaction and higher alkali concentration leads to a higher silica dissolution. Consequently, more reaction will occur, similarly with fly ash. The amount of silica in the aggregate determined by XRF analysis (Table 4.3) cannot define the aggregate reactivity, since the type of silica crystal is more important than the quantity for reactivity (Thomas 2011).
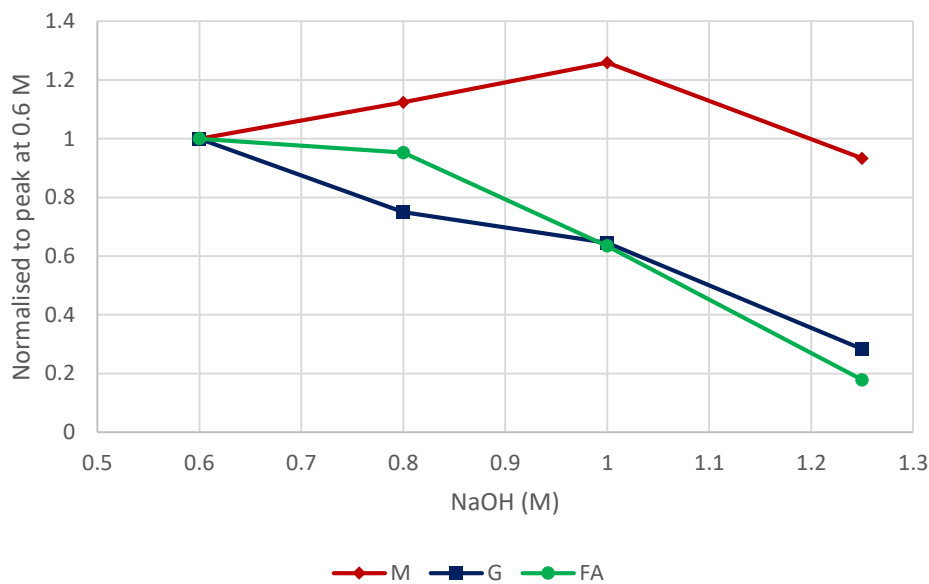
Figure 5-9: Quartz peak normalised to the intensity of the 0.6 M NaOH solution specimen.

5.4 Effect of alkali solution on the expansion of mortar bars and on the composition of mortars

The accelerated mortar bar test (AMBT) is a relatively rapid method to assess the reactivity of aggregates. This test method was used to investigate the effect of alkali solution concentration on expansion and the potential of fly ash to mitigate expansion due to ASR. The AMBT expansion tests were carried out based on the Standard Australia's standard AS 1141.60.1 accelerated mortar bar test (AMBT) with the two modifications; (i) the use of three

sodium hydroxide solutions (0.7 M, 1.0 M and 1.3 M NaOH) and (ii) the incorporation of a blended cement containing 25% fly ash. The mix design is described in Section 4.4.

Table 5-3: AMBT aggregate reactivity classification

Mean mortar bar expansion (E), %		AS 1141.60.1 aggregate reactivity classification
Duration of specimens in 1 mol/L NaOH 80°C		
10 days	21 days	
-	E < 0.10	Non-reactive
E < 0.10	$0.10 \leq E < 0.30$	Slowly-reactive
$E \geq 0.10$	-	Reactive
-	$0.30 \leq E$	Reactive

The criteria for categorisation aggregate reactivity, based on AS 1141.60.1, are listed in Table 5-3 and are based on mortar bar expansion at 10 and 21 days, being that the standard period of the test is 21 days. Aggregates classified as reactive or slowly reactive are deemed to have an elevated risk of deleterious ASR. These standard limits are also used for the discussion of the mortar bar expansion for the prisms aged in 0.7 M and 1.3 M NaOH solution. The standard test duration is 21 days, but the measurement continued up to 54 days for the investigation of the potential threshold alkali content. The expansion data are listed in Table 5-4 as the average of the three mortar bars for each mix and plotted in Figures 5-10 to 12.

Table 5-4: Average mortar bar expansion according to solution concentration (conc.) versus age

Age (days)	Micro-diorite (MD)			Greywacke (GW)		
	0.7 (M)	1.0 (M)	1.3 (M)	0.7 (M)	1.0 (M)	1.3 (M)
1	0.010	0.010	0.011	-0.003	0.001	0.005
5	0.011	0.015	0.022	0.017	0.035	0.049
7	0.018	0.032	0.049	0.029	0.066	0.082
12	0.041	0.073	0.093	0.059	0.134	0.170
14	0.052	0.088	0.108	0.084	0.183	0.222
21	**0.095**	**0.137**	**0.158**	**0.165**	**0.299**	**0.353**
28	0.131	0.176	0.193	0.248	0.405	0.473
42	0.180	0.230	0.252	0.367	0.555	0.655
54	0.205	0.265	0.284	0.440	0.649	0.781

The micro-diorite data of the specimens stored in three different sodium hydroxide concentrations 0.7 M, 1.0 M and 1.3 M- is plotted in Figure 5-10. The data shows that within the Australian Standard limits the mortar bars stored at 1.0 M NaOH expanded on average 0.14% in 21 days. This result classifies micro-diorite as a slowly-reactive aggregate and aligns with previous analysis. Adopting the same classification for the other two concentrations, the mortar stored in the lower concentration solution (0.7 M) had an expansion of 0.09% which classifies the aggregate as non-reactive and the most concentrated solution (1.3 M) had an expansion of 0.16% which classifies the aggregate as slowly-reactive. Considering the results according to the standard test method duration of 21 days, the increase in the concentration from 0.7M to 1.0M and then 1.3M, caused an expansion proportional to the increase of the concentration.
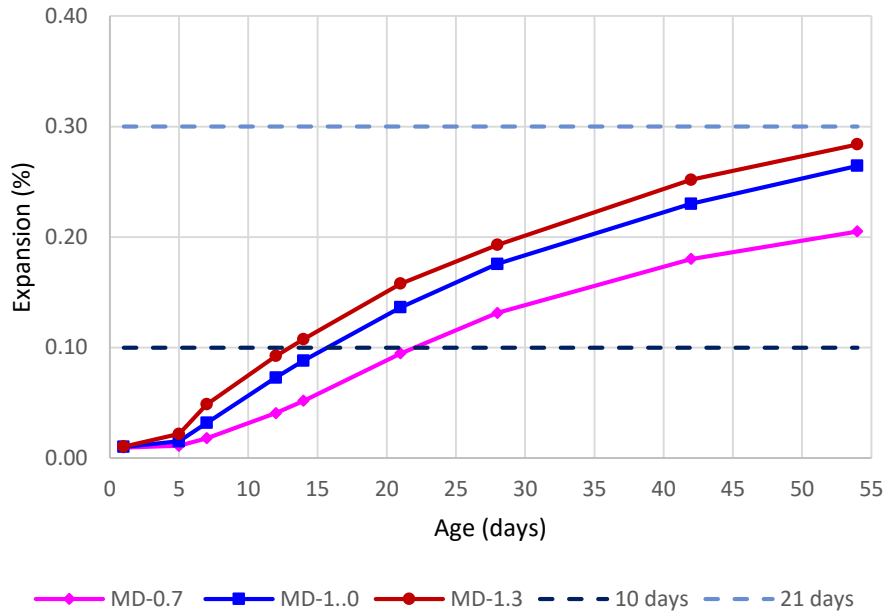
Figure 5-10: Micro-diorite expansion of AMBT specimens in NaOH solutions

The expansion data for the mixes prepared with greywacke without the addition of fly ash is shown in Figure 5-11. The mortar bars mixes were stored in the same baths containing the three different sodium hydroxide concentrations- 0.7 M, 1.0 M and 1.3 M.

Following the AS1141.60.1 limits, the mortar bars stored at 1.0 M NaOH had an average expansion of 0.30% at 21 days. This result classifies greywacke as a reactive aggregate and aligns with previous analysis of this material. The classification of greywacke would be different if the standard solution of this test method was 0.7 M. The specimens stored in the lower concentration solution (0.7 M) had an expansion of 0.16% which classifies the aggregate as slowly-reactive after 21 days. These data suggest that expansion rate is a function of alkali concentration. Therefore, a lower concentration used do not reduce reactivity, just a longer time is required for the test where this is the consequence of an accelerated test.

The AMBT type test and the expansion rate may suggest that despite the pH is changing, because the specimens have excess amount of alkali, there is continue supply of alkali to the reaction site and that may be the cause of the continue reaction. That means that in an accelerated test, it might need a longer period of time, but it may also mean that in a field situation the alkali content is irrelevant as reaction will occur irrespective of the alkali content, but at a lower rate. i.e. cracking is observed at a later stage. Therefore, threshold cannot be determined with AMBT because of the high level of alkali.
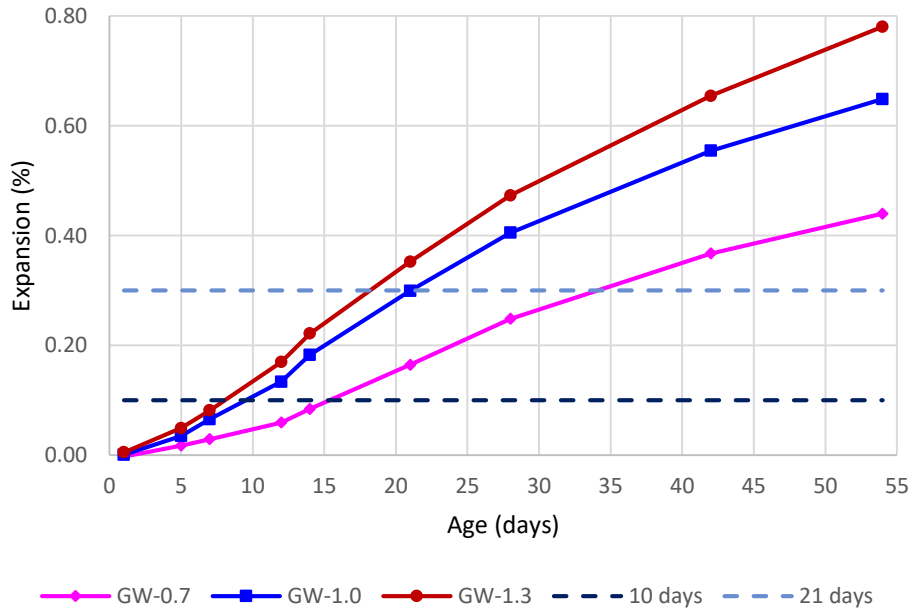
Figure 5-11: Greywacke expansion of AMBT specimens in NaOH solutions

For comparison of the relative reactivity of the two aggregates studies, Figure 5-12 shows the expansion of both aggregates over time. It is evident that as the alkali content of the solution increases, so does the expansion of the specimens, regardless of the aggregate type although the nature of the aggregate significantly affects the degree of expansion (Berra, Mangialardi & Paolini 1999a; Berra, Mangialardi & Paolini 1999b).

GW contains a large amount of strained quartz which is reactive while MD contain less strained and more crystalline quartz, based on the petrographic analysis. Additionally, the amount of quartz is also identifiable by XRD and is reported above on the relative reactivity of the quartz. As shown previously, greywacke released much more silica than micro-diorite (Figure 5-5) in NaOH solution which indicates that greywacke contains more free silica, hence it is easily released therefore more reactive.

Moreover, a more restrictive precaution has to be taken when choosing the aggregate instead of only considering the alkali concentration of the cement in preventing ASR. If reactive aggregate is going to be used, then the alkali content in the concrete mix has to be considered. The data suggests only that a reduction in alkali content may simply delays reactivity and the observation of cracking. This suggests that alkali only influences the rate of reaction rather than whether the reaction occurs or not. And it is important to remember that this does not account for any changes in the second mechanism of the process i.e. the actual

expansion and cracking of the concrete. If low alkali is used, then it is possible that the Ca content of the gel is high leading to a less expandable gel.

A concrete structure with a high-alkali cement could still probably be used with a non-reactive aggregate or perhaps even slowly-reactive aggregate without causing a deleterious ASR. Consequently, for reactive systems low alkali content is required while for non-reactive systems elevate alkali content may be tolerated due to the reduced risk of deleterious ASR forming.
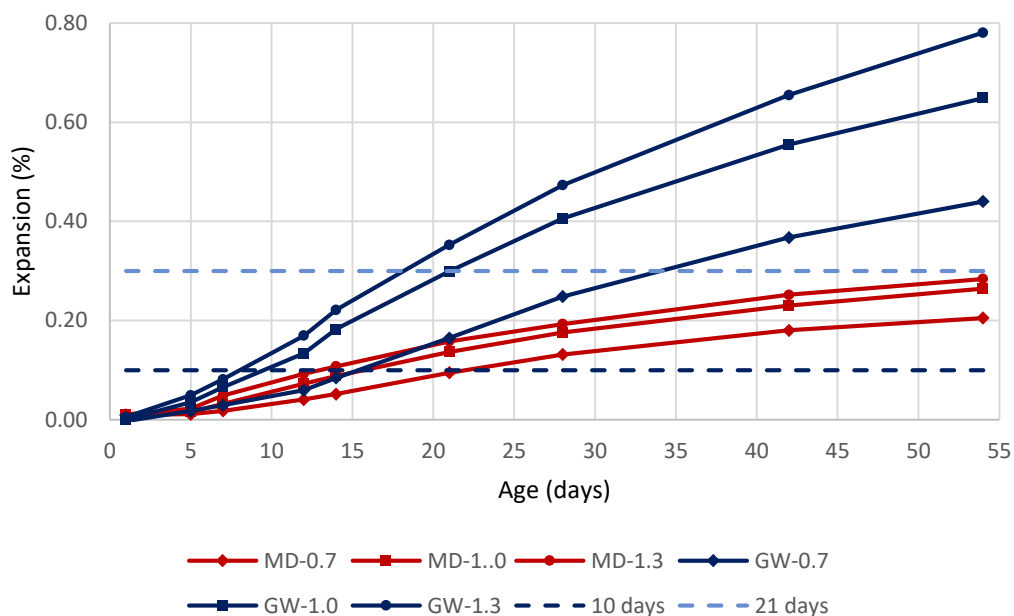
Figure 5-12: AMBT expansion of micro-diorite and greywacke during 54 days

It is clear that the degree of expansion of the mortars is dependent on the alkali concentration of the solution so the concentration of the sodium hydroxide storage solution certainly affects the expansion of the mortar bar (Berra et al. 1991). A large amount of the mortar was crushed with ring mill which could cause CSH and carbonate decomposition, and the sample was then used for phase development analysis. The analysis of the mortars prepared with the AMBT batch material showed no significant difference between micro-diorite and greywacke for the analysis of CH and CSH in Figures 5.13 and 5.14, respectively. The consumption of CH and dehydration of the CSH phase indicates the degree of reaction, and surprisingly, the MD and GW show little difference for the mortar mix. That might be because the ASR gel is localised and therefore is likely to be limited in quantity - more from the GW

than from the MD. CH across the specimen is not necessarily involved in the reaction and the same amount of consumption of CH is showed for both aggregates at the same rate, although there is greater expansion for GW specimens than MD specimens. So it is reasonable to make the assumption that there is more ASR gel produced by GW. As there is approximately the same amount of CH consumed and if it is consumed by the ASR gel then it must follow that the calcium content of the ASR gel in MD is greater than the content in the GW gel. This means that the GW gel is more expansive (less C binding together).
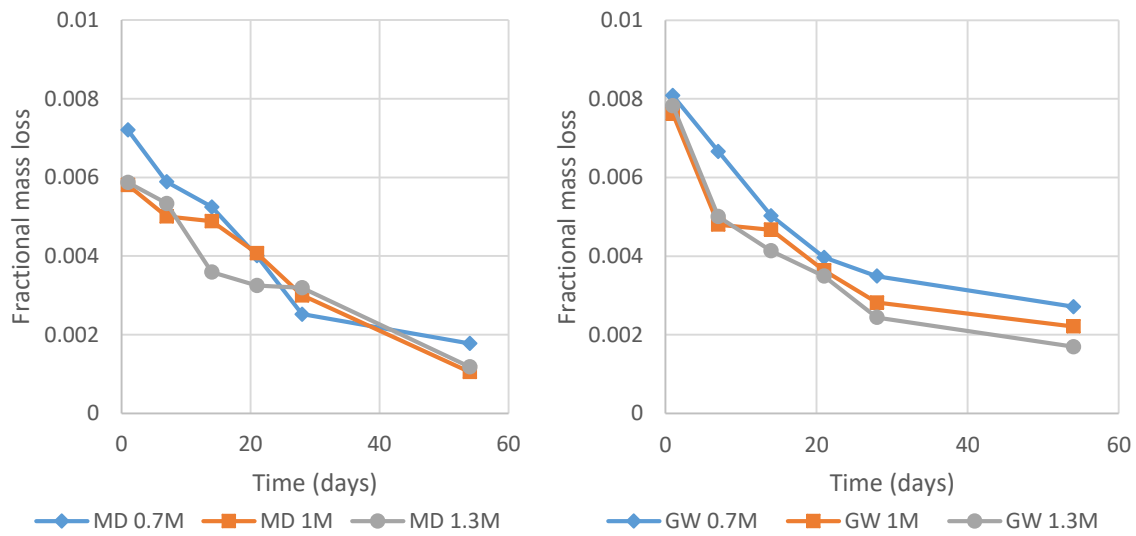
Figure 5-13: Fractional mass loss as a function of time
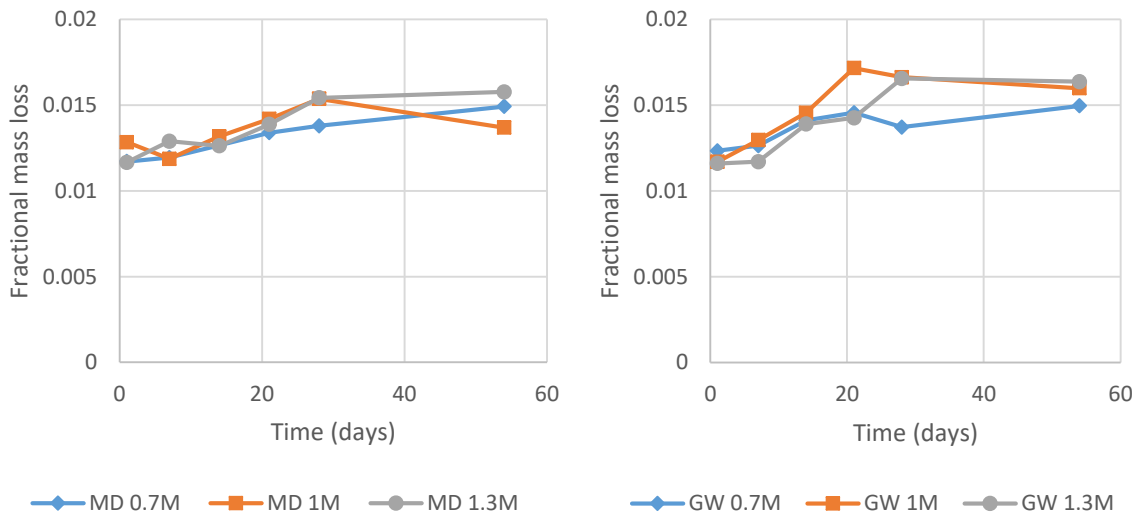
Figure 5-14: Dehydration of CSH phase as a function of time

The XRD data in Figure 5.15 shows the CH peak and seems consistent with TG data and FTIR data except for the early specimens. More quartz appeared to be consumed in the XRD data for the GW than the MD. The large degree of scatter makes detailed interpretation difficult. CH consumption occurred over time at a very similar rate for both aggregates and no difference was indicated between the sodium hydroxide solutions. Therefore, these results indicate that the aggregates reacted in a similar manner and also that the level of alkali content had no impact. Figure 5-16 shows the quartz peak respectively against age from day 1 to day 54. The FTIR consolidate data in Figure 5-17 shows a significant difference between both aggregates until 14 days but after that the samples indicated the same CH-OH peaks.
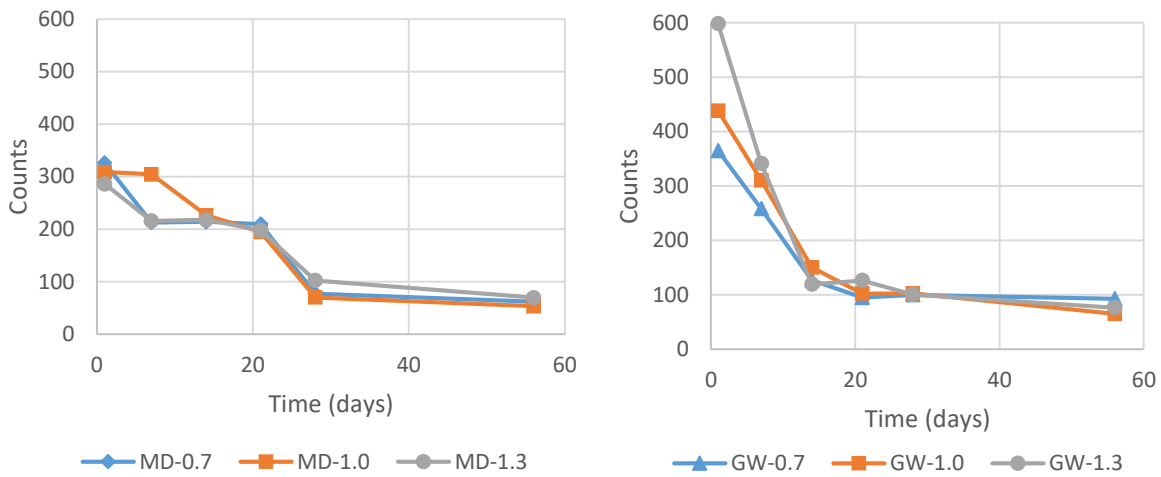
Figure 5-15: CH peak intensities at 18° 2ϑ plotted against time
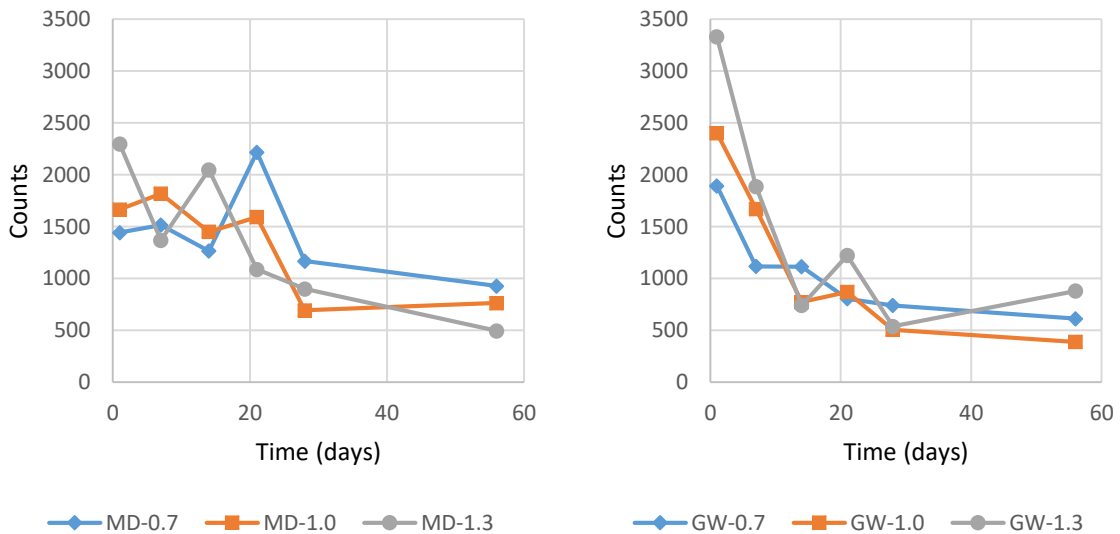
Figure 5-16: Quartz peak intensities at 26.6° 2ϑ plotted against time

81
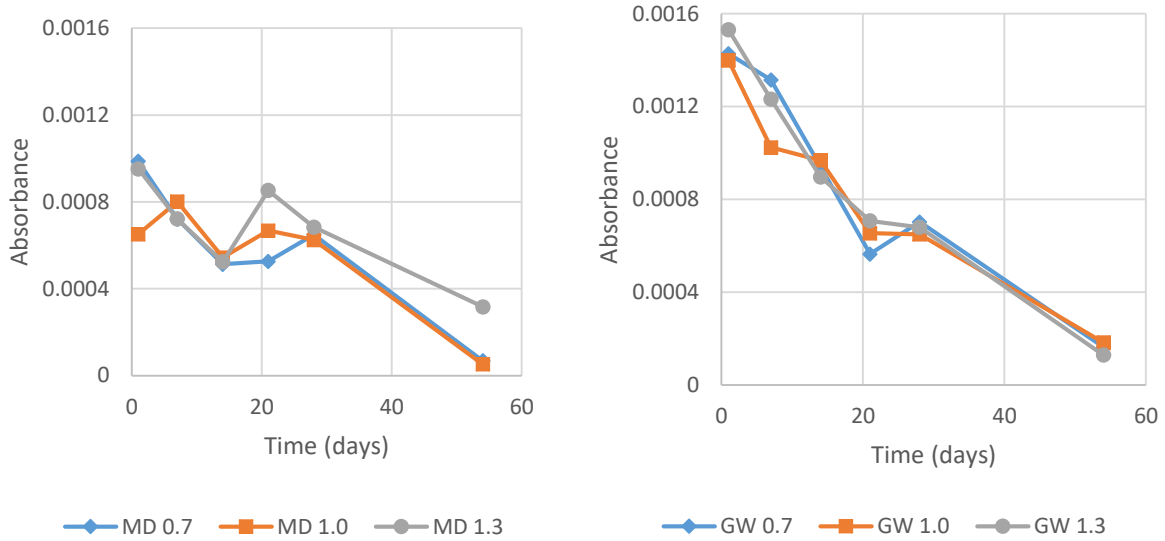
Figure 5-17: CH-OH stretch in CSH region against time

5.5 Effect of alkali solution and fly ash replacement on the expansion and composition of mortar bars

The replacement of cement with 25% fly ash was investigated to ascertain the potential of ASR mitigation by different alkali concentrations and fly ash. Table 5-5 shows the average expansion of the specimens prepared with 25% fly ash cement replacement for both aggregates, micro-diorite and greywacke.

Table 5-5: Average expansion of the mortars with the addition of 25% cement replacement with fly ash

Age (days)	Micro-diorite with fly ash (MD-F)			Greywacke with fly ash (GW-F)		
	0.7 (M)	1 (M)	1.3 (M)	0.7 (M)	1 (M)	1.3 (M)
1	-0.006	-0.007	-0.007	0.009	0.009	0.013
5	-0.006	-0.004	-0.005	0.020	0.020	0.025
7	-0.005	-0.004	-0.004	0.024	0.024	0.027
11	0.002	0.004	0.005	0.030	0.033	0.035
14	0.003	0.009	0.009	0.039	0.043	0.046
21	**0.013**	**0.024**	**0.027**	**0.043**	**0.052**	**0.062**
28	0.017	0.029	0.040	0.047	0.058	0.078
42	0.032	0.051	0.073	0.056	0.068	0.091
54	0.06	0.068	0.094	0.061	0.076	0.112

Figure 5-18 illustrates the expansion of the specimens prepared with micro-diorite aggregate and fly ash. As can be seen, the 25% replacement of cement with fly ash was highly effective in reducing the expansion regardless of the alkali concentration in the solution. All the micro-diorite specimens had less than 0.10% expansion up to the 54th day of the tests. At 10 and 21 days (durations for 0.1 and 0.3 % expansion to classify reactivity) the expansion was observed to be significantly less than 0.1% for each solution. The relative reactivity in AMBT conditions with FA blended cement is reduced. The rate of reaction is still influenced by alkali concentration, as a more reactive environment cause greater rate of reaction. Therefore, it results match the expectations. This reduction of reactivity is due to the competitive reactant present. Consequently, FA is mitigating the ASR reaction due to the competitive reaction of a more reactive component.
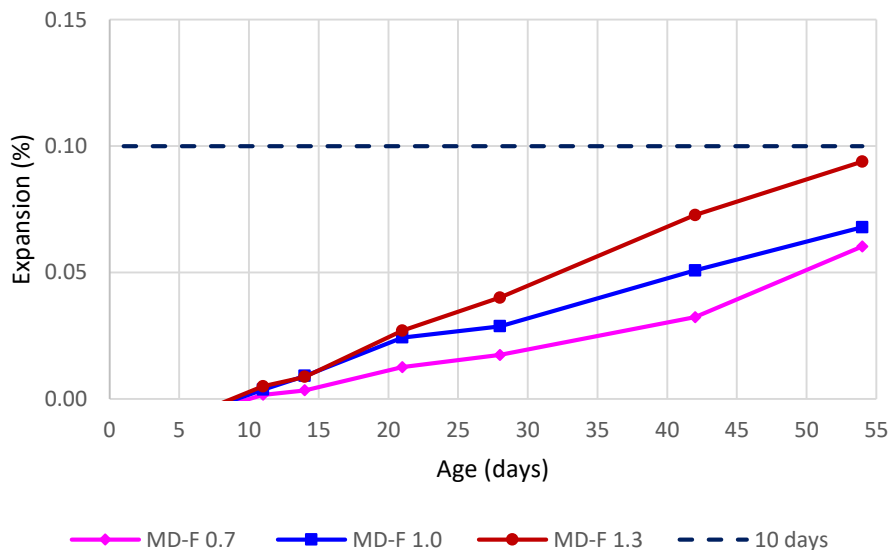
Figure 5-18: Micro-diorite specimens with 25% fly ash cement replacement

Figure 5-19 is a plot of the average expansion of specimens prepared with greywacke. Fly ash performed very well in controlling expansion at a replacement level of 25% for the greywacke specimens and the degree of expansion was much lower than the specimens prepared without SCM.

The three alkali solutions have affected the greywacke specimens where the highest concentration had significant expansion although the differences in the expansion of the mortars was noted only after 14 days of exposure. The higher alkali concentration of 1.3M NaOH led to a slightly higher expansion so even with 25% fly ash cement replacement, the

samples were sensitive enough to behave differently in a concentration environment with a higher alkali. GW is more reactive and so more expansion is likely to be observed. The fact that even at 1.3M the GW-F only reaches the 0.1% limit at 54 days suggests that FA has the potential to mitigate deleterious ASR. The effectiveness of FA is related to many variables such as pozzolanic reaction, particle size and chemical composition (Kawamura & Takemoto 1988) but it seems like the alkalinity of the pore solution can have a major influence on properly mitigating ASR.
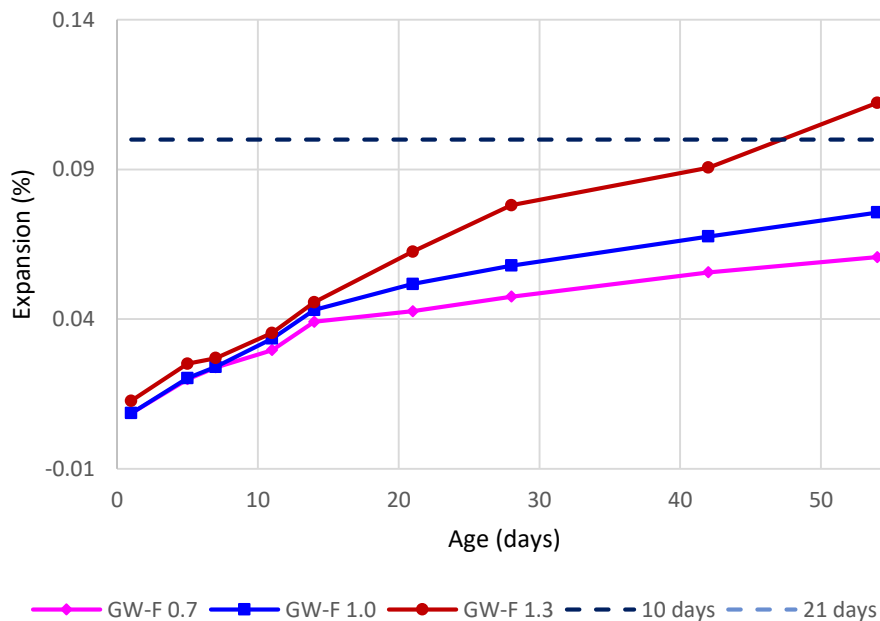
Figure 5-19: Greywacke specimens with 25% fly ash cement replacement

The specimens at 0.7 M and 1.0 M had minimal expansion after 54 days. However, the expansion of the specimens in 1.3 M NaOH did not demonstrate the expansion ceasing and continuously increased for 54 days due to the highly reactive environment. There are two possible reasons to obtain these results. FA consumption just acts as an inhibitor i.e. it reacts first and after it is consumed the aggregate reacts so the reaction rate is slowed and hence inevitable deleterious ASR gel is delayed. Another processes in parallel, such as the swelling process of the gel, the gel composition or importantly if FA can permanently remove the alkali from the reaction medium, are other mechanisms involved that can significantly impact the mitigation.

. The application of high alkaline with reactive aggregate suggests that it is possible to have elevated Na_2O_e levels without the risk of deleterious ASR. Ideally, this system would be

tested following the concrete prism test (CPT) for 24 months to demonstrate the efficacy of FA mitigation in high alkaline concrete mixtures.

These results indicate that 25% replacement of fly ash can reduce expansion of less than 0.1% even after 42 days. However, more research has to be investigate the effectiveness of FA, as AMBT is designed for assessing aggregate reactivity only.

The Australian standard AS 1141.60.1 (AMBT) does not recommend this test method for the investigation of ASR mitigation with SCMs. The American Standard ASTM C1260 was not developed to evaluate SCM mitigation (Oberholster & Davies 1986) although it has been used in many studies that show that the results can provide a good prediction of concrete behaviour with the addition of SCMs (Berra, Mangialardi & Paolini 1994; Thomas et al. 2007).

The fly ash used in this research contains low calcium content (CaO <10%) and is considered more effective than high calcium fly ash. The replacement of cement with low calcium fly ash will produce cement hydrates with low Ca/Si ratios and subsequently more alkalis are bound, reducing the pore solution alkalinity (Shehata, Thomas & Bleszynski 1999b) therefore mitigating ASR. For this reason, it is important to assess the type of fly ash available and consider the SCM composition to prevent unreliable conclusions.

The phase analysis of the mortars with micro-diorite and greywacke with an additional 25% fly ash cement replacement was also investigated. The thermogravimetric analysis (TG) in Figure 5-20 below shows that mortars with different aggregates had a very similar consumption of calcium hydroxide (CH). The formation of CSH in Figure 5-21 was also very close for both aggregates however a significant difference between the alkali concentrations for the reactive aggregate greywacke was observed.
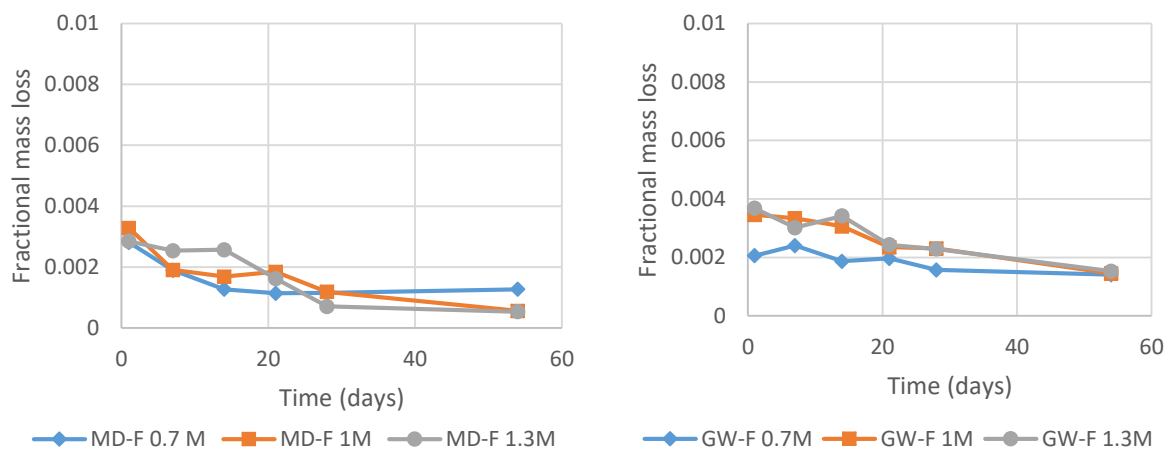
Figure 5-20: MD and GW fractional mass loss of CSH with fly ash as a function of time
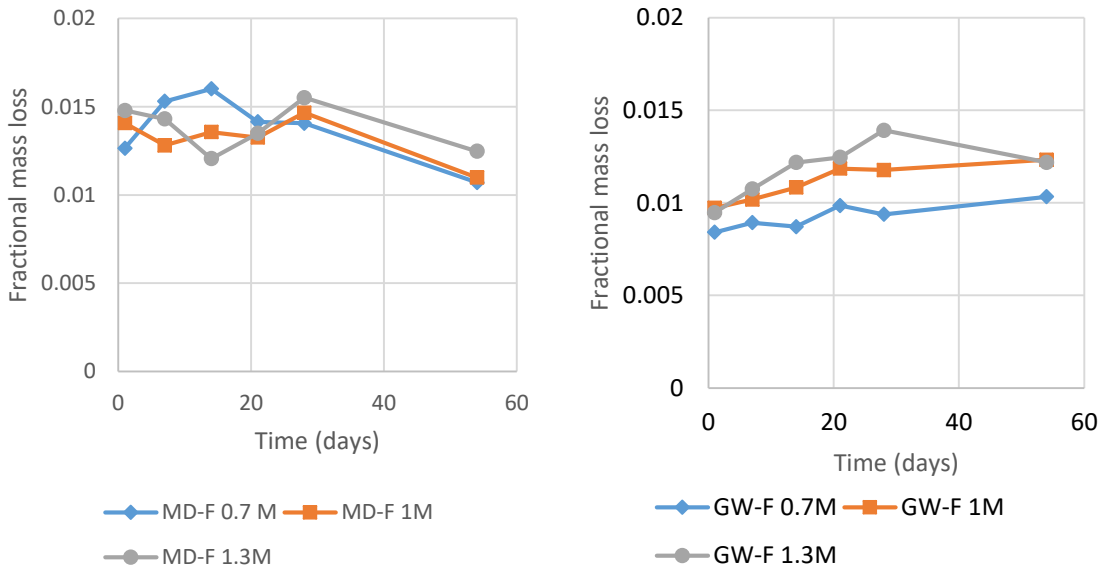
Figure 5-21: MD and GW fractional mass loss of CSH with fly ash as a function of time

The XRD data in Figure 5.22 and 5.23 shows the calcium hydroxide peak (CH) and the quartz peak respectively against age from day 1 to day 54. Significant amount of CH consumption occurred over time at a very similar rate for both aggregates as the data shows low intensity. These qualitative data indicate no difference between the sodium hydroxide solutions. This is a complicated methodology and it's difficult to do the measurements. The FTIR consolidated data in Figure 5.24 shows no significant difference between both aggregates on the analysis of the CH-OH bound peaks.
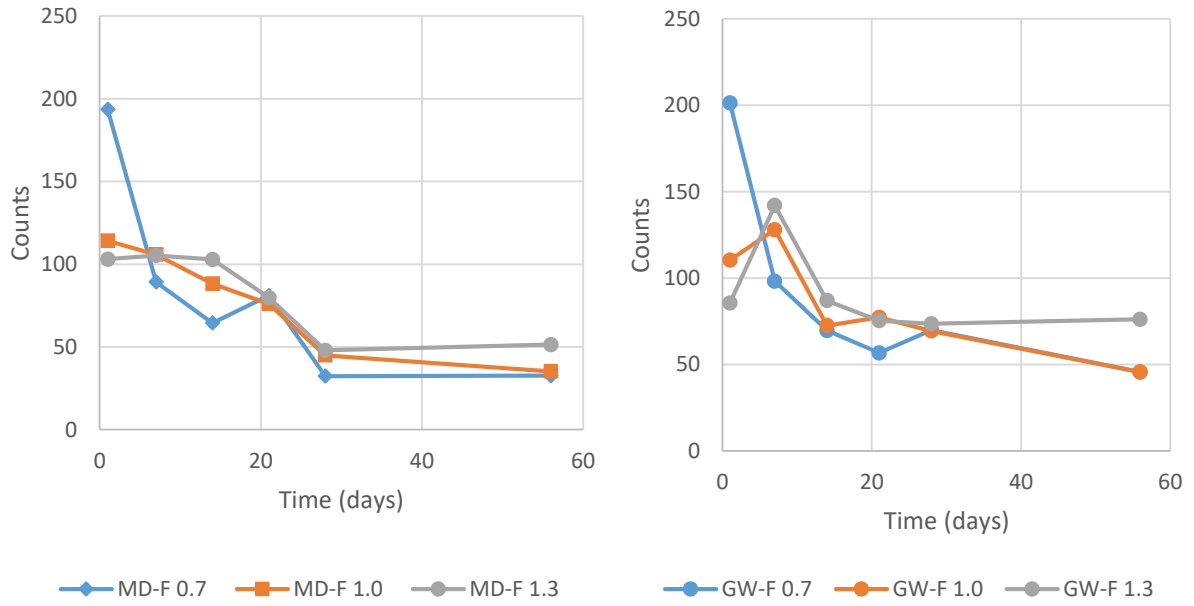
Figure 5-22: MD and GW with fly ash: CH peak intensities at 18° 2ϑ plotted
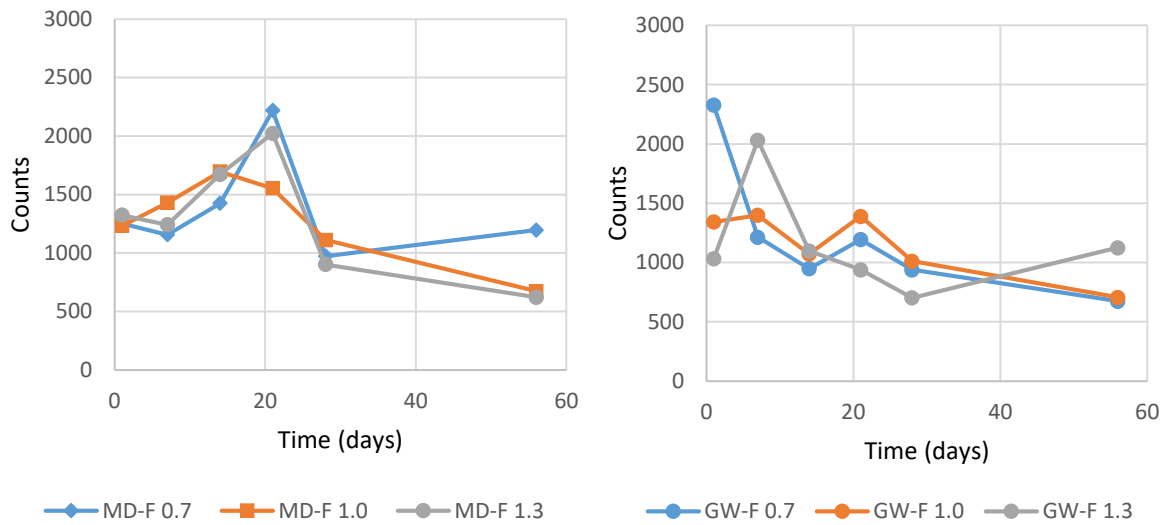
Figure 5-23: MD and GW with fly ash: Quartz peak intensities at 68° 2ϑ plotted against time
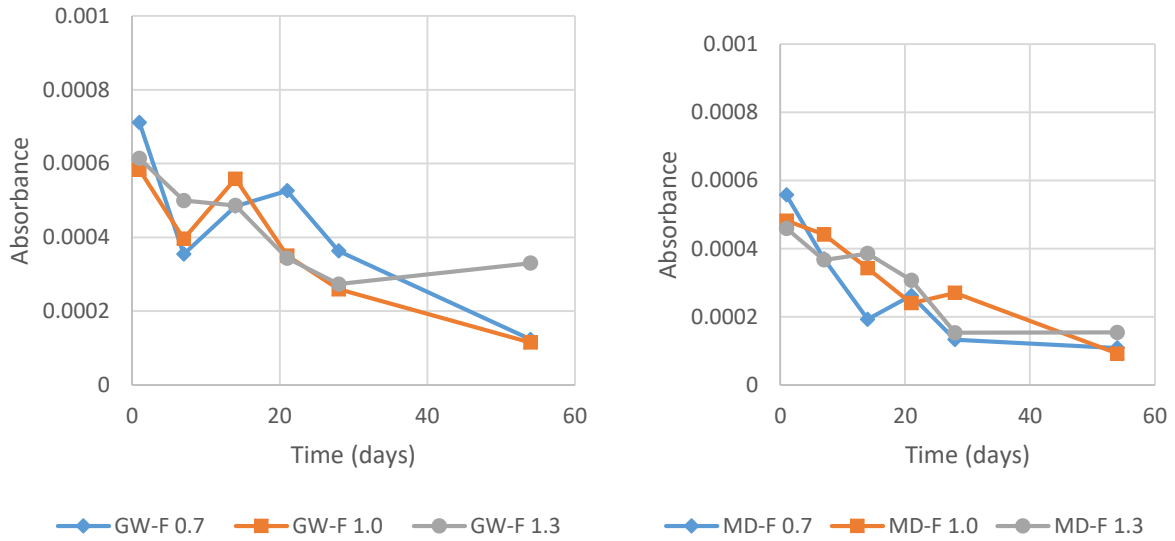
Figure 5-24: MD and GW with fly ash: CH-OH stretch in CSH region

5.6   Effect of alkali solution on fine aggregate mortars at 60°C

The investigation of the balanced alkali in cementitious systems and the potential for an alkali balance was further evaluated using fine aggregates mortars prepared in a less aggressive environment compared to AMBT. The specimens were prepared following the ACPT test method where the alkali boost is calculated considering the alkali already existing in the cement and the alkali level in the mix was increased by adding sodium hydroxide into the mix water. The fine aggregates mortars were then placed in sealed HDPE tubes and stored in a 60°C oven until the date of evaluation. This investigation looked at the role of alkalis in ASR by evaluating the alkali concentration effect and the reactivity of different mixes and solution concentrations. This study focusses on the consumption of calcium hydroxide and the current chapter describes the analysis of fine aggregates mortars with the reactive and slowly reactive aggregate, with and without fly ash. The samples' identification based on the results is indicated in Table 5-6.

Table 5-6: Samples nomenclature

Sample ID	Material	Alkali boost (%Na$_2$O$_{eq}$)
MD 0.6	Micro-diorite	0.6
MD 0.8		0.8
MD 1.0		1.0
MD 1.25		1.25
GW 0.6	Greywacke	0.6
GW 0.8		0.8
GW 1.0		1.0
GW 1.25		1.25

The thermogravimetric (TG) analyses were carried out with the specimens collected in a period of 4 months, from day 7 until day 112. Baseline correction was used to adjust the CH decomposition peak to consequently separate the other phases from CH due to the common dissolution and decomposition of other components besides CH that overlap (Donato, Lazzara & Milioto 2010).

The data presented in Figure 5.25 shows the ACPT-conditioned specimens with greywacke (GW) and micro-diorite (MD) with no cement replacement. Overall, GW consumed more CH than MD which confirms the previous AMBT results. The effect of the four different alkali concentrations did not show a significant difference between the specimens for both aggregates. The low concentration tends to consume more CH in few specimens, more specifically for the last samples at day 112. The result of the no alkali effect is similar to the previous TG analysis of the fine aggregates mortars under AMBT conditions.
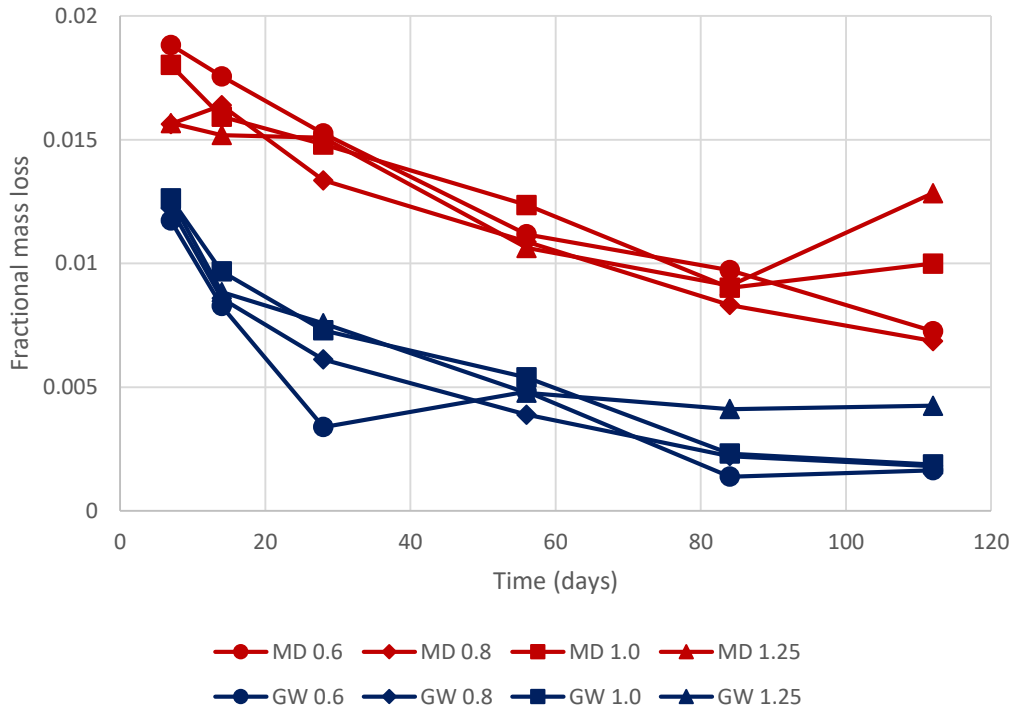
Figure 5-25: Micro-diorite and greywacke fractional mass loss as function of time

In addition, the specimens were tested with XRD analysis and the results are plotted in Figure 5-26. The results agree with the TG result and shows that there is a relationship between CH consumption and aggregate reactivity. Contradictory to what was expected, the alkali concentration had no consistent and no significant effect on the CH peak, although a slight difference of the alkali levels can be observed in the micro-diorite specimens at day 112. Over time, as the peak intensity indicates the amount of CH in the sample, the amount of CH decreases as it has been consumed for reaction. Therefore, greywacke (GW) specimens indicates more reactivity since less calcium was present in the form of CH.
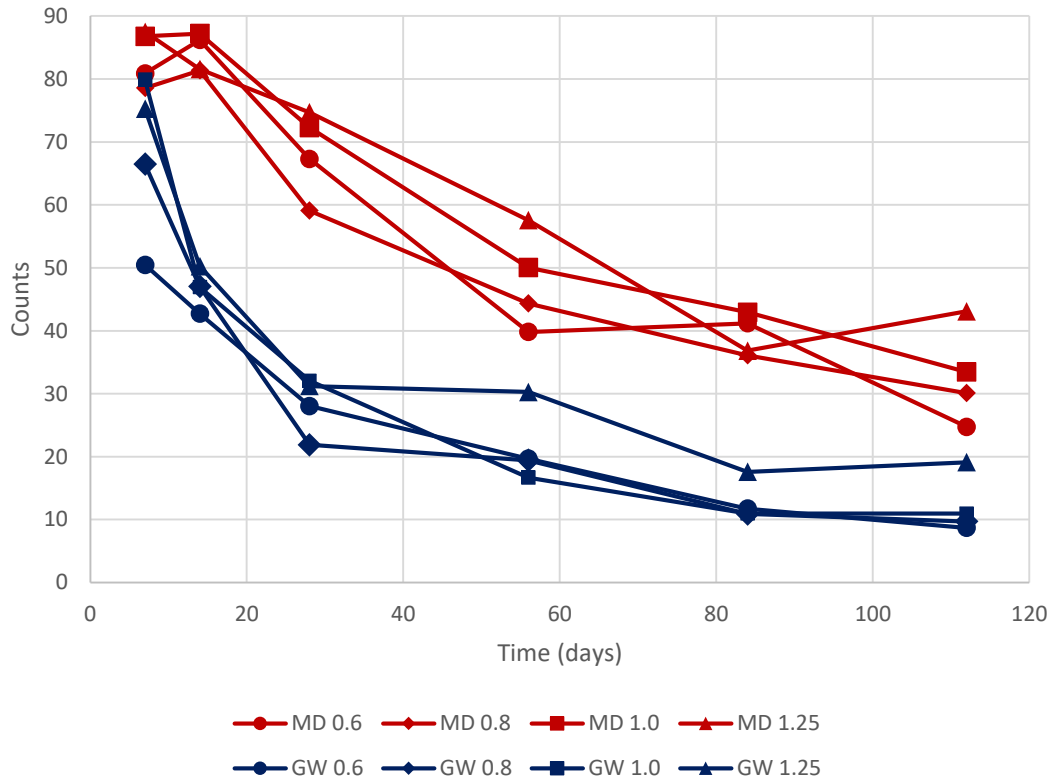
Figure 5-26: CH peak intensities (counts) of the specimens at 18° 2ϑ plotted

5.7   Effect of alkali solution and fly ash replacement on fine aggregates mortars at 60°C

The previous investigation was extended to examine the effect of fly ash (FA) in ASR mitigation. The specimens were prepared in the same conditions and 25% of cement was replaced with FA. This experiment also aimed to investigate the effect of alkali concentration into ASR but additionally, the FA ash effect on the system at 60°C as a function of time. The TG results shown in Figure 5-27 indicate consumption of CH with the SCM. The addition of FA significantly reduces the reaction rate since less CH is consumed therefore changing the reactivity of the aggregates. The results show that greywacke is more reactive than micro-diorite where the system with FA seems more reactive than without the SCM. This might occur due to one of the pozzolanic reaction mechanisms in which portlandite in the fine aggregates mortars is depleted by the pozzolanic reaction and binds alkali ions from the pore solution (Duchesne & Bérubé 1994b).

The effect of alkali concentration shows a consistent trend where lower NaOH concentration results in higher CH consumption. According to the literature, the greater alkali

concentration reflects the decrease of the CH dissolution due to solubility product (Ksp) (Glasser, Lachowski & Macphee 1987). The decrease of calcium ions in solution will cause less consumption of the CH for reaction hence it might produce silica gel with lower Ca^{2+} content. If the gel is formed, it may result in a low calcium/silica ratio gel which may be more expansive as it contains more alkali ions. The addition of FA may cause higher CH consumption due to the formation of more CSH phases, therefore reducing the calcium available in the pore solution to recycle with the alkalis.
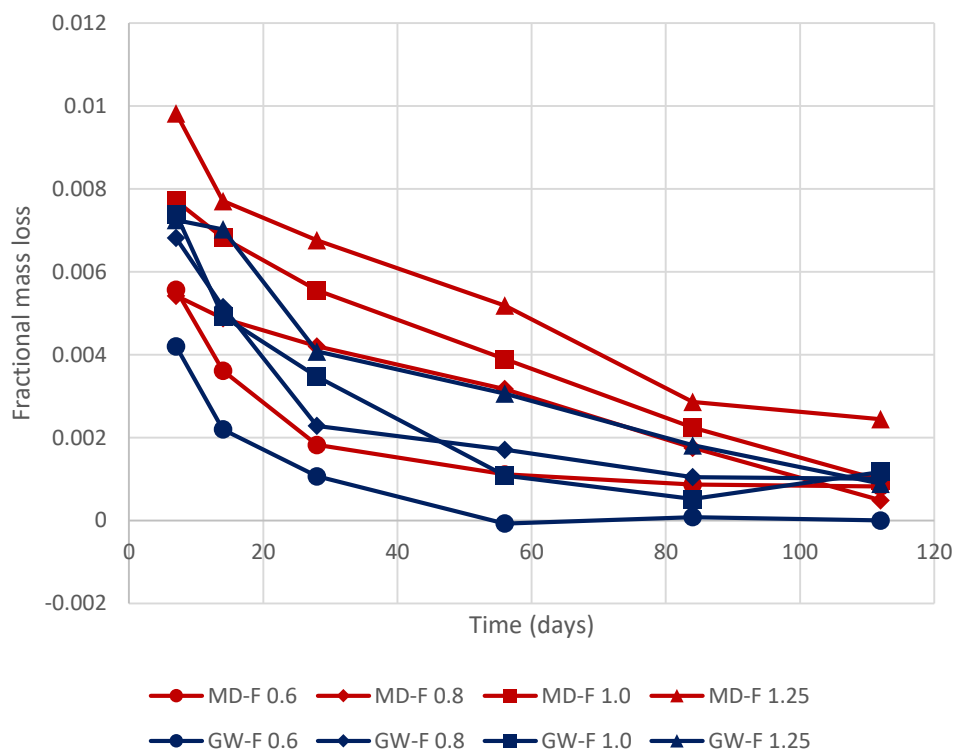
Figure 5-27: MD and GW fractional mass loss with fly ash as a function of time

Additionally, the XRD analysis results can be seen in Figure 5-28. The addition of fly ash indicates that there are fewer differences between the reactivity of the aggregates since the results among the specimens are more similar. Moreover, the addition of this SCM demonstrated the effect of alkali concentration in which the CH peak increased with the NaOH concentration.
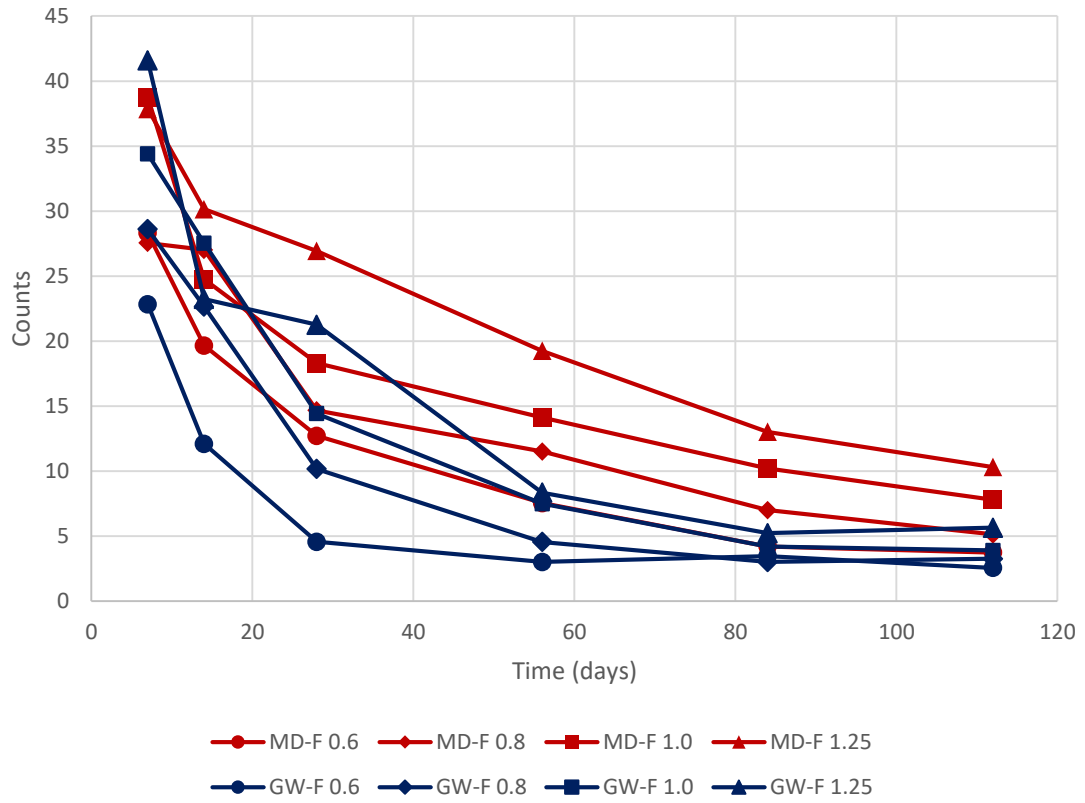
Figure 5-28: MD and GW with fly ash: Consolidate XRD data of CH peak intensities at 18° 2ϑ plotted

6   Conclusions

ASR is a deleterious reaction that has the potential to cause cracking in concrete resulting in the necessary remediation or replacement of affected structures. Currently the approach to mitigation of the risk of ASR is to use low alkali contents in concrete (2.8 kg.m^{-3} in Australia resulting in a cement specification limit of 0.6% Na$_2$O$_e$) in conjunction with testing aggregates for potential reactivity to ASR (Standards Australia Handbook HB79). The conservative concrete alkali content limits are imposed irrespective of the potential risk or consequence of deleterious ASR. The necessity of a flexible approach to mitigate ASR in Australia is, therefore, required and one approach is by permitting flexible alkali content limits in a concrete mix by considering the aggregate reactivity and the potential risk of ASR.

This thesis aimed to investigate the chemical part of the mechanistic process by investigating the influence of alkali content on the potential of non-reactive (micro-diorite) and reactive (greywacke) aggregates to cause ASR through measurement of their relative reactivity using chemical tests and phase analysis. In addition, as fly ash is known to aid in mitigation of ASR, the reactivity of fly ash in parallel reactions was also investigated.

The reactivity the aggregates, micro-diorite and greywacke, which have a similar composition but distinct reactivity, were investigated for their relative reactivity to alkali, initially by investigating the influence of temperatures and alkali concentration on slurries of finely ground aggregate. The results demonstrated, as might be expected, that higher pH and higher temperature increased the rate of reaction. The test was also able to discriminate between the two aggregates showing greater reactivity for the reactive aggregate, greywacke.

To further investigate the reactivity of the aggregates, dissolution tests were carried out. The measurement of the concentration of cations release into solution by the aggregates was carried out in neutral pH and in 1 M NaOH. In this test the dissolution of ions from cement and fly ash was also carried out. Neutral pH was used to demonstrate that the main source of alkalis available to the concrete pore water solution is the cement and was confirmed by these tests where little or no dissolution of ions was observed at neutral pH with the exception of the release of significant quantities of alkali ions from the cement. In alkaline media, however, significant quantities of alkali and, in particular, significant quantities of silica were released into solution. The degree of release of silica correlated with the reactivity of the two aggregates, but was most significant for the fly ash.

As the ASR gel generally contains calcium as well as alkali ions, the influence of calcium ions on the formation of the ASR gel was investigated by carrying out slurry tests in the presence and absence of calcium hydroxide (CH) as a co-reactant with aggregates and fly ash. It was found that little reaction happened without the addition of CH, while in the presence of CH, significant amounts of ASR gel were formed. This was demonstrated by investigating the water and CH content of the solid phases using TG and the CH and quartz content using XRD. It is interesting to note that water content of the solid phase increased with increasing pH, but the CH consumption as determined by fractional mass loss was not significantly influenced by pH suggesting that, while reactivity increased with pH, CH consumption did not increase. It is likely that the increased pH reduced the calcium ion solubility in solution and thus the calcium ion content of the gel reduced reducing the degree of CH consumption despite greater degree of reactivity at higher pH. To confirm this hypothesis further characterisation should be carried out on the composition of the gel product.

Even though a lack of a strong pH dependence on the consumption of CH in the slurry tests was observed, the presence of CH was demonstrated to be significant in the degree of reaction; in the absence of CH little reaction was observed, while in the presence of CH significant reaction occurred. Additionally, the tests in the presence of CH demonstrated that the degree of consumption of CH (as well as the degree of formation of hydrated gels) was indicative of the relative reactivity of the aggregates and fly ash. The CPT reactive greywacke was found to be more reactive than the CPT non-reactive micro-diorite while the fly ash was found to me the most reactive material in the slurry tests.

In order to test the effect of alkali content on the reactivity of the aggregates, the investigation of the physical effect of ASR was investigated in mortar systems following the Australian standard procedure AS 1141.60.1, the AMBT. The results classified micro-diorite as slowly-reactive and the greywacke as a reactive aggregate (note that AMBT is considered to be a conservative test and that the micro-diorite has been classified as non-reactive using CPT). The data showed that the increase of pH changes the rate of expansion, but does not inhibit expansion at low pH, simply the rate of expansion is reduced with decreasing pH. Similarly, the rate of expansion is increased with increasing pH.

Interestingly, phase analysis of parallel aged mortar specimens prepared from excess mortar from the preparation of the AMBT prisms showed limited variation between the aggregates and little dependence on pH. The dependence of pH is not necessarily expected as the reactions are complex and variation was not observed in the slurry tests, however,

differences were predicted, but not observed in phase development between the reactive and non-reactive aggregate. This lack of variation might be ascribed to the difference in specimen type. Slurries of fine ground aggregate have significant surface area and hence availability for reaction while for AMBT specimens the aggregates are graded in a particle size rage of 0.15 to 5 mm thus having significantly reduced surface available for reaction. Additionally, the tests were carried out in different ratios; slurry tests were carried out with either pure aggregate (or fly ash) or a 1:1 aggregate (or fly ash) to CH ratio while in the AMBT mortars a 1:2.25 cement to aggregate was used making the relative sensitivities to aggregate reactivity more difficult to identify in the mortar specimens.

The use of blended cement containing 25% fly ash in the AMBT tests showed significant difference in the expansions observed. Although AMBT is not generally considered to be a test suitable for testing the mitigation, this reduction in expansion strongly suggests that fly ash has the potential to mitigate ASR. For both the CPT reactive greywacke and the CPT nonreactive micro-diorite, the partial substitution of the cement with fly ash resulted in significant reduction in expansion. The rate of expansion was higher for the reactive greywacke and remained dependent on the pH indicating that the aggregates continued to react, but at a significantly reduced rate. The reduced rate of expansion is consistent with the presence of fly ash acting in its role as competitive reactant and in this case, the phase analysis showed significant reduction in the CH content of the mortars which is consistent with the pozzolanic reaction of fly ash with CH. Additionally, the fly has added to form the blended cement had a cement fineness and is therefore expected to be reactive.

The dissolution tests, slurry tests and AMBT were carried out under the reactive conditions of the AMBT conditions of 80°C with samples submerged in alkali with concentrations varying around the 1M NaOH concentration. In order to investigate the effect of alkali concentration under reduced reactivity conditions, fine aggregates mortars tests were carried out at 60°C replicating the RILEM ACPT temperature. These test again demonstrated that aggregate fines based accelerated tests have the potential to discriminate between aggregate reactivity as, based on phase analysis, the greywacke was again demonstrated to be significantly more reactive than micro-diorite. The alkali concentration, however, did not show a significant difference between aggregate.

The mortars systems evaluated with fly ash at 60°C showed that fly ash is more reactive than greywacke. This observation is consistent with model of fly ash mitigation of ASR through a competitive reaction. Fly ash reacts rapidly and as fly ash is finely dispersed the silica gel

formed from the alkali-silica reaction with fly ash silica is finely dispersed and is unlikely to be able to be involved in expansion. In this series of samples, a pH effect is observed. The relative consumption of CH in the fly ash pastes decreases with increasing alkali concentration. This inverse trend in CH consumption with alkali concentration is consistent with the depression of calcium ion solubility with increasing pH resulting in reduced availability of calcium ions and hence reduced consumption of CH during the gel formation. The reduced CH consumption indicates that gel composition is likely to be significantly affected by pore solution pH and hence the expansive properties of an ASR gel is likely to be affected by pH of the pore water.

Final Remarks

The current investigation has focused on chemical part of the ASR process by investigating the reactivity of silica in aggregates and fly ash. The experimental focus was on investigating the potential of alkali concentration thresholds in aggregate reactivity. This was addressed by varying the alkali concentrations of the immersion solutions. In all the test carried out in this study following reactivity, varying the alkali concentration simply resulted in a variation in the rate of reaction. Reduced alkali concentrations resulted in reduced rate of reaction while increased concentrations resulted in increased rates of reaction. These results suggest that the alkali-silica reaction will occur irrespective of the alkali content of the reaction system. The fact that the reaction continues irrespective of the alkali content of the system, does not necessarily mean that deleterious ASR is inevitable as deleterious ASR is a two-step process of gel formation followed by action of the gel on the concrete to yield cracking. To identify the potential of a threshold in alkali content, an understanding of the second stage of the deleterious ASR process is required; that is can the gel act on the concrete in a manner which results in cracking and what conditions are required. This is a topic for the next stage of the research.

This study also investigated the role of fly ash in the reaction. The introduction of a finely divided reactive silica resulted in a preferential reaction. The incorporation of fly ash in the mix thus provided a competitive reaction to the aggregate reaction. The provision of a fly ash to the reaction mix indicates that the mechanism of mitigation as a sacrificial reactant where the fly ash reacts in preference to the aggregate.

The AMBT test and tests that use 80°C to accelerate the reaction (e.g. the slurry tests used in this study) are considered to be extremely reactive and in aggregate screening produce

false positives (such as in the case of the micro-diorite used in this study). To demonstrate finely ground aggregate tests have the potential to screen aggregates for reactivity, test the role of alkali in ASR and test SCMs for their efficacy, a 60°C test was carried out showing significant success. Paste tests of this nature therefore have the potential to both screen for aggregate reactivity and investigate SCM potential for mitigation.

Finally, it should be noted that this study has only investigated the alkali dependence of the silica reactivity. This is the first step in the deleterious ASR reaction. Further investigation is therefore required to determine the potential of the silica gel produced to cause deleterious cracking and the conditions required for the generation of cracking. This investigation provides a basis for further investigation.

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