THE USE OF LITHIUM SALTS AND SUPPLEMENTARY CEMENTING MATERIALS TO CONTROL REACTIVITY OF RECYCLED CONCRETE AGGREGATE

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ABSTRACT

The Use of Lithium Salts and Supplementary Cementing Materials to Control Reactivity of Recycled Concrete Aggregate

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This thesis covered the second phase of a study that focused on the reactivity of recycled concrete aggregate (RCA) produced from concrete affected by alkali-silica reaction (ASR). The first phase investigated the reactivity of ASR-affected RCA and the use of Supplementary Cementing Materials (SCM) as a preventive measure. The second phase was carried out to study the efficacy of lithium nitrate, when used individually and in combination with SCM, in suppressing the reactivity of RCA. The use of different dosages of lithium nitrate combined with SCMs reduced expansion due to ASR. However, the expansion results showed that increasing the dosage of lithium beyond a certain level does not help in suppressing the expansion. The high reactivity of the tested RCA was attributable to its relatively high alkalis and calcium hydroxide contents that fuel further ASR. The alkalis consumed or contributed from RCA were evaluated through leaching the aggregate particles in distilled water and alkaline solutions at different molarities with and without lithium nitrate. Alkalis consumption was found to decrease when lithium was presented in the leaching solutions. Examining RCA samples under scanning electron microscope (SEM) showed that the crushing process of the RCA exposes fresh surfaces of the reactive virgin aggregate and creates cracks within the particles that provide an easy path of alkalis to reactive sites within the RCA. Examination of the composition of the ASR gel showed that exposing the RCA to lithium solution decreased the calcium content and Ca/Si of the gel. This could add to the suggested mechanisms by which the lithium mitigates ASR.

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Dedication:

To the sole of my Father

List of Abbreviations

AAR	Alkali Aggregate Reaction
ACR	Alkali Carbonate Reaction
ASR	Alkali Silica Reaction
ASSHTO	American Association of State Highway and Transportation Officials
ASTM	American Society for Testing Materials
CH	High Calcium
CI	Intermediate Calcium
CSA	Canadian Standards Association
C-S-H	Calcium Silica Hydrate
F	Low Calcium
FA	Fly Ash
GU	General Use
HA	High Alkali
LA	Low Alkali
MTO	Ontario Ministry of Transportation
PC	Portland Cement
RCA	Recycled Concrete Aggregate
RH	Relative Humidity
SCM	Supplementary Cementing Materials
SEM	Scanning Electron Microscope
SF	Silica Fume
SSD	Saturated Surface Dry
w/c	Water to Cementing Materials Ratio
Ca/Si	Calcium to Silica ratio

Chapter 1

Introduction

1.1 General

Conventional concrete aggregates usually contain natural fine and coarse aggregates. However, there is a growing interest in finding alternative aggregate materials due the major environmental concerns resulting from disposal of construction waste and depletion of natural aggregate sources. Many major infrastructures are due for replacement as a result of aging, lack of serviceability or other structural concerns. This increases the demand of recycling the debris produced from demolishing these structures. Each year 200 million tons of construction waste is continuously discarded in landfills (Gomez-Soberon, 2002).

Deteriorations take place in concrete due to sever environmental conditions and chemical attack such as the repeated cycles of freezing and thawing and the use of de-icer salts. Sometimes, deteriorations are caused by concrete constituents as a result of damaging reactions even without severe environmental conditions or exposure to external chemicals attack. For instance, alkalis inside the concrete react with some forms of reactive silica inside the aggregates producing expansive gel that causes damage of concrete structures. In many cases repairs are more difficult and more expensive to implement, and removal may be the best solution.

Hence, the debris resulting from demolishing these structures is of a concern if recycled as aggregate for new concrete structures. The quality of concrete with recycled concrete aggregate (RCA) is very dependent on the quality of the recycled material properties. Unfortunately most of the RCA with history of ASR is used as a landfill or as a sub-base,

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which are not the best use of it if the demolished structure is in a remote area with scarce natural aggregate sources. This necessitates the need of finding preventive measures to counteract ASR in new concrete containing RCA.

1.2 Objective

The purpose of this study is to determine if deterioration continues in new concrete containing RCA affected by ASR, the extent of the deterioration, and whether or not the deterioration can be controlled. This was carried out in two phases.

Phase 1:

This phase focused on evaluating the reactivity of RCA produced from ASR-affected concrete. This was accomplished by testing aggregates without preventive measures. In addition, preventative measures in the form of binary and ternary blends of supplementary cementing materials (SCM) were investigated. The investigated blends included various levels of silica fume, fly ash, slag, ternary blends of silica fume and fly ash or silica fume and slag, low alkali cement, and pre-washing aggregates to remove excess alkalis.

Phase 2:

Phase 2 presented in this thesis covers the following:

1- Investigate the effects of SCMs; at higher replacement levels than those used in Phase 1; to reduce expansion in new concrete with ASR-affected RCA.

2- Evaluate the reactivity of the ASR-affected RCA when used as partial replacement of coarse aggregate.

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3- Investigate the effect of using the lithium nitrate at different molar ratios to mitigate the expansion of concrete containing ASR-affected RCA

4- Investigate the synergy effect of using the lithium nitrate in combination of SCMs with different molar ratios.

5- Evaluate the amount of alkalis contributed from the ASR-affected RCA when immersed in solutions of alkalis concentrations representing those likely to be encountered in concrete pore solution.

6- Studying the composition of ASR gel found in the original RCA, gel in the concrete prisms and gel in the RCA after exposed to alkaline solutions with and without lithium. The objective is to find out if the lithium has an effect on the gel composition.

1.3 Organization of thesis

In this thesis:

- Chapter 2 provides a literature review of the ASR and its common preventative measures.

- Chapter 3 presents the materials and experimental program.

- Chapter 4 discusses the results obtained and possible reasons for the obtained trends.

- Chapter 5 covers the conclusions and recommendations for possible further studies.

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Chapter 2
Literature Review

A review of literature is presented pertaining to alkali silica reaction and the role of SCMs and lithium salts as preventative measures against ASR expansion.

2.1 Recycled Concrete Aggregate (RCA)

2.1.1 General

Recycling of concrete is a relatively simple process. It involves demolishing old concrete structures, removing non-concrete materials and crushing existing concrete into a material with a specified size. The quality of concrete with recycled concrete aggregates is very dependent on the quality of the recycled material used. If the demolished concrete was exposed to de-icer salts, the RCA produced will contain salt ions (Prieur & Nikitine 2006). Similarly, if the demolished concrete had history of ASR, the produced RCA will contain portions of the reactive aggregate including ASR gel.

Removal of reinforcements and other contaminating materials is essential to obtain quality aggregate to be used as aggregate for new concrete. Figure 1 illustrates the typical steps required to process recycled material. Technology primarily involves crushing, sizing, and blending to provide aggregates suitable for a variety of applications. Concrete and asphalt recycling plants can be used to process natural sand and gravel, but sand and gravel plants usually won't process recycled material (David & Thomas, 1998).

Another advancement in the use of Recycled Concrete Aggregate is the advantage of using a mobile crusher to recycle concrete in place of demolition to be used as a sub-base or in new concrete, if applicable.
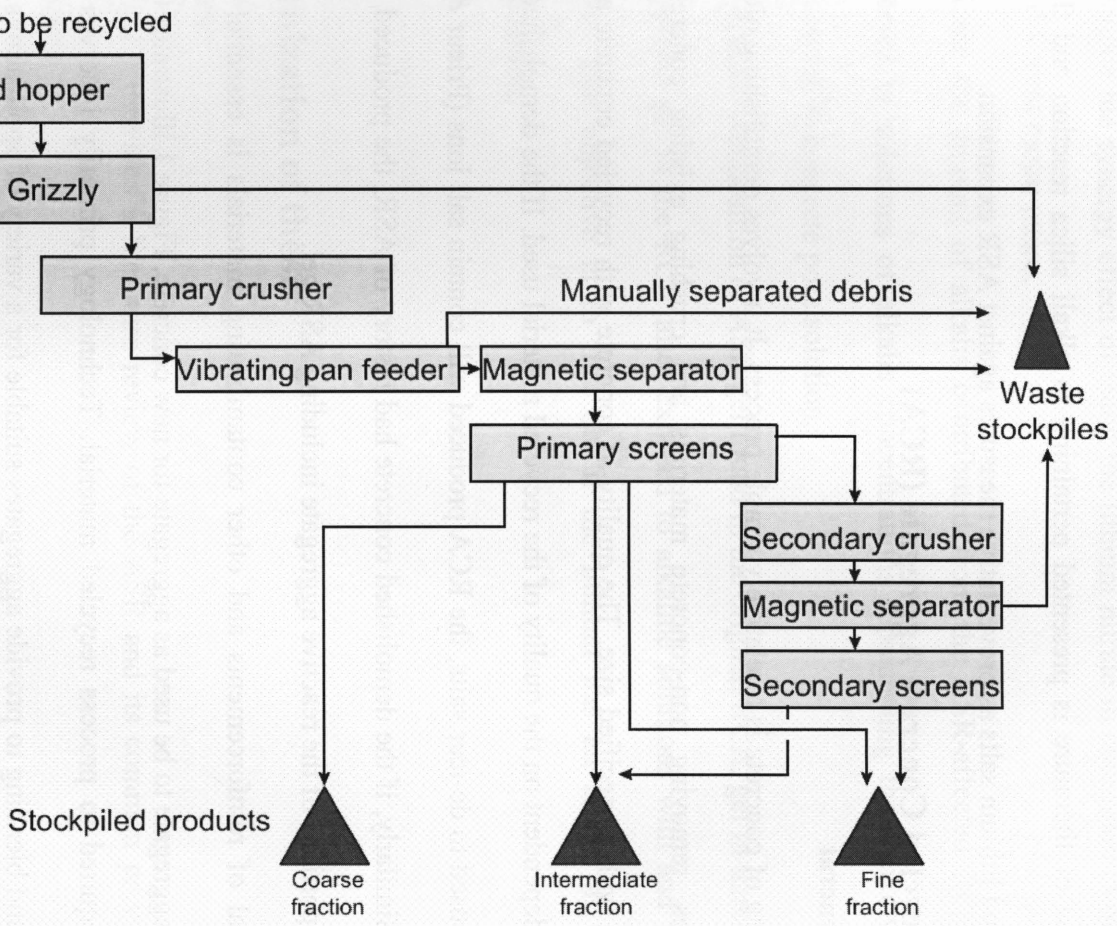
Figure 1. Generalized flow diagram for an aggregates recycling operation.

(David & Thomas, 1998).

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2.1.2 Recycled concrete Properties

RCA consists of part of original aggregate attached to residues of the old concrete mortar. The mortar attached to the aggregate particles affects the performance of the new concrete as it alters the aggregate absorption and density and affects the mechanical compressive strength than the original recycled concrete (Ajdukiewicz & Kliszczewicz, characteristics of the new concrete. Recycled coarse aggregate was found to have absorptions of 5% to 6%; whereas recycled fine aggregate absorptions was 9% to 10% (McGovern, 2002). Compressive strength of concrete decreases as the percentage of RCA increases as seen in Figure 2.
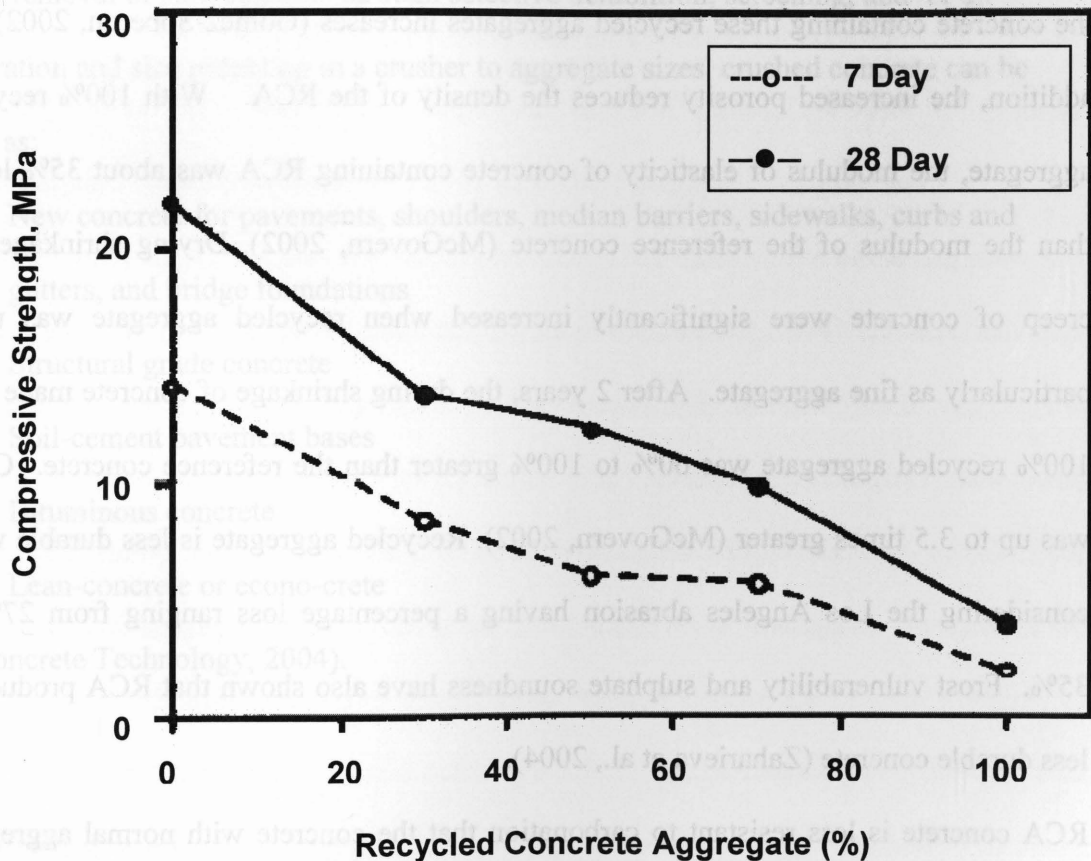
Figure 2: Changes in compressive strength due to varying replacement quantities of recycled aggregate (Topcu, 1997).

When RCA is used as 100% of the coarse and fine aggregates in concrete the reduction in strength could be as much as 80% compared to concrete without RCA (Topcu, 1997). Although concrete containing RCA has been demonstrated to have a lower compressive strength, it is possible to produce concrete containing RCA with equal to or greater compressive strength than the original recycled concrete (Ajdukiewicz & Kliszczewicz, 2002). Tensile strength is approximately 10% lower in concrete containing RCA than in concrete containing limestone aggregate (Ajdukiewicz & Kliszczewicz, 2002). According to Gomez-Soberon (2002), recycled aggregates have a lower density and higher porosity than natural aggregates. As the replacement level of the RCA increases, the porosity in the concrete containing these recycled aggregates increases (Gomez-Soberon, 2002). In addition, the increased porosity reduces the density of the RCA. With 100% recycled aggregate, the modulus of elasticity of concrete containing RCA was about 35% lower than the modulus of the reference concrete (McGovern, 2002). Drying shrinkage and creep of concrete were significantly increased when recycled aggregate was used, particularly as fine aggregate. After 2 years, the drying shrinkage of concrete made with 100% recycled aggregate was 60% to 100% greater than the reference concrete. Creep was up to 3.5 times greater (McGovern, 2002). Recycled aggregate is less durable when considering the Los Angeles abrasion having a percentage loss ranging from 27% to 35%. Frost vulnerability and sulphate soundness have also shown that RCA produces a less durable concrete (Zaharieva et al., 2004).

RCA concrete is less resistant to carbonation that the concrete with normal aggregates (Otsuki et al., 2003).

2.1.3 Recycled concrete Applications

In general, applications without any processing include:

- Many types of general bulk fills
- Bank protection
- Base or fill for drainage structures
- Road construction
- Noise barriers and embankments

After removal of contaminants through selective demolition, screening, and /or air separation and size reduction in a crusher to aggregate sizes, crushed concrete can be used as:

- New concrete for pavements, shoulders, median barriers, sidewalks, curbs and gutters, and bridge foundations
- Structural grade concrete
- Soil-cement pavement bases
- Bituminous concrete
- Lean-concrete or econo-crete

(Concrete Technology, 2004).

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2.2 Alkali Silica Reaction

2.2.1 General

Alkali-Silica Reaction (ASR) is the reaction between the soluble alkalis in the pore solution and some types of aggregates that contain poorly crystallized silica. The reaction results in the ASR gel formation that is not stable, and upon absorption of water expands causing rupture of the aggregate fragments. Hence, these cracks propagate into the concrete structure. Aggregates that contain opaline silica as a mineral, as primary or secondary materials, are highly reactive; aggregates that contain chalcedony as a mineral are moderately reactive such as cherts and flints; and aggregates that contain volcanic glass are reactive in some cases such as basalt and rhyolites (Swamy, 2003).

Alkali-Silica Reaction (ASR) was first identified by Stanton from investigation of cracking in concrete pavements and bridges in 1940 (Stanton 1940). Since then, ASR has been recognized in more than 50 countries around the world. It is likely that the problems associated with ASR exist in a larger number of countries, but the deterioration of the concrete may have been attributed to other causes (Fournier & Bérubé, 2000). ASR can cause extreme deterioration problems when combined with other forms of deterioration, such as chloride attack (Neville, 1996). When recycled concrete aggregate (RCA) that was affected by ASR is used as partial or full replacement for coarse aggregate, some of the alkalis contained in the aggregate contributes to raise the available alkalis in the pore solution, and the ASR expansion obtained from that type of RCA was found to be similar to the one obtained from the original natural aggregate. It was found that the early expansion was even higher with RCA due to early age moisture swelling of the past portion of the RCA (Scott & Gress, 2004).

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2.2.2 Alkali Silica Reaction Mechanism

It is generally recognized that the alkali silica reaction is a multi stage process, with the first step being the dissolution of silica on the surface of aggregate particles (Diamond, 1997). The Polar water molecules react with SiO_2 creating silanol moieties (-Si-OH) in their place, which can be expressed by the following equation:

$$H_2O + Si-O-Si \rightarrow Si-OH \ldots OH-Si \qquad (1)$$
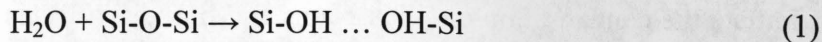
In highly alkaline environment, such as concrete pore solution, hydroxyl ions will attack the silanol bonds created in equation (1), which will yield some free Si-OH molecules that are no longer bound to the larger mineral structure, the free Si-OH groups react with free alkali ions, creating alkali silica molecules as shown in equation (2). These molecules cluster at the surface of the aggregate, creating the ASR gel

$$Si-OH + NaOH \rightarrow Si-O-Na + H_2O \qquad (2)$$
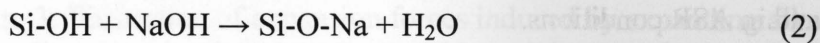
Silica is an amphoteric material, which means that it dissolves at extreme pH in strongly acidic or strongly alkaline conditions, but not at natural pH. In the alkali-silica reaction, there are three forms of silicon; the undissolved silica contained in the aggregate; the dissolved silica in the alkaline solution and the undisclosed ASR gel. Only the solute silicon is present in the solution and is measured as dissolved silica (Feng et al, 2005).

At first the ASR gel is restrained from expanding into the cement paste. However, cracking occurs when the tensile stresses that are developed exceed the tensile strength of the cement paste as shown in Figure 3. As soon as adequate micro cracking has occurred, the gel spreads out freely through the cracks in the cement paste. It continues spreading, but gradually loses its expansive properties with the absorption of calcium.

The calcium enters the system through an ion-exchange process with the hydrates of the paste (Fournier & Bérubé, 2000).

The Role of Calcium in ASR is controversial. Some researchers stated that the presence of calcium is essential for the formation of ASR gel and thus the expansion due to ASR. They suggested that without calcium ions the residual solution is merely an alkali-silica solution. Thus calcium ions initiate the condensation of silicate ions and link the silicates species in order to form a solid (Nieto & Zanni, 1997).

Two categories of ASR reactive rocks were recognized in Canada according to the silica form involved:

1) Rock types incorporating poorly crystalline or meta-stable silica minerals. Concrete structures that incorporate even as little as 1 to 2% of these silica minerals have shown to greatly expand in ASR conditions.

2) Rocks that contain very fine quartz grains or some variety of macro-granular quartz. This category is common in Eastern Canada. It is characterized by an initial delay of expansion, followed by deterioration cracks that can take 10 to even 25 years to become apparent in field conditions (Fournier & Bérubé, 2000).

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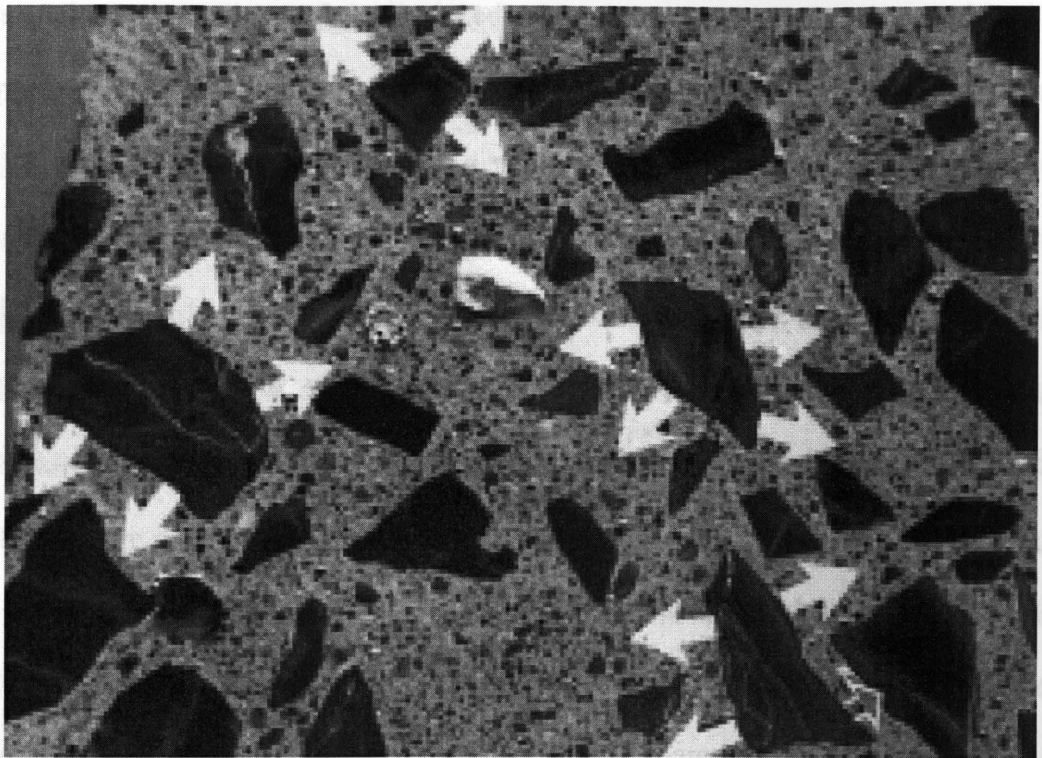
Figure 3: Illustration of expansion forces induced by expanding alkali–silica reactive siliceous limestone particles causing cracking of the particles and the surrounding cement paste (Fournier & Bérubé, 2000).

2.2.3 Factors affecting alkali silica reaction

Three derivative conditions mainly control the ASR formation in concrete; presence of reactive aggregate, available soluble alkalis in concrete pore solution and the presence of adequate moisture (Neville, 1996).

2.2.3.1 Presence of reactive aggregate

With the mixture proportions being constant, the reactivity level will generally increase with an increased amount of reactive particles in the aggregate. The reactivity level will also increase as the aggregate particle size decreases, or in other words increasing the surface area of the aggregate (Fournier & Bérubé, 2000).

It is said that a maximum expansion can be obtained for a given proportion and size fraction of such reactive particles. It should be noted also that all natural rocks react to some extent with the alkaline pore solution in concrete (Rogers et al., 2000). Although, introducing fresh faces of aggregate that still have un-reacted reactive silica; and introducing the poor structure with many cracks such as in case of ASR-affected RCA; this would drive more ASR expansion to take place in new concrete with RCA exactly as with virgin natural aggregate. Hence, the ASR reaction is proportional to the amount of replacement of RCA in concrete.

2.2.3.2 Available soluble alkalis in concrete pore solution

Available soluble alkalis in the pore solution are usually introduced by the internal ingredients of concrete (cement, water, aggregate, SCMs and additives), some external quantities may become available in concrete due the excess exposure to De-icer salts. Aggregates generally expand in the concrete with an increased amount of total alkali content in the form of sodium hydroxides, as seen in Figure 4 (Shehata & Thomas, 2000). However, the amount of alkali content needed to initiate and sustain ASR varies from one aggregate to another (Fournier & Bérubé, 2000).

Alkalis contained in the aggregate can be expelled into the pore solution. This is particularly true with feldspar-rich aggregates (Bérubé et al., 2002). RCA with history of ASR contains considerable amount of alkalis in the ASR gel and from the de-icing salts contained with the RCA that have determinate effect on ASR of the new concrete.

The alkalis from Portland cement and RCA in concrete creates very high initial pH levels that are more aggressive than those seen in concrete where cement is the only alkali source (Scott & Gress 2004).

Unwashed sea dredged sands can contribute to the increase of the available alkalis due to the salt content of these aggregates. Chemical admixtures such as superplasticizers have been known to contain alkalis. Hard water also can contain moderate levels of alkalis (Neville, 1996).

The high alkali content of the SCMs such as fly ashes (Shehata, & Thomas 2000), silica fume (Boddy et al., 2003), and slag (Hooton, 2000) contributes in the gel formation due ASR. Total alkalis available to various testing solutions for samples containing high-alkali fly ash were much higher than those contributed by fly ash of lower alkali contents. These fly ashes may be expected to provide considerable sources of alkalis if the alkalinity of the pore solution drops due to alkali being consumed by the reactive aggregate (Shehata & Thomas 2006).
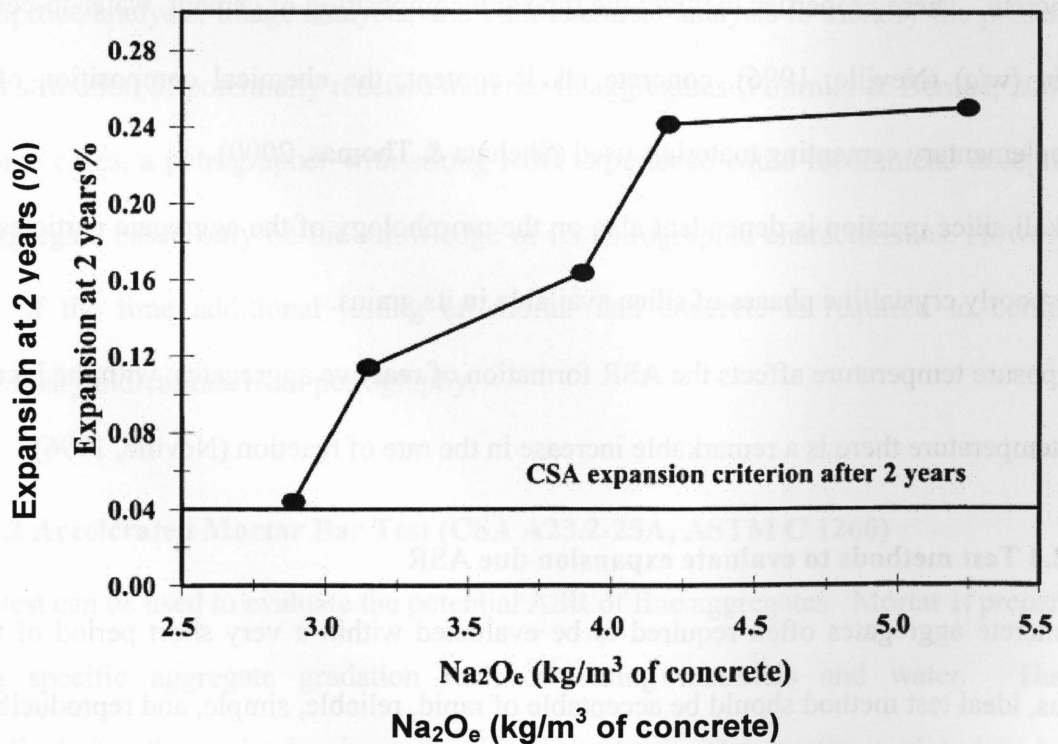
Figure 4: Effect of alkali content of concrete on the 2-year expansion of concrete prisms containing Sprat aggregate (Shehata & Thomas, 2000).

2.2.3.3 Adequate moisture content

The alkali-silica gel needs water to swell, which causes expansive pressure on the concrete. Alkali-aggregate reactivity typically occurs in concretes that are exposed to internal relative humidity of approximately 80 to 85% (Neville, 1996). Investigations have shown that partially dehydrated gel due to drying of the specimen can be re-hydrated and expand if additional water is supplied to the specimen (Fournier & Bérubé, 2000). However, dried and carbonated gels are unlikely to regain their expansive properties (Neville, 1996).

2.2.3.4 Other Factors affecting ASR

The chemical properties of the components added to the concrete mix affect the ASR in concrete. These properties include: the type and composition of cement, water-to-cement ratio (w/c) (Neville, 1996), concrete alkali content, the chemical composition of the supplementary cementing materials used (Shehata & Thomas, 2000).

Alkali silica reaction is dependent also on the morphology of the aggregate particles and the poorly crystalline phases of silica available in its grains.

Exposure temperature affects the ASR formation of reactive aggregates; with the increase in temperature there is a remarkable increase in the rate of reaction (Neville, 1996).

2.2.4 Test methods to evaluate expansion due ASR

Concrete aggregates often required to be evaluated within a very short period of time, thus, ideal test method should be acceptable of rapid, reliable, simple, and reproducible to evaluate the potential for ASR expansion for particular combination of materials.

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2.2.4.1 Petrographic examination (ASTM 295)

ASTM C295-03 Standard outlines procedures for the petrographic examination of samples representative of materials proposed for use as aggregates in cementitious mixtures or as raw materials for use in the production of such aggregates. Essentially this is the first step in testing aggregates for ASR. Petrographic analysis uses microscopic techniques described in ASTM 295. Some of the items that can be reviewed by petrographic examination include paste, aggregate, supplementary cementing materials and air content. Also, distress effects due to frost, sulphate attack, and alkali aggregate reactivity can be reviewed by this method (Kosmatka et al, 2002).

However, a standard petrographic analysis is sometimes accompanied by other methods such as X-ray diffraction, infrared spectroscopy, Scanning Electron Microscope (SEM), microprobe analysis, image analysis, and bulk chemical analysis to identify the presence and distribution of potentially reactive material in aggregates (Fournier & Bérubé, 2000). In some cases, a petrographer with strong ASR experience could recommend accepting an aggregate based only on the knowledge of its petrographic characteristics. However, most of the time additional testing on mortar and concrete is required to confirm preliminary indications from petrography.

2.2.4.2 Accelerated Mortar Bar Test (CSA A23.2-25A, ASTM C 1260)

This test can be used to evaluate the potential ASR of fine aggregates. Mortar is prepared using specific aggregate gradation with cementing materials and water. These ingredients are then mixed using a specific procedure. The mortar is placed in bars approximately 25 X 25 X 285 mm in size. After 24 hours of moist curing in their

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moulds, the bars are placed in a sealed plastic container filled with water at 23°C, and the container is stored in an oven at 80°C. The next day, an initial length measurement is taken, and the bars are transferred to a 1 N NaOH solution at 80°C. Measurements occur several times over a 2-week time period. Reactive aggregates are determined based on a 14-day expansion of approximately 0.10%. This test is typically an effective method to determine the ASR reactivity of aggregates within 2 weeks. However, it was found to be misleading for several aggregates with good field performance, but greatly expansive mortar bars (Fournier & Bérubé, 2000). Therefore, the Accelerated Mortar Bar Test should not be used for rejecting aggregates. Further testing using the concrete prism test as per CSA A23.2-14A, ASTM C 1293 is required.

2.2.4.3 Concrete Prism Test (CSA A23.2-14A, ASTM C 1293)

This test is used to evaluate the potential alkali-reactivity of coarse aggregates. Prisms are prepared using a specific quantity of cement, coarse-to-fine aggregate ratio, and water. The water cement ratio (w/c) should be 0.42 to 0.45, except when supplementary cementing materials are used. In the case of using SCMs, the CSA 2004 limits the w/c to 0.35 to 0.40. The prisms are kept in their molds for 24 h at 23°C, and then stored above water in a sealed plastic container lined with a damp material. After the one-day curing, the prisms are placed in a room controlled at 38°C. Length change measurements are made periodically up to 1 year with concrete containing no SCM and 2 years with concrete containing SCM. Aggregates can show different expansion rates in the Concrete Prism Test. Generally, the more rapid the onset of expansion and the development of micro-cracking due to ASR, the faster the leaching of alkalis out of the

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test prisms and the levelling off of the expansion curve (Rogers et al., 2000). Reactive aggregates are determined based on an expansion of approximately 0.04%. There are a number of disadvantages to this test. One disadvantage is that the testing period is too long for most construction projects. Another disadvantage is that depending on the storage conditions, some alkali leaching from the prisms is evident which would slow down or stop the expansion (Rogers et al., 2000).

2.2.4.4 Accelerated Concrete Prism Test method

In 1992, Rance and Debray proposed accelerating the rate of expansion in the concrete prism test, hence, shortening its duration by increasing the exposure temperature to 60 C°. Since then, there have been a number of studies on the accelerated test (Fournier et al, 2004) although the test method has yet to be standardized. Some research work showed reasonable correlation between the 3-month expansion of prisms at 60 C° and the 12-month expansion at 38 C° for concrete with and without preventive measures (Air-entrainment, SCMs and lithium nitrate) (Touma et al, 2001). Other researchers have not been able to reproduce the good correlation that was reported by Touma. It has been observed that the higher temperature in the accelerated concrete prisms test increases the rate of alkali leaching during test, and reduces the pore solution pH due to sulfate ions replacing some of the hydroxyl ions in the solution. Acceptance of this Test method is not yet approved due the uncertainty of its correlation.

2.2.5 Preventative measures for ASR

2.2.5.1 Aggregate selection

The most effective measure against ASR is the use of non-reactive aggregates. This solution may not be practical or economical because non-reactive aggregates may not be locally available or must be transported over long distances to a construction site. On the other hand, in some cases such as in demolishing deteriorated structures to produce RCA with history of ASR, it could be the best option available as source of aggregate in place of construction.

2.2.5.2 Limiting the alkali content in concrete

Portland cement contains some alkalis (from within Na_2O and K_2O) that cannot be eliminated completely from the cement produced. In modern cement plants, the hot gases leaving the upper end of kiln preheat raw materials. These gases contain a significant proportion of the volatile alkalis, which ultimately contributes in raising alkalinity in the cement. However, by bleeding off a part of the gases, the alkali content can be controlled (Neville 2006). ASR can be considerably reduced or even prevented by the use of low-alkali cement or by limiting the total alkali content of concrete under a limiting value. Low alkali cement with upper limit of 0.60 percent of sodium oxide equivalent (Na_2O + $0.658K_2O$) has been standardized and used in the USA for nearly 50 years in the cement to minimize the risk of ASR (Neville 2006).

2.2.5.3 Use of Supplementary Cementing Material (SCMs).

SCMs are found to be effective in controlling ASR. The use of any SCM reduces the permeability of the concrete, which reduces the ability of the gel to absorb water and expand (Neville, 1996). Alkali dilution and consumption of $Ca(OH)_2$ through pozzolanic reaction are also thought to play a role in the beneficial effect of SCMs against ASR (Fournier & Bérubé, 2000). The efficacy of SCMs in mitigating ASR is attributed, mainly, to their ability to reduce the alkalinity of pore solution (Shehata & Thomas, 1999). It was stated that due to chemical and mineralogical composition variation and the distinct alkali release characteristics, each SCM imparts specific role in controlling ASR. Fly ash contributes 17%, GGBFS 50%, and silica fume 100% of its total Na_2Oe to the pore solution (Hobbs, 1988). This nearly in good agreement with the proposed revision of Appendix B of the Canadian CSA A23.1 and A 23.2 standards as 15 % of total Na_2O_e for fly ash, 50% for both GGBFS and silica fume (Duchense & Bérubé, 1994). Experimental results of studies showed that some fly ashes were found to release more alkali in the pore solution than the suggested level (Shehata and Thomas 2006).The role of each SCM in controlling ASR is covered in the following subsections.

2.2.5.3.1 Fly Ash

Fly ash has proven to be an effective SCM in reducing ASR expansion. The amount of alkalis and calcium content in the fly ash were important factors in the amount of reduction that occurred. Of course, an increased amount of alkalis in the fly ash increases the expansion that occurs. In addition, high calcium fly ash is not effective in mitigating ASR, specially, at lower replacement levels. The reason for the lower efficiency of a

class C fly ash is likely due to the greater portion of the silica in the fly ash that is tied up by lime, lowering the amount of silica available to control the alkali-silica reaction (Mindess et al, 2003). Experimental results elsewhere showed that low calcium fly ash is effective in suppressing ASR. The main reason behind the effectiveness of such fly ash is due its higher alkali binding capacity (Shehata & Thomas 2006). The Reduction of alkalinity in the pore solution is due to the incorporation of more alkalis in the secondary C-S-H (Duchense and Bérubé 1994). It was also noted that the increase in total silica content of the fly ash increased the effectiveness of the fly ash to reduce expansion.

In a study by Shehata and Thomas (2000) on concrete made using reactive siliceous limestone (Spratt) a relationship was developed between expansion and CaO of the ash as shown in Figure 5.There is a slight increase in the expansion as the CaO content increases ranging from 5% to 20% with a sudden and remarkable increase above $20\pm 22\%$ CaO. In nearly all cases, fly ashes (with low to moderate alkali) that meet the CSA specification for Type F or Type CI were effective in limiting the 2-year expansion of concrete prism to $\leq 0.04\%$ when used at replacement level of 25%.

The relation in Figure 6 was established from the same experimental results in an attempt to correlate the fly ash composition and replacement levels with the expansion of the concrete prisms. Multiple regression analyses were performed between expansion as the dependent variable and the CaO, Na_2Oe, and SiO_2 contents of the fly ash as the independent variables. The best fit was achieved when the Na_2Oe and CaO were normalized to the SiO_2 content. The graph shows a general trend of increasing expansion as the Na_2Oe and CaO contents of the fly ash increase and as its silica content decreases. The graph also indicates that fly ash with chemical composition that satisfies the

condition $[(10 \ Na_2Oe + 4.45CaO)/ \ SiO_2 \leq 2]$ will likely meet the 0.04% expansion criterion of the concrete prism test after 2 years when used at a replacement level of 25% (Shehata & Thomas 2000).
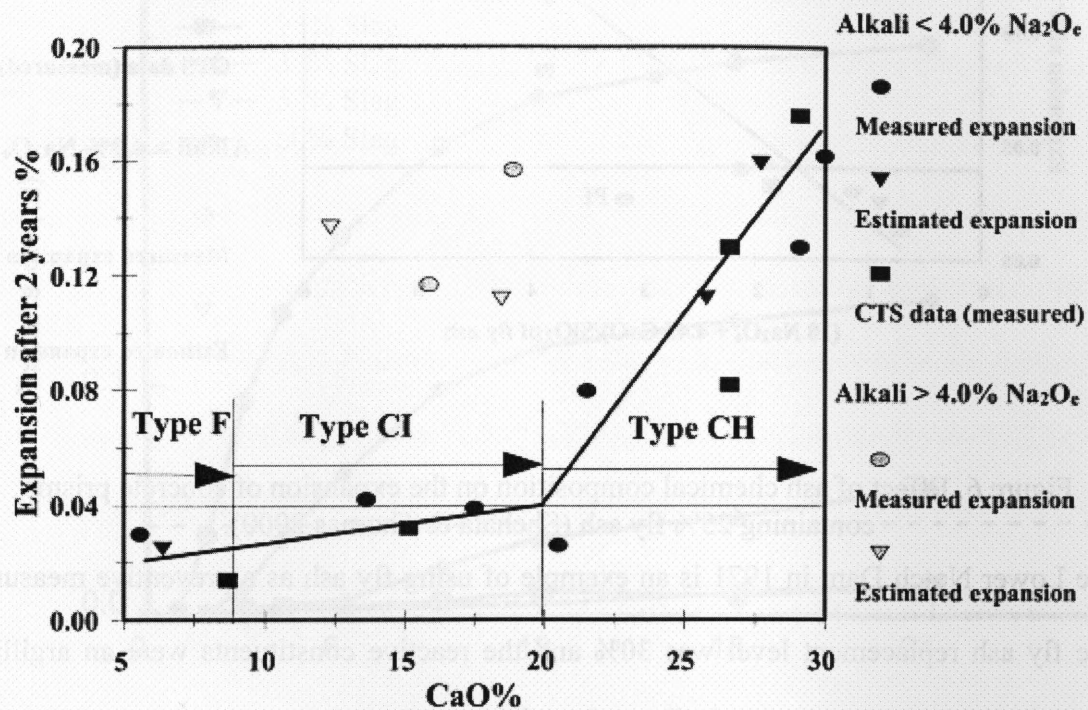
Figure 5. Effect of CaO content of fly ash on expansion of concrete containing 25% fly ash (Shehata & Thomas 2000).
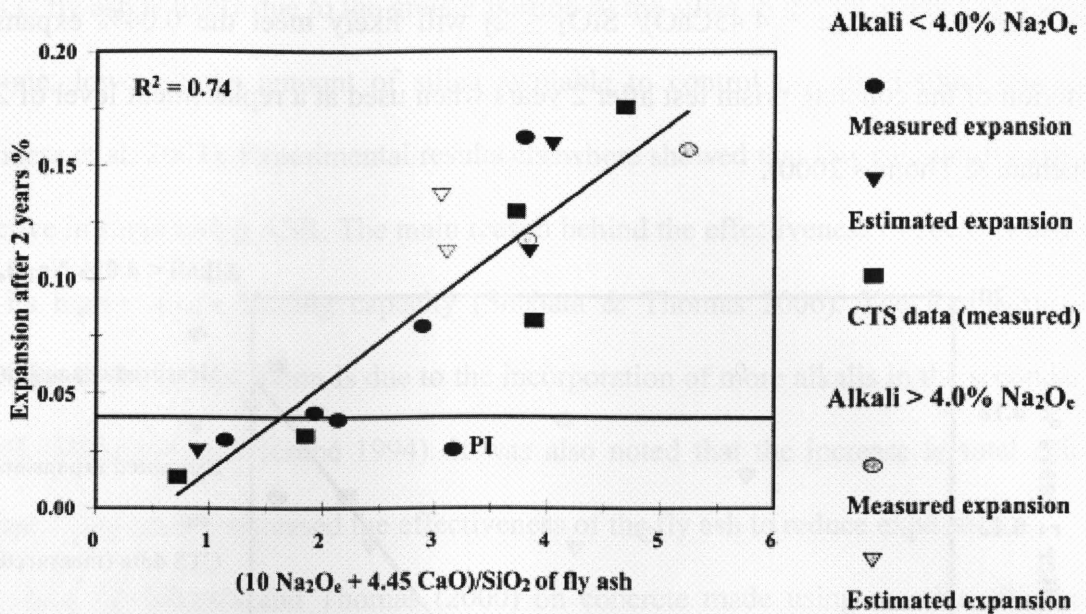
Figure 6. Effect of ash chemical composition on the expansion of concrete prisms containing 25% fly ash (Shehata & Thomas 2000).

The Lower Notch Dam in 1971 is an example of using fly ash as a preventive measure. The fly ash replacement level was 30% and the reactive constituents were an argillite aggregate (Rogers et al., 2000). It was the only known instance in Canada where the use of a known alkali reactive aggregate was permitted with high alkali cement combined with fly ash (Rogers et al., 2000).

2.2.5.3.2 Granulated Ground Blast Furnace Slag (GGBFS)

Thomas & Innis (1998) reported that high proportions of slag are necessary to reduce expansion as shown in Figure 7. In their study on four alkali-silica reactive aggregates (siliceous limestone, sandstone, greywake and granite) they found that the minimum replacement level of slag required to control expansion to an acceptable level (0.04% in 2

years) varied depending on the nature of aggregate and the amount of alkali present in the concrete.
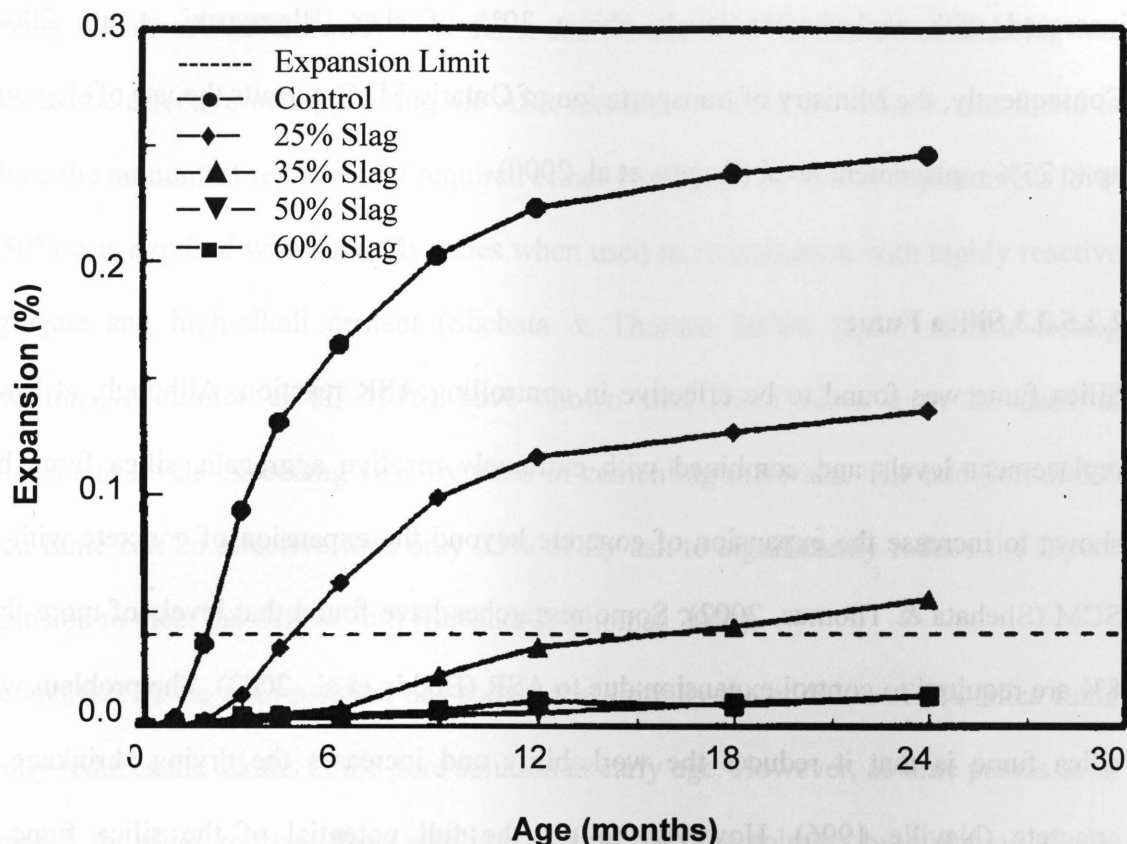
Figure 7: Expansion of concrete with Spratt aggregate alkalis = 1.25% Na_2O_e (by mass of cement) (Thomas & Innis, 1998).

Slag replacement level ranging from 25% to 65% was found to be effective in retarding the rate of expansion. However, the effectiveness of slag was found to be decreasing with the increase in the alkali content of cement. Thomas & Innis (1998) believed that slag helps to reduce the hydroxyl ion content of the pore solution; this is achieved by incorporating higher levels of alkalis into the C-S-H matrix compared to the C-S-H that is produced when Portland cement is used alone. The efficacy of slag was attributed to the dilution effect as well as the stabilization and immobilization of alkalis.

A disadvantage with the use of slag as a preventative measure is the amount required which may lead to other deleterious problems such as salt scaling that shown to be increased with replacement levels above 30% of slag (Bleszynski et al., 2002). Consequently, the Ministry of transportation of Ontario MTO permits the use of slag only up to 25% replacement level (Rogers et al, 2000).

2.2.5.3.3 Silica Fume

Silica fume was found to be effective in controlling ASR reaction. Although, at lower replacement levels and combined with extremely reactive aggregate, silica fume has shown to increase the expansion of concrete beyond the expansion of concrete with no SCM (Shehata & Thomas, 2002). Some researches have found that levels of more than 8% are required to control expansion due to ASR (Boddy et al., 2003). The problem with silica fume is that it reduces the workability and increases the drying shrinkage of concrete (Neville 1996). However, to get the full potential of the silica fume in controlling ASR, its quantity should be sufficient in the concrete mix. The efficacy of silica fume is due to its effect in reducing the calcium hydroxide contents of cement paste and pore solution due the pozzolanic reaction forming secondary C-S-H. Those reaction products decrease the porosity and cause retardation of transportation of Na^+ and K^+ ion towards aggregate (Hooton, 1993). But, Silica fume doesn't have a high capacity to retain alkalis in its hydration products; however, ternary blends containing silica fume and fly ash have excellent capacity to bind and retain Alkalis (Shehata & Thomas, 2002 and 2006).

2.2.5.3.4 Ternary Blends

Ternary blends of Portland with silica fume and fly ash or with silica fume and slag was found to be effective in suppressing the ASR reaction in concrete. Also, it was found to reduce the amount of replacement required either by slag or fly ash. A replacement level of 50% was required with some fly ashes when used in combination with highly reactive aggregate and high-alkali cement (Shehata & Thomas 2000). Under similar testing conditions, (Fournier et al, 1995) have shown that silica fume must be used at replacement levels exceeding 10% by mass of cementing materials. The addition of 5% silica fume can be effective with only 25% of fly ash to significantly reduce the 2-year expansion to meet the 0.04% limit (Shehata & Thomas 2002).

The analysis of the pore solution has shown that initially the addition of 5% silica fume greatly reduces the alkalis in the pore solution at early age. However, as time passes as in Figure 8, the silica releases these alkalis back into the pore solution by replacing alkalis for calcium. The presence of both SF and FA results in a low pore solution alkalinity at both early and late ages. Hence, the synergy that exists between SF and FA can be explained on the basis of their different effects over time. SF is very effective in reducing the alkalinity at early age whereas FA becomes increasingly effective at later ages. The combination of the two materials produces a pore solution that is initially low in alkalis and remains that way as seen in Figure 9 (Shehata & Thomas, 2002).

The very low range of the permeability of the ternary blended concrete can reduce the permeation of moisture, which is essential for ASR expansion into the concrete. Also the

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low range of permeability can reduce the ease of ionic diffusion of the soluble Alkalis in the pore solution.
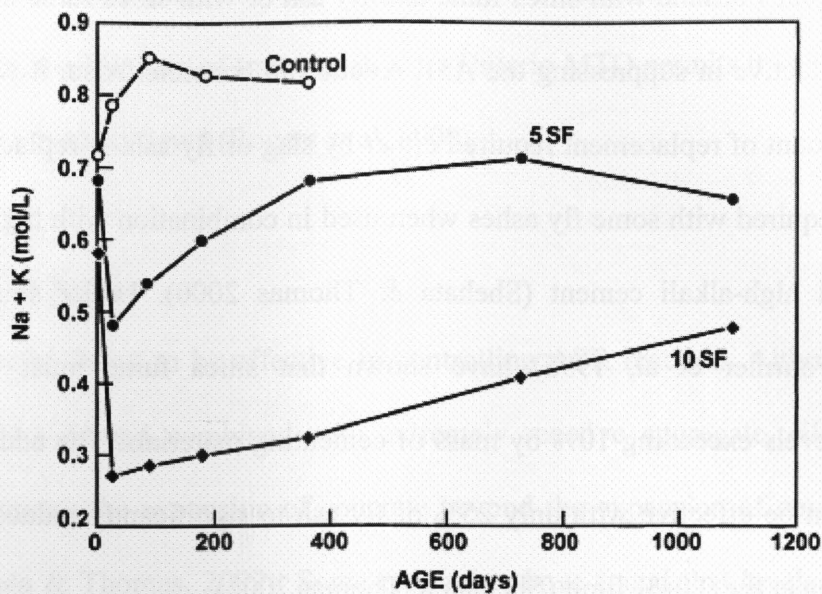
Figure 8: Effect of Silica Fume on the alkalinity of pore solution of pastes, represented by the sum of alkali cations in the pore solution (Shehata & Thomas, 2002).
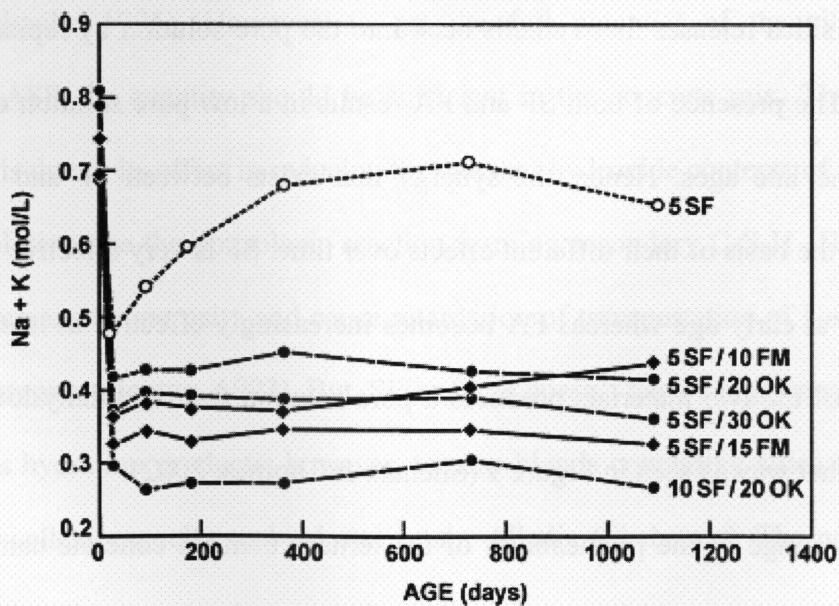
Figure 9: Effect of Silica fume (SF) & Fly Ash (OK) and combination of SK/OK on pore solution alkalinity (Shehata & Thomas, 2002).

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2.2.5.4 Use of Lithium Salts

Since McCoy and Caldwell in 1951 found that Lithium-based compounds were probably among the most effective chemical compounds against ASR, many researchers have investigated the effects of lithium hydroxide and several lithium salts on the ASR. It is known that some Li-bearing compounds including, $LiOH$, $LiNO_3$, LiF, $LiCl$ and Li_2CO_3 are able to suppress the expansion caused by the ASR when used at an adequate dosage (Stark et al, 1994). However, the mechanism of the lithium behaviour is not yet well understood (Ramyar et al, 2004).

Lithium nitrate has shown high efficacy in mitigating expansion due to ASR in both new and in service concrete. The efficacy of $LiNO_3$ was recognized as it appears not to be susceptible to pessimum effects and does not increase the pH of the pore solution contrarily to $LiOH$ and some other Lithium salts (Stokes et al, 1997). A significant increase in the pore solution OH^- ion concentration (and pH) by lithium hydroxide and inadequate dosages are known to result in increased, rather than decreased expansion (Diamond, 1999). Generally, $LiNO_3$ was found to be more effective against ASR than $LiOH$ at Similar $Li/(Na+K)$ molar ratios (Fournier and Bérubé, 2001). Although the Li^+ is still adsorbed into the hydration products, the release of NO_3 does not seem to have a negative effect in the concrete and also does not increase the amount of alkalis in the pore solution.

It has been reported by Diamond et al (1992) that when $NaOH$ is added into cement paste for accelerating the alkali silica reaction, about 25% of the added Na ions will be bound by the cement hydration products. Only the remaining 75% would be available for driving the ASR. Similarly, when lithium containing compound is added to the system,

the fate of the Li ions is similar to that of the Na ions. Only, about 60% of the Li^+ ions will be available for suppressing the ASR expansion and 40% will be bound by the cement hydration products (Diamond et al 1992).

Some researchers believe that the lithium ion Li^+ has both a smaller ionic radius and higher surface charge density than Na^+ or K^+ (Mo et al., 2003). This allows the Li^+ to enter the ASR product more readily than Na^+ or K^+. As the Lithium ions enter the ASR product, this produces a crystalline and non-expansive gel (Mo et al., 2003). Another mechanism was suggested by Kurtis et al (2000), is that some of the Lithium salts may prevent re-polymerization of the gel.

Others believe that lithium decreases the rate of silica dissolution (Shomglin et al., 2003). Feng et al (2005) conducted a study on two reactive aggregates that were ground to the size between 150μm and 300μm and placed in plastic containers at 1 N NaOH solution with and without $LiNO_3$ at 0.74 Molar ratio in presence and absence of calcium. Solution filtrates were then separated from aggregate residues and were analyzed by induction coupled plasma emission spectrometry (ICP-ES) to determine the silicon concentration, and by flame atomic emission to determine the Li^+ and Na^+ ion concentrations in the immersing solution. In presence of calcium, silica dissolution was much less; this was attributed to the formation of C-S-H. But the trend in Na and Li ion concentrations reduction were similar compared to the trend in the absence of calcium. Feng et al (2005) believed that the reduction of both Na^+ and Li^+ ions from the solution may indicate there are insoluble reaction products such as sodium-silicate, and lithium-sodium-silicate forming in the system. There was no significant difference between the aggregates that respond to the lithium effect to mitigate ASR expansion in concrete prism test and the

other that did not in terms of the amount of reduction of silica dissolution, or lithium and alkalis consumed as seen in Figure 11. Thus, the different response to Lithium exhibited by the aggregates may be due to textural differences rather than mineralogical differences. The Lithium Nitrate was effective to suppress the ASR expansion in case of NB aggregate (rhyolite), but not for the NS aggregate (greywacke). The NB is coarse grained, and almost all quartz likely coexists with albite while NS is fine grained with preferred orientation, and quartz likely exist alone Fig 10   (Feng et al, 2005).
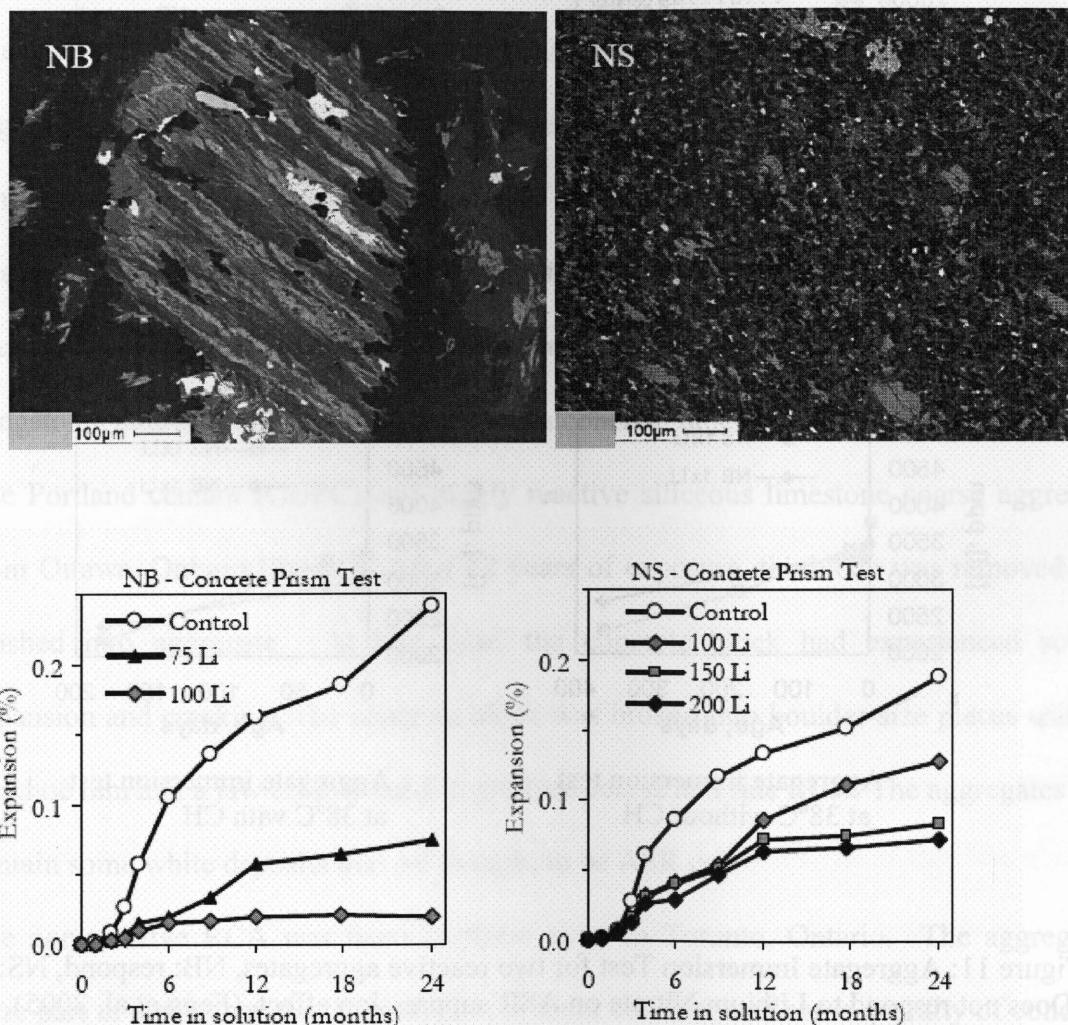
Figure 10: Aggregate microstructure by SEM, NB: respond, NS: Did not respond to Lithium Nitrate on ASR suppression effect, (X.Feng et al, 2005).

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No CH

[Si], ppm

8000
6000
4000
2000
0

- - -◇- - - NB control
- - -△- - - NS control
—▲— NS 1x Li
—◆— NB 1x Li

0   100   200   300   400
Age, days

With CH

[Si], ppm

480
400
320
240
160
80
0

- - -△- - - NS control
- - -◇- - - NB control
—▲— NS 1x Li
—◆— NB 1x Li

0   50   100   150   200
Age, days

No CH

[Na], ppm

22000
20000
18000
16000
14000
12000
10000

—■— NB 1x Li
—▲— NS 1x Li
- - -□- - - NB control
- - -△- - - NS control

0   100   200   300   400
Age, days

With CH

[Na], ppm

22000
20000
18000
16000
14000
12000
10000

—◆— NB 1x Li
—▲— NS 1x Li
- - -◇- - - NB control
- - -△- - - NS control

0   50   100   150   200
Age, days

No CH

[Li], ppm

5000
4500
4000
3500
3000
2500
2000

—■— NS 1x Li
—◆— NB 1x Li

0   100   200   300   400
Age, days

With CH

[Li], ppm

5000
4500
4000
3500
3000
2500
2000

—■— NS 1x Li
—◆— NB 1x Li

0   50   100   150   200
Age, days

Aggregate immersion test
at 38°C without CH

Aggregate immersion test
at 38°C with CH

Figure 11: Aggregate Immersion Test for two reactive aggregates, NB: respond, NS: Does not respond to Lithium Nitrate on ASR suppression effect, (Feng et al, 2005).

Chapter 3

Materials and Experimental Program

3.1 Materials

3.1.1 Coarse Aggregates

The properties of all the aggregates used in the first phase of this study were covered by Christidis (2006) and are reported here in Table 1. Four different types of coarse aggregates were tested; two reactive and two non-reactive.

The reactive aggregates were Spratt and ASR-affected RCA. The two non-reactive aggregates were limestone and Non-ASR recycled concrete aggregate. The 3/4'' coarse limestone was received from Acton, Ontario.

The Spratt aggregates were obtained from Ottawa, Ontario. The RCA used in this study was obtained from the Ontario Ministry of Transportation outdoor exposure site in Kingston, Ontario. The concrete was part of a concrete block placed in 1991 with General Use Portland cement (GUPC) and highly reactive siliceous limestone coarse aggregate from Ottawa, Ontario (Spratt). After 12 years of exposure, the block was removed and crushed into aggregate. At that time, the concrete block had experienced severe expansion and cracking. The concrete block was broken into boulder-size pieces using a backhoe ram and a jaw crusher used to produce coarse and fine RCA. The aggregates still contain some white deposits that are thought to be ASR gel.

The non-reactive RCA was from Dufferin plant in Toronto, Ontario. The aggregates were part of a pile that mostly contained leftover concrete and some quantity of concrete

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collected from the demolition of old concrete structures. Most of the non-concrete debris was removed.

The RCA was separated in 3 sizes for testing of coarse material conforming to ASTM C1293. The coarse ASR-affected RCA was not washed to avoid removing the pre-existing alkalis. Heating the aggregates was avoided because it was assumed that the heat would destroy some of the ASR gel.

In the second phase of the program which is covered in this thesis, the coarse aggregates used were:

- Two reactive aggregates: The same ASR-affected RCA used in phase 1 and Spratt aggregate obtained from Ottawa, Ontario.

- Two non-reactive aggregates: Non-reactive limestone from Ontario, and non-ASR recycled concrete aggregates obtained from Dufferin plant (demolished RCA)

3.1.2 Fine Aggregates

The fine aggregates used in the first phase :

There were four different types of fine aggregate tested; three reactive and one non-reactive. The reactive aggregates were natural sand, Jobe, and ASR recycled concrete aggregate that was primary crushed and secondary crushed. The one non-reactive was Ottawa sand. The natural fine aggregate was from Orangeville Ontario. This sand was found to correspond with the gradation limits in ASTM C136. Jobe was from New Mexico and has been proven to be very reactive with respect to alkali silica reaction. ASR fine recycled concrete aggregate that was primary crushed was obtained from the original crushing of the deteriorated out door-exposure of the concrete block and contain the white deposits similar to the coarse aggregate. The secondary re-crushed fine RCA

was acquired from re-crushing the ASR coarse aggregates, mentioned above, into the appropriate gradations.

Second phase only used the non-reactive natural sand from Sunderland, Ontario which is similar to the natural sand from Orangeville Ontario used in phase 1.

Fine aggregates were separated in 5 sizes for testing conforming to ASTM standard C1260.

3.1.3 Cementing materials

The cement and supplementary cementing materials used in this study were received by various suppliers. The chemical analysis for cement, slag, and silica fume are shown in Table 2. The chemical analysis for the fly ash can be seen in Table 3. Carbon content was measured with Leco SC444DR Carbon/Sulfur Analyzer. The chemical analysis was performed on a dry, ignited basis for the fly ash and on a dry basis for the slag, silica fume and cement using a Bruker S4 X-ray fluorescene spectrometer according to ASTM D4326. Cement used for Phase 2 of this study was of 0.97 Alkali content.

3.1.4 Lithium Nitrate LiNO₃

The lithium compound used in this study was in the form of a 30% lithium nitrate solution. This was used to evaluate the dosage used based on molar ratio of Li/Na+K where the Na + K are obtained form the Portland cement alkali content in the concrete mix.

Table 1: Aggregate Properties using ASTM Standards

Aggregate Type	Bulk Relative Density (Dry) (Kg/m^3)	SSD Bulk Relative Density (Kg/m^3)	Apparent Relative Density (Kg/m^3)	Dry Rodded Density (Kg/m^3)	Absorption
Coarse Aggregate					
Limestone	2680	2694	2718	-	0.51
Spratt	2665	2680	2706	-	0.58
ASR Recycled Concrete	2333	2441	2615	1385	5.07
Non-ASR Recycled Concrete	2249	2400	2647	-	6.69
Fine Aggregate					
Ottawa Sand	2417	2418	2419	-	0.00
Natural	2648	2660	2691	-	0.60
Jobe	2515	2534	2564	-	0.77
Primary ASR Recycled Concrete	2023	2203	2469	-	8.94
Secondary ASR Recycled Concrete	2107	2217	2367	-	5.21

Table 2: Chemical analysis of cement, slag, and silica fume

Sample Material	1.06 Alkali Cement	0.97 Alkali Cement *	0.96 Alkali Cement	0.89 Alkali Cement	0.55 Alkali Cement	Slag	Silica Fume
Carbon Content	0.48	-	-	-	-	0.21	-
Silicon Dioxide, SiO_2	19.51	19.55	19.58	19.92	20.12	34.40	96.19
Aluminum Oxide, Al_2O_3	4.94	5.51	5.35	5.57	4.43	7.40	0.35
Iron Oxide, Fe_2O_3	2.65	2.39	2.29	2.10	2.80	0.94	0.10
Sulfur Trioxide, SO_3	4.24	4.39	4.10	3.86	3.60	0.83	-
Calcium Oxide, CaO	62.65	62.63	62.84	63.02	62.41	43.20	0.27
Sodium Oxide, Na_2O	0.31	-	0.21	0.20	0.27	0.57	0.11
Magnesium Oxide, MgO	2.56	2.48	2.43	2.55	3.01	9.30	0.23
Potassium Oxide, K_2O	1.13	-	1.13	1.05	0.44	0.58	0.51
Phosphorus Pentoxide, P_2O_5	0.16	-	0.11	0.12	0.13	175ppm	-
Titanium Dioxide, TiO_2	0.28	-	0.31	0.31	0.23	0.44	-
Chloride, Cl	786ppm	-	-	0.01	-	-	-
Manganese Oxide, Mn_2O_3	0.07	-	0.07	0.05	0.13	-	-
Strontium Oxide, SrO	0.11	-	0.08	0.09	-	-	-
Na_2O_e	1.05	0.97	0.95	0.89	0.56	0.95	0.44

Note: All cements in study were Type 10 Portland cements
Silica Fume was not palletized
A dash (-) represents that no data was available
* St Lawrence cement used in phase 2 of this study

Table 3: Chemical analysis of fly ash

Sample Material	Fly ash F, LA	Fly ash F, HA	Fly ash CI, LA	Fly ash CH, LA #1	Fly ash CH, LA #2	Fly ash CH, LA #3
Carbon Content	1.58	-	1.29	-	-	-
Silicon Dioxide, SiO_2	55.74	61.29	40.15	33.26	35.92	31.39
Aluminum Oxide, Al_2O_3	27.35	16.81	21.37	18.24	21.18	18.54
Iron Oxide, Fe_2O_3	5.59	4.62	9.92	6.45	5.85	5.22
Sulfur Trioxide, SO_3	0.26	1.12	2.46	2.59	1.29	2.62
Calcium Oxide, CaO	4.43	6.42	16.97	28.73	24.48	29.83
Sodium Oxide, Na_2O	0.44	3.68	1.36	1.94	1.70	2.10
Magnesium Oxide, MgO	1.56	2.15	4.23	5.32	4.46	5.22
Potassium Oxide, K_2O	2.29	0.98	1.04	0.33	0.48	0.31
Phosphorus Pentoxide, P_2O_5	0.31	0.54	1.10	0.88	1.36	1.20
Titanium Dioxide, TiO_2	0.67	0.95	1.39	1.45	1.68	1.60
Chloride, Cl	-	-	-	-	-	-
Manganese Oxide, Mn_2O_3	-	-	-	-	0.03	0.11
Strontium Oxide, SrO	-	-	-	-	0.44	0.55
Na_2O_e	1.95	4.33	2.04	2.16	2.02	2.30

Note: F = Low Calcium< 8% CaO, CI = Intermediate Calcium 8-20% CaO, CH = High Calcium >20% CaO
LA = Low Alkali, HA = High Alkali
A dash (-) represents that no data was available.

3.2 ASR concrete prisms (CSA A23.2-14A, ASTM C 1293)

3.2.1 Mix procedures

The concrete prism test (CPT) [CSA A23.2-14A] was used to evaluate the reactivity of the RCA and the efficacy of preventive measures. Water/cement ratio was kept between 0.42 and 0.45 as per ASTM C1293. Whenever binary blends used w/c was kept as of 0.4 except when used ternary blends where a w/c of 0.43 was required to achieve a relatively workable mix. When superplasticizers EUCON was used (2.7-3.1 l/m3) a w/c ratio of 0.40 was workable enough for the concrete prisms of the ternary blends. Since the RCA has a relatively low relative density, a volume of dry-rodded coarse aggregate of 0.69% of unit volume of concrete was found to produce workable and homogeneous mixtures. This ratio, which lies within the limit of CSA A23.2-14A, was then used in all the tested samples. The RCA was not washed so as to eliminate any leaching of alkalis from the residual mortar.

In Phase 1: In order to increase the total alkalinity of the concrete to 1.25% by mass of the cement, NaOH was dissolved in the total mixing water in accordance with ASTM C1293. However, NaOH was dissolved in half of the total mixing water and the other half of clean mixing water was mixed for one minute with the coarse RCA prior to adding the cement and the non-reactive fine aggregates. The remaining water (with the NaOH) was then added to the mixer. This was done to prevent the NaOH that was dissolved in the water from being rapidly absorbed by the high porosity RCA.

The mix sequence involved one minute of mixing the coarse RCA with half the total clean mixing water, then the mixer was stopped and the cement was added on top the RCA and the fine aggregate was added on top the cement. The mixing time was: three

minutes mix, two minutes rest, two minutes mix, two minutes rest, and 1 minute mix. The NaOH dissolved in half of the mixing water was slowly added in the first 30 seconds, after the PC and SCMs were introduced.

In phase 2: For all the samples prepared with lithium nitrate solution, no alkalis were added to achieve the 1.25 % by mass of cement assuming that the alkalis contributed from the RCA would be more than enough to reach that ratio of alkali content of the concrete mix (5.25 Kg/m^3). Also, the lithium nitrate was added with the 2nd half of the mixing water instead of the sodium hydroxide.

The molds were filled in two layers with concrete. Each layer was tamped with a standard metal tamper 20 times and the ends, where the studs were, were spaded 10 times to insure that the studs were covered with concrete. Each layer was also consolidated by lifting and dropping the ends of the mould for one time. Care was taken to avoid bleeding. The top surface of the material was finished with a metal spade. The samples were cured for one day by covering the molds using damped burlap at room temperature. After de-molding, a reading of the initial length was taken and recorded. The samples were then placed in 20 litre buckets with wicking cloth from the inside as per test standard to maintain a relative humidity of approximately 100%. Samples were placed in a heat room at a temperature of 38°C. Subsequent comparator readings were taken after removal of the container from the heat room to room temperature 16 – 20 hours before measuring. Expansions of the concrete prisms were measured periodically as per test standard. It should be noted that every time a measurement was taken, the buckets always contained water but not touching the prisms.

3.2.2 Concrete mixes

Phase 1 focused on evaluating the reactivity of the RCA and the efficacy of different SCMs to prevent ASR. The mixes used in Phase 1 are listed on Table 4. Alkalis content were calculated based only on the alkalis content of the Portland cement. No alkalis were taken into calculations from the alkali contributed from the RCA or the SCMs.

Phase 2 focused on the efficacy of the lithium nitrate to mitigate ASR expansion in concrete prisms with and without SCMs. Different molar ratios of Li/Na+K calculated based on the cement alkali content was investigated to evaluate the optimum dosage of $LiNO_3$ for use with the ASR- affected RCA. Ternary Blends of silica with slag that failed to suppress the ASR expansion in Phase 1 were investigated with addition of different dosages of $LiNO_3$.

In attempt to investigate the efficacy of introducing lithium nitrate to the ASR- affected RCA before used in concrete, 4 samples were prepared by pre-soaking the RCA with half of the mixing water and all the dosage of the lithium nitrate for 24 hour prior to mixing.

Dilution of the RCA in concrete mix was also investigated by blending the RCA with natural non-reactive limestone to evaluate the efficacy of partial replacement of the coarse aggregate in suppressing the ASR in concrete. Dilution of virgin aggregate (Spratt) was also investigated for use as a benchmark to which the dilution of RCA can be compared.

Two RCA non-reactive aggregates were tested to evaluate the swelling effect due the presence of paste or mortar on the overall expansion of the samples.

In addition, the efficacies of ternary blends at replacement levels higher than those used in Phase 1 were investigated. Also, the blends of high calcium fly ahs and slag were investigated. The mixes investigated in Phase 2 are listed on Tables 5 and 6.

Table 4: Mix Design for ASR Prisms – Phase 1

Binary Blends		RCA Mixes										Jobe Mixes					Spratt Mixes		
		5	8	10	15	20	25	30	35	40	50	7	10	15	20	25	15	20	25
Fly ash F, LA						X	X	X												
Fly ash F, HA				X		X	X		X					X	X	X	X	X	X
Fly ash CI, LA						X		X												
Fly ash CH, LA #1							X	X			X									
Silica Fume		X	X	X									X	X						
Slag							X	X			X									
Ternary Blends																				
5% SF	FA F LA				X	X		X							X					
5% SF	FA F HA					X	X												X	X
5% SF	FA CI LA					X	X													
5% SF	FA CH LA					X	X	X												
5% SF	Slag						X	X		X										
5% SF	FA CH LA #3																X			
3% SF	FA CH LA #2																X			

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Table 5: Mix Design for ASR Prisms – Phase 2

		RCA Mixes											Spratt Mixes			
		0	5	10	15	20	25	30	35	40	45	50	0	15	20	25
Ternary Blends																
5% SF	FA F LA						X	X								
5% SF	Slag										X					
20% FA F LA	Slag							X								
Partial Replacement (70%RCA , 30%ST MARY)																
Control		X														
Fly ash F, LA							X									
Fly ash CI, LA							X									
Slag												X				
Partial Replacement (50%Sprat & 50%StMary)														X		
(70%Sprat & 30%StMary)														X		

Table 6: Mix Design for ASR Prisms with Lithium– Phase 2

Mixes	Lithium molar Ratio Li/(Na+K) of Portland cement							
	0.5	0.74	1	1.5	2.25	3	4	5
RCA control		X	X	X	X	X	X	X
RCA Pre-soaked	X	X	X	X				
RCA with 20% Fly Ash Type "F" LC, LA	X	X	X	X				
RCA with 25% Fly Ash Type HC, LA	X	X	X	X				
RCA with 40% Fly Ash Type HC, LA	X							
RCA with 30% Slag	X	X	X	X				
RCA with 50% Slag	X							
RCA with 5% Silica & 30% Slag	X	X	X	X				

3.3 Scanning Electron Microscopy (SEM)

Polished thin sections were prepared and sputtered with carbon in an Edwards Vacuum Coating System Model # 306A using ultra pure Carbon, Grade UF4S. The sections were analysed in a JEOL JSM6380LV scanning electron microscope equipped with Oxford INCAx-sight Energy Dispersive X-Ray analysis (EDS) System as seen in Figure 12. The backscattered electron images (BSE) were taken at an accelerated voltage of 20Kv under high vacuum of about 1^{-4} Torr and probe current in the range from 1pA to 1 μA.

Two samples were prepared from the RCA of size between 9.5-13.2 mm to investigate the amount of ASR gel that already exists in the coarse aggregates before usage in new concrete. Another Sample was prepared from a concrete prism with ASR-affected RCA after 2 years passed on ASR Concrete Prism testing. This was to investigate the changes that happened during testing and the nature of the ASR Gel formation.

Three samples were prepared from RCA particles of size 9.5 -13.2mm after left in alkaline solution of 0.7 M- (Na + K) for 4 weeks; one with 0.7 M- (Na + K) without lithium, and the other two samples with 0.7 M- (Na + K) with lithium at molar ratio of Li/(Na+K) of 1:1.

This was performed to investigate the differences of the gel composition in absence and presence of the $LiNO_3$ and the distribution of the alkalis in the RCA particles due releasing or absorbing of alkalis from the leaching solutions.

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Figure 12: Scanning Electron Microscope - SEM

3.4 Alkali Contribution Test

This test was conducted to evaluate the available alkalis from the RCA to the pore solution when used in new concrete. Spratt aggregate is known to contain an amount of alkalis but not readily available to pore solution (Chris Rogers- personal communication). When RCA aggregate was ground and sieved to pass from 300μm and retained on 150μm and examined by XRF, the total alkalis from the RCA was 0.57% by mass. Some of these alkalis are not soluble and thus they don't contribute to the ASR in concrete. Hence, leaching solutions with different molar of 0, 0.25, 0.4 and 0.7 concentrations were used to evaluate the available soluble alkalis from the RCA.

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Furthermore, lithium nitrate with molar ratio 1:1 [Li/ (Na+K)] was prepared to investigate the difference of the consumption or contribution of alkalis from RCA in the presence of Lithium in the test solution. Three different sizes of RCA were used: 9.5-13.2mm, 4.75 –9.5 mm and 150μm - 300μm.

Each sample was prepared with aggregate to solution ratio of 1:10 by weight. The samples were immersed into the solution and maintained on a shaker at temperature of 38°C in closed containers for 4 weeks. RCA moisture content was determined at the time of the immersion to calculate the dry mass of the aggregate.

After 4 weeks, one sample of each of these leaching solutions were taken from the large size aggregate (9.5-13.2mm) and examined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP AES). The compositions of the soaking solutions were compared to the compositions of the original solution. An increase in the concentration of a particular ion (Na, K or Li) indicated that the RCA released this ion into the solution. A reduction in concentrations indicated that the RCA absorbed alkalis from the soaking solution. The amount of the contributed or absorbed (negative contribution) ions were calculated and presented as a percentage of the dry mass of the RCA.

Chapter 4

Results and discussion

4.1 ASR concrete prisms

4.1.1 Reactivity of RCA

ASR expansions in concrete prisms were measured periodically according to ASTM C1293. Expansions of the tested blends are listed in Appendix A. It was expected that the ASR affected RCA shall have less reactivity due to the consumption of the reactive silica during the past service life. Also, it was expected due to carbonation of its content of the ASR gel that it may possess less tendency to absorb water causing swelling and rupture of the new concrete. In the contrary, the RCA concrete showed even higher expansion at the early age and continued with the same rate of expansion compared to the natural reactive aggregate. Furthermore, it is expected that the RCA concrete will continue to expand more than the virgin Spratt aggregate after the test period of 2 years as can be seen from the expansion curve in Figure 12. It is believed that the swelling of the old paste was one of the major causes of the expansion of the RCA rather than the new ASR gel formation and the swelling of the old gel.

It was similarly noticed when we tested two other non-reactive RCA aggregates. The two aggregate samples obtained expansion values between 0.028% and 0.035% at 1 year respectively as seen in Figure 13. Also, the non-reactive RCAs were soaked in half of the mixing water for 24 hr before used in concrete to evaluate the reduction of the swelling of the RCA paste. It was noticed that a slight improvement occurred but was not enough to prevent the further swelling afterwards.

The RCA aggregate was found to have many cracks on its surface due to the demolition process as seen in Figure 14. These cracks facilitate the water and the alkali ions to penetrate to the old ASR gel. Also, the demolishing process introduces new surfaces of the un-reacted reactive silica. These new surfaces are readily introduced to the ASR gel formation process due to the high alkalis retained in the RCA in addition to the alkalis from the cementing materials.

It was previously reported by Shehata & Thomas (2000) that the Spratt aggregate reaches acceptable expansion at an alkali content of approximately 0.7% Na_2Oe. But, in case of the reactive RCA, it would require more preventative measures to reduce the expansion to the ASTM expansion limit of 0.04%. The Use of SCMs and dilution of the RCA with natural non-reactive aggregate are measures to be considered to reduce the effect of the swelling of RCA concrete.
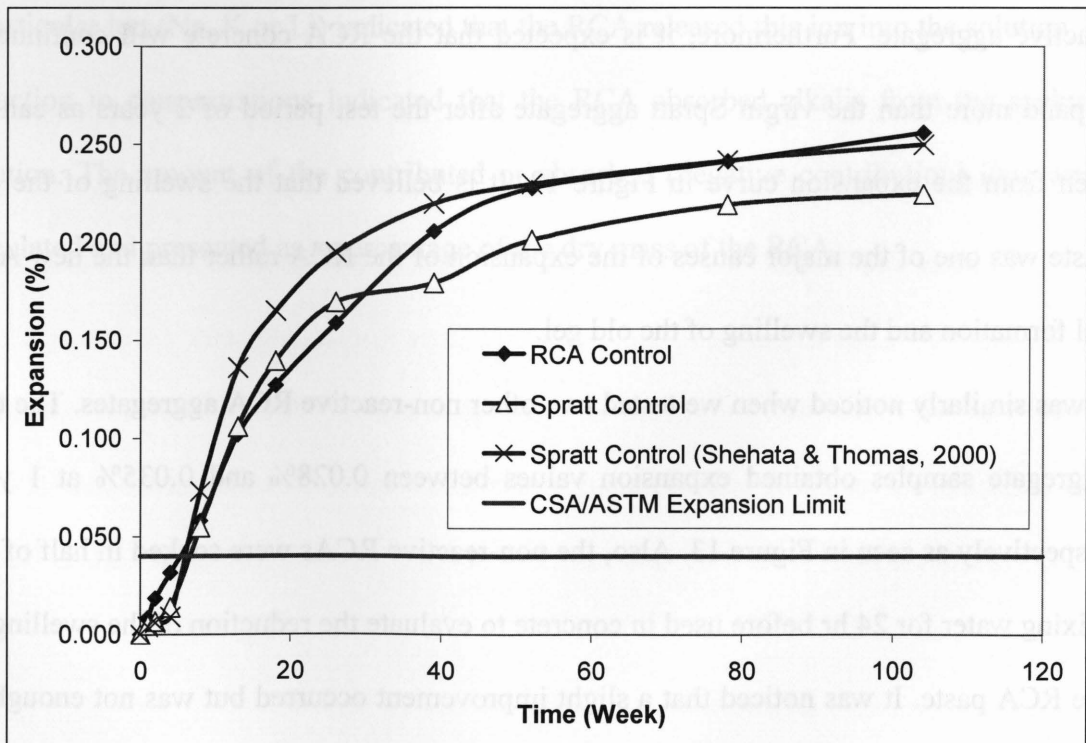
Figure 12: RCA and Spratt aggregate concrete prisms expansions

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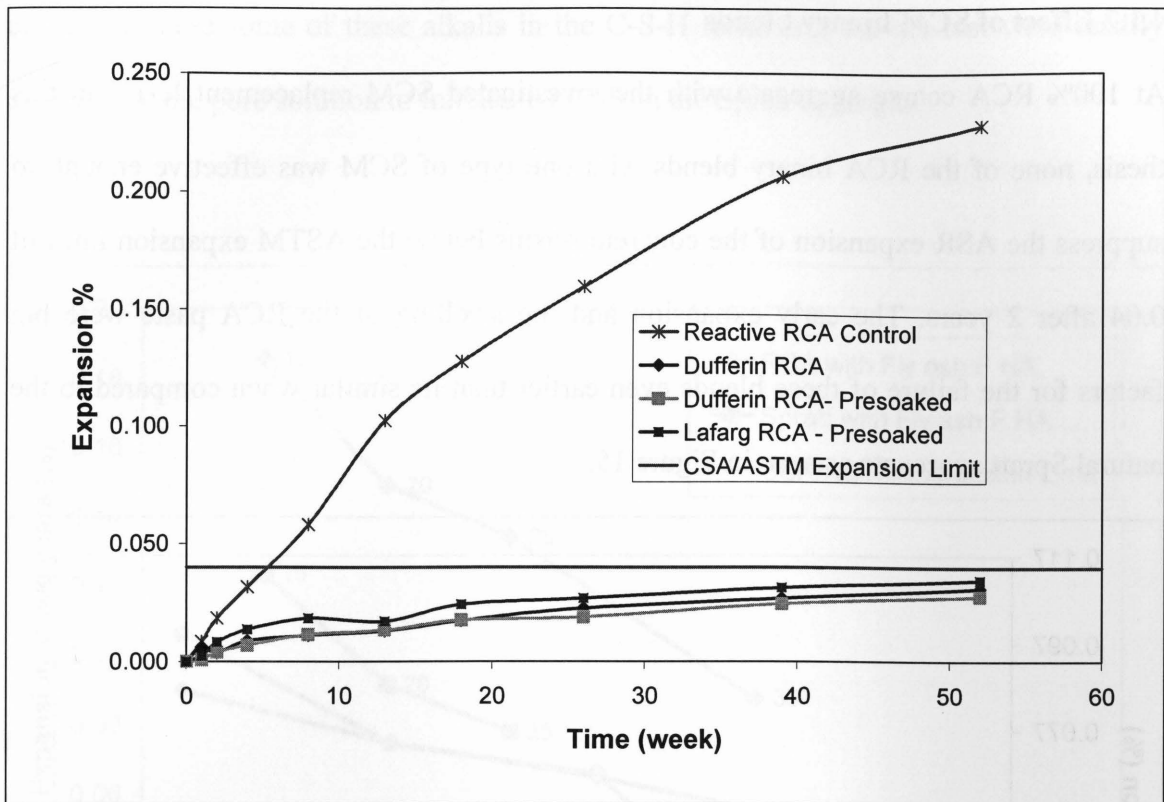
Figure 13: Comparison of the ASR concrete prisms expansions between the ASR affected RCA and two non Reactive RCAs
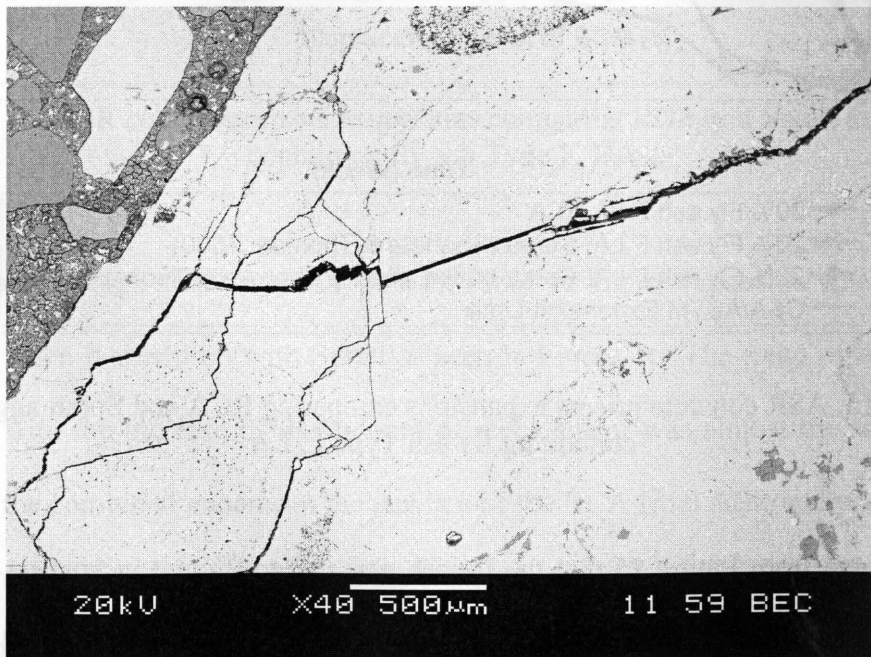
Figure 14: RCA Mechanical cracks

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4.1.2 Effect of SCM binary blends

At 100% RCA coarse aggregate with the investigated SCM replacement levels in this thesis, none of the RCA binary blends with one type of SCM was effective enough to suppress the ASR expansion of the concrete prisms below the ASTM expansion limit of 0.04 after 2 years. The early expansion and the swelling of the RCA paste were big factors for the failure of these blends even earlier than its similar when compared to the natural Spratt aggregate as seen in Figure 15.
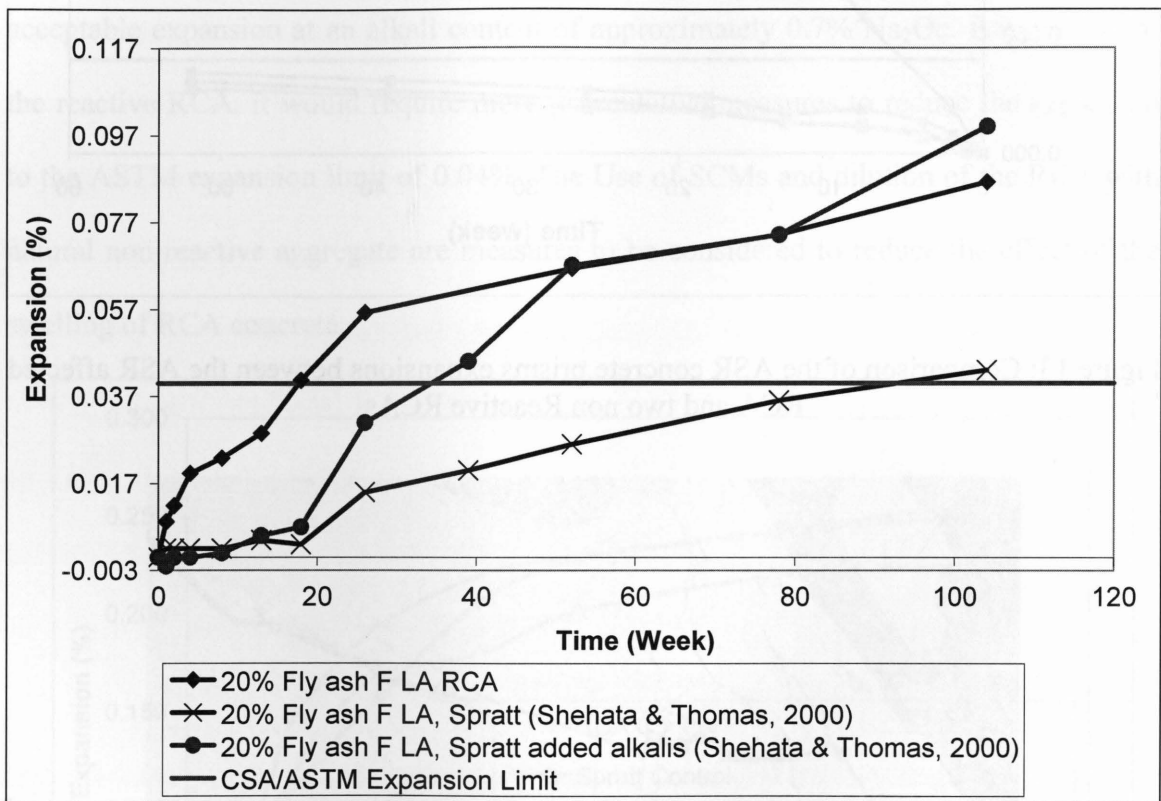
Figure 15: ASR concrete prisms expansions comparing RCA and Spratt aggregate containing fly ash Type F, LA

It is also noted from Figure 15 that the fly ash was more efficient in binding the alkalis when presented from the cementing material than when it was introduced as added alkalis to the mixing water. With the increased alkalinity from the added alkalis, the fly ash

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could only bind some of these alkalis in the C-S-H formation but the rest were readily available in the pore solution to initiate the ASR in the Spratt aggregate.
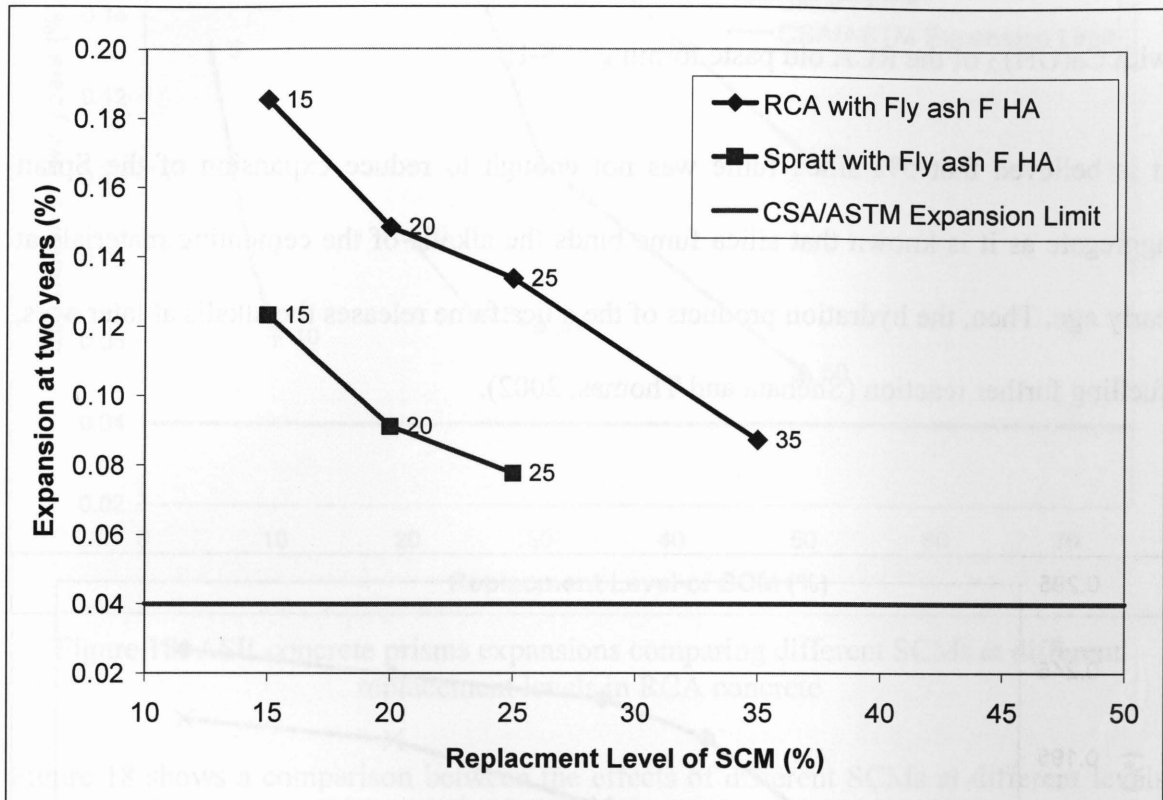
Figure 16: ASR concrete prisms expansions comparing RCA and Spratt aggregate containing fly ash Type F, HA

The low calcium high alkali fly ash type F HA showed higher expansion when used with RCA than when it was used with Spratt as seen in Figure 16. The trend of lowering the expansion with the increase of the amount of replacement was almost the same in both cases. But the combined expansion mechanism of the RCA from ASR and paste swelling is presenting a difference of 0.056% of the expansions.

However, this was not the case when compared the effect of 5% replacement with silica fume as seen in Figure 17. RCA showed higher expansion in the early age more than the

Spratt aggregate as it was expected like the other SCMs. But after 26 weeks the Spratt aggregate showed higher expansion than the RCA. This could be attributed to the effect of the silica fume to enhance the permeability of the concrete with RCA reducing the amount of water reaching the aggregate and hence, its swelling. The silica tends to bind with $Ca(OH)_2$ of the RCA old paste forming C-S-H.

It is believed that 5% silica fume was not enough to reduce expansion of the Spratt aggregate as it is known that silica fume binds the alkalis of the cementing materials at early age. Then, the hydration products of the silica fume releases the alkalis at later ages, fuelling further reaction (Shehata and Thomas, 2002).
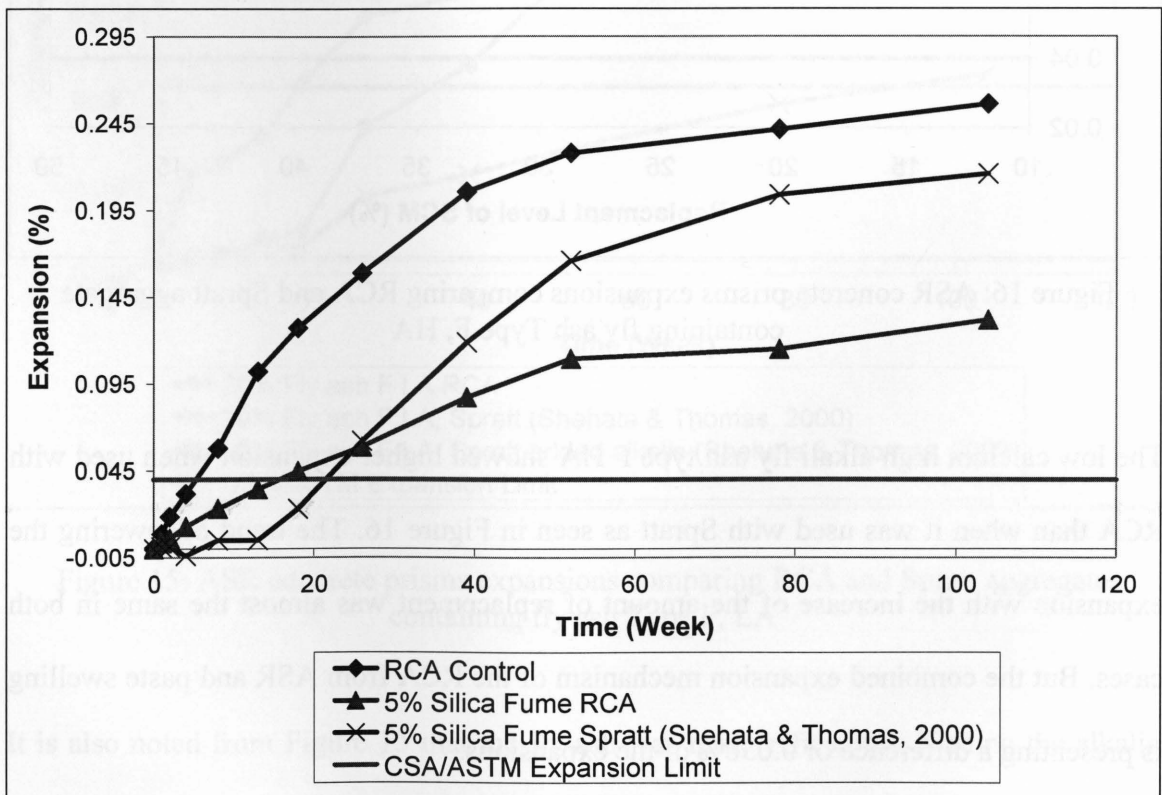
Figure 17: ASR concrete prisms expansions comparing RCA and Spratt aggregate containing 5% silica fume

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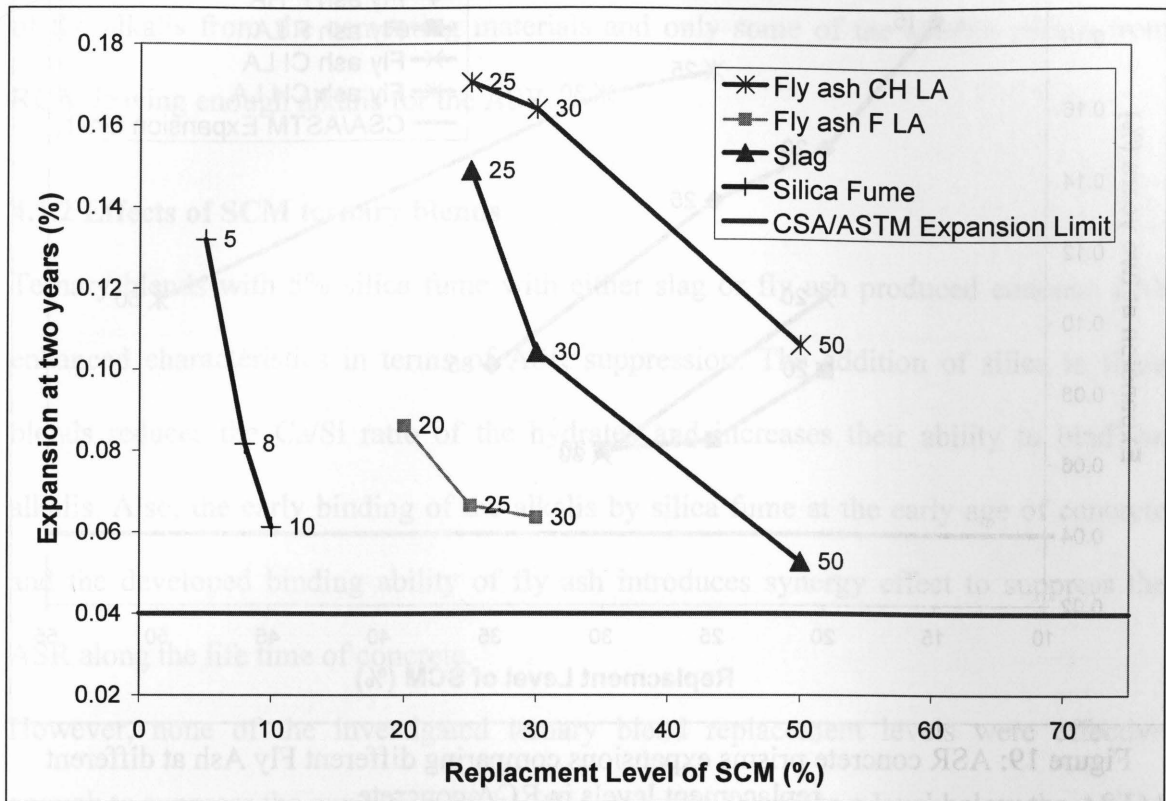
Figure 18: ASR concrete prisms expansions comparing different SCMs at different replacement levels in RCA concrete

Figure 18 shows a comparison between the effects of different SCMs at different levels of replacements to suppress the ASR expansion in RCA concrete prisms. It can be deduced that a replacement level of almost 60% of slag would be required to maintain the expansion of the RCA concrete prisms at acceptable limit.

A 10% replacement with silica fume was not sufficient to reduce the expansion and a higher replacement level may be required. This may not be suitable due the low workability of such produced concrete with RCA. However, it still may not be effective to suppress the swelling effect of the RCA concrete. Also, it may not be suitable from the workability prospective of the RCA concrete.
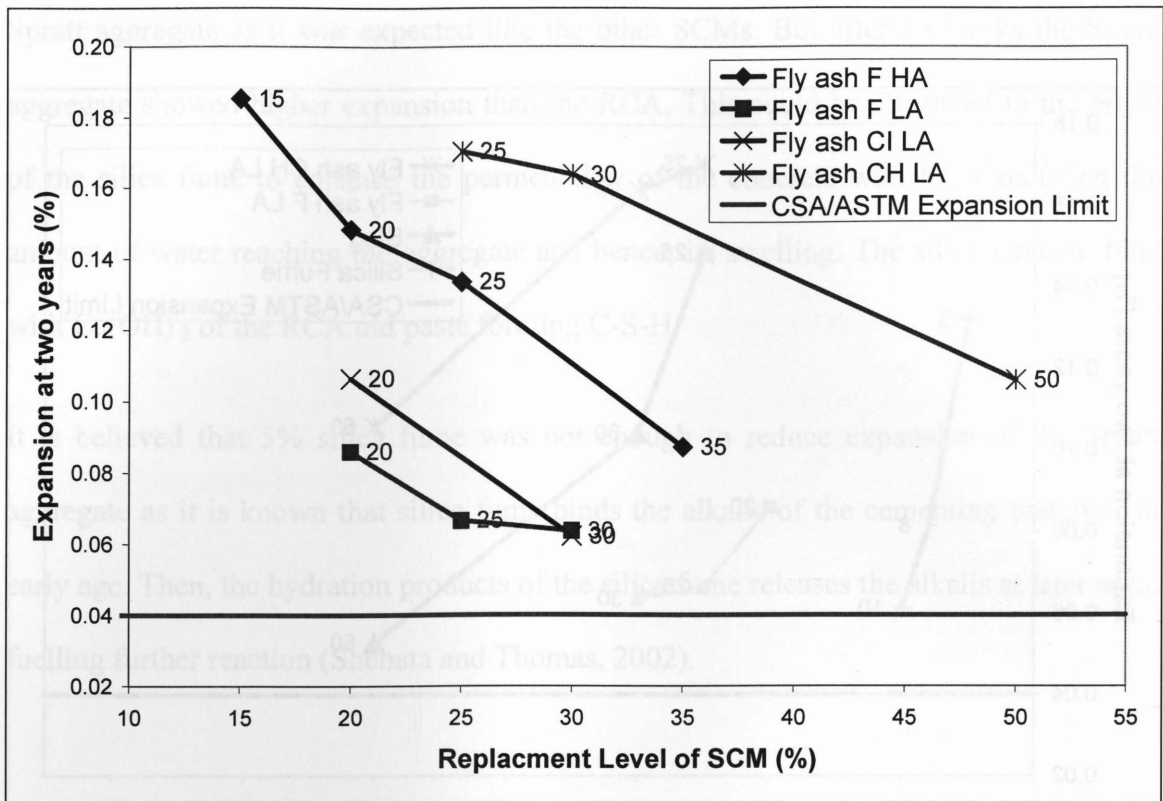
Figure 19: ASR concrete prisms expansions comparing different Fly Ash at different replacement levels in RCA concrete

Figure 19 shows the effect of different types of fly ashes at different replacement levels in ASR affected RCA concrete. The fly ashes with the low and medium calcium and low alkali content showed superior performance than the high calcium and high alkali fly ashes at 2 years. As previously reported by Shehata and Thomas (2000), the lower the calcium content of the fly ash the better its efficacy to suppress ASR. Also, the alkalis from the ashes contribute partially to raise the alkalinity of the pore solution. Hence, the high alkali fly ashes are less effective in reducing alkalis available for ASR in concrete when compared to its counterpart with low alkalis content. Fly ash binds alkalis from the pore solution in their C-S-H, but the high alkalis concentrations contained in the RCA aggregate are readily consumed by the reactive silica to form the ASR gel in the presence

of the high calcium of the old paste. On other words, the binding was only viable to some of the alkalis from the cementing materials and only some of the soluble alkalis from RCA, leaving enough alkalis for the ASR.

4.1.2 Effects of SCM ternary blends

Ternary blends with 5% silica fume with either slag or fly ash produced concrete with enhanced characteristics in terms of ASR suppression. The addition of silica to these blends reduces the Ca/Si ratio of the hydrates and increases their ability to bind the alkalis. Also, the early binding of the alkalis by silica fume at the early age of concrete and the developed binding ability of fly ash introduces synergy effect to suppress the ASR along the life time of concrete.

However, none of the investigated ternary blend replacement levels were effective enough to suppress the expansion of the RCA concrete prisms to a level below the ASTM expansion limit. Though, the Ternary blends with 5% silica and 25% fly ash CI LA marginally met the expansion limit as can be seen from Figure 20.

Similar replacement levels of 25% and 30% of fly ash F LA with 5% silica are still under investigation and only complete 1½ year of the test period. These samples had expansion of 0.04% and 0.037% respectively after 78 weeks and are expected to be within the same range of expansion just above 0.04% as seen in Figure 20

Also, a replacement level of 45% slag with 5% silica was investigated and produced an expansion of 0.049% after 78 weeks which show a minimal improve in reducing expansion compared to the mix of 40% slag with 5% silica as seen in Figure 20.
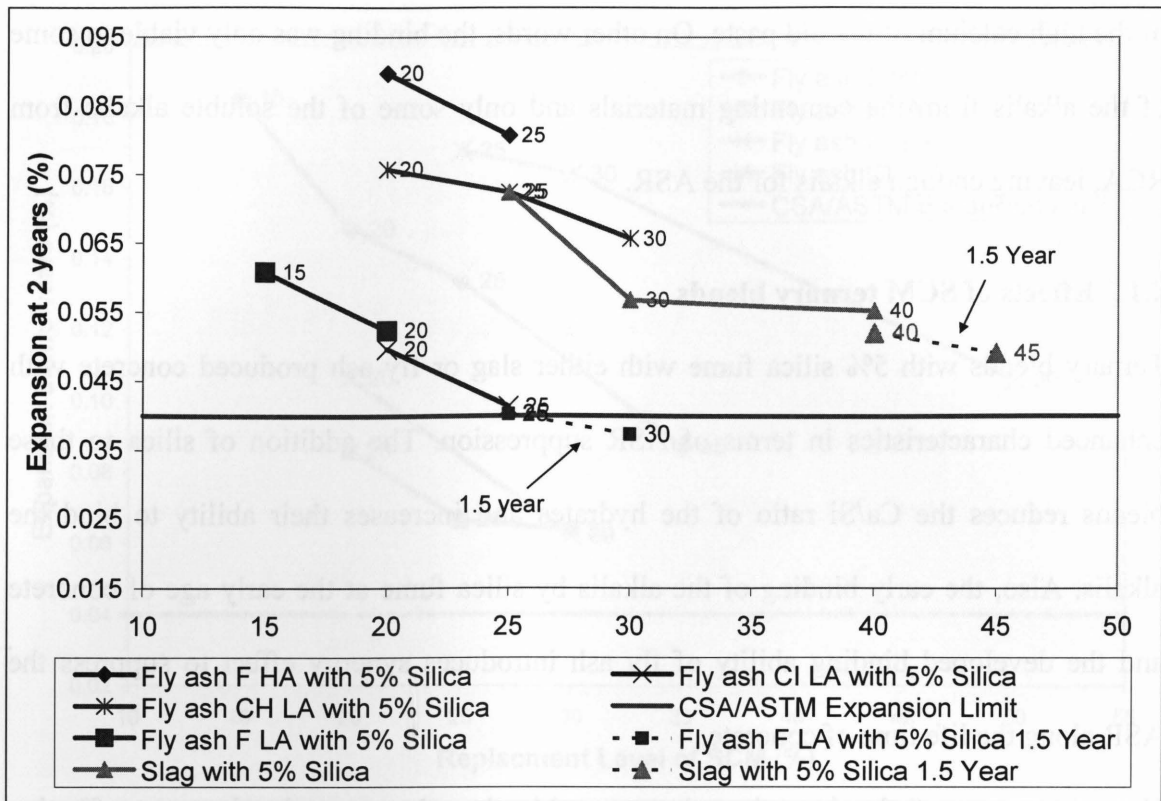
Figure 20: ASR concrete prisms expansions comparing different Fly Ash at different ternary blends replacement levels in RCA concrete

The addition of 5% silica with slag to blends reduced the expansion of the concrete prism to 50% of the samples with only slag replacements as seen in Figure 21. But, it is noted that the expansion reduction rate when 5% silica was added to 25% and 30% of slag is much higher than when it was added to 40% slag or more.

The high calcium low alkali fly ash performance was much improved by adding 5% silica to these blends. The reduction of expansion was almost 60% of the samples with fly ash only. Though, it was not enough to suppress the expansion below the ASTM limit.
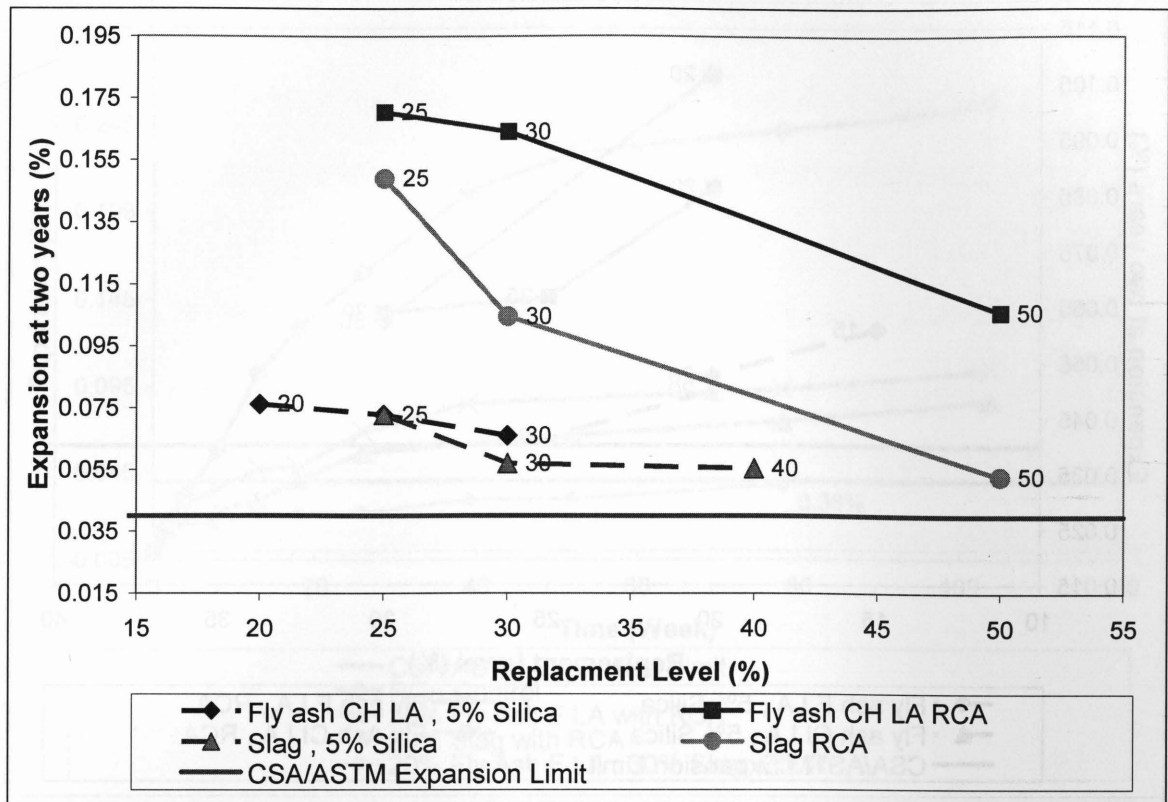
Figure 21: ASR concrete prisms expansions comparing ternary blends versus binary blends in RCA concrete

Figure 22 shows the improvement of adding 5% silica fume to both moderate and low calcium fly ashes in the ternary blends. The expansion reduction was even higher in case of the moderate calcium low alkali fly ash type CI than the low calcium fly ash type F. Both of these fly ashes have low alkali content as seen in Table 3. But, this may be attributable to the fineness of the fly ash type CI that enabled it to perform better when reducing the overall Ca/Si ratio of the blend by adding 5% silica.
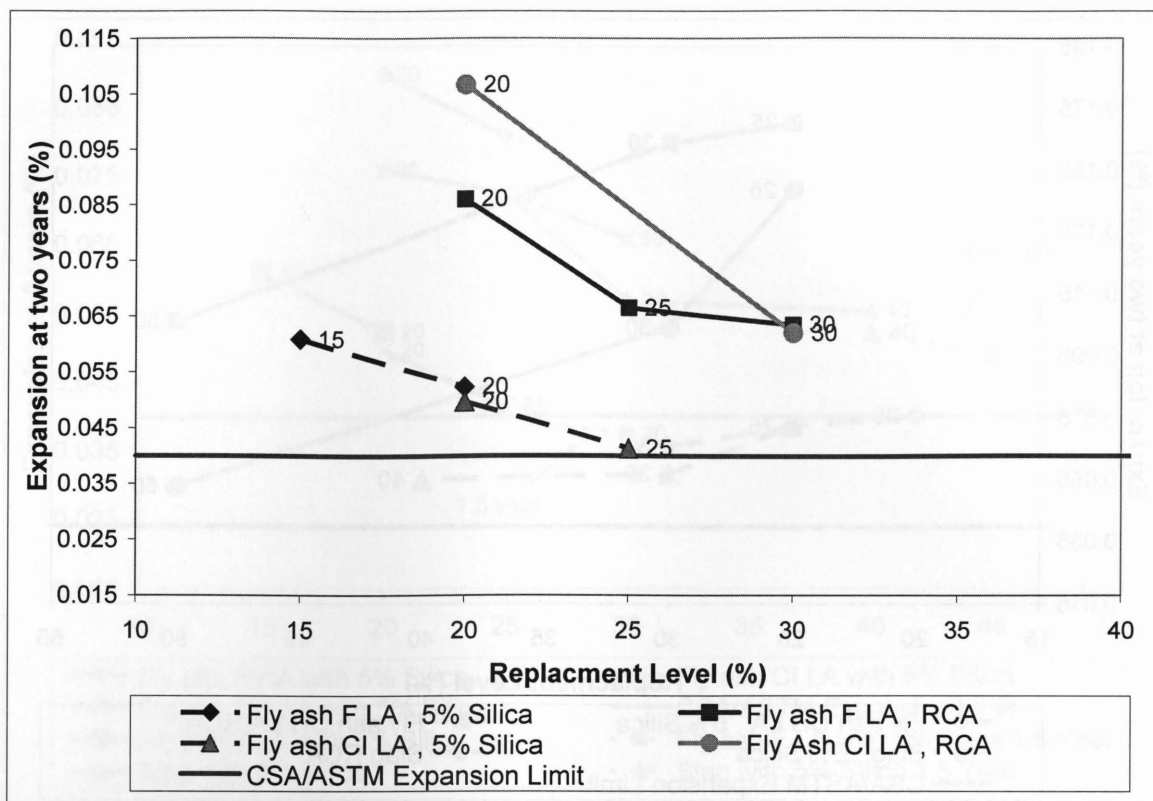
Figure 22: ASR concrete prisms expansions comparing ternary blends versus binary blends in RCA concrete

Figure 23 shows another combination of ternary blends that was investigated in this study using 20% fly ash F LA with 30% slag replacement. The concrete prisms expansions didn't complete the test period but it provides a good indication of the expected success that may be obtained from this blend. The synergy shown in suppressing the expansion in the concrete prisms gives hope that this combination may produce RCA concrete within the acceptable expansion limit of 0.04% after 2 years.
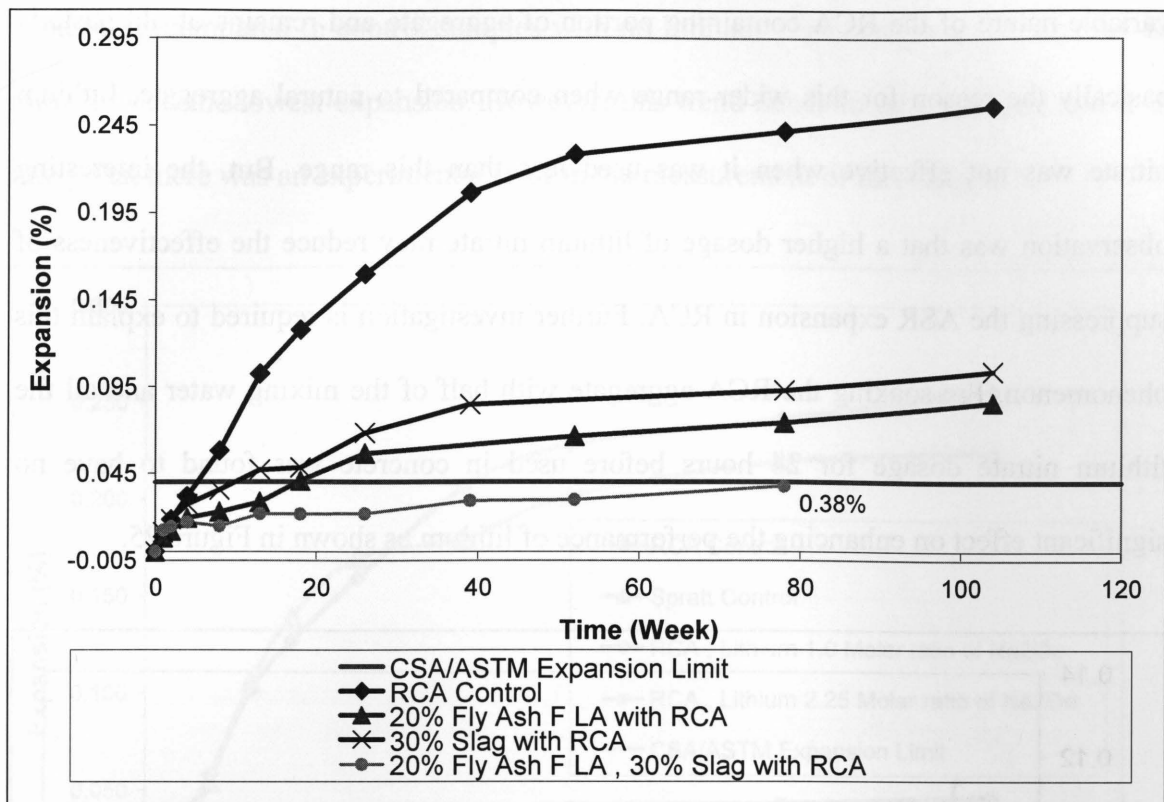
Figure 23: ASR concrete prisms expansions comparing ternary blends versus binary blends in RCA concrete

4.2 ASR concrete prisms test for blends containing lithium nitrate

4.2.1 Effect of lithium nitrate on RCA reactivity

Lithium nitrate was known to be effective in suppressing the ASR reaction in some natural reactive aggregates. The appropriate dosage of Lithium was found to be varying from one reactive aggregate to the other with no correlation with the aggregate reactivity or the petrographic nature of the aggregate. In some research work on natural aggregate the optimum dosage was found to lie between 0.74 and 1.04 [Li]: [Na+K] molar ratios (Tremblay et al, 2007). The investigated ASR affected RCA was found to require a higher molar ratio to suppress the expansion in ASR concrete prisms as seen in Figure 24. The range of the Lithium nitrate dosage required varied between 1 to 2 molar ratios. The

variable nature of the RCA containing portion of aggregate and remains of old paste is basically the reason for this wider range when compared to natural aggregate. Lithium nitrate was not effective when it was used less than this range. But, the interesting observation was that a higher dosage of lithium nitrate may reduce the effectiveness of suppressing the ASR expansion in RCA. Further investigation is required to explain this phenomenon. Pre-soaking the RCA aggregate with half of the mixing water and all the lithium nitrate dosage for 24 hours before used in concrete was found to have no significant effect on enhancing the performance of lithium as shown in Figure 25.
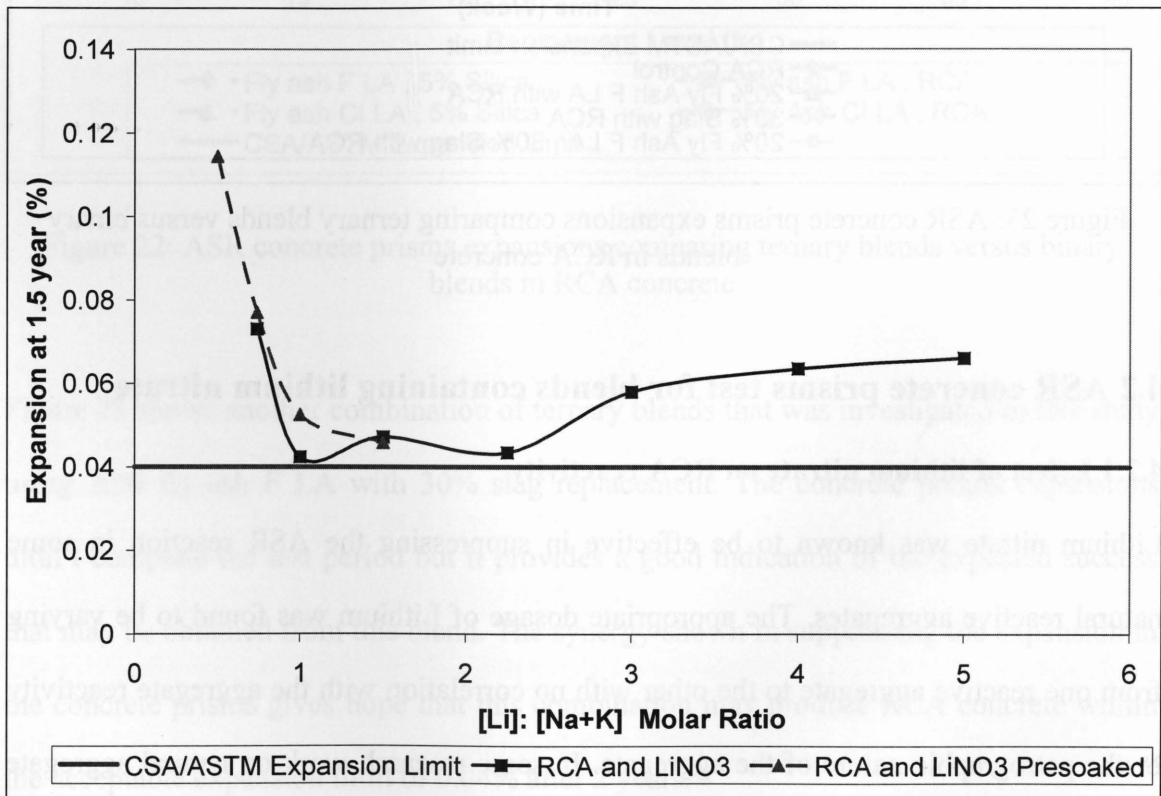
Figure 24: ASR concrete prisms expansions of RCA with different Molar Ratio of [Li]: [Na+K]

All the tested lithium dosages resulted in concrete expansion higher than the 0.04% at the age of 78 weeks. However, there was a considerable reduction of the concrete prism

expansions compared to control samples with no lithium. The sample at 1:1 Li: Na+ K
ratio showed the lowest expansion. However, this trend needs to be confirmed and it is
likely that there was an experimental error in the measurement of this sample.
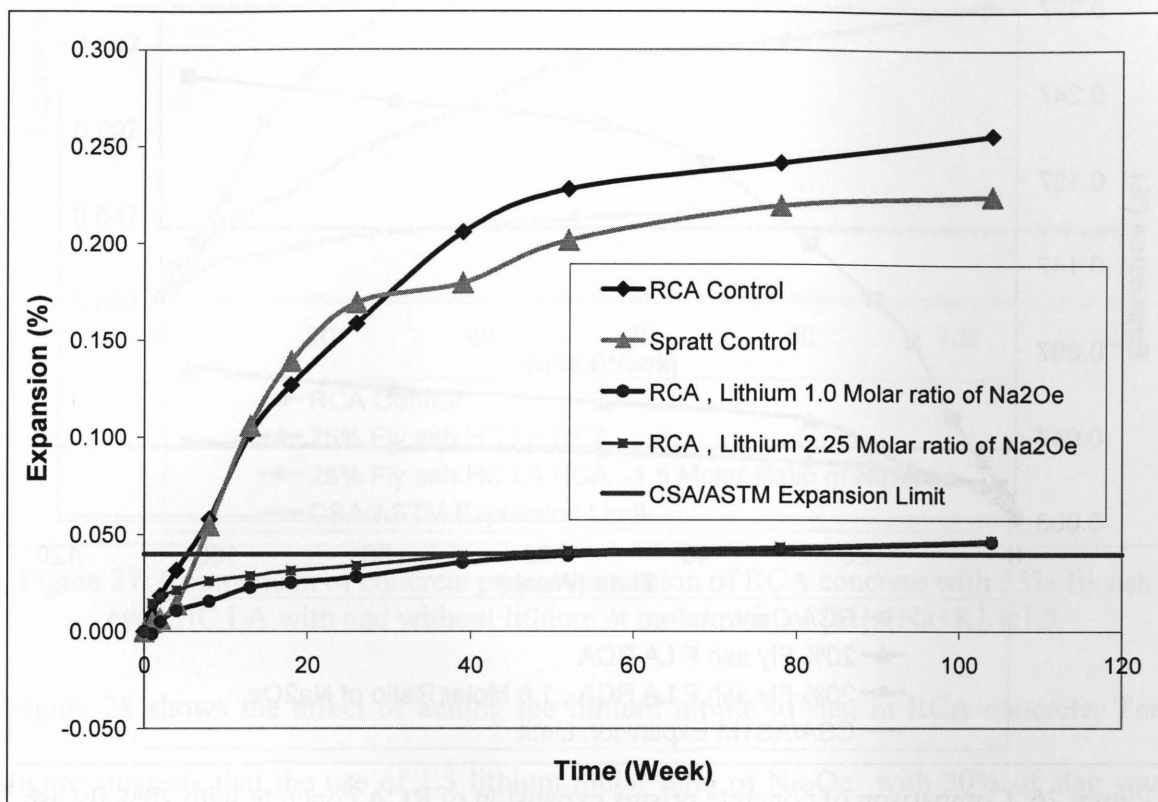
Figure 25: Comparison of concrete prisms expansion of RCA concrete with and without
lithium at molar ratio of [Li]: [Na+K] 1:1

4.2.2 Effect of using lithium nitrate with SCMs

As discussed previously, fly ashes of low and high calcium content with low alkalis were
not capable of suppressing the expansion of the RCA to the specified limit when used in
binary blends. The use of lithium nitrate in combination of these fly ashes provided a
synergy suppression effect on the concrete prisms expansion; the expansion was less than
50% of the samples with fly ash alone. Figure 26 shows the comparison of using 20% of
Fly ash type F LA with and without lithium. The expansion of the sample with low

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calcium fly ash and lithium can be considered to marginally meet the 0.04% expansion limit. Perhaps higher level of either materials or using fly ash of higher fineness may be able to reduce the expansion to lower than 0.04%.
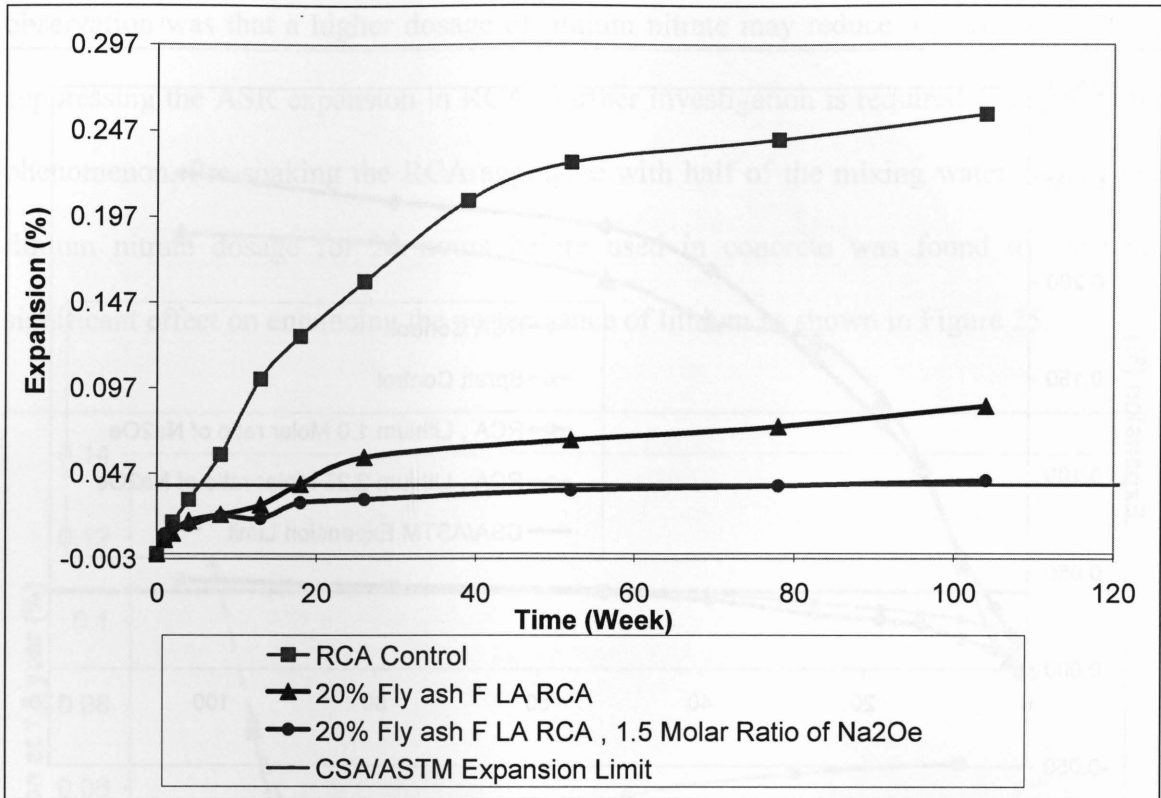
Figure 26: Comparison of concrete prisms expansion of RCA concrete with 20% fly ash type F LA with and without lithium at molar ratio of [Li]: [Na+K] 1:1.5

Lithium and high calcium fly ash was not effective in limiting the expansion to lower or close to 0.04%. However, a significant reduction in the expansion was achieved when lithium (at a ratio of 1:1.5) was added to high-calcium fly ahs as shown in Figure 27.
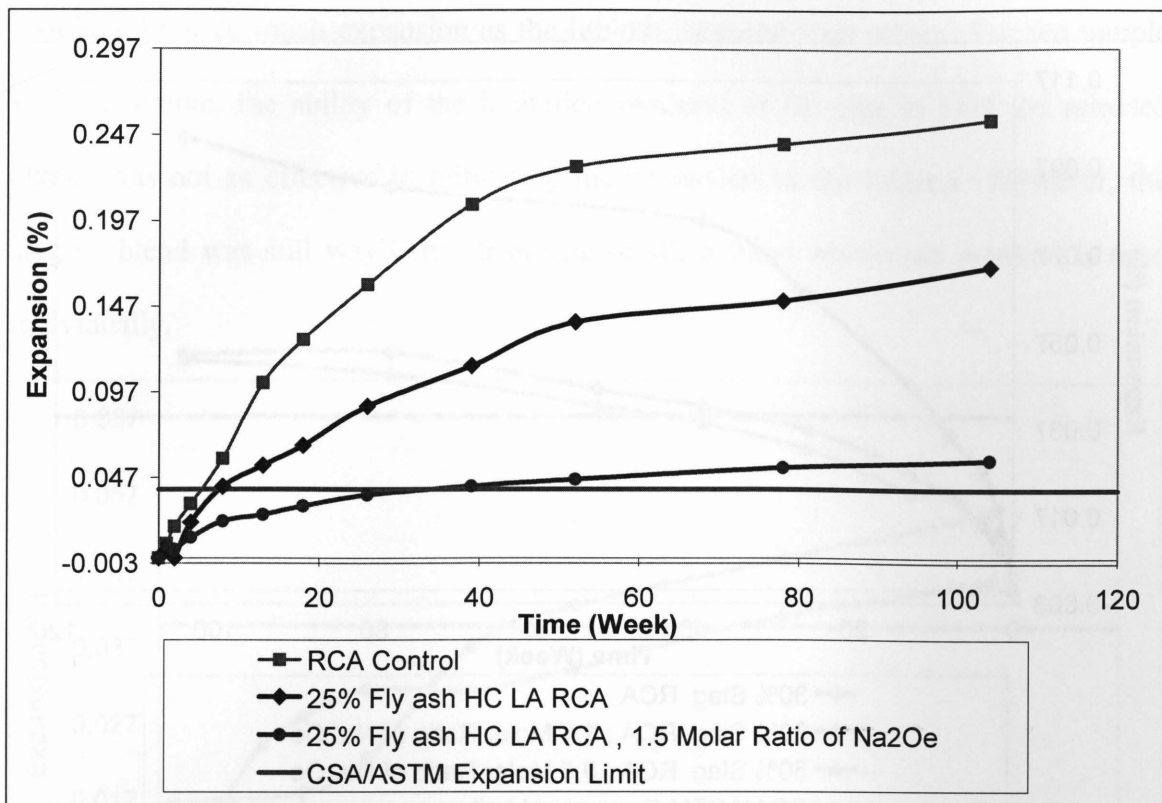
Figure 27: Comparison of concrete prisms expansion of RCA concrete with 25% fly ash type HC LA with and without lithium at molar ratio of [Li]: [Na+K] 1:1.5

Figure 28 shows the effect of adding the lithium nitrate to slag in RCA concrete. The figure suggests that the use of 1.5 lithium molar ratio of Na_2Oe with 30% of slag was almost of the same effect as using only 0.5 lithium molar ratio with 50% slag.

The Lithium use in combination with SCMs was not effective in lowering the expansion to acceptable limit. It is believed that the high alkali concentrations retained in the RCA and the swelling of the old gel are predominantly causing the inability of these preventive measures to counteract the expansion. More effective measures may require more lithium and higher SCMs replacement levels to control that expansive action of the RCA. However, higher levels may not be practical from the economical standpoint. Also, as it was mentioned previously in the literature review, excess use of SCM can lead to other deleterious effects of salt scaling.
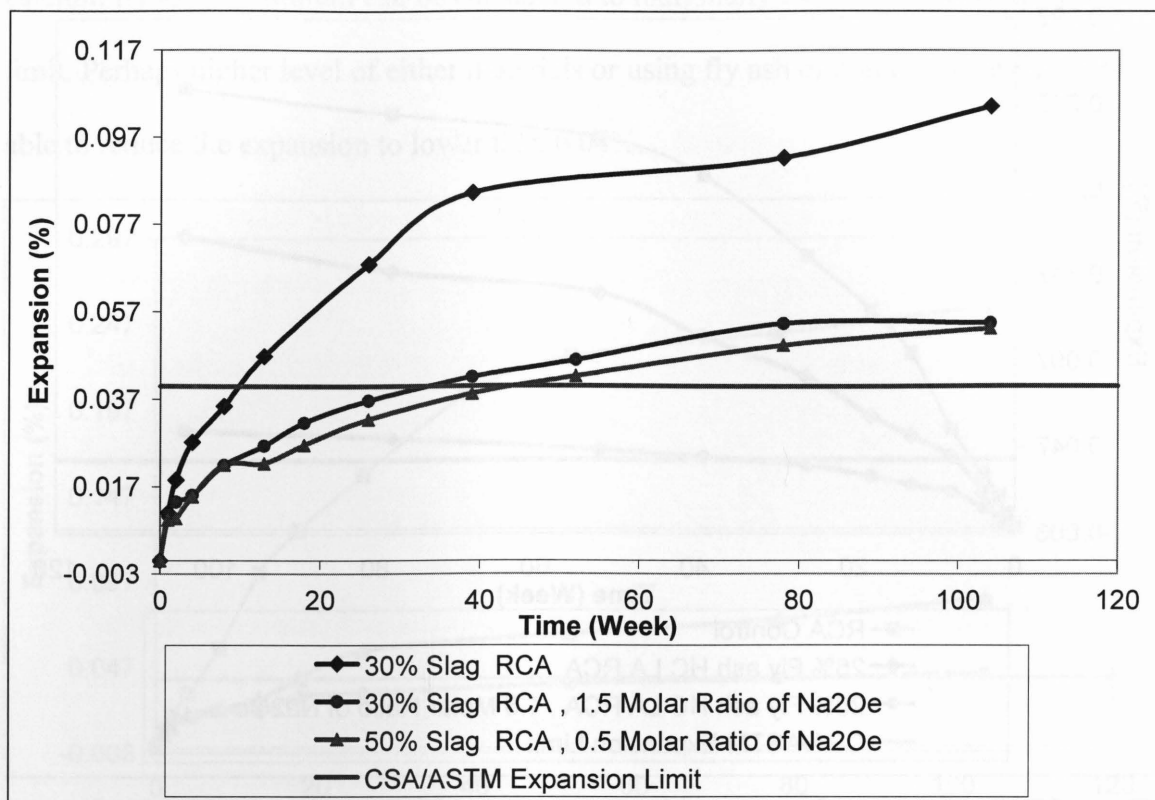
Figure 28: Comparison of concrete prisms expansion of RCA concrete with Slag replacements with and without lithium

Ternary blends with 5% silica and 30% slag was also investigated with and without lithium as seen in Figure 29. It was expected that the addition of 5% silica may be effective in lowering the permeability and pore solution alkalinity of the RCA-concrete and reduces its expansion furthermore than the binary blends. However, this also was not enough to counteract the expansion of the RCA concrete prisms to acceptable limits.

The early expansion of this blend was higher when lithium was used up to 28 weeks. Afterwards, the lithium sample maintained a steady rate of expansion while the no-lithium sample slid to a little higher expansion. Then, both maintained the same rate of expansion. It may be deduced that silica tend to release alkalis at a later age and bind with the released $Ca(OH)_2$ of the hydration products. At the presence of lithium, the released

alkalis did not do much expansion as the lithium hindered their effects. For the sample without lithium, the ability of the hydration products of the slag to bind the released alkalis was not as effective in mitigating the expansion as the lithium. However, the slag/SF blend was still way better than slag or silica fume when each material is used individually.
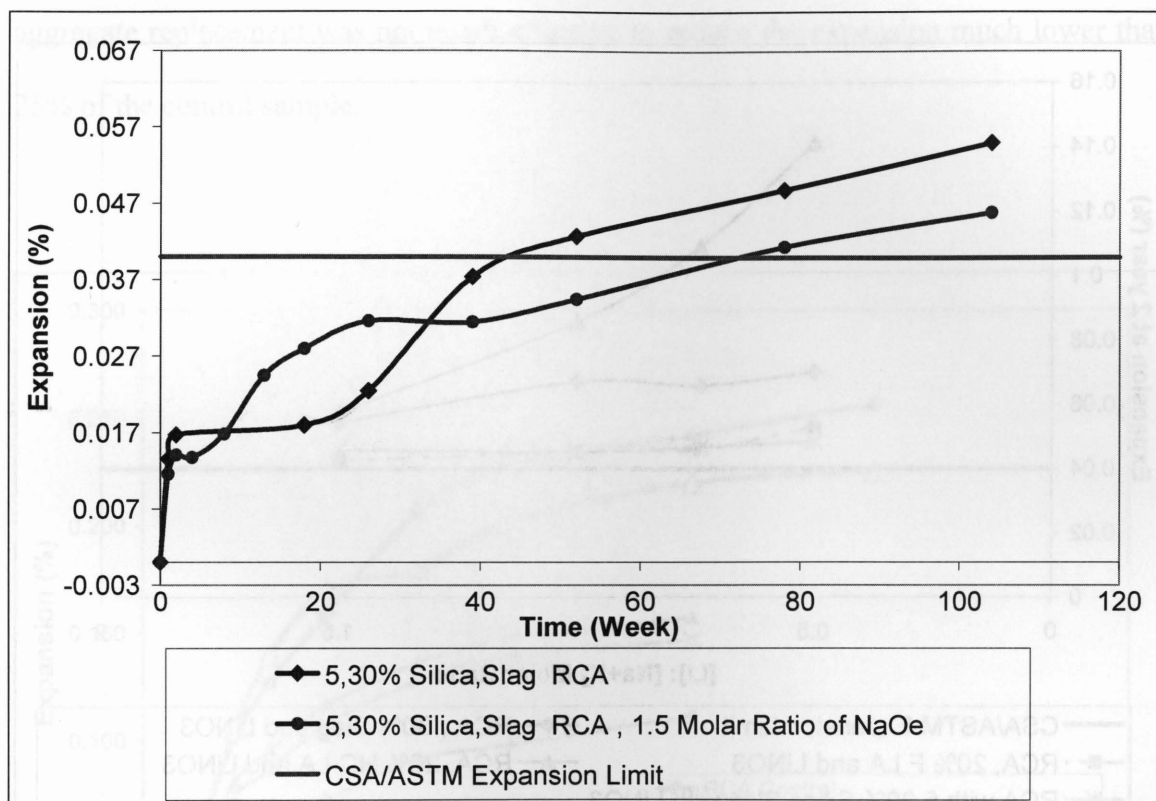
Figure 29: Comparison of concrete prisms expansion of RCA concrete with ternary blend of 5% silica and 30% slag replacements with and without lithium

Figure 30 provides a comparison of the efficacy of some SCM blends used with lithium at different molar ratios of [Li]:[Na+K] of the Portland cement. The figure shows that the addition of lithium was not effective with the silica/slag combination. Also, it shows that introducing lithium nitrate to 30% slag or 20% fly ash F LA slightly reduced the expansion, particularly with the increase of the lithium nitrate added to the mix. However, with the high calcium fly ash with low alkali HC LA, the expansion was

dramatically improved with increasing the lithium dosage. It is the author's opinion that this may be attributed to the less ability of the high calcium fly ahs to bind the lithium in its hydration products compared to the other types of SCMs. This synergy effect of lithium and this type of fly ash reducing the available soluble alkalis in the system enhanced the reduction of expansion due ASR.
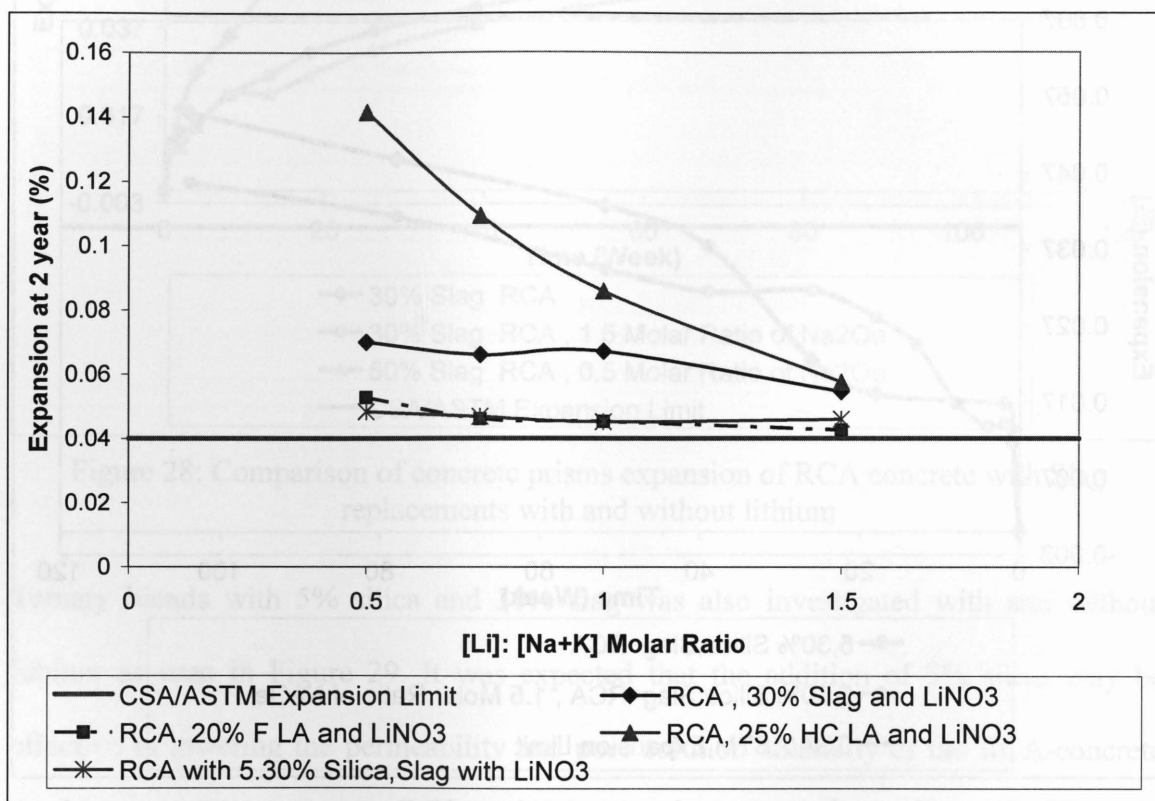
Figure 30: Comparison of concrete prisms expansion of RCA with fly ashes and slag binary and ternary blends at different molar ratio of [Li]: [Na+K]

4.2.3 Dilution effect of the reactive aggregate

As seen from the concrete prism expansions, the SCMs and the lithium nitrate were not enough to suppress the expansions in concrete containing reactive RCA. Hence, dilution of the aggregate was investigated to reduce the source of the deleterious effect from concrete. For other practical considerations, RCA is usually used in concrete as part of

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the total coarse aggregate. So, the concept of diluting the RCA content in concrete is a feasible option from the construction standpoint. As seen in Figure 31, dilution of the virgin Spratt aggregate with 30% replacement with non reactive natural aggregate was useful to reduce 25% of the concrete prisms expansion while it reduced almost 50% of the expansion in case of RCA dilution. Further dilution of Spratt with 50% coarse aggregate replacement was not much effective to reduce the expansion much lower than 25% of the control sample.
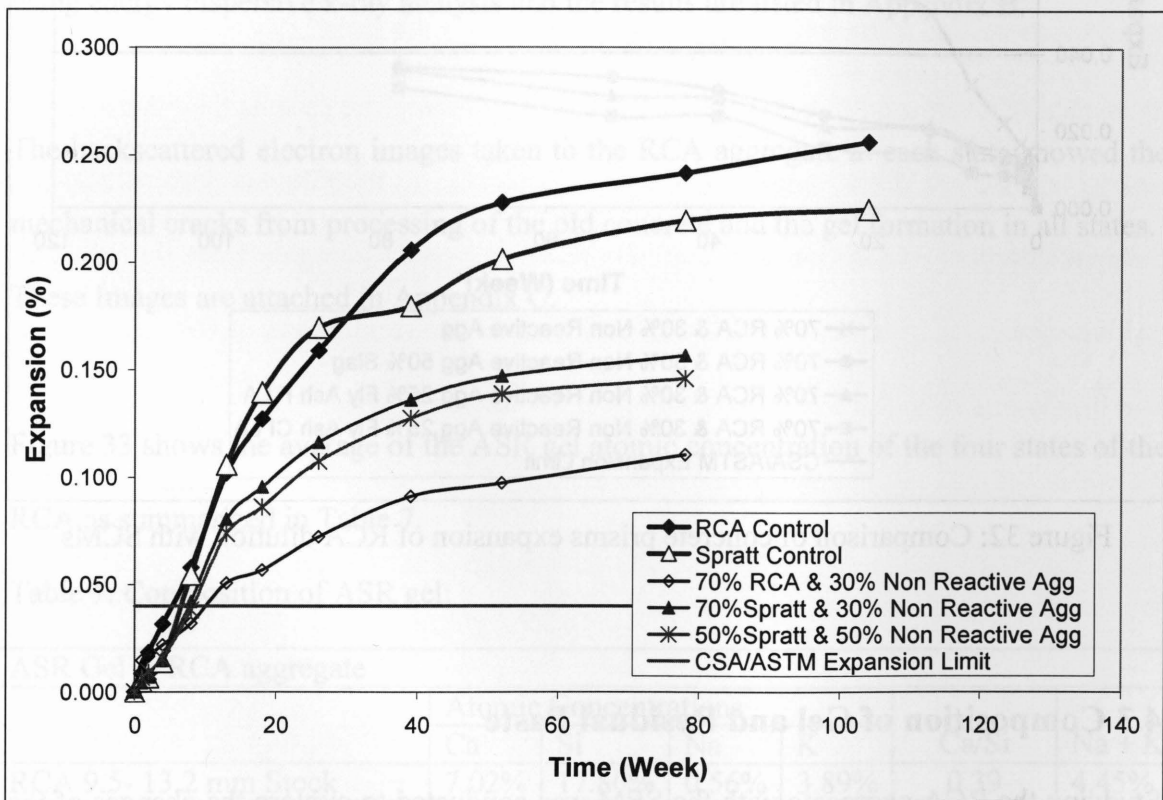
Figure 31: Comparison of concrete prisms expansion of RCA and Spratt when coarse aggregate replacement with non reactive aggregate is used for dilution

Dilution of the RCA was also investigated with SCM replacements of 25% fly Ash F LA, 25% fly Ash CI LA and 50% slag in binary blends. The expansions of these samples are expected to satisfy the ASTM limit at 2 years as it can be exported from the expansion curves in Figure 32.
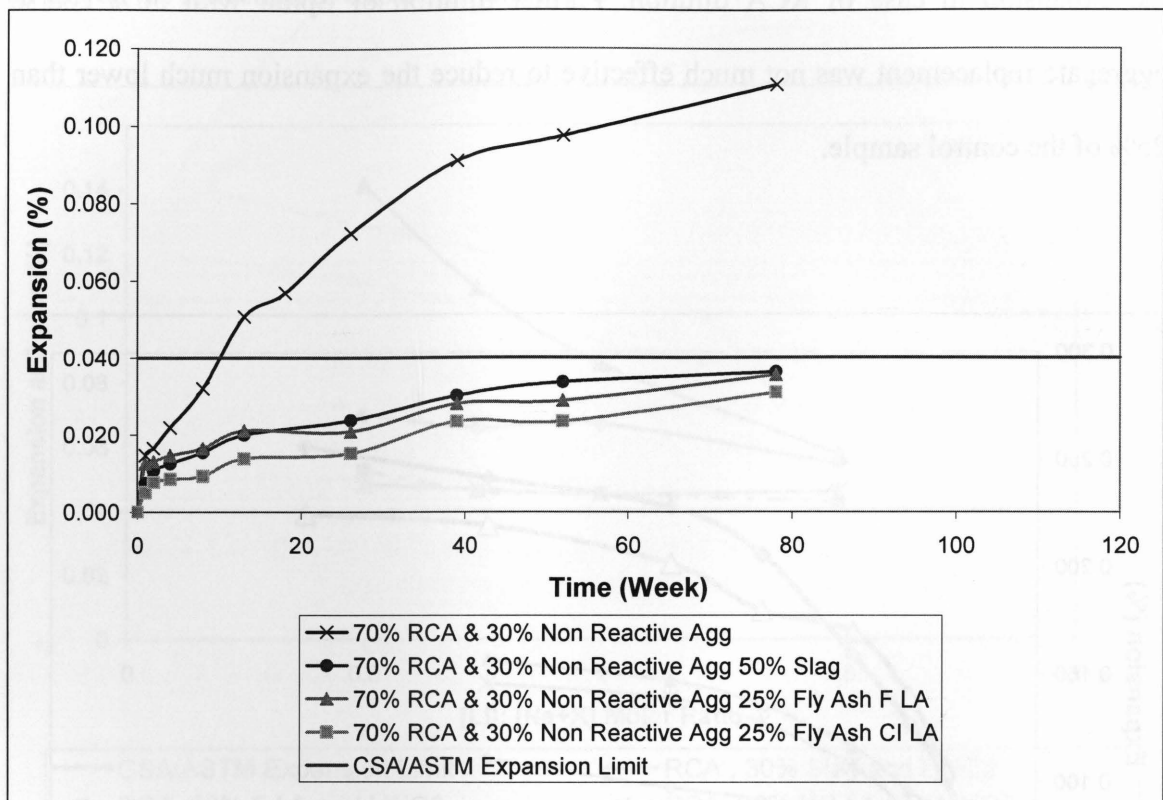
Figure 32: Comparison of concrete prisms expansion of RCA dilution with SCMs

4.3 Composition of Gel and Residual Paste

Studying the RCA aggregate with the SEM was conducted to explore the changes of the RCA gel and paste after soaking in 0.7 M-solution with and without lithium at [Li]:[Na+K] ratio of 1:1. RCA aggregate samples were prepared from aggregate of the

size from 9.5-13.2 mm. Four Types of RCA samples were chosen for this study based on their service exposure as follows:

- ASR-affected RCA stock pile

- ASR-affected RCA used in concrete prism – Prism was broken and a sample was taken.

- ASR-affected RCA in 0.7 Molarity without lithium for 4 weeks

- ASR-affected RCA in 0.7 Molarity with [Li]:[Na+K] of 1:1 for 4 weeks

Quantitative atomic concentrations of the ASR gel and the RCA paste were performed using energy dispersive x-ray analysis and the results are listed in Appendix B.

The backscattered electron images taken to the RCA aggregate at each state showed the mechanical cracks from processing of the old concrete and the gel formation in all states. These Images are attached in Appendix C.

Figure 33 shows the average of the ASR gel atomic concentration of the four states of the RCA as summarized in Table 7.

Table 7: Composition of ASR gel:

ASR Gel in RCA aggregate						
	Atomic Concentrations				Ca/Si	Na + K
	Ca	Si	Na	K		
RCA 9.5- 13.2 mm Stock	7.02%	17.80%	0.56%	3.89%	0.39	4.45%
RCA in concrete prism	5.88%	20.72%	1.09%	4.72%	0.28	5.81%
RCA in solution 0.7 Molarity of Li: (Na + K) 1:1	4.64%	21.88%	0.83%	2.49%	0.23	3.32%
RCA in solution 0.7 Molarity without Lithium	7.54%	19.17%	0.30%	2.94%	0.40	3.24%

Figure 34 shows the average of the RCA paste atomic concentration of the four states of

the RCA summarized in Table 8.

Table 8: Alkali content of RCA Paste:

RCA Paste					
	Atomic Concentrations				
	Ca	Si	Na	K	Na+K
RCA 13.2 Agg Stock	11.02	11.78	0.53	0.34	0.87%
RCA in concrete prism	11.72	12.72	0.65	0.40	1.05%
RCA in solution 0.7 Molarity of Li: (Na + K) 1:1	14.24	9.66	0.09	0.11	0.20%
RCA in solution 0.7 Molarity without Lithium	17.76	6.81	0.15	0.15	0.30%

The above tables and the following figures illustrate that the RCA ASR gel gained 1.36%

more alkalis when used in concrete prism. This is normally the case as the alkalis in the

second service life of the aggregate is due the exposure to the alkaline pore solution of

the new concrete in addition to the alkalis retained in the aggregate from the previous

service cycle. This was also manifested in the alkalis concentrations of the paste which

was 0.18% higher in the second service life in the concrete prism.

Figure 32: Atomic concentrations in RCA ASR gel
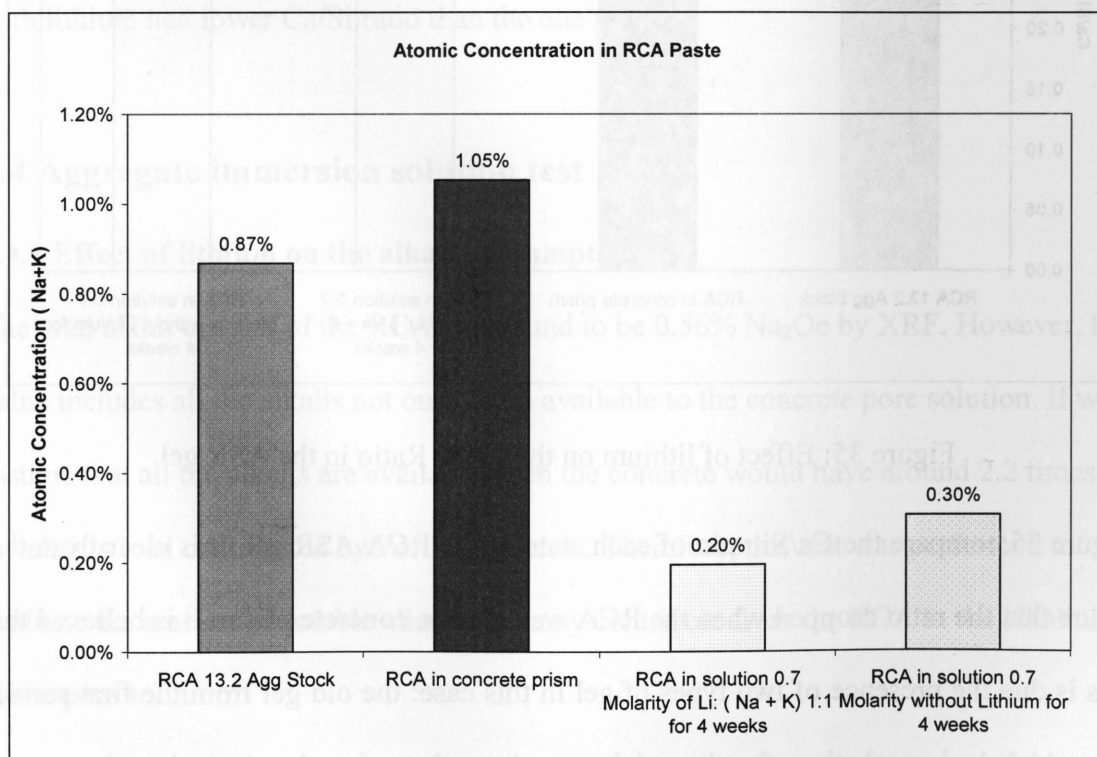
Figure 33: Atomic concentrations in RCA Paste

When the RCA was placed in 0.7 Molarity solutions, the alkali concentrations of the ASR gel dropped as they were leached out in both cases with or without lithium. The alkali concentrations in the gel were almost the same but slightly higher in presence of lithium. The opposite can be seen in the paste alkalis concentrations as it dropped 0.1% in the presence of lithium. It is believed that the tendency of the paste to retain some lithium, at the expense of sodium and potassium, was the reason of that small drop of the alkalis.

Effect of Lithium on the Ca/Si Ratio in RCA ASR Gel
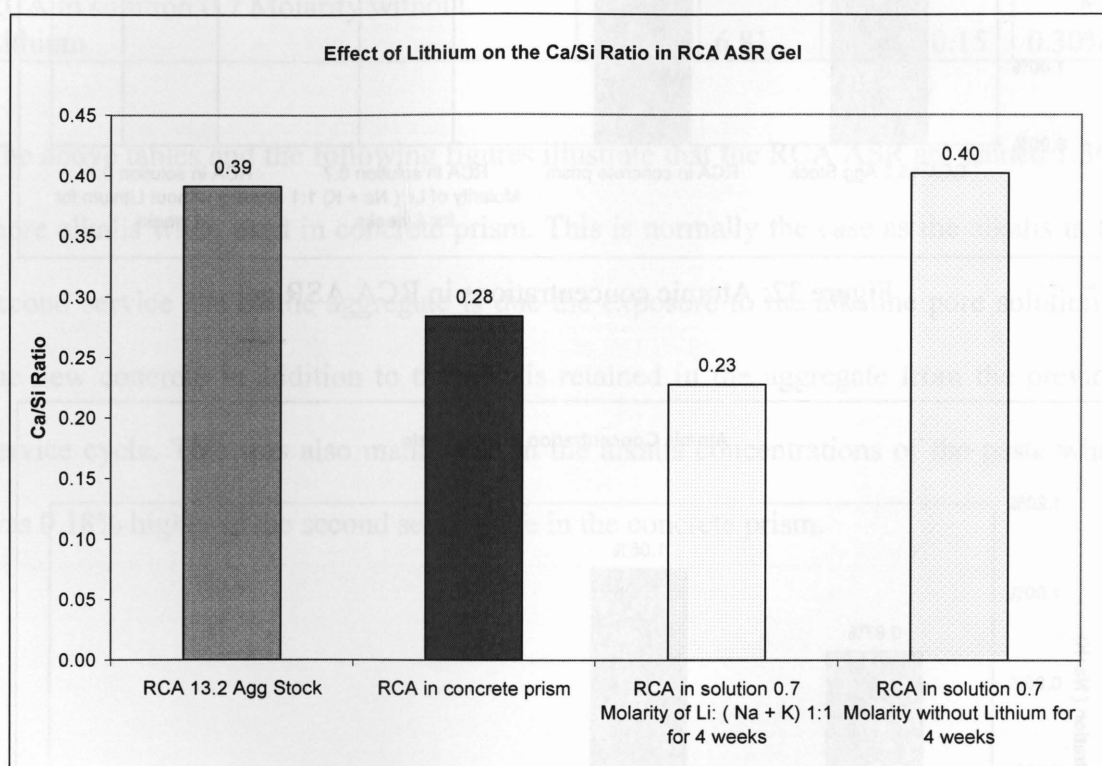
Figure 35: Effect of lithium on the Ca/Si Ratio in the ASR gel

Figure 35 compare the Ca/Si ratio of each state of the RCA ASR gel. It is clear from this figure that the ratio dropped when the RCA was used in concrete prism. It is believed that this is due the presence of two types of gel in this case: the old gel from the first service life which had much time for the calcium to inter the gel and polymerize, the second

when the RCA was used in concrete which is new and the calcium is still not as much as the old gel. That dropped the average of the Ca/Si ratio to 0.28 instead of 0.39 in the RCA stock. This can be deduced as the value obtained is the average of the Ca/Si ratio of both old ASR gel of the RCA and the new ASR gel formed from the new reactions in the second service life. The new gel didn't have much time to exchange as much calcium as the old gel.

When the RCA was kept in solution 0.7 M without lithium for 4 weeks, no noticeable change occurred to the Ca/Si ratio of the ASR gel. However, when lithium was used, the value dropped from 0.40 to 0.28, which is significant. A gel of lower Ca/Si ratio, within the range obtained here, is likely to cause less expansion and disruption.

It was stated by Feng et al (2005) from their work that the Lithium was found to reduce the silica dissolution. This could be the reason why the sample placed in 0.7 M solution with lithium had lower Ca/Si ratio than the one without.

4.4 Aggregate immersion solution test

4.4.1 Effect of lithium on the alkali consumption

The total alkali content of the RCA was found to be 0.56% Na_2Oe by XRF. However, this value includes all the alkalis not only those available to the concrete pore solution. If we assume that all the alkalis are available, then the concrete would have around 2.2 times the alkalis load contributed by Portland cement. Therefore, this test was performed to evaluate the amount of soluble alkalis that may contribute from the RCA to the alkalinity of the pore solution.

Figure 36 presents the amount of the contributed or absorbed (negative contribution) ions as a percentage of the dry mass of the RCA. It was found that the amount of available water-soluble alkalis of the RCA ranges from 0.13% to 0.16% of the dry mass of RCA. It was also found that at 0.25 Molarity the alkalis concentration are in equilibrium between the RCA and the leaching solution. This caused the alkalis neither to be leached out of the RCA nor to be consumed from the immersion solution. Furthermore, it was found that the alkalis consumed by the RCA are much less when lithium is used in the immersing solutions. It should be noted that it is likely that some ASR reaction continues while the RCA is placed in the solution. Indeed all ingredients for the reaction to proceed are available, reactive silica, alkalis and calcium hydroxide which is leached from RCA. The alkalis removed from the solutions are those likely to be used in fuelling reaction as the ability of the residual paste in RCA to retain alkali is not high, as will be shown later. The fact that less alkalis (Na +K) were removed from solution when lithium was available confirmed that the use of lithium reduces the alkalis absorbed by the reactive aggregates. This in turn reduces the formation of expansive ASR gel.

75
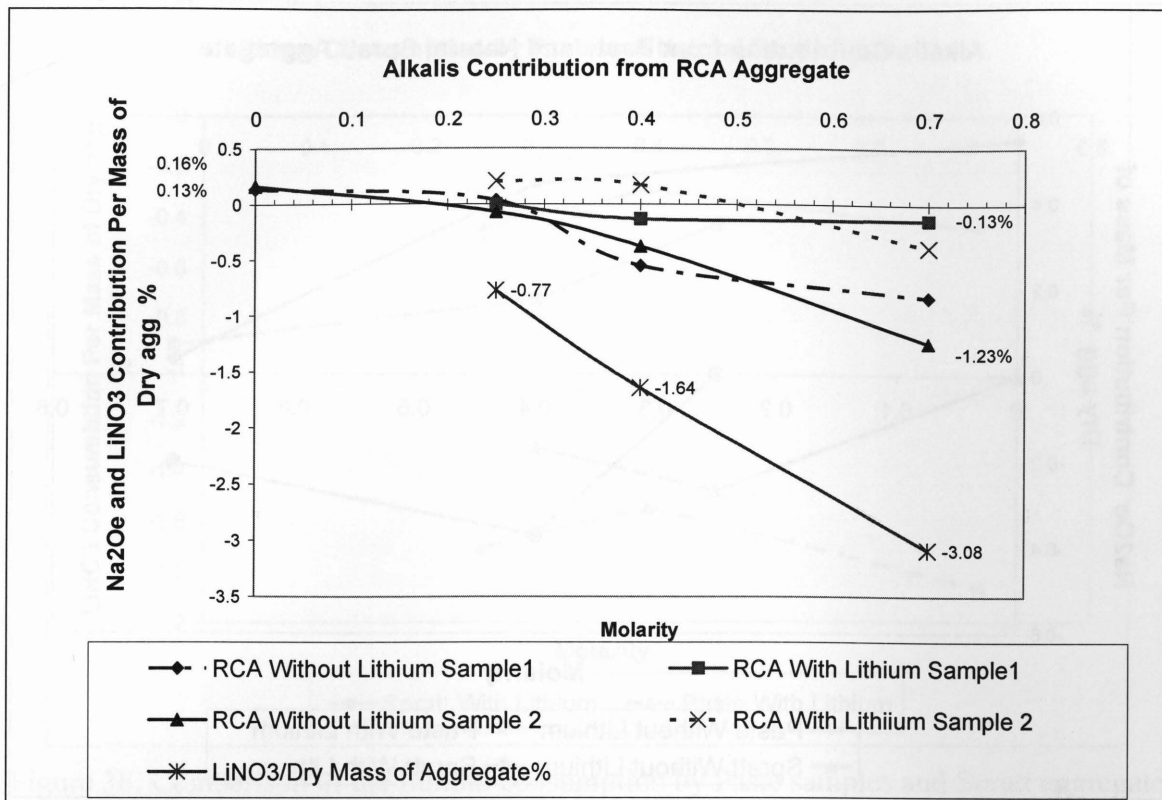
Figure 36: Comparison of alkali consumption when RCA was immersed for 6 month in alkali solution with lithium of Li: Na+K of 1:1 and when immersed in alkali solution without lithium

For better understanding of the role of the residual paste and aggregate portions of the RCA in terms of their characteristics to release or consume alkalis, paste and Spratt samples were soaked in solutions of the same Molarity as those used with the samples of the RCA. For the Spratt samples, $Ca(OH)_2$ was added to the immersing solution to mimic the composition of the pore solution around the aggregate in actual concrete. As shown in Figure 37, the paste mainly contributed alkalis to the host solution. This confirms that the alkalis that were bound by RCA were mainly consumed in ASR reaction or perhaps bound by the gel. The Spratt consumed some alkalis which could be due to some binding of alkali cations by the reactive silica initiating the first stages of ASR.
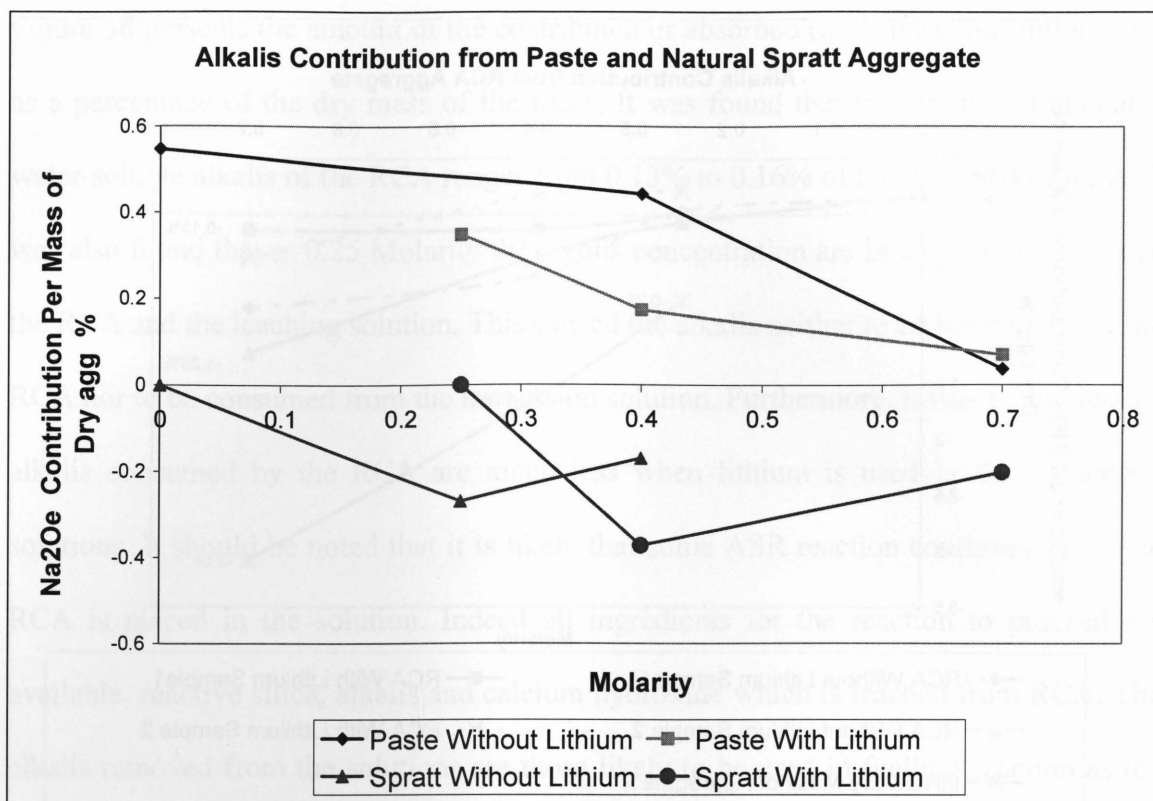
Figure 37: Comparison of alkalis consumption by the Paste and Spratt aggregate when immersed for 4 weeks in alkali solution with lithium of Li: Na+K of 1:1 and when immersed in alkali solution without lithium

Both Spratt and the paste didn't have much difference in their alkalis release or consumption with or without lithium in the immersing solutions. Furthermore, the amount of the lithium consumed by the unit mass of the paste was almost 4 times the amount consumed by the unit mass of the Spratt aggregate as can be seen in Figure 38. It should be noted that the paste used here is control PC paste with no SCM to represent the residual paste of RCA. If PC+ SCM paste was used, the paste could have bound more of both alkalis and lithium.
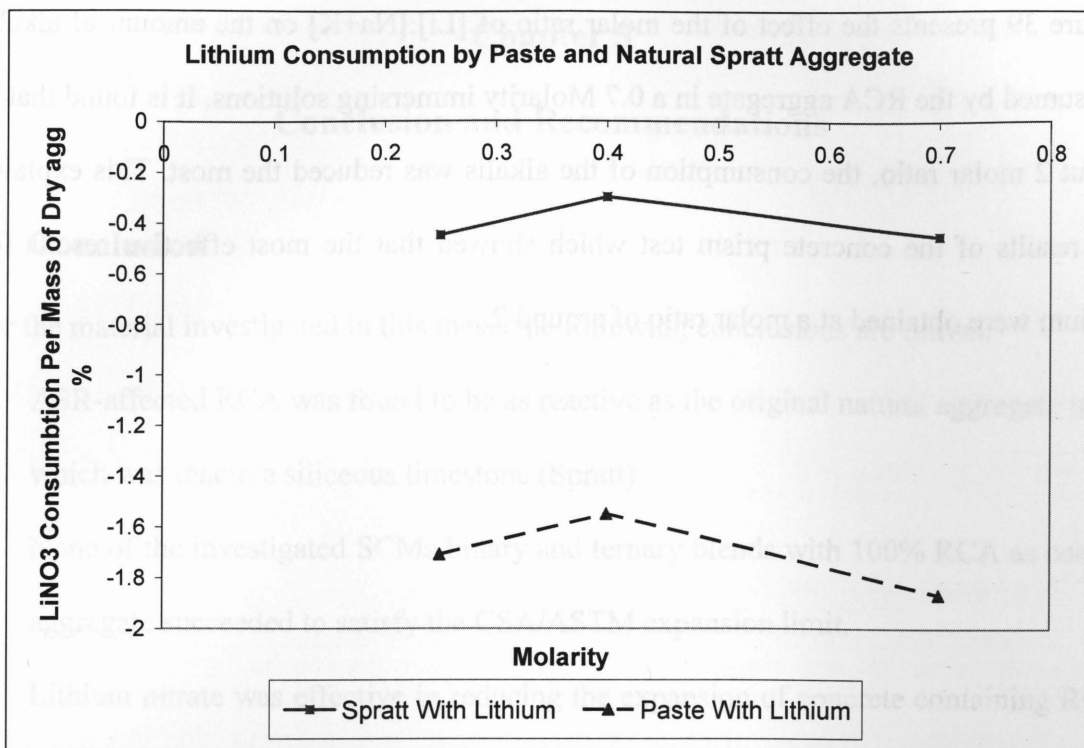
Figure 38: Comparison of the lithium consumption by Paste samples and Spratt aggregate when immersed in solution with Li: Na+K of 1:1 for 4 weeks
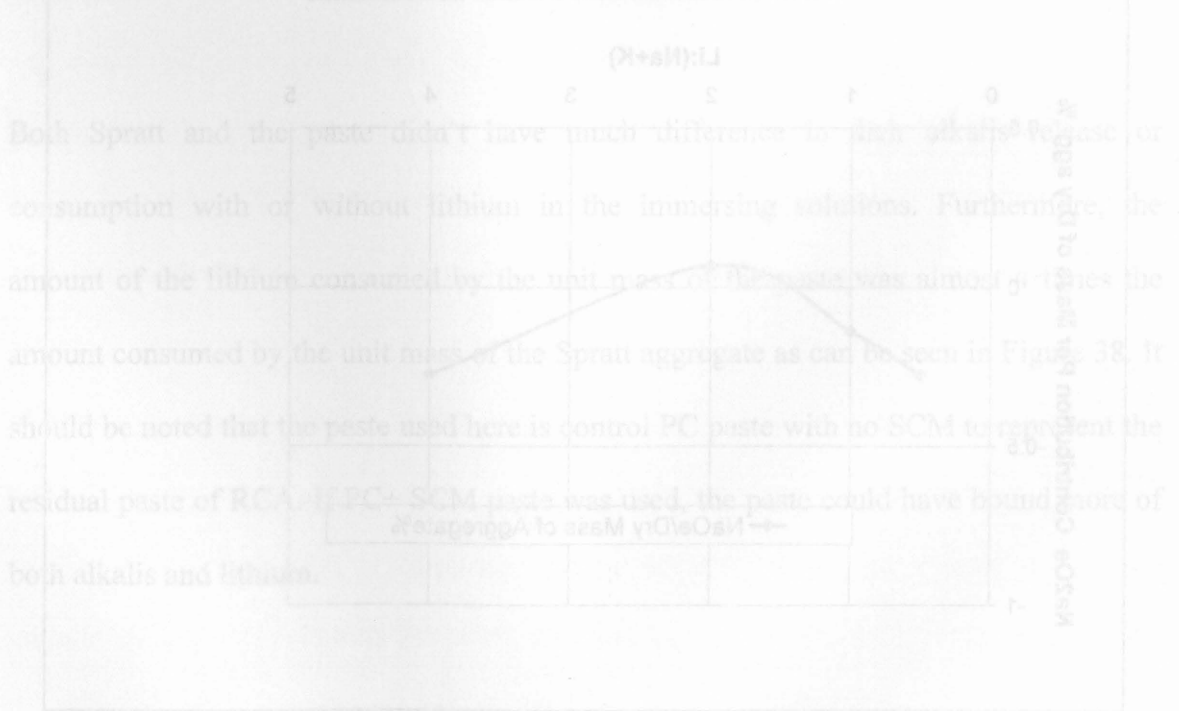
Figure 39: Effect of Li :(Na+K) Molar Ratio on the Alkali contribution or Consumption From RCA in 0.7 Molarity Solution

Figure 39 presents the effect of the molar ratio of [Li]:[Na+K] on the amount of alkalis consumed by the RCA aggregate in a 0.7 Molarity immersing solutions. It is found that at about 2 molar ratio, the consumption of the alkalis was reduced the most. This explains the results of the concrete prism test which showed that the most effective results for lithium were obtained at a molar ratio of around 2.

Chapter 5

Conclusion and Recommendations

5.1 Conclusion

For the material investigated in this thesis the following conclusions are drawn:

1. ASR-affected RCA was found to be as reactive as the original natural aggregate used which was reactive siliceous limestone (Spratt).

2. None of the investigated SCMs binary and ternary blends with 100% RCA as coarse aggregate succeeded to satisfy the CSA/ASTM expansion limit.

3. Lithium nitrate was effective in reducing the expansion of concrete containing RCA but the range of dosages presented in this study did not suppress the expansion to the allowable limit.

4. Swelling of the residual mortar of the RCA, old ASR gel swelling and the higher alkalis retained in the aggregate from the previous service life are mainly the causes of the early expansion of RCA concrete.

5. The addition of the lithium nitrate enhances the RCA concrete performance in binary blends but was not sufficient to reduce expansion to acceptable limits when RCA was used as the total coarse aggregate in the mix.

6. Dilution of the RCA with natural non-reactive coarse aggregate is required along with other preventative measures to reduce the expansion of the concrete to acceptable limits.

7. Quantitative SEM atomic concentration analysis showed a considerable reduction of the Ca/Si ratio of the ASR gel when RCA was exposed to lithium nitrate.

8. The addition of lithium nitrate to ternary blends of silica and slag didn't improve the reduction of the concrete expansion. However, the use of lithium with high calcium fly ash showed significant improvement.

9. The synergy effect of lithium nitrate with high calcium low alkalis fly ash is effective in reducing the RCA concrete expansion dramatically and can be a very successful approach if used with dilution of the coarse aggregate. However, the investigate blend with 100% RCA did not satisfy the ASTM expansion limit.

5.2 Recommendations

This study presented preliminary steps in understanding the mechanism of expansion in concrete containing reactive RCA. The study also looked at the mechanism by which lithium reduces the expansion in concrete with reactive aggregates. Further mechanistic work is recommended. Such work should include investigating the pore solution of the concrete with RCA and binary and ternary blends of SCMs with and without lithium nitrate.

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Appendix A: Expansion of Concrete Prisms

Phase1:

	RCA Expansion %										
	CONTROL										
Bucket #	#9	#47	#1	#6	#2	#13	#22	#72	#15	#66	#65
Type	0.69 Con	0.69 Con	60:40 Con	0.70 Con	0.69 Con	0.69 Con	0.69 Con	0.69 Con	0.69 Con	60:40 Con	60:40 Con
Na_2O_e	2.31 (kg/m^3)	3.36 (kg/m^3)	5.25 (kg/m^3)	5.25 (kg/m^3)	5.25 (kg/m^3)	5.25 (kg/m^3)	5.25 (kg/m^3)	5.25 (kg/m^3)	6.30 (kg/m^3)	5.25 (kg/m^3)	5.25 (kg/m^3)
	0.55 Alkali	0.80 Alkali	1.25 Alkali	1.25 Alkali	1.25 Alkali	1.25 Alkali	1.25 Alkali	1.25 Alkali	1.5 Alkali	1.25 Alkali	1.25 Alkali
Weeks							Ottawa Sand	WASHED		FINE AGG.	N.A.
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	0.009	0.010	0.018	0.021	0.007	0.008	0.016	0.012	0.010	0.010	0.005
2	0.020	0.017	0.029	0.025	0.011	0.018	0.027	0.022	0.015	0.015	0.007
4	0.025	0.032	0.036	0.035	0.020	0.032	0.035	0.021	0.025	0.018	0.009
8	0.036	0.041	0.066	0.067	0.037	0.058	0.058	0.046	0.053	0.030	0.015
13	0.049	0.059	0.101	0.122	0.085	0.102	0.082	0.076	0.097	0.040	0.024
18	0.056	0.080	0.123	0.157	0.118	0.127	0.111	0.101	0.125	0.046	0.026
26	0.062	0.107	0.144	0.192	0.146	0.159	0.000	0.134	0.164	0.057	0.031
39	0.081	0.127	0.161	0.223	0.187	0.206	0.203	0.171	0.211	0.051	0.034
52	0.098	0.122	0.177	0.244	0.205	0.228	0.235	0.190	0.237	0.066	0.044
78	0.089	0.133	0.188	0.259	0.219	0.242	0.275	0.206	0.255	0.086	0.063
104	0.100	0.145	0.201	0.276	0.240	0.256	0.294	0.217	0.275	0.089	0.067

RCA Expansion %										
	SILICA			**FLY ASH Type F, HA**				**FLY ASH Type F, LA**			
Bucket #	#3	#8	#14	#10	#16	#17	#68	#48	#49	#73	#50
Type	0.69 RCA	0.69 RCA	0.69 RCA	Type F, HA	Type F, HA	Type F, HA	Type F, HA	Type F, LA	Type F, LA	Type F, LA	Type F, LA
Na$_2$O$_e$	4.99 (kg/m^3)	4.83 (kg/m^3)	4.73 (kg/m^3)	4.46 (kg/m^3)	4.20 (kg/m^3)	3.94 (kg/m^3)	3.41 (kg/m^3)	4.20 (kg/m^3)	3.94 (kg/m^3)	3.94 (kg/m^3)	3.68 (kg/m^3)
	5% SF	8% SF	10% SF	15% FA	20% FA	25% FA	35% FA	20% FA	25% FA	25% FA	30% FA
Weeks										**WASHED**	
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	0.003	-0.001	-0.004	0.005	0.008	0.012	0.015	0.008	0.008	0.011	0.007
2	0.006	-0.002	-0.001	0.006	0.009	0.014	0.013	0.012	0.010	0.016	0.016
4	0.013	0.006	0.002	0.018	0.021	0.018	0.000	0.019	0.017	0.015	0.018
8	0.023	0.014	0.009	0.037	0.030	0.031	0.007	0.023	0.017	0.020	0.021
13	0.034	0.022	0.012	0.050	0.043	0.042	0.019	0.029	0.021	0.032	0.028
18	0.045	0.028	0.016	0.061	0.050	0.049	0.000	0.041	0.031	0.039	0.033
26	0.059	0.031	0.026	0.079	0.071	0.065	0.029	0.056	0.042	0.038	0.038
39	0.087	0.050	0.037	0.115	0.096	0.084	0.048	0.072	0.050	0.047	0.052
52	0.110	0.065	0.050	0.144	0.124	0.103	0.060	0.066	0.049	0.053	0.051
78	0.115	0.066	0.051	0.159	0.129	0.117	0.074	0.074	0.055	0.056	0.058
104	0.132	0.082	0.061	0.185	0.149	0.134	0.087	0.086	0.067	0.062	0.064

RCA Expansion %								
	FLY ASH CI, LA		FLY ASH Type CH LA			SLAG		
Bucket #	#45	#46	#18	#19	#20	#35	#32	#26
Type	Type CI, LA	Type CI, LA	Type CH	Type CH	Type CH	0.69 RCA	0.69 RCA	0.69 RCA
Na_2O_e	4.20 (kg/m^3)	3.68 (kg/m^3)	3.94 (kg/m^3)	3.68 (kg/m^3)	2.63 (kg/m^3)	3.94 (kg/m^3)	3.68 (kg/m^3)	2.63 (kg/m^3)
	20% FA	30% FA	25% FA	30% FA	50% FA	25% Slag	30% Slag	50% Slag
Weeks								
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	0.012	0.005	0.005	0.005	0.001	0.008	0.011	0.010
2	0.015	0.005	0.000	0.000	0.021	0.019	0.019	0.018
4	0.015	0.005	0.021	0.022	0.024	0.032	0.027	0.022
8	0.026	0.013	0.042	0.034	0.027	0.044	0.035	0.028
13	0.037	0.017	0.054	0.051	0.036	0.059	0.047	0.025
18	0.049	0.026	0.065	0.063	0.042	0.070	0.048	0.028
26	0.062	0.034	0.088	0.082	0.054	0.089	0.068	0.000
39	0.078	0.047	0.112	0.108	0.065	0.107	0.084	0.041
52	0.071	0.036	0.137	0.138	0.083	0.124	0.100	0.042
78	0.089	0.047	0.150	0.139	0.088	0.133	0.092	0.050
104	0.107	0.062	0.170	0.164	0.106	0.149	0.104	0.053

	FLY ASH F, HA		FLY ASH F, LA		FLY ASH CI, LA		

RCA Expansion %

Ternary Blends

Bucket #	#33	#34	#51	#52	#53	#55	#69
Type	Type F, HA	Type F, HA	Type F, LA	Type F, LA	Type CI	Type CI	Type CI
Na$_2$O$_e$	3.94 (kg/m^3)	3.68 (kg/m^3)	4.20 (kg/m^3)	3.94 (kg/m^3)	3.94 (kg/m^3)	3.68 (kg/m^3)	3.68 (kg/m^3)
	5% Silica	5% Silica	5% Silica	5% Silica	5% Silica	5% Silica	5% Silica
	20% FA	25% FA	15% FA	20% FA	20% FA	25% FA	25% FA
Weeks							
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	0.008	0.012	0.003	0.010	0.003	0.000	-0.001
2	0.011	0.011	0.010	0.012	0.004	0.002	-0.003
4	0.014	0.016	0.012	0.009	0.006	0.005	-0.013
8	0.014	0.019	0.014	0.011	0.009	0.014	-0.005
13	0.026	0.026	0.021	0.018	0.013	0.016	0.008
18	0.028	0.026	0.028	0.025	0.020	0.019	0.000
26	0.042	0.046	0.031	0.026	0.022	0.027	0.009
39	0.055	0.055	0.047	0.041	0.038	0.023	0.021
52	0.061	0.068	0.046	0.039	0.035	0.033	0.029
78	0.073	0.065	0.054	0.048	0.043	0.035	0.032
104	0.090	0.081	0.061	0.052	0.050	0.041	0.038

RCA Expansion %							
Ternary Blends							
	FLY ASH Type CH LA			SLAG			
Bucket #	#29	#30	#31	#54	#56	#70	#71
Type	Type CH	Type CH	Type CH				
Na$_2$O$_e$	3.94 (kg/m^3)	3.68 (kg/m^3)	3.41 (kg/m^3)	3.68 (kg/m^3)	3.41 (kg/m^3)	3.41 (kg/m^3)	2.89 (kg/m^3)
	5% Silica	5% Silica	5% Silica	5% Silica	5% Silica	5% Silica	5% Silica
	20% FA	25% FA	30% FA	25% Slag	30% Slag	30% Slag	40% Slag
Weeks							
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	0.004	0.001	-0.002	0.010	0.007	0.014	0.016
2	0.008	0.003	0.000	0.017	0.006	0.017	0.020
4	0.010	0.007	0.007	0.018	0.013	0.006	0.014
8	0.012	0.010	0.008	0.025	0.020	0.008	0.017
13	0.019	0.015	0.012	0.033	0.024	0.016	0.020
18	0.027	0.023	0.015	0.042	0.028	0.000	0.000
26	0.039	0.032	0.023	0.045	0.036	0.022	0.029
39	0.057	0.045	0.033	0.062	0.034	0.037	0.042
52	0.046	0.040	0.030	0.060	0.044	0.043	0.047
78	0.063	0.059	0.053	0.064	0.050	0.049	0.052
104	0.076	0.072	0.066	0.072	0.057	0.055	0.055

JOBE Expansion %								
	TAYLORVILLE				DEELY	COMANCHE	ST. LAWRENCE	
	FLYASH			BLEND	BLEND	BLEND	SILICA	
Bucket #	#41	#42	#43	#44	#57	#58	#59	#60
Type	Type F, HA	Type F, HA	Type F, HA	Type F, HA				
Na_2O_e	4.46 (kg/m^3)	4.20 (kg/m^3)	3.94 (kg/m^3)	3.94 (kg/m^3)	3.78 (kg/m^3)	3.68 (kg/m^3)	4.88 (kg/m^3)	4.73 (kg/m^3)
	15% FA	20% FA	25% FA	5% Silica	3% Silica	5% Silica	7% Silica	10% Silica
				20% FA	25% FA	25% FA		
Weeks								
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	0.002	0.001	0.002	-0.003	-0.001	-0.008	0.000	-0.001
2	0.012	0.009	0.004	-0.003	-0.001	-0.006	0.005	0.001
4	0.039	0.011	0.007	-0.001	0.006	0.000	0.014	0.009
8	0.124	0.044	0.010	0.004	0.011	0.001	0.019	0.014
13	0.205	0.092	0.029	0.005	0.016	0.008	0.028	0.020
18	0.272	0.142	0.056	0.010	0.019	0.012	0.042	0.024
26	0.341	0.200	0.088	0.014	0.031	0.020	0.208	0.028
39	0.455	0.287	0.146	0.029	0.022	0.026	0.366	0.019
52	0.452	0.320	0.151	0.026	0.038	0.065	0.421	0.022
78	0.560	0.412	0.244	0.065	0.082	0.168	0.484	0.175
104	0.573	0.431	0.274	0.122	0.154	0.263	0.493	0.299

	CONTROL		FLYASH					BLEND		
SPRATT Expansion %										
Bucket #	#67	#74	#61	#62	#63	#23	#24	#75	#64	#28
Type	60:40 Con	60:40 Con	Type F, HA	Type F, HA	Type F, HA	Type F, HA	Type F, HA	Type F, HA	Type F, HA	Type F, HA
Na_2O_e	5.25 (kg/m^3)	5.25 (kg/m^3)	4.46 (kg/m^3)	4.20 (kg/m^3)	3.94 (kg/m^3)	4.46 (kg/m^3)	3.94 (kg/m^3)	3.94 (kg/m^3)	3.94 (kg/m^3)	3.68 (kg/m^3)
	1.25 Alkali	1.25 Alkali	15% FA	20% FA	25% FA	15% FA	25% FA	5% Silica	5% Silica	5% Silica
								20% FA	20% FA	25% FA
Weeks										
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	0.005	0.005	-0.002	-0.005	0.004	0.002	0.002	-0.005	-0.004	-0.002
2	0.007	0.002	-0.001	-0.004	0.003	0.007	0.006	-0.005	-0.001	0.000
4	0.014	0.002	0.006	0.002	0.008	0.008	0.002	-0.010	-0.001	-0.001
8	0.055	0.023	0.011	0.006	0.012	0.016	0.011	-0.005	0.004	0.003
13	0.106	0.083	0.023	0.015	0.022	0.026	0.016	0.002	0.012	0.010
18	0.140	0.123	0.040	0.023	0.029	0.036	0.023	0.001	0.015	0.015
26	0.170	0.163	0.055	0.031	0.044	0.053	0.033	0.005	0.024	0.017
39	0.180	0.200	0.069	0.039		0.047	0.025	0.010	0.015	0.019
52	0.202	0.214	0.085	0.054	0.048	0.074	0.046	0.016	0.015	0.020
78	0.219	0.220	0.110	0.080	0.071	0.096	0.067	0.018	0.031	0.033
104	0.225	0.227	0.123	0.091	0.078	0.104	0.073	0.024	0.036	0.036

Phase2:

RCA Expansion %				
Ternary Blends				
	FLY ASH Type F LA		**SLAG**	
Bucket #	#30	#31	#32	#33
	5% Silica	5% Silica	5% Silica	20% F LA
	20% F LA	25% F LA	45% Slag	30% Slag
Weeks				
0	0.000	0.000	0.000	0.000
1	0.012	0.010	0.013	0.012
2	0.013	0.011	0.016	0.014
4	0.017	0.015	0.022	0.017
8	0.016	0.014	0.021	0.015
13	0.024	0.022	0.030	0.022
18	0.023	0.021	0.030	0.021
26	0.024	0.022	0.031	0.022
39	0.032	0.029	0.040	0.029
52	0.033	0.031	0.041	0.030
78	0.040	0.037	0.049	0.038
104				

RCA With Lithium Expansion %											
CONTROL											
Bucket #	#1	#2	#3	#4	#27	#28	#29	#5	#6	#7	#8
Li / Na+ K	0.74	1.0	1.5	2.25	3	4	5	0.5	0.74	1.0	1.5
Weeks								Pre Soaked	Pre Soaked	Pre Soaked	Pre Soaked
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	0.013	-0.001	0.014	0.014	0.022	0.020	0.022	0.010	0.009	0.009	0.010
2	0.019	0.005	0.019	0.018	0.028	0.026	0.029	0.015	0.013	0.013	0.014
4	0.027	0.011	0.023	0.021	0.031	0.029	0.033	0.020	0.020	0.020	0.019
8	0.033	0.016	0.029	0.026	0.040	0.038	0.037	0.042	0.039	0.035	0.034
13	0.042	0.023	0.033	0.029	0.044	0.044	0.046	0.053	0.043	0.031	0.031
18	0.047	0.025	0.035	0.031	0.046	0.045	0.049	0.063	0.050	0.035	0.034
26	0.055	0.028	0.037	0.034	0.047	0.047	0.051	0.077	0.057	0.039	0.036
39	0.063	0.036	0.043	0.039	0.049	0.050	0.054	0.092	0.063	0.042	0.037
52	0.069	0.039	0.046	0.042	0.051	0.053	0.059	0.101	0.069	0.046	0.040
78	0.073	0.042	0.047	0.043	0.058	0.064	0.066	0.114	0.077	0.053	0.046
104	0.079	0.046	0.050	0.047				0.118	0.081	0.054	0.047

RCA With Lithium Expansion %

Bucket #	FLY ASH F LA				FLY ASH Type CH LA				
	#9	#10	#11	#12	#13	#14	#15	#16	#17
Li / Na+ K	0.5	0.74	1.0	1.5	0.5	0.5	0.74	1.0	1.5
	20% F LA	20% F LA	20% F LA	20% F LA	40% CH LA	25% CH LA	25% CH LA	25% CH LA	25% CH LA
Weeks									
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	0.010	0.010	0.010	0.012	0.000	0.008	0.007	0.005	0.007
2	0.015	0.013	0.016	0.016	0.000	0.012	0.007	0.007	0.005
4	0.018	0.016	0.017	0.017	0.006	0.017	0.015	0.014	0.012
8	0.022	0.019	0.020	0.022	0.016	0.031	0.023	0.021	0.021
13	0.026	0.020	0.021	0.020	0.023	0.043	0.033	0.030	0.025
18	0.031	0.026	0.030	0.030	0.031	0.056	0.041	0.035	0.030
26	0.036	0.030	0.033	0.032	0.044	0.078	0.056	0.044	0.037
39	0.040	0.033	0.032	0.030	0.051	0.093	0.070	0.055	0.042
52	0.045	0.038	0.038	0.037	0.067	0.111	0.081	0.063	0.046
78	0.053	0.047	0.041	0.039	0.081	0.126	0.100	0.077	0.053
104	0.053	0.046	0.045	0.043	0.092	0.141	0.109	0.086	0.057

RCA With Lithium Expansion %					
	SLAG				
Bucket #	#18	#19	#20	#21	#22
Li / Na+ K	0.5	0.5	0.74	1	1.5
	50% Slag	30% Slag	30% Slag	30% Slag	30% Slag
Weeks					
0	0.000	0.000	0.000	0.000	0.000
1	0.009	0.004	0.007	0.009	0.010
2	0.010	0.012	0.013	0.017	0.014
4	0.015	0.013	0.015	0.018	0.015
8	0.022	0.022	0.025	0.026	0.022
13	0.022	0.028	0.030	0.033	0.026
18	0.027	0.034	0.036	0.038	0.032
26	0.032	0.043	0.043	0.045	0.037
39	0.038	0.051	0.050	0.051	0.042
52	0.042	0.058	0.056	0.055	0.046
78	0.049	0.069	0.065	0.066	0.054
104	0.053	0.070	0.066	0.067	0.054

RCA Expansion %				
Ternary Blends				
Bucket #	#23	#24	#25	#26
Li / Na+ K	0.5	0.74	1	1.5
	5% Silica	5% Silica	5% Silica	5% Silica
	30% Slag	30% Slag	30% Slag	30% Slag
Weeks				
0	0.000	0.000	0.000	0.000
1	0.008	0.007	0.009	0.012
2	0.010	0.012	0.011	0.014
4	0.013	0.012	0.013	0.014
8	0.015	0.015	0.015	0.017
13	0.022	0.021	0.023	0.024
18	0.026	0.025	0.024	0.028
26	0.032	0.029	0.031	0.032
39	0.031	0.031	0.030	0.031
52	0.037	0.036	0.034	0.034
78	0.044	0.041	0.041	0.041
104	0.048	0.047	0.045	0.046

RCA Dilution Expansions %				
70% RCA , 30% Non reactive natural aggregate (St Mary)				
Bucket #	#34	#35	#36	#37
	Control	25% Fly Ash	25% Fly Ash	50% Slag
Type	-	F LA	CI LA	
Weeks				
0	0.000	0.000	0.000	0.000
1	0.015	0.013	0.005	0.007
2	0.017	0.013	0.008	0.011
4	0.022	0.015	0.009	0.013
8	0.032	0.017	0.009	0.015
13	0.051	0.021	0.014	0.020
18	0.057	0.018	0.011	0.017
26	0.072	0.021	0.015	0.024
39	0.091	0.028	0.023	0.030
52	0.097	0.029	0.023	0.034
78	0.111	0.035	0.031	0.036
104				

Spratt / St Mary Dilution Expansions %		
	50% Spratt & 50% St Mary	**70% Spratt & 30% St Mary**
Bucket #	#38	#39
Weeks		
0	0.000	0.000
1	0.007	0.004
2	0.009	0.007
4	0.015	0.015
8	0.038	0.042
13	0.074	0.081
18	0.086	0.095
26	0.107	0.116
39	0.127	0.136
52	0.139	0.147
78	0.146	0.157
104		

	Non Reactive RCA Expansion %			
	Dufferin	**Lafarg**	**Dufferin**	**Lafarg**
Bucket #	#40	#41	#42	#43
			Pre Soaked	Pre Soaked
Weeks				
0	0.000	0.000	0.000	0.000
1	0.006	0.005	0.001	0.002
2	0.004	-0.001	0.004	0.008
4	0.009	0.000	0.007	0.014
8	0.011	0.002	0.011	0.018
13	0.013	0.003	0.013	0.017
18	0.017	0.007	0.018	0.024
26	0.023	0.010	0.019	0.027
39	0.027	0.012	0.025	0.031
52	0.031	0.017	0.028	0.035
78				
104				

Appendix B: Atomic Concentrations

| | sample # | Atomic Concentrations | | | | | | | | | | Total | | Ca/Si | Na + K |
		O	Na	Mg	AL	Si	P	S	K	Ca	Fe				
Gel-1	#4	70.43%	0.94%	0.17%		18.16%			2.86%	7.44%		100.00%		0.41	3.80%
	#7	73.68%	0.31%			16.46%			3.28%	6.27%		100.00%		0.38	3.59%
Gel -2	#7	64.07%	0.39%			19.65%	0.55%		4.93%	10.41%		100.00%		0.53	5.32%
	#7	69.44%	0.43%			18.17%			3.95%	8.02%		100.01%		0.44	4.38%
	#7	71.60%	0.37%			17.70%			3.71%	6.60%		99.98%		0.37	4.08%
	#7	71.85%	0.92%			17.66%		0.41%	3.62%	5.54%		100.00%		0.31	4.54%
Gel -3	#7	72.06%	0.64%			16.00%		2.04%	4.51%	4.76%		100.01%		0.30	5.15%
	#7	69.99%	0.99%			18.78%		0.67%	3.85%	5.72%		100.00%		0.30	4.84%
	#7	70.23%	0.86%	1.01%		17.01%		1.63%	4.01%	5.25%		100.00%		0.31	4.87%
	#7	73.61%	0.30%			16.40%	0.14%		3.28%	6.26%		99.99%		0.38	3.58%
Gel -4	#7	64.07%	0.39%			19.65%	0.55%		4.93%	10.41%		100.00%		0.53	5.32%
	#7	69.34%	0.42%			18.09%	0.20%		3.94%	8.00%		99.99%		0.44	4.36%
	#7	71.55%	0.37%			17.64%	0.15%		3.70%	6.59%		100.00%		0.37	4.07%
Average		70.15%	0.56%	0.59%		17.80%	0.32%	1.19%	3.89%	7.02%		100.00%		0.39	4.45%
SD		3.03%	0.27%	0.59%		1.15%	0.21%	0.77%	0.61%	1.80%		0.01%		0.07842986	0.00616

RCA Stock – SEM Samples

	sample #	O	Na	Mg	AL	Si	P	S	K	Ca	Fe	Total	Ca/Si	Na + K
						Atomic Concentrations								
Gel-1	#1	59.33%	1.34%	0.20%	0.48%	21.64%			6.18%	10.56%	0.27%	100.00%	0.49	7.52%
Gel-2	#1	67.99%	1.24%	0.35%		20.24%			4.56%	5.61%		99.99%	0.28	5.80%
	#1	67.61%	1.41%			18.99%			4.76%	7.24%		100.01%	0.38	6.17%
Gel-3	#1	69.18%	0.92%	0.09%		20.19%			4.43%	5.19%		100.00%	0.26	5.35%
	#1	69.38%	0.82%	0.13%		20.23%			4.14%	5.30%		100.00%	0.26	4.96%
	#1	64.64%	0.98%	0.10%		23.46%			4.92%	5.91%		100.01%	0.25	5.90%
	#1	68.28%	1.34%	0.27%		20.64%			4.40%	5.08%		100.01%	0.25	5.74%
Gel-4	#1	67.12%	1.10%	0.26%		21.64%			4.65%	5.22%		99.99%	0.24	5.75%
	#1	69.95%	0.84%	0.28%		19.93%			4.35%	4.66%		100.01%	0.23	5.19%
	#1	68.66%	0.89%	0.19%		20.58%			4.76%	4.92%		100.00%	0.24	5.65%
	#1	68.46%	1.16%	0.23%		20.42%			4.73%	4.99%		99.99%	0.24	5.89%
Average		67.33%	1.09%	0.21%		20.72%			4.72%	5.88%	0.27%	100.00%	0.28	5.81%
SD		3.00%	0.22%	0.08%		1.17%			0.54%	1.70%		0.01%	0.08	0.66%

RCA in concrete prism – SEM Samples

		Atomic Concentrations													
	sample #	O	Na	Mg	AL	Si	P	S	K	Ca	Fe	Total		Ca/Si	Na + K
Gel-1	#4	68.60%	1.42%			23.86%	0.92%	0.87%	1.40%	2.93%		100.00%		0.12279966	2.82%
	#4	68.13%	1.05%	0.75%		19.58%	3.18%	0.33%	0.93%	6.04%		99.99%		0.30847804	1.98%
	#4	65.92%	1.13%	0.33%		24.25%	2.00%	0.94%	1.48%	3.93%		99.98%		0.16206186	2.61%
	#4	69.00%	1.00%	0.28%		23.75%	1.51%	1.04%	0.92%	2.48%		99.98%		0.10442105	1.92%
Gel-2	#4	67.19%	0.23%	0.37%		25.22%	2.18%	0.24%	1.75%	2.81%		99.99%		0.11141951	1.98%
	#4	65.52%	0.29%	0.13%		26.94%	1.80%	0.38%	1.93%	3.02%		100.01%		0.11210097	2.22%
	#4	64.71%	0.24%	0.27%		28.02%	1.79%	0.27%	1.84%	2.87%		100.01%		0.10242684	2.08%
	#4	64.91%	0.24%	0.21%		27.96%	2.04%	0.26%	1.41%	2.96%		99.99%		0.10586552	1.65%
	#4	65.38%	0.41%	0.31%		25.60%	2.17%	0.28%	2.10%	3.74%		99.99%		0.14609375	2.51%
Gel-3	#4	69.00%	1.00%	0.28%		23.75%	1.51%	1.04%	0.92%	2.48%		99.98%		0.10442105	1.92%
	#4	65.92%	1.13%	0.33%		24.25%	2.00%	0.94%	1.48%	3.93%		99.98%		0.16206186	2.61%
	#4	68.13%	1.05%	0.75%		19.58%	3.18%	0.33%	0.93%	6.04%		99.99%		0.30847804	1.98%
	#4	68.44%	1.36%	0.24%		23.85%	0.92%	0.86%	1.40%	2.93%		100.00%		0.12285115	2.76%
Gel-4	#2	70.97%	1.43%	1.17%		18.86%			2.90%	4.68%		100.01%		0.24814422	4.33%
	#2	71.17%	1.03%	1.00%		19.99%			2.85%	3.96%		100.00%		0.19809905	3.88%
	#2	68.36%	1.07%	0.88%		22.35%			3.03%	4.32%		100.01%		0.19328859	4.10%
	#2	70.09%	0.86%	0.89%		19.63%			3.39%	5.14%		100.00%		0.26184412	4.25%
Gel-5	#2	68.62%	0.55%	0.53%		17.13%		0.43%	4.41%	8.33%		100.00%		0.48628138	4.96%
	#2	70.51%	0.41%	0.49%		17.08%			4.10%	7.42%		100.01%		0.43442623	4.51%
	#2	70.10%	0.51%	0.36%		17.60%			4.24%	7.19%		100.00%		0.40852273	4.75%
	#2	69.58%	0.40%	0.55%		17.92%		0.32%	4.20%	7.03%		100.00%		0.39229911	4.60%
Gel-6	#2	70.49%	0.94%	0.78%		18.86%		0.38%	3.55%	5.00%		100.00%		0.26511135	4.49%
	#2	72.62%	1.04%	0.53%		17.49%	0.41%		3.15%	4.76%		100.00%		0.27215552	4.19%
	#2	65.40%	0.99%	0.93%		22.10%			4.16%	6.14%	0.29%	100.01%		0.27782805	5.15%
	#2	66.26%	0.99%	0.96%		21.40%	0.61%		3.72%	5.78%	0.28%	100.00%		0.27009346	4.71%
Average		68.20%	0.83%	0.56%		21.88%	1.75%	0.56%	2.49%	4.64%	0.29%	100.00%		0.22726292	3.32%
SD		2.22%	0.39%	0.30%		3.46%	0.81%	0.32%	1.23%	1.72%	0.01%	0.01%		0.1152634	1.21%

RCA in solution 0.7 Molarity with Li: Na+ K of 1:1 for 4 weeks – SEM Samples

	sample #	Atomic Concentrations										Total		Ca/Si	Na + K
		O	Na	Mg	AL	Si	P	S	K	Ca	Fe				
Gel-1	#1	68.77%	0.32%	0.51%		17.05%			2.47%	10.88%		100.00%		0.63812317	2.79%
	#1	69.90%	0.45%	0.29%		18.42%			2.77%	8.16%		99.99%		0.44299674	3.22%
	#1	69.54%	0.38%	0.26%		19.75%			3.30%	6.76%		99.99%		0.34227848	3.68%
	#1	69.52%	0.32%	0.45%		19.39%			3.04%	7.28%		100.00%		0.37545126	3.36%
Gel-2	#1	68.53%	0.33%	0.33%		20.21%			3.41%	7.19%		100.00%		0.35576447	3.74%
	#1	70.18%	0.15%	0.41%		18.50%			3.12%	7.66%		100.02%		0.41405405	3.27%
	#1	70.49%	0.25%	0.24%	0.21%	18.00%			2.86%	7.94%		99.99%		0.44111111	3.11%
Gel-3	#1	69.50%	0.50%			21.24%			3.27%	5.50%		100.01%		0.25894539	3.77%
	#1	70.44%	0.44%			18.54%			3.55%	7.03%		100.00%		0.37918015	3.99%
	#1	72.24%	0.39%	0.44%		15.59%			2.01%	8.83%		99.50%		0.56638871	2.40%
	#1	67.81%	0.16%			21.81%			3.34%	6.88%		100.00%		0.31545163	3.50%
Gel-4	#1	69.50%	0.21%	0.65%		21.17%			2.57%	5.90%		100.00%		0.27869627	2.78%
	#1	69.55%	0.05%	0.37%		19.48%			2.52%	8.03%		100.00%		0.41221766	2.57%
Average		69.69%	0.30%	0.40%	0.21%	19.17%			2.94%	7.54%		99.96%		0.40158916	3.24%
SD		1.07%	0.13%	0.13%		1.75%			0.45%	1.35%		0.14%		0.10658515	0.50%

RCA in solution 0.7 Molarity without Lithium for 4 weeks– SEM Samples

Spectrum #	Atomic concentrations									Na + K
	O	Na	Mg	Al	Si	P	S	K	Ca	
Spec-1	70.13	0.52	2.14	1.2	13.73	0.34	0.94	0.34	10.65	0.86
Spec-2	70.81	0.69	1.88	0.65	13.99	0.42	0.71	0.44	10.41	1.13
Spec-3	70.26	0.34	1.61	1.38	13.01	0.58	1.27	0.28	11.27	0.62
Spec-4	72.1	0.47	1.64	1.41	12.66	0.26	1.15	0.32	9.99	0.79
Spec-1	70.58	0.48	1.24	1.47	11.14		1.94	0.37	12.78	0.85
Spec-2	71.74	0.64	0.73	1.13	11.75		1.55	0.38	12.08	1.02
Spec-3	71.76	0.6	2.52	2.01	10.35		1.48	0.37	10.91	0.97
Spec-4	77.72	0.36	0.72	6.42	2.26		0.4	0.15	11.98	0.51
Spec-1	70.29	0.52	2.15	1.2	13.85		0.96	0.34	10.68	0.86
Spec-2	71.01	0.69	1.9	0.65	14.14		0.73	0.44	10.44	1.13
Spec-4	72.22	0.48	1.65	1.41	12.74		1.16	0.33	10.01	0.81
Average		0.53			11.78			0.34	11.02	0.87
SD		0.12			3.39			0.08	0.91	0.19

Paste of RCA Stock – SEM Samples

Spectrum #	Atomic concentrations									Na + K
	O	Na	Mg	Al	Si	P	S	K	Ca	
Spec-1	69.16	0.76	1.98	1.77	14.7	0.21	0.51	0.49	10.42	1.25
Spec-2	68.89	0.62	2.79	1.38	15.8	0.05	0.58	0.57	9.32	1.19
Spec-3	68.38	0.7	1.8	1.73	15.28	0.27	0.31	0.33	11.19	1.03
Spec-4	71.34	0.71	2.77	1.17	14.04	0.24	0.28	0.34	9.11	1.05
Spec-5	70.84	1.18	1.14	3.75	9.75	0.15	0.68	0.63	11.9	1.81
Spec-3	70.72	0.61	1.42	1.25	13.89	0.27	0.42	0.28	11.13	0.89
Spec-4	65.12	0.13	2.19	3.62	8.07	0.15	2.66	0.28	17.77	0.41
Spec-2	69.48	0.52	3.58	1.87	10.24	0.16	0.99	0.28	12.89	0.8
Average		0.65			12.72			0.40	11.72	1.05
SD		0.29			2.92			0.14	2.75	0.40

Paste of RCA in concrete prism – SEM Samples

Spectrum #	Atomic concentrations										Na + K
	O	Na	Mg	Al	Si	P	S	K	Ca	Fe	
Spec-1	72.62	0.03	2.43	1.24	7.93	0.67	0.8	0.13	13.82	0.33	0.16
Spec-2	71.43	-0.02	0.9	1.27	7.84	0.89	1.09	0.1	16.24	0.24	0.08
Spec-3	70.54	0.02	1.02	3.15	3.4	1.55	0.63	0.03	19.39	0.26	0.05
Spec-4	72.66	-0.03	1.14	2.23	5.82	1.74	1.09	0.14	14.95	0.24	0.11
Spec-1	70.51	0.03	0.63	1.76	7.46	1.51	1.46	0.02	16.24	0.39	0.05
Spec-2	64.07	0.37	0.92	1.57	16.09	1.79	2.1	0.27	12.43	0.38	0.64
Spec-3	64.74	0.21	2.04	2.25	17.89	0.84	2.39	0.06	9.01	0.57	0.27
Spec-4	69.36	0.09	1.01	2.04	10.84	0.85	3.44	0.11	11.87	0.39	0.2
Average		0.09			9.66			0.11	14.24	0.35	0.20
SD		13.70%			5.01			0.08	3.19	0.11	0.20

Paste of RCA in Solution 0.7 Molarity with Li: Na+K of 1:1 for 4 weeks – SEM Samples

Spectrum #	Atomic Concentrations										Na + K
	O	Na	Mg	Al	Si	P	S	K	Ca	Fe	
Spec-1	75.99	0.34	1.48	0.92	3.23	0.23	0.3	0.37	16.21	0.94	0.71
Spec-2	72.34	0.13	2.04	2.15	5.95		0.43	0.09	16.49	0.38	0.22
Spec-3	70.24	0.03	1.22	3.17	9.24	0.59	0.64	0.14	14.15	0.58	0.17
Spec-4	70.39	0.24	2.53	1.81	5.74		0.37	0.15	18.19	0.58	0.39
Spec-1	69.14	0.04	2.66	2.66	7.33	0.44	0.7	0.14	15.32	1.57	0.18
Spec-2	68.74	0.18	2.17	1.04	11.45	0.46		0.12	15.4	0.45	0.3
Spec-3	71.8	0.06	1.55	1.31	8.74		0.63	0.12	15.33	0.46	0.18
Spec-4	63.98	0.18	0.5	0.4	2.83		0.64	0.1	30.97	0.4	0.28
Average		0.15			6.81			0.15	17.76	0.67	0.30
sd		0.11						0.09	5.47	0.41	0.18

Paste of RCA in Solution 0.7 Molarity without Lithium for 4 weeks - SEM Samples

Appendix C: Backscattered Electron Images for RCA

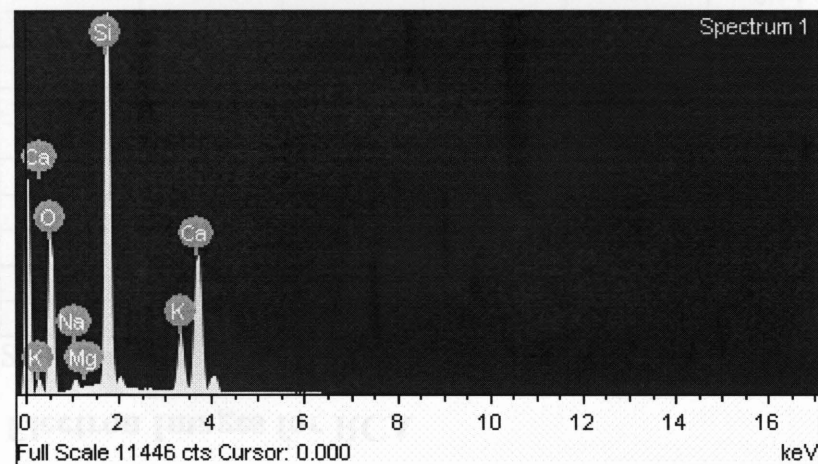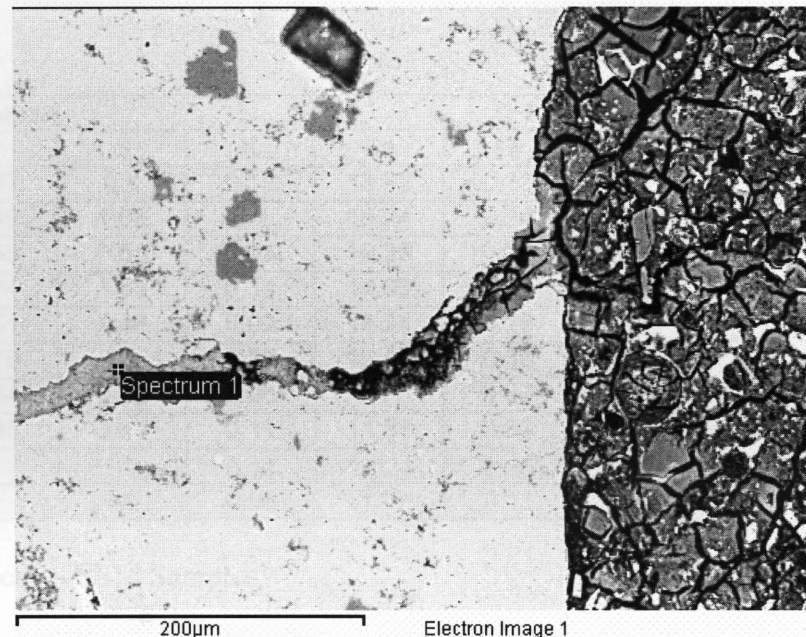# RCA aggregate stock
Gel-1

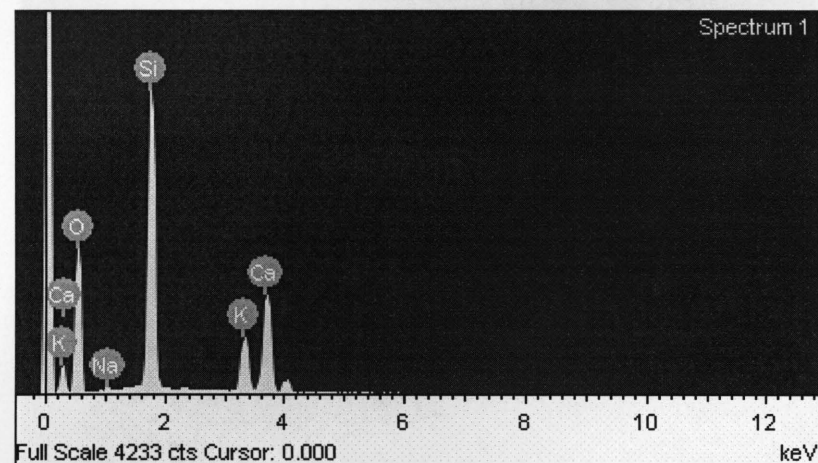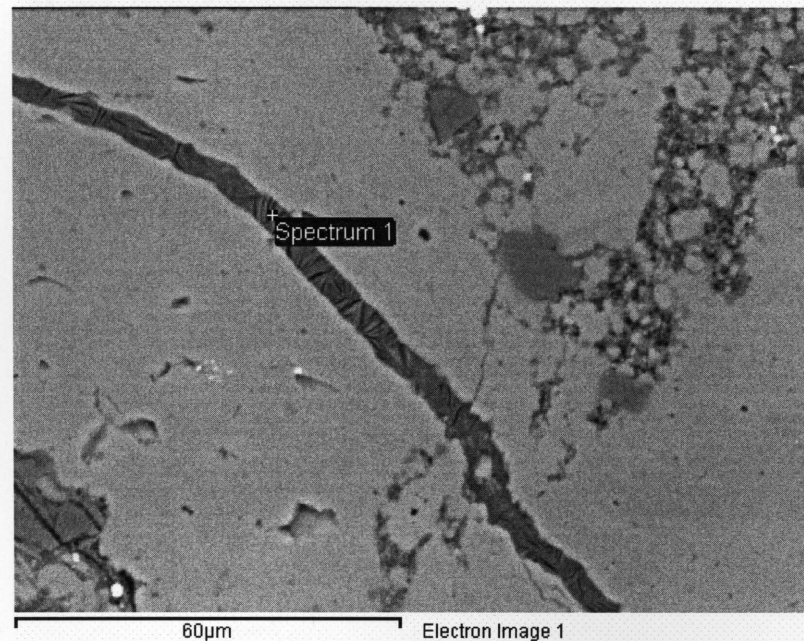Spectrum processing:
No peaks omitted

Processing option: All elements analyzed (Normalised)
Number of iterations = 5

Standard:
O   SiO2   1-Jun-1999 12:00 AM
Na   Albite   1-Jun-1999 12:00 AM
Mg   MgO   1-Jun-1999 12:00 AM
Si   SiO2   1-Jun-1999 12:00 AM
K   MAD-10 Feldspar   1-Jun-1999 12:00 AM
Ca   Wollastonite   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	54.37	70.43
Na K	1.04	0.94
Mg K	0.20	0.17
Si K	24.61	18.16
K K	5.39	2.86
Ca K	14.39	7.44
Totals	100.00	

200µm   Electron Image 1

Spectrum 1

Full Scale 11446 cts Cursor: 0.000   keV

RCA aggregate stock
Gel-2

Spectrum processing:
Peak possibly omitted: 2.308 keV

Processing option: All elements analyzed (Normalised)
Number of iterations = 6

Standard:
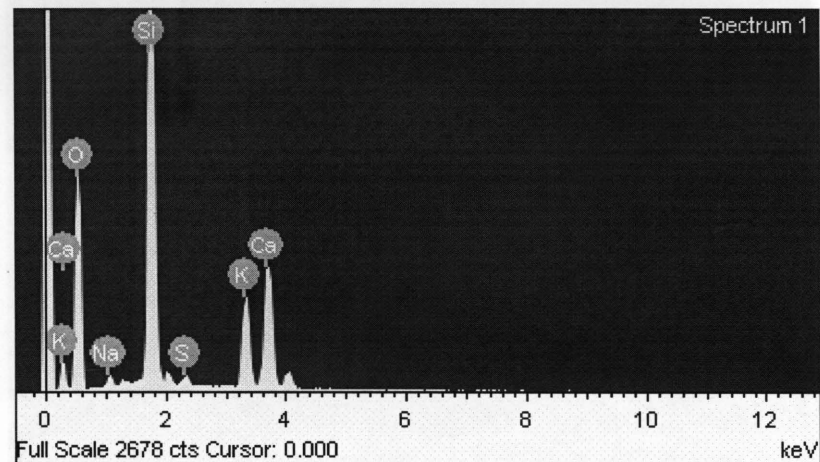O   SiO2   1-Jun-1999 12:00 AM
Na   Albite   1-Jun-1999 12:00 AM
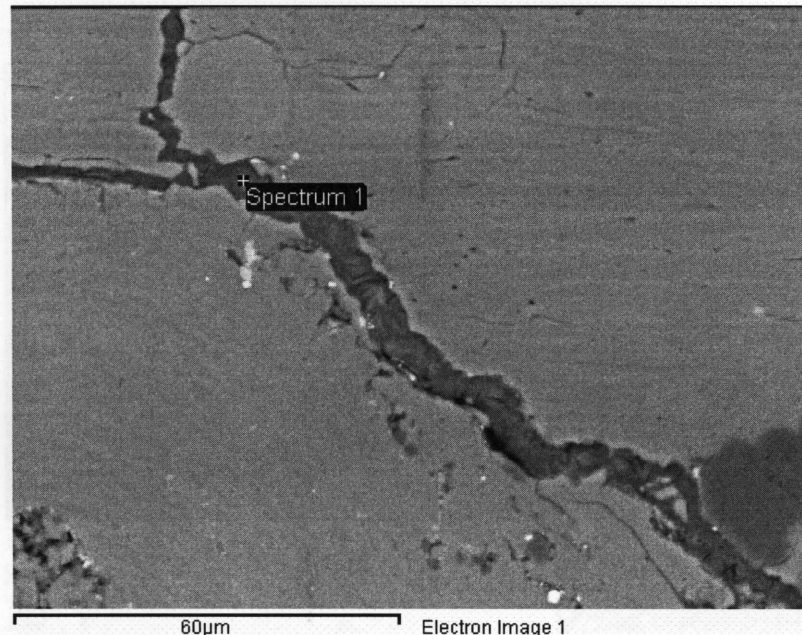Si   SiO2   1-Jun-1999 12:00 AM
K   MAD-10 Feldspar   1-Jun-1999 12:00 AM
Ca   Wollastonite   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	58.13	73.68
Na K	0.35	0.31
Si K	22.80	16.46
K K	6.33	3.28
Ca K	12.40	6.27
Totals	100.00	

60µm   Electron Image 1

Spectrum 1

Full Scale 4233 cts Cursor: 0.000   keV

110
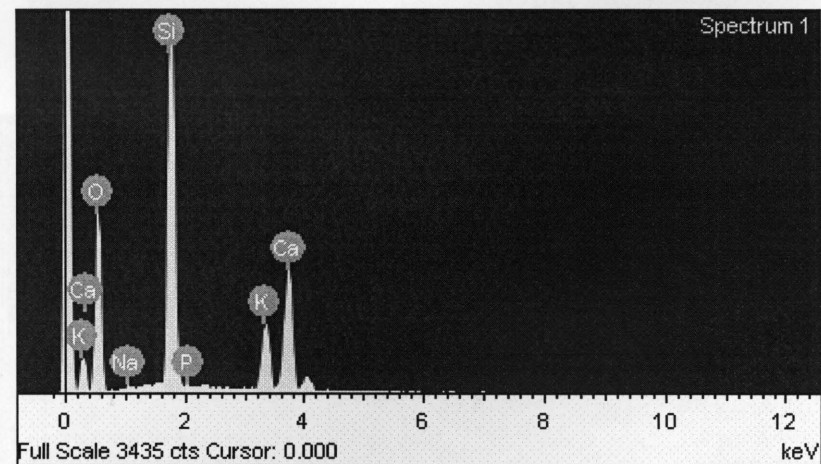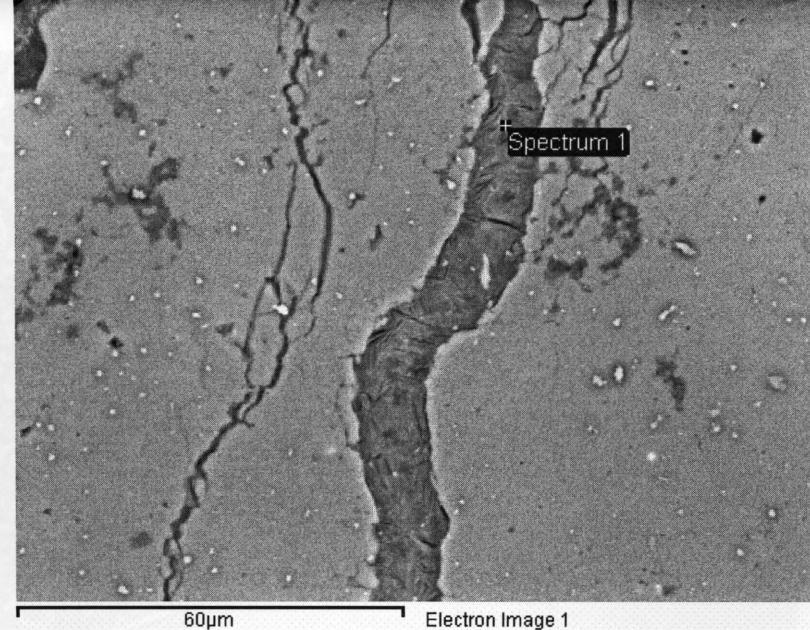
RCA aggregate stock
Gel-3

Spectrum processing:
No peaks omitted

Processing option: All elements analyzed (Normalised)
Number of iterations = 5

Standard:
O   SiO2   1-Jun-1999 12:00 AM
Na   Albite   1-Jun-1999 12:00 AM
Si   SiO2   1-Jun-1999 12:00 AM
S   FeS2   1-Jun-1999 12:00 AM
K   MAD-10 Feldspar   1-Jun-1999 12:00 AM
Ca   Wollastonite   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	56.25	71.85
Na K	1.03	0.92
Si K	24.28	17.66
S K	0.65	0.41
K K	6.93	3.62
Ca K	10.86	5.54
Totals	100.00	

60µm   Electron Image 1

Spectrum 1

Full Scale 2678 cts Cursor: 0.000   keV

111

RCA aggregate stock
Gel-4
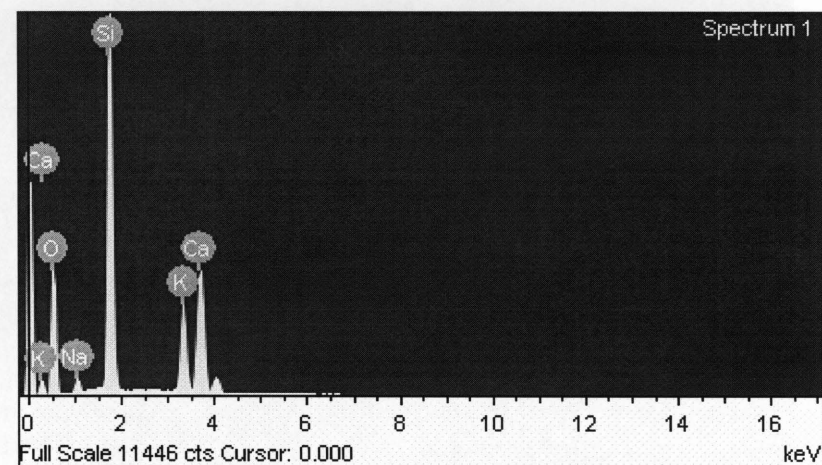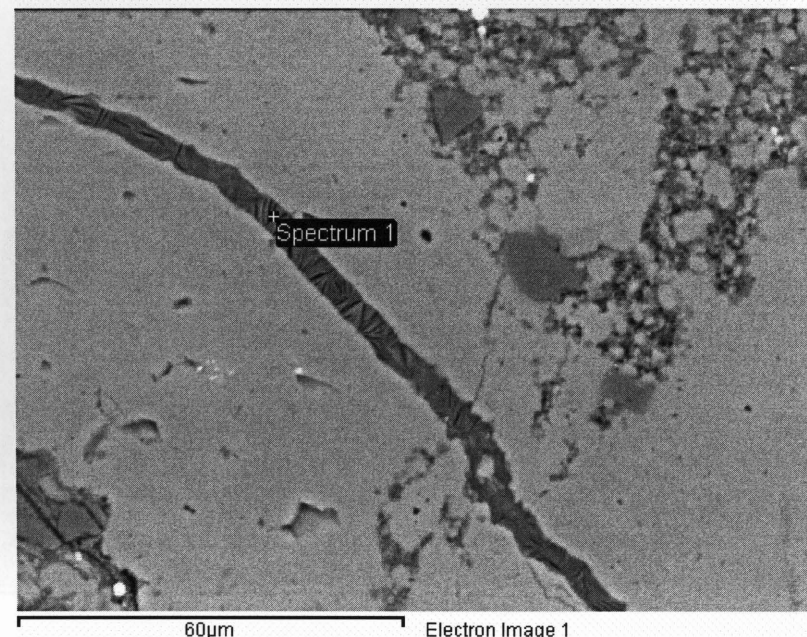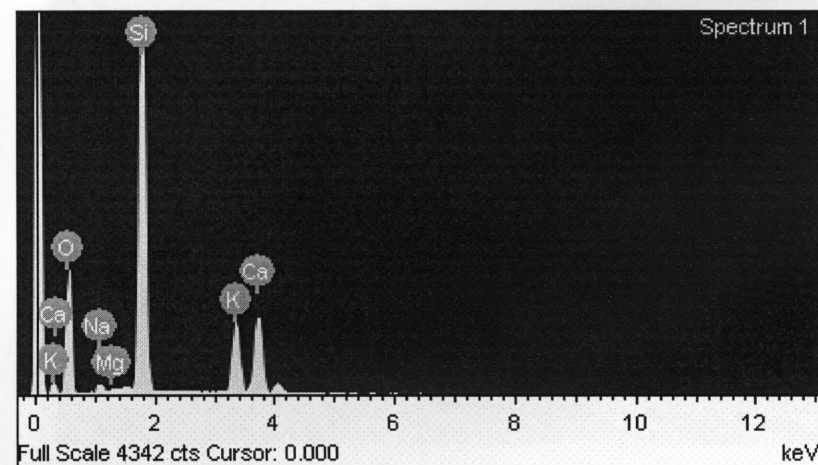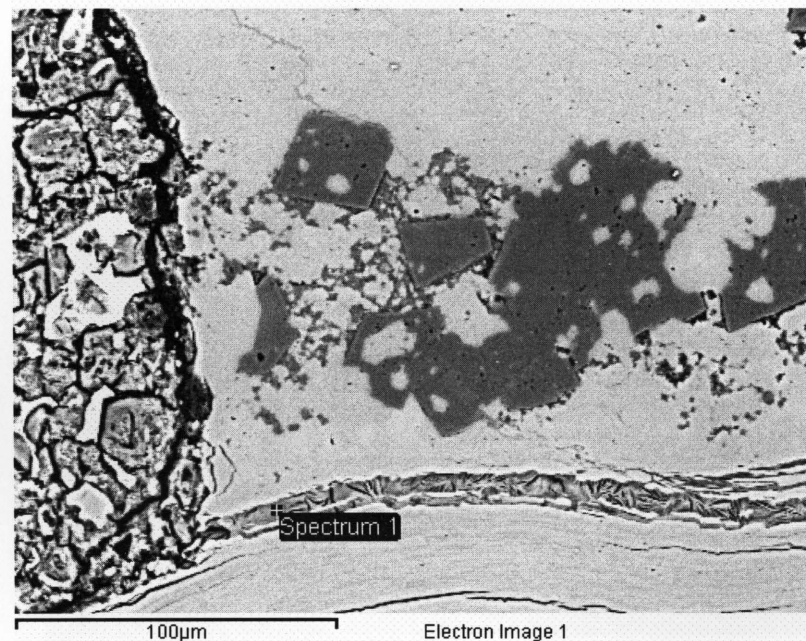
Spectrum processing:
No peaks omitted

Processing option: All elements analyzed (Normalised)
Number of iterations = 6

Standard:
O   SiO2   1-Jun-1999 12:00 AM
Na   Albite   1-Jun-1999 12:00 AM
Si   SiO2   1-Jun-1999 12:00 AM
P   GaP   1-Jun-1999 12:00 AM
K   MAD-10 Feldspar   1-Jun-1999 12:00 AM
Ca   Wollastonite   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	58.04	73.61
Na K	0.35	0.30
Si K	22.71	16.40
P K	0.21	0.14
K K	6.32	3.28
Ca K	12.37	6.26
Totals	100.00	

Electron Image 1

RCA aggregate in concrete prism
Gel-1

Spectrum processing:
Peak possibly omitted: 10.500 keV

Processing option: All elements analyzed (Normalised)
Number of iterations = 5

Standard:
O   SiO2   1-Jun-1999 12:00 AM
Na   Albite   1-Jun-1999 12:00 AM
Si   SiO2   1-Jun-1999 12:00 AM
K   MAD-10 Feldspar   1-Jun-1999 12:00 AM
Ca   Wollastonite   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	50.94	67.61
Na K	1.52	1.41
Si K	25.11	18.99
K K	8.76	4.76
Ca K	13.66	7.24
Totals	100.00	

60µm   Electron Image 1

Spectrum 1

Full Scale 11446 cts Cursor: 0.000   keV

113

RCA aggregate in concrete prism
Gel-2

Spectrum processing:
No peaks omitted

Processing option: All elements analyzed (Normalised)
Number of iterations = 4

Standard:
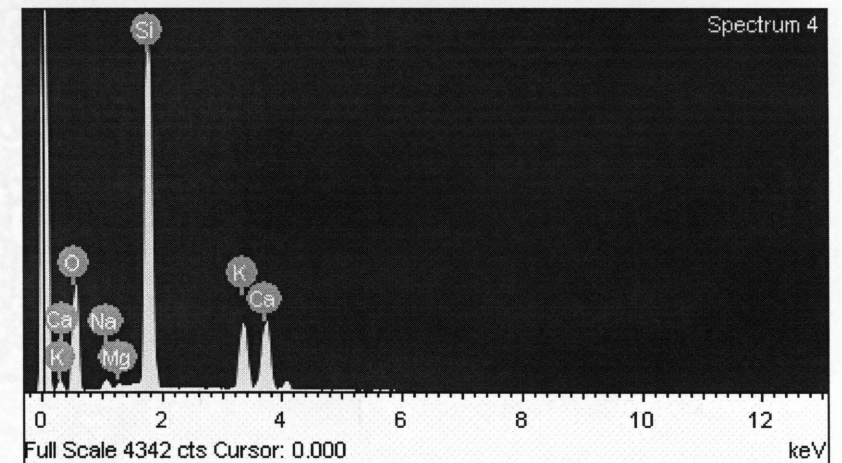O   SiO2   1-Jun-1999 12:00 AM
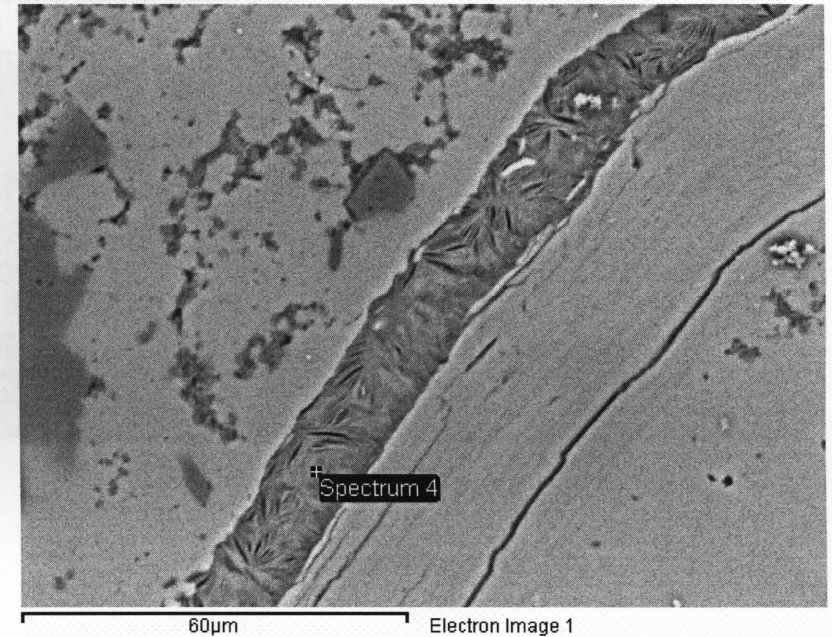Na   Albite   1-Jun-1999 12:00 AM
Mg   MgO   1-Jun-1999 12:00 AM
Si   SiO2   1-Jun-1999 12:00 AM
K   MAD-10 Feldspar   1-Jun-1999 12:00 AM
Ca   Wollastonite   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	53.25	69.18
Na K	1.01	0.92
Mg K	0.11	0.09
Si K	27.29	20.19
K K	8.34	4.43
Ca K	10.01	5.19
Totals	100.00	

100µm   Electron Image 1

Spectrum 1

Full Scale 4342 cts Cursor: 0.000   keV

114

RCA aggregate in concrete prism
Gel-3

Spectrum processing:
No peaks omitted

Processing option: All elements analyzed (Normalised)
Number of iterations = 5

Standard:
O   SiO2   1-Jun-1999 12:00 AM
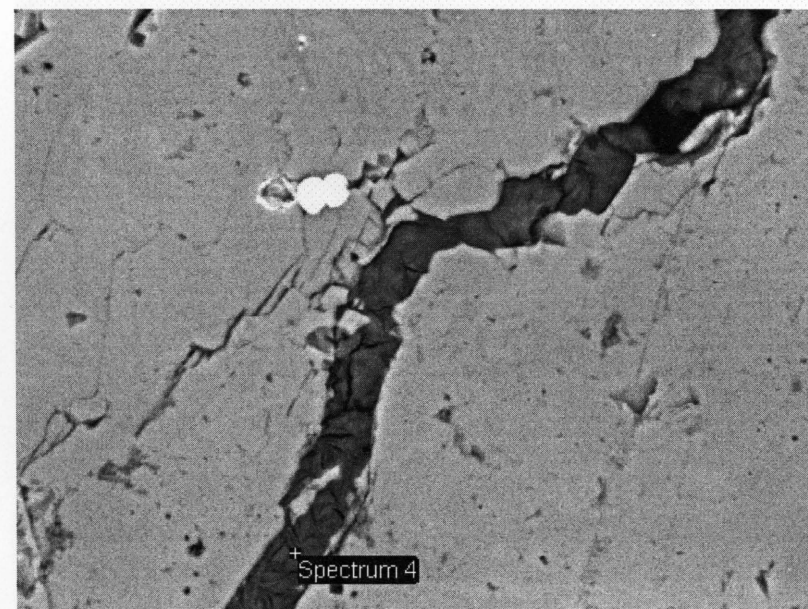Na   Albite   1-Jun-1999 12:00 AM
Mg   MgO   1-Jun-1999 12:00 AM
Si   SiO2   1-Jun-1999 12:00 AM
K   MAD-10 Feldspar   1-Jun-1999 12:00 AM
Ca   Wollastonite   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	51.03	67.12
Na K	1.21	1.10
Mg K	0.30	0.26
Si K	28.87	21.64
K K	8.64	4.65
Ca K	9.95	5.22
Totals	100.00	

60µm   Electron Image 1

Spectrum 4

Full Scale 4342 cts Cursor: 0.000   keV

RCA aggregate in Solution 0.7 Molarity
Li: Na+k of 1:1
Gel-1

Spectrum processing:
No peaks omitted

Processing option: All elements analyzed (Normalised)
Number of iterations = 5

Standard:
O   SiO2   1-Jun-1999 12:00 AM
Na   Albite   1-Jun-1999 12:00 AM
Si   SiO2   1-Jun-1999 12:00 AM
P   GaP   1-Jun-1999 12:00 AM
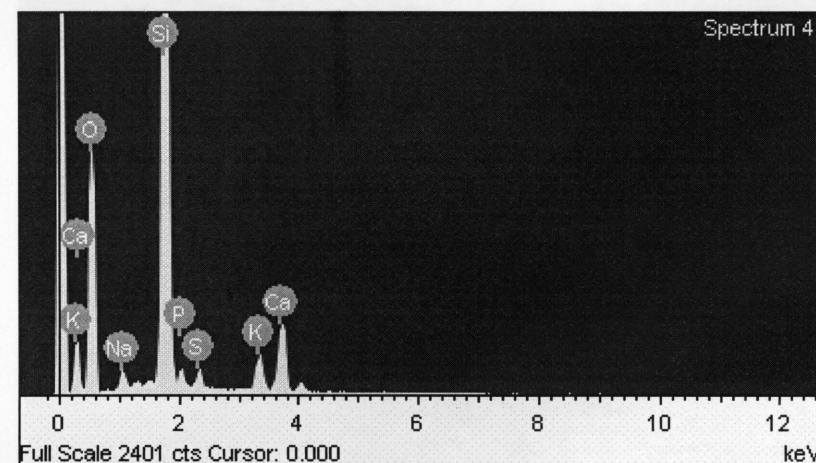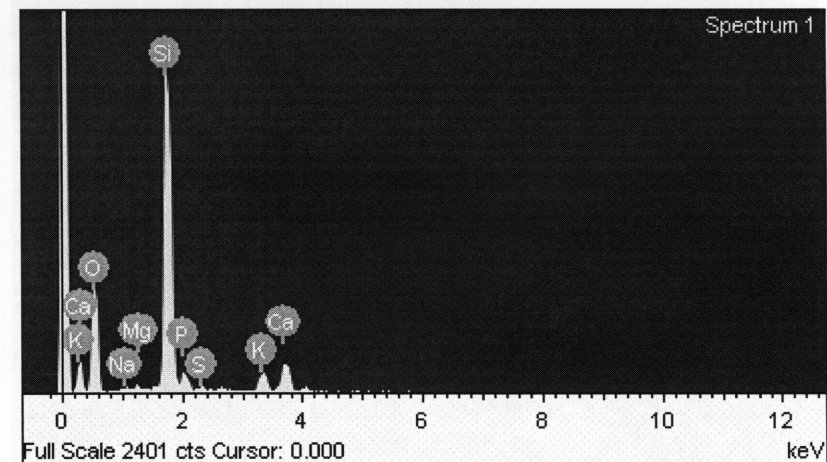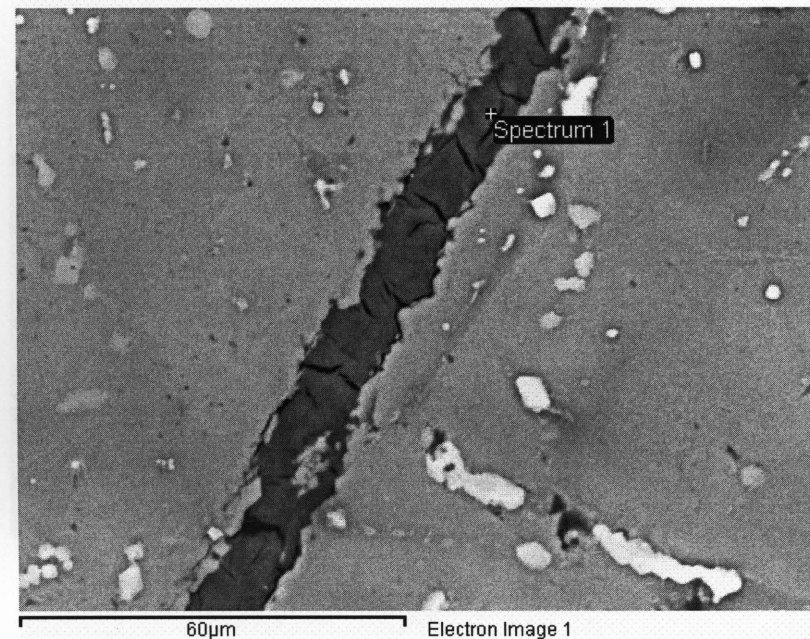S   FeS2   1-Jun-1999 12:00 AM
K   MAD-10 Feldspar   1-Jun-1999 12:00 AM
Ca   Wollastonite   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	54.10	68.60
Na K	1.61	1.42
Si K	33.03	23.86
P K	1.40	0.92
S K	1.37	0.87
K K	2.70	1.40
Ca K	5.80	2.93
Totals	100.00	

60µm   Electron Image 1

Spectrum 4

Full Scale 2401 cts Cursor: 0.000   keV

116

RCA aggregate in Solution 0.7 Molarity
Li: Na+k of 1:1
Gel-2

Spectrum processing:
No peaks omitted

Processing option: All elements analyzed (Normalised)
Number of iterations = 5

Standard:
O   SiO2   1-Jun-1999 12:00 AM
Na   Albite   1-Jun-1999 12:00 AM
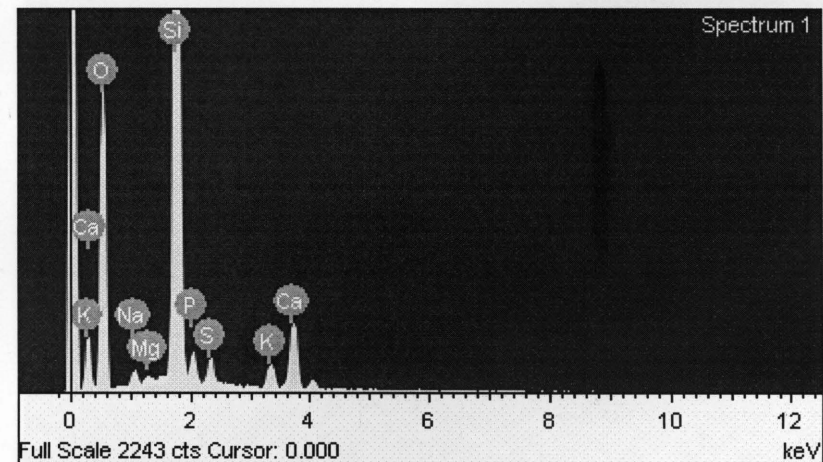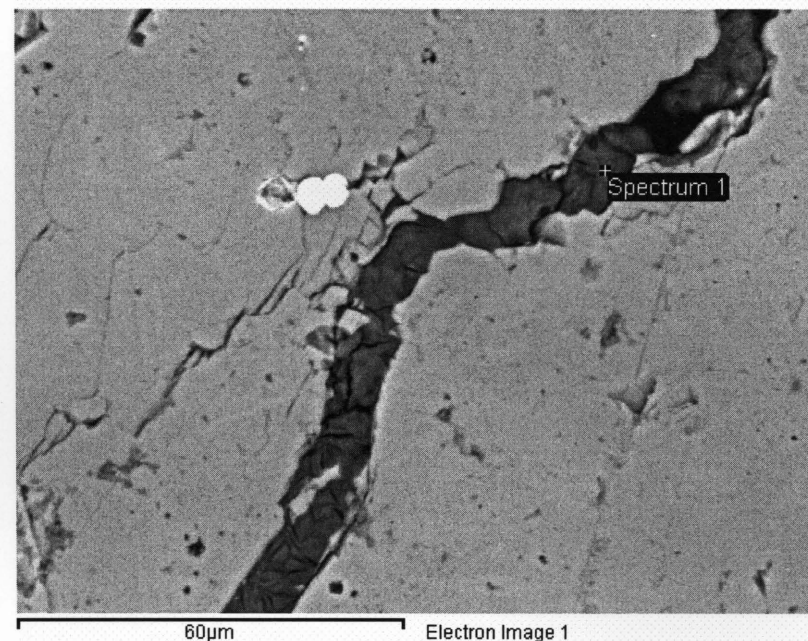Mg   MgO   1-Jun-1999 12:00 AM
Si   SiO2   1-Jun-1999 12:00 AM
P   GaP   1-Jun-1999 12:00 AM
S   FeS2   1-Jun-1999 12:00 AM
K   MAD-10 Feldspar   1-Jun-1999 12:00 AM
Ca   Wollastonite   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	52.33	67.19
Na K	0.25	0.23
Mg K	0.44	0.37
Si K	34.48	25.22
P K	3.29	2.18
S K	0.38	0.24
K K	3.34	1.75
Ca K	5.49	2.81
Totals	100.00	

Electron Image 1

RCA aggregate in solution 0.7 Molarity
Li: Na+k of 1:1
Gel-3

Spectrum processing:
No peaks omitted

Processing option: All elements analyzed (Normalised)
Number of iterations = 5

Standard:
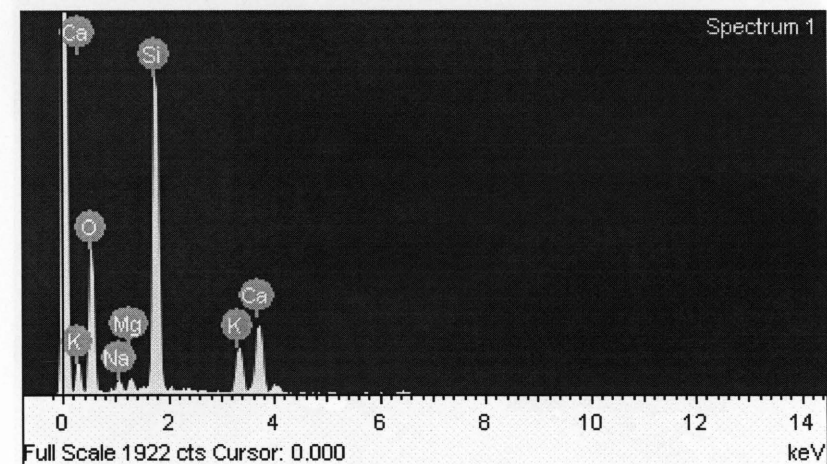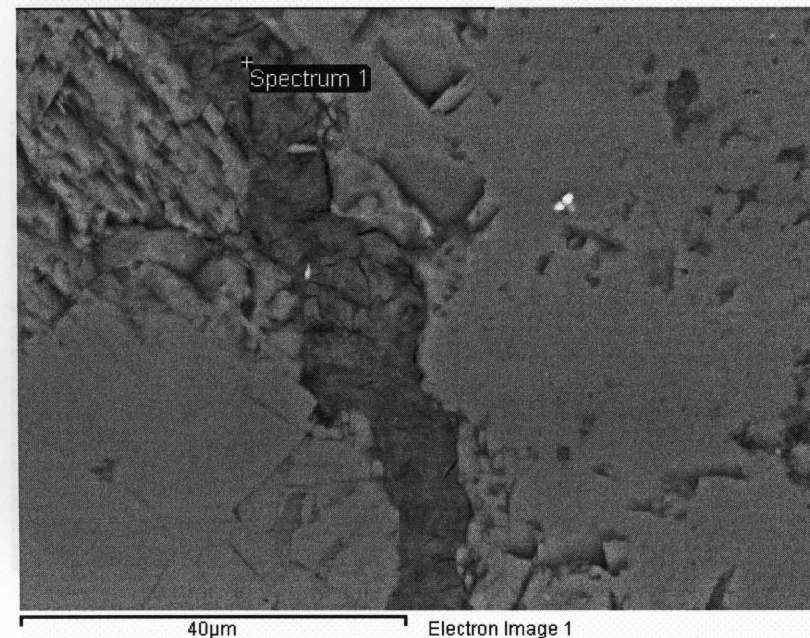O   SiO2   1-Jun-1999 12:00 AM
Na   Albite   1-Jun-1999 12:00 AM
Mg   MgO   1-Jun-1999 12:00 AM
Si   SiO2   1-Jun-1999 12:00 AM
P   GaP   1-Jun-1999 12:00 AM
S   FeS2   1-Jun-1999 12:00 AM
K   MAD-10 Feldspar   1-Jun-1999 12:00 AM
Ca   Wollastonite   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	54.74	69.00
Na K	1.15	1.00
Mg K	0.34	0.28
Si K	33.08	23.75
P K	2.32	1.51
S K	1.66	1.04
K K	1.78	0.92
Ca K	4.93	2.48
Totals	100.00	

60µm   Electron Image 1

Spectrum 1

Full Scale 2243 cts Cursor: 0.000   keV

RCA aggregate in solution 0.7 Molarity
Li: Na+K of 1:1
Gel-4

Spectrum processing:
No peaks omitted

Processing option: All elements analyzed (Normalised)
Number of iterations = 5

Standard :
O   SiO2   1-Jun-1999 12:00 AM
Na   Albite   1-Jun-1999 12:00 AM
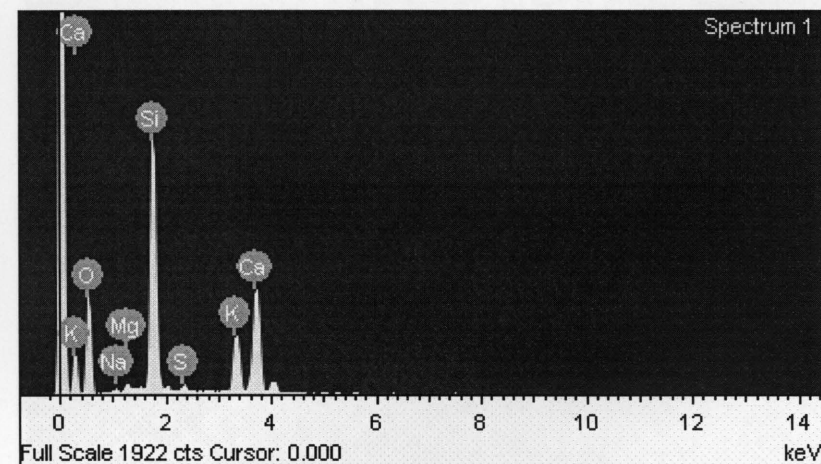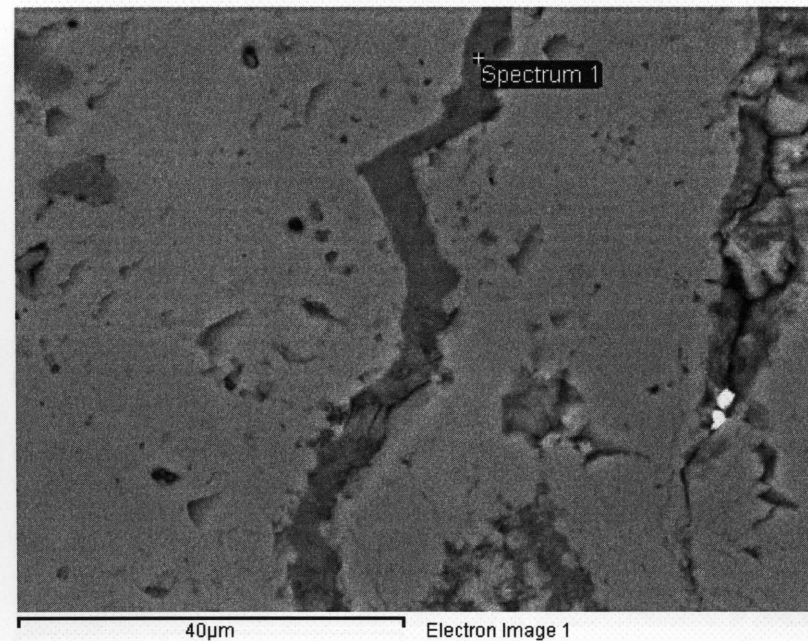Mg   MgO   1-Jun-1999 12:00 AM
Si   SiO2   1-Jun-1999 12:00 AM
K   MAD-10 Feldspar   1-Jun-1999 12:00 AM
Ca   Wollastonite   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	56.01	70.97
Na K	1.62	1.43
Mg K	1.40	1.17
Si K	26.12	18.86
K K	5.60	2.90
Ca K	9.25	4.68
Totals	100.00	

40µm   Electron Image 1

Spectrum 1

Full Scale 1922 cts Cursor: 0.000   keV

RCA aggregate in solution 0.7 Molarity
Li: Na+K of 1:1
Gel-5

Spectrum processing:
No peaks omitted

Processing option: All elements analyzed (Normalised)
Number of iterations = 4

Standard:
O   SiO2   1-Jun-1999 12:00 AM
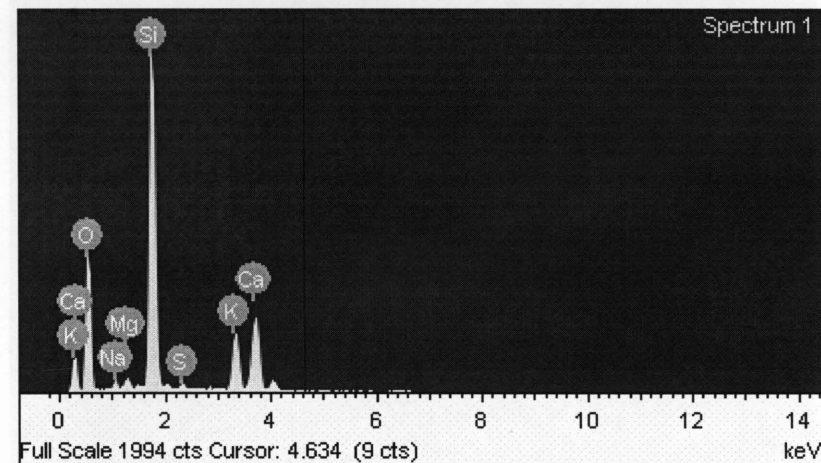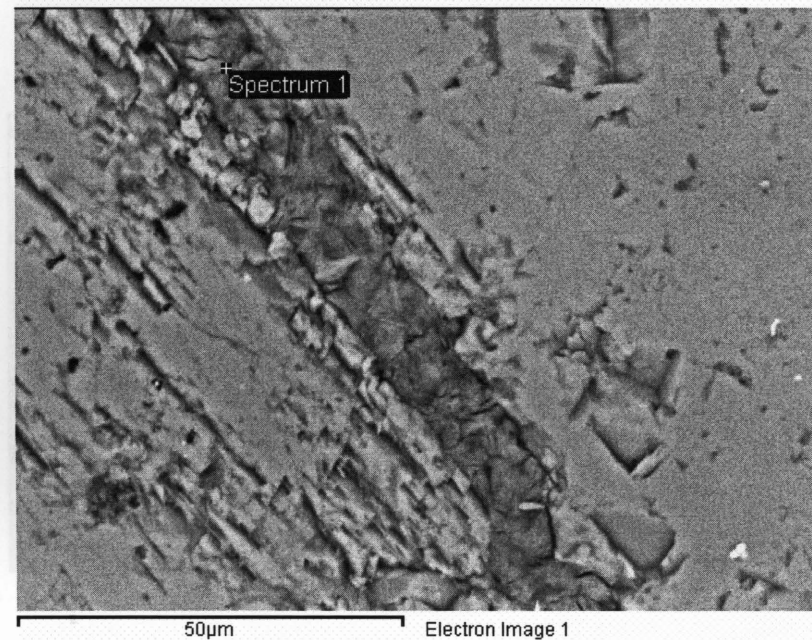Na   Albite   1-Jun-1999 12:00 AM
Mg   MgO   1-Jun-1999 12:00 AM
Si   SiO2   1-Jun-1999 12:00 AM
S   FeS2   1-Jun-1999 12:00 AM
K   MAD-10 Feldspar   1-Jun-1999 12:00 AM
Ca   Wollastonite   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	51.68	68.62
Na K	0.60	0.55
Mg K	0.61	0.53
Si K	22.64	17.13
S K	0.65	0.43
K K	8.12	4.41
Ca K	15.71	8.33
Totals	100.00	

40µm   Electron Image 1

RCA aggregate in solution 0.7 Molarity
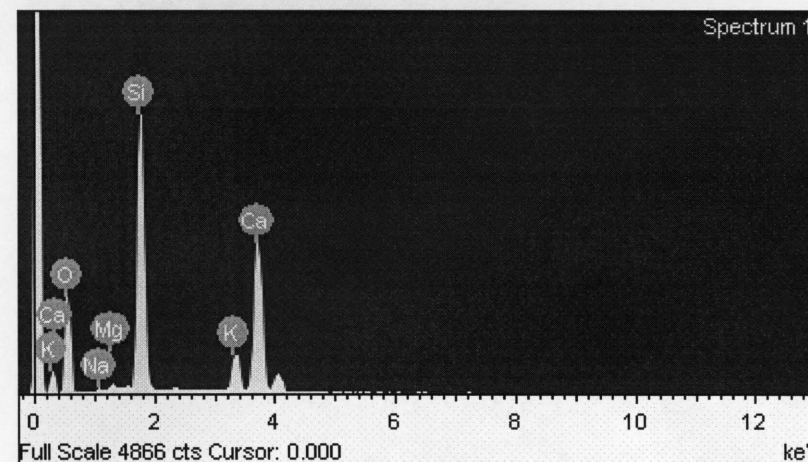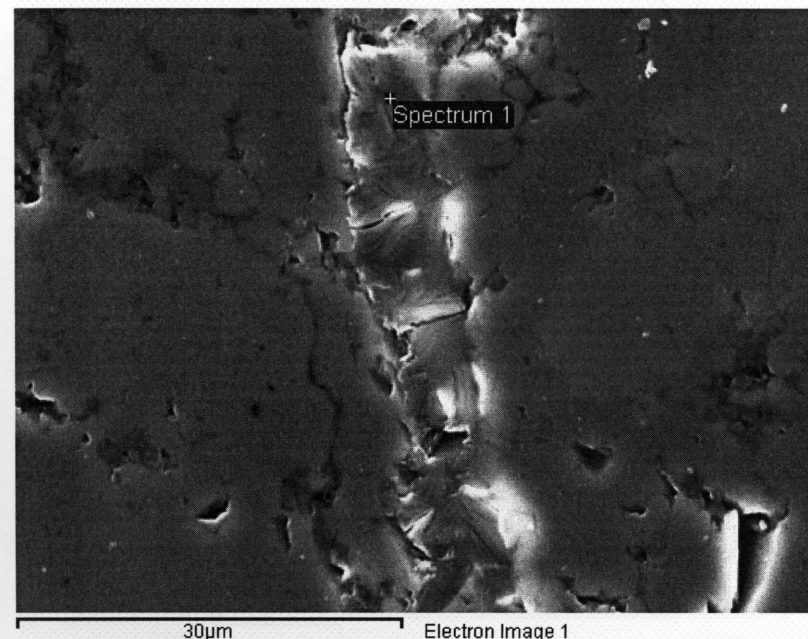Li: Na+K of 1:1
Gel-6

Spectrum processing:
Peak possibly omitted: 6.400 keV

Processing option: All elements analyzed (Normalised)
Number of iterations = 5

Standard:
O   SiO2   1-Jun-1999 12:00 AM
Na   Albite   1-Jun-1999 12:00 AM
Mg   MgO   1-Jun-1999 12:00 AM
Si   SiO2   1-Jun-1999 12:00 AM
S   FeS2   1-Jun-1999 12:00 AM
K   MAD-10 Feldspar   1-Jun-1999 12:00 AM
Ca   Wollastonite   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	55.02	70.49
Na K	1.06	0.94
Mg K	0.92	0.78
Si K	25.85	18.86
S K	0.59	0.38
K K	6.78	3.55
Ca K	9.77	5.00
Totals	100.00	

50µm   Electron Image 1

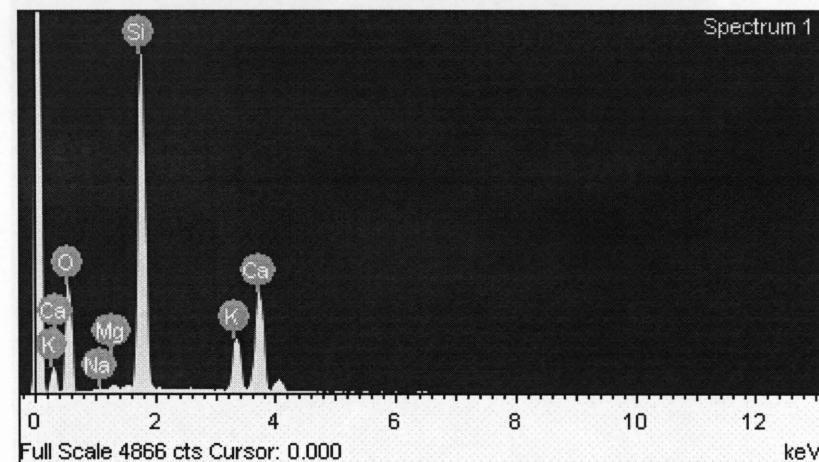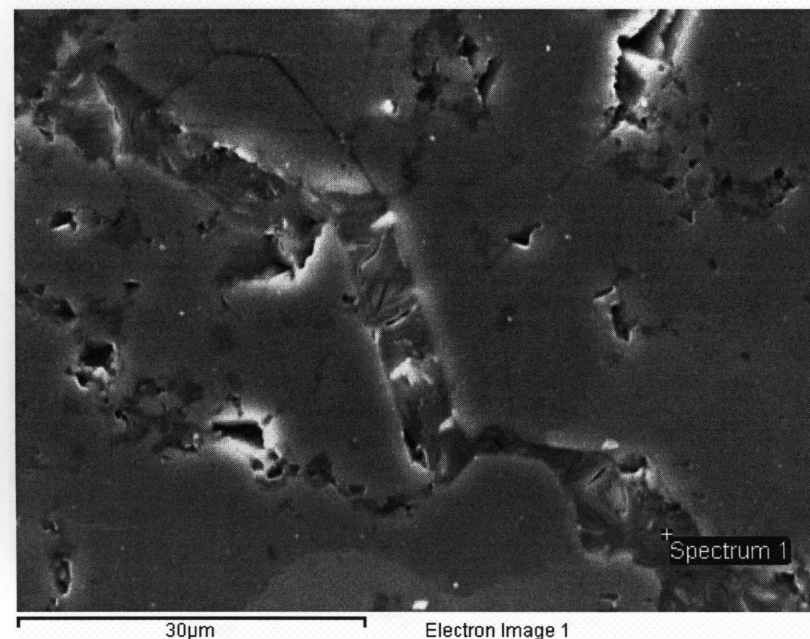## RCA aggregate in solution 0.7 Molarity without Lithium Gel-1

Spectrum processing:
Peak possibly omitted: 7.200 keV

Processing option: All elements analyzed (Normalised)
Number of iterations = 5

Standard:
O   SiO2   1-Jun-1999 12:00 AM
Na   Albite   1-Jun-1999 12:00 AM
Mg   MgO   1-Jun-1999 12:00 AM
Si   SiO2   1-Jun-1999 12:00 AM
K   MAD-10 Feldspar   1-Jun-1999 12:00 AM
Ca   Wollastonite   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	51.61	68.77
Na K	0.34	0.32
Mg K	0.58	0.51
Si K	22.47	17.05
K K	4.53	2.47
Ca K	20.46	10.88
Totals	100.00	

30μm   Electron Image 1

Spectrum 1

Full Scale 4866 cts Cursor: 0.000   keV

RCA aggregate in solution 0.7 Molarity without Lithium
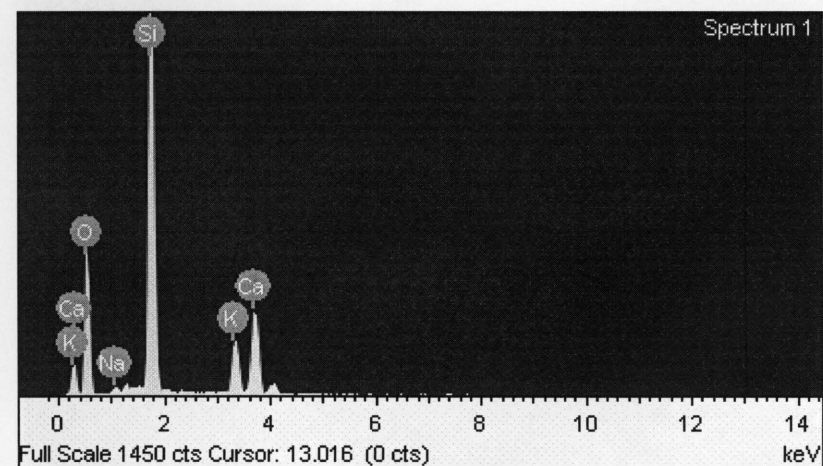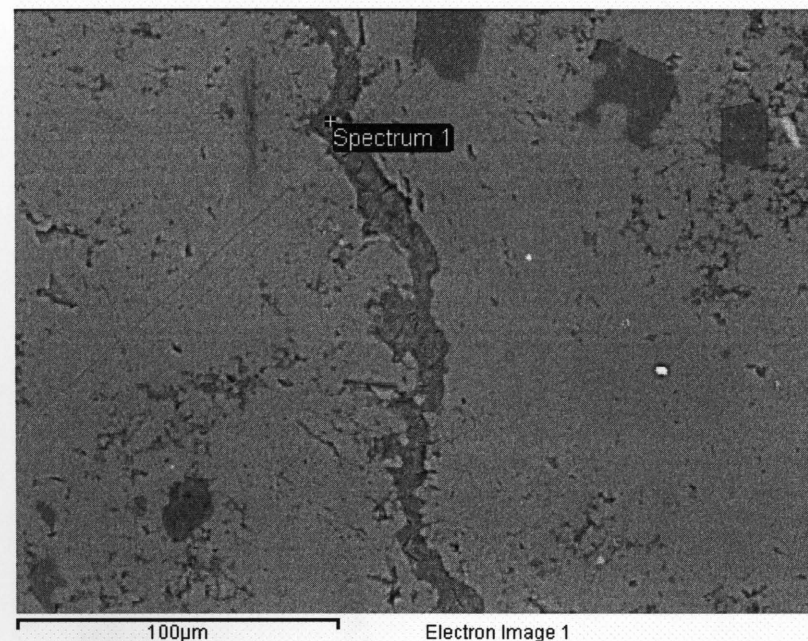## Gel-2

Spectrum processing:
No peaks omitted

Processing option: All elements analyzed (Normalised)
Number of iterations = 4

Standard:
O   SiO2   1-Jun-1999 12:00 AM
Na   Albite   1-Jun-1999 12:00 AM
Mg   MgO   1-Jun-1999 12:00 AM
Si   SiO2   1-Jun-1999 12:00 AM
K   MAD-10 Feldspar   1-Jun-1999 12:00 AM
Ca   Wollastonite   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	52.18	68.53
Na K	0.36	0.33
Mg K	0.38	0.33
Si K	27.01	20.21
K K	6.35	3.41
Ca K	13.72	7.19
Totals	100.00	

30µm   Electron Image 1

Spectrum 1

Full Scale 4866 cts Cursor: 0.000   keV

RCA aggregate in solution 0.7 Molarity without Lithium Gel-3

Spectrum processing:
No peaks omitted

Processing option: All elements analyzed (Normalised)
Number of iterations = 4

Standard:
O   SiO2   1-Jun-1999 12:00 AM
Na   Albite   1-Jun-1999 12:00 AM
Si   SiO2   1-Jun-1999 12:00 AM
K   MAD-10 Feldspar   1-Jun-1999 12:00 AM
Ca   Wollastonite   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	53.77	69.50
Na K	0.55	0.50
Si K	28.84	21.24
K K	6.19	3.27
Ca K	10.65	5.50
Totals	100.00	

100μm   Electron Image 1

Spectrum 1

Full Scale 1450 cts Cursor: 13.016 (0 cts)

RCA aggregate in solution 0.7 Molarity without Lithium Gel-4

Spectrum processing:
No peaks omitted

Processing option: All elements analyzed (Normalised)
Number of iterations = 4

Standard:
O   SiO2   1-Jun-1999 12:00 AM
Na   Albite   1-Jun-1999 12:00 AM
Mg   MgO   1-Jun-1999 12:00 AM
Si   SiO2   1-Jun-1999 12:00 AM
K   MAD-10 Feldspar   1-Jun-1999 12:00 AM
Ca   Wollastonite   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	53.87	69.50
Na K	0.23	0.21
Mg K	0.77	0.65
Si K	28.80	21.17
K K	4.88	2.57
Ca K	11.45	5.90
Totals	100.00	

60µm   Electron Image 1

Spectrum 1

Full Scale 1770 cts Cursor: 0.000   keV
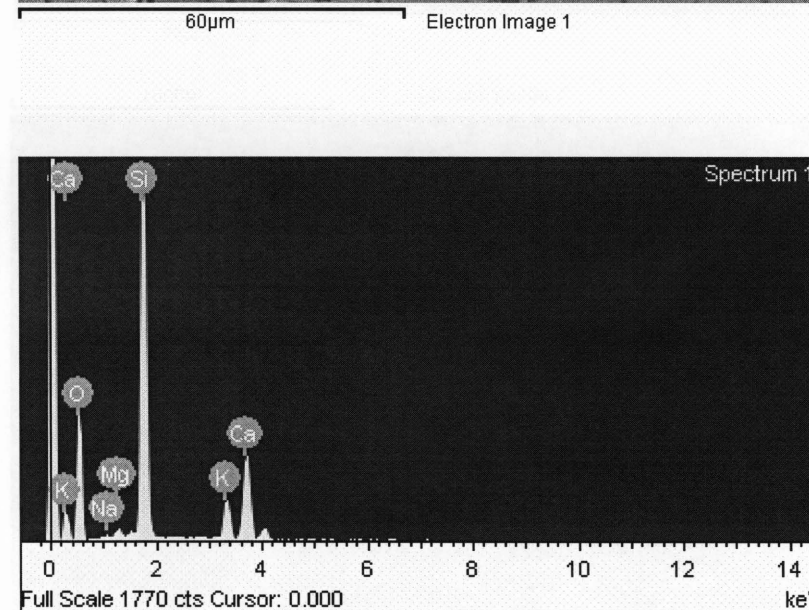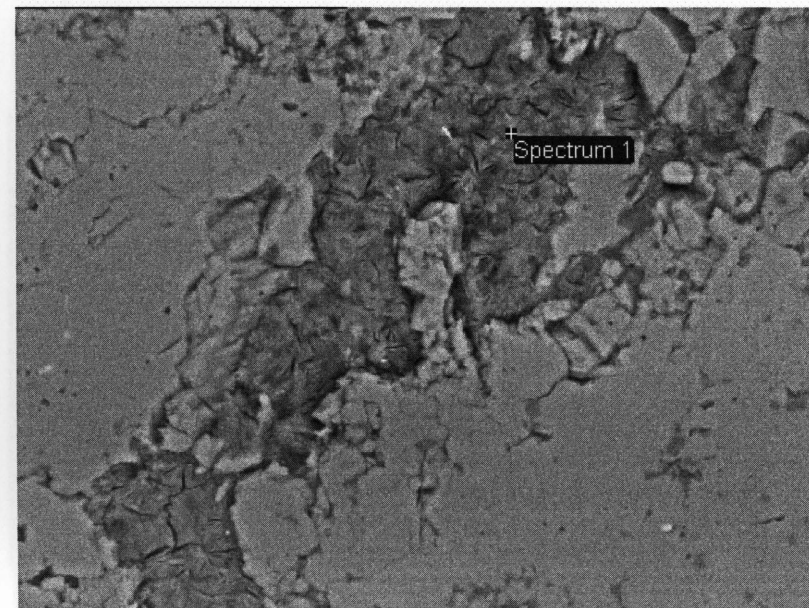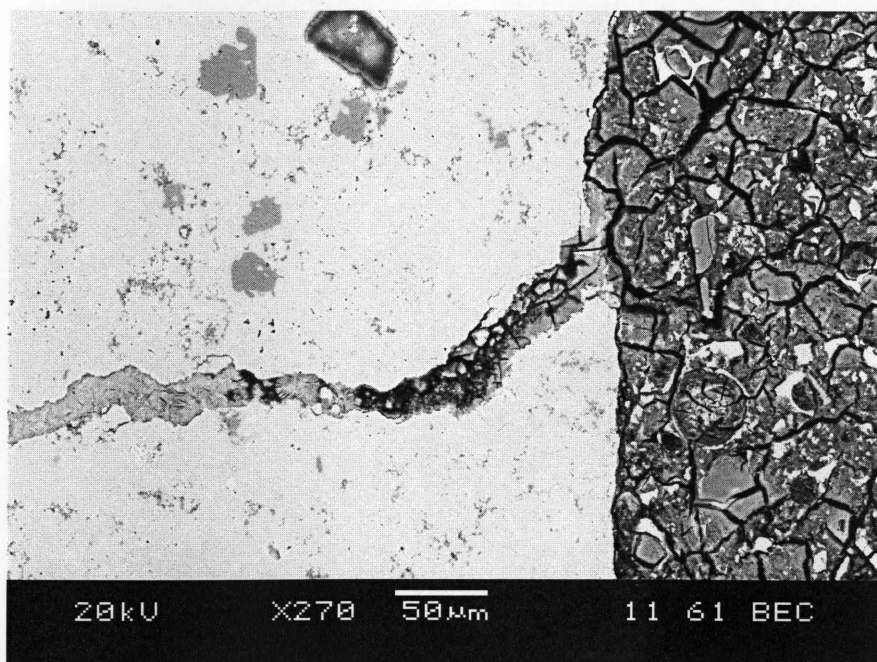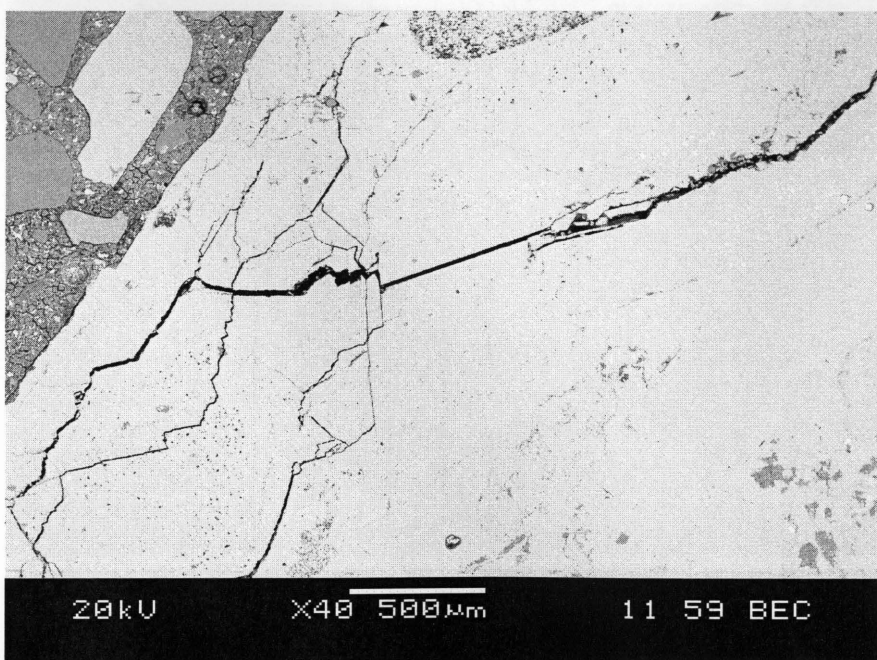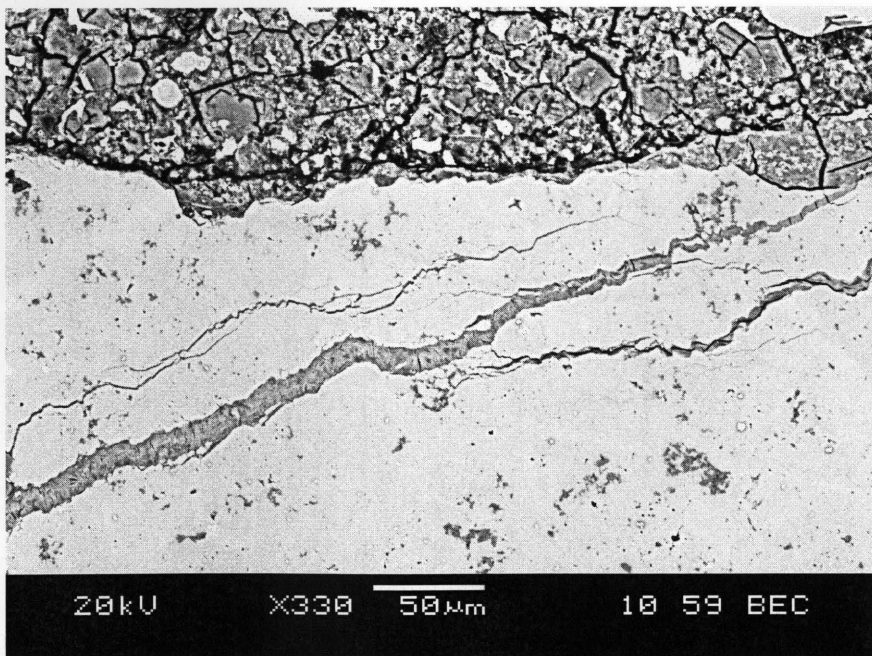
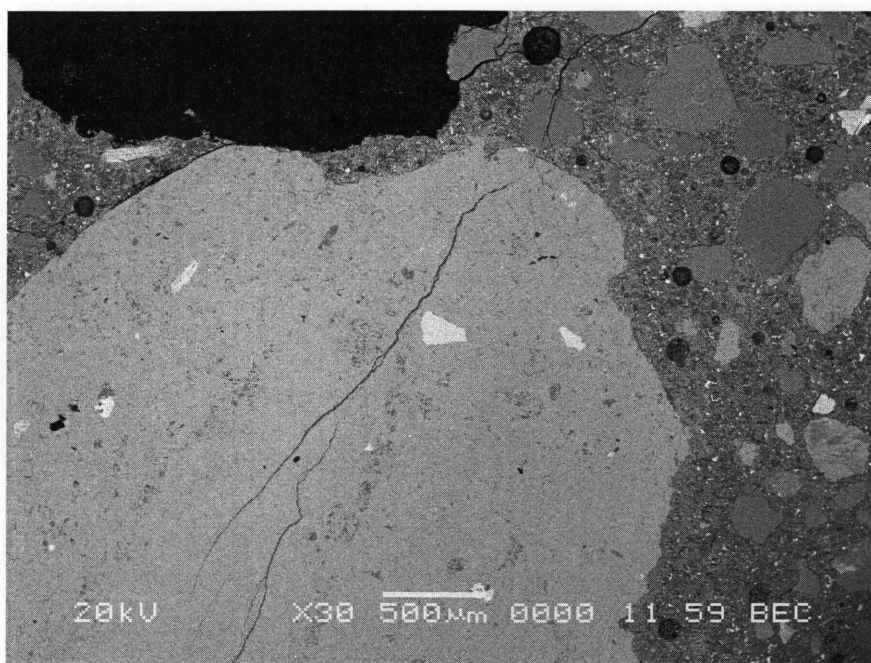RCA aggregate stock

RCA aggregate stock
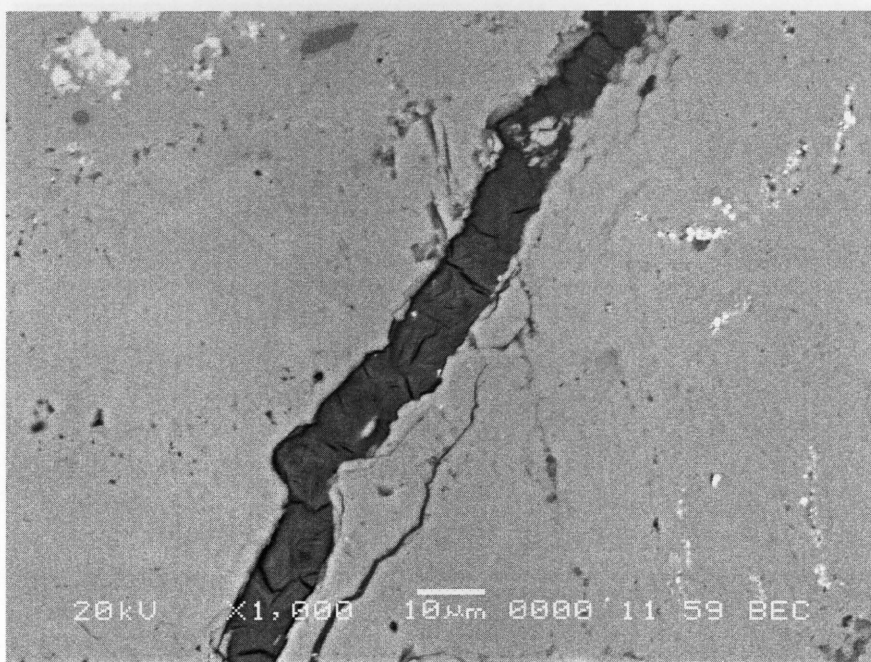
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RCA aggregate in concrete prism
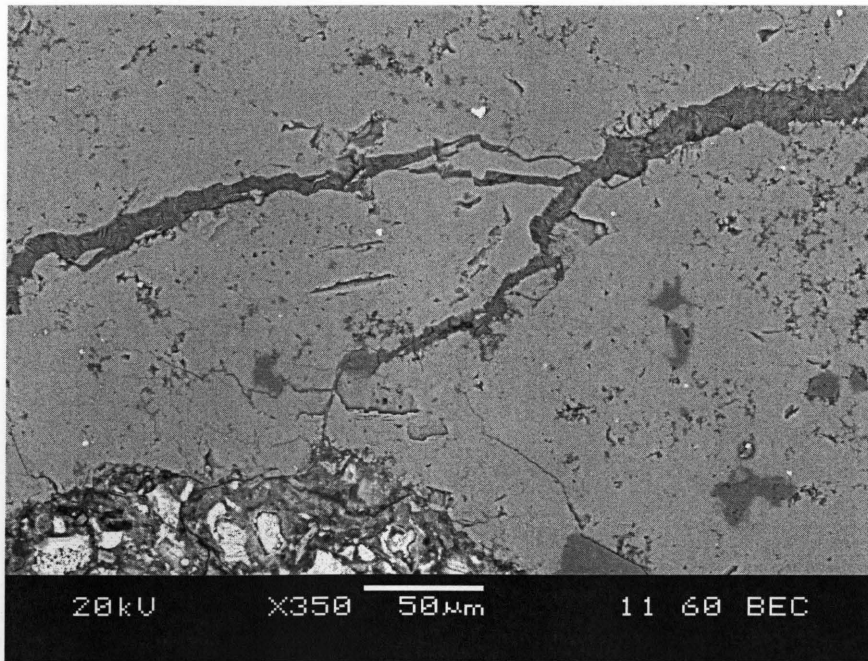

RCA aggregate in concrete prism

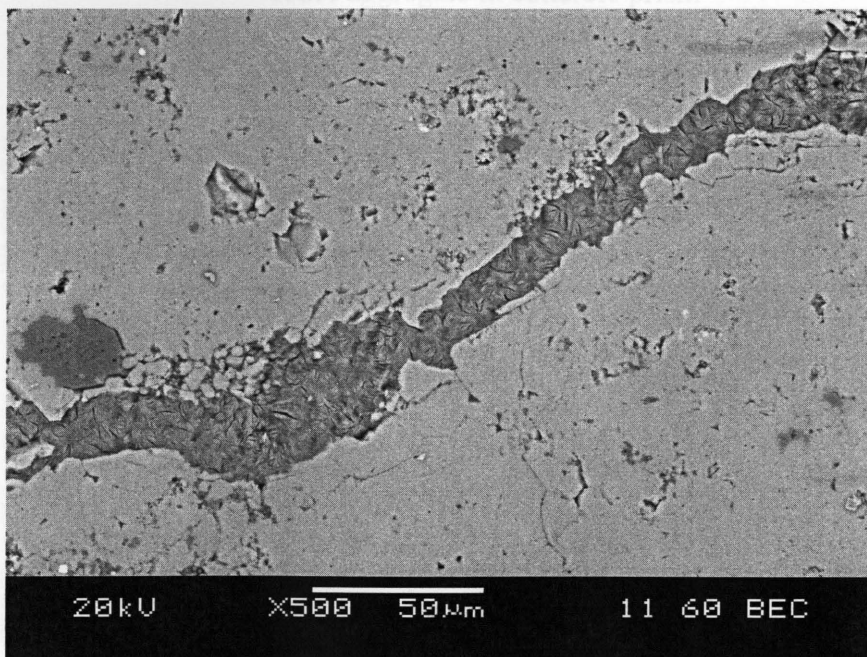RCA aggregate in solution 0.7 Molarity with Li: Na+K of 1:1

RCA aggregate in solution 0.7 Molarity with Li: Na+K of 1:1

RCA aggregate in solution 0.7 Molarity without Lithium

RCA aggregate in solution 0.7 Molarity without Lithium