ROLE OF SUPPLEMENTARY CEMENTING MATERIALS ON REDUCING DAMAGE DUE TO INTERNAL SULPHATE ATTACK IN CONCRETE

Ву

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Abstract

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The effect of supplementary cementing materials (SCM) on internal sulphate attack in mortars was evaluated. Different types and levels of SCM were investigated where a mixture of hemihydrate and calcium carbonate fillers were used in the mixtures as a source of sulphate and carbonate, respectively. In addition, mixtures containing aggregates with high sulphate content were also examined to understand the role of sulphate from aggregate on the expansion. It has been found that the internal sulphate attack can be reduced through the use of SCM with high reactive alumina such as Metakaolin. It was hypothesised that the beneficial effect of Metakaolin lies in its ability to reduce ion mobility within the matrix, and perhaps raise the alumina/sulphur in the system favoring the formation of non-expansive monosulphoaluminate. However, at high levels of sulphate, none of the SCM provided successful protection against internal sulphate attack.

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Chapter 1

Introduction

There has been research conducted by European Scientists on the Sulphate resistance of Concrete as early as the 19th Century with reported cases in Canada of damage due to the presence of sulphate as early as 1908. (Marchand, Odler, and Skalny 2003a). The damage on concrete was due to excessive sulphate ions and is commonly referred to as Sulphate attack. Examples of this type of concrete deterioration include but not limited to expansion, cracking, spalling, strength loss and loss of adhesion which reduces the service life of the concrete (Collepardi and Mario 1999).



Figure 1.1: Deteriorated sample due to Internal Sulphate Attack

As the source of sulphate can present both inside and outside the concrete in applications such as foundations, backfill, pavements and sewer pipes, it is crucial to understand the mechanism of the reactions in order to reduce the frequency and severity of these reactions if not stopping them all together. This thesis is on the mechanisms and mitigation techniques of internal sulphate attack focusing primarily on two types of phases or types of sulphate attack; Ettringite formation/attack and Thaumasite sulphate attack (TSA).

Depending on when Ettringite is formed, it can cause deleterious expansions. Ettringite formation that occurs during hydration, also known as Primary Ettringite Formation (PEF), does not result in any expansion. The formation of Ettringite after concrete has hardened due to presence of excessive amounts of sulphates is known as Secondary Ettringite Formation (SEF). SEF is known can have detrimental effects if enough expansion occurs. Excessive amounts of sulphates resulting in an imbalance of sulphate will turn the available aluminate phases (Tricalcium Aluminate and monosulphoaluminate) into Ettringite.

Thaumasite has a similar crystal structure of Ettringite where the main difference is between the Aluminate and the Silicate. The Silicate in Thaumasite is usually taken from the Calcium Silicate Hydrate which adheres the concrete together. However Thaumasite formation does not necessarily result in the loss of adhesion known as Thaumasite Sulphate Attack (TSA).

Available literature will be reviewed on conventional sulphate attack as well as Thaumasite Sulphate attack. Mechanisms and mitigation techniques will be reviewed in the following sections to obtain a better understanding on the subject.

1.1 Research Significance

There has been a significant amount of research done on sulphate attack from external sources but has a limited amount of research on sulphate attack due to internal sources. The primary goal was to better understand the mechanisms which affect both conventional sulphate attack and Thaumasite Sulphate attack and ways to mitigate these reactions. There is currently no standard that tests for Thaumasite Sulphate attack using blended hydraulic cements for internal sources of sulphate. The ultimate goal is to provide information to contribute towards developing a standard which can predict the performance of concrete susceptible to Thaumasite Sulphate Attack.

1.2 Thesis Outline

The following paragraphs outline the contents of this thesis

- 1. Chapter 1: Outlines the objective and introduces the two forms of sulphate attacks studied in this thesis.
- 2. Chapter 2: Provides a review on the mechanisms, research done thus far and the use of supplementary cementing materials.
- 3. Chapter 3: Summarizes the properties of the materials used in this research program as well as a summary of the methodologies carried out in the various phases in this program.
- 4. Chapter 4: Provides the results and in depth discussions of all phases conducted in this research program.
- 5. Chapter 5: Presents the conclusions based on the results obtained from the phases in this research program and recommendations for further studies.

Chapter 2

Literature Review

2.1 Internal Sulphate Attack

"Sulphate attack is the term used to describe a series of chemical reactions between sulphate ions and the components of hardened concrete" (Skalny, Marchand, & Odler, 2001). Internal Sulphate Attack (ISA) refers to the source of sulphate required for sulphate attack to occur is already present within the hardened concrete. In other words, the source of sulphate is from either the cementing material, aggregate or concrete additives (Marchand, Odler, and Skalny 2003b). There are two types of chemical sulphate attacks, which are Ettringite and Thaumasite. The main reaction products within the scope of work of sulphate attack include the following: calcium sulphate, Ettringite and Thaumasite which will be discussed in details in the proceeding sections. Current preventative measures in standards include limiting the C_3A in sulphate resistant Portland cement and limiting the amount of sulphate that can be present in cement (varying between 2.3% to 3% SO_3^{2-} depending on the class of cement) (ASTM C1157, 2011)

2.1.1 Calcium Sulphate

Calcium sulphate is a common reactant added to the cement clinker in order to retard the hydration product associated with Tri-Calcium Aluminate (abbreviated as C_3A) in order to prevent flash set from occurring. Common sources of Calcium Sulphate come in the form of Calcium Sulphate Dihydrate (CaSO₄•2H₂O), also known as gypsum, Calcium Sulphate Anhydrite (CaSO4) and Calcium Sulphate Hemihydrate (CaSO4•½H₂O), commonly found as "Plaster of Paris". It is noted that the reaction between C_3A and calcium sulphate occurring prior to the hardening of concrete, also known as Primary Ettringite Formation (PEF) does not cause

distress in the concrete. However, it is the formation after the hardening that can cause internal stresses within the concrete to form cracks (Marchand, Odler, and Skalny 2003b). Calcium Sulphate Hemihydrate is said to have low solubility when compared to Calcium Sulphate Anhydrite which results in higher amounts of monosulphoaluminate phases. A study has also shown that there is a slow release of sulphate ions from Calcium Sulphate Hemihydrates while there is little to none when using Calcium Sulphate Anhydrite. (Xu, Wang, & Zhang, 2012) In comparison to gypsum, the Hemihydrate/carbonate blend has a higher solubility which results in a higher rate of dissolution of SO_3^{2-} (Aitcin, 2011).

2.1.2 Ettringite

As mentioned previously, the initial reaction between C_3A and Calcium Sulphate known as Primary Ettringite Formation (PEF) causes no damage to the concrete. However, it is the formation of the Ettringite after the concrete is hardened that causes the damage as a build-up of internal stresses that cause expansion and perhaps cracking (Marchand, Odler, and Skalny 2003b). There are two main categories of Ettringite formation when it comes to ISA, which are: Delayed Ettringite Formation (DEF) and Secondary Ettringite Formation (SEF). Both categories of Ettringite formation have the following chemical reaction that contributes to Internal Sulphate attack at ambient temperature is given in equation below

$$Ca_{3}Al_{2}O_{6} + CaSO_{4} \bullet 2H_{2}O + 26H_{2}O \rightleftharpoons [Ca_{3}Al (OH)_{6} \bullet 12H_{2}O]_{2} \bullet (SO_{4})_{3} \bullet 2H_{2}O \text{ (Equation 2-1)}$$

DEF is related to the curing of concrete at an elevated temperature. In general, Ettringite is formed before the concrete is hardened but in the case of curing at a high temperature, Ettringite is not stable and the sulphates will be absorbed by the Calcium Silicate Hydrate (Taylor, Famy, and Scrivener 2001). Ettringite formation is the cause for what is known as, conventional

sulphate attack. Ettringite in hardened concrete is formed when the following conditions are present: late sulphate release, a source of water and micro cracking. Previous studies have been performed on the causes and mitigation techniques to prevent the formation of Ettringite after the concrete has been hardened. These mitigation techniques have been to limit the amount of sulphate in Portland cement, sulphate in aggregate and the amount of alumina (Al₂O₃) in cementing material (Taylor, Famy, and Scrivener 2001).

2.1.3 Thaumasite

There have been a history incidents of Thaumasite occurring all over the world but it became a growing concern in the 1990's when the foundation of major motorways in the United Kingdom were found to have severe deterioration due to a sulphate attack that is known as Thaumasite Sulphate Attack (TSA). It is to be noted that when the motorways were built, it satisfied all the recommendations that were present for conventional sulphate attack which included limiting the amount of C_3A and sulphate within the concrete (Crammond 2003).

Crammond (2003) has identified five key factors for TSA to occur which include the following: source of Sulphate ions, source of Silicate ions, source of Carbonate ions, a source of water and low temperatures. The factors are commonly agreed upon but the direct relationship is still relatively unknown. An example of these unknown relationships is that it is agreed that carbonate ions are needed for Thaumasite to occur but there is a debate about whether an increase in carbonate will result in no detrimental effect, a higher degree of deterioration or result in higher amounts of Thaumasite produced (Hooton, R., Nokken, M., & Thomas, M. 2007). Literature has also found that Thaumasite can occur at higher temperatures that are close to room temperature though it is commonly agreed that Thaumasite is more favourable at lower temperatures as a decrease in temperature will result in a higher coordination number which will allow the concrete to form Thaumasite (Pipilikaki et al. 2008).

Previous scholars have conducted research where they have found that specimens with small or no amounts of Ettringite resulted in no detectable TF. The specimens that had Ettringite present detected TF of varying amounts. The paper concluded that Ettringite has a considerable effect on the rate of Thaumasite formation where it uses Ettringite as an initial template of nucleation as will be explained by the dissolution and precipitation mechanism (Köhler, Heinz, and Urbonas 2006). In other research, it was found that Thaumasite was only found after all of the Al was consumed to form Ettringite while having a molar ratio between SO_3^- and Al_2O_3 to be over 3 which would support Kohler's findings (Schmidt, Lothenbach, Romer, Scrivener, Rentsch, & Figi, 2008).

It is important to note here that there is a significant difference between Thaumasite Formation (TF) and TSA. Thaumasite Formation refers to the finding of Thaumasite within voids and cracks without any signs of deterioration to the mortar bonding whereas, Thaumasite Sulphate Attack refers to the damage to the Calcium Silicate Hydrate (C-S-H) Matrix where the matrix is replaced by Thaumasite resulting in what some have referred to and visualized as "mush" (Shi et al. 2012).

There are two mechanisms that have been hypothesized of how Thaumasite forms which include dissolution, precipitation and topochemical conversion from Ettringite to Thaumasite. The dissolution precipitation mechanism reaction is presented below.

$$3Ca^{2+} + SiO^{3-} + CO_3^{2-} + SO_4^{2-} + 15H_2O \rightleftharpoons 3CaO \bullet SiO_2 \bullet CO_3 \bullet SO_3 \bullet 15H_2O$$
 (Equation 2-2)

This mechanism suggests that when there is enough sulphate ions present in the pore solution, it will form Thaumasite in the presence of a carbonate source after all of the C_3A is consumed to

form Ettringite and enough Portlandite (Ca(OH)₂) is consumed to reduce the pH of the concrete to below 13 but higher than 10.5(Shi et al. 2012).

The topochemical conversion mechanism, the typical route, explains that the structures of Thaumasite $CaCO3 \cdot CaSiO_3 \cdot CO_3 \cdot CaSO_4 \cdot 15H_2O$) and Ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$) are similar. In order to obtain Thaumasite, the Silicate ions replace the Alumina ions and hence releasing Aluminum ions back into the pore solution which allows additional formation of Ettringite which is presented in Equation 2-3.

 $C_3S_2H + C_6A\bar{S}H_{32} + 2C\bar{C} + 4H \rightarrow 2C_3S\bar{C}\bar{S}H_{15} + C\bar{S}H + AH_3 + 4CH$ (Equation 2-3)

These two structures are difficult to distinguish when there are only low concentrations of either Thaumasite or Ettringite (Shi et al. 2012). However, this mechanism cannot explain the rapid TF that occurs as the topochemical conversion mechanism is only applied to the outermost layer of the molecule (Shi et al. 2012; Köhler, Heinz, and Urbonas 2006). It has been found that lower amounts of Alumina may be beneficial for the formation of Thaumasite yet it is suggested in other literature that Ettringite is needed to form Thaumasite and hence Alumina is still needed.

However, a different study performed by Hartshorn et al. (1999) has shown that the use of magnesium sulphate as a source the main source of sulphate resulted in the formation of Thaumasite and Brucite. The reaction is different from both the mechanisms listed above as it consumes the Portlandite as opposed to producing it when in the presence of Magnesium ions and is shown in Equation 2-4 (Hartshorn, Sharp, & Swamy, 1999). The source of Magnesium ions is not limited to Magnesium Sulphate solutions, other sources can include the cementing material itself, water or from aggregate such as dolomite. It was noted that it is easy to misinterpret as the majority of the Thaumasite and Brucite fall off the actual specimen and the majority of what is left is the sound specimen which contains mainly Ettringite and Gypsum (Rahman & Bssuoni, 2014).

$C_3S_2H_3 + 3CH + 2C\bar{C} + 4M\bar{S} + 32H \rightarrow 2C_3S\bar{C}\bar{S}H_{15} + 2C\bar{S}H_2 + 4MH$ (Equation 2-4)

Using thermodynamic analysis, calculating the difference Gibbs free energy, it can be shown if the ratio between Calcium (Ca^{2+}) and Silicon (Si^{4+}) is greater than 1.7 and in the presence of Portlandite (Ca(OH)₂), which is a product of hydration, can still produce Thaumasite even at very low concentrations of Sulphate. In this study, three different scenarios were used, which included a ratio of Calcium to Silicon to be 1.7 or more with and without Portlandite and also Calcium to Silicon ratio of 1.1. The high ratio in the presence with the presence of Portlandite represents the use of General Use Portland Cement, the high ratio without the presence of Portlandite represents the use of sufficient SCM which through pozzolanic reactions that would convert all of the Portlandite to CSH or other phases. The third case represents the use of SCM at a later phase where all of the Portlandite has reacted to form CSH therefore reducing the ion concentration of Ca^{2+} which in turn reduces the Calcium to Silicon Ratio to 1.1 or lower. This theory was put to the test for over five years and the only damaged samples that contained Thaumasite were the samples that consisted high calcium to silicon ratio within the Calcium Silicate Hydrate. It has been suggested that controlling the calcium to silicon ratio can result in a higher resistance to Thaumasite formation at higher levels of sulphate as the reduction of Portlandite leads to a decrease in pH within the pore solution therefore requiring higher levels of sulphate to form Thaumasite thus increasing the chemical resistance. It is also mentioned that the increase in physical resistance was also found from the use of some samples containing low ratios where pores was found to be narrower. This physical resistance is said to not completely prevent the formation of Thaumasite. However, it hinders the rate of formation (Bellmann & Stark, 2007). The decrease of Ca to Si ratio was seen to result in less Thaumasite formed in other studies where the decrease in Portlandite resulted in a lower pH which favoured secondary gypsum formation opposed to Thaumasite formation. The lower pH helps reduce the formation of Thaumasite as levels greater than 12.5 or higher is favorable. (Schmidt, Lothenbach, Romer, Scrivener, Rentsch, & Figi, 2008; Nielsen, Nicolai, Darimont, & Kestemont, 2014)

In a previous study it was found that the Thaumasite formed after the formation of Ettringite and gypsum when exposed to a sodium sulphate solution. The Thaumasite formed at a high rate which resulted in expansion and disintegration at a later stage due to TSA. It is hypothesized that the extensive cracking within the sample is a prerequisite for Thaumasite to form (Ramezanianpour, Mohammad, & Hooton, 2012).

A different study supported the claim of deterioration caused by expansive Thaumasite. In this study, samples were found to contain a white phase which occupied the central part of the specimen. Through Scanning Electron Microscope (SEM) analysis, the absence of Al³⁺ and peaks of Si⁴⁺, S²⁻ and Ca²⁺ confirmed that the white mass was Thaumasite and was the mechanism of expansion which leads to the breaking down of the samples (Aguilera, Martinez-Ramirez, Pajares-Colomo, & Blanco-Varela, 2003).

2.2 Effect of Mix Properties on Sulphate Resistance

2.2.1 Water to Cement Ratio

It is well known that the water to cement (w/c) ratio has a very important role in determining both the strength and the porosity of a concrete mix. It is necessary to control the w/c as it also controls the spacing of the voids and the size of the voids as stated by the Power's Spacing factor. In literature, it has been observed that both Ettringite and Thaumasite are detected within the voids and cracks. CSA3004-C5 is the current standard for Internal Sulphate attack which uses a w/c ratio of 0.485. It has also been observed when a w/c ratio of 0.60 is used, which would represent a specimen which has a larger void size and a less space between voids, a higher w/c ratio would promote sulphate attack (Mulenga, Stark, and Nobst 2003). However, a w/c ratio of 0.45 is said to the threshold to determine whether the resistance to deleterious material is a function of its chemistry or a function of its physical characteristics. Having a w/c ratio which is lower than the threshold would suggest that the resistance to deleterious material is a function of the physical characteristics (Smallwood, Wild, & Morgan, 2003).

2.2.2 Fly Ash Class F (Low Calcium)

A Fly ash that has low calcium content, also known as class F, is Pozzolanic cement where it reacts with the calcium hydroxide that is a common product for hydraulic cement reactions. The general use of mineral admixture helps to lower the permeability and help refine the pore to the structure and hence the performance of concrete (Tsivilis et al. 2003). This type of fly ash has shown improved durability when it comes to conventional sulphate attack, mitigating Ettringite formation, whether it is used with ordinary Portland cement (OPC), Portland Limestone Cement (PLC) or sulphate resistant Portland cement (SRPC). This is due to the increase of Al₂O₃ which encourages the formation of monosulphoaluminate opposed to Ettringite (Ramlochan, Zacarias, Thomas, & Hooton, 2003). All the cements that were used in the study by Mulenga et al. passed

the recommendation of having less than 3% of C_3A and 3% Sulphate. The study showed that with the incorporation of low calcium fly ash, it was possible for Thaumasite to still occur. It has been reported that PLC is not sulphate resistant as it expands more than the allowable amount (Hooton, R., Nokken, M., & Thomas, M., 2007). After 14 days of curing and submersion in their respective baths, it has been shown that temperature has a strong effect on the Thaumasite formation of mixes containing 30% - 50 % fly ash replacement. Mulenga et al. (2003) concluded that depending on which cements were used combined with fly ash can either promote or limit the amount of Thaumasite that can form. Ramlochan et al. (2003) explained that the performance of fly ash is variable depending on the calcium, sulphate and alkali content. With all the research that has been done, there is no consistent trend on whether the use of low calcium fly ash will reduce the formation of Ettringite and Thaumasite. Perhaps the reason may be that the not all of the Al₂O₃ may be in a reactive phase, with phases such as mullite, and hence actually have less Al₂O₃ available to form monosulphoaluminate and hence more prone to forming Ettringite.

2.2.3 Ground Granulated Blast Furnace Slag

One of the by products from an iron blast furnace can be used as a supplementary cementing material (SCM) after being grinded down into very fine particles. This SCM is commonly known as Ground Granulated Blast Furnace Slag or GGBFS for short. GGBFS is a Pozzolanic material which has similar effects as to low calcium fly ash in terms of enhanced durability that include decreasing permeability and enhancing the pore structure within the concrete. According to a research conducted, replacement levels of 70% GGBFS were used to test specimens at various temperatures and under various conditions. They have concluded that the use of GGBFS has shown to have a significant improvement in terms of resistance to TSA with carbonate aggregates when compared to mixes that only contain Portland cement. However, this was not enough to mitigate the TSA with any specimens containing inferior carbonate aggregates (Higgins and Crammond 2003). Research has also been conducted indicating that replacement levels of 50% GGBFS have shown significant improvement however replacement level with

only 30% was still susceptible to TSA which would coincide with the CSA standards where a minimum of 40% Slag is needed for concrete in favorable conditions for TSA (Ramezanianpour and Hooton 2012). It should be noted that the use of GGBFS is more susceptible to conventional sulphate attack (Higgins and Crammond 2003) and depending on the rate of reaction of the pozzolanic material it can further reduce both conventional and Thaumasite Sulphate Attack (TSA) (Tsivilis et al. 2003).

2.2.4 Metakaolin

Although, there is limited literature on the effect of Metakaolin on TSA, there are still some promising results thus far. After 11 months of testing there have been no signs of deterioration with the mixes with 10% Metakaolin opposed to other specimens that may have either started to deteriorate or even completely deteriorated. This may be due to the fact that Metakaolin is a fast reacting pozzolanic material due to the fineness of the material (Tsivilis et al. 2003). The strengths of the specimens were measured and concluded that there was strength gain using this SCM. Specimens which used only Portland cement seemed to lose strength over time, this can be attributed to the loss of CSH gel which contributes to strength.

Metakaolin is said to improve both the physical resistance and the chemical resistance to TSA. The physical resistance towards TSA is enhanced by densifying the hydration products within the matrix which is due to the fine particle size (Smallwood, Wild, & Morgan, 2003). The densification of the hydration products decreases the ability in which ions can mobilize within the sample. As mentioned earlier, the presence of magnesium ions either from an internal or external source can cause the Portlandite to be become a reactant opposed to a product when forming Thaumasite. The use of pozzolanic materials such as Metakaolin can help reduce the amount of available Portlandite that is available and hence increasing the chemical resistance. It was speculated that a 15% replacement of Portland cement with Metakaolin can restrict the

amount of Portlandite that is available to form Thaumasite. It was noted in the journal that there was a sharp increase in expansion in the early stages of storage. At the time of 11 months, no visual deterioration and have the ability to prevent Thaumasite in the short term and therefore has potential to fully prevent TSA (Smallwood, Wild, & Morgan, 2003). In a different study it showed that the use of Metakaolin resulted in severe deterioration in the presence of magnesium sulphate at ambient temperatures. It was reported that an increase in Metakaolin resulted in the most deterioration as the CSH was replaced with Magnesium Silicate Hydrate (MSH), a non-binding material. Although Metakaolin proves to provide beneficial attributes to other samples, in the case presented by Lee et al. it clearly had a negative impact stating the need for further research in this area (Lee, Moon, Hooton, & J.P., 2005).

2.2.5 Silica Fume Cement

Silica fume is a common product in the Canadian market that can be found in blended Portland cement which constitutes around 8% of the blend. In a study done by Attahan & Dikme (2011), it was found that it was very effective to incorporate silica fume even at low replacement levels of 2% - 6% by limiting the amount of expansion due to conventional sulphate attack (Atahan and Dikme 2011). Literature involving the effect of Thaumasite formation is very limited and in most literatures it is commonly agreed that the use of SCM may reduce and perhaps even mitigate Thaumasite. As the surface area of Silica fume is much higher when compared to ordinary Portland cement (OPC) it has a much faster rate of reaction as compared to other SCM and hence would help mitigate Thaumasite formation (Bellmann and Stark 2007).

2.2.6 Limestone Filler

A common way for practicing greener construction is to use Portland Limestone Cement (PLC). Opposed to using 100% General Use cement, which creates about a tonne of CO₂ emission for every tonne of cement produced, the PLC replaces up to 20% of GU cement with limestone. By using limestone as a filler it requires less energy to obtain the same fineness as GU cement and hence providing a smaller carbon footprint (Hooton, R., Nokken, M., & Thomas, M. 2007). However, there are growing concerns of whether or not this will affect TSA as it will become a major source of carbonate ions within the mixture itself, which would be the main source of carbonates besides limestone aggregate if TSA were to occur. When comparing GU cement and PLC, there is a small difference between the two in terms of resistance to the conventional sulphate attack (Hooton, R., Nokken, M., & Thomas, M. 2007). Studies have shown that a potential of reducing the activity in cement by grinding the limestone with the clinker as the limestone fineness would be finer than the clinker resulting in less surface area of the clinker in the final product which leads to lower optimum sulphate content. (Ingram & Daugherty, 1991). PLC has inconsistent trends and hence needs more research to be conducted. It is also noted that the majority of the research was done with external sulphate sources opposed to internal sulphate sources. In addition, the majority of the researches conducted thus far have been conducted with cements that have high C₃A levels which would not be used in sulphate environments as per the Canadian Standard Association (CSA)(Hooton, R., Nokken, M., & Thomas, M. 2007).

Chapter 3

Material and Experimental Details

3.1 Scope of Work

3.1.1 Test Development

Current standards in Canada test for internal (CSA A3004-C5) and external (CSA A3004-C6) sulphate attack for Portland cement only test specimens at $23 \pm 2^{\circ}$ c which is optimal for Ettringite formation. An amendment was noted in A3004-C6, test for external Sulphate attack, to accommodate testing at 5°c which is favourable for Thaumasite formation. A test for external sulphate attack for blended hydraulic cement (CSA A 3004-C8) is also currently in place but there is no standard for internal sulphate attack for blended mortars thus far or a standard for Internal Sulphate attack at low temperatures. Currently, in CSA A 3001 Table 9 sub clause 3, it recommends the use of supplementary cementing materials to obtain moderate or highly sulphate resistant blended hydraulic cements, which include; minimum 40% slag, minimum 25% Fly Ash Class F, 15% Metakaolin, 5% Type SF Silica Fume + 25% slag, or 5% Type SF Silica Fume + 20% Fly Ash Class F.

For the purpose of this study, specimens were tested at optimum temperatures of $23 \pm 2^{\circ}C$ to test conventional sulphate attack and $5 \pm 2^{\circ}c$ to test Thaumasite sulphate attack which is similar to the C8 standard. Also, additional time was given to cure when using supplementary cementing materials. The change was modified so that an additional 72 hours of curing (after it has been demolded) was added to all curing times for samples done in this study in order for the samples to cure before storage at 5°C. Another modification of this test was made to the first length measurement of the samples which was taken after 24 hours ± 15 minutes after the specimens has gone through the curing period and stored in water opposed to 24 ± 15 minutes after the

mixing water and cement are mixed together. Finally, to maintain the amount of sulphate added and the amount of cementing material to the mortar designs, the amount of sulphate was subtracted from the aggregate opposed to being subtracted from the cementing material. In attempt to accelerate the test, a higher water cement ratio of 0.65 was used and compared to the 0.485 as per the CSA standards.

For all samples, 14 day measurements were taken as per CSA standards and were periodically monitored after accompanied by visual inspection of the specimens to identify deleterious reactions, non-linear expansion and formation on the surface of the specimens. From the CSA standards, cementing materials can exceed the maximum allowed amount of SO_3^- provided that the expansion of the blended hydraulic cements does not exceed 0.02% @ 14 days. Adopting the limits from the C8 standard will help provide a better idea of the level of sulphate resistance in this program.

3.1.2 Sample Preparation

All samples were moulded to 25 x 25 x 285 mm with a gauge stud on each end of the sample and every sample having the gauge length corrected to 254 mm. A length comparator was used following CSA 3004-C5 to take length measurements for each sample where the ends of the gauge studs were wiped thoroughly to ensure no build up was present. The mixing procedure outlined in CSA A3004-C1 was used for all samples to ensure consistent mixing procedures (without the use of the lid) throughout the program. All specimens are placed in a moist environment immediately after it has been moulded and are covered to prevent water from dripping onto the specimen.

3.2 Materials

3.2.1 Aggregate

Two types of fine aggregates were used in this study for the production of mortar specimens. The first is graded silica sand which meets ASTM C778 standards and will be used as the control specimens. The other is a sulphate bearing dolomite aggregate, which has a nominal size of 19mm and will be used as comparison to the control to represent a different source of sulphate within the specimen itself where the chemical compositions is shown in Table 3.1.

3.2.1.1 Graded Silica Sand

The graded silica sand is a commercial product which can be purchased from suppliers. The aggregate must pass through the No. 20 sieve (0.841 mm) and retained on the No. 30 sieve (0.595 mm) as per ASTM C778. This is the same graded sand that is used for the three standards in CSA 3004-C5, CSA 3004-C6 and CSA 3004-C.

3.2.1.2 Sulphate Bearing Aggregate

The sulphate bearing aggregates is a dolomite which was obtained from a quarry located in Stoney Creek, Ontario along the Niagara Escarpment. The nominal size of the aggregate obtained was 19 mm. As the maximum nominal size for mortar bar specimens are 4.75 mm, the aggregate was sieved through a No. 4 sieve and is referred to as SAP (sulphate aggregate passing) from here on. The aggregate which was retained on the No. 4 sieve was crushed using jaw crushers and sieved through the No.4 sieve again until all of the aggregate passed the No. 4 sieve and is referred to as SAC (sulphate aggregate crushed). In the following Figure 3.1, a gradation curve is given for the crushed and the passing aggregate as well as a table of the chemical composition determined by a third party testing company. It is important to determine the amount of sulphate and the amount of carbonates that are present within the as it will help determine the total amount of sulphates within the specimens and also to ensure the supply of CO_3^{2-} is readily available. There are two types of sulphates that are identified; total and dissolvable. The total amount of sulphates and carbonates were found using the Combustion Infrared Detection method using pulverized pulp samples. The amount of dissolvable sulphates was found using the Ion Chromatography which analyzes the water that is leached from the same pulp sample. The difference between the two types of sulphates will be used to help explain the results obtained for this research.

	Sulphata Aggragata Crushad	Sulphate Aggregate -	
		Passing 4.75 mm	
Amount of CaCO ₃ (%)	43.9	30.7	
Amount of Mg(CaCO ₃) (%)	45.6	43.2	
Amount of Total SO ₄ (%)	3.6	4.6	
Amount of Water Soluble SO ₄ (%)	1.44	1.86	

Table 3.1: Chemical Composition of Sulphate-Bearing Aggregate



Figure 3.1: Sulphate Bearing Aggregate Gradation Curve

3.2.2 Cementing Materials

This section will outline the components of each cementing material as well as the proportions of the compounds of the cementing materials determined through X-ray fluorescence analysis.

Parameter	PC Type GU	FA-LC	GGBFS	HSF	Metakaolin
LOI, %	2.51	1.96	2.05	2.61	1.7
SiO ₂ , %	19.47	47.78	36.95	26.26	63.18
Al ₂ O ₃ , %	5.03	20.5	8.18	4.69	29.91
Fe ₂ O ₃ , %	2.09	20.43	0.51	2.15	1.13
CaO, %	62.95	3.05	38.51	56.06	0.69
MgO, %	2.27	1.18	1.047	2.06	0.48
SO ₃ , %	4.06	1.78	2.7	4.08	0.26
K ₂ O, %	1.16	1.38	0.52	1.13	1.17
Na ₂ O, %	0.24	0.5	0.33	0.2	0.21
TiO ₂ , %	0.26	0.95	0.53	0.24	0.062
SrO, %	0.09	0.06		0.08	0.01
P ₂ O ₅ , %	0.12	0.22	0.02	0.12	0.03
Cl, %	0.04	0	0.06	0.04	0
ZnO, %	0.01	0.02		0.03	0.01
Cr ₂ O ₃ , %	0.01	0.03		0.01	0.01
Mn ₂ O ₃ , %	0.06	0.04	0.034	0.17	0.01

Table 3.2: Chemical Analysis of Cementing Materials

3.2.2.1 General Use Portland Cement

General Use (GU) Portland cement was used in all samples in this study. The GU cement was obtained from what was called the Holcim plant located in Mississauga, Ontario. A detailed chemical analysis is provided in the table below.

Compound	Amount (%)
C ₃ S	51.87
C ₂ S	16.89
C ₃ A	10.16
C ₄ AF	6.58

Table 3.3: Chemical Compound of OPC

3.2.2.2 Ground Granulated Blast Furnace Slag

Ground Granulated Blast Furnace Slag (GGBFS) was used in this study using two different amounts of replacement of the total cementing material, 30% and 50%. These two amounts have been used in previous literature by Hooton et. al (2003). This study will help confirm whether these amounts will help mitigate the two different types of internal sulphate attacks. Table 2 lists the results of a chemical analysis done on the GGBFS using the X-Ray Fluorescence (XRF) method.

3.2.2.3 Low Calcium Fly Ash

Low Calcium Fly Ash (FA-LC) was used at 25% replacement of the total cementing material. This will help in determining the effect of FA-LC as there were varying results (Mulenga, Stark, and Nobst 2003). Table 2 displays the chemical composition of the cementing material.

3.2.2.4 Metakaolin

For the purpose of this study, a replacement level of 10% Metakaolin was chosen as it is the middle value of the suggested amounts of Metakaolin which is usually between 8-12%. This will help determine the effectiveness of this fast reacting pozzolanic cementing material. Refer to Table 2 for the chemical analysis of Metakaolin.

3.2.2.5 High Silica Fume Cement

High Silica Fume (HSF) Cement was used in this study as a tertiary blend of cement with general use Portland cement and also GGBFS. Silica Fume has been sought to be a solution for conventional sulphate attack at low amounts. HSF cement is blended together at the Holcim plant in Mississauga, Ontario and contains 8% Silica Fume within the blend. The chemical analysis is listed in table 2.

3.2.3 Limestone Filler

The limestone filler used in this research is a commercially available. This product was chosen as to be used as the lime filler for this research. It will provide the supply of CO_3^{2-} as well as perhaps improving the pore structures within the samples. Samples that are made with lime filler have 8% of total cementing material added as part of the aggregate weight.

3.2.4 Hemihydrate/carbonate blend (Hemihydrate + Calcium Carbonate filler)

Hemihydrate/carbonate blend (HCB) is one of the listed sources of sulphate. The HCB contains Calcium Sulphate hemihydrate (CaSO4 $\frac{1}{2}$ H2O), calcium carbonate and also silica sand. This product provides sulphates in the form of hemihydrate as opposed to Dihydrate in gypsum which is the general form of sulphate added to cement in order to prevent flash set from occurring. The Hemihydrate/carbonate blend was added with the cement although it was considered as part of the mass of aggregate. There were different amounts of sulphates added to the mix which include 1.45%, 2.90%, 3.89% and 5.83%. The percentages listed are in terms of SO₃²⁻ and was determined by stoichiometry. The chemical composition of the Hemihydrate/carbonate blend is presented below in Table 3.4.

Compound	Amount (%)
$CaSO_4 \bullet \frac{1}{2} H_2O$	51.83
CaCO ₃	43.89
SiO ₂	3.47

Table 3.4: Chemical Analysis of Hemihydrate/carbonate blend
3.3 Experimental Program

3.3.1 Experimental Program

The mix design for mortar in this study was based on the standards outlined in CSA 3004-C5 and CSA 3004-C6. This includes having a proportion of 1 part cement to 2.75 part aggregate by mass. Two water cement ratios were used which include 0.485 and 0.65. Similar designs with SCM replacements were used which included 30% Slag, 50% Slag, 25% Low Calcium Fly Ash, 10% Metakaolin and 5% Silica fume with 30% Slag. In addition to the SCM, Hemihydrate/carbonate blend was added to the mix where the material acted as part of the aggregate. Through stoichiometric calculations, HCB was added in terms of SO_3^{2-} until it amounted to 1.45%, 2.90%, 3.89% and 5.83%. Another parameter was whether there was a limestone filler addition in the mix or not. The amount of limestone filler added amounted to 8% CO_3^{2-} through stoichiometric calculations. In the later stages of this study, aggregate that contained sulphate was investigated as well. The research conducted is broken down into six phases summarized in Figure 3.2. This experimental program will help to better understand the mechanism of formation of both Ettringite and Thaumasite due to ISA as well as investigating possible mitigation techniques against ISA. Table 3.5 shows the ratio and a sample of the mixes used for each water to cement ratio.

Water to		0.485		0.65	1.92		
Cement Ratio	Ratio Sample Mass (g)		Ratio	Sample Mass (g)	Ratio Sample Mass (g		
Cementing Material	Cementing Material 1 500		1	500	1	160	
Total Aggregate2.75		1375	2.75 1375		11	1760	
Water	0.485	242.5	0.65	325	1.92	307.2	

Table 3.5: Mortar mix design for mixes used



Figure 3.2: Summary of Phases

3.3.1.1 Phase 1: Sulphate Attack in cementing system with high w/cm

3.3.1.1.1 High w/cm systems with the addition of Hemihydrate/carbonate blend

In the preliminary stages of the research conducted a water cement ratio of 0.65 was chosen to try to study possibility of sulphate attack in high w/cm systems, and accelerate the rate of reaction for an earlier indication of sulphate attack. Eight bars were cast at a time to ensure identical proportions which were subsequently stored in saturated lime solutions at temperatures that would favour Thaumasite formation (5°C) and Ettringite formation (23°C). As expansion was expected, mitigation techniques using SCM were used and compared to the sample without SCM. Different levels of SO_3^{2-} were used to see what the optimum amount of SO_3^{2-} was. The source of SO_3^{2-} was from Hemihydrate/carbonate blend.

%SO3 of cementing material	1.45	2.90	3.89	5.83
Cementing material (g)	500	500	500	500
Graded Silica Sand(g)	1349.64	1324.28	1306.97	1273.04
Water(g)	325	325	325	325
HCB(g)	25.36	50.72	68.03	101.96

Table 3.6: Sample Mixes for Phase 1 Part 1

3.3.1.1.2 High w/cm systems with the addition of Hemihydrate/carbonate blend with limestone filler

Upon reading literature and the increasing use of Portland Limestone Cement, the addition of Limestone filler was decided upon. The amount to be added was fixed at 8% CO_3^{2-} by mass of cementing material used. Thaumasite needs a source of CO_3^{2-} ions in the sample in order to promote Thaumasite formation. With the addition of limestone filler, the effect on the formation of Ettringite also needed to be determined. All of the mixes from phase one were casted again with the limestone addition.

%SO3 of cementing material	1.45	2.90	3.89	5.83
Cementing material(g)	500	500	500	500
Graded Silica Sand (g)	1282.97	1257.62	1240.30	1206.37
Water (g)	325	325	325	325
HCB (g)	25.36	50.72	68.03	101.96
Limestone Filler(g)	66.67	66.67	66.67	66.67

Table 3.7: Sample Mixes for Phase 1 Part 2

3.3.1.1.3 Comparison of high w/cm systems with or without Limestone filler

Comparing the high w/cm systems with or without Limestone filler will help to better define the role of CO_3^{2-} on the formation of Thaumasite. It will also help determine the effect of limestone filler on the formation of Ettringite which is thought to form mostly in the voids within a sample.

3.3.1.2 Phase 2: Effect of w/cm ratio

This phase consisted of all the samples from Phase 1 with the water to cement ratio of 0.485 as per CSA 3004-C5 and CSA 3004-C6. This was done in order to determine the effect of water to cement ratio on both conventional sulphate attack and Thaumasite sulphate attack.

%SO3 of cementing material	3.89
Cementing material (g)	500
Graded Silica Sand (g)	1240.30
Water (g)	242.5
HCB (g)	68.03
Limestone Filler (g)	66.67

Table 3.8: Sample Mix for Phase 2

3.3.1.2.1 Determination of Absorption

It is important to help better understand the physical characteristics such as the pore structure of the mixes used. Determining the absorption allows the comparison of the pore structures from mix to mix and will be determine by first casting two samples for each mix. Submerge all samples in water in a vacuum sealed system for 24 hours followed by storing the samples in an oven set at 100°C for 24 hours. The determination of absorption is the quotient of the difference between the wet mass of sample and the dry mass of the sample over the dry mass of the sample multiplied by 100 and expressed as a percentage.

 $\frac{wet mass of sample-dry mass of sample}{dry mass of sample} (100) = \% absorption (Eq 3-1)$

3.3.1.3 Phase 3: Effect of initial formation of Ettringite on late Thaumasite Formation

From the research conducted by Köhler et al., 2006, it hypothesized that the Ettringite can control the rate at which Thaumasite is formed. In the study performed, the mixes from Phase 1 were casted again. These samples were stored at 23°C to promote Ettringite formation and then 5°C to promote Thaumasite formation. The study of this phase will help determine whether an increase in Ettringite formation will result in a faster rate of Thaumasite formation.

3.3.1.4 Phase 4: Internal sulphate attack due to sulphate from the aggregates

Internal Sulphate attack is due to the components that are already within the mix itself and thus far the only major source of sulphate is from the Hemihydrate/carbonate blend. However, a major component of any mix design is the aggregate. The use of inferior dolomite aggregate was chosen to provide the source of sulphate. In this phase, mortar bar samples were cast at the same ratio of cement to aggregate as previously which was 1 part cement to 2.75 part aggregate. The water cement ratios chosen were 0.485 and 0.65 which coincides with phases 1 and 2 but also 1.92 which represents controlled low strength materials (CLSM). For the CLSM sample a mix was chosen which used the same aggregate and used a cement to aggregate ratio of 1:11. As the aggregate came with a nominal size of 19mm the aggregates were separated by the No 4. Sieve. Material passing was labeled as SAP and everything that was retained was crushed and was labeled as SAC.

Table 3.9:	Sample	mixes o	f Phase 4

Water to Cement ratio	0.485	0.65	1.92
Cementing material (g)	500	500	160
Sulphate Bearing Aggregate (g)	1375	1375	1760
Water (g)	242.5	325	307.2

3.3.1.5 Phase 5: Comparison of Sources of Sulphates

In order to compare the sources of sulphates the amount of sulphates present needed to be fixed. This was done by stoichiometric calculations so that the amount of sulphates which the sulphate bearing aggregates contributed was equal to 3.890% SO₃²⁻ which would equate to the same amount of sulphate as the samples prepared in Phase 1. As expansion was expected to occur at the same rate or greater, supplementary cementing materials were used to help mitigate the Internal Sulphate Attack (ISA)

Table 3.10: Sample Mix of Phase 5

%SO3 of cementing material	4.70
Cementing material (g)	500
Graded Silica Sand (g)	864.12
Water (g)	242.5
Sulphate Bearing Aggregate (g)	510.88

3.3.2 Scanning Electron Microscopy (SEM)

The microstructure of specimens of interest was broken into pieces and was prepared by polishing and then carbon coated so that it could be examined by using a Scanning Electron Microscopy (SEM). The SEM was performed using a JEOL model JSM-6380-LV. Using this machine it can either perform a Secondary Electron scan (SE) or a Backscatter Electron Scan (BSE). The most common type of scan that is included with all SEM machine is SE. The machine scans the sample with a ray of electrons which in turn produce signal patterns. These signals (Energy Dispersive X-rays (EDS)) can be interpreted to display the topography and the chemical composition of the sample being scanned. The beams being emitted can be focused and

magnify an area of interest so that it is only a few nanometers. Using the SEM, it helps illustrate the pore structures of the specimens and it will also help differentiate between the two key crystals of interest. As mentioned before, Ettringite and Thaumasite of similar crystal structures and is hard to differentiate, except by composition. Using the SEM, the chemical composition can be determined. Areas containing Sulfur, Aluminum and Calcium should indicate Ettringite formation and areas containing Aluminum, Silicon, Carbon and Calcium should indicate Thaumasite Formation. It is noted that the carbon is hard to detect using this method (Sahu, Exline, & Nelson, 2002). Another study had a slight variance in terms of the peaks when listing the ratios between Sulfur/Calcium, Aluminum/Calcium and Silicon/Calcium. The ratios for Thaumasite and Ettringite respectively are as follow S/Ca = 1/3, Al/Ca = 0, Si/Ca = 1/3 and S/Ca = 1/2, Al/Ca = 1/3, Si/Ca = 0 (Yang & Buenfeld, 2000). The difference between the two studies is whether or not there is aluminum in Thaumasite. Both studies will be taken into consideration in this thesis.

		Ettringite	Thaumasite
Vong & Puonfield	S/Ca ratio	1/3	1/2
rang & Buenfield,	Al/Ca ratio	0	1/3
2000	Si/Ca ratio	1/3	0
Sahu et al	Peaks	S, Al, Ca	Al, Si, C, Ca

	Table 3.11: Summary	′ of c	characteristics	of Ettring	ite and	Thaumasite	when	using	EDS	anal	vsis
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3.4 Thermogravemetric Analysis

Thermogravemetric Analysis (TGA) is commonly used with Differential Thermal Analysis (DTA) to help identify material and to help identify the amount of certain compounds. The Machine that is used to perform the TGA was the Mettler Toledo TGA 2 which is supposed to have high temperature ranges with high sensitivity so that both the TGA and DTA can be performed. Samples are prepared by grinding the material with a mortar and pestle and then sieved through a No. 200 sieve (75 microns). Samples are then quartered and placed into crucibles made specifically for the TGA machine. Once the sample is ready, it is placed into the machine where it is heated at a uniform rate until it reaches the maximum allowable temperature which is about 1000°C. As the sample is heated, the change of energy (1 mW = 1 J/s) which can be used later to determine the material. Identifying areas of peaks on the DTA, it will help determine the amount of material on TGA.

Chapter 4

Results and Discussion

4.1 Phase 1: Sulphate Attack in cementing system with high w/cm

As previously mentioned in section 3.3.1, six set of eight bars were made for each level of $SO_3^$ in this phase, one for each of the following supplementary cementing material replacement; no SCM replacement, 30% Slag replacement, 50 % Slag replacement, 25% Fly Ash Class F, 10% Metakaolin and 5% Silica Fume + 30% Slag. For this study four different levels of SO_3^{2-} were chosen; 1.45%, 2.90%, 3.89% and 5.83% of cementing materials. Each set of mortar bars were split evenly to be tested at 23°C and 5°C. A sample mix used in this phase can be viewed in Table 3.6.

4.1.1 Cementing Systems Containing Hemihydrate/carbonate blend (hemihydrate + CaCO₃)

The first part of this phase was to test the different cement mixtures with just the addition of SO_3^{2-} in the form of Hemihydrate/carbonate blend. The graphs below are presented to show the results obtained for all mixture in the first part of the phase (Figure 4.1– Figure 4.7). The samples that were intended to be tested at 5°C were removed from the storage temperature due to insufficient space with the exception of the bars that were casted with 5.83% SO_3^{2-} .

By analyzing the data collected for the mixes with 1.45% SO_3^{2-} tested at 23°C, it can be said that all of the mixes are within the expansion limit of 0.02% at 14 days and would probably not result in conventional sulphate attack as there is probably not enough internal source of SO_3^{2-} available for Secondary Ettringite Formation. The mix containing 100% PC will serve as a control sample in this thesis as there is no standard for ISA after 14 days.



Figure 4.1: Comparison of various cementing systems with 1.45% SO_3^{2-} , as mass of cementing material, added using Hemihydrate/carbonate blend and tested at 23°C



Figure 4.2: Same data presented in Figure 4-1 but using larger scale on Y-Axis

The effects of adding 2.90% SO_3^{2-} at 23°C are shown in Figure 4.3. Analyzing the data, there is not much difference in terms the amount of expansion between the different samples with the exception with the sample made with 10% Metakaolin replacement which has a clear improvement in terms the amount of expansion. The majority of the mixes exceeds the 0.02% limit at 14 days except the mixes a replacement level of 25% Fly Ash Class F and 10% Metakaolin. Further measurements for the samples revealed that all mixes with an addition of 2.90% SO_3^{2-} did not exceed of 0.05% at 6 months. As there is not a clear difference between the majority of the mixes, an increase of SO_3^{2-} is needed.



Figure 4.3: Comparison of various cementing systems with 2.90% SO_3^{2-} , as mass of cementing material, added using Hemihydrate/carbonate blend and tested at 23°C



Figure 4.4: Same data presented in Figure 4-3 but using larger scale on Y-Axis

In Figure 4.5 and Figure 4.6, the expansion of the samples containing only Portland Cement has clearly shown a substantial amount of expansion. With the addition of $3.89\% SO_3^{2-}$ and $5.83\% SO_3^{2-}$, a maximum expansion of 0.151% and 2.021% has been measured respectively. The amount of expansion and the rate of expansion can be allotted to the increase of availability of SO_3^{2-} . The expansion of the sample containing $5.83\% SO_3^{2-}$ was expected to further increase but was not able to be measured as the length exceeded the maximum length of the measuring apparatus. It is apparent that for all samples that an increase in availability of SO_3^{2-} resulted in an increase in expansion. By analyzing the results of using supplementary cementing materials, it is apparent that it significantly reduces the amount of expansion. This is due to the decrease in amount of Ordinary Portland Cement which in turn reduces C₃A in the mixtures.



Figure 4.5: Comparison of various cementing systems with 3.89% SO_3^{2-} , as mass of cementing material, added using Hemihydrate/carbonate blend and tested at 23°C



Figure 4.6: Comparison of various cementing systems with 5.83% SO_3^{2-} , as mass of cementing material, added using Hemihydrate/carbonate blend and tested at 23°C

The use of both Metakaolin and Low-Calcium Fly Ash resulted in a reduction to the amount of expansion. The use of Metakaolin in literature enhances the pore structure of the sample due to the fineness of the particles and later the pozzolanic reaction to form CSH gel. A comparison of the water-accessible pores was done by measuring the absorption of the samples shown in Table 4.1. The absorption of the samples is determined by following the procedure outlined in section 3.3.1.2.1. The enhanced pore structure, reduction in SO_3^{2-} by dilution of Portland Cement, the early strength gain of Metakaolin and large amounts of active alumina are believed to help mitigate the formation of Ettringite in the samples presented in this study.

Table 4.1: Comparison of Absorption using Metakaolin

	Sample		Absorption (%)
	100% Portland Cement	w/o Limestone	6.903
3.89%	10% Metakaolin	Filler	5.521
SO ₃ ²⁻	100% Portland Cement	w/ Limestone	7.024
	10% Metakaolin	Filler	5.518

A ternary blend of OPC, GGBFS and Silica Fume also resulted in a reduction of expansion. Silica Fume was added in the form of blended cement which comprised of 92% OPC and 8% Silica Fume which will be referred to as HSF. The chemical composition of HSF and OPC does not vary by much as outlined in Table 3.1. As the fineness of Silica Fume is known to be higher than that of OPC an enhanced pore structure was expected. This can be used to explain the reduction in expansion between the ternary mix and the mix containing just 30% GGBFS.



Figure 4.7: Comparison of various cementing systems with 5.83% SO_3^{2-} , as mass of cementing material, added using Hemihydrate/carbonate blend and tested at 5°C

From Figure 4.7, rate of expansion for all samples can be said to high which is shown by the slope in the figure with the highest being the sample containing 10% Metakaolin. The samples containing slag, Metakaolin and HSF clearly have an effect of reducing the amount of expansion that occurs. Taking a look at the 6 month expansions outlined later in Table 4.23 on page 67, the highest expansion would be the sample containing only OPC then the following samples in descending order, 25% Fly Ash Class F, 30% Slag, 10% Metakaolin, 5% SF & 30% Slag and 50% Slag. It was expected for the OPC to be the worst which was the case but the amount of

expansion from the sample containing Fly Ash Class F was unexpected but may be due to the slow reacting Pozzolanic reaction of the Fly Ash and the limited amount of reactive alumina. In previous studies, Fly Ash has been found to be inconsistent in the results that it produces depending on the properties of the cement used where some were found to mitigate Thaumasite Formation while others were found to have no effect (Mulenga, Stark, & Nobst, 2003). The use of 50% GGBFS has been found by Hooton et al. (2003) to help reduce the amount of Thaumasite that is formed which is confirmed in this study to show the least expansion of the samples with the same amount of added SO_3^{2-} .

Metakaolin and Silica Fume are known to decrease permeability of a mix even at low replacement levels. The effects of both SCM can be seen in Figure 4.7 as the addition of either results in a reduction in expansion. It is thought that the reduction in permeability limits the ion migration that is needed for Thaumasite and Ettringite to form and hence increase the physical resistance.

4.1.2 Cementing Systems Containing Hemihydrate/carbonate blend (Hemihydrate + CaCO₃) and Limestone Filler

The second part of the phase was to add additional limestone filler to further promote Thaumasite formation by providing additional amounts of CO_3^{2-} . This was done by adding a fixed percentage of 8% CO_3^{2-} by mass of cementing material in the form of limestone filler, as replacement for aggregate. A sample of the mixes used in this portion of the phase can be viewed in Table 3.7. Samples were tested at both of the testing temperatures to see the effect of CO_3^{2-} addition on the formation of Ettringite and Thaumasite. The graphs below show the results of this part of the phase for both testing temperatures.

Analyzing the expansion results in the Figure 4.8 and 4.9, it can be said that the samples are resistant to an addition of 1.45% SO_3^{2-} at 23°C as they did not exceed limit of for 14 days. The low expansion is due to the low amounts of SO_3^{2-} ions that are available to promote the formation of Ettringite.



Figure 4.8: Comparison of various cementing systems with $1.45\% SO_3^{2-}$, as mass of cementing material, added using Hemihydrate/carbonate blend, added limestone filler and tested at $23^{\circ}C$



Figure 4.9: Data presented in Figure 4-8 using larger Y-Axis Scale.

With the addition of 2.90% SO_3^{2-} the maximum expansion seen was 0.050% occurring in the sample with 100% Portland cement. Viewing the trends presented in Figure 4.10, there is not a large difference between the majorities of the mixes with the exception of Metakaolin which can be explained by the decreased amounts of voids where Ettringite tends to form.



Figure 4.10: Comparison of various cementing systems with 2.90% SO_3^{2-} , as mass of cementing material, added using Hemihydrate/carbonate blend, added limestone filler and tested at 23°C

From Figure 4.11, it is evident that the increase in SO_3^{2-} has led to an increase in the expansions both at 14 days and at 6 months with the exception of Metakaolin. When comparing the expansions between the Metakaolin samples with and without limestone filler - 0.037% and 0.016% at 6 months, respectively - it is apparent that the sample containing limestone filler resulted in less expansion. Comparing the two amount of absorption of the two samples shown in Table 4.1, there is not much of a difference. Hence, the differences in expansion cannot be attributed to differences in pore structure or availability of moisture. Perhaps, the additional limestone did not result in more expansion since there is already enough limestone in the system in relation to the available sulphate. However, the reason for decreased expansion when limestone filer is used is not known. It should be noted that the expansions in both cases were < 0.04% at 6 months. There is a possibility that the limestone filler reduces the size of pores and hence resist the formation of growth of Ettringite crystals.



Figure 4.11: Comparison of various cementing systems with 3.89% SO_3^{2-} , as mass of cementing material, added using Hemihydrate/carbonate blend, added limestone filler and tested at 23°C

When comparing the expansion in Figure 4.12 and Figure 4.6, the effect of each SCM can be said to be similar. Comparing the absorption of the two 100% PC samples, there is about a 0.10% difference due to the addition of limestone filler. When comparing the two expansions of 100% PC at 23 °C, the expansions are slightly different with the sample containing limestone filler to possess less expansion at the same time of testing.



Figure 4.12: Comparison of various cementing systems with 5.83% SO_3^{2-} , as mass of cementing material, added using Hemihydrate/carbonate blend, added limestone filler and tested at 23°C

The mixes containing 1.45% SO_3^{2-} is expected to have low expansion due to the internal sulphate attack when being stored at 5°C since the amount of sulphate is relatively low. This has been the case as shown in Figure 4.13 and Figure 4.14.



Figure 4.13: Comparison of various cementing systems with $1.45\% SO_3^{2-}$, as mass of cementing material, added using Hemihydrate/carbonate blend, added limestone filler and tested at 5°C



Figure 4.14: Data is Figure 4-13 using larger scale on the Y-Axis

The expansion of samples with 2.90% SO_3^{2-} at 5 °C is shown in Figure 4.15. There is an apparent benefit when SCM are used, where Metakaolin showed the best performance.



Figure 4.15: Comparison of various cementing systems with $2.90\% SO_3^{2-}$, as mass of cementing material, added using Hemihydrate/carbonate blend, added limestone filler and tested at 5°C

In Figure 4.16, it is clear that $3.89\% SO_3^{2-}$ is the level of SO_3^{2-} at which there is a significant amount of expansion at which the sample containing no SCM showed significant expansion. The use of SCM clearly has a positive impact in reducing the amount of expansion within these samples. The SCM that has the least amount of reduction in terms of expansion a is the sample containing 25% Fly Ash Class F. Although this sample follows the guidelines set by CSA, 3000 for external sulphate attack, the sample in this study does not seem to support findings in which that Fly Ash is beneficial in reducing the expansion when tested at 5 °C. This could be due to the low amount of active Al₂O₃ is type of fly ash (Ramlochan, Zacarias, Thomas, & Hooton, 2003). Other samples used in the study showed promising results with the addition of $3.89\% SO_3^{2-}$. For the case of the addition of Silica Fume, the enhancement of pore structure may play a key role.



Figure 4.16: Comparison of various cementing systems with 3.89% SO_3^{2-} , as mass of cementing material, added using Hemihydrate/carbonate blend, added limestone filler and tested at 5°C

Ground Granulated Blast Furnace Slag (GGBFS) evidently has a positive effect on reducing the amount of expansion that occurs at 5°C. An increase in GGBFS leads to an increased reduction in expansion as seen in the difference in expansion from the samples containing 50% and 30% GGBFS. The use of this SCM reduces the amount of C_3A available to form Ettringite and increases the amount of Al_2O_3 to form monosulphoaluminate. Whether using the topochemical theory or the dissolution-precipitation theory, both agree that the formation of Ettringite occurs first before the formation of Thaumasite. Determining whether or not there is enough SO_3^{2-} available after the formation of Ettringite will be the next step to help determine if there was Thaumasite formation that occurred. From Figure 4.17, the addition of 5% Silica Fume + 30% Slag clearly has a positive impact on the amount of expansion. The use of silica fume reduces the size of the capillaries due to the fine particle sizes of silica fume and hence limiting the amount of ion migration needed for products to form.



Figure 4.17: Comparison of various cementing systems with 5.83% SO_3^{2-} , as mass of cementing material, added using Hemihydrate/carbonate blend, added limestone filler and tested at 5°C

The effect of the sample containing 10% Metakaolin on expansion is similar to the sample containing 30% Slag and 5% Silica Fume. The reason being the increased amount of available Al_2O_3 to form monosulphoaluminate and also the refinement of the pore structure as the particle size is similar to that of Silica Fume. As the replacement level of Metakaolin is only at 10% and the CSA guideline is 15% for external sulphate, an additional sample with that will help better define the effect of Metakaolin. Comparing the expansion of the same sample at both storing temperatures, the significant difference in expansion can be seen. As storage at 23°C is said to be favourable for Ettringite formation it is assumed that Ettringite and monosulphoaluminate are the major sulphate-bearing phases to form.

4.1.3 Microstructure Examination of Samples Tested in Phase 1

To further identify the mechanisms which caused expansion, SEM images was taken and an EDS analysis was performed for the following specimen at the specified time:

- 5.83% SO_3^{2-} 10% Metakaolin with limestone filler stored at 5°C @ 105 days
- 5..83% SO_3^{2-} 25% Fly Ash Class F with limestone filler stored at 5°C @ 399 days

Using the identification summarized in Table 3.1, Ettringite has been found in the sample containing Metakaolin with traces of Thaumasite as shown in Figure 4.18 and Figure 4.19. From the EDS it can be seen that the peaks for Figure 4.18 is Calcium, aluminum and sulfur which are the same main peaks as Ettringite. Ettringite is known to form in voids or in this case a micro crack as show in the image. In Figure 4.19 it has the both Ettringite and Thaumasite



Figure 4.18: SEM image and EDS analysis of 5.83% SO_3^{2-} 10% Metakaolin w/limestone filler stored at 5°C showing possible Ettringite



Figure 4.19: SEM image and EDS analysis of 5.83% SO_3^{2-} 10% Metakaolin w/limestone filler stored at 5°C showing possible of both mixture of both Ettringite and Thaumasite.

The least effective replacement at 5.83% SO_3^{2-} being 25% Fly Ash Class F has an expansion of 0.194% at 6 months and 1.392% at 12 months. In comparison to the sample containing only OPC which has an expansion of 0.421% at 6 months and maximum expansion measured before sample curling (due to excessive expansion) of 1.392% which occurred before 12 months. It is clear here that the replacement of Fly Ash has reduced the amount of expansion thus far. Similar to the case of Metakaolin, the amount of expansion stored at 5°C is significantly higher than the samples that are stored at 23°C. This could be due to the formation of Thaumasite but further analysis is needed in order to determine the products that lead to expansion. In Figure 4.20 it can be said that Thaumasite is present within the sample. This is concluded from the ratios which use the amounts shown in the figure. The ratios of S/Ca and Si/Ca are both greater than 1/3 which is a sign of Thaumasite that has formed in that area.



Figure 4.20: SEM image and EDS analysis of 5.83% SO_3^{2-} 25% Fly Ash Class F w/limestone filler stored at 5°C showing possible Thaumasite

4.1.4 Comparison of Cementing Systems Containing Hemihydrate/carbonate blend with or without Limestone Filler

It is known that a source of CO_3^{2-} is needed for Thaumasite to form whether it is from the cementing material, aggregate or perhaps even the atmosphere in some cases. The samples were made with varying SO_3^{2-} which originated from Hemihydrate/carbonate blend. The composition of the Hemihydrate/carbonate blend used in this study can be seen in Table 3.4. An additional 8% CO_3^{2-} was added to each mix (as % of cementing materials) in the second part of this phase in the form of limestone filler. Table 4.2 shows the amount of CO_3^{2-} added for the varying levels of SO_3^{2-} .

$%SO_3^{2-}$	CO_3^{2-} from	CO_3^{2-} from Limestone Filler (g)	Total CO_3^{2-1} added (g)
	Hemihydrate/carbonate		
	blend(g)		
1.45	6.8		42.0
2.90	12.90	35.2	48.7
3.89	18.2		53.4
5.83	27.0		62.2

Table 4.2: Amount of CO_3^{2-} added based on 440g of cementing materials

Table 4.3 and Table 4.4 show the expansion values at 14 days, 6 months and 12 months, if available. The comparison in Tables 4.3 and 4.4 is used to evaluate the effect of additional CO_3^{2-} on the formation of both Ettringite and Thaumasite. From analyzing the values of expansion in terms of storage at 23°C, the effects vary when comparing the mix with or without limestone with the same SCM. However, the majority is seen to have a positive effect in reducing the expansion. The reason for this is not known, although the addition of filler might have reduced the size of pores. While the absorption of samples with and without limestone is the same, this represents the total porosity. Two samples can have the same total porosity but the pore distribution of average size of pores may vary.

The increase in CO_3^{2-} seems to also have a varying effect on the formation of Thaumasite. As the mixes containing OPC, 30% Slag, Fly Ash Class F and 30% Slag + 5% Silica Fume resulted in an increase in expansion when adding 8% CO_3^{2-} . On the other hand the addition of the Limestone filler seemed to decrease the amount of expansion for mixes containing 10% Metakaolin and 50% Slag. Hence it is hard to conclude the direct relationship of CO_3^{2-} on the rate of formation of Thaumasite. It should be noted that if sulphur is consumed in the formation of sulphur-bearing phases such as monosulphoaluminate, Ettringite, or Thaumasite, additional lime filler in the mix will not result in formation of any additional Thaumasite as sulphur is

missing. When comparing the expansion results at 6 months for the OPC mixes at 5.83% SO_3^{2-} , and 5 C, there is a significant amount of expansion which could suggest that increasing the availability of CO_3^{2-} may increase the severity of TSA when it occurs.

	Cementing Material	1	LOO% Portla	and Cemen	t	30)% GGBFS F	Replaceme	nt	50)% GGBFS F	Replacemei	nt
	% SO ₃ ²⁻	1.45	2.90	3.89	5.83	1.45	2.90	3.89	5.83	1.45	2.90	3.89	5.83
	14 days	0.004	0.027	0.031	0.027	0.008	0.024	0.042	0.042	0.011	0.014	0.025	0.049
	6 months	0.009	0.037	0.133	0.551	0.018	0.039	0.063	0.129	0.021	0.034	0.038	0.122
HCB @ 23	12 months	0.020	0.050	0.149	Curled	0.033	0.054	0.081	0.153	0.037	0.053	0.055	0.134
	14 days	0.005	0.011	0.018	0.010	0.005	0.019	0.019	0.013	0.002	0.012	0.020	0.023
	6 months	\ge	$\left \right\rangle$	$\left \right\rangle$	0.246	$\left \right\rangle$	$\left \right\rangle$	$\left \right\rangle$	0.158	$\left \right\rangle$	$\left \right\rangle$	$\left \right>$	0.126
HCB @ 5	12 months	\ge	$\left \right\rangle$	$\left \right\rangle$	0.842	$\left \right\rangle$	$\left \right\rangle$	$\left \right\rangle$	0.186	\ge	$\left \right\rangle$	$\left \right>$	0.136
	14 days	0.007	0.025	0.023	0.008	0.006	0.018	0.032	0.039	0.007	0.019	0.040	0.047
HCB & LF @	6 months	0.010	0.050	0.100	0.529	0.012	0.038	0.056	0.135	0.013	0.036	0.062	0.109
23	12 months	>	0.054	0.102	Curled	>	0.051	0.062	0.155	>	0.041	0.066	0.123
	14 days	0.004	0.013	0.012	0.008	0.005	0.017	0.024	0.011	0.002	0.006	0.019	0.020
HCB & LF @	6 months	0.028	0.066	0.123	0.421	0.029	0.046	0.065	0.184	0.033	0.038	0.057	0.110
5	12 months	\geq	0.068	0.137	Curled	\ge	0.051	0.070	0.209	\ge	0.043	0.062	0.117

Table 4.3: Phase 1 expansion results of mixes containing 100% OPC, 30% GGBFS and 50% GGBFS

										5% Silica Fume + 30% GGBFS			
	Cementing Material	25% Fly Ash Class F Replacement			10% Metakaolin Replacement				Replacement				
	% SO ₃	1.45	2.90	3.89	5.83	1.45	2.90	3.89	5.83	1.45	2.90	3.89	5.83
HCB @ 23	14 days	0.002	0.015	0.026	0.030	0.001	0.000	0.037	0.086	0.000	0.029	0.048	0.050
	6 months	0.005	0.016	0.043	0.195	0.014	0.011	0.061	0.097	\geq	0.037	0.067	0.133
	12 months	\geq	\triangleright	0.045	0.198	0.030	0.026	0.078	0.101	\geq	>	0.073	0.150
	14 days	-0.003	0.004	0.006	0.014	0.003	-0.001	\triangleright	0.043	0.003	0.020	0.025	0.024
	6 months	\geq	\searrow	0.077	0.158	\ge	\ge	\geq	0.164	\geq	0.037	0.067	0.129
HCB @ 5	12 months	\geq	\geq	0.086	0.602	\ge	$\left \right\rangle$	\geq	0.166	\geq	\searrow	0.071	0.143
HCB & LF @ 23	14 days	0.002	0.026	0.031	0.031	0.005	0.000	0.008	0.065	0.002	0.022	0.045	0.054
	6 months	\geq	\geq	0.059	0.187	0.013	0.016	0.016	0.077	\geq	0.035	0.068	0.131
	12 months	\geq	\triangleright	0.061	0.190	\triangleright	0.021	0.019	0.081	\geq	>	0.074	0.153
HCB & LF @ 5	14 days	0.004	0.012	0.013	0.014	0.005	0.006	0.022	0.030	0.002	0.017	0.024	0.029
	6 months	\geq	\triangleright	0.091	0.194	0.026	0.029	0.040	0.139	\geq	0.033	0.063	0.148
	12 months	\triangleright	\triangleright	0.114	0.651	\triangleright	0.035	0.044	0.142	\triangleright	\triangleright	0.067	0.163

Table 4.4: Phase1 expansion results for mixes containing 25% Fly Ash Class F, 10% Metakaolin and 5% Silica Fume 30% Slag

4.2 Phase 2: Effect of W/cm ratio

As mentioned in Section 3.3.1, sets of mortar bars were made with water to cement ratio of 0.485 which is the conventional water to cement ratio used by CSA standards CSA 3004 C5 and C6. This will help determine the effect of the water to cement ratio on both conventional sulphate attack and Thaumasite Sulphate attack. It is thought that a reduction in the water to cement ratio would help enhance the pore structure and hence reduce the expansion. Four different cementing combinations was chosen for this phase, which consisted a combination of Portland Cement, 10% Metakaolin, a ternary blend of 30% Slag and 5% Silica Fume and limestone filler addition. The specimens were tested at both 23 and 5 and the results can are presented in Figure 4.21 and 4.22, respectively. For all mixes the added SO_3^{2-} and CO_3^{2-} was 3.89% and 8% respectively of the total cementing material. It is noted here that the proportions will change slightly as there will be more cementing material by using a lower water to cement ratio and keeping the same cement to aggregate ratio. A sample mix for this phase is provided in Table 3.8.



Figure 4.21: Comparison of various cementing systems with 3.89% SO_3^{2-} , as mass of cementing material, added using Hemihydrate/carbonate blend, with a w/cm of 0.485 and tested at 23°C



Figure 4.22: Comparison of various cementing systems with 3.89% SO_3^{2-} , as mass of cementing material, added using Hemihydrate/carbonate blend, with a w/cm of 0.485 and tested at 5°C

The mixes in this phase exhibit similar trends when being storied at 23°C in terms of reducing the expansion when compared to mixes with only Portland Cement. From Figure 4.22, there is no clear visual trend in terms of reduction in expansion when using reduced water to cement ratio. However this does not conclude that a reduction in water to cement ratio does not reduce the expansion. The reason for no visual trend is due to the increase of cementing material increasing the amount of PC in each sample and therefore increasing the amount of C_3A . Also, more SO_3^{2-} is added as it is expressed as % of cementing materials. Hence, more reactants are included in mixtures with lower w/c ratio. This may have counteracted the enhancement in pore structure due to the use of lower w/cm.

The comparisons of the same cement replacements from Phase 1 with $5.83\% SO_3^{2-}$ and with limestone addition is used to demonstrate the effect of water to cement ratio at 23°C and 5°C in Figures 4.23 and 4.24, respectively. The comparison of the two water to cement ratios stored at 5°C shows that the decrease of water to cement ratio results in a reduction expansion. When comparing the rate of expansion between the two mixes containing only OPC, it is apparent that the rate of expansion is much lower at for the sample containing a lower water to cement ratio. It is noted that the sample is still expanding compared to the other mixes which has already seemed to have plateaued. By decreasing the water to cement ratio, it is apparent that the physical resistance to expansion has increased at a storage temperature of 5°C by reducing the amount of ion migration. There is a possibility that storing samples with high w/c in lime solution could have resulted in reduced pH within the mortar due to migration of lime solution to the mortar bars. The reduced pH could have favoured the formation of Thaumasite.



Figure 4.23: Comparison of expansion results at 6 months for mixes with different w/c ratio stored at 23°C containing 3.89% SO₃²⁻, as mass of cementing material



Figure 4.24: Comparison of 6 month expansion results for samples with different w/c ratio stored at 5°C containing 3.89% SO₃²⁻, as mass of cementing material
	w/c			0.485		0.65				
Temperature	Cementing Material	100% PC w/ I F	10% MK	10% MK w/ I F	5% SF + 30% GGBFS w/1 F	100% PC w/	10% MK	10% MK w/ LF	5% SF + 30% GGBFS w/ LF	
	14 days	0.012	0.014	0.013	0.022	0.012		0.022	0.024	
	6 months	0.058	0.020	0.019	0.047	0.123	\geq	0.040	0.063	
5	12 months		\triangleright			0.137	\geq	0.044	0.067	
	14 days	0.023	0.008	0.007	0.033	0.023	0.037	0.008	0.045	
	6 months	0.106	0.018	0.017	0.046	0.100	0.061	0.016	0.068	
23	12 months	\triangleright	\geq			0.102	0.078	0.019	0.074	

Table 4.5: Comparison of expansion results with different w/c ratio with 3.89% SO_3^{2-} , as mass of cementing material

4.3 Phase 3: Effect of initial formation of Ettringite on late Thaumasite Formation

As outlined in section 3.3.1, a set of mortar bars were batched using the same mix of 0.65 water to cement ratio, 2.75 aggregate to cement ratio, 3.89% SO_3^{2-} and 8% CO_3^{2-} where it was stored at 23 for 28 days then 5 degrees thereafter. The mix for this phase follows the same mix as Phase 1 part 2, a sample of this mix can be viewed in Table 3.7. The change in storage temperatures was meant to promote the formation of Ettringite before the formation of Thaumasite to study the effect of initial Ettringite formation on late Thaumasite formation. In previous studies it has been hypothesized that an increase in Ettringite. The results of these samples have been illustrated in Figure 4.25 and are compared to the same mix stored only at 5°C in Table 4.6.



Figure 4.25: Comparison of various cementing systems with 3.89% SO₃²⁻, as mass of cementing material, added using Hemihydrate/carbonate blend, with a w/cm of 0.65 where the samples were tested at 23°C for 28 days and then tested at 5°C

The use of supplementary cementing materials clearly has a positive effect on reducing the expansion. The one trend that differs from previous results is the mixes which pertains slag. It appears that the increase of slag did not further reduce the amount of expansion. The reason for this warrants further investigation.

		5 °C		28 days at 23°C then 5°C			
			6			6	
Sample	14 days	28 days	months	14 days	28 days	months	
100% PC	0.012	0.024	0.123	0.027	0.038	0.102	
30% Slag	0.024	0.035	0.065	0.038	0.045	0.052	
50% Slag	0.019	0.029	0.057	0.030	0.038	0.050	
25% Fly Ash Class F	0.013	0.019	0.091	0.031	0.048	0.097	
10% Metakaolin	0.022	0.023	0.040	0.016	0.018	0.023	
5% Silica Fume + 30%							
Slag	0.024	0.034	0.063	0.040	0.046	0.053	

Table 4.6: Comparison for samples stored at 5°C and samples stored at 23°C then 5°C both with 3.89% SO_3^{2-} , as mass of cementing material

Comparing the initial 28 days of expansion, all samples, except for metakaolin, have higher expansion when stored at 23°C. However, at 6 months, all samples that were initially stored at 23°C resulted in a decreased expansion. The reduction in late expansion could be related to the findings in previous studies which hypothesized that enough SO_3^{2-} must be present after the formation of monosulphoalumuinate and Ettringite in order for Thaumasite to form. (Schmidt, Lothenbach, Romer, Scrivener, Rentsch, & Figi, 2008).

4.4 Phase 4: Internal sulphate attack due to sulphate from the aggregates

Thus far the source of SO_3^{2-} originated from the Hemihydrate/carbonate blend was investigated; a study for an alternate source is needed to compare the results. As mentioned in section 3.3.1 a sulphate- bearing dolomite aggregate was chosen and was separated into passing the No. 4 sieve (SAP) and retained on the No. 4 sieve (SAC). The aggregate retained on the No. 4 sieve was further crushed using a jaw crusher so that all of the contents passed the No. 4 sieve. The chemical composition of the separated aggregate is shown in Table 3.1. The expansion results for samples stored at 5°C and 23°C are shown in Figure 4.26 and Figure 4.27 respectively for aggregate passing the No.4 sieve and Figure 4.28 and Figure 4.29 respectively for aggregate passing No. 4 sieve. Mixes used in this phase can be viewed in Table 3.9.



Figure 4.26: Comparison of various w/cm using Sulphate bearing aggregate passing No.4 sieve (SAP) tested at 5°C

Using the sulphate bearing aggregate passing the No. 4 sieve has exceeded the sample with silica sand and the least amount of added sulphate $(1.45\% SO_3^{2-})$ which was expected due to the increase in SO_3^{2-} from the aggregate. Further monitoring is required for the mixes with a water to cement ratio of 0.65 and 0.485 to see if the expansion will increase. It is clear, however, that the controlled low strength concrete mix did not perform well as it quickly lost cohesiveness before 50 days of storage at 5°C (shown in Figure 1.1) and failed due to curling before 200 days of storage at 23°. The reasons for failure could be due to the low strength of the concrete, low cement content and high amounts of SO_3^{2-} in proportion to the cementing material the mix. However further analysis is needed to determine the mechanism of failure for the CLSM.



Figure 4.27: Comparison of various w/cm using Sulphate bearing aggregate passing No.4 sieve (SAP) tested at 23°C

The expansion results for the sample with a w/c ratio of 0.485 were unexpectedly higher when compared to the sample with a w/c ratio of 0.65. The reason for this was due to the increased amount of cement material and an increase in the amount of aggregate in the mix when compared to the mix with a water to cement ratio of 0.65. Having more Portland Cement would increase the amount of C_3A and an increase in aggregate increases the amount of available SO_3^{2-} resulting in more Ettringite being formed. When comparing the use of SAP and SAC, SAC has a lower expansion. This is due to the difference in amount of SO_3^{2-} in Table 3.1.



Figure 4.28: Comparison of various w/cm using crushed sulphate bearing aggregate retained on No. 4 sieve (SAC) tested at 5°C

The crushed Sulphate bearing aggregate holds similar trend lines to that of the passing sulphate bearing aggregate but results in less expansion as there is less SO_3^{2-} as shown in Table 3.1. This is true with the exception of the sample made with SAC and water to cement ratio of 1.92. Although there has yet to be a rapid expansion within the sample, there is still a steady rate of expansion occurring. Further monitoring will be needed to determine whether the rapid expansion will occur or not.



Figure 4.29: Comparison of various w/cm using crushed Sulphate bearing aggregate retained on No. 4 sieve tested at 23°C

4.4.1 Microstructural Analysis of Samples with Sulphate Bearing Aggregates

To further identify the mechanisms which caused failure, SEM images was taken and an EDS analysis was performed for the following specimen at the specified time:

- SAP stored at 5°C with a w/c ratio of 1.92 @ 91 days
- SAP stored at 23°C with a w/c ratio of 1.92 @ 386 days

At 91 days, the sample containing SAP stored at 5°C had lost the ability to bind which is shown in Figure 1.1 and is analyzed in Figure 4.31. At 386 days the sample had lost complete cohesion similar to that of the sample stored at 5°C as shown in Figure 4.30 and is analyzed in Figure 4.32.



Figure 4.30: SAP(1.92) @ 23 loss of cohesion at 386 days



Figure 4.31: SEM image and EDS analysis of SAP @ 5°C @ 91 days showing possible signs of Thaumasite mixed with Ettringite.

Using Table 3.11, the EDS analysis of the SAP sample stored at 5°C it can be said that there is a fair amount of both Ettringite and Thaumasite. Thaumasite is outlined by the peaks of Ca^{2+} , S^{2-} , Si^{4+} and C^{4+} and Ettringite is outlined by the peaks of Ca^{2+} , S^{2-} and Al^{3+} in Figure 4.31.

In Figure 4.32, the EDS analysis high peaks in Ca^{2+} , Si^{4+} with smaller peaks in S^{2-} and Al^{3+} . This suggests that there is a presence of Thaumasite with some Ettringite. Looking at the Scanning Electron Microscope, it is hard to differentiate between Thaumasite and Ettringite as they have similar structures.



Figure 4.32: SEM image and EDS analysis of SAP @ 23 @ 386 days showing crystals of Thaumasite with traces of Ettringite.

4.4.2 Thermogravemetric Analysis of Sulphate Bearing Aggregate

Using TGA analysis it was determined that the sulphate originating from the aggregate is in the form of Gypsum as indicated by the loss of mass in between the temperatures of 120°C - 150°C. The TGA analysis also verified that the aggregate is dolomite represented by the change in mass between 750 and 900. (Ramachandran & Beaudoin, 2001). Figure 4.33 and 4.34 show the results of the TGA for both the crushed portion and the portion passing the No. 4 sieve.



Figure 4.33: TGA Analysis of Crushed Sulphate Aggregate retained on No. 4 sieve



Figure 4.34:TGA Analysis of Sulphate Aggregate passing the No. 4 Sieve

4.5 Phase 5: Comparison of Sources of Sulphates

From the results of Phase 4, it was clear that the addition of sulphate-bearing aggregate opposed to graded silica sand could have detrimental due to the effects of internal sulphate attack. However it is unclear on how it would compare to the alternative source of sulphate, represented by Hemihydrate/carbonate blend. For Phase 5 samples were casted with water to cement ratios of 0.485 and 0.65 and an aggregate to cement ratio of 2.75. Samples of the mixes used in this phase is provided in Table 3.10 where the value used to determine the amount of sulphate was the total sulphate of the sulphate bearing aggregate. The mixes consisted of cementing systems with 100% Ordinary Portland Cement, 40% GGBFS replacement, 25% Fly Ash Class F replacement and 10% Metakaolin replacement. To compare the sources, an amount of 4.7% total SO_3^{2-} as % of cementing material was selected. The sulphate-bearing aggregate was added so that the total amount of SO_3^{2-} in the aggregate amounted to $4.7\% SO_3^{2-}$. The mass of sulphate bearing aggregate mass was added using graded silica sand. It is noted that using a 4.70% of total SO_3^{2-} is equivalent of using a 1.93% of soluble SO_3^{2-} . The results of the mixes are presented in Figure 4.35 to Figure 4.38 and in Table 4.7.



Figure 4.35: Comparison of various cementing systems with 4.70% total SO_3^{2-} (1.93% soluable sulphate), as mass of cementing material, added using Sulphate-Bearing Aggregate with a w/c ratio of 0.65 stored at 5°C

Figure 4.35 and Figure 4.36 show that the sample was resistant to internal sulphate attack with 4.70% *total* SO_3^{2-} added through the aggregate as the samples had expansions less than 0.02%. This may be due to the difference between soluble and the total SO_3^{2-} . As shown in Table 3.1, the total SO_3^{2-} of SAP (Sulphate Aggregate Passing No. 4 Sieve) was 4.6% and the soluble SO_3^{2-} in SAP was 1.86%, less than half of the total SO_3^{2-} . With the low amounts of expansion it is also hard to determine the effect of the addition of various levels of SCM when adding sulphate bearing aggregate as the source of SO_3^{2-} .



Figure 4.36: Comparison of various cementing systems with 4.70% total SO_3^{2-} (1.93% soluable sulphate), as a mass of cement material, added using Sulphate Bearing Aggregate with a w/c ratio of 0.65 stored at 23°C



Figure 4.37: Comparison of various cementing systems with 4.70% total SO_3^{2-} (1.93% soluable sulphate), as a mass of cement material, added using Sulphate Bearing Aggregate with a w/c ratio of 0.485 stored at 5°C



Figure 4.38: Comparison of various cementing systems with 4.70% total SO_3^{2-} (1.93% soluable sulphate), as a mass of cement material, added using Sulphate Bearing Aggregate with a w/c ratio of 0.485 stored at 23°C

As mentioned earlier in this thesis, the use of water to cement ratio of 0.485 and the same aggregate to cement ratio of 2.75 will result in an increase of cementing material and increase in aggregate per unit volume of the mix. This explains the increase of expansion at 0.485 compared to 0.65.

Comparing the expansion at 6 months, in Figure 4.39 and Figure 4.40, between 1.93% soluble SO_3^{2-} originating from the SAP, 1.45% SO_3^{2-} originating from Hemihydrate/carbonate blend, it is evident that the expansion when using sulphate bearing aggregate is slightly lower at 5°C and almost the same at 23°C at the same level of SO_3^{2-} . The difference between the expansions of the two samples at 5°C could be due to the solubility difference between hemihydrate and the aggregate (gypsum). It is also noted that the higher expansion with hemihydrate as the source of SO_3^{2-} could be attributable to the high fineness of Hemihydrate/carbonate blend which would result in a higher dissolution rate. While the same factors exist at 23 °C, the difference in expansion was not evident as the level of expansion was very low in both cases.



Figure 4.39: Comparison of expansion at 6 months for sources of sulphates with water to cement ratio of 0.65 stored at 5° C where SO_3^{2-} is expressed as a percent of cementing material



Figure 4.40: Comparison of expansion at 6 months for sources of sulphates with water to cement ratio of 0.65 stored at 23°C where SO_3^{2-} is expressed as a percent of cementing material



Figure 4.41: Comparison of different sources of sulphates using 100% OPC & w/c = 0.65 stored at 5°C, SO_3^{2-} expressed as a % of cementing material mass,



Figure 4.42: Comparison of different sources of sulphates using 100% OPC & w/c = 0.65 stored at 23°C, SO_3^{2-} expressed as a % of cementing material mass

			1.93% Soluble SO_3^{2-} from Aggregate			3.890% SO_3^{2-} from HCB & LF					
w/c	Temperature	Sample	100% PC	40% Slag	25% FA	10% MK	100% PC	30% Slag	50% Slag	25% FA	10% MK
		14 days	0.006	0.006	0.003	0.004	0.012	0.024	0.019	0.013	0.022
		6 months	0.012	0.017	0.008	0.015	0.123	0.065	0.057	0.091	0.040
	5	12 months	\geq	\triangleright	>	\geq	0.137	0.070	0.062	0.114	0.044
		14 days	0.006	0.006	0.003	0.004	0.023	0.032	0.040	0.031	0.008
		6 months	0.012	0.017	0.008	0.015	0.100	0.056	0.062	0.059	0.016
0.65	23	12 months	\geq	\triangleright	\triangleright	\geq	0.102	0.062	0.066	0.061	0.019
		14 days	0.016	0.006	0.007	0.009	0.012			\triangleright	0.013
		6 months	0.035	0.014	0.014	0.018	0.058	>			0.019
	5	12 months	\geq	\triangleright	\triangleright						
		14 days	0.017	0.011	0.006	0.010	0.023	\searrow		\triangleright	0.007
		6 months	0.030	0.020	0.012	0.024	0.106	\geq	\triangleright	\triangleright	0.017
0.485	23	12 months	\triangleright	\triangleright	\supset	\supset	\supset	\supset	\triangleright	\triangleright	\triangleright

Table 4.7: Comparison of SO_3^{2-} sources with % SO_3^{2-} expressed as a % of cementing material (1)

Table 4.8: Comparison of SO_3^{2-} sources with % SO_3^{2-} expressed as a % of cementing material (2)

			1.45% SO_3^{2-} HCB & LF					
w/c	Temperature	Sample	100% PC	30% Slag	50% Slag	25% FA	10% MK	
		14 days	0.004	0.005	0.002	0.004	0.005	
		6 months	0.028	0.029	0.033	\triangleright	0.026	
	5	12 months	\ge	\ge	\ge	\searrow	$\left \right\rangle$	
		14 days	0.007	0.006	0.007	0.002	0.005	
		6 months	0.010	0.012	0.013	\triangleright	0.013	
0.65	23	12 months	\geq	\geq	\geq	\triangleright	>	

Chapter 5

Summary, Conclusion and Recommendations for Further Studies

For the materials investigated in this thesis, the following conclusions and recommendations are made:

- The levels of sulphate used in this study are for the purpose of investigating the effect of SCM and cannot be used as to set limits for a safe level of sulphate in concrete. The performance of concrete may be different than that of mortars particularly that the proportions of ingredients are not the same in mortars and concrete.
- An increase in internal sources of SO₃²⁻ at 23°C will result in an increase in expansion where the SO₃²⁻ is believed to react with the reactive alumina (Al₂O₃) forming Ettringite.
- Increasing the internal source SO₃²⁻ at 5°C resulted in an increase in expansion where both Ettringite and Thaumasite were found to co-exist without having rapid Thaumasite formation occur when sufficient SO₃²⁻ was available for Thaumasite to form.
- The use of pozzolans with high alumina contents did not necessarily result in a reduction in expansion for both storage temperatures, in the case of Fly Ash Class F used in this thesis
- The use of pozzolans with high amounts of reactive alumina resulted in a reduction in the amount of expansion at both storage temperatures. The alumina is more likely to react with the available SO₃²⁻ consuming all sulphur in the formation of non-expansive monosulphoaluminate before the formation of Ettringite and Thaumasite.
- Replacement level of 25% Fly Ash Class F did not seem to have much of an effect on the mitigation of expansion for both storage temperatures even though a high alumina content was found in a X Ray Fluorescence analysis. It is likely that this alumina in a non-reactive form mullite
- GGBFS replacement has shown to be an effective way of reducing expansion due to internal sulphate attack. This reduction is due to the dilution of Portland cement and refinement of pore structure.
- Metakaolin has shown to be the most effective at low replacement levels. The use of Metakaolin is believed to increase both the physical and chemical resistance of the samples.

The pore structure was thought to be enhanced by reducing the size of capillaries and voids hence increasing the physical resistance to Internal Sulphate Attack. The high amounts of reactive alumina in Metakaolin contributed to the increase in chemical resistance. However due to the limited amounts of Metakaolin that can be added to a mix before a significant loss in workability, Metakaolin will only be effective up to a certain amount of SO_3^{2-} .

- The effect of Silica Fume blended cement can be seen to have a considerable contribution to the reduction of expansion at 5°C. This is due to the refinement of pore structure within the sample. The use of Silica Fume also had a minor impact of the expansion at 23°C.
- Increasing the availability of CO₃²⁻beyond a certain level did not result in additional Thaumasite Formation in this thesis when the SO₃²⁻ is consumed in the production of sulphoaluminate phases or Thaumasite formation. However, the increase in CO₃²⁻ may increase the severity of Thaumasite Sulphate Attack.
- A decrease in water to cement ratio reduces the rate of expansion, likely due to the reduced sizes in capillaries and hence reducing the ability for ions to migrate, or crystals to grow. However, this was difficult to show as the amount of cementing material was increased when the water to cement ratio was reduced when comparing the mix as a whole. Having SO₃²⁻ expressed as a percentage of total cementing materials, an increase in cementing material would lead to an increase in SO₃²⁻.
- Allowing the formation of Ettringite to form first before Thaumasite, by storing the specimens at 23°C for 28 days before storing the specimens at 5°C, did not result in a higher expansion.
- The aggregate used for this thesis showed detrimental effects of loss of bonding in the case of a w/c ratio of 1.92 which was not seen when the source of sulphate originated from the Hemihydrate/carbonate blend. This is attributed to the higher amounts of SO₃²⁻ due to large volume of aggregate per mix and lower strength of the sample.
- The expansion of mixtures with sulphate from aggregate and sulphate from hemihydrate/carbonate blend was closer when the water-soluble sulphate of the aggregate was used. When total sulphate was used, the expansion of samples with sulphate from the aggregate was significantly lower, since not all sulphate was readily available.

• The slightly higher expansion at 5 °C of samples with added hemihydrate compared to samples with aggregate of similar sulphate content could be attributable to better distribution of sulphate within the samples in case of added sulphate in addition to higher dissolution rate due to the high fineness of Hemihydrate/carbonate blend.

Recommendations for Further Studies

Based on the obtained results, the following recommendations for future studies are suggested

- Testing using concrete prisms opposed to mortar bar tests will provide more reliable results but will take a longer time to provide additional results. Hence, a longer testing program is needed to address this.
- Conduct a more thorough mechanistic investigation to understand how each SCM affects internal sulphate attack which includes strength testing and visual inspections.
- Carry out Field studies to come up with an expansion limit using mortar bar tests when evaluating internal sulphate attack.
- Conduct additional testing with increased levels of SO_3^{2-} to see the effect of the availability of CO_3^{2-} on the severity Thaumasite Sulphate Attack.

<u>Appendix</u>

Determination of Total Sulphate Content using Combustion Infrared Detection

The following is obtained from Activation Laboratories Ltd.

"A 0.2 g sample is combusted in a resistance furnace at 550 $^{\circ}$ C in a pure oxygen environment. During combustion, sulphur-bearing elements are reduced, releasing sulphur, which binds with oxygen to form SO₂. Sulphur is measured as a SO₂ in the infrared cell. An Eltra CS-2000 used for analysis.

According to ASTM E1915 in regards to sulphide sulphur, "In the absence of sulphate forms of sulphur, total sulphur may be used to estimate the sulphide sulphur concentration. The pyrolysis loss sulphur may be the best estimate of sulphide sulphur, particularly where the acid generation potential due to iron sulphides is desired. The nitric acid loss method may be appropriate where the sulphide forms are primarily pyrite and marcasite and pyrrhotite is absent, since pyrrhotite may react with acid. The sodium carbonate residual sulphur method is most appropriate where the concentration of metal sulphide minerals in addition to iron are desired in the absence of barite, alunite, jarosites, orpiment and realgar.""

Determination of Water Soluble Sulphate using Ion Chromatography

The following is obtained from Activation Laboratories Ltd.

"Un-acidified water samples are analyzed using the DIONEX DX-120 Ion Chromatography System to determine and quantify a group of seven anions. This analysis is applicable to concentrations less than 75 mg/L for Cl, NO_2 and NO_3 ; less than 50 mg/L for F; less than 125 mg/L for PO_4 ; less than 250 mg/L for Br and less than 375 mg/L for SO₄. Samples exceeding this range (with high total dissolved solids) must be diluted to avoid over-saturation. Measurement uncertainty is evaluated and controlled by an appropriate quality assurance program, including the use of regular laboratory duplicates of samples and verification of the precision/calibration of the instrument through regular runs of various primary dilution standard solutions

"

Refernces

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