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Inhibiting alkali silica reaction in concrete with lithium salts.

Nana K. Banahene

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INHIBITING ALKALI SILICA REACTION IN CONCRETE WITH LITHIUM SALTS

by

NANA K. BANAHENE

A Thesis Submitted to the Faculty of Graduate Studies through the Department of Geology and Geological Engineering in Partial Fulfilment of the Requirements for Degree of Master of Applied Science at the University of Windsor

Windsor, Ontario 1991
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Nana Banahene

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Abstract

A study into the effectiveness of various lithium salts and two lithium-containing minerals to prevent damage to concrete resulting from alkali-silica reaction is presented.

A series of tests were performed. These included:

i. Linear expansion tests on mortar cores containing reactive aggregate, with and without admixtures of the lithium salts and lithium-containing minerals;

ii. Silica analysis of a reactive aggregate;

iii. Strength tests on mortar cores;

iv. pH determination of cement paste with and without admixtures of lithium salts;

v. Examination of thin sections.

An accelerated testing method recently proposed by Hudec and Larbi was used as the expansion test. Length changes were measured with a double linear variable differential transformer connected to a TRS-80 Model III computer. Three reactive aggregates and one unreactive aggregate were used.

Lithium carbonate, lithium chloride, lithium fluoride, and lithium hydroxide were found to be effective in reducing expansions due to alkali-silica reaction. Four other salts, lithium acetate, lithium bromide, lithium nitrate, and lithium perchlorate were not effective in reducing the expansion. The lithium-containing minerals also proved to be ineffective against alkali silica reaction.

It is concluded that the effectiveness of the lithium salts against alkali-silica reaction is related to the ionic structure of lithium. With a small radius, the lithium ion probably exercises a binding effect on some of the OH⁻ ions in the pore solution, and consequently limits the extent
of OH attack on reactive silica.

With lithium ions in the pore solution, a predominantly lithium silicate gel is formed. It is proposed that the positive charges of the lithium ions neutralise the residual negative charges on the internal surfaces of the gel, to which water molecules would otherwise be attracted. The ability of the gel to attract water is therefore restricted. The strong electrostatic attraction of the lithium ion probably gives the gel structure enough rigidity to resist the tendency to swell.

The effectiveness of lithium salts appears to depend on their equivalent weights. Salts of small equivalent weights are more effective, by reason of yielding more lithium ions in solution at equal concentrations.
DEDICATED TO MY MOTHER
Acknowledgements

My primary vote of thanks goes to Dr. Peter Hudec for his supervision of this work. Dr. Hudec also suggested the topic for this research.

Some members of staff of the department of Geology and Geological Engineering rendered various forms of assistance with the experimental work, and I owe them a debt of gratitude. They are Dr. Paul Holm, for the strength tests; Dr. Iain Samson, for the preparation of the photomicrographs; Mr. Antun Knitl, for the preparation of the thin sections; Mrs. Ingrid Churchill, for the silica analysis.

I wish to express my gratefulness to the staff of the central research shop of the University of Windsor, for their invaluable assistance with dimpling the mortar cores. Miss Haleh Hobooti of the department of Electrical Engineering also assisted with the expansion tests, and her help is very much appreciated. To all those through whose contributions in diverse ways this study become possible, I say a big "thank you".

My final expression of gratitude goes to all my friends, for their friendship and moral support, and to God, for the strength and determination.
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Chapter One

Introduction

1.1 Overview of the Problem

Reaction between cement alkalis and concrete aggregates has been known and studied since 1940, when it was first discovered. After investigations into widespread incidences of cracking in concrete structures in southern California, Stanton (1940) concluded that the cracking was due to expansion in the concrete subsequent to reaction between the cement alkalis and silica minerals in the aggregates. Studies by other researchers revealed the existence of other reactions involving the cement alkalis and some carbonate rocks (Swenson 1957), as well as with some silicate rocks (Duncan et al. 1973). Together these became known as alkali-aggregate reactions.

Rocks containing amorphous and poorly crystallized silica minerals such as opal, chalcedony, cristobalite, and tridymite have been identified as being very susceptible to alkali attack. Some carbonate rocks that consist of roughly equal proportions of dolomite and calcite are also prone to alkali attack. Examination of such carbonate rocks reveals the presence of dolomite rhombs dispersed in a clay matrix.

The current shortage of unreactive aggregate near some areas of intense urban development has necessitated the use of marginal aggregates (Grattan-Bellew 1978), and focused much attention on the problem of alkali reactivity. Research work on the phenomenon has therefore intensified, resulting in a large number of publications on the subject in the past decade. A number of international conferences have also been held to discuss research developments relating to alkali reactivity.
The alkalis are derived mainly from cement, though other sources, such as deicing salts and sea water, are recognized. It has been established that an alkali content of less than 0.6 percent in the cement is necessary to avoid expansive reaction in concrete (Powers and Steinour 1955; Stanton 1940). Modern cements, however, rarely meet this criterion. A survey of Canadian cements by Rogers (1989) provides an excellent illustration of this. He found that in most parts of Eastern Canada normal portland cements (CSA Type 10) have alkali contents of more than 0.9 percent.

The high level of alkalis in modern cements is attributed to the use of raw materials that naturally have high contents of alkalis (Grattan-Bellew et al. 1978), and the greater recycling of alkali-rich kiln dust and gases. The latter practice is inspired by energy and environmental considerations (Dolar-Mantuani 1983; Tuthill 1982).

The reaction often leads to expansion, cracking, loss of strength, and in extreme cases, to the complete destruction of the concrete (Dolar-Mantuani 1983). External cracks occur in a characteristic pattern referred to as "map" cracking. An alkali silicate gel produced by the silica reaction is often exuded onto the surface of affected structures through cracks. This gel is colorless and viscous, but on exposure to air it carbonates and turns whitish. The carbonate reaction however, produces no such gel. In nature, damage due to alkali aggregate reaction is often reinforced by other processes of concrete deterioration such as freezing and thawing.

Alkali-aggregate reactions are generally slow, and symptoms of distress in affected concrete may not be apparent for 20 to 30 years (Rogers 1989). Cases have been reported though, where cracking occurred within 2 to 5 years (Stark 1980).
Occurrence of alkali reaction has been reported in structures worldwide, including those in several U.S. states and in Canada. In Ontario, more than 130 structures have suffered the effects of alkali reactions (Rogers 1986). Affected structures include highways (Morgan 1990), bridges, dams, a seawall (Tuthill 1982), a sidewalk (Rogers 1983), a hydroelectric plant (Kammer and Carlson 1941), and a retaining wall (Grattan-Bellew 1983). In some cases, the deterioration has affected the integrity of the structure enough to warrant a complete replacement of the structure. The cost of repairs to affected structures is estimated in millions of dollars.

Research efforts over the years have successfully provided useful insights into the mechanisms of reaction and expansion, though such knowledge is still considered far from definitive. Further to this, a host of testing methods for identifying reactive aggregates have been established and some of them standardised by ASTM and CSA. These tests have however been criticized for being too slow, such that at times results only become available when the structure is already under construction, or even completed (Rogers 1989). In response to this drawback, a number of tests have been developed which yield results in reasonable time.

Where the use of reactive aggregate in concrete is unavoidable, it is advised that low-alkali (less than 0.6 percent) cement be used. The high cost of this cement, as well as the fact that alkalis are often introduced into concrete from other sources, often makes this measure unattractive. In practice, pozzolanic and other mineral admixtures are usually introduced into the concrete mix in a bid to prevent reaction. Fly ash, silica fume, and ground blast-furnace slag have all proved fairly successful in reducing expansion when used in appropriate quantities. Using these mineral admixtures has the attendant advantage of reducing cement cost and the heat of hydration. However, the rate of strength development, especially at early age, is often
adversely affected.

1.1 Objective of the Study

The possibility of using chemical additives to inhibit the occurrence of alkali-aggregate reaction in concrete has long been suggested. The effectiveness of certain organic and inorganic compounds in preventing expansion has been studied at one time or another in the past. In particular, some salts of lithium and barium, and some phosphate compounds have been found to be reasonably effective. However, none of these has been used in practice. This is probably due to the fact that small quantities of chemical compounds often have substantial effects on some properties of concrete, such as rate of strength development and setting time.

In 1951, McCoy and Caldwell studied the effect of some chemicals on alkali silica reaction in concrete. They found that some lithium salts were able to reduce expansion considerably. However, they did not recommend the use of these salts, because they felt the cost would be too high. A survey of the literature shows that not much work has been done either to confirm the above findings, or to search for other chemical additives that might be effective. In fact, ACI committee 212 (1981) acknowledges this fact and recommends that further work should be done on this aspect of alkali-silica reaction research.

This study was therefore undertaken to investigate:

i. the effectiveness of a number of lithium salts in controlling alkali silica reaction,

ii. the possibility of using some lithium-containing minerals as admixtures to prevent the reaction at an economic cost.
Chapter Two

Literature Review

2.1 Concrete as a Construction Material

Concrete is a composite material comprising aggregate, cement and water, and occasionally incorporating mineral or chemical admixtures for the purpose of influencing a particular property. It is one of the most widely used materials for construction, due mainly to its ability to be cast into any desired shape, and also due to its economy of use (Mindess and Young 1981). When concrete is well designed, manufactured and placed with good quality control, it is usually of high durability. It suffers the disadvantage, however, of having low tensile strength. This latter point is very important since it gives the concrete little resistance to expansive forces generated by chemical reactions between certain aggregate-cement combinations, as will be discussed later.

2.1.1 Aggregate

Aggregate forms the bulk of concrete mass, making up about 75 percent of the volume (Mindess and Young 1981; Neville 1981). A host of materials can be used as aggregate in concrete but ordinary rocks are mostly used. Traditionally, aggregate is divided into "coarse" and "fine" fractions. Coarse aggregate consists of fragments retained on No.4 (4.75mm) sieve, whilst anything passing that is described as fine (ASTM 1989).

Aggregate in concrete serves primarily as filler, although its role in determining the quality and performance of concrete is generally recognised (Dolar-Mantuani 1983). Selection
of the right aggregate therefore forms an important part of the design of concrete mixtures. Aggregate for concrete used to be selected solely on the basis of physical eligibility, since, as Diamond (1978) put it, "the proper role of aggregate in concrete is usually perceived as mechanical rather than chemical". Since the discovery of alkali-aggregate reactions however, it has become imperative that close attention be paid to the chemical properties of concrete aggregates, especially when the cement to be used has a high alkali content.

2.1.2 Cement Paste

The cement paste is a mixture of cement and water. It is the most important component of concrete, since its quality determines the rate of strength development of concrete. The level of strength that can be attained by concrete is primarily a function of the ratio, by weight, of water to cement in the paste. The smaller this ratio, the greater the strength though there is a minimum value that is compatible with hydration requirements, workability and placement (Mindess 1981).

The chemical composition of the cement is also important, in that the presence of certain chemical elements can adversely affect the service performance of the concrete. Any admixtures used in the concrete usually influence the chemical constitution of the paste.

2.2 Mortar

Perhaps a distinction between the terms "concrete" and "mortar" is in order at this juncture. Whilst "concrete" includes both coarse and fine aggregate, "mortar" contains only fine aggregate. Simply put, mortar is concrete without coarse aggregate.
2.3 **Alkali-Aggregate Reaction**

Alkali aggregate reaction (AAR) is a reaction that occurs in concrete or mortar between certain minerals in some aggregates and alkali hydroxides in concrete pore solutions, usually resulting in expansion and/or cracking. It is essentially a reaction between reactive (siliceous or carbonate) material in the aggregate and hydroxide (OH⁻) ions in the pore solution (Diamond 1989; Nixon and Page 1987), the extent of reaction being largely influenced by the concentration of alkalis (Na and K).

Three forms of the reaction are recognised. These are:

i. Alkali-Silica Reaction

ii. Alkali-Silicate Reaction

iii. Alkali-Carbonate Reaction

2.3.1 **Alkali-Silica Reaction (ASR)**

The alkali silica reaction is the most common form of the alkali-aggregate reaction, and also the most widely studied. ASR occurs between aggregates containing reactive forms of silica and the alkali (Na and K) hydroxide ions in the pore solution, producing an alkali-silicate gel complex (Hansen 1944; Stanton 1940). The gel swells by absorbing water through an osmotic process, causing expansion and cracking. The reaction can be summarised as follows:

alkali hydroxide + silica + water ----> alkali-silicate complex(gel)

Materials susceptible to such alkali attack include vitreous, poorly crystalline, and strained forms of silica (Grattan-Bellew and Gilliot 1987). Such material occurs in minerals such as opal, chert, chalcedony, tridymite, cristiobalite and quartz (Dolar-Mantuani 1983). Quartz
is believed to be unreactive in its normal form. However when strained by tectonic action it becomes reactive (Grattan-Bellew and Gilliot 1987).

Rocks containing silica-reactive minerals fall under all the three categories: igneous, sedimentary and metamorphic. Among them are chert, flint, silicified carbonates, opal-bearing shales, sandstones, dacites, rhyolites, andesites and their tuffs, and quartzites (Dolar-Mantuani 1983). In Iceland, Gudmundsson and Asgeirsson (1975), found basaltic glass to be slowly reactive. Table 2.1 shows a description of reactive silica minerals and rocks.

2.3.1.1 Mechanism of Reaction and Expansion

The actual mechanism of reaction is still far from clear. That the reaction is initiated by OH⁻ ion attack has been confirmed by many researchers (Chatterji 1989; Diamond 1989; Nixon 1987; Powers and Steinour 1955). The roles of alkalis and calcium in the reaction mechanism are, however, still open to debate.

According to a hypothesis presented by Powers and Steinour (1955), the reaction is initiated through an attack by the OH⁻ ions in the pore solution on silanol molecules (Si-O-H) on the surface of the silica particles as follows;

\[
\text{Si-O-H} + \text{Na}^+ + \text{OH}^- \rightarrow \text{Si-O-Na}^+ + \text{H}_2\text{O}
\]

This opens up the particle, allowing the alkali hydroxide ions access to the inner siloxane molecules, which are then attacked.

\[
\text{Si-O-Si} + 2\text{Na}^+ + 2\text{OH}^- \rightarrow 2\text{Si-O-Na}^+ + \text{H}_2\text{O}
\]

The reaction produces a gel which, depending on the relative concentrations of alkali and calcium ions, is either a free-swelling alkali-silicate gel complex, or a calcium-alkali-silicate gel
Table 2.1: Deleteriously Reactive Rocks, Minerals, and Synthetic Substances

<table>
<thead>
<tr>
<th>Reactive Substance</th>
<th>Chemical Composition</th>
<th>Physical Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>Opal Chalcedony</td>
<td>SiO₂, nH₂O, SiO₂</td>
<td>Amorphous Microcrystalline to cryptocrystalline; commonly fibrous</td>
</tr>
<tr>
<td>Certain forms of quartz</td>
<td>SiO₂</td>
<td>Microcrystalline to cryptocrystalline; Crystalline, but intensely fractured, strained, and/or inclusion-filled</td>
</tr>
<tr>
<td>Cristobalite</td>
<td>SiO₂</td>
<td>Crystalline</td>
</tr>
<tr>
<td>Tridymite</td>
<td>SiO₂</td>
<td>Crystalline</td>
</tr>
<tr>
<td>Rhyolitic, dacitic latitic, or andesitic glass or cryptocrystalline devitrification products</td>
<td>Siliceous, with lesser proportions of Al₂O₃, Fe₂O₃, alkaline earths, and alkalis</td>
<td>Glass or cryptocrystalline material as the of volcanic rocks or fragments in tuffs</td>
</tr>
<tr>
<td>Synthetic siliceous glasses</td>
<td>Siliceous, with lesser proportions of alkalis, alumina, and/or other substances</td>
<td>Glass</td>
</tr>
</tbody>
</table>

The most important deleteriously alkali reactive rocks (that is, rocks containing excessive amounts of one or more the substances listed above) are as follows:

- Opaline cherts Andesites and tuffs
- Chalcedonic cherts Siliceous shales
- Quartzose cherts Phyllites
- Siliceous limestones Opaline concretions
- Siliceous dolomites Fractured, strained, and Rhyolites and tuffs inclusion-filled quartz
- Dacites and tuffs and quartzites

Source: ACI Manual of Concrete Practice (1981)
complex of limited swelling potential.

Chatterji et al. (1986) have proposed a different mechanism. They postulated that \( \text{OH}^- \) ions hydrolyse siloxane bonds according to the equation,

\[
\text{Si-O-Si} + \text{OH}^- \rightarrow \text{SiOH} + \text{SiO}^-
\]

This creates more openings in the particle being attacked, leading to further attack and the "liberation" of silica which diffuses out of the particle.

Whilst Powers and Steinour suggested that calcium contributes to lower expansion through the formation of a limited swelling gel, Chatterji and his team argued that the presence of calcium rather enhances expansion by reducing the diffusion of silica out of the reacting particles. Results obtained by Struble and Diamond (1989) in a recent study seem to lend credence to this latter view.

In 1944, Hansen proposed a mechanism for the expansion that accompanies alkali-silica reaction. His idea was that once formed the gel absorbs water by an osmotic process, with the paste acting as a semi-permeable membrane. The osmotic pressure thus generated produces expansion in the concrete. Other researchers are in agreement with this idea (Dent-Glasser and Kataoka 1981; Diamond 1989), though current thinking holds that the semi-permeable membrane is not required (Dent-Glasser 1979; Halstead and Chaiken 1958). It has subsequently been demonstrated (Pike 1958; Verbeck and Gramlich 1955) that osmotic pressures of considerable magnitude can be generated in the manner described by Hansen (1944).

It has also been suggested that the expansion is due to mechanical pressure resulting from an increase in volume of the reaction products (Chatterji 1989; Hobbs 1980). Perhaps Moore (1978) was right when he stated that there is no general agreement that osmotic forces are
responsible for the expansion.

2.3.1.2 The "Pessimum" Effect

Early investigations into the alkali silica reaction phenomenon led to the finding that some reactive materials, usually the fastest reacting ones (Hobbs 1987), gave maximum expansion when a certain optimum quantity is used with high-alkali cements in concrete. The term "pessimum" was used by Stanton (1940) to describe this behaviour. It is customary therefore, for researchers to refer to the pessimum proportion for a given reactive aggregate. The value is different for different materials.

It is thought that this behaviour is due to the fact that the reaction attains maximum rate when the ratio of alkali to reactive silica reaches an optimum value (Hobbs 1987). Clearly then, the pessimum proportion for any concrete aggregate will depend on the alkali level of the cement, and therefore its value should always be related to the percentage of alkali in the cement.

Recently, Hudec (1990) has proposed that the distribution of, and the distances between, reactive particles may be the reason for the pessimum behaviour rather than the alkali to reactive silica ratio. He reasoned that, since in the rapid test proposed by Oberholster and Davies (1986) there is an excess of alkali (sodium) ions, the pessimum effect should not occur. However, a sample of chert he tested using the rapid test mentioned above, still showed pessimum behaviour. He considered each reactive particle to have an osmotic sphere of influence to which water is attracted for expansion. He then theorized that with more reactive particles, the osmotic spheres of influence will interfere with each other, thus reducing the imbibition of water,
resulting in less expansion.

2.3.2 Alkali-Silicate Reaction

Another type of alkali-aggregate reaction is believed to take place between the alkali hydroxides in the pore solution and the siliceous aggregate particles in a characteristically different way. Unlike the silica reaction, it is not very widespread perhaps because it is much slower, and not as thoroughly investigated. It has been identified as being responsible for expansion and cracking of a number of concrete structures, including some in Nova Scotia (Gilliot et al. 1973) and Ontario (Dolar-Mantuani 1971).

Rocks which have been found to react in this manner include greywackes, argillites, phyllites, and schists. Similarities between this and the silica reaction have been found. Reaction products of the latter have been observed in concrete affected by the silicate reaction (Gilliot 1975). This is probably because microcrystalline or strained quartz is often present in aggregate containing phyllosilicates.

2.3.2.1 Mechanism of Reaction and Expansion

The reaction mechanism is not well understood. It has been suggested that the alkali hydroxides in the pore solution react with interlayer precipitates in reactive particles causing exfoliation (Gilliot et al. 1973). Subsequent water adsorption by previously dry alumino-silicate surfaces in the particle causes expansion and cracking. This reaction is much slower than the silica reaction.
2.3.3 Alkali-Carbonate Reaction (ACR)

Alkali-carbonate reaction involves reaction between carbonate rocks and alkali hydroxides in the pore solution. The reaction is notably different from that involving siliceous rocks. The carbonate reaction is more sensitive to alkalis (Dolar-Mantuani 1983), such that a lower content of alkalis in cement is required for damage to occur (Hadley 1961). This reaction produces no gel, and no "pessimum effect" has been observed (Walker 1978). Pozzolans and lithium chloride, known to inhibit the silica reaction, had no effect on the carbonate reaction (Grattan-Bellew and Gilliot 1987). Expansive forces that are generated lead to cracking in similar fashion as for the silica reaction. Outward manifestations associated with ASR in field structures, such as the closing of joints, are also observed with ACR (Walker 1978).

Rocks affected by this reaction are fine-grained, argillaceous, dolomitic limestones, usually containing more or less equal quantities of calcite and dolomite (Walker 1978). The microstructure consists of rhombs of dolomite dispersed in a matrix of clay and disseminated calcite (Hadley 1961). They possess a high specific surface, low porosity, and generally good physical properties (Pagano and Cady 1982, Swenson and Gilliot 1964). Rocks of this nature have been encountered in Ontario (Swenson 1957), Iowa, Illinois, and Indiana (Hadley 1961), Virginia (Newlon and Sherwood 1962), Michigan, Tennessee, and Maine (Pagano and Cady).
2.3.3.1 Mechanism of Reaction and Expansion

The reaction is initiated with an attack on the dolomite grains by the alkali hydroxide causing a dedolomitization reaction as follows (Hadley 1961):

$$\text{CaMg(CO}_3\text{)}_2 + 2\text{MOH} \longrightarrow \text{Mg(OH)}_2 + \text{M}_2\text{CO}_3 + \text{CaCO}_3$$

$$M=\text{Na or K.}$$

A regeneration of alkali hydroxide subsequently occurs through reaction of the alkali carbonate with the calcium hydroxide produced by cement hydration:

$$\text{M}_2\text{CO}_3 + \text{Ca(OH)}_2 \longrightarrow 2\text{MOH} + \text{CaCO}_3$$

Reaction therefore proceeds until all the dolomite has reacted or all the alkali is used up. This alkali regeneration makes the carbonate reaction "faster" than any of the other reactions, resulting in deterioration within a short period after placement of the concrete.

The mechanism of expansion has, as yet, not been clearly explained. A host of hypotheses that attempt to explain it have been presented. Two of these, by Hadley (Hadley 1961) and Swenson and Gilliot (1960), are based on osmotic pressure. Hadley postulated that the alkali carbonate produced by the dedolomitization reaction, being soluble, forms a highly concentrated solution which is "trapped" around the dolomite rhomb by the interstitial clay, acting as a semi-permeable membrane. With the surrounding pore fluid being less concentrated, osmotic pressures are set up, causing expansion.

Swenson and Gilliot however, suggested that the dolomite contains an "active" clay, which they established as illite which is dried up as a result of the geological processes that led to the formation of the rock. On dedolomitization, this clay becomes exposed to water. Subsequent uptake of water then results in expansion.
2.4 Cracking due to ASR

Cracking is the most striking expression of internal distress produced by alkali-silica reaction in concrete. Cracking in a concrete structure develops when the tensile stress due to the combined effects of ASR, structural loads, and/or reinforcement restraint exceeds the tensile strength of concrete (Wood et al. 1986). This is further aggravated by differential expansion in the concrete (Gilliot 1975).

Both micro- and macro-cracks are usually formed, the former being only visible under a suitable magnifying device. Figg (1986) described a model micro-crack formation in which 3 cracks originate at a common centre, usually at an angle of 120° to each other, in response to local swelling pressures. Further pressure from intrusion of gel widens these cracks to macro dimensions.

In a study of concrete prisms undergoing ASR expansion, Kobayashi et al. (1989) found that cracks first form perpendicular to the longitudinal direction, and these are later connected by longitudinal cracks (fig.2.1). Visible surface cracks usually form pseudo-hexagonal shapes (Walker 1978), enclosing apparently sound blocks of the concrete, with their widths increasing with time (Dolar-Mantuani 1983). They are normally about 24mm to 45mm deep, but may be as much as 110mm in depth (Hobbs 1987). Widths are commonly less than 1mm, but may be up to 4mm wide.

This characteristic configuration of the cracks is referred to as "map" cracking (see fig.2.2). Investigations by a number of researchers (Figg 1986; Hobbs 1987; Kobayashi et al. 1989), have revealed that the actual configuration of cracks is influenced by loading and reinforcement, and that "map" cracking obtains only in situations where concrete is neither
Fig. 2.1: ASR Cracking in a Concrete Prism
Source: Kabayashi et al. (1989)

Fig. 2.2: Map Cracking in Concrete Affected by AAR
Photo by Dr. P. P. Hudec
reinforced nor restrained. In reinforced concrete, cracks have been found to be more parallel to the direction of reinforcement (Figg 1986; Hobbs 1987).

Microcracks in affected structures can usually be found on closer examination under a microscope. Cracks radiating into the cement paste from the aggregate are often seen in thin sections examined under a polarizing microscope (Dolar-Mantuani 1983).

2.5 Conditions of Reaction

Like all reactions involving chemical compounds, alkali-aggregate reaction proceeds under a set of conditions. These conditions which must all occur simultaneously (Dolar-Mantuani 1983) are:

i. the presence of reactive aggregate in the concrete,

ii. the availability of alkalis in the pores of the cement paste,

iii. availability of moisture.

2.5.1 Presence of Reactive Aggregate

This is by far the most important condition of all, since the use of non-reactive material surely guarantees no reaction. It is also the least difficult to control. In fact, concern about alkali-aggregate reactions has peaked only because sources of unreactive aggregate are becoming increasingly harder to find.

For aggregate that is silica reactive, the type of reactive mineral present will determine the extent of reaction and expansion, and how much of the reactive proportion will give the greatest damage, since the different reactive minerals have different levels of reactivity and
pessimum proportions.

2.5.2 **Availability of Alkalis**

The availability of alkali ions in appropriate quantities in the pore solution of cement paste is essential for alkali reaction to occur. Although, as mentioned in an earlier section, the reaction is primarily between \( \text{OH}^- \) ions and the reactive material in the aggregate (Diamond 1989), it is the soluble alkalis whose presence is regarded as being necessary for the reaction to occur. This is because the \( \text{OH}^- \) ions exist in abundant quantities in hydrated cement paste in the form of insoluble \( \text{Ca(OH)}_2 \) (Neville 1981). Reaction with alkali compounds brings these ions into solution in sufficient quantities for deleterious reaction to occur.

Of the alkalis known to exist, only sodium and potassium are commonly found in concrete pore solutions. The quantity of each of these present influences the extent of reaction. The rate of expansion is higher when a greater quantity of potassium is present, although ultimate expansion is decreased (Davies 1958). The percentage, by weight, of alkalis present in concrete is normally expressed as the \( \text{Na}_2\text{O} \) equivalent. This is calculated as the percentage of \( \text{Na}_2\text{O} \) plus 0.658 times the percentage of \( \text{K}_2\text{O} \).

2.5.2.1 **Sources of Alkalis**

A number of sources are known to contribute to the amount of alkalis in concrete. Chief among these is the cement. Alkalis in cement are derived largely from the raw materials used to manufacture the cement (Diamond 1975; Grattan-Bellew et al. 1978). Modern cements are generally higher in alkalis than those of the past due to the use of raw materials naturally having
a higher content of these alkalis (Grattan-Bellew et al. 1978), and the greater recycling of kiln gases for energy conservation and air pollution reduction (Diamond 1975). According to Diamond (1975), Na and K in cement consist of "water-soluble" and "water-insoluble" fractions. The water-soluble proportion consists mainly of sulphates, while the insoluble portion usually occurs in solid solution in the dicalcium silicate, tricalcium aluminate, calcium aluminoferrite components in the cement clinker.

Work by Stanton (1942), and later Powers and Steinour (1955), established that an alkali level of 0.6 percent or higher is required for harmful reaction to occur. Although this figure is generally accepted, and is used in ASTM specifications (1989), the "rule" has to be observed with caution since lower proportions of alkalis in cement are known to have caused alkali reaction in some instances (Stark 1980; Tuthill 1982). It appears that the percentage of alkalis that will lead to deleterious expansion depends on the type of reactive material present. A lower percentage of alkalis has been recommended for concrete containing reactive carbonate rocks (Swenson and Gilliot 1960).

Some aggregate minerals containing high proportions of soluble alkalis, especially feldspars, have also been found to release alkalis into the concrete pores (Hansen 1944; Powers and Steinour 1955; Stark and Bhatt 1986; Visvesvaraya et al. 1986). Salt used as deicing agent in winter also increases the alkali content in pavements (Nixon et al. 1986), more so when the concrete has suffered some cracking. In marine environments, sea water also forms a source of alkalis in concrete. Other recognised sources of alkalis include mixing water (Neville 1981), and seeping waters (Diamond 1975).
2.5.3 Availability of Moisture

Access of moisture to concrete is a required condition for alkali reaction to take place. Water initially serves as the medium of reaction, then causes expansion of the gel by absorption. This condition is realised when either the concrete is in direct contact with water, or the ambient humidity is very high. However, it has been reported that reaction occurred in concrete that was apparently dry (Vivian 1950).

2.6 Extent of Reaction and Expansion

The need to differentiate expansive reaction in concrete from harmless reaction has been emphasized by some writers (Diamond 1989). The reaction itself is of no significance if it does not result in expansion and subsequent damage. A number of factors which tend to affect the extent of reaction and expansion are discussed below.

2.6.1 Temperature

An increase in temperature promotes an increase in the rate of reaction especially in the early stages (Dolar-Mantuani 1983). This was demonstrated in Iceland (Gudmundsson and Asgeirsson 1975) where it was thought at first that the low temperatures would prevent reaction from taking place. It was later discovered that some structures had been damaged by ASR. Of interest is the fact that the sides of these structures facing the sun suffered more deterioration than the shaded areas. This temperature effect is probably in accordance with kinetic considerations associated with all chemical reactions.
2.6.2 **Water:Cement Ratio**

Since a low water:cement (w:c) ratio implies a large number of alkali and other ions concentrated in a small volume of solution, one would expect this to lead to greater reaction. However, work by Gilliot (1975) shows that expansion due to the silica reaction is reduced at low water:cement ratios. Hobbs (1980) found that expansion increases up to a maximum at a water:cement ratio of about 0.4 and decreases beyond that. This behaviour is probably due to the fact that a progressively higher fraction of the cement grains are hydrated with increasing water:cement ratio, thus yielding more alkalis in solution. After no more unhydrated grains are left, at about w:c of 0.4 (Neville 1981), the increased quantity of water produces a weaker pore solution, thus reducing expansion.

2.6.3 **Size of Reactive-Aggregate Particles**

The size of reactive-aggregate particles in concrete significantly influences the rate of alkali reaction and expansion. For very reactive siliceous rocks, greater expansions have been observed to occur with a reduction in size, down to about No. 200 (75μm) sieve (McConnell et al. 1947; Stanton 1940). Figure 2.3 shows increasing expansion with aggregate particle sizes ranging from 13mm to 0.15mm. Perhaps this can be explained on the basis of a higher surface area being exposed to attack from the pore solution with decreasing size of particles. The opposite has commonly been the case however, for less reactive siliceous rocks (McConnell et al. 1947), and carbonates (Dolar-Mantuani 1983).

Particles passing the No. 300 (53μm) sieve are normally considered to retard reaction and expansion. This reasoning is based on the fact that these particles react quickly to produce gel
Concrete: moist cured, 20 °C; opaline silica; uncrushed coarse aggregate; Na₂O = 5.0 kg/m²

**Fig. 2.3: Influence of Reactive Particle Size on the Relationship Between Expansion and Age**
Source: Hobbs (1987)
even before the concrete hardens, so that any resultant volume increase is easily accommodated (Neville 1981). Diamond and Thaulow (1974) using a sample of opal, showed that on the contrary, large expansions can actually result when using such fine aggregate.

2.7 The Chemistry of Pore Solutions

The chemistry of cement paste pore solutions, both with and without aggregate, has evolved into one of the most important aspects of investigations into alkali reactivity. The development of devices with which pore fluids can be squeezed from mature specimens (Barneyback 1981) has led to significant advances in this subject.

Hydration of cement releases various ions into the pore solution. These include mainly sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺), hydroxide (OH⁻), and sulphate (SO₄²⁻) ions (Diamond 1989; Mindess and Young 1981). Silicon (Si⁴⁺), aluminium (Al³⁺), and iron (Fe³⁺) ions occur in negligible amounts. The pore solution therefore consists of these ions, as well as any others that may be introduced through the mixing water, and is highly alkaline (pH of about 13.5).

Initial hydration reactions produce calcium, hydroxide, potassium, sodium and sulphate ions in significant quantities. The concentrations of calcium and sulphate ions however, decrease rapidly to trace quantities (Diamond 1983), whilst the concentrations of sodium, potassium, and hydroxide ions increase. After 24 hours only the sodium, potassium, and hydroxide ions exist in the solution in appreciable concentrations (Nixon et al. 1986), and these concentrations stabilize after about 30 days (Diamond 1989). The decline in the concentrations of the calcium and sulphate ions has been attributed to the formation and precipitation of ettringite, which
results from the reaction of tricalcium aluminate with calcium and sulphate ions (Nixon and Page 1987).

The total concentration of the alkalis (Na and K) in the pore solution depends on the alkali level in the cement. Initial concentrations are reportedly high, with about 3 times more potassium than sodium. Final (equilibrium) concentrations are estimated at 70 to 80 percent of the alkali content of the cement. For example, cement of 0.91 percent equivalent Na₂O content, gave a combined alkali concentration of about 0.72N (Diamond 1983).

Concentrations of hydroxide ions increase with time and reach the highest levels of all as shown in figure 2.4 (Diamond 1983). The rapid increase in hydroxide ion concentration results from continued dissolution of alkali ions and the concomitant reduction in "free" water as hydration proceeds (Nixon et al. 1986). It has also been suggested (Diamond 1983) that after solid gypsum is exhausted, precipitation of ettringite depresses the concentration of sulphate ions. More hydroxide ions then come into solution to maintain the charge balance. A study by Diamond (1989) revealed that final (equilibrium) concentration of hydroxide ions is linearly related to the alkali content of cement, expressed as Na₂O equivalent (fig.2.5).

Much of the investigation into pore solution chemistry has been made on "neat" pastes. Data on pore solution compositions of mortar and concrete are very scarce. Nixon and Page (1987) compared data on hydroxide ion concentrations of mortars with those obtained using pastes of the same water:cement ratio. They found consistently lower concentrations in the mortars. No significant differences, however, appear to exist between concentrations in mortar and concrete.
Fig. 2.4: Concentrations of Ca\(^+\), Na\(^+\), K\(^+\), SO\(_4\)\(^2-\), and OH\(^-\), Expressed from Cement Pastes up to 1 Day
Source: Diamond (1983)

Fig. 2.5: Relation Between Equilibrium OH\(^-\) Ion Concentrations of Pore Solution and Alkali Content of Cement
Source: Diamond (1989)
The use of reactive aggregate in mortar results in appreciable decreases in concentrations of alkali and hydroxide ions (Diamond 1983). This is probably because they are used up during the reaction, thus lending support to the notion that these ions play a major role in the reaction mechanism.

The chemistry of pore solutions in paste containing silica fume, fly ash, and blast-furnace slag has also been closely studied (Diamond 1983; Glasser and Marr 1984). Silica fume, when used to replace up to 30 percent of the cement substantially reduced alkali and hydroxide ion levels. Page and Vannesland (1983) determined the concentrations of alkali and hydroxide ions in a paste containing silica fume, and found them to be nearly equal.

Fly ash, when used with high-alkali (>0.6%) cements, has been found to be effective in lowering alkalinity (Diamond 1983; Nixon and Page 1987). Negligible reductions were obtained when low-alkali cement was used.

Granulated blast-furnace slag also resulted in lower hydroxide ions concentrations in the pore solution, when added in large quantities. Bakker (1981) has opined that this is due to reduced alkali ion diffusivity and water permeability in the hydrated cement-slag paste system.

2.8 Structure and Composition of Reaction Products

The alkali-silicate gel is the main product of the alkali-silica reaction. It is of variable chemical composition which depends on the relative amounts of alkalis and reactive silica (Dolar-Mantuani 1983).

Chemical analyses made on gels of various origins have revealed that it is made up predominantly of SiO₂, with moderate amounts of potassium (K), sodium (Na), and calcium
(Ca), in the form of their oxides, as well as water (Regourd-Moranville 1989). Berube and Fournier (1986) reported the following ranges of chemical composition for the gel:

\[
\text{SiO}_2 \quad 56-86\% , \quad \text{K}_2\text{O} \quad 2-8\% , \quad \text{Na}_2\text{O} \quad 0.4-2\%
\]

\[
\text{CaO} \quad 1-28\% , \quad \text{H}_2\text{O} \quad 10-30\%
\]

The content of potassium or sodium is influenced by their respective contents in the pore solution (Davis and Oberholster 1958).

The gel is credited with cation adsorption and exchange properties. Use has been made of this fact to develop two methods for identifying ASR products in affected concrete, by employing the fluorescent nature of the uranyl ion under ultraviolet light (Natesaiyer and Hoover 1988), and the blue coloration associated with the copper (Cu\(^{2+}\)) ion (Poole et al.). Sodium (Na\(^+\)), potassium (K\(^+\)), and calcium (Ca\(^{2+}\)) ions are usually adsorbed by the gel, and can easily be replaced by other cations.

Studies with the scanning electron microscope have revealed that gels are either massive or textured (Regourd and Hornain 1986; Shayan and Quick 1989). Massive gel constitutes the main material in the dark reaction rim usually seen around aggregate particles in affected concrete (Regourd et al. 1981). It is the first product formed and usually fills cracks that originally existed in the aggregate (St. John 1985).

Textured gels develop from massive gels with time, and are richer in calcium (Regourd and Hornain 1986). They may be grainy, spongy, or foliated, according to the amount of calcium ions available in the gel. Crystalline products have also been identified in recent studies (Davies and Oberholster 1988; Regourd and Hornain 1986; Regourd-Moranville 1989; Shayan and Lancucki 1986). These are described as rosette, lamella, and fibrous crystals. They are
all silicates, containing variable quantities of alkali, calcium and aluminium ions. It has been suggested (Diamond 1989) that these are probably secondary products of crystallization from the gel stage, and are unlikely to play a role in expansion and cracking.

2.9 Effect of ASR on the Mechanical Properties of Concrete

When ASR occurs in a concrete structure, it usually results in the depreciation of some mechanical properties of the concrete. Among these are compressive and tensile strengths, and elastic modulus.

Quite a substantial amount of data has been gathered by various researchers on the effect of ASR on the tensile and compressive strength of concrete. Table 2.2 is a summary of results obtained by various investigators. These data generally suggest that ASR results in a reduction in both compressive and tensile strengths, in some instances by a considerable percentage. Shayan and Ivanusec (1989), on the other hand, found little effect on compressive strength, though they obtained appreciable reductions in tensile strength. Additional data obtained by Hobbs (1987) indicate that the reduction in strength is a function of the level of expansion.

Elastic modulus of concrete is also affected by ASR, even to a greater extent. In a 1983 study, Hobbs concluded that if the extent of reaction is such as to induce up to 0.3 percent expansion, elastic modulus is reduced by about 50 percent. Similar results were obtained by Blight and Alexander (1985).
2.10 Alkali-Silica Reaction in Field Concrete

Occurrence of alkali reaction in field structures is usually manifested in the form of "map" cracking, the presence of gel and reaction rims (Dolar-Mantuani 1983; Hadley 1961; Stanton 1940). Sometimes the cracks are only visible when the surface is moistened with water (Gilliot 1975). The reader should bear in mind that the presence of cracks and reaction rims in a concrete structure is by no means diagnostic of alkali reaction, since other phenomena affecting concrete can produce similar effects. Only the alkali-silicate gel is considered diagnostic of alkali-silica reaction (McConnell et al. 1947), though the absence of gel is not conclusive proof that reaction has not occurred (Gilliot 1975).

The gel is usually found filling voids and lining cracks, and may exude via cracks to the surface (Hobbs 1987). It is colourless when wet, but it turns white when dry due to carbonation, and may also undergo shrinkage cracking (Dolar-Mantuani 1983; Shayan and Ivanusec 1989). It appears isotropic under a petrographic microscope (Regourd and Hornain 1986). Reaction rims are more commonly found when the affected concrete contains carbonate aggregate. They occur as dark bands surrounding reacting particles (Dolar-Mantuani 1983).

In most cases damage occurs after several years of service, but some structures reportedly started showing signs of reaction only 2 to 5 years after the concrete was placed (Hobbs 1987; Rogers 1983; Stark 1980).

It is important, in assessing damage to a service structure, to distinguish between effects on the structural integrity and damage to the concrete properties (Diamond 1989). This is because a structure may show no sign of cracking, yet expansion may cause buckling (Walker 1978) and/or misalignment of structural members (Dolar-Mantuani 1983), causing serious
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Source: Hobbs (1987)
problems to the structure. This is especially true for structures such as turbines and lift bridges which require accurate alignment of adjacent members. On the other hand, a structure that looks severely cracked may still be structurally sound (Diamond 1989).

2.11 Identification and Testing of Reactive Material

The magnitude of damage caused by alkali-silica reaction in concrete structures makes it imperative that the alkali reactive potential of any aggregate whose record of field performance is unknown be well investigated before use in concrete. This is usually achieved through petrographic examination and accepted testing methods.

2.11.1 Petrographic Examination of Concrete Aggregate

The importance of petrographic examination of aggregate before use in concrete has often been stressed in the literature (Pitts and Stanger 1987; Power and Hammersley 1979). This fact has assumed greater significance in recent times due to environmental and economic factors necessitating the use of marginal aggregates (Power and Hammersley 1979).

Petrographic examination offers a large contribution, in diverse ways, to the investigation, selection, testing, and control of concrete aggregate in general. It aims to determine the relative abundance of particular mineral constituents that are considered harmful and affect the durability of concrete as a result of freezing and thawing, alkali reactivity, and/or wetting and drying (Mielenz 1954). Of importance are characteristics such as particle shape, surface texture, pore dimensions, hardness, the presence or otherwise of surface coatings, and the potential for alkali reaction.
With respect to alkali reactivity, the objective is to establish the proportion of reactive components in the aggregate, and based on that, determine whether further testing is necessary, and if so, which tests are appropriate (ASTM 1989). This is important since some of the established testing methods are known to be unsuitable for some aggregate types.

With petrographic examination the basic nature of any aggregate of unknown record can be established, so that its probable field performance can be determined by comparison to aggregates of similar petrographic characteristics whose field records are well documented (Mielenz 1958). This approach was used by Wakazaka et al. (1987) to correctly estimate the reactive potential of aggregate from an unfamiliar source. ASTM Standard C-295 lists the main mineralogical components to be noted in relation to alkali-silica reaction.

Techniques involving the use of polarizing and stereo-microscopes are mostly used. In some instances, additional procedures such as X-ray diffraction analysis, differential thermal analysis, and scanning electron microscopy are employed (Grattan-Bellew 1987). For fine aggregate, thin sections are usually a useful tool for determining the mineralogical constitution of the aggregate, in which case the various mineral particles can be assessed by the point count method (ASTM 1989; Pitts and Stanger 1987). Investigative tools of petrographic analysis include a small knife, a hand lens, and dilute acid to confirm the presence of carbonate particles (Dolar-Mantuani 1983). It is important that the examination be carried out on a sample that is representative of the source of aggregate.
2.11.2 Testing Methods

2.11.2.1 Standard Tests

A number of test methods for assessing the reactive potential of aggregate have been suggested over the years. Some of these have been adopted into the standards of the American Society for Testing and Materials (ASTM) and the Canadian Standards Association (CSA). These include:

i. the mortar bar test (ASTM C-227),

ii. the rock cylinder test (ASTM C-586),

iii. the quick chemical test (ASTM C-289), and

iv. the concrete prism test (CSA A23.2-14A).

2.11.2.1.1 Mortar Bar Test (ASTM C-227)

This is the most widely used of the standard tests, since it is thought to be the one that most closely simulates actual behaviour of field concrete (Diamond 1978). In this method, mortar bars (25mm x 25mm x 300mm), are prepared from a graded sand-sized sample of the aggregate, are exposed to conditions of controlled temperature and humidity, and the resulting expansions are measured. Details of the sample selection and preparation, appropriate apparatus, and the general test procedure are provided in ASTM standard designation C-227.

The alkali content of the cement should be above 0.8 percent (expressed as Na₂O), or else the mix is adjusted by the addition of sufficient NaOH. The mortar bars are stored at a temperature of 38°C and length measurements are taken periodically. The threshold of deleterious expansion is set at 0.1 percent at 6 months. However, where results are needed in
less time, an expansion of 0.05 percent at 3 months is accepted as suggesting potential harmful reactivity. ASTM makes it clear that the "line of demarcation between non-reactive and reactive combinations is not clearly defined" (ASTM 1989).

The method is used for testing only siliceous reactive aggregate, and is considered inappropriate for testing carbonate-reactive rocks. To ensure that expansions obtained are not due to other forms of concrete expansion phenomena, it is recommended that confirmation be sought using petrographic examination (ASTM C-295) and/or the chemical test (ASTM C-289). Inspection of mortar bars at the end of the test for reaction products is also considered good practice.

2.1.2.1.2 Quick Chemical Test (ASTM C-289)

The quick chemical test involves determining the reactive potential of siliceous aggregate through reaction with sodium hydroxide solution. This method is fast, providing results in a matter of days. This, coupled with the fact that it requires only a small sample of the reactive aggregate, makes it a favourite test (Sims 1981).

The aggregate is crushed to a size passing No. 50 (300μm) sieve and retained on No. 100 (150μm). It is then reacted with standard 1N sodium hydroxide solution in a closed plastic container at 80°C for 24 hours. The suspension is then allowed to cool, and is filtered. The filtrate obtained is analyzed for the amount of dissolved silica, as well as the reduction in alkalinity of the original solution. Further details of the required apparatus, and the test procedure are available in ASTM standard designation C-289.
The results are expressed graphically, with the reduction in alkalinity on the ordinate axis against the quantity of dissolved silica (log scale). The graph (fig. 2.6) is divided into 3 areas designated as "innocuous", "deleterious", and "potentially deleterious". The division is based on the results of correlation tests between this test and the mortar bar test, petrographic examinations, and the performance of field structures (Chaiken and Halstead 1960). Aggregates whose test results fall in the area labelled "potentially deleterious" need further testing using ASTM C-227 (Kammer and Carlson 1941).

Interpretations based on this test should usually be supported by the results of petrographic examinations and service records (Diamond 1978; Dolar-Mantuani 1983). The test is not recommended for carbonate rocks.

2.11.2.1.3 Rock Cylinder Test (ASTM C-586)

This method is used for testing carbonate rocks. It is based on the fact that if a rock reacts with cement alkalis it will also react with sodium hydroxide solution. ASTM does not recommend this for testing siliceous rocks (ASTM 1989), but it has been successfully used for testing reactive silicate rocks (Dolar-Mantuani 1969; Duncan et al. 1973).

Cylinders of the reactive rock about 35mm in length and 9mm in diameter are made. These should be drilled perpendicular to the stratification of the rock, since expansions in that direction have been found to be larger than those in the direction parallel to the layering (Gilliot 1963). They are equilibrated in distilled water after which their initial lengths are taken. Then they are immersed in 1M sodium hydroxide solution and the lengths measured at given intervals. The test is described in greater detail under C-586 in the ASTM annual book of standards.
Fig. 2.6: Evaluation Graph for Reactivity of Siliceous Rocks by the Quick Chemical Method (ASTM)
Source: Dolar-Mantuani (1981)
The limit of expansion is given as 0.1 percent without any stated period in which to achieve this. It is believed however, that expansive tendencies of the rock should be apparent after 28 days (ASTM 1989; Walker 1978). In this test the aggregate does not react within cement paste, but the results indicate nevertheless, that it gives a good prediction of the likely behaviour of the aggregate in concrete. It is recommended that the results of this test be used only to support results of other tests (Walker 1978).

2.11.2.1.4 Concrete Prism Test (CSA A23.2-14A)

The concrete prism test is used to evaluate the expansion potential of coarse, alkali-silica or alkali-carbonate reactive aggregate. Fine aggregate used for the test should be non-reactive when tested by ASTM C-227.

The prisms are required to be of dimensions not less than 75mm x 75mm x 350mm, and not more than 120mm x 120mm x 450mm. Cement of alkali content 0.9 percent (expressed as Na₂O equivalent) is used, with reagent grade NaOH being added to raise the alkali level to 1 percent. After initial length measurements, they are stored at 100 percent relative humidity and 23°C temperature, with further measurements being taken at specified times. Visual examinations for cracks and surface deterioration are required to be made after each measurement.
2.11.2.2 Rapid Methods of Testing

Although the tests discussed above have been quite successful in evaluating aggregates for alkali reactive potential, a major shortcoming, namely duration of testing, still remains. It takes unacceptably long for credible results to become available using these tests. The chemical test (ASTM C-289), which can give results in a short time, is only used to complement other tests. In a bid to overcome this problem, concrete designers have often resorted to what Sims (1981) described as "the questionable expedient of accepting earlier indications (of expansions) than those recommended".

As the need for shorter testing times mounted, the idea of using elevated temperatures in testing was conceived. Chatterji (1978) proposed that high temperature and an excess of alkali salt can successfully be used to accelerate testing. Subsequently, a number of "rapid" tests have been developed, though none of them has been standardised by ASTM or CSA. Some of these are summarised below.

2.11.2.2.1 Accelerated (NBRI) Mortar Bar Test

This is perhaps the most widely used of the "rapid" tests. It involves preparing mortar bars according to ASTM C-227. On demoulding the bars, they are cured in water at 80°C for 24 hours. Lengths are then measured, and the bars are stored in 1N sodium hydroxide solution at 80°C. Measurements are made everyday for 14 days. An expansion of more than 0.1 percent in 12 days has been suggested as indicative of potentially deleterious behaviour (Oberholster and Davies 1986).

* National Building Research Institute of South Africa
A variant of this test has been proposed by Hudec and Larbi (1989). Their method employs small-size mortar cylinders, 60mm in length and 26mm in diameter. Measurement of length changes is done using a double linear variable differential transformer (LVDT). The test takes about 28 days to complete. The aggregate is considered deleteriously reactive if expansion exceeds 0.171 percent at 12 days or 0.330 percent at 22 days. This method was used in experiments for this study.

2.11.2.2.2 **Chemical Shrinkage Test**

This test is based on the decrease in volume or "chemical shrinkage" that occurs when reactive silica reacts with alkali. 25 grams of sand is put in a reaction flask containing 50ml. of 10M NaOH at 50°C. The decrease in volume that takes place is recorded through a narrow pipette. An apparatus for performing this test automatically, the Konometer, has been developed (Knudsen 1986).

2.11.2.2.3 **Japanese GBRC** Test

This involves preparing mortar bars (40mm x 40mm x 160mm) with alkali content adjusted to 2.5 percent Na₂O equivalent by the addition of sodium hydroxide. The bars are then cured for one day in moulds, and another day in water before being put in boiling water under a pressure of 0.15 MPa for 2 hours (Tamura 1986).

Specimens are visually inspected for cracks just before and after the boiling process. Any changes in their ultrasonic pulse velocity and dynamic Young's modulus are also noted and

** General Building Research Corporation of Japan
used to establish potential for harmful reaction.

2.12 Prevention of ASR

A number of measures have been suggested to prevent alkali reaction in concrete when the aggregate to be used has been certified as having the potential to undergo deleterious reaction. Some of these are described below.

2.12.1 Use of Alternative Source of Aggregate

This appears to be the simplest way of preventing alkali reaction in concrete, since no reaction occurs when non-reactive aggregate is used. However, a number of factors often make this approach unattractive. In particular, where the non-reactive aggregate source is much farther from the construction site than the reactive aggregate, the extra transportation cost might be prohibitive. Political considerations may also play a role in ruling out the use of aggregate from another source (Grattan-Bellew 1983). An example of this is when such an action can lead to the closure of a quarry with consequent loss of jobs.

2.12.2 Use Low Alkali Cement

This is the method most often employed to avoid damage due to alkali reactivity. The maximum percentage of alkalis allowed in the cement is set at 0.6 percent (ASTM 1989), though for carbonate rocks a lower value, 0.4 percent, has been suggested (Walker 1978). However, instances where low alkali cement concrete expanded and cracked have been reported (Stark 1980; Tuthill 1982; Woolf 1952). Possible failure of this approach could stem from a number
of factors.

Firstly, several sources of alkalis in concrete exist other than the cement, though the latter is recognised as the major source (see sec. 2.5.2.1). Expansive reaction is possible when using low-alkali cement, if alkalis are contributed by any of the other sources, effectively making the cement high-alkali. Using a low-alkali cement and a very reactive rock could still satisfy the pessimum proportions of that cement-aggregate combination, and hence cause expansion and damage (French 1980; Hobbs 1978). A higher content of cement in field concrete than used in testing can also lead to increased alkali levels in the concrete (Grattan-Bellew 1983).

On some projects it becomes difficult to ensure that specified low-alkali cement is actually used. Instances of this have been noted by Tuthill (1982). Lastly, the high cost of low alkali cement (Grattan-Bellew et al. 1978; Neville 1981) makes its use on certain projects simply uneconomical.

2.12.3 Use of Pozzolans

The use of pozzolans in concrete to prevent alkali reaction has been practised since the pioneering work of Stanton (1949). The materials which have been used include mainly fly ash, slag, and silica fume (Diamond 1983; Grattan-Bellew 1983; Oberholster and Westra 1981). Others are diatomite and calcined shale. These are used to replace a proportion of the cement, usually in quantities of 35 to 75 percent by weight of the cement. Since these materials are less dense than cement, their introduction in concrete leads to an increased water requirement, which in turn results in a lower rate of strength development (Grattan-Bellew 1983; Tuthill 1982), and also causes shrinkage cracks. On the other hand, using these pozzolans has a number of
advantages. They are more economic to use, produce a lower rate of heat (of hydration) evolution, and increase the resistance of the concrete to aggressive chemicals.

The mechanism by which pozzolans work is yet to be clearly explained. It has been suggested that the finely divided siliceous component reacts with calcium hydroxide to produce a gel similar to that produced by the hydration of cement particles (Gilliot and Swenson 1973; Newlon and Sherwood 1962). The production of this gel, together with the removal of calcium hydroxide which is susceptible to leaching, leads to a reduction in the porosity and permeability of the concrete (Bakker 1981; Mills 1981).

It has often been suggested that the beneficial effect of pozzolans on alkali reaction is due to a dilution of the alkalinity of the pore solution, which results from partial replacement of cement. Grattan-Bellew (1983) dismissed this as incorrect, citing data obtained by Bakker (1981). Bakker replaced 65 percent of portland cement with slag in mortar bars, and added Na₂SO₄.10H₂O to raise the alkali level to 1.49 percent. Expansion was reduced in the mortar bars, whilst other mortar bars containing Na₂SO₄.10H₂O without slag showed increased expansion. Since the introduction of Na⁺ ions would obviously offset any dilution effects of the slag on the alkalinity of the cement, Grattan-Bellew argued that the mortar bars containing both slag and Na₂SO₄.10H₂O would have expanded, if the slag served to dilute the alkalinity of the cement. He then suggested that the gel probably incorporates sodium and potassium ions in its lattice, thus lowering their concentration in the pore solution, and hence preventing expansive reaction (Grattan-Bellew 1983).

Studies of the chemical composition of fly ash, slag, and silica fume turned up an interesting finding. These materials were found to contain alkalis in quantities that are not
negligible. Quantities ranging from 0.48 percent for silica fume, to 3.78 percent for fly ash have been detected (Grattan-Bellew 1983). Although a sizeable proportion of the alkali is insoluble, it is thought that a greater quantity will probably dissolve in the pore solution (Nixon and Page 1987).

2.12.4 Beneficiation of Aggregate

It is possible to prevent alkali reaction in concrete through beneficiation of the aggregate. A number of techniques can be used to achieve this, depending on the type of rock and the deposit in which it occurs (Grattan-Bellew 1983). Selective quarrying and density separation are two of the most commonly used methods of beneficiation.

Selective quarrying is usually used for carbonate rocks which occur in horizontal layers (Smith 1974), as well as igneous rocks with intrusions of reactive material (Grattan-Bellew 1983). Density separation is used when there is a marked difference in specific gravity between the reactive and non-reactive materials.

2.12.5 Use of Chemical Additives

The possibility of introducing chemical substances into a concrete mix to avert the occurrence of alkali reaction was first considered nearly four decades ago (McCoy and Caldwell 1951), though there is no known instance of its use in practice (Grattan-Bellew 1983).

McCoy and Caldwell (1951) investigated the effectiveness of an array of inorganic and organic chemicals. Their results show that 1 percent (by weight of cement) of lithium carbonate and fluoride reduced expansion of mortar bars containing pyrex glass and high alkali cement by
more than 90 percent. The beneficial effect of lithium was demonstrated even more vividly when they tested a set of three mortar bars containing pyrex glass and high alkali cement. Two of the mortar bars were mix-treated with 1.0 percent and 0.72 percent (by weight of cement) of Na₂CO₃ and Li₂CO₃ respectively. After 8 weeks, the untreated bar had expanded by 0.243 percent, while that containing Na₂CO₃ had expanded by 0.374 percent. The Li₂CO₃-treated mortar bar had expanded only by 0.02 percent (see fig. 2.7). In their conclusions however, McCoy and Caldwell expressed reservations, on the basis of high cost, about using lithium salts to prevent ASR.

It has been suggested that barium salts are also effective. However, the presence of barium salts in the pore solution will lead to the precipitation of insoluble barium sulphate. It should be mentioned that the experiment with barium salts (Hansen 1960) was done using a

![Graph showing expansion over time for different mortars.](image)

*Fig. 2.7: Effect of Equivalent Amounts of Sodium Carbonate and Lithium Carbonate on Expansion of Pyrex Glass Mortar Bars made with High Alkali Cement.*

*SOURCE: McCoy and Caldwell (1951)*
special gypsum-free cement.

Other proposals have come from Pagano and Cady (1982), who found 11 percent ferric chloride to be effective against alkali-carbonate reaction. It is feared, however, that ferric chloride can affect the setting of concrete and cause corrosion if the concrete is reinforced (Grattan-Bellew 1983). Sakaguchi et al. (1989) studied the effects of LiOH.H₂O, LiNO₃, and Li₂CO₃. They added quantities of these salts to mortar bars to give various molar ratios of Li/Na. All the mortar bars contained high-alkali cement. Lithium carbonate, at a Li/Na molar ratio of 0.63 proved quite effective. In another experiment in which they added LiOH.H₂O to mortar bars containing reactive aggregate and high-alkali cement, they took the weights of the bars after each length measurement. The result was that the mortar bars that expanded least, gained the least weight.

Recently, Hudec and Larbi (1989) have suggested that the use of acidified monocalcium phosphate monohydrate or apatite concentrate is effective in controlling alkali reaction.

2.12.6 Other Methods

Other methods of preventing alkali reaction in concrete include dilution of reactive aggregate with a non-reactive aggregate (Grattan-Bellew 1983). There is a danger here that pessimum conditions could be created by such action, and therefore elaborate testing of the blended aggregate is necessary.

It is also possible to prevent alkali reaction through careful considerations in design. Such a design should aim at minimizing the amount of water that gets to the structure (Grattan-Bellew 1983). In practice however, this is very difficult to achieve.
Chapter Three

Petrography of Aggregates

3.1 Sources of Aggregates Used in the Study

Four types of rocks were used as aggregates in this study. These consisted of three reactive rocks of known service records, and an unreactive rock. The three reactive rocks were designated as "PUT", "SUD", and "KIN", and are respectively alkali-silica, alkali-silicate, and alkali-carbonate reactive.

Two of these reactive rock samples ("SUD" and "KIN") were obtained from stockpiles of reactive aggregate established by the Ontario Ministry of Transportation for the calibration of new and existing test procedures on alkali-aggregate reaction (Rogers 1989). Samples of the "PUT" aggregate were collected from the New Bigging Pit, Putnam, Ontario.

The unreactive aggregate, a dolostone from Manitoulin Island, was obtained from Standard Aggregates Incorporated, Windsor. This was designated as "INACT". The locations of the reactive aggregates are shown on figure 3.1.

3.2 Petrography of Reactive Aggregates

The reactive aggregate designated as "PUT" is a chert of middle to lower Devonian age (Giliot 1986). This aggregate is silica reactive, and the reactive mineral is chert. It is fine-grained in texture, often containing patches of sand, and occurs in nodules in glacially-derived gravels near Putnam, Southwestern Ontario. When fresh, the nodules are light to medium grey in colour. They are however, usually slightly weathered, giving them a brownish yellow color.
Fig. 3.1: Map Showing General Geology and Locations of Reactive Aggregate Samples
Source: Rogers (1983)
The rock is hard, dense and has a conchoidal fracture. Petrographic data obtained by Aduamoah-Larbi (1987) show that this aggregate is mainly a mixture of chert and cherty limestone, which are of fair physical condition. A petrographic number (Ontario Ministry of Transportation Standard) of 274.7 was obtained for this aggregate. Results of petrographic analysis on this aggregate are shown in appendix B.

The "SUD" reactive aggregate is a gravel whose reactive constituents are argillites, greywackes, and quartzitic sandstones of the Huronian Supergroup, which is middle Precambrian in age (Dolar-Mantuani 1969). Gneisses, quartzites, granites and diabases are also present. This aggregate is found in Northern Ontario from the Blind River through Sudbury to New Liskeard. In the Sudbury area, where the sample used for this research is mined, the proportion of reactive material (mentioned above) in the gravel ranges from 65 to 90 percent (Magni et al. 1986). Petrographic analysis (see appendix B) shows that the various rocks that make up this aggregate are generally in good physical condition, giving the aggregate a petrographic number of 120.6.

The "KIN" reactive aggregate is alkali-carbonate reactive. It forms part of the Gull River formation (Lake Ontario Basin) and the Ottawa Limestone (Ottawa-St. Lawrence Lowlands) which is Devonian in age (Swenson and Gilliot 1960). According to Aduamoah-Larbi (1987), it consists largely of fine-grained, and hard dolomitic limestone, which is brownish grey in colour. Slightly-shaley limestone, medium grey in colour and fine-grained in texture, is also present. Results of petrographic analysis of this aggregate is provided in appendix B, and it shows a petrographic number of 124.2.
Chapter Four

Experimental Procedures

4.1 Outline

Four different experiments were carried out for this study as follows:

i. expansion tests on mortar cylinders containing reactive and unreactive aggregate and high alkali cement,

ii. silica analysis of "PUT" aggregate,

iii. unconfined compressive strength tests on mortar cylinders,

iv. pH tests on cement pastes incorporating lithium salts.

4.2 Mortar Expansion Tests

A series of linear expansion measurements on mortar cylinders exposed to hot NaOH solution constituted the main experiments done for this study. These involved length measurements of mortar cylinders containing reactive aggregates and high-alkali cement, some with and others without chemical additives to the mix water. Length changes of mortar cylinders made with unreactive aggregate and the same high-alkali cement were also determined.

A modified version (see section 2.11.2.2.1) of the rapid alkali reactivity test proposed by Oberholster and Davies (Oberholster and Davies 1986) was used in these expansion tests. Small-size mortar cylinders were reacted in an excess of 1N NaOH solution at a temperature of 80°C.
4.2.1 Chemical Treatments

Chemical treatments were performed by dissolving the chemicals given below in the mix water:

1. lithium acetate,
2. lithium bromide,
3. lithium carbonate,
4. lithium chloride,
5. lithium fluoride,
6. lithium hydroxide,
7. lithium nitrate,
8. lithium perchlorate.

Two lithium-containing minerals, amblygonite and spodumene, were also used as powder additives in some mortars. Spodumene is an alumino-silicate of lithium (\(\text{LiAlSi}_2\text{O}_6\)), having 4 to 7.5 percent of \(\text{LiO}_2\). Amblygonite is a phosphate compound (\(\text{LiAlFPO}_4\)), and contains a lower proportion of \(\text{LiO}_2\) than spodumene. Both of these minerals are mined commercially.

4.2.2 Mix Proportions

The distribution of particle sizes, in accordance with ASTM C 227, was as shown on the table below. For "PUT" specimens, 75 percent of unreactive aggregate was mixed with 25 percent of the Putnam chert, since previous research (Hudec and Larbi 1989) has established a pessimum quantity of 25 percent for the chert. CSA Type 10 portland cement with a \(\text{Na}_2\text{O}\) equivalent of 0.8 percent was used. The water:cement ratio was 0.42, and the aggregate:cement ratio was 4.
Table 4.1: Particle Size Distribution of Mortar Aggregate

<table>
<thead>
<tr>
<th>Sieve Size</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Passing</td>
<td>Retained on</td>
</tr>
<tr>
<td>No.4(4.75mm)</td>
<td>No.8(2.36mm)</td>
</tr>
<tr>
<td>No.8(2.36mm)</td>
<td>No.16(1.18mm)</td>
</tr>
<tr>
<td>No.16(1.18mm)</td>
<td>No.30(600μm)</td>
</tr>
<tr>
<td>No.30(600μm)</td>
<td>No.50(300μm)</td>
</tr>
<tr>
<td>No.50(300μm)</td>
<td>No.100(150μm)</td>
</tr>
</tbody>
</table>

4.2.3 Specimen Preparation

Preparation of specimens began with crushing of the aggregates to the appropriate particle sizes. The quantity of each fraction needed to cast one block of mortar (120mm x 60mm x 70mm) was weighed into plastic (ziplock) bags, and cement was added. The bags were tightly sealed to prevent hydration of the cement by atmospheric moisture prior to mixing. Mixing was performed according to ASTM C-305, using a Hobart-type mixer (fig. 4.1). After mixing, the material was cast into blocks in plastic containers, sealed over water and allowed to set at room temperature for 24 hours. After demolding, the blocks were cured in water for another 24 hours at a temperature of 80°C.
Fig. 4.1: Hobart-type Mixer used in Mixing Mortar Samples
Three cores, each of length 60mm and 26mm in diameter, were drilled from each block and the ends squared. Small dimples were then put at the centre of each end face of the cores (fig. 4.2). The dimples were placed so that the core could be properly seated in the instrument used for measuring lengths. Each core was then labelled, and was ready for measurement.

Fig. 4.2: Cured Mortar Blocks and Dimpled Cores Ready for Length Measurement
4.2.4 Measurement of Length

The initial lengths of the cores were determined at room temperature and in a wet state, before being reacted in 1N NaOH solution at 80°C. Lengths were then measured every 2 days till day 10, after which measurements were taken every 3 days. The measurements were taken for a period of 22 days. All measurements were made with a linear variable differential transformer, described in the next section.

Linear expansions were determined by expressing incremental changes of length over the initial length as a percentage of the initial length.

4.2.4.1 The Linear Variable Differential Transformer

Measurement of the lengths of the mortar cylinders was done using a double linear variable differential transformer (LVDT) connected to a TRS-80 model III computer, which recorded the data. This equipment was designed by Dr. P. Hudec of the University of Windsor. It was constructed by the Central Research Laboratory of the University of Windsor.

The LVDT is an electromechanical transformer which produces an electrical voltage as a function of the displacement of a movable magnetic core. The magnetic core is positioned in the centre of a cylindrical insulating form around which are three equally spaced coils (fig. 4.3). A magnetic flux generated by the magnetic core links the three coils. Depending on the position of the core, a net voltage output of appropriate sign is produced as shown in figure 4.4. The position of zero net voltage is called the balance or null point. The output is linearly related to the displacement. For a fuller description of the mechanism of the LVDT, the reader is referred
Fig. 4.3: Configuration of LVDT
Source: Lama and Vutukuri (1978)

Fig. 4.4: LVDT Output as a Function of Rod Position
Source: Lama and Vutukuri (1978)
to Lama and Vutukuri (1978). The LVDT is highly sensitive to big changes in ambient temperature, as well as to the presence of stray magnetic fields of considerable magnitude.

Two in-line LVDTs, the "coarse" and the "fine", of different sensitivities, were used. This, as explained by Hudec and Larbi (1989), enables the utilization of the sensitivity of the LVDT mechanism while allowing the removal of the core to its environment. The "coarse" LVDT serves to bring the core within measuring range, through a micrometer dial, so that the "fine" can measure the length changes. The LVDTs are fixed to a thick ceramic plate of low coefficient of thermal expansion, which is in turn supported by an aluminium plate. Brass rods of rounded tips extend from the LVDTs and serve as sample holders. Figures 4.5 and 4.6 show a schematic diagram and a photograph of the double LVDT and computer arrangement.

The "coarse" LVDT scale is in millimetres, and measures to the nearest 0.001mm. The fine scale measures in micrometres, and has a range of ±2000 micrometres. Ravina (1987) obtained a linear relationship between the two scales.

4.2.4.2 Measurement Procedures

Measurements are computer-controlled through a program in "Basic" Language. The procedure involves a sequence of steps in which the operator is prompted by the computer to enter pertinent information about the sample or press a particular key. Steps in the process designed to increase the accuracy of the readings obtained are listed below:

1. At the beginning of measurements on each day, a ceramic core of low coefficient of thermal expansivity is used to calibrate the LVDT to a length of 60.000mm.

2. For each length determination, the core length is measured seven times. The mean and standard deviation of the seven readings are calculated. Those readings that fall within
Fig. 4.5: Schematic Representation of the Double LVDT and Computer Arrangement

Fig. 4.6: The Double LVDT and Computer Arrangement
one standard deviation of the mean are then averaged to yield a single value which is used in expansion calculations.

3. The length of a second ceramic core, also of low thermal expansivity, is measured after measuring each set of three cores (representing one sample). Since this ceramic core is of known length, any drifting in the LVDT can easily be detected. If drifting is found to have occurred, the instrument is recalibrated before the next set of cores is measured.

4. Each core is always measured in the same orientation relative to the instrument to ensure consistency.

4.3 Silica Analysis

A test based on the quick chemical test (ASTM C-289) was used to investigate the ability of the lithium salts to limit the solubility of silica (from reactive aggregate) in an environment of high alkalinity. The idea was that for any chemical additive to be effective against ASR, it should be capable of doing one of the following:

i. prevent silica from dissolving into the pore solution, or

ii. reduce the ability of the alkali silicate gel to absorb water.

The "PUT" aggregate was used in this test.

4.3.1 Test Procedure

A pulverised sample of the aggregate, passing no.50 and retained on no.100 sieve, was prepared. 0.5N solutions of lithium salts and a 2N NaOH solution were also prepared. Twenty-five millilitres of the 2N NaOH solution was added to 25ml of each of the lithium salt solutions in plastic bottles. Ten grams of the aggregate powder was then added to the lithium salt/sodium
hydroxide mixture, and thoroughly stirred. A control specimen with only aggregate and sodium hydroxide was also prepared. The plastic bottles were put in an oven at a constant temperature of 80°C. After 24 hours the suspensions were cooled, filtered, and their silica contents determined by atomic absorption spectrometry.

4.4 pH Tests

A number of pH tests were performed on portland cement pastes containing some lithium salts in different concentrations. The purpose was to determine the effect of the lithium salts on the level of alkalinity of the pore solution in concrete at early age.

Forty grams of water was added to 20 grams of cement with quantities of lithium salts added to provide concentrations of 4, 10, and 20 percent. The mixture was continuously stirred for 5 minutes, and allowed to stand for 24 hours. The supernatant solution was then decanted and its pH determined. A paste containing no chemical additive was used as control.

In another set of tests, 10 percent solutions of LiCl, NaCl, and KCl were added to a saturated solution of Ca(OH)₂ and the pHs determined. A Beckman Century SS-1 pH meter was used in the tests.

4.5 Compressive Strength Tests

Unconfined compressive strength tests were performed on some of the mortar cylinders to determine whether the introduction of the lithium salts had any adverse effect on the strength of mortars. Due to limitations imposed by the dimensions of the testing apparatus, cores of diameter 19mm were used. The length of each core was 38mm, to satisfy the ASTM requirement of a length/diameter ratio of 2. It should be pointed out that neither the size of
specimens used nor the testing equipment was strictly in conformity with ASTM specifications. The maximum size of aggregate used was, however, within the limits of the specifications.

The significance of the test results therefore lies solely in the difference in strength between the untreated and the treated specimens. The values obtained however, compare favourably with average compressive strength values for standard concrete. A Donath Triaxial Deformation Apparatus was used in this test.

4.6 Thin Sections

Standard thin sections were made of selected specimens. Both reacted and unreacted specimens were used. The thin sections were examined for the presence of microcracks, alkali silicate gel, and other signs of alkali reaction. The results were qualitatively correlated to the expansions obtained in the mortar experiments. Photomicrographs of some of the thin sections are shown in appendix B.
Chapter Five

Results and Discussion

5.1 Sources of Error

A number of sources of error were identified with the expansion tests, and appropriate measures taken to limit the occurrence of errors in the results obtained. These include:

(i) Since the LVDT mechanism is very sensitive to large changes in temperature, a thermometer was affixed to the double LVDT, so that the ambient temperature could be measured during measurements. In this way, it was always ensured that the ambient temperature was within the optimum operating temperature range of the LVDT.

(ii) It was also important that all the different sets of mortar specimens were reacted (in the 1 NaOH) at the same temperature (80°C). This also applies to the curing of the mortar blocks. To this end, another thermometer was inserted into the top of the oven to ensure the maintenance of a constant temperature.

(iii) Errors could potentially occur from deposition of solid sodium hydroxide on the tips of the two LVDTs, and within the dimples of the mortar cores, through drying. These surfaces were therefore cleaned regularly to keep them as free of the NaOH as possible.

(iv) There could also have been errors through a depreciation in strength of the 1 NaOH solution. Changes in the strength of the solution were therefore monitored by measuring the refractive index of the solution from time to time. If a decline in strength was indicated, the solution was replaced by a fresh 1 normal solution.

(v) During measurements, the specimens were allowed to cool from the oven temperature to room temperature. This could potentially lead to errors in the results. However,
since the same procedure was used for all the specimens, any error introduced in this way is considered insignificant.

5.2 Results of Expansion Tests

The results of the linear expansion tests are presented in several tables and graphs. The data shown are averages of the measured linear expansions of the 3 cores representing each treatment. Linear expansion values for the untreated reactive and the unreactive are plotted on all graphs to compare the effectiveness or otherwise of the treatments used in these tests. The reader should note, that (as mentioned in section 2.11.2.2.1) a linear expansion of 0.33 percent or greater at 22 days was established by Hudec and Larbi (1989) as indicative of deleterious expansion.

5.2.1 Lithium Salts Treatments

Four lithium salts proved quite effective in reducing linear expansion of the mortar cores. These are the lithium carbonate, lithium chloride, lithium fluoride, and lithium hydroxide. Table 5.1 shows the percentage linear expansions obtained for "PUT" mortar cores treated with 4, 10, and 20 percent concentrations (by weight of water) of the above mentioned salts. These data have also been graphically illustrated in figures 5.1 to 5.7. In figures 5.1 to 5.3, the effects of the four salts at different concentrations are shown. The same data are plotted in figures 5.4 to 5.7, this time showing how effective each salt was at the different concentrations.

The slopes of the linear expansion-time plots (representing the rates of linear expansion) are also shown on table 5.1. These were calculated using simple linear regression analysis.
Slope (a) was calculated over the first 10 days, whilst slope (b) covers days 10 to 22. Table 5.2 presents the percentage reductions in linear expansion achieved by the various treatments. The percentage reductions and the slopes were calculated to facilitate comparison of the effectiveness of different treatments.

The untreated "PUT" specimen expanded by 0.53 percent at 22 days of reaction. With the exception of lithium chloride at 10 percent, all the salts mentioned above were successful at all concentrations used, reducing linear expansion by 54 to 95 percent. Twenty percent of lithium carbonate produced the lowest linear expansion of 0.03 percent at 22 days of reaction, a reduction of 95 percent.

Generally, the salts were more effective the higher the concentration used for treatment. A few departures from this trend were, however, observed. For example, there was little difference between the linear expansions of specimens treated with 4 and 10 percent of lithium carbonate (see fig. 5.4). This may have resulted from the fact that the numbers of lithium ions produced in the pore solution at the two concentrations were more or less the same. This is quite possible, given the low solubility of lithium carbonate. In figure 5.5, it is noticed that, with a treatment of 10 percent lithium chloride, the linear expansion increased sharply after 13 days, and at 22 days was well above the linear expansion of the specimen treated with 4 percent lithium chloride. The writer can see no mechanism-related reason for this behaviour, and believes it was due to experimental error. A similar behaviour was observed for the specimen treated with 10 percent lithium fluoride (fig. 5.6).

An inspection of the values of slopes (a) and (b) reveals that there was not much difference in the effectiveness of the treatments during the first half of the reaction period.
Table 5.1: *Expansion of "PUT" Aggregate Mortar Cores Treated with some Lithium Salts

<table>
<thead>
<tr>
<th>Aggregate Type</th>
<th>Treatment Chemical</th>
<th>Conc., %</th>
<th>% Expansion on Exposure for Specified no. of days</th>
<th>slope a</th>
<th>slope b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inact</td>
<td>None</td>
<td>0</td>
<td>0 0.01 0.01 0.01 0.01 0.01 0.01 0.02 0.02 0.02 0.03</td>
<td>0.000</td>
<td>0.001</td>
</tr>
<tr>
<td>Put</td>
<td>Untreated</td>
<td>0</td>
<td>0 0.03 0.09 0.16 0.21 0.26 0.31 0.38 0.47 0.53</td>
<td>0.030</td>
<td>0.023</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Carbonate</td>
<td>4</td>
<td>0 0.01 -0.00 0.02 0.02 0.05 0.08 0.13 0.17 0.23</td>
<td>0.006</td>
<td>0.015</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Chloride</td>
<td>4</td>
<td>0 0.00 0.00 0.02 0.04 0.03 0.06 0.09 0.16 0.21</td>
<td>0.004</td>
<td>0.015</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Fluoride</td>
<td>4</td>
<td>0 0.01 -0.00 0.02 0.03 0.04 0.05 0.06 0.09 0.13</td>
<td>0.005</td>
<td>0.007</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Hydroxide</td>
<td>4</td>
<td>0 0.01 0.01 0.02 0.03 0.04 0.07 0.09 0.12 0.16</td>
<td>0.005</td>
<td>0.009</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Carbonate</td>
<td>10</td>
<td>0 0.01 0.01 0.01 0.02 0.04 0.06 0.09 0.17 0.24</td>
<td>0.003</td>
<td>0.018</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Chloride</td>
<td>10</td>
<td>0 0.01 0.01 0.01 0.01 0.04 0.03 0.14 0.31 0.45</td>
<td>0.003</td>
<td>0.037</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Fluoride</td>
<td>10</td>
<td>0 0.01 0.03 0.03 0.04 0.06 0.03 0.12 0.17 0.23</td>
<td>0.005</td>
<td>0.016</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Hydroxide</td>
<td>10</td>
<td>0 0.02 0.02 0.02 0.02 0.01 0.03 0.05 0.09 0.16</td>
<td>0.000</td>
<td>0.011</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Carbonate</td>
<td>20</td>
<td>0 0.01 -0.00 0.01 0.01 0.00 0.02 0.02 0.02 0.03</td>
<td>0.000</td>
<td>0.002</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Chloride</td>
<td>20</td>
<td>0 0.01 0.00 0.01 0.02 0.02 0.04 0.05 0.06 0.10</td>
<td>0.002</td>
<td>0.006</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Fluoride</td>
<td>20</td>
<td>0 0.01 0.01 0.02 0.05 0.07 0.10 0.12 0.13 0.14</td>
<td>0.008</td>
<td>0.006</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Hydroxide</td>
<td>20</td>
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<td>0.001</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Slope (a) -- covers days 2 to 10
Slope (b) -- covers days 10 to 22

* Refers to linear expansion
Table 5.2: % Reduction in *Expansion obtained for different Treatments of "PUT" Mortar Cores

<table>
<thead>
<tr>
<th>Aggregate Type</th>
<th>Treatment Chemical</th>
<th>Conc., %</th>
<th>Expansion, %</th>
<th>% Exp. Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Put</td>
<td>Untreated</td>
<td>0</td>
<td>0.31</td>
<td>0</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Carbonate</td>
<td>20</td>
<td>0.02</td>
<td>94</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Hydroxide</td>
<td>20</td>
<td>0.03</td>
<td>89</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Chloride</td>
<td>20</td>
<td>0.04</td>
<td>87</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Fluoride</td>
<td>4</td>
<td>0.05</td>
<td>83</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Fluoride</td>
<td>20</td>
<td>0.10</td>
<td>67</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Hydroxide</td>
<td>10</td>
<td>0.03</td>
<td>89</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Hydroxide</td>
<td>4</td>
<td>0.07</td>
<td>78</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Chloride</td>
<td>4</td>
<td>0.06</td>
<td>81</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Fluoride</td>
<td>10</td>
<td>0.03</td>
<td>90</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Carbonate</td>
<td>4</td>
<td>0.08</td>
<td>76</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Carbonate</td>
<td>10</td>
<td>0.06</td>
<td>82</td>
</tr>
<tr>
<td>Put</td>
<td>Spodumene</td>
<td>15</td>
<td>0.15</td>
<td>51</td>
</tr>
<tr>
<td>Put</td>
<td>Spodumene</td>
<td>20</td>
<td>0.14</td>
<td>54</td>
</tr>
<tr>
<td>Put</td>
<td>Amblygonite</td>
<td>15</td>
<td>0.17</td>
<td>46</td>
</tr>
<tr>
<td>Put</td>
<td>Spodumene</td>
<td>10</td>
<td>0.18</td>
<td>41</td>
</tr>
<tr>
<td>Put</td>
<td>Amblygonite</td>
<td>10</td>
<td>0.19</td>
<td>39</td>
</tr>
<tr>
<td>Put</td>
<td>Amblygonite</td>
<td>20</td>
<td>0.21</td>
<td>33</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Chloride</td>
<td>10</td>
<td>0.03</td>
<td>92</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Nitrate</td>
<td>10</td>
<td>0.09</td>
<td>70</td>
</tr>
<tr>
<td>Put</td>
<td>Amblygonite</td>
<td>5</td>
<td>0.29</td>
<td>6</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Bromide</td>
<td>10</td>
<td>0.12</td>
<td>63</td>
</tr>
<tr>
<td>Put</td>
<td>Spodumene</td>
<td>5</td>
<td>0.41</td>
<td>-31</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Acetate</td>
<td>10</td>
<td>0.12</td>
<td>63</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Perchlorate</td>
<td>10</td>
<td>0.40</td>
<td>-29</td>
</tr>
</tbody>
</table>

* Refers to linear expansion

** Figures in brackets indicate number of days of reaction

65
Fig. 5.1: Expansion of Mortar Cores Treated with 4% of Various Lithium Salts
Aggregate Used: "PUT"

Fig. 5.2: Expansion of Mortar Cores Treated with 10% of Various Lithium Salts
Aggregate Used: "PUT"
Fig. 5.3: Expansion of Mortar Cores Treated with 20% of Various Lithium Salts
Aggregate Used: "PUT"

Fig. 5.4: Expansion of Mortar Cores Treated with Various Percentages of Lithium Carbonate
Aggregate Used: "PUT"
Fig. 5.5: Expansion of Mortar Cores Treated with Various Percentages of Lithium Chloride
Aggregate Used: "PUT"

Fig. 5.6: Expansion of Mortar Cores Treated with Various Percentages of Lithium Fluoride
Aggregate Used: "PUT"
Fig. 5.7: Expansion of Mortar Cores Treated with Various Percentages of Lithium Hydroxide
Aggregate Used: "PUT"

Fig. 5.8: Expansion of Mortar Cores Treated with 10% of some Lithium Salts
Aggregate Used: "PUT"
The differences in the effectiveness of the treatments became obvious during the latter stage of the reaction period.

Lithium acetate, lithium bromide, lithium nitrate, and lithium perchlorate were used as treatments at a concentration of 10 percent, but without much success. For "PUT" cores, all four produced increased linear expansion at 22 days. Data for these salts are shown on table 5.3, and plotted in figure 5.8. Lithium perchlorate was the least effective, causing an increase in linear expansion of 54 percent. Lithium acetate resulted in an linear expansion of 0.71 percent, an increase of 34 percent.

All the salts used to treat the "PUT" mortar cores were also used as treatments on mortar cores containing "SUD" aggregate. The linear expansion results, as well as slope data, are presented on table 5.4. These data are also plotted in figures 5.9 to 5.13. Percentage reductions in linear expansion are shown on table 5.5. The untreated specimen expanded by 0.44 percent. With 10 percent of each of lithium hydroxide and lithium carbonate as treatment, there were linear expansions of 0.03 and 0.06 percent at 22 days respectively. These constitute respectively 94 and 87 percent reductions in linear expansion. Only the perchlorate caused an increase in linear expansion. Lithium acetate and lithium bromide, however, achieved reductions of only 11 and 35 percent.

Linear expansion data for cores containing "KIN" aggregate are shown on table 5.6, and illustrated graphically in figure 5.14. Only those lithium salts which were successful as treatments for the "PUT" cores were used to treat the "KIN" cores. They were each applied at a concentration of 4 percent (by weight of water). These treatments were not very effective, producing a maximum reduction in linear expansion of only 36 percent at 22 days of reaction.
Table 5.3: Data on *Expansion of Mortar Cores Treated with 10% of some Lithium Salts

<table>
<thead>
<tr>
<th>Aggregate Type</th>
<th>Treatment Chemical</th>
<th>% Expansion after Exposure for specified number of days</th>
<th>Slope a</th>
<th>Slope b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inact</td>
<td>None</td>
<td>0 0.01 0.01 0.01 0.01 0.02 0.02 0.02 0.03</td>
<td>0.000</td>
<td>0.001</td>
</tr>
<tr>
<td>Put</td>
<td>Untreated</td>
<td>0 0.03 0.09 0.16 0.21 0.26 0.31 0.37 0.47 0.53</td>
<td>0.030</td>
<td>0.023</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Acetate</td>
<td>0 0.01 0.03 0.03 0.04 0.07 0.12 0.26 0.53 0.71</td>
<td>0.007</td>
<td>0.057</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Bromide</td>
<td>0 0.00 0.02 0.03 0.04 0.08 0.12 0.26 0.45 0.58</td>
<td>0.009</td>
<td>0.044</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Nitrate</td>
<td>0 0.01 0.01 0.01 0.03 0.09 0.22 0.40 0.58 0.81</td>
<td>0.004</td>
<td>0.046</td>
</tr>
<tr>
<td>Put</td>
<td>Li-Perchlorate</td>
<td>0 0.02 0.07 0.08 0.17 0.26 0.40 0.61 0.69 0.81</td>
<td>0.029</td>
<td>0.047</td>
</tr>
<tr>
<td>Sud</td>
<td>Untreated</td>
<td>0 0.02 0.03 0.06 0.11 0.16 0.23 0.33 0.39 0.44</td>
<td>0.019</td>
<td>0.023</td>
</tr>
<tr>
<td>Sud</td>
<td>Li-Acetate</td>
<td>0 -0.00 0.01 0.01 0.02 0.04 0.07 0.16 0.29 0.39</td>
<td>0.005</td>
<td>0.031</td>
</tr>
<tr>
<td>Sud</td>
<td>Li-Bromide</td>
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<td>0.004</td>
<td>0.022</td>
</tr>
<tr>
<td>Sud</td>
<td>Li-Nitrate</td>
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<td>0.001</td>
<td>0.009</td>
</tr>
<tr>
<td>Sud</td>
<td>Li-Perchlorate</td>
<td>0 0.01 0.03 0.04 0.08 0.12 0.22 0.33 0.41 0.44</td>
<td>0.013</td>
<td>0.028</td>
</tr>
</tbody>
</table>

Slope (a) -- covers days 2 to 10
Slope (b) -- covers days 10 to 22

* Refers to linear expansion
<table>
<thead>
<tr>
<th>Aggregate Type</th>
<th>Treatment Chemical</th>
<th>Conc., %</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>13</th>
<th>16</th>
<th>19</th>
<th>22</th>
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<th>slope b</th>
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<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
<td>0.000</td>
<td>0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sud</td>
<td>Untreated</td>
<td>0</td>
<td>0.02</td>
<td>0.03</td>
<td>0.06</td>
<td>0.11</td>
<td>0.16</td>
<td>0.23</td>
<td>0.33</td>
<td>0.39</td>
<td>0.44</td>
<td>0.019</td>
<td>0.023</td>
<td></td>
</tr>
<tr>
<td>Sud</td>
<td>Li-Carbonate</td>
<td>4</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.03</td>
<td>0.05</td>
<td>0.07</td>
<td>0.12</td>
<td>0.13</td>
<td>0.17</td>
<td>0.005</td>
<td>0.010</td>
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<tr>
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<td>Li-Chloride</td>
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<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.04</td>
<td>0.07</td>
<td>0.09</td>
<td>0.14</td>
<td>0.20</td>
<td>0.004</td>
<td>0.012</td>
<td></td>
</tr>
<tr>
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<td>Li-Fluoride</td>
<td>4</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>0.02</td>
<td>0.04</td>
<td>0.06</td>
<td>0.11</td>
<td>0.003</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>Sud</td>
<td>Li-Hydroxide</td>
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<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>0.04</td>
<td>0.07</td>
<td>0.10</td>
<td>0.15</td>
<td>0.003</td>
<td>0.010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sud</td>
<td>Li-Carbonate</td>
<td>10</td>
<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.04</td>
<td>0.05</td>
<td>0.06</td>
<td>0.003</td>
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<td></td>
</tr>
<tr>
<td>Sud</td>
<td>Li-Hydroxide</td>
<td>10</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
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<td>0.02</td>
<td>0.03</td>
<td>0.000</td>
<td>0.001</td>
<td></td>
</tr>
</tbody>
</table>

Slope (a) -- covers days 2 to 10
Slope (b) -- covers days 10 to 22

* Refers to linear expansion
Table 5.5: % Reduction in *Expansion obtained for different Treatments of "SUD" Mortar Cores

<table>
<thead>
<tr>
<th>Aggregate Type</th>
<th>Treatment Chemical</th>
<th>Conc., %</th>
<th>Expansion, % <strong>(13)</strong></th>
<th>Expansion, % <strong>(22)</strong></th>
<th>% Exp. Reduction <strong>(13)</strong></th>
<th>% Exp. Reduction <strong>(22)</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sud</td>
<td>Untreated</td>
<td>3</td>
<td>0.23</td>
<td>0.44</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sud</td>
<td>Li-Hydroxide</td>
<td>10</td>
<td>0.02</td>
<td>0.03</td>
<td>93</td>
<td>94</td>
</tr>
<tr>
<td>Sud</td>
<td>Li-Carbonate</td>
<td>10</td>
<td>0.02</td>
<td>0.06</td>
<td>92</td>
<td>86</td>
</tr>
<tr>
<td>Sud</td>
<td>Li-Fluoride</td>
<td>4</td>
<td>0.02</td>
<td>0.11</td>
<td>91</td>
<td>75</td>
</tr>
<tr>
<td>Sud</td>
<td>Li-Nitrate</td>
<td>10</td>
<td>0.03</td>
<td>0.12</td>
<td>87</td>
<td>71</td>
</tr>
<tr>
<td>Sud</td>
<td>Li-Hydroxide</td>
<td>4</td>
<td>0.04</td>
<td>0.15</td>
<td>81</td>
<td>65</td>
</tr>
<tr>
<td>Sud</td>
<td>Li-Carbonate</td>
<td>4</td>
<td>0.07</td>
<td>0.17</td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td>Sud</td>
<td>Li-Chloride</td>
<td>4</td>
<td>0.07</td>
<td>0.20</td>
<td>71</td>
<td>55</td>
</tr>
<tr>
<td>Sud</td>
<td>Spodumene</td>
<td>15</td>
<td>0.13</td>
<td>0.25</td>
<td>42</td>
<td>43</td>
</tr>
<tr>
<td>Sud</td>
<td>Spodumene</td>
<td>20</td>
<td>0.13</td>
<td>0.26</td>
<td>43</td>
<td>41</td>
</tr>
<tr>
<td>Sud</td>
<td>Li-Bromide</td>
<td>10</td>
<td>0.05</td>
<td>0.29</td>
<td>79</td>
<td>35</td>
</tr>
<tr>
<td>Sud</td>
<td>Amblygonite</td>
<td>10</td>
<td>0.16</td>
<td>0.39</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>Sud</td>
<td>Spodumene</td>
<td>10</td>
<td>0.17</td>
<td>0.34</td>
<td>25</td>
<td>21</td>
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<tr>
<td>Sud</td>
<td>Li-Acetate</td>
<td>10</td>
<td>0.07</td>
<td>0.39</td>
<td>71</td>
<td>11</td>
</tr>
<tr>
<td>Sud</td>
<td>Li-Perchlorate</td>
<td>10</td>
<td>0.22</td>
<td>0.44</td>
<td>5</td>
<td>-2</td>
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<tr>
<td>Sud</td>
<td>Amblygonite</td>
<td>5</td>
<td>0.23</td>
<td>0.46</td>
<td>-0</td>
<td>-6</td>
</tr>
<tr>
<td>Sud</td>
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<td>5</td>
<td>0.26</td>
<td>0.48</td>
<td>-11</td>
<td>-10</td>
</tr>
</tbody>
</table>

* Refers to linear expansion

** Figures in brackets indicate number of days of reaction
Table 5.6: *Expansion of "KIN" Mortar Cores Treated with 4% of some Lithium Salts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>% Expansion on Exposure for Specified No. of days</th>
<th>% Exp. Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chemical</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Inact</td>
<td>None</td>
<td>0</td>
<td>0.01</td>
</tr>
<tr>
<td>Kin</td>
<td>Untreated</td>
<td>0</td>
<td>0.00</td>
</tr>
<tr>
<td>Kin</td>
<td>Li-Carbonate</td>
<td>0</td>
<td>0.01</td>
</tr>
<tr>
<td>Kin</td>
<td>Li-Chloride</td>
<td>0</td>
<td>0.01</td>
</tr>
<tr>
<td>Kin</td>
<td>Li-Fluoride</td>
<td>0</td>
<td>0.01</td>
</tr>
<tr>
<td>Kin</td>
<td>Li-Hydroxide</td>
<td>0</td>
<td>0.01</td>
</tr>
</tbody>
</table>

* Refers to linear expansion

** Figures in brackets indicate number of days of reaction
Fig. 5.9: Expansion of Mortar Cores Treated with 4% of Various Lithium Salts
Aggregate Used: "SUD"

Fig. 5.10: Expansion of Mortar Cores Treated with 10% of Various Lithium Salts
Aggregate Used: "SUD"
Fig. 5.11: Expansion of Mortar Cores Treated with Various Percentages of Lithium Carbonate
Aggregate Used: "SUD"

Fig. 5.12: Expansion of Mortar Cores Treated with Various Percentages of Lithium Hydroxide
Aggregate Used: "SUD"
Fig. 5.13: Expansion of Mortar Cores Treated with 10% of some Lithium Salts
Aggregate Used: "SUD"

Fig. 5.14: Expansion of Mortar Cores Treated with 4% of Various Lithium Salts
Aggregate Used: "KIN"
Since the "KIN" cores are alkali carbonate reactive, the inability of the lithium salts to inhibit the linear expansions may be related to the fact that no gel is produced by the carbonate reaction. This line of thought is based on the premise that the effectiveness of the lithium salts against ASR is mainly due to lithium ion action on the alkali silica gel, as will be discussed in section 5.6.

An examination of all the data above, as well as the accompanying graphs, reveals an interesting finding. It is noticed that, generally, the treatments significantly suppressed linear expansion, with much lower rates of linear expansion until about 13 to 16 days, when linear expansions rose sharply. It appears the effect of the lithium ion is overwhelmed at that stage of reaction. This is probably because by that time sodium and potassium ions dissolve into the pore solution in sufficient numbers as to strongly counter the effect of the lithium ions. If the concentration of lithium ions is high enough, however, its effect prevails, keeping the rate of linear expansion to a minimum.

It is interesting to note that data obtained by McCoy and Caldwell (1951) showed a similar effect. For example, using 0.5 percent (by weight of cement) of lithium chloride to treat mortar bars, there was a 75 percent reduction in linear expansion at 2 weeks, but at 8 weeks there was a reduction of only 34 percent. When the concentration of the salt was increased to 1.0 percent, the linear expansion was reduced by 90 percent at 2 weeks, and by 88 percent at 8 weeks. With 0.5 percent lithium carbonate as treatment, linear expansion was reduced by 89 and 62 percent at 2 and 8 weeks respectively. However, when the concentration was increased to 1.0 percent, linear expansion reduction at 2 weeks was 94 percent, whilst 91 percent was achieved at 8 weeks.
5.2.2 **Treatment with Minerals**

Linear expansion data for mortar cores treated with the lithium-containing minerals amblygonite and spodumene are given in Table 5.7 and in Figures 15 to 18. These treatments were used for "PUT" and "SUD" cores only.

The minerals were not as effective for treatment as the salts. At 5 percent concentration, both treatments caused increased linear expansion at 22 days. With increased concentration, however, the linear expansion was reduced, but not significantly even at 20 percent concentration. In general, spodumene appeared to perform better than amblygonite.

Despite the disappointing results obtained for the above treatments, the writer hesitates to write off the two minerals as ineffective treatments against alkali-silica reaction. Attention is drawn to the fact other minerals such as silica fume and slag have to be used in large amounts for them to be effective, as discussed in Chapter two. It should also be borne in mind, that the samples of spodumene and amblygonite were used "by addition to cement", instead of "by replacement of cement" as silica fume and the others are usually used.

If part of the cement had been replaced by the minerals, it stands to reason that greater reductions in linear expansion could have been achieved, since the quantity of alkalis in the mix would have been reduced. It must be pointed out nevertheless that these minerals can only be used to replace cement in sizeable quantities if, and only if, such usage will not compromise the strength development of the mortar or concrete. Additionally, the economics of using these minerals in large amounts may make the practice unattractive.
Table 5.7: *Expansion Data for Mortar Cores Treated with Lithium-containing Minerals

<table>
<thead>
<tr>
<th>Aggregate Type</th>
<th><strong>Treatment</strong></th>
<th>Conc., %</th>
<th>% Expansion on Exposure for Specified No. of Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inact</td>
<td>None</td>
<td>0</td>
<td>0 0.01 0.01 0.01 0.01 0.01 0.02 0.02 0.02 0.03</td>
</tr>
<tr>
<td>Put</td>
<td>Untreated</td>
<td>0</td>
<td>0 0.03 0.09 0.16 0.21 0.26 0.31 0.38 0.47 0.53</td>
</tr>
<tr>
<td>Put</td>
<td>Spodumene</td>
<td>5</td>
<td>0 0.02 0.09 0.18 0.24 0.30 0.41 0.49 0.56 0.62</td>
</tr>
<tr>
<td>Put</td>
<td>Spodumene</td>
<td>10</td>
<td>0 0.01 0.04 0.06 0.09 0.12 0.18 0.24 0.25 0.33</td>
</tr>
<tr>
<td>Put</td>
<td>Spodumene</td>
<td>15</td>
<td>0 0.01 0.04 0.06 0.08 0.10 0.15 0.22 0.24 0.30</td>
</tr>
<tr>
<td>Put</td>
<td>Spodumene</td>
<td>20</td>
<td>0 0.00 0.03 0.04 0.05 0.09 0.14 0.23 0.23 0.30</td>
</tr>
<tr>
<td>Put</td>
<td>Amblygonite</td>
<td>5</td>
<td>0 0.02 0.07 0.13 0.17 0.20 0.29 0.37 0.43 0.58</td>
</tr>
<tr>
<td>Put</td>
<td>Amblygonite</td>
<td>10</td>
<td>0 0.02 0.04 0.05 0.08 0.13 0.15 0.26 0.28 0.34</td>
</tr>
<tr>
<td>Put</td>
<td>Amblygonite</td>
<td>15</td>
<td>0 0.00 0.02 0.04 0.07 0.11 0.17 0.24 0.26 0.31</td>
</tr>
<tr>
<td>Put</td>
<td>Amblygonite</td>
<td>20</td>
<td>0 0.01 0.04 0.06 0.09 0.15 0.21 0.31 0.32 0.39</td>
</tr>
<tr>
<td>Sud</td>
<td>Untreated</td>
<td>0</td>
<td>0 0.02 0.03 0.06 0.11 0.16 0.23 0.33 0.39 0.44</td>
</tr>
<tr>
<td>Sud</td>
<td>Spodumene</td>
<td>5</td>
<td>0 0.00 0.03 0.09 0.12 0.18 0.26 0.33 0.41 0.48</td>
</tr>
<tr>
<td>Sud</td>
<td>Spodumene</td>
<td>10</td>
<td>0 -0.00 0.02 0.05 0.08 0.11 0.17 0.24 0.26 0.34</td>
</tr>
<tr>
<td>Sud</td>
<td>Spodumene</td>
<td>15</td>
<td>0 -0.00 0.02 0.04 0.05 0.08 0.13 0.18 0.19 0.25</td>
</tr>
<tr>
<td>Sud</td>
<td>Spodumene</td>
<td>20</td>
<td>0 -0.01 0.02 0.04 0.06 0.08 0.13 0.18 0.20 0.26</td>
</tr>
<tr>
<td>Sud</td>
<td>Amblygonite</td>
<td>5</td>
<td>0 -0.00 0.03 0.08 0.11 0.16 0.23 0.30 0.38 0.46</td>
</tr>
<tr>
<td>Sud</td>
<td>Amblygonite</td>
<td>10</td>
<td>0 0.00 0.02 0.05 0.08 0.12 0.18 0.26 0.27 0.34</td>
</tr>
</tbody>
</table>

* Refers to linear expansion

** Minerals added in powder form
Fig. 5.15: Expansion of Mortar Cores Treated with Various Percentages of Spodumene
Aggregate Used: "PUT"

Fig.5.16: Expansion of Mortar Cores Treated with Various Percentages of Spodumene
Aggregate Used: "SUD"
Fig. 5.17: Expansion of Mortar Cores Treated with Various Percentages of Amblygonite
Aggregate Used: "PUT"

Fig. 5.18: Expansion of Mortar Cores Treated with Various Percentages of Amblygonite
Aggregate Used: "SUD"
5.2.3 Statistical Analyses

Statistical analyses were carried out to determine the significance of the difference in linear expansions between the treated and untreated specimens, using the F-test. Similar comparisons were also made for the four salts which were effective as treatments (Li₂CO₃, LiCl, LiF, LiOH) to test for statistical variations in their linear expansions. Data for 20 percent treatments were used for these analyses. The results are shown on tables 5.8 and 5.9. Data for the minerals treatments were also analysed to determine if there were significant variations between the untreated and treated specimens. The results are presented on table 5.10.

On table 5.8, each of the salts was compared to the untreated specimen, whilst on table 5.9 comparisons were made between lithium carbonate and each of the other salts. The results show that there were significant variations, to a 5 percent level of significance, between the untreated specimens and the treated. In other words, the linear expansions of the untreated and treated specimens were significantly different, statistically. The test also showed that there were not any significant variations in the linear expansions of the treated specimens. For the minerals treatments, no significant variations were found between the untreated and treated specimens.

5.3 Results of Silica Analysis

The results of the silica analysis on "PUT" aggregate are presented on table 5.11 and in figure 5.19. They show very little reductions in the concentration of silica, with three treatments (Li₂CO₃, LiNO₃, and LiClO₄) causing no reductions at all. No relationship between these results and the linear expansions of the mortar cores treated with the respective salts is discerned.
### Table 5.8: Statistical Comparison of Untreated and Lithium Salts-Treated Mortar Cores

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Sample Size</th>
<th>Variance</th>
<th>F-value</th>
<th>Significance Level,</th>
<th>F</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>15</td>
<td>0.0095</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20% Li-Carbonate</td>
<td>15</td>
<td>0.0001</td>
<td>95.0</td>
<td>0.05</td>
<td>2.98</td>
<td>Significant Variation</td>
</tr>
<tr>
<td>20% Li-Chloride</td>
<td>15</td>
<td>0.0001</td>
<td>95.0</td>
<td>0.05</td>
<td>2.98</td>
<td>Significant Variation</td>
</tr>
<tr>
<td>20% Li-Fluoride</td>
<td>15</td>
<td>0.0002</td>
<td>47.5</td>
<td>0.05</td>
<td>2.98</td>
<td>Significant Variation</td>
</tr>
<tr>
<td>20% Li-Hydroxide</td>
<td>15</td>
<td>0.0001</td>
<td>95.0</td>
<td>0.05</td>
<td>2.98</td>
<td>Significant Variation</td>
</tr>
</tbody>
</table>

### Table 5.9: Statistical Comparison Between Mortar Core Treatments

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Sample Size</th>
<th>Variance</th>
<th>F-value</th>
<th>Significance Level,</th>
<th>F</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% Li-Carbonate</td>
<td>15</td>
<td>0.0001</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20% Li-Chloride</td>
<td>15</td>
<td>0.0001</td>
<td>1</td>
<td>0.05</td>
<td>2.98</td>
<td>No Significant Variation</td>
</tr>
<tr>
<td>20% Li-Fluoride</td>
<td>15</td>
<td>0.0002</td>
<td>2</td>
<td>0.05</td>
<td>2.98</td>
<td>No Significant Variation</td>
</tr>
<tr>
<td>20% Li-Hydroxide</td>
<td>15</td>
<td>0.0001</td>
<td>1</td>
<td>0.05</td>
<td>2.98</td>
<td>No Significant Variation</td>
</tr>
</tbody>
</table>

### Table 5.10: Statistical Comparison of Untreated and Minerals-treated Mortar Cores

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Sample Size</th>
<th>Variance</th>
<th>F-value</th>
<th>Significance Level,</th>
<th>F</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>15</td>
<td>0.0095</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20% Amblygonite</td>
<td>15</td>
<td>0.0072</td>
<td>1.3</td>
<td>0.05</td>
<td>2.98</td>
<td>No Significant Variation</td>
</tr>
<tr>
<td>20% Spodumene</td>
<td>15</td>
<td>0.0054</td>
<td>1.6</td>
<td>0.05</td>
<td>2.98</td>
<td>No Significant Variation</td>
</tr>
<tr>
<td>15% Amblygonite</td>
<td>15</td>
<td>0.0052</td>
<td>1.8</td>
<td>0.05</td>
<td>2.98</td>
<td>No Significant Variation</td>
</tr>
<tr>
<td>15% Spodumene</td>
<td>15</td>
<td>0.0045</td>
<td>2.1</td>
<td>0.05</td>
<td>2.98</td>
<td>No Significant Variation</td>
</tr>
</tbody>
</table>

F-value = $s_f^2 / s_i^2$; $s_f^2 > s_i^2$
### Table 5.11: Results of Silica Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Silica Conc., ppm</th>
<th>Reduction in Silica, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUT</td>
<td>Li-Acetate</td>
<td>6750</td>
<td>350</td>
</tr>
<tr>
<td>PUT</td>
<td>Li-Bromide</td>
<td>6250</td>
<td>850</td>
</tr>
<tr>
<td>PUT</td>
<td>Li-Carbonate</td>
<td>7100</td>
<td>0</td>
</tr>
<tr>
<td>PUT</td>
<td>Li-Chloride</td>
<td>5750</td>
<td>1350</td>
</tr>
<tr>
<td>PUT</td>
<td>Li-Fluoride</td>
<td>6750</td>
<td>350</td>
</tr>
<tr>
<td>PUT</td>
<td>Li-Hydroxide</td>
<td>6750</td>
<td>350</td>
</tr>
<tr>
<td>PUT</td>
<td>Li-Nitrate</td>
<td>7100</td>
<td>0</td>
</tr>
<tr>
<td>PUT</td>
<td>Li-Perchlorate</td>
<td>7100</td>
<td>0</td>
</tr>
</tbody>
</table>

![Graphical Illustration of Silica Analysis Results](image.png)

*Fig. 5.19: Graphical Illustration of Silica Analysis Results*
5.4 Results of pH Tests

Data on the pH tests are shown on table 5.12 and in figures 5.20 and 5.21. These data represent the pH values of the pore solutions of the various mortar specimens at the commencement of the linear expansion tests. The pH of untreated cement paste was determined as 13.4. This is quite close to the value of 13.5 given by Diamond (1983) for hardened cement paste.

For each treatment there was a consistent decrease in the pH of the paste with increasing concentration of salt treatment. A comparison of the pH values for pastes treated with the chlorides of lithium, sodium, and potassium shows that there was an increase in pH from lithium chloride treatment to potassium chloride treatment. This means there is an increase in pH the larger the size of the cation of the treatment chemical.

There was a similar trend when the three chlorides were used to treat saturated calcium hydroxide. The pH of the saturated calcium hydroxide was found to be 12.5. Using lithium chloride treatment the pH was 11.5, compared to 12.2 for sodium chloride and 12.7 for potassium chloride.

5.5 Results of Strength Tests

The results of the strength tests (table 5.13 and fig. 5.22) show that most lithium salts can be used to treat mortar (against ASR) without sacrificing its strength. Only mortar cores treated with lithium carbonate showed a substantial decrease in strength. The strength was reduced by 25 percent. This is similar to what McCoy and Caldwell (1951) obtained when they tested a hardened cement paste treated with lithium carbonate.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Conc., %</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement Paste</td>
<td>Untreated</td>
<td>0</td>
<td>13.4</td>
</tr>
<tr>
<td>Cement Paste</td>
<td>Li-Chloride</td>
<td>4</td>
<td>12.4</td>
</tr>
<tr>
<td>Cement Paste</td>
<td>Li-Chloride</td>
<td>10</td>
<td>11.8</td>
</tr>
<tr>
<td>Cement Paste</td>
<td>Li-Chloride</td>
<td>20</td>
<td>11.1</td>
</tr>
<tr>
<td>Cement Paste</td>
<td>Li-Carbonate</td>
<td>4</td>
<td>12.8</td>
</tr>
<tr>
<td>Cement Paste</td>
<td>Li-Carbonate</td>
<td>10</td>
<td>12.4</td>
</tr>
<tr>
<td>Cement Paste</td>
<td>Li-Carbonate</td>
<td>20</td>
<td>12.1</td>
</tr>
<tr>
<td>Cement Paste</td>
<td>Li-Fluoride</td>
<td>4</td>
<td>12.9</td>
</tr>
<tr>
<td>Cement Paste</td>
<td>Li-Fluoride</td>
<td>10</td>
<td>12.6</td>
</tr>
<tr>
<td>Cement Paste</td>
<td>Li-Fluoride</td>
<td>20</td>
<td>12.0</td>
</tr>
<tr>
<td>Cement Paste</td>
<td>Li-Hydroxide</td>
<td>4</td>
<td>12.9</td>
</tr>
<tr>
<td>Cement Paste</td>
<td>Li-Hydroxide</td>
<td>10</td>
<td>12.5</td>
</tr>
<tr>
<td>Cement Paste</td>
<td>Li-Hydroxide</td>
<td>20</td>
<td>12.2</td>
</tr>
<tr>
<td>Cement Paste</td>
<td>Li-Perchlorate</td>
<td>10</td>
<td>12.6</td>
</tr>
<tr>
<td>Cement Paste</td>
<td>Li-Acetate</td>
<td>10</td>
<td>12.7</td>
</tr>
<tr>
<td>Cement Paste</td>
<td>Li-Bromide</td>
<td>10</td>
<td>12.4</td>
</tr>
<tr>
<td>Cement Paste</td>
<td>Li-Nitrate</td>
<td>10</td>
<td>12.2</td>
</tr>
<tr>
<td>Cement Paste</td>
<td>Na-Chloride</td>
<td>10</td>
<td>12.8</td>
</tr>
<tr>
<td>Cement Paste</td>
<td>K-Chloride</td>
<td>10</td>
<td>13.3</td>
</tr>
<tr>
<td>Sat.ed Ca-Hydroxide</td>
<td>Untreated</td>
<td>0</td>
<td>12.5</td>
</tr>
<tr>
<td>Sat.ed Ca-Hydroxide</td>
<td>Li-Chloride</td>
<td>10</td>
<td>11.5</td>
</tr>
<tr>
<td>Sat.ed Ca-Hydroxide</td>
<td>Na-Chloride</td>
<td>10</td>
<td>12.2</td>
</tr>
<tr>
<td>Sat.ed Ca-Hydroxide</td>
<td>K-Chloride</td>
<td>10</td>
<td>12.7</td>
</tr>
</tbody>
</table>

Concentration by weight of water
Fig. 5.20: Effect of some Lithium Salts on the pH of Cement Paste

Fig. 5.21: Effect of Different Alkalis on the pH of Cement Paste
### Table 5.13: Results of Unconfined Compressive Strength Tests on Mortar Cores

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Strength, psi(MPa)</th>
<th>% Change in Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUT</td>
<td>Untreated</td>
<td>4080.3(28.6)</td>
<td>0.0</td>
</tr>
<tr>
<td>PUT</td>
<td>10% Li-Carbonate</td>
<td>3056.3(21.4)</td>
<td>-25.1</td>
</tr>
<tr>
<td>PUT</td>
<td>10% Li-Chloride</td>
<td>4557.4(31.9)</td>
<td>11.7</td>
</tr>
<tr>
<td>PUT</td>
<td>10% Li-Fluoride</td>
<td>4300.7(30.1)</td>
<td>5.4</td>
</tr>
<tr>
<td>PUT</td>
<td>10% Li-Hydroxide</td>
<td>3994.2(28.0)</td>
<td>-2.1</td>
</tr>
<tr>
<td>SUD</td>
<td>Untreated</td>
<td>4910.7(34.4)</td>
<td>0.0</td>
</tr>
<tr>
<td>SUD</td>
<td>10% Li-Carbonate</td>
<td>3395.3(23.8)</td>
<td>-30.9</td>
</tr>
<tr>
<td>SUD</td>
<td>105 Li-Hydroxide</td>
<td>4020.0(29.4)</td>
<td>-14.4</td>
</tr>
</tbody>
</table>

### Fig. 5.22: Effect of 10% of Various Lithium Salts on Compressive Strength of Mortar made with "PUT" Aggregate
On the contrary, cores treated with lithium fluoride and lithium chloride actually showed increases in strength. Lithium hydroxide treatment resulted in a decrease in strength of only 2 percent. The large reduction in unconfined compressive strength caused by lithium carbonate may be due to the formation of insoluble calcium carbonate, which fills the capillary pores. These deposits then form weak spots in the paste which fail easily under stress. It is also probable that the carbonate ions interfere with (decrease) the rate of formation of hydration products (which give the paste, and therefore the mortar, its strength), thus decreasing the strength.

5.6 Thin Sections

Photomicrographs of some of the thin sections are shown in appendix B. The thin sections correlated well with the results of the linear expansion tests. As expected, the untreated specimens showed all the symptoms of ASR occurrence; gel, cracks, and reaction rims. Some evidence of ASR can also be seen in thin sections of the specimens whose treatments were ineffective. Aggregate particles affected by ASR can also be seen.

Figure B.1 is a photomicrograph of untreated mortar made with "PUT" aggregate. Cracks induced by ASR can be seen in the aggregate on the right side of the figure. On the left edge of the aggregate, one crack opens into a gel-filled void. In figure B.3, the photomicrograph of a similar mortar treated with lithium hydroxide is shown. No cracks are seen in either the aggregate particles or the paste.
5.7 Proposed Mechanism of Lithium Ion Control of ASR Expansion

In this section, an attempt is made to explain how lithium, though an alkali, is able to inhibit ASR reaction and expansion, a problem that is caused by the presence in pore solution of other alkalis, namely sodium and potassium.

Among other things, any measures to prevent or control ASR should be able to do the following:

i. control the pH of the pore solution,

ii. alter the alkali silicate gel to restrict its ability to absorb water.

The presence of lithium in the pore solution appears to meet the above requirements.

The reason for the effectiveness of lithium in inhibiting ASR may probably be traced to its ionic structure. The small size of the lithium ion gives it and its salts physical and chemical properties quite distinct from those of the other alkalis. For example, the lithium ion exerts a much stronger attractive force on the hydroxide ion than does either sodium or potassium (Wood 1986). In a solution of lithium hydroxide, therefore, fewer "free" hydroxide ions are encountered than in a solution of sodium or potassium hydroxide. This is why lithium hydroxide solution has a lower pH compared to solutions of sodium or potassium hydroxide.

As explained in chapter two, the pore solution of admixture-free portland cement paste contains mainly hydroxide, potassium, and sodium ions. It is suggested that when the lithium ion is introduced into the pore solution, the much stronger attractive force it exerts will restrain a large number of hydroxide ions, making them unavailable for reaction. Thus the level of alkalinity (pH) of the pore solution is depressed, and initial attack on the reactive silica by the hydroxide ions is decreased.
The concept that the lithium ion restricts some of the hydroxide ions from attack on silica particles explains why, for pastes treated with equal concentrations of LiCl, NaCl, and KCl, the pH was lowest for the LiCl-treated paste, and highest for the KCl-treated paste (see fig. 5.21). It also explains the fact that for a particular lithium salt treatment, the higher the concentration the bigger the pH reduction (fig. 5.20).

The lithium ions will likely exist in the pore solution in greater concentrations than sodium and potassium ions, which are derived mainly from the cement grains as mentioned in chapter two. For example, 20 percent LiOH will yield a lithium ion concentration of 8.4N, which is well above the combined concentration of sodium and potassium that normally exists in the pore solution. With lithium ions being present in the solution in superior numbers, any alkali-silicate gel formed will contain more lithium ions than potassium or sodium. This is corroborated by an analysis of gel recovered from ASR-affected concrete, which was shown to contain more potassium than sodium (see section 2.8). It is recalled that potassium ions outnumber sodium ions by a ratio of about 3 to 1 in the pore solution.

It is suggested that residual negative charges on the internal surfaces of the gel are neutralised by the positive charges of the lithium ions. Thus, attraction of water molecules onto the internal surfaces of the gel is reduced. The strong attractive force of the lithium ion also probably gives the gel a very rigid structure, thus boosting its resistance to expansion. The above principle has been successfully employed by Hudec and Larbi (1989) to treat aggregates against ASR in the past.
It is further suggested that the ineffectiveness of some of the lithium salts (lithium acetate, lithium bromide, lithium nitrate, and lithium perchlorate) in inhibiting ASR may be related to their equivalent weights. All the salts which were not effective as treatments have large equivalent weights (see table 14). At a given concentration the salts of large equivalent weights will furnish fewer lithium ions into the pore solution than salts of small equivalent weights. For example, a 20 percent concentration of lithium perchlorate only yields about 1.9N of lithium ions in solution, compared to 8.4N for the same concentration of lithium hydroxide. Hence, lithium hydroxide is more effective than lithium perchlorate at equal concentrations.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Equivalent Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Hydroxide</td>
<td>23.94</td>
</tr>
<tr>
<td>Lithium Fluoride</td>
<td>25.94</td>
</tr>
<tr>
<td>Lithium Carbonate</td>
<td>36.95</td>
</tr>
<tr>
<td>Lithium Chloride</td>
<td>42.39</td>
</tr>
<tr>
<td>Lithium Acetate</td>
<td>65.96</td>
</tr>
<tr>
<td>Lithium Bromide</td>
<td>86.85</td>
</tr>
<tr>
<td>Lithium Nitrate</td>
<td>68.95</td>
</tr>
<tr>
<td>Lithium Perchlorate</td>
<td>106.39</td>
</tr>
</tbody>
</table>
Chapter Six

Conclusions and Recommendations

6.1 Conclusions

i. It is observed that some lithium salts are effective in inhibiting expansion due to alkali silica reaction. In this respect, salts of small equivalent weights are more effective than those of large equivalent weights.

ii. It is proposed that the lithium ion "binds" some of the "free" OH\(^-\) ions in the pore solution through electrostatic attraction. The number of OH\(^-\) ions available for attack on reactive silica therefore decreases, so that the extent of reaction is reduced.

iii. It is further proposed that the lithium ion also influences the chemistry of the alkali-silica gel, such that a predominantly lithium silicate gel is formed. The lithium ions probably neutralise the residual negative charges on the internal surfaces of the gel. Attraction of water molecules to the gel is therefore reduced. Additionally, the lithium ions probably increase the ability of the gel to resist swelling by making the structure more rigid through a stronger electrostatic attraction.

iv. The lithium-containing minerals spodumene and amblygonite are not effective in controlling alkali-silica reaction when added to the mix in small concentrations. They could probably be effective if greater quantities are used to replace part of the cement.
v. The use of lithium chloride, lithium fluoride, and lithium hydroxide as admixtures in mortar does not adversely affect the strength of the mortar. However, lithium carbonate appears to reduce the strength.

vi. The lithium salts have very little effect on the alkali-carbonate reaction. This may be because the lithium ion inhibits expansion mainly by acting on the gel, and the carbonate reaction produces no gel.
6.2 Recommendations for Further Research

It is recommended that:

i. The compositional changes within the pore solution as the reaction proceeds should be investigated. This, it is hoped, will provide an insight into the cause of the sudden increase in the rate of expansion observed for most of the mortar cores tested. The chemistry of the alkali silica gel in an environment of sodium, potassium, and lithium ions should also be studied.

ii. The potential of the minerals amblygonite and spodumene to control ASR should be studied further. In particular, a greater quantity than used in this study should be used to replace a portion of the cement to see what effect they will have. The minerals should be used at a greater fineness than they were used in this study.

iii. The effectiveness of the lithium salts over an extended period should be monitored. This will help to determine how long it will take for the expansion levels to attain equilibrium.
References


Buck, A.D., and Mather, K. 1978. Alkali Silica Reaction Products from Several Concretes: Optical, Chemical, and X-Ray Diffraction Data. 4th Int. Conf. on Effects of Alkalis in Cement, Purdue, pg. 73-85.


Chatterji, S. 1979. The role of Calcium Hydroxide in the Breakdown of Portland Cement Concrete Due to Alkali Silica Reaction. Cement and Concrete Research, vol. 9, pg.185-188.


Diamond, S. 1983. Alkalis Reactions in Concrete Pore Solutions. 6th ICAAR, Copenhagen, Denmark, pg. 155-166.


Moore, A.E. 1978. An Attempt to Predict the Maximum Forces that Could be Generated by Alkali-Silica Reaction. 4th ICAAR, Purdue, Indiana, pg. 363-368.


Rogers, C. 1989. Alkali Aggregate Reactivity in Canada. 8th ICAAR, Tokyo, Japan, pg.57-63.


APPENDIX A

"Basic" Program for Controlling Measurements on the Double LVDT
5 CLEAR 5000
10 GOTO 3000
20 IF A$="Standard" GOSUB 7300
90 REM **** READ DIGIT-1 ****
100 OUT 236,16
110 D1=INP(126)
120 IF ( D1 AND 240 ) <> 16 THEN GOTO 100
190 REM **** READ DIGIT-3 ****
200 OUT 236,16
210 D3=INP(126)
220 IF ( D3 AND 240 ) <> 32 THEN GOTO 200
290 REM **** READ DIGIT-2 ****
300 OUT 236,16
310 D2=INP(126)
320 IF ( D2 AND 240 ) <> 64 THEN GOTO 300
390 REM **** READ DIGIT-4 ****
400 OUT 236,16
410 D4=INP(126)
420 IF ( D4 AND 240 ) <> 128 THEN GOTO 400
490 REM **** ASSEMBLE DATA ****
500 D1=D1 AND 15
510 D2=(D2 AND 15) * 10
520 D3=(D3 AND 15) *100
530 P=(D4 AND 8)
540 D4=(D4 AND 3) *1000
550 IF P=0 THEN P$="-": GOTO 570
560 P$=" +"
570 A=D4+D3+D2+D1
580 A$=STR$(A)
590 IF LEN(A$)=5 THEN B$=A$ : GOTO 640
600 B$=A$
610 FOR X=1 TO 5-LEN(A$)
620 B$=" +B$
630 NEXT X
640 A$=P$+B$
690 REM **** DISPLAY READOUT ****
700 RETURN
800 IF P=0 THEN A=A*-1
810 RESET(G,10)
820 G=((A+20)/40)+63
825 IF G>126 THEN G=126
826 IF G<0 THEN G=0
830 SET(G,10)
840 K$=INKEY
1000 RETURN
1990 REM **** DRAW GRID FOR BARGRAPH ****
2000 FOR X=0 TO 126 : PPSET(X,5) : NEXT X
2010 X=13: GOSUB 2020
2011 X=38: GOSUB 2020
2013 X=88: GOSUB 2020
2014 X=113: GOSUB 2020
2015 GOTO 2060
2020 FOR Y=3 TO 7
2030 SET(X,Y)
2040 NEXT Y
2050 RETURN
2060 FOR Y=1 TO 9 : PPSET (63,Y) : NEXT Y
2100 LOCATE 5,32: PRINT "0"
2500 RETURN
3000 CLS
3050 GOSUB 7200 'Open Output File
3070 GOSUB 7000 'LVDT Setting Instructions
3100 GOSUB 4100 'Standard Placement
3200 GOSUB 5010 'Standard Data Acquisition
3300 GOSUB 4000 IF O=2 OR O=1 THEN 3550 'Sample Description
3400 GOSUB 4200 'Open Input File
3500 GOSUB 4300 'Record Standard Length
3550 GOSUB 7400 'Comparison Standard #2 Length Measurement
3600 INPUT "No. of Cores for this Sample"; NN
3601 IF NN <=6 GOTO 3605
3602 IF NN >6 PRINT " " : PRINT " No. of Ceres should be less than 7"
3603 PRINT
3604 GOTO 3600
3605 GOSUB 4240 'Record Conditions
3610 FOR KK=1 TO NN
3615 INPUT "Core No."; CN$
3617 CM$="" : INPUT" Any comments about this core or sample? Press ENTER if none"; CM$
3620 GOSUB 5000 'Measure Core
3630 GOSUB 4300 'Record Conditions
3640 NEXT KK
3700 PRINT "Do you want to:" : O=0
3710 PRINT "1. Re-calibrate with the standard"
3720 PRINT "2. Continue with another sample"
3730 PRINT "3. Quit"
3740 INPUT "Your Choice? "; O
3750 ON O GOTO 3100,3300,3800
3800 CLOSE #1
3810 END
4000 'Sample Description
4004 PRINT "Same conditions as previous sample-- Y/N"
4006 INPUT "Press 'Y' if same, 'N' if different conditions"; OS
4008 IF OS="y" OR OS="Y" THEN GOTO 4050
4009 PRINT "If and error is made, correct after last entry! If no change for hit ENTER!" :
        Print
4010 PRINT, , TC$
4012 INPUT "Treatment Chemical ('none' if no treatment)"; TC$
4019 PRINT, , TP
4020 INPUT "Solution Concentration (0 if no treatment)"; TP
4029 PRINT, , TF
4030 INPUT "Frequency of Treatment(1 if mixwater, 0 if none)"; TF
4039 PRINT, , TM$
4040 INPUT "Which was treated: Mix, Core, Agg, None"; TM$
4041 PRINT, , AT$: INPUT "Aggregate used (eg: SUD)"; AT$
4042 PRINT, , ES: INPUT "Temperature of room, deg. C"; ES
4043 PRINT, , DE: INPUT "No. of Days of Exposure,(0 at start)"; DE
4045 PRINT "Last Date/Time of Measurement "; DT$
4047 INPUT "Write a sentence description (no commas) of this sample"; SD$
4049 GOSUB 8000
4050 PRINT : PRINT "Is the above information correct? Y/N"
4052 INPUT "Y/N? (Change the wrong entry only)"; OI$
4055 IF OI$="N" OR OI$="n" THEN GOTO 4000
4070 RETURN
4100 'STANDARD DATA
4140 CL.=60000!: CN$="Standard"
4150 RETURN
4200 'FILE OPENING & DESCRIPTIVE DATA INPUT
4205 IF O=2 OR O=1 THEN RETURN
4210 CLOSE #1
4220 INPUT "File Name, eg: AGGTREAT (if new)"; SN$
4222 INPUT "Is this a New (N) or Continuing (C) experiment?"; O$
4230 OPEN "E",1,SN$+":1"
4232 IF O$="N" THEN GOTO 4233 ELSE GOTO 4239
4233 PRINT #1,"ExpName";",";"Chemical";",";"Concentration";",";
4234 PRINT #1,"TreatFreq";",";"Mix/Core/Agg";",";"AggType";",";
4235 PRINT #1,"DaysExposed";",";"Date"
4237 PRINT #1,"CoreNo";",";"AbsLength";",";
4238 PRINT #1,"Re1Length";",";"No.Readings";",";"Comment"
4239 RETURN
4240 'Conditions Data
4242 PRINT #1,SN$",";TC$",";TP",";"
4250 PRINT #1,TF",";";TM$",";AT$",";ES",";
4259 DTS=TIMES$
4260 PRINT #1,DE",";DT$",";SD$",";SL",";LN
4270 RETURN
4300 'Core Length Data
4310 PRINT #1,cN$",";";LN",";";SL",";";C2",";";CM$
4315 LN=0: SL=0: C2=0
4320 RETURN
5000 'DATA ACQUISITION
5005 PRINT "Place sample in holder"
5010 INPUT "Key in Full COARSE LVDT setting";CL :
       CD=CL-10*INT(CL/10)
5020 GOTO 5040
5030 REM
5035 INPUT "Coarse LVDT Setting (LAST DIGIT ONLY)";CD
5040 C=C+1:GOSUB 90
5100 'Fine LVDT Data Acquisition
5130 FL(C)=VAL(A$)
5131 'FL(C)=INT(100*RND(CD))
5140 CL(C)=CD
5145 PRINT "Coarse and Fine LVDT Readings: "; CD,FL(C)
5150 IF C>8 THEN GOSUB 6000 : RETURN 'Mean Calculation
5160 PRINT : PRINT : PRINT "Run No.: "; C : PRINT
5162 PRINT "Turn sample and Turn Coarse LVDT Micrometer Screw"
5165 PRINT "Allow changes only in the last digit on the COARSE LVDT"
5170 IF C<8 THEN GOTO 5030
5180 RETURN
6000 'STATISTICAL ROUTINE
6100 FOR K=1 TO 7
6110 GOSUB 6500
6120 S=S+L
6130 SS=SS+L*L
6140 NEXT K
6200 'MEAN & STAND. DEV. (ORIGINAL)
6210 M=S/7
6220 SD=1/7 * SOR(7*SS - S*S) 'STD. DEV.
6230 PRINT "Orig. Mean & Std. Dev. ": M,SD
6300 'CLEARING OUTLIERS
6305 C=0: S=0: SS=0: C2=0: S2=0
6310 FOR K=1 TO 7
6315 GOSUB 6500
6320 IF L> (M+2*SD) OR L<(M-2*SD) THEN GOTO 6350
6330 C2=C2+1
6340 S2=S2+L

111
6350 NEXT K
6360 M2=S2/C2 'Clean Mean
6365 PRINT ,"Cleaned Mean :"; M2
6367 PRINT ,"No. of samples in the cleaned mean : ";C2
6380 SL=10 * INT(CL/10) + M2
6390 PRINT ,"Average Apparent Sample Length is "; SL
6391 IF CN4="Standard" THEN LN = SL*SL/60005: GOTO 6394
6393 LN=SL*ST/60065
6394 PRINT ,"ABSOLUTE SAMPLE LENGTH IS "; LN
6395 PRINT : PRINT
6400 RETURN
6500 L = CL(K) + FL(K)/9.5821
6510 RETURN
7000 CLS : PRINT "STANDARD PLACEMENT - DO EVERY TIME!!!": PRINT
7010 PRINT "Seat the standard by rotating it a few times."
7020 PRINT "Turn the micrometer until fine LVDT is near 0".
7025 PRINT ,"ALWAYS TURN CLOCKWISE !!!"
7030 PRINT ,"Reset the Coarse LVDT by:"
7040 PRINT ,"Press 'Zero Reset' Button
7050 PRINT ,"Press White 'Preset' Button
7060 PRINT ,"Press Blue '+ ' Button
7070 PRINT
7080 PRINT "Press any key to start program
7090 G$=INKEY$: IF G$="" THEN GOTO 7090 ELSE RETURN
7200 !INPUT "New File (N), or Existing File (E)"; O2$
7202 IF O2$="N" THEN RETURN
7204 INPUT "File Name ";SN$
7209 OPEN "I", 2,SN$+" +1"
7210 INPUT #2, A$
7220 IF A$="Standard" GOSUB 7300
7230 IF EOF (2) THEN CLOSE 2: GOSUB 8000: INPUT "Hit ENTER to continue"; XX$: RETURN
7240 GOTO 7210
7300 INPUT #2, A,A,A
7310 !INPUT #2, X$,SN$,TC$,TP
7320 INPUT #2, TF,TM$,AT$,ES
7330 INPUT #2, DE,DT$,SD$
7340 RETURN
7400 'OPEN "E", 3, "CERAM2:1"
7410 PRINT, "Comparison Standard #2 ": PRINT
7430 GOSUB 5000
7435 ST=SL
7440 'PRINT #3, AT$; ";LN;" ;SL;" ";C2; " ;DT$
7450 'CLOSE #3: RETURN
8000 PRINT "Conditions Same? ", O$
8010 PRINT "Chemical", TC$
8020 PRINT "Solution Concentration", TP
8030 PRINT "Treat. Freq.", TF
8040 PRINT "Which Treated ", TMS
8050 PRINT "Aggregate type", AT$
8060 PRINT "Temperature", ES
8070 PRINT "Days Exposed", DE
8080 PRINT "Last Measurement Date", DT$
8085 PRINT "General Description", SD$
8090 PRINT : RETURN
9000 PRINT "ERROR HAS OCCURED - FILE IS SAVED"
9010 PRINT "RE-START THE PROGRAM WITH STANDARD, THEN PROCEED WITH THE MEASUREMENT OF WHICH ERROR OCCURED"
9020 PRINT CLOSE
9030 RESUME 9040
9040 END
APPENDIX B

Petrographic Data on Reactive Aggregates

Source: Aduamoaah-Larbi (1987)
COARSE AGGREGATE PETROGRAPHIC ANALYSIS

Source: New Bigging Pit, Putnam, Ontario. Lab No.: 1
Type: Crushed Rock (PUT)  Size Fraction: —  Date: June, 1987.

<table>
<thead>
<tr>
<th>LITHOLOGIC DESCRIPTION</th>
<th>MTC Type</th>
<th>Weight g.</th>
<th>Percent of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chert - cherty carbonates, dark blue, light grey, nodular;</td>
<td>Fair</td>
<td>252.50</td>
<td>25.51</td>
</tr>
<tr>
<td>Carbonates - cherty limestone, light grey, whitish in colour;</td>
<td>Fair</td>
<td>612.30</td>
<td>61.84</td>
</tr>
<tr>
<td>Carbonates - crystalline, white, medium-to fine-grained, hard;</td>
<td>Good</td>
<td>125.20</td>
<td>12.65</td>
</tr>
</tbody>
</table>

**TOTAL**

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent Good.</td>
<td>12.65 x 1</td>
<td>12.65</td>
</tr>
<tr>
<td>Percent Fair.</td>
<td>87.35 x 3</td>
<td>262.05</td>
</tr>
<tr>
<td>Percent Poor.</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Percent Deleterious</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Percent crushed: 100.00
Percent Flats and Elongate: —

PETROGRAPHIC NUMBER

BASIC: 274.70
CONCRETE & HOT MIX: —
GRANULAR "A" & 5/8" Cr: —
COARSE AGGREGATE PETROGRAPHIC ANALYSIS

Source: Pioneer Construction Pit, Sudbury, Ont
Lab No.: 1
Type: Gravel (SUD)
Size Fraction: —
Date: June, 1987

<table>
<thead>
<tr>
<th>LITHOLOGIC DESCRIPTION</th>
<th>MTC Type</th>
<th>Weight g</th>
<th>Percent of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandstone - medium hard, medium-grained,</td>
<td>Good</td>
<td>99.00</td>
<td>9.90</td>
</tr>
<tr>
<td>Gneiss, schist - hard;</td>
<td>Good</td>
<td>75.30</td>
<td>7.40</td>
</tr>
<tr>
<td>Quartzite - hard, medium-grained;</td>
<td>Good</td>
<td>141.00</td>
<td>14.10</td>
</tr>
<tr>
<td>Greywacke, arkose - medium-grained, hard;</td>
<td>Good</td>
<td>328.00</td>
<td>32.80</td>
</tr>
<tr>
<td>Volcanic - hard and slightly weathered;</td>
<td>Good</td>
<td>120.00</td>
<td>12.00</td>
</tr>
<tr>
<td>Granite, diabase - hard;</td>
<td>Good</td>
<td>140.00</td>
<td>14.00</td>
</tr>
<tr>
<td>Argillite - light grey, fine-grained;</td>
<td>Fair</td>
<td>99.00</td>
<td>9.90</td>
</tr>
</tbody>
</table>

**TOTAL**

|                |          | 1002.00  | 100.00 |

Percent Good: \(90.10 \times 1\) \(90.10\)
Percent Fair: \(9.90 \times 3\) \(29.7\)
Percent Poor: —
Percent Deleterious: —

Percent Crushed: \(100.00\)
Percent Flats and Elongate: —

PETROGRAPHIC NUMBER

<table>
<thead>
<tr>
<th>BASIC</th>
<th>120.60</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONCRETE &amp; HOT MIX</td>
<td>—</td>
</tr>
<tr>
<td>GRANULAR &quot;A&quot; &amp; 5/8&quot; Cr</td>
<td>—</td>
</tr>
</tbody>
</table>
# COARSE AGGREGATE PETROGRAPHIC ANALYSIS

**Source** Pittsburg Quarry, Kingston, Ontario  
**Lab No.** 1  
**Type** Crushed Rock (KIN)  
**Size Fraction**  
**Date** June, 1987

<table>
<thead>
<tr>
<th>LITHOLOGIC DESCRIPTION</th>
<th>MTC Type</th>
<th>Weight</th>
<th>Percent of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonates - brownish grey, hard, fine-grained, dolomitic limestone;</td>
<td>Good</td>
<td>691.00</td>
<td>69.30</td>
</tr>
<tr>
<td>Carbonates - wackestone, sandy, hard;</td>
<td>Good</td>
<td>185.00</td>
<td>18.60</td>
</tr>
<tr>
<td>Carbonates - medium grey, fine-grained, slightly shaley limestone;</td>
<td>Fair</td>
<td>121.10</td>
<td>12.10</td>
</tr>
</tbody>
</table>

**TOTAL**  
87.90 x 1 87.90  
Percent Good ................. 87.90  
Percent Fair .................. 36.30  
Percent Poor ...................  
Percent Deleterious ............  
Percent Flats and Elongate .....  
Percent crushed 100.00

**PETROGRAPHIC NUMBER**  
BASIC ......................... 124.20  
CONCRETE & HOT MIX .............  
GRANULAR "A" & 5/8" Cr ........
### Table B.1: Physical Properties of Reactive Aggregates

<table>
<thead>
<tr>
<th>DATA</th>
<th>PUT</th>
<th>SUD</th>
<th>KIN</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.N.</td>
<td>274.700</td>
<td>120.600</td>
<td>124.200</td>
</tr>
<tr>
<td>BSG</td>
<td>2.545</td>
<td>2.669</td>
<td>2.679</td>
</tr>
<tr>
<td>ASG</td>
<td>2.503</td>
<td>2.656</td>
<td>2.649</td>
</tr>
<tr>
<td>% Absp.</td>
<td>1.651</td>
<td>0.466</td>
<td>1.120</td>
</tr>
</tbody>
</table>

P.N. -- Petrographic Number (Ontario Ministry of Transportation)
B.S.G.-- Bulk Specific Gravity
A.S.G -- Apparent Specific Gravity
% Absp. -- Absorption (%)  
L.A. -- Los Angeles Abrasion Test
APPENDIX C

Photomicrographs of some Treated and Untreated Mortar Specimens
Fig. B.1: Photomicrograph of untreated mortar made with "PUT" aggregate. Notice cracks in aggregate on the right side. One crack appears to open into gel-filled void. X10

Fig. B.2: Photomicrograph of untreated mortar made with "PUT" aggregate. A gel-filled crack can be seen. X10
Fig. B.3: Photomicrograph of LiOH-treated mortar made with "PUT" aggregate. No cracks can be seen. X10

Fig. A.4: Photomicrograph of LiClO₄-treated mortar made with "PUT" aggregate. A cracked aggregate with gel-filled paste is seen. X10
Fig. B.5: Photomicrograph of untreated "SUD" mortar. It features a crack through an aggregate. X10

Fig. B.6: Photomicrograph of Li$_2$CO$_3$-treated mortar made with "SUD" aggregate. No cracks are seen. X10
Vita Auctoris

Name: Nana Kwame Banahene.

Date of Birth: 3rd April, 1961.

Place of Birth: Kumasi, Ghana.


B.Sc (Hons) Geological Engineering.


M.A.Sc Geological Engineering.