Development of a Quantitative Accelerated Sulphate Attack Test for Mine Backfill

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ABSTRACT

Mining operations produce large amounts of tailings that are either disposed of in surface impoundments or used in the production of backfill to be placed underground. Their mineralogy is determined by the local geology, and it is not uncommon to come across tailings with a relatively high sulphide mineral content, including pyrite and pyrrhotite. Sulphides oxidize in the presence of oxygen and water to produce sulphate and acidity. In the concrete industry, sulphate is known to produce detrimental effects by reacting with the cement paste to produce the minerals ettringite and gypsum. Because mine backfill uses tailings and binders – including cement – it is therefore prone to sulphate attack where the required conditions are met. Currently, laboratory tests on mine backfill mostly measure mechanical properties such as strength parameters, and the study of the chemical aspects is restricted to the impact of tailings on the environment. The potential of sulphate attack in mine backfill has not been studied at length, and no tests are conducted on binders used in backfill for their resistance to attack.

Current ASTM guidelines for sulphate attack tests have been deemed inadequate by several authors due to their measurement of only expansion as an indicator of attack. Furthermore, the tests take too long to perform or are restricted to cement mortars only, and not to mixed binders that include pozzolans. Based on these, an accelerated test for sulphate attack was developed in this work through modifying and compiling procedures that had been suggested by different authors. Small cubes of two different binders were fully immersed in daily-monitored sodium sulphate and sulphuric acid solutions for a total of 28 days, after 7 days of accelerated curing at 50°C. In addition, four binders were partially immersed in the same solutions for 8 days for an accelerated attack process. The two procedures were conducted in tandem with leach tests using a mixed solution of ethylene glycol and methanol solution, which enabled the quantification of ettringite and gypsum that had formed due to the attack.

Combining the partial immersion technique with the dissolution of ettringite and gypsum in the organic solutions, a new quantitative accelerated test for sulphate attack was developed.

RÉSUMÉ

Les opérations minières produisent de grandes quantités de rejets miniers qui sont soit stockés en surface dans des haldes, soit réutilisés comme remblais sous terre. La minéralogie de ces déchets est dictée par la géologie des lieux, et il est commun de trouver des rejets qui ont une teneur élevée en minéraux sulfurés comme la pyrite et la pyrrhotite. Les sulfures sont oxydés en présence d'eau et d'oxygène et produisent une eau acide et riche en sulfates. Dans l'industrie du béton, un des grands problèmes provient de la réaction des sulfates de sources externes avec le ciment du béton pour former de l'ettringite et du gypse. Étant donné que les remblais dans les mines se servent des rejets et d'agents de liaison comme le ciment, ils sont sensibles aux attaques des sulfates si les conditions sont propices. En ce moment dans les laboratoires, on s'intéresse surtout aux paramètres mécaniques comme la résistance en compression et l'impact chimique que les rejets miniers ont sur l'environnement. Aucune recherche concrète n'a été faite sur les dangers de l'attaque des sulfates sur les remblais dans les mines et sur les différents agents de liaisons, afin de déterminer leurs résistances à de telles attaques.

Les directives actuelles de l'ASTM pour tester l'attaque des sulfates se sont avérées inadéquates. En effet, ces tests sont seulement basés sur l'expansion, ce qui ne se produit pas forcément lors de l'attaque par des sulfates. De plus, ces tests sont trop longs et ne peuvent s'appliquer qu'à certains mélanges spécifiques de ciment et pas à d'autres comme la pouzzolane. Sur ces faits, un test accéléré a été mis en place par certains chercheurs. Après un séchage accéléré dans un four à 50°C, des échantillons sont immergés dans des solutions de sulfate de sodium et d'acide sulfurique pendant 28 jours d'une part. D'autre part, d'autres échantillons sont immergés à moitié dans ces mêmes solutions pendant 8 jours pour une attaque accélérée. Ces deux procédures sont suivies par un filtrage des échantillons qui sont séchés par une solution 3:1 d'éthylène glycol et de méthanol, un mélange qui permet de déterminer la quantité d'ettringite formée. Ainsi, non seulement nous avons pu étudier des échantillons qui ont subi une attaque accélérée de sulfates, mais aussi nous avons pu évaluer l'ampleur de l'attaque en mesurant la quantité d'ettringite formée dans les échantillons.

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LIST OF ABBREVIATIONS

A:	aluminum oxide [Al ₂ O ₃]
AA:	atomic absorption spectrometer
AFt:	ettringite
AFm:	monosulphate
C:	quicklime [CaO]
C_2S :	dicalcium silicate (alite)
C ₃ S:	tricalcium silicate (belite)
C ₃ A:	tricalcium aluminate
C ₄ AH:	ferrite
CH:	lime, calcium hydroxide [Ca(OH) ₂]
C S :	gypsum [CaSO ₄ .2H ₂ O]
CSH:	calcium silicate hydrate
DEF:	delayed ettringite formation
DTA:	differential thermal analysis
EGM 13:	1:3 mix of ethylene glycol and methanol
EGM 31:	3:1 mix of ethylene glycol and methanol
F:	ferric oxide [Fe ₂ O ₃]
H:	water [H ₂ O]

HS:	2% (by volume) sulphuric acid [H ₂ SO ₄] solution
IC:	ion chromatograph
ICP-OES:	inductively-coupled plasma – optical emission spectrometer
NS:	4% (by weight) sodium sulphate [Na2SO4] solution
PC:	cement-only binder
PF:	cement-fly ash binder
PS:	cement-slag binder
PSF:	cement-slag-fly ash binder
S:	silica, silicon oxide [SiO ₂]
S :	sulphur trioxide [SO ₃]
SEM-EDX:	scanning electron microscope – energy dispersive x-ray
UCS:	unconfined compressive strength
XRD:	x-ray diffraction

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CHAPTER: 1 INTRODUCTION

1.1. TAILINGS GEOCHEMISTRY

Mining operations invariably produce large quantities of waste called tailings that need to be deposited in a special pond or reused in the production of backfill. In the case of the former, tailings are deposited continuously in a constructed dam, which is usually covered and vegetated at the end of mining operations. Tailings reused in the production of backfill are mixed with an assortment of binders and pumped back underground to fill in stope cavities and provide support for ongoing operations in the vicinity.

The geology of the region determines the mineral assemblages found in both the ore and tailings portions at a particular mine. For example, in the Val d'Or region of northern Quebec, volcanogenic massive sulphides and sulphide vein intrusions dominate the geology of the area. The variation in local lithology affects not only the type of ore being extracted, but also the characteristics of the tailings produced during operations. Several mines in Quebec produce tailings with large metal sulphide contents of which pyrite [FeS₂] is the most ubiquitous. Whereas all metal sulphides exhibit some degree of oxidation in the presence of oxygen and water, the extent and speed of pyrite reactivity is well documented, placing it at the top of the list. In simple terms, pyrite oxidizes to produce sulphuric acid, ferrous [Fe⁺²], and ferric [Fe⁺³] iron, which lower the pH of their immediate environment and leach out other metals from the tailings stockpile.

1.2. SULPHATE ATTACK IN MINE BACKFILL

Pyrite oxidation could leave an undesirable environmental footprint were its products to escape the confines of the tailings dam. In addition, it could have a significant negative impact on mine backfill. Apart from its acidity, any leachate produced by pyrite oxidation would naturally be extremely rich in sulphate ions $[SO_4^{-2}]$. Since backfill integrity is provided by cement and other binders, the effect of abundant sulphate would be to severely test the chemical durability of the solidified product. Sulphate attack is one

of the most pervasive problems within the concrete industry and as such has been extensively studied. Detailed regulations limit the availability of sulphate – whether from aggregate or mixing water – within the concrete recipe to avoid problems. Furthermore, the main binding component in concrete, which is cement, is usually present in a given recipe at about 10-15% of the total weight (PCA 2008). In contrast, mine backfill does not - and cannot - enjoy the luxury of choice. Tailings are its main component, the mineralogy of which is predetermined and cannot be modified. The total percentage of binder used is usually 5 to 7%, with cement constituting 50 to 70% of the binder weight. Therefore, mines operating in regions where metal sulphides prevail could face the problem of sulphate attack within the backfill. Relatively few studies have been conducted so far on such attacks despite the disadvantageous mineralogy inherent in the tailings of certain mines, with the main focus of tests being the strength parameters of backfill. Although the binder ratio is relatively small when compared to concrete, one advantage of backfill preparation is that the binders used and their ratios can be easily modified to suit the needs of the site as long as the mechanical and economical requirements are met.

1.3. SULPHATE ATTACK TESTS

Sulphate attack in concrete takes place when tricalcium aluminate – one of the main components of cement – combines with sulphate ions to produce the mineral ettringite [3CaO.Al₂O₃.3CaSO₄.32H₂O]. The ingress of external sulphate ions produces a secondary or delayed phase of ettringite formation (DEF), which is expansive in nature and results in cracking within the structure. More sulphate content enters these cracks and accelerates the deterioration process, and the reactions quickly degenerate into a vicious circle. Although the expansive nature of ettringite has been discussed and debated, there is no question that its formation at later stages is always associated with sulphate attack in concrete. Mehta (1975) notes that in addition to this mineral, gypsum [CaSO₄.2H₂O] is also indicative of sulphate attack. With the presence of sulphide-rich tailings, it is obvious that backfill could be tested much more severely than concrete in terms of such attacks.

Where new binder components or various proportions are used in mine backfill, the primary testing protocol is the unconfined compressive test (UCS). As yet, there are no regulatory tests designed to study the effects of tailings geochemistry on the final backfill product, and no sulphate attack tests are done on binder combinations normally used in mines. Within the concrete industry, tests for sulphate attack are mandatory in regions where the structure is likely to be faced with ionic ingress. The two main ASTM tests are C 1012 and C 452, which measure the extension of mortar prisms cured in 0.35M sodium sulphate solutions and water, respectively. However, there have been calls from the research community to modify these tests in order to better reflect the conditions faced by structures in the field. Mehta and Gjörv (1974) and Mehta (1975) have noted that whereas these tests define deterioration as consisting of expansion – and are therefore geared towards its measurement – sulphate attack in the field does not always exhibit this feature. They point to the fact that unlike expansion, the presence of secondary ettringite and gypsum in concrete is much more indicative of sulphate attack. In addition, the tests currently available require a relatively long time – up to six months – to provide final results and are cumbersome in the tight construction schedules faced by contractors. These time frames are even more unpractical for mining companies and their operational schedules. Hence, a meaningful test that can measure the presence of realistic attack symptoms in a short period of time would be an extremely useful tool for the design of binder mixes in backfill.

Mehta and Gjörv (1974) and Monteiro et al (2000) proposed an accelerated test in which the solution is constantly refreshed and kept at a constant pH to severely attack the test cubes. These authors further proposed a method of accelerated curing in an oven at 50°C, which would be especially useful for pozzolans since they require longer periods of time than cement to completely cure at room temperature. Clifton et al (1999) drew attention to the fact that a partial immersion in a solution would accelerate the attack process even more than a full immersion. Several methods can be used for the detection of secondary ettringite produced by the attack - x-ray diffraction (XRD) being one option – but quantifying its amount and monitoring its rise or decline is much more challenging. Uchikawa and Uchida (1974) reported a novel method of quantifying ettringite by dissolving it in a mixture of ethylene glycol and methanol. Amongst the different phases

in hydrated cement, the organic mixture dissolved ettringite exclusively and almost completely, thus providing a relatively simple method for its quantitative assessment. Odler and Abdul-Maula (1984) tested the method on different types of ettringite and compared it to both XRD and differential thermal analysis (DTA) and recommended it over other procedures. With accelerated curing and sulphate attack procedures, a rapid and easy method for quantifying ettringite would combine to produce a novel and fast procedure that is able to assess the resistance of different binders against sulphate attack within weeks rather than months.

1.4. PROBLEM DEFINITION

The discussions above can be summarized in the following sequence:

- Tailings are the major component of mine backfill operations and based on the local geology, they could contain large amounts of sulphides.
- The sulphides could oxidize and produce sulphate, which would attack the small amount of binder used to hold the backfill together, resulting in the formation of secondary ettringite and gypsum, and leading ultimately to failure.
- Mines are flexible with the use of different binder components at various percentages by weight of tailings, but do not test them for resistance to sulphate or acid attack.
- The relevant sulphate attack tests currently available take a long time to complete and measure only expansion – and not the amount of ettringite or gypsum formed – which does not always take place in the field in the case of an attack.
- A new combination of accelerated curing, sulphate attack, and quantitative ettringite measurement can give results regarding binder durability in a few weeks rather than months.

1.5. OBJECTIVES AND SCOPE OF THE RESEARCH PROJECT

Based on the discussion above, the research project had several objectives as its guiding principles. In terms of experimental steps, they could be listed in the following manner:

- Assessing the ability of ethylene glycol and methanol in various combinations to dissolve ettringite and gypsum, confirming the results through traditional XRD analysis
- Subjecting a number of typical backfill binders to accelerated curing
- Immersing the binders fully in two attack solutions refreshed on a daily basis to expose them to sulphate and acid attack
- Immersing the binders partially in the same solutions to expose them to an accelerated form of these attacks
- Monitoring the quantity of ettringite and gypsum in the binders over time using the most efficient combination of ethylene glycol and methanol to assess the amount of attack

The scope of research was limited to the testing of binders for ettringite and gypsum content, and evaluating the mix that would be the most resistant to sulphate attack. It included preliminary work with the formation and testing of these two minerals in the laboratory. Since the scope of work was limited to establishing the fundamentals of an accelerated sulphate attack test for binders, it did not include their testing when mixed with tailings, which could form the basis of future work in this area. In addition, because the focus of the project was on the chemical aspects of sulphate attack, no strength tests were performed on the cured samples, an area that can adequately be explored through future work as well.

1.6. THESIS OUTLINE

Apart from the current introduction, the thesis is divided into the following sections:

- Chapter 2 provides a review of tailings geochemistry with a special emphasis on sulphide-rich tailings and their oxidation
- Chapter 3 reviews sulphate attack in general, detailing its causes, mechanisms, effects, current available tests, as well as the role of ettringite and gypsum
- Chapter 4 discusses mine backfill operations in general, focusing on the types of backfill, its various components, the effect of tailings mineralogy on it, and the various test procedures that are currently used on backfill
- Chapter 5 presents the materials and methodology adopted for the project
- Chapter 6 provides the test results obtained and relevant discussion
- Chapter 7 closes the thesis with conclusions and recommendations for future work, and makes a statement about the originality of the research conducted

CHAPTER : 2 THE GEOCHEMISTRY OF SULPHIDE-RICH MINE TAILINGS

2.1. INTRODUCTION

Mining wastes consist of waste rock, overburden, and the portion of ore that is not economically profitable. From a geological perspective, mining wastes are a reflection of the local lithology from which the profitable portion has been extracted, and are therefore heterogeneous in composition and mineralogy. They are processed at a mill and typically undergo washing, crushing, and treatment operations. Subsequent to this process, they are designated as tailings, the size fraction of which ranges from clay to fine sand.

The wastes produced by the mining industry are inherently large due to the relatively small percentage of ore found in nature. For example, whereas sand, gravel, and aggregate producers are able to use most, if not all, of the material they extract from nature, metalliferous mining operations extract only a minor percentage of the removed materials owing to the nature and lithology of the mined ore. It is only logical, therefore, to expect a very large waste to ore ratio where such operations are concerned.

2.2. TAILINGS PRODUCTION

The extraction of metals from the Earth involves the fragmentation, crushing, and grinding of rocks that host the ore in order to liberate it. The goal is to facilitate its separation from the gangue material. Apart from the small concentration of the metals being mined, the rest of the material constitutes what is termed as mine waste that includes rock, water, and tailings. For example, the Canadian mining industry generates about 1 million tons of waste rock and 950,000 tons of tailings per day and this comes to a total of 650 million tons of waste per year (Government of Canada 1991; cited in Environmental Mining Council of BC 2000). It is interesting to note that more than 10% of all tailings in Canada are located at Copper Cliff, occupying more than 2225 hectares (Shaw et al 1998). In metal mining operations, more than 99% of the material mined

usually ends up as tailings (Lottermoser 2007). These consist of solid and liquid components, and vary in their physical and chemical properties.

The size of solid particles ranges from clay to sand (2 µm to 2 mm), with dry tailings typically consisting of 70 to 80% of sand-sized particles and 20 to 30% of claysized ones (Lottermoser 2007). Al et al (1994a) report that the tailings at the Kidd Creek mine initially contain 17% of solids by weight but are then thickened to 62% solids by weight. Other authors specify the solids content in typical slurries at 20 to 40% with less than 10% falling in the range of clay particles (Robertson 1994). Brown (2002) states that conventional tailings are in slurry form with 30-50% solids while dewatering would produce thickened tailings containing 50-60% solids. Paste tailings, on the other hand, would consist of 60% solids if the grain size is fine and 80% solids for coarser material. Jambor (1994) confirms that most tailings particles are either sand or silt in size, using the designation of the mineral industry where the former ranges from 20 to 200 µm and the latter runs from 5 to 20 µm. As for the mineralogical and geochemical properties, they are site-specific and even change after deposition due to ongoing reactions between the various components. The impoundments into which the tailings are discharged are specially constructed structures for retaining the solid and liquid wastes produced by mining activities, and it is estimated that there are about 3500 such dams in the world (Davies and Martin 2000; cited in Lottermoser 2007).

2.3. QUEBEC SULPHIDE DEPOSITS

Quebec boasts a rich mineral industry and associated history. The Abitibi region in the northwest of the province is the main hub of activities and hosts about a dozen operating mines in a relatively small region (Figure 2-1). The region is dominated by the geology of the Abitibi belt, which is composed of volcano-sedimentary rocks that have been metamorphosed to the greenschist facies (Simard et al 1990). It is the largest Archaean greenstone belt in the world and has been extensively studied (Windley 1984; cited in Simard et al 1990). The main metals produced are gold, silver, copper, and zinc,





Figure 2-1 – Map of operating mines in Quebec

Most of the base metals are extracted from volcanogenic massive sulphide deposits in the Rouvn-Noranda, Mattagami, and Val d'Or areas, and sulphide-rich vein deposits are common in the Chibougamau region. Sulphide minerals found most commonly in these deposits include pyrite, pyrrhotite $[Fe_{1-x}S_x]$, chalcopyrite $[CuFeS_2]$, and sphalerite [(Zn,Fe)S] with the first two comprising around 80% of the total sulphides (Chartrand and Cattalani 1990), with Murray (1977; cited in Jambor 1994) reporting up to 39% sulphur in massive sulphide deposits. Minor and trace sulphides include galena [PbS], tetrahedrite [Cu₁₂Sb₄S₁₃], molybdenite [MoS₂], and arsenopyrite [FeAsS], while the rest of the gangue minerals are restricted mainly to silicates and carbonates such as chlorite, quartz, talc, sericite, calcite, and others. The Kidd Creek mine tailings in northern Ontario comprise 10-25% pyrite, 1-2% pyrrhotite, 1-2% sphalerite and chalcopyrite, 75-85% gangue minerals, and 7-8% carbonates (Al et al 1994a). Therefore, it can easily be seen as to why the geochemistry of sulphides and their chemical reactions are important for mining operations. Since pyrite and pyrrhotite fall within the gangue minerals, which constitute about 99% of the material being mined, a large amount of waste material with chemically reactive components will eventually need to be safely disposed of.

2.4. SULPHIDE OXIDATION

Sulphide minerals are those that have the element sulphur combined with different types of metals, such as iron, and they constitute an integral part of metallic ores. When mining operations extract and expose these minerals to oxygen and water, they undergo a complex set of spontaneous chemical reactions called oxidation, and produce waters rich in acid, which in turn leach out other metals. Amongst the various sulphides, the most ubiquitous is undoubtedly pyrite [FeS₂], which is associated with both metal and coal deposits (Evangelou 1995), and its oxidation causes the most challenging environmental problem facing the mining industry, which is acid mine drainage (Lottermoser 2007). Petruk (2000) estimates that the pyrite and/or pyrrhotite content in mine wastes ranges from less than 1% up to around 60%. Whereas in the past waste rock piles and tailings could be left next to a mine after operations ceased, legislation passed since 1970 has

prohibited abandonment in North America and elsewhere (Jambor and Blowes 1998; cited in Petruk 2000). Hence, the estimate of managing potentially acid generating wastes in Australian mines, for example, runs around \$60 million per year (Harries 1997; cited in Parker and Robertson 1999). In Canada, the estimate of acid generating metal mine tailings runs at about 2 billion tonnes out of a total of 7 billion tonnes (Feasby and Tremblay 1995; cited in Parker and Robertson 1999).

2.4.1. MECHANISMS OF SULPHIDE OXIDATION

The chemical stability of sulphide minerals is attained in reducing environments characterized with low oxygen content. Exposure to an atmosphere rich in oxygen destabilizes them and commences a series of chemical and biological reactions that alters them significantly. As pyrite is the most common mineral in terms of sulphide oxidation, it has been studied extensively by various authors such as Evangelou (1995). Pyrite can vary greatly in size and morphology and the most reactive forms are reported to be the framboidal ones – which are "grape-like" agglomerations of about 0.25 µm diameter crystals – due to their large surface areas (Caruccio and Geidel 1978, Caruccio et al 1997; cited in Evangelou 1995). The reactions that take place during pyrite oxidation upon exposure to air and water are as follows:

$$FeS_{2} + 7/2 O_{2} + H_{2}O = Fe^{2+} + 2 SO_{4}^{2-} + 2 H^{+}$$

$$Fe^{2+} + 1/4 O_{2} + H^{+} = Fe^{3+} + 1/2 H_{2}O$$

$$Fe^{3+} + 3 H_{2}O = Fe(OH)_{3} + 3 H^{+}$$

$$FeS_{2} + 14 Fe^{3+} + 8 H_{2}O = 15 Fe^{2+} + 2 SO_{4}^{2-} + 16 H^{+}$$

Although there are many more intermediate reactions that take place, the four equations above summarize the main components in pyrite oxidation (Evangelou 1995). In the first instance, the mineral reacts with oxygen and water and produces ferrous iron with a double positive charge, acidity in terms of the hydrogen ion, and sulphate. In the second equation, ferrous iron oxidizes to produce the ferric form of the metal, which

combines with water to produce ferric hydroxide and more acidity as shown in the third equation. Lastly, ferric iron reacts with the remaining pyrite to produce further acidity and sulphate. Hence, if a balance of all components is made, it can be seen that for every mole of pyrite oxidized, four moles of acidity are produced. In addition, once oxidation is initiated and ferric iron is produced, it continues unabated since Fe^{3+} starts to act as the driving force behind the reaction (Levens et al 1996). Nordstrom (1992; cited in Evangelou 1995) states that at a lower pH range (< 4.5), pyrite oxidation is mainly driven by ferric iron rather than oxygen, and iron-oxidizing bacteria such as *Thiobacillus ferrooxidans* can accelerate the rate of its production by a factor of 10⁶ (Singer and Stumm 1970; cited in Evangelou 1995). At neutral and alkaline pH conditions, the concentration of ferric iron decreases significantly due to its incorporation into ferric hydroxide, which precipitates as coatings on pyrite surfaces. However, due to the production of sulphuric acid, the coating is quickly removed and a fresh surface of pyrite is exposed to oxidation, thus continuing the cycle.

2.4.2. FACTORS AFFECTING SULPHIDE OXIDATION

The oxidation of pyrite requires a fresh surface of the mineral in the presence of water, oxygen, and ferric iron. It accelerates significantly in the presence of bacteria and at certain temperature levels (Nicholson 1994). Therefore, it is not surprising that these criteria constitute the principle factors affecting sulphide oxidation reactions and are also the main preventive tools used in mitigating it.

2.4.2.1 Exposure and extent of surface area

According to Evangelou (1995), the work of a large body of researchers has pointed out that pyrite oxidation is a surface controlled reaction regardless of whether the oxidant is O_2 , Fe^{3+} , or hydrogen peroxide [H₂O₂]. Mention was already made that framboidal pyrite is the most reactive type due to its relatively large surface area. The speed of surficial reactions is directly proportional to the ratio of the object's surface area to its volume, with a larger ratio implying a faster penetrating reaction rate. Hence, it could be that framboidal pyrite, due to its agglomerate-like shape, presents a larger surface-to-volume ratio than the octahedral or cubic types. Once oxidation occurs, iron oxides precipitate and cover the surfaces of pyrite grains, thus inhibiting the ingress of oxygen and further reactions. However, due to the presence of sulphuric acid and the associated low pH, the iron oxide film is dissolved and a fresh pyrite surface is once again exposed to the elements for a new reaction.

2.4.2.2 Oxygen

Oxygen is the main requirement in any oxidation reaction and that of pyrite is no exception. It is significant to note that prior to its extraction and exposure, pyrite is found in a reducing environment and thus shows no signs of reaction. However, once it is removed from its natural environment and brought into contact with oxygen, the potential for its oxidation increases dramatically should the other reaction components be also available. Maximum reactivity occurs immediately after the deposition of tailings as oxygen is readily available to the top part of the pile (Blowes and Ptacek 1994). It is not surprising that one of the main prevention tools for sulphide oxidation is the restriction of its access to oxygen, whether in the form of underwater submersion (Environmental Mining Council of BC 2000) or encapsulation of the individual grains (Evangelou 1995, Evangelou 1996, Evangelou 2001, Georgopoulou et al 1996, Zhang and Evangelou 1998, Vandiviere and Evangelou 1998, Nicholson et al 1990, Fytas and Bousquet 2002).

2.4.2.3 Ferric iron

Along with oxygen, ferric iron is one of the main oxidants of pyrite and other sulphide minerals. Its solubility is low under neutral or alkaline pH conditions and it therefore precipitates as hydroxides above pH 3. However, its hydrolysis provides acidity in the form of H^+ , which lowers the pH and dissolves the hydroxides. For example, Cravotta (1994) reported on the formation of ferric hydroxides on the surface of pyrite grains, which dissolve at later stages and release Fe³⁺ and SO₄²⁻ into the vicinity. This, in turn, releases Fe³⁺ into the solution and accelerates the reaction even more. Lapakko and Antonson (1994) report a six- to seven-fold increase in sulphate release in pyrrhotite

samples between pH 3.5 and 4.05 than between 5.35 and 6.1. The only method for preventing ferric iron to play its detrimental role is to raise the pH significantly and keep it at an elevated level with the use of additives.

2.4.2.4 Water

Water is required for the first oxidation reaction to occur, as stated above, and it also reacts with iron to form the iron oxide coatings. It has been observed that pyrite weathers differently under varying humidity conditions (Borek 1994). An abundance of water or submersion, however, would restrict or significantly slow down oxygen ingress and prevent the reaction from taking place. Reardon and Moddle (1985; cited in Robertson 1994) estimate that the rate of oxygen diffusion through porous media decreases by more than three orders of magnitude as water saturation increases. Soil or artificial covers are sometimes used to prevent both water and oxygen from reaching sulphide-rich tailings underneath. This will be discussed in more detail in upcoming sections.

2.4.2.5 Bacteria

The presence of bacteria in the reactions and products of pyrite oxidation has been observed for some time. The most prominent and widely studied amongst these is *Thiobacillus ferrooxidans*, an acidophilic species able to oxidize Fe^{2+} , S^0 , metal sulphides, and other inorganic sulphur compounds (Evangelou 1995). Another relevant species is *Thiobacillus thiooxidans*, which can oxidize both elemental sulphur and sulphide to sulphuric acid, but is unable to oxidize Fe^{2+} (Brierley 1982, Lundgren and Silver 1980, Harrison 1984; cited in Evangelou 1995). The main benefit of these bacteria in oxidizing sulphides resides in the energy they obtain from the process, which they use for growth (Suzuki et al 1994). Although bacteria accelerate the rate of pyrite oxidation (biotic), the process could also take place in their absence and involve only chemical means (abiotic). However, observations in the field confirm that biotic pyrite oxidation is ten to one hundred times faster than the abiotic chemical one (Olson 1991; cited in Ritchie 1994).

2.4.3. RATES OF SULPHIDE OXIDATION

Singer and Stumm (1970) have stated that Fe^{3+} is the driving force behind pyrite oxidation in the acidic pH ranges, while O₂ takes over in the neutral to alkaline range. More recently, Moses et al 1987 (cited in Ritchie 1994) confirmed that oxidation rates below a pH of 3 – attributed to ferric iron – are ten to one hundred times faster than by oxygen. The same authors and other research in recent years, however, have shown that Fe^{3+} can be dominant even in the neutral pH range (Moses et al 1987, Moses and Herman 1991, Brown and Jurinak 1991; cited in Evangelou 1995). It was specifically shown that even at very small concentrations, Fe^{3+} was very effective as an oxidant between pH 2 and 9. The ability of ferric iron to outperform oxygen in the rate of sulphide oxidation stems from its ability to bind chemically to the pyrite surface (Luther 1987; cited in Evangelou 1995).

Although its oxidation reaction rates have been studied extensively, pyrite is by no means the sole sulphide mineral that undergoes alteration. Others such as pyrrhotite, sphalerite, and galena have been studied as well (Rimstidt et al 1994) and some authors report that pyrrhotite oxidation proceeds at a faster rate than that of pyrite (Petruk 2000, Nicholson and Scharer 1994), while others give a specific oxidation ratio of twenty to one hundred times when compared to pyrite (Shaw et al 1998). Jambor (1994) states that the rate of reaction is determined by the pyrite to pyrrhotite ratio rather than the total amount of sulphur present.

There are two sets of reactions that determine the overall rate of oxidation. The first is the dissolution of pyrite into ferrous iron and sulphate, and it is dependent on the presence of bacteria, the ferric to ferrous iron ratio, and the nature of sulphide, and is usually about 0.1 gm Fe^{2+} per gm of pyrite per day. The second is the oxidation of ferrous to ferric iron or ferric hydroxide. If the latter is purely chemical, it takes place in minutes at pH 7, in 300 days at pH 4.5, and 1000 days at pH 3.5. However, the biological version of this reaction can be a million times faster than the chemical one (Hutchison and Ellison 1992).

2.5. ACID MINE DRAINAGE

The process of sulphide oxidation itself is a chemical and biological phenomenon and has been covered from those angles in the section above. However, it is not restricted to a laboratory study but occurs in the field on a large-scale basis when tailings rich in metal sulphides are exposed to the atmosphere. It is in this capacity that sulphide oxidation concerns the mining industry and is its main environmental issue. Hence, the research and measures taken against acid mine drainage are actually geared at preventing sulphide oxidation on a larger scale, and they will be presented in the following sections.

2.5.1. DEFINITION AND SCOPE

Acid mine drainage is the result of pyrite and pyrrhotite oxidation in mine tailings in the presence of water, oxygen, and bacteria. The reactions result in the generation of sulphuric acid that not only contaminates the soil and water in the area, but also leaches metals from the tailings pile and into the environment. The reactions involved have been presented in a preceding section. Metal drainage becomes significant below a pH of 5.5, as most metals are soluble within the acidic range. It should be noted that a neutral drainage does not necessarily translate into an absence of metals because the likes of antimony, arsenic, cadmium, molybdenum, and zinc would still be soluble (Price and Errington 1998).

Acid mine drainage is the most serious environmental issue related to the mining industry. In Canada, estimated numbers run at 351 million tons of waste rock, 510 million tons of sulphide tailings, and more than 55 million tons of other mining sources that could produce acid drainage (Government of Canada, 1991; cited in Environmental Mining Council of BC 2000). Others mention that acid rock drainage liability associated with Canadian tailings and waste rock is about \$2-5 billion (Feasby and Tremblay 1995). Acid generation in Canada occurs at coal, nickel, zinc, copper, lead, gold, and uranium mines (MAC 1991; cited in Gould et al 1994). Lime treatment for the Noranda-group of companies alone was estimated at around \$5 million per annum (Kuyucak et al 1991; cited in Blowes et al 1994). In British Columbia, preventing acid drainage and metal

leaching is the most costly issue facing the mining industry (Price and Errington 1998). In the US, the industry spent over \$1 million per day to treat acid waters two decades ago (Kleinman 1989).

2.5.2. EFFECTS AND EXAMPLES

The main problem associated with acid drainage is its ability to mobilize and leach out heavy metals present in the tailings. These metals, even in small amounts, have a significant negative impact on the ecosystem into which they eventually drain. Acid drainage is toxic to aquatic life, vegetation, and to the terrestrial life that feeds on them (Price and Errington 1998), and this is the reason behind more stringent regulations regarding the responsibility for remediation. The produced waters are acidic, iron- and sulphate-rich, and can either react with other sulphides to accelerate oxidation, undergo partial evaporation and precipitate as hydrated iron sulphates, or contact host rocks and be neutralized (Lapakko 2002). The problem with iron sulphates is that they can act as temporary reservoirs for acid and metal storage, which can be released at a later stage when contacted by water.

A major factor that enhances the effects of acid drainage is the relatively fine size of tailings produced by the mill, which increases the particle surface area-to-volume ratio and translates into more oxidation per weight of sulphide minerals. The finer fractions are also problematic when used in backfill operations. Until the advent of paste technology that utilizes the entire gradation of tailings, the slime portion was always removed from the backfill mix and had to be dumped into the tailings pond.

2.5.3. NEUTRALIZATION

Within the suite of minerals in the gangue portion, a series of carbonates and silicates can also be found alongside the sulphides. The presence of these minerals provides a natural response mechanism to sulphide oxidation and specifically to the acid generation process it comprises. Whereas oxidation results in sulphuric acid generation, the presence of carbonates such as calcite provides a neutralization operation to counter

the acidity of the system. Sulphuric acid dissolves carbonates and hydroxides, which raises the pH of the system and halts the advance of acidity for a while (Blowes and Ptacek 1994). The overall equations of neutralization by calcite and dolomite are given below:

$$CaCO_3 + H_2SO_4 = CaSO_4 + H_2O + CO_2$$
$$CaMg(CO_3)_2 + 2 H_2SO_4 = CaSO_4 + MgSO_4 + 2 H_2O + 2 CO_2$$

Further oxidation would naturally release fresh acid, which would need fresh carbonate in order to be neutralized, and the chemical contest between the two is decided by the relative abundance of either one. An important consideration is that carbonate dissolution is relatively fast when compared to other mechanisms that control pyrite oxidation, and that it takes some time for acid to be produced afresh. From chemical equations, it is calculated that 200 g of calcite are needed to neutralize 120 g of pyrite (Hutchison and Ellison 1992). Once calcite is depleted, however, pore water pH declines at a rapid rate that forces the dissolution of other carbonates such as siderite [FeCO₃].

The most common carbonates found in Canadian acid-generating impoundments are calcite, dolomite, ankerite [Ca(Fe,Mg,Mn)(CO₃)₂], and siderite (Jambor 1994). Blowes and Ptacek (1994) list minerals that are responsible for neutralization at various pH levels. Calcite is the first mineral to dissolve in order to counter acidity and upon its depletion, pH levels drop to between 4.8 and 6.3 and cause siderite to solubilise. After siderite, aluminum hydroxides dissolve and the pH drops further to 4 to 4.3. Then, ferric hydroxides such as goethite [α -FeOOH] react and the pH is buffered between 2.5 and 3.5. At this stage, aluminosilicates such as muscovite, biotite, and feldspars start to dissolve, thus increasing the level of Al and Si in the pore water (Ritchie 1994, Blowes and Ptacek 1994). Although they can raise the pH, they are not as effective as carbonates in neutralizing acidity (Hutchison and Ellison 1992), and neutralization rates estimated by the same authors are observed as being fastest with calcite, followed by limestone and aluminum silicates, with silicates being the slowest.

2.5.4. PREDICTION

Based on new regulations for mining operations, the prediction of acid drainage has become an important tool in the assessment of potentially problematic conditions at a given site. Prediction is centered on identifying the amount of acid-generating and acid-neutralizing minerals in tailings, the presence of potential contaminants, and the conditions under which exposure and transportation would take place (Environmental Mining Council of BC 2000). A recent prediction manual by Price (1997) is currently being used as the main guideline for the evaluation of acid drainage potential. In essence, prediction is rather difficult as the process of oxidation could start after a mine ceases its operations and closes down (Price and Errington 1998). Nevertheless, some guidelines have been put forward by concerned governmental agencies, both at the provincial and federal government levels, such as the BC Ministry of Energy and Mines and Mine Effluent Neutral Drainage (MEND), which have been summarized below:

- Identification and description: it includes material characterization such as lithology, grain size, and degree of alteration.
- Prediction of metal release and acid drainage potential and timing: it comprises testing for individual samples, whole strata, and for the entire mine components. The tests are divided into two categories; static and kinetic. The former is made up of elemental analysis, acid-base accounting to assess the natural neutralization potential of the material, and mineralogy. Kinetic tests comprise the use of humidity cells, in-situ field tests, on-site test pads, and monitoring of weathering progress.
- Development of mitigation and monitoring programs: it includes the prevention and reduction of metal release and acid drainage, the assessment of available mitigation strategies, and the preparation of contingency plans.

2.5.5. CLASSIFICATION AND TESTING

Classification is the main requirement for predicting the acid-generating or acidneutralization potential of tailings, and this is achieved through laboratory or field testing. There are a number of recognized or recommended test procedures that are widely recognized, which includes the Waste Extraction Test that uses a 10:1 buffered 0.2M sodium citric acid solution at a pH of 5. The US Environmental Protection Agency recommends the use of its Method 1311, known as the Toxicity Characteristic Leaching Procedure (TCLP), or Method 1312, which is a modified TCLP. Both methods use a dilute acetic acid solution to extract metals, and wastes are classified based on their results (Hutchison and Ellison 1992).

The same authors list a series of other tests that are used for classifying tailings and these are categorized into static tests such as the modified Sobek and the Net Acid Production procedures, and kinetic tests such as the Shake Flask, the Soxhlet Extraction, and Humidity Test cells. Static tests are used to provide an estimation of the acidgenerating and neutralization potentials of a waste, are relatively cheap to conduct, and take a few days to complete at the most (White et al 1999; cited in Lapakko 2002). Leinz et al (1999, 2000; cited in Lapakko 2002), for example, developed leach tests that are able to extract different phases in mine tailings, dividing them into water-soluble, ion exchangeable, carbonate-associated, amorphous iron oxide, crystalline iron oxide, sulphide, and silicate phases.

On the other hand, kinetic tests are more complicated as they tend to accelerate the oxidation processes in the laboratory, and need clearly defined objectives in order to choose the appropriate methodology. A good summary of the two types of tests would be that while the static ones assess acid-generation and neutralization potential, kinetic ones estimate the oxidation rate and time needed for these processes to take place (Lee 1999). The same source states that the Australian Center for Mining Environment Research is in the process of preparing a manual for testing wastes, which will classify them into the following five categories; acid consuming and non-sulphidic, non-acid forming and low sulphur, non-acid forming and high sulphur, potentially acid forming with low capacity, and potentially acid forming with high capacity.

An assessment of the sulphur content in a given waste is crucial if the acidgenerating potential is to be determined. In static tests such as acid-based accounting, the acid potential is determined by measuring the total sulphur content. However, this will overestimate the value due to the inclusion of non acid-generating sulphates like gypsum or barite [BaSO₄]. On the other hand, measuring only sulphide sulphur will underestimate the acid-producing value due to its omission of minerals like jarosite [KFe₃(SO₄)₂(OH)₆] that can act as secondary basins of acid generation. Lapakko (2002) lists the various methods used in measuring sulphur in mine wastes and these include procedures such as ASTM E 1019, E 395-70, and E 1915-97 (ASTM 2000). He further adds that based on his personal communication with two separate authors, new tests are in the process of being finalized that will be able to analyze the various species of sulphur in order to better assess acid-producing potentials.

2.5.6. PREVENTION

It is an unfortunate fact that once acid drainage processes start, current technology would not be able to stop it and return the situation to what it was before. Hence, prevention is a more desirable option in this case than subsequent treatment and is usually less costly. Sulphide oxidation and the subsequent acid drainage require three essential components to occur, which are oxygen, water, and bacteria. The latter actually accelerates the oxidation rate and its absence does not completely prevent acid drainage, but slows it down considerably. Therefore, it is logical that preventive methods revolve around inhibiting oxygen and water from reaching the sulphides or applying bactericides to slow down acid generation. Some of the common acid drainage preventive methods in use today are covered in the paragraphs below.

2.5.6.1 Underwater storage

The underwater placement of acid generating tailings has gained popularity in recent years since it effectively prevents oxygen from reaching the sulphides. Underwater placement could mean disposal in a natural or artificial water body, or submarine disposal for mines located in proximity to the coastline. Although effective in some ways, underwater disposal should consider two important factors; the existing concentrations of soluble contaminants within the tailings, and the potential for aerial weathering prior to disposal (Price and Errington 1998). Since water saturation would increase the dissolution of metals and other water-soluble species, it is very important to evaluate the amount of such materials in the tailings so as not to contaminate the bottom sediments of the water body. Studies are currently being conducted to assess the long-term effects of underwater disposal on the ecosystem.

Two major drawbacks in this method of prevention are the need for a natural lake that does not have special social or ecological sensitivities, and is located in proximity of the site, or the existence of favourable morphological features to construct an artificial one. Furthermore, if tailings that have been placed underwater were to be re-exposed at a later date, they would simply resume undergoing oxidation reactions. Underwater placement renders them immune only as long as they stay in that state.

Examples of underwater storage include the Placer Dome Equity Silver Mine in BC where 42 million tons were submerged and BHP's Island Copper Mine where submarine storage was used (Environmental Mining Council of BC 2000).

2.5.6.2 Blending of wastes

A second method of prevention is the blending and co-deposition of acid generating wastes with materials that have an excess neutralization potential. The principle reactions are similar to the natural neutralization of acidity by carbonates. For maximum blending performance, a thorough mixing of both materials needs to take place, e.g., tailings slurry and crushed limestone. Some of the major constraints for the blending method have been summarized by Price and Errington (1998), and can be listed as follows:

- High cost related to materials handling and amendment
- Performance limitations since metals could leach even in a neutral pH
- Technical uncertainty based on the current understanding of complex processes
- Demanding information requirements about the materials prior to blending

2.5.6.3 Covers

The main purpose of covers for tailings impoundments is to inhibit or restrict the access of water and oxygen to the sulphide minerals. The disadvantage of this method is that it involves large surface areas and costs are therefore high. In Canada, covers are used primarily to reduce drainage into already oxidized tailings to limit the total volume of contaminant leachate. Clay, soil, and synthetic materials could all be used as covers, and there are even the types that consume oxygen so as to completely prevent it from reaching the tailings. Recent research has focused on the concept of a multi-layer cover that consists of a fine material sandwiched between two coarser layers (Aubertin 1996). Major drawbacks in cover systems are the long-term performance and monitoring requirements since the method relies heavily on the durability of the cover material. Being constantly exposed to the elements, natural covers run the risk of erosion and synthetic ones need to be monitored to ensure constant integrity (Blowes et al 1994). In order to be effective, covers should be applied shortly after tailings deposition as this is the time when sulphide oxidation risks are at their peak due to the fresh surfaces being exposed and the availability of oxygen. With time and the deposition of secondary alteration minerals, the path of oxygen ingress to fresh sulphide surfaces would substantially lengthen in time.
2.5.6.4 Bactericides

The role of bacteria in enhancing sulphide oxidation was covered in a preceding section. Therefore, it is not surprising to find that one of the preventive tools for acid generation in mine tailings is the use of bactericides to try to slow down considerably – if not completely prevent – the suite of reactions that lead to acid generation. Bactericides can be sprayed either directly on the surface of tailings or mixed with them in the impoundment (Erickson and Ladwig 1985; cited in Blowes et al 1994). One drawback of this method is that bactericide application should be renewed periodically and is therefore thought of as a short-term or limited solution.

2.5.6.5 Coatings

Since acidity originates with sulphide oxidation, several authors have researched methods of coating the pyrite grains in order to cover their surfaces, thus providing immunity against reactions with the atmosphere. Coatings could include ferric phosphate (Huang and Evangelou 1994; cited in Blowes et al 1994) and ferric oxyhydroxides (Ahmed 1991; cited in Blowes et al 1994). Kalin et al (1998) used natural phosphate rock to test with those taken from base metal mines in Quebec. Their goal was to precipitate iron phosphate as a coating based on the fact that it is stable at low pH levels, which is ideal for an acidic environment.

2.5.7. TREATMENT

At most mine sites, especially the ones that have closed down or that have been abandoned, prevention of acid drainage is no longer an option. Oxidation has already taken place and the only mitigation measure left is to treat the acidic waters that continue to be generated. The costs of treating acid drainage fluctuate dramatically based on the most feasible method. Figures range from negligible for natural wetlands to \$1.5 million per year for lime treatment and sludge disposal (Price and Errington 1998).

Effective treatment processes require a substantial amount of information, e.g., water quality and quantity, effectiveness of drainage collection systems, effectiveness of

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treatment process, treated effluent discharge, disposal of secondary waste products, and long-term operational costs. Some constraints associated with the various methods include the high cost of long-term active chemical treatment, and the inability of passive systems such as wetlands to handle high metal loads or high flow rates.

The most common method of acid water treatment is lime precipitation (Kleinmann 1997). Lime is added to the water and soluble ferrous iron is oxidized to the ferric type, and is followed by precipitation as an iron oxide or oxyhydroxide. Other metals precipitate as well since the pH of the system is raised to the neutral range. This method requires the continuous provision of lime and generates a calcium sulphate and iron oxide sludge that could pose significant problems due to its chemical composition and sheer volume. Furthermore, all precipitation methods such as the use of calcite, sodium hydroxide, sodium carbonate, and anhydrous ammonia leave behind a metalladen sludge that needs to be disposed of in a safe manner (Pennsylvania DEP 2002). The sludge is usually referred to as floc and contains iron oxides, metals, and sulphate at pH levels of 6 to 8.5, and researchers noted that a high sulphate content and SO₄:Fe ratio retard precipitation and settlement processes (Lenter et al 2002). Remediation controls vary between old and new sites in that whereas they include collection, treatment, and infiltration controls at the former, the latter involve mostly sulphide oxidation controls to prevent acid production (Blowes et al 1994).

While active treatment involves lime neutralization, passive methods can include wetlands, wood waste, peat logs, and activated carbon, all of which treat the acidic water by precipitating the metals from them. Other authors used steel slag as an alternative to treatment by limestone (Skousen 1995, Ziemkiewicz and Skousen 1998; cited in Simmons et al 2002). The main reasoning behind passive treatments is to allow the natural reaction of sulphide oxidation to occur within the treatment system and not in the receiving body. An important consideration is that their maintenance is relatively cheap (Pennsylvania DEP 2002).

2.6. SECONDARY MINERALS

In addition to releasing acid and metals, sulphide oxidation liberates other cations and anions in the immediate vicinity, thus producing saline leachates. Although some of these ions are adsorbed to clay surfaces where they are present, most of them will interact with the solutions and upon reaching saturation levels, precipitate as secondary minerals. Lottermoser (2007) states that this is the most common form of fixation for metals in sulphide-rich wastes and cites several other researchers (Lin 1997; Lin and Herbert 1997) who support this premise. Other researchers have noted such occurrences associated with both sulphide oxidation and acid mine drainage, and have even classified the minerals into several categories based on their relative age of precipitation. Bigham (1994) reported that the rapid oxidation and hydrolysis of iron lead to the precipitation of secondary minerals with very small particle size (<10 nm). It must be noted that although secondary minerals form whenever sulphides outcrop naturally – as in the formation of gossans – or are otherwise exposed to the atmosphere, for the purposes of this work they shall be taken to mean only those that form as a result of mining and milling processes.

2.6.1. CATEGORIES

Jambor and Owens (1993; cited in Jambor 1994) categorize minerals found in weathered tailings piles into the following four sets:

- 1. Primary; constituting the main ore and gangue assemblages.
- 2. Secondary; forming in impoundments through the precipitation of constituents from oxidation reactions.
- Tertiary; crystallizing after samples have been removed from the impoundment, and cementing particles together (e.g., covellite [CuS], gypsum, and ferrihydrite [(FeOOH)₅(H₂O)₂]).
- 4. Quaternary; forming by surficial oxidation during the storage of the dried samples.

Hence, these authors state that the primary ones are those minerals that are found originally in the tailings, and the secondary ones are those that are formed directly from sulphide oxidation, whereas the last two types form during the drying and storage stages. Jambor (1994) adds that the saturated zone in the tailings impoundment usually hosts the primary minerals while the secondary ones are found in the vadoze zone where oxygen and water co-mingle. It must be kept in mind that it is precisely because of the availability of both oxygen and water in the vadoze zone that the sulphides are able to oxidize. Saturation would keep them underwater at all times and restrict their access to oxygen.

2.6.2. HARDPAN LAYER

In more matured tailings, Jambor (1994) observes the formation of a new layer at a certain depth, which indicates a zone of increasing pH. This is due to the fact that when neutralization takes place in tailings because of calcite and siderite dissolution, the higher pH levels produced allow for the precipitation of minerals belonging to the iron oxide family that includes amorphous species, ferrihydrite, goethite, and schwertmannite $[Fe_8O_8(OH)_6(SO_4).nH_2O]$. Others such as iron and calcium sulphates also precipitate. These iron oxides act as cementing agents by forming a hardpan layer with other secondary minerals (Blowes and Ptacek 1994). For example, Jambor (1994) reports ferrihydrite and bassanite $[CaSO_4.1/2H_2O]$ in the hardpan layer at the Waite Amulet mine in Quebec, while melanterite $[FeSO_4.7H_2O]$ and gypsum are found at Heath Steele. He states that the most abundant secondary minerals found in tailings impoundments are gypsum and goethite, while melanterite is reported by other authors to be the most common iron sulphate mineral, occurring mainly as pore-filling cement in hardpan layers (Blowes et al 1994).

McGregor and Blowes (2002) report on three hardpan layers at different mine sites near Sudbury. They state that tailings at all three sites contain pyrrhotite and it is the oxidation of this mineral that has produced the cemented hardpan layers. At the first location, it is at the surface of the impoundment and measures 20 cm in thickness. At the second one, it is at a depth of 19 cm and is 12 cm thick. At the last location, the authors report an 8 cm thick layer present at a depth of 25 cm. Boulet and Larocque (1998) place the hardpan layer at two sites in New Mexico at 46 cm below the surface, consisting of gypsum and iron oxyhydroxides laden with metals.

In addition to natural reactions, treatment methods for acid drainage can also produce hardpan layers due to the neutralization reactions involved. Doerr et al (2003) reported on the findings from a reactive barrier where secondary phases such as jarosite, goethite, and ferrihydrite had formed as part of a hardpan layer. The latter two minerals were observed in the unsaturated vadoze zone, which was separated from the saturated one by a hardpan layer. Tests showed that the iron oxides forming this layer were soluble in a 0.5M HCl solution.

Based on the properties of hardpan layers in cementing tailings particles together and preventing oxygen and water percolation to the materials below, researchers have tried to artificially create them in tailings. Ahmed (1994) deduced that a hardpan layer can be produced by converting sulphides into goethite. He tested pyrrhotite-rich tailings from the Sudbury region and induced reactions by bubbling air through them and adding tap water at certain pH levels. After six weeks, he reported hardpan layers in all the samples, and examination revealed goethite and lepidocrocite as their main components.

2.6.3. IRON OXIDES

Iron oxides and oxyhydroxides are the main categories of secondary minerals that form due to sulphate oxidation. Since pyrite – an iron sulphide – is the main component in acid-producing mine tailings, the hydrolysis of liberated iron inevitably produces an entire series of oxides, e.g., goethite, lepidocrocite [γ -FeO(OH], ferrihydrite, schwertmannite, and jarosite. While goethite – the most stable form of ferric iron oxide – and jarosite are well crystallized minerals, others like ferrihydrite and schwertmannite are poorly crystallized and their names have even been used as a synonym for amorphous iron oxides (Bigham 1994).

It is well known that iron oxide minerals have adsorption abilities and act as reservoirs for other metals. A commercial process called FERROX binds metals found in municipal solid waste into amorphous iron oxide phases, which transform into crystalline ones over time (Sørensen et al 2000, Christensen et al 2000, Lundtorp et al 2000). Another process called JAROFIX stabilizes tailings rich in jarosite and transforms them into inert waste (Benoit and Getahun 2003). Based on this property, the dissolution of iron oxides in the mine tailings environment would be the start of a renewed release of metals that had been liberated by acid generation but had been retained by iron oxide adsorption and co-precipitation (Blowes et al 1994, Yun et al 2001). In addition, iron oxides such as jarosite buffer the pore water at a low pH by releasing acidity in the form of ferric iron, in addition to other metals that had been adsorbed on their surfaces (Al et al 1994b). Holmström et al (2001) reported the adsorption of copper on iron oxyhydroxides at the Kristineberg Mine in Sweden. Shaw et al (2003) conducted several leach extraction tests to quantify the chemistry of soluble secondary minerals such as iron oxides. Yun et al (2001) discussed the ability of goethite in scavenging for metals through adsorption or co-precipitation at specific pH level for metal mine tailings in Korea. Research in this area has also been conducted at McGill University, where Potter (1999) studied the retention of copper and lead on synthetic iron and aluminum oxides, while Gao (2001) looked at anion adsorption on goethite and iron oxyhydroxide surfaces.

2.6.4. TESTING AND ANALYSIS

As with acid-producing or neutralization potentials, the amount of secondary minerals, and specially iron oxides, needs to be assessed in order to evaluate their role in the formation of hardpan layers and to determine the stage of oxidation at which the tailings stand. Furthermore, the different types of iron oxides and oxyhydroxides need to be differentiated so as to better understand the role played by each species in retaining other metals.

2.6.4.1 Debye-Scherrer method of x-ray diffraction

It is known that regular x-ray diffraction can detect the presence of amorphous minerals but cannot identify them, and this is a drawback when it comes to secondary iron oxyhydroxides (Lapakko 2002). The Debye-Scherrer method uses regular diffraction

techniques and principles but instead of the diffracted rays being captured by a detector, they are imprinted on a special circular x-ray film. Jambor (1994) recommends the use of this method, in addition to thin sections, as the best way of studying secondary minerals such as sulphates and iron oxyhydroxides. Another related methodology he recommends is the use of diffraction on the tailings prior to and after washing them with water, which would indicate the subsequent absence of any water-soluble minerals such as gypsum. When using glass slides for XRD analysis, the author recommends great care in not using water at any stage of sample preparation because of the solubility of certain secondary minerals. Instead, it is suggested to use acetone or another type of alcohol to avoid dissolution (Boulet and Larocque 1998).

2.6.4.2 Thin sections

A second useful method in the analysis of secondary minerals and iron oxides is the thin section technique with a petrographic microscope. Special care should be taken in preparing the tailings slides for this method as water cannot be used at any stage of the sample preparation process. Instead, organic solvents and oil-based products like kerosene must be employed to prevent accidental dissolution (Boulet and Larocque 1998, Shaw et al 1998). The technique is similar to the one employed for the preparation of concrete samples where hydration products are sensitive to water.

2.6.4.3 Sequential extraction

Various authors have used different solutions to extract the various phases of iron oxides found in mine tailings. Some of them have focused on this particular family of minerals while others have taken a more global approach in applying their methodology to the entire suite of minerals found in tailings. For example, Bigham (1994) states that a 2- to 4-hour extraction with a 0.2M ammonium oxalate solution at pH 3 in the dark would dissolve amorphous iron oxides but not crystalline ones. McGregor and Blowes (2002) used a 2M hydroxylamine hydrochloride [NH₂OH.HCl] in a 25% (v/v) acetic acid [CH₃COOH] solution for 24 h at 95°C with occasional agitation to extract crystalline iron oxides, following a method proposed by Ribet et al (1995). Sørensen et al (2000)

extracted amorphous iron oxide using 0.2M ammonium oxalate for 2 hours in the dark. In a previous section, mention was made of a sequential leaching protocol developed by Leinz et al (1999, 2000) where different phases of minerals found in mine wastes could be extracted separately. Holmström et al (2001) used a technique stipulated by Hall et al (1996) to sequentially extract metals in oxidized and treated mine tailings in Sweden. Moore (2005) categorized metals found in sediments into the following groups; exchangeable, bound to carbonates, bound to Fe- or Mn-oxyhydroxides, bound to organic matter, and part of the crystalline minerals. He further specified extraction methods to analyze each category and recommended the following solutions:

- Exchangeable: 1M MgCl₂ at pH 7 at room temperature or 1M sodium acetate at pH 8.2 at room temperature
- Carbonates: 1M sodium acetate-acetic acid buffer at pH 5 at room temperature
- Fe-Mn oxyhydroxides: sodium dithionite + sodium citrate-citric acid at 96°C or hydroxylamine hydrochloride + acetic acid at 96°C
- Organics: nitric acid + hydrogen peroxide + ammonium acetate at 85°C
- Crystalline minerals: hot HF + HClO₄ or hot HF + HNO₃

2.6.4.4 Ferrous and ferric iron

Another important requirement to better understand iron oxides is the ability to differentiate between ferrous and ferric iron compounds. Several methods including colorimetry and atomic absorption can be adopted but the solutions used allow for the analysis of only one type of iron at a time, and an additional step is required to determine the other. Karamanev et al (2002) developed a new method that simultaneously determines the amount of ferrous and ferric iron in acid drainage waters. The procedure involves the use of a 5-sulfosalicylic acid solution and measures its absorbance on a spectrophotometer at a wavelength of 500 nm.

2.7. CONCLUSIONS

The mineralogy of tailings is an important factor in their disposal and reuse, and one that needs to be addressed especially when they include a high percentage of sulphide minerals. The main problem associated with this type of minerals is their potential for oxidation, a process that releases acid and sulphate into the environment. Due to the large amounts of tailings produced, problems associated with sulphide oxidation have a significant environmental and economical impact, the foremost of which is acid drainage. Research has been conducted in this area, and tests have been put into place to predict or mitigate the problem. Another aspect of oxidation is the formation of secondary minerals, most of which are iron oxides or oxyhydroxides. Their ability to adsorb metals has been exploited commercially, but they can also act as reservoirs for secondary sulphate and acid release in tailings. In addition, the iron oxides form a hardpan layer at certain depths within the tailings where both oxygen and water abound, and act as impervious barriers with respect to the material below. Therefore, several authors have attempted to create artificial hardpan layers either as a cementing tool or as a natural barrier to the ingress of oxygen and water into the deeper levels of tailings impoundments.

CHAPTER: 3 SULPHATE ATTACK

3.1. INTRODUCTION

Sulphate attack is one of the better documented processes in the concrete industry due to its detrimental effects. It occurs mainly as a result of an interaction between the calcium silicate hydrate gel formed due to cement hydration and sulphate anions found either in water (mixing or external) or in aggregates. The long-term effect of exposure is an undesirable loss of mechanical strength properties leading ultimately to structural failure. Hence, the cement and concrete research community has studied the problem extensively and the tolerance levels towards any form of sulphate exposure – whether internal or external – is severely curtailed through guidelines and procedures. Sulphate attack was already the subject of study in the 19th century in Europe, and at the beginning of the 20th century it was also reported by American and Canadian engineers (Skalny et al 2002). Limiting tricalcium aluminate [C₃A] content in the clinker and lowering the water-to-cement ratio were two methods of curbing the extent of the damage at that time. In this chapter, after a brief introduction to cement hydration, a more rigorous review of the mechanisms, types, and available tests for sulphate attack will be conducted.

3.2. CEMENT AND CONCRETE

Concrete is the most widely used construction material in the world today. The world consumption of cement – the main ingredient of concrete – was 1.6 billion tons for 1999 (PCA 2000; cited in Skalny et al 2002). Cement is produced by grinding clinker – obtained by burning limestone and clays together – with gypsum and mineral components such as slag, pozzolans, or limestone, and is composed of several anhydrous phases that react with water and form hydrated compounds. It is important to realize that the process is not a dissolution one but rather the result of these phases being unable to exist in their original forms when in contact with water. On the other hand, their hydrated products are at equilibrium with aqueous solutions and able to exist when in contact with them (Lea 1970).

3.2.1. CEMENT COMPONENTS

Ordinary Portland cements are composed of four main reactive phases;

- tricalcium silicate C₃S [3CaO.SiO₂]
- dicalcium silicate C₂S [2CaO.SiO₂]
- tricalcium aluminate C₃A [3CaO.Al₂O₃]
- ferrite C₄AF [4CaO.Al₂O₃.Fe₂O₃]

In addition to the above, they could also include minor amounts of free lime [CaO], gypsum, and other calcium sulphates, which are used to regulate concrete setting and hardening. The first phase hydrates and sets within hours, attaining the majority of its strength within seven days, while the second phase requires a few days to hydrate and provides strength over time. The presence of the third phase assists mainly in hydration and the development of strength. The fourth phase is known to hydrate rapidly but its contribution is not well known (Lea 1970).

3.2.2. CEMENT HYDRATION

The main product of C_3S and C_2S hydration is a calcium silicate hydrate gel [CSH gel] that has a very poor crystalline or nearly amorphous structure, although the rates of hydration for the two phases are different. In the presence of gypsum, sulphate is seen to enter the CSH gel and to slightly change its morphology. The ratio of Ca:Si varies greatly within this gel and typical numbers range from 1.5 to 1.7 (Skalny et al 2002). The second important hydration product is calcium hydroxide [Ca(OH)₂], which is sometimes called portlandite and is designated as CH. These two – the CSH gel and CH – play important roles in the chemical durability of concrete, especially during sulphate attack, and the topic will be explored in more detail further on.

C₃A hydrates very rapidly and the end product, after a few intermediate ones, is a stable compound with the formula 3CaO.Al₂O₃.6H₂O. Along with C₄AF, products of C₃A

hydration also include tricalcium aluminate trisulphate hydrate, known as ettringite (AFt phase), and tricalcium aluminate monosulphate hydrate, known as monosulphate (AFm phase). The hydration of C_3A can sometimes be radically modified when gypsum is present because the sulphate component allows for large amounts of ettringite to precipitate in the form of fine needles. The presence of a minimal amount of gypsum is necessary, though, since its absence allows C_3A to react very rapidly and to stiffen immediately, a process that is called flash set (Henderson and Revell 2005).

The most chemically active component of a concrete system is naturally the cement paste, which is the matrix holding the various components together. It determines the permeability, durability, and mechanical strength of the final product and it has been designated as the "heart" of concrete (Brunauer 1968; cited in Skalny et al 2002). Since the hydration products are more voluminous than their inert counterparts, the pore space between the various components is continuously filled with these new products after the hydration processes start, which reduces the volume of voids and decreases the overall permeability.

3.2.3. COMPONENTS OF CONCRETE

3.2.3.1 Cement

The different components in Portland cement were covered in section 3.2.1 above. It suffices to mention that cement is the sole binding agent in a concrete mix, with the other components assisting it in performing its main function. The primary active phases are the calcium silicates, aluminate and ferrite present in cement, and their roles were covered in the said section.

3.2.3.2 Aggregates

Aggregates form the highest percentage in concrete based on volume. Depending on the required properties of the end product, the mass percentage of aggregates can range between 3.5 and 7.5 times that of the cement used (Skalny et al 2002). The particle size properties of the aggregates are largely based on the application for which the product is prepared, and its quality depends on the environment into which it will be placed.

3.2.3.3 Mineral admixtures

Chemical and mineral admixtures are widely used in the concrete industry today. Their role is to facilitate or retard the occurrence of certain reactions or to control them in a manner congruent to the use of the final product. Some of the functions for chemical additives include water reduction, set control, workability improvement, strength increase, and durability improvement. As for mineral admixtures, they include granulated blast-furnace slag, high-calcium and low-calcium fly ash, silica fume, and rice husk ash. The latter ones are know as pozzolans and they have been used at an increasing rate in recent years as cement replacement components. The use of mineral additives has been reported extensively in the literature and the reader is referred to specialized textbooks for a more comprehensive average of their utilization coverage. Table 3-1 provides the oxide components of regular cement and some of the more common mineral aggregates used in the industry for comparison (Skalny et al 2002).

Oxide	Symbol	Clinker	Fly ash	GBF Slag	Microsilica
CaO	С	64-65	1-20	30-50	
SiO ₂	S	20-22	10-50	25-45	90-98
Al ₂ O ₃	Α	4-7	10-30	5-13	trace
Fe ₂ O ₃	F	3-5	1-15	<1	trace
MgO	М	1-4	1-4	1-20	
SO3	S	0.3-1.5	0-5	<3	
Na ₂ O	Ν	0.1-1.5	0-4	<2	trace
K ₂ O	K	0.1-1.5	0-3	<2	trace

Table 3-1 – Typical compositions of clinker and admixtures (mass %)

3.2.3.4 Water

Water is a crucial ingredient in a concrete mix without which hydration would not occur. The ratio of water used is therefore quite important for two reasons; firstly, it

determines the rate of hydration and therefore the final void ratio and permeability of the concrete, and secondly, it determines the workability of the mixture. It is usual to have water in ratios ranging from 25% to 50% by weight of cement, although 20-22% is enough for cement to hydrate completely (Skalny et al 2002). Hearn and Young (1999) indicate that the water-to-cement ratio can vary between 0.28 and 0.75 but that 0.45 to 0.60 are the more frequent ones to be used. Many authors have studied the relationship between this ratio and permeability and it is now well known that the latter increases dramatically above a ratio of 0.45-0.50 (Powers 1958; cited in Skalny et al 2002). These numbers are important to bear in mind as permeability is one of the important factors in determining the amount of sulphate ingress into concrete, and hence in assessing the severity of an attack. Powers et al (1959; cited in Hearn and Young 1999) studied the relationship of this ratio to the time required for the pores to achieve discontinuity, which would prevent infiltration. Their conclusions were that whereas a ratio of 0.40 would require only 3 days to disrupt communications between pores, a ratio of 0.50 would require 14 days to do so, and a ratio of 0.60 would require 6 months (Table 3-2).

W:C ratio	Time required		
0.4	3 days		
0.45	7 days		
0.5	14 days		
0.6	6 months		
0.7	1 year		
>0.7	impossible		

Table 3-2 – Age required for pore discontinuity (Powers et al 1959)

In a similar manner, Skalny et al (2002) recommend a maximum upper limit of 0.5 for the water-to-cement ratio with the optimal value being 0.4. Based on their studies, Hearn and Young (1999) categorize the water retained into three components:

- Non-evaporable water, which constitutes about 23% by weight of the original cement
- Gel water held by the CSH
- Capillary water in the spaces not occupied by hydration products

3.3. DEFINITION OF SULPHATE ATTACK

The durability of concrete is not necessarily associated with strength only, but is that characteristic whereby concrete is able to resist chemical or physical "pressures" (Skalny et al 2002). Specifically, chemical durability refers to the ability of concrete to resist internal or external reactions that may compromise its performance or shorten the service life expected from it. These reactions could include the action of carbonates, sulphates, and chlorides, as well as other species. Sulphate attack is the term given to a complex set of reactions that occur between cement components and sulphate ions. Nevertheless, there is still some confusion in the research community and literature as to what processes and results are included in the definition of sulphate attack and where its limitations stand. For example, expansion due to ettringite formation is one narrow definition of the term that only looks at reactions between external sources of sulphate and C_3A (Skalny et al 2002).

Under normal conditions, aluminum converts to the trisulphate ettringite (AFt) form first, which subsequently transforms to the monosulphate (AFm) one. Upon exposure to sulphates, this phase reverts back to ettringite and produces expansion, cracking, and a loss of cohesion. The mechanism and chemical processes of sulphate attack are independent of the source of sulphate anions. Regardless of the many overlapping reactions and as yet unanswered questions about its identity, the ACI's guide to durable concrete (ACI 1992; cited in Skalny et al 2002) defines two mechanisms as constituting sulphate attack; formation of gypsum and formation of ettringite. Similarly, Diamond and Lee (1999) quote Thorvaldsen (1952) and Mehta (1992) in defining sulphate attack as the formation and deposition of ettringite and to some extent gypsum.

3.4. TYPES OF SULPHATE ATTACK

Several types of sulphate attack have been observed in concrete and they have been categorized based on their source and the nature of the reactions involved. Hence, there are chemical vs. physical sulphate attacks based on the reactions involved, and there are internal vs. external attacks based on the source of sulphate. The distinction between the first two categories has been deemed to be artificial in that they are based on visual observations and not on the nature of the reactions themselves. The main recognized categories, therefore, are the internal vs. external attacks.

3.4.1. CHEMICAL AND PHYSICAL ATTACK

Chemical sulphate attack comprises reactions involving SO_3 [S] such as when monosulphate and gypsum combine to form ettringite:

$$C_4ASH_{12} + 2CSH_2 + 16H = C_6AS_3H_{32}$$
 (C = CaO, A = Al₂O₃, H = H₂O)

Physical attack is sometimes called salt crystallization and involves the formation of sodium sulphate decahydrate from solution, followed by its repeated transfer into sodium sulphate anhydrite, and vice versa. Although the reactions themselves are no less chemical than others, the term physical refers to the observed expansion-contraction of the concrete volume.

 $2 \text{ Na}^{+} + \text{SO}_{4}^{2-} = \text{Na}_2\text{SO}_{4.10\text{H}_2\text{O}}$ (evaporation) Na₂SO₄.10H₂O = Na₂SO₄ (repeated recrystallization)

3.4.2. INTERNAL ATTACK

Internal attack refers to the source of the sulphate ions, which could come from any of the components used in the preparation of concrete, such as pozzolans, aggregates, or mixing water. A good example of an internal attack is the process called delayed ettringite formation (DEF). One internal source is the calcium sulphates used in the production of cement, and their original intended role is to accelerate the hydration of calcium silicates. The overall SO₃ content ranges between 2.2% for type IV cement and 3.5% for type III (PCA 1996; cited in Skalny et al 2002). Another source is the aggregate used and the sulphate or sulphide minerals present therein. The best example of the latter is pyrite, a mineral that could readily be available in mine tailings. Pyrite found in gravels that are used as aggregate could result in problems since its oxidation could cause local spalling. A sequence of freeze and thaw actions could further deteriorate the concrete and although the overall durability is not affected, the quality of the product would naturally be questioned (Figg 1999). From the standpoint of chemical attack, pyrite is unique in that its oxidation may contribute to concrete deterioration both through sulphate and acid attack mechanisms due to its production of sulphuric acid. This is because the oxidation of pyrite does not simply produce an abundance of sulphate ions that are detrimental to concrete, but also results in acidity and the associated lowering of the pH. Skalny et al (2002) succinctly state that "unlike other types of attack, a chemical corrosion by sulphuric acid is not a pure sulphate attack, but a combined acid-sulphate attack", and that "an attack by free sulphuric acid is more severe than any with a neutral sulphate solution".

A final, although improbable, source of internal attack could be the mixing water since at certain localities, the tap water itself could have a high sulphate percentage. However, in practice, the main internal source of sulphate that has been observed to cause problems comes from the aggregate used. Casanova et al (1996; cited in Skalny et al 2002) specifically warn of aggregates with pyrite inclusions due to the latter's susceptibility to oxidation and sulphate production. The basic control mechanism for curbing internal attack is to limit the amount of C₃A and sulphate in the cement. For example, sulphate-resistant type V cement can have up to 5% C₃A according to ASTM C 150, 25% C₄AF + 2(C₃A), and 2.3% SO₃ (ASTM 1995).

3.4.2.1 Delayed ettringite formation (DEF)

Since the late 1980's, the term delayed ettringite formation has been prominent in the literature, and it is important to understand clearly what it entails. Skalny et al (2002) designate it as an internal form of sulphate attack in that all the necessary chemical ingredients for it are already present in the concrete at the time of preparation, although additional external water might be needed to produce the characteristic expansion. Furthermore, nomenclature in this regard is unnecessarily confusing since various authors use terms like "delayed", "secondary", "heat-induced", and the such, thus differentiating between what has been called "primary" or "good" ettringite, and the "secondary" one. Instead, Skalny et al (2002) propose a new designation derived from petrology whereby all phases that form as a product of initial reactions are called primary, and subsequent ones that derive from recrystallization processes are termed secondary.

There does not seem to be any credible evidence for DEF occurring in concrete cured at ambient temperatures, and it is a phenomenon that is observed to take place at curing temperatures above 65-70°C, which would make it a heat-induced phenomenon. Although it is unlikely to have internal sulphate attack due to an excess in sulphate within concrete-making materials, all necessary precautions are nevertheless taken to limit these as much as possible, especially when heat-curing or changes in humidity are anticipated (Skalny et al 2002).

Some of the visual characteristics of DEF or heat-induced ettringite formation are map cracking and spalling while microscopic observations include expansion of cement paste to form gaps around aggregate particles (Johansen et al 1993; cited in Skalny et al 2002), the filling of these gaps with ettringite, formation of ettringite "nests" (Marusin 1993; cited in Skalny et al 2002), and micro-cracking. Although there is still some debate whether paste expansion occurs or if it is responsible for the gaps, micro-analytical methods available nowadays are able to provide the clues to a better understanding of this issue. The main tool in conducting analysis is the scanning electron microscope (SEM) with the back-scattered electron imagery option. While highly informative, the method remains solely qualitative and is used to confirm results from other forms of analysis.

3.4.3. EXTERNAL ATTACK

External attacks take place when the sulphate source comes from without such as from groundwater, soil, industrial waste, or atmospheric SO₃. Groundwater contaminated with sulphates from mining wastes could be an important external source, while industrial wastes from coal combustion and the metallurgical industry could contribute based on their concentration of sulphates and their proximity to circulating water. During an external attack, the ingress of sulphate ions into the concrete could be accompanied by a partial dissolution and decomposition of the CSH gel, which involves the removal of Ca²⁺

from the product. Marchand et al (1999) cite several authors to prove the point that the decalcification of the CSH gel results in a major decrease in the mechanical strength of concrete. Such a severe form of attack usually takes place due to ammonium sulphate or sulphuric acid reactions.

Amongst the external sulphate sources, the most common one is groundwater, which would typically include alkali-, calcium-, or magnesium-sulphates. In an external attack, the reactions start at the cement paste-water interface and move gradually inwards. Gollop and Taylor (1992-1996; cited in Skalny et al 2002) report that the reaction front penetrated about 0.5-1.0 mm deep in a paste immersed in 0.25M Na₂SO₄ solution after six months of curing. Skalny et al (2002) cite their own work where sulphate-resistant cement was cured in 0.5M Na₂SO₄ solution and the reaction front was located at 0.26 mm after 3 days, at 0.60 mm after 28 days, and 1.1 mm after 106 days (Werner et al 2000). The presence of a layered progression of the attack front was confirmed by Wang (1994; cited in Skalny et al 2002) who immersed cement pastes in a sodium sulphate solution of 350 mmol/l and pH 6 for fourteen days. He observed layers of ettringite, gypsum, and portlandite in the samples through minute XRD analysis after coating all but two of the faces of each sample, one of which was exposed to air and the other to the solution.

3.4.3.1 Na₂SO₄ and K₂SO₄

The usual mode of alkali sulphate attack is the reaction of the anion with monosulphate formed in concrete during the hydration process, with the aluminum provided from the latter and the calcium coming from the dissolution of portlandite.

$$2 \text{ SO}_4^{2-} + \text{Ca}_4\text{Al}_2(\text{OH})_{12}.\text{SO}_4.6\text{H}_2\text{O} + 2 \text{ Ca}^{2+} = \text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_3.26\text{H}_2\text{O}$$

At the point where aluminum is depleted but sulphate ions are still available, they react with calcium to form gypsum instead of ettringite. One of the characteristic effects of alkali sulphate attack is the temporary increase in strength resulting from ettringite infilling within the pore spaces (Brown 1981, Brown and Taylor 1999; cited in Skalny et al 2002). One of the defences against this type of attack has been to reduce the Al_2O_3 in the clinker, which is found in the C_3A phase. Another technique, according to Gollop and

Taylor (1992-1996; cited in Skalny et al 2002) is to increase the gypsum content within the limits of SO₃ allowed, which would form primary ettringite instead of monosulphate, bearing in mind that the latter's conversion back to ettringite following an attack is the main reason of expansion. The basis for this logic is the fact that only the aluminum in monosulphate is available for reaction with the sulphates and not the one found in the CSH gel or elsewhere in the concrete product. Gollop and Taylor's (1992-1996; cited in Skalny et al 2002) research also showed that even when pozzolans such as slag are used in concrete, the only aluminum originating from that source that would be incorporated into ettringite would be the portion that goes into the initial monosulphate formation during hydration. The conclusion of these researchers is that when slag and Portland cement are used together, the damage caused by alkali-sulphate attack would be reduced.

Brown and Taylor (1999) present four equations that take place sequentially to precipitate ettringite:

$$Ca_4Al_2(OH)_{12}.SO_4.6H_2O + 2 Ca^{2+} + 2 SO_4^{2-} + 20 H_2O = Ca_6Al_2(OH)_{12}(SO_4)_3.26H_2O$$

(eq. 1)

$$Ca(OH)_2 = Ca^{2+} + 2 OH^{-}$$
 (eq. 2)

$$Ca^{2+} + SO_4^{2-} + 2 H_2O = CaSO_4.2H_2O$$
 (eq. 4)

In the first equation, ettringite forms due to the reaction of monosulphate with calcium, which is provided through the dissolution of calcium hydroxide presented in the second equation. Once it is depleted, the decalcification of the CSH gel commences as per equation 3, and gypsum is formed as per equation 4. These authors further elaborate that a combined attack of Na_2SO_4 and CO_2 would cause severe destruction of the CSH gel, with thaumasite formation especially at temperatures below 5°C.

3.4.3.2 CaSO₄

Waters rich in anhydrite or gypsum would be limited in aqueous sulphate ions by the low solubility of calcium sulphate (15.2 mmol/l or 1.46g SO_4^{2-}/l) at 20°C. Yet again, it is the monosulphate phase in the paste that reacts with the sulphate to form ettringite. However, unlike a case of an alkali-sulphate attack, the CSH gel is not decalcified and it remains intact.

3.4.3.3 MgSO₄

Attack by magnesium sulphate produces brucite $[Mg(OH)_2]$ and gypsum in addition to the gradual decomposition of the CSH gel. The unique aspect of this process is its rapidity due to the insoluble nature of brucite and the low pH of the solution. In addition, the main effect of MgSO₄ attack on concrete is the loss of strength rather than expansion.

3.4.3.4 H₂SO₄

The interaction of sulphuric acid and concrete cannot be considered as merely a form of sulphate attack, but is rather a combined sulphate-acid attack in which several mechanisms operate. The source of the acid could be any of the following; acid found in groundwater through pyrite oxidation, acid in industrial wastewater, acid in sewers, and acidic rainwater. The first step of such an attack is the formation of gypsum with calcium hydroxide and the CSH gel found in concrete. Diamond and Lee (1999) observe that calcium hydroxide acts as a preservative for the gel, keeping the pore solution pH above 12.5. During an attack, calcium hydroxide dissolves due to the drop in pH and when it is depleted, CSH gel decalcification starts. Hence, the dissolution of the CH phase is a harbinger of the onset of strength deterioration (Marchand et al 1999). Any ettringite or monosulphate present cannot withstand the low pH environment induced by the acid and they convert to gypsum and aluminum sulphate, except within the deeper parts of the concrete body where a higher pH regime may still prevail. Attacks through sulphuric acid

are the most severe a concrete structure could undergo due to their intense degradation of the hydrated cement paste (Skalny et al 2002).

3.5. CHARACTERISTICS OF SULPHATE ATTACK

The four main hydrated calcium sulphate components that form as a result of sulphate attack are gypsum (formed subsequent to attack and not the initial component), ettringite, monosulphate, and thaumasite (Taylor 1997, Brown and Taylor 1999; cited in Skalny et al 2002). Certain researchers have designated the two characteristic results of sulphate attack as expansion through ettringite formation and progressive loss of strength and mass (Mehta and Monteiro 1993; cited in Skalny et al 2002). It should be noted that high permeability and cracks in concrete greatly accelerate the reach of external solutions into the structure and therefore its deterioration without significant volumetric expansion (Skalny et al 2002). As for its manifestations, they include the visually discernible ones such as spalling, cracking, and delamination, which are the result of complex chemical reactions occurring within the concrete system. Researchers have classified these into one or more of the following processes:

- Dissolution or removal of calcium hydroxide
- Decomposition of unhydrated clinker components
- Decomposition of previously formed hydration products
- Formation of brucite and magnesium silicate hydrate
- Formation of thaumasite, gypsum, and ettringite

3.5.1. FORMATION OF ETTRINGITE

As noted in previous sections, ettringite [Ca₃Al(OH)₆.12H₂O]₂.(SO₃)₃.2H₂O is the main mineral associated with sulphate attack and would therefore require a more detailed review. It forms initially in fresh concrete and controls the rate of set, and is therefore

beneficial in this aspect. It is its formation in hardened concrete that is detrimental and associated with attack (Brown and Taylor 1999). In solutions, ettringite is stable only above a pH of 10-11, which translates into a highly alkaline environment, and requires a relatively high amount of sulphate to precipitate. In sulphate-deficient environments, monosulphate forms instead since it requires only one third the amount of the anion when compared to ettringite (Diamond and Lee 1999). The solubility of ettringite in water has been determined by Damidot and Glasser (1992; cited in Skalny et al 2002) to be as follows:

$$K_{sp} = (Ca^{2+})^6 . (Al(OH^-)_4)^2 . (SO_4^{2-})^3 . (OH^-)^4 = 2.80E - 45$$

It is important to keep in mind that ettringite formation in concrete may or may not be coupled with volumetric expansion, since this phenomenon is related to various chemical and mineralogical factors. In order for any expansion to occur, several conditions must first be met, which include ettringite crossing a threshold amount, the orientation of crystals pointing towards neighbouring solids, and formation occurring after setting has taken place. Ettringite can form through a variety of reactions based on the source of sulphates, and the two presented below are from the natural hydration of tricalcium aluminate in the presence of gypsum (eq. 1) and the reaction of monosulphate with an external sulphate source (eq. 2).

$$C_{3}A + 3 CSH_{2} + 26 H = C_{6}AS_{3}H_{32}$$
 equation 1
 $C_{4}ASH_{12} + 2 CSH_{2} + 16 H = C_{6}AS_{3}H_{32}$ equation 2

Researchers have reported the formation of ettringite and gypsum in sulphate attack tests but have been unable to agree on the relative amounts or whether expansion is proportional to the amount of ettringite formed (Brown and Taylor 1999). Diamond and Lee (1999) indicated that in a sulphate-deficient environment, such as in fly ash and cement mixes, monosulphate would form instead of ettringite during an attack. Although other authors have questioned its relevance to sulphate attack, a large body of work links the damage with ettringite formation and presence. Brown and Taylor (1999) stress the

point that one of the basic reasons for a lack of agreement in this matter is the absence of any reliable methods to quantify ettringite.

3.5.1.1 Test methods for determining ettringite

Brown and Taylor (1999) cite x-ray diffraction and thermal methods for the determination of ettringite content but present their reservations due to dehydration taking place during sample preparation. Others like Glasser (1999) propose scanning electron microscopy in backscatter mode with x-ray analysis (SEM-EDX) as the best method for identifying the mineral. These methods, although helpful qualitatively are nevertheless inadequate for a quantitative determination of ettringite. Uchikawa and Uchida (1974) first reported a method for determining the amount of ettringite through leaching with various combinations of ethylene glycol and methanol. They confirmed that almost 100% of the ettringite sample tested was dissolved in a 3:1 mixture, and that the analysis of aluminum proved to be the best method of calculating the amount of ettringite present. Odler and Abdul-Maula (1984) conducted tests with the 3:1 solution and reported that amongst the various new phases formed after cement hydration, ettringite was the only one with aluminum in its formula that was dissolved in appreciable amounts. They compared the test method to XRD and DTA and preferred its use in the quantitative measurement of ettringite at weight-to-volume ratios of 0.67. Bernier et al (1999) used the same method for monitoring secondary ettringite formation in mine backfill, which was made with pyrrhotite tailings and cured for six months.

3.5.2. FORMATION OF GYPSUM

Apart from ettringite, gypsum is the other mineral normally associated with sulphate attack. It usually forms in concrete when external solutions rich in sulphate interact with the calcium hydroxide found in cement paste, although whether it causes expansion or not is still a matter of debate amongst researchers:

$$2 \text{ Me}^{+} + \text{SO}_4^{2-} + \text{Ca}^{2+} + 2 \text{ OH}^{-} = \text{CaSO}_4.2\text{H}_2\text{O} + 2 \text{ Me}^{+} + 2 \text{ OH}^{-}$$

The formation of gypsum is sometimes associated with pyrite found in aggregates used in concrete preparation. Sulphate ions produced from pyrite oxidation react with the calcium hydroxide and yield gypsum. The interaction of sulphates is not restricted only to the aluminum-bearing phases in cement paste as they could even react with the CSH gel formed from C_3S hydration. Experiments conducted by authors such as Bentur (1976) and Mehta et al (1979; cited in Skalny et al 2002) showed that significant strength losses were registered as a result of this interaction in which gypsum was formed. The tests available for gypsum determination are laborious, especially in light of the relatively low solubility of the mineral in water, involving its dissolution in water or other solutions and the measurement of sulphur (Sokolovich and Evdokimova 1997, Berigari and Al-Any 1994). In their quantitative tests on ettringite, Odler and Abdul-Maula (1984) reported that 69.6% of gypsum could be dissolved in the ethylene glycol and methanol solution, and this could be a promising test should no other sulphate bearing mineral be included in the test sample.

3.5.3. PHYSICAL CONSEQUENCES

Apart from the chemical and mineralogical consequences of a sulphate attack as discussed in the preceding sections, the main concern for engineers is the physical aspect of such attacks. The mineralogical changes enumerated converge and result in a weakening of the concrete product, leading ultimately to failure. These changes are not without their observable physical characteristics, such as swelling, spalling, and volume instability, which will be reviewed in the following sections.

3.5.3.1 Internal sulphate attack

The sources of internal sulphate attack were discussed at length previously, and they are restricted to excessive amounts of calcium sulphates in the cement or aggregate portions. Test samples prepared with high compositional amounts of sulphates showed significant cracking and strength loss at 0.3% expansion (Ouyang et al 1988; cited in Skalny et al 2002), and it is noteworthy that ASTM C 1038 (Standard Test Method for Expansion of Hydraulic Cement Mortar Bars Stored in Water) allows a maximum

expansion of 0.02% after fourteen days of immersion in water. As for heat-induced or DEF sulphate attack, the main observations are map cracking and the factors affecting its initiation include moisture, temperature, and the alkali concentration in the surrounding environment (Day 1992; cited in Skalny et al 2002).

3.5.3.2 External sulphate attack

ASTM C 1012 is a typical test for samples undergoing external sulphate attack whereby they are immersed in solutions and their changes in mass and volume monitored at regular intervals. Analysis of results shows that after an initial period where no major swelling occurs, the samples experience constant expansion until total disintegration (Brown 1981; cited in Skalny et al 2002). Based on similar results, a number of expansion limits have been proposed by authors over the years, ranging from 0.05% to 0.5%. Visual inspections have been extensively used to assess degradation, with various numerical values attached to different stages, but these should be used with caution. Day and Ward (1988; cited in Skalny et al 2002), for example, observed 1% expansions and reduction in mechanical strength in cement–fly ash combined samples without any visual signs of degradation.

Although cracking is the main visual feature of concrete attacked by external sulphate sources, spalling and exfoliation are its other characteristics. These are observed especially when slabs or foundations are placed directly on top of sulphate-rich soils, an action that produces a typical efflorescing material like sodium sulphate prior to inducing damage. For example, Diamond and Lee (1999) cite the penetration of sulphate-bearing groundwater into slabs, which results in the deposition of sodium sulphate (thenardite) at the top and indicates a progressive upward alteration. As discussed previously, some authors classify this type as a physical or salt crystallization attack (Haynes 2000, Haynes et al 1996, Hime and Mather 1999; cited in Skalny et al 2002).

3.6. PREVENTION OF SULPHATE ATTACK

Different types of cements are generally designated as being sensitive or resistant to sulphate attack. Since the main suspect component is the aluminum found in the C_3A phase, resistance is significantly improved through its limitation. Sulphate-resistant Portland cement, for example, has a reduced Al_2O_3 component that limits the amount of ettringite formed should unfavourable conditions be present. Fly ash–Portland cements replace up to 30% of the clinker with ash gathered from coal combustion, bearing in mind that class F fly ash tends to be more effective than class C (Soroushian and Alhozami 1992, Biricik et al 2000; cited in Skalny et al 2002). Similar mixes have been tried with natural pozzolans or with silica fume. All of these replacement components share a common characteristic in that they limit the amount of calcium hydroxide and increase the amount of CSH gel formed. Slag–Portland cement mixes go even further in that the former can make up to 60% of the mixed blend, and the same reduction in C_3A is behind the added resistance to sulphate attack.

Apart from limiting the C_3A phase, another prevention tool sometimes cited by authors is the reduction of permeability of concrete. External sulphate-rich water would induce more damage if it were able to infiltrate into the concrete mass. Decreasing the permeability would therefore be an excellent tool in combating sulphate ingress, and this can be done by lowering the water-to-cement or the water-to-cementitious materials ratio, which is a recognized technique by international regulatory publications such as the ACI 201's Guide to Durable Concrete (cited in Skalny and Pierce 1999). Authors who have reviewed the issue at length (Skalny and Pierce 1999, Skalny et al 2002) conclude that a ratio of 0.4 would be optimal in minimizing porosity and permeability in concrete. Others (Diamond and Lee 1999) have purposely used very high ratios such as 0.60 in order to maximize these properties and to study the effects of sulphate attack.

The use of additives in concrete is currently a common practice, and these include silica fume, blast furnace slag, fly ash, rice husk ash, and others. The literature studying their general usage in concrete is voluminous, and their effect on its resistance to sulphate attack has also been looked into. Lagerblad (1999) tested concrete mixed with silica fume

and slag, and found that decreasing the amount of cement invariably lessened the amount of attack and damage. Mixing of silica fume was observed to limit the damage, due to spalling without much expansion as opposed to the pure cement pastes, while mixing slag gave even better results. Mehta (1986) looked into concrete made with a mix of cement and fly ash in terms of sulphate resistance and his results were positive (Clifton et al 1999).

3.7. TESTING FOR SULPHATE ATTACK

Deterioration due to sulphate attack has been evaluated in a variety of tests and procedures that include visual assessment, wear rating, loss of mass, hardness, and compressive strength, all of which are usually codified into standards (Skalny et al 2002). There are currently two main tests that evaluate the performance of concrete when subjected to sulphate attack, and these are ASTM C 1012 and C 452. ASTM C 1012 is applicable for both Portland and blended cements where the water-to-cement ratio is fixed, and a 20 MPa compressive strength is required of the mortar samples before testing can commence. The test comprises the immersion of mortar bars into a 50 g/l solution of sodium sulphate or magnesium sulphate with expansion measured periodically for up to 6 months. Clifton et al (1999) assess this test as being closer to field conditions than C 452. As for the latter, it involves the addition of gypsum to cement prior to making the mortar bars such that the SO₃ content is 7%. The bars are then cured in water for 14 days and their expansion is measured at that time. One drawback of this method is its application to Portland cement only and not to the blended ones. Another is that it does not simulate field conditions in terms of sulphate attack.

Mehta and Gjörv (1974) developed a full immersion test with constant pH and sulphate concentrations, with 10 mm cube samples prepared at a high water-to-cement ratio. The pH was controlled by adding dilute sulphuric acid either manually or with an automatic titration machine. Compared to ASTM C 1012, the solution had a constant pH of 7, which accelerated the rate of attack significantly.

Brown and Taylor (1999) observed that expansion and strength measurements on mortars in Na_2SO_4 solutions show that the two parameters are related. Furthermore, they stressed that the rate of attack is dependent on the pH regime of the solution, with lower values seen to accelerate the process. Authors who wished to increase the level of attack for study purposes used a higher water-to-cement ratio in their experiments, such as 0.60 by Diamond and Lee (1999), and 0.55, 0.45, and 0.35 by Lagerblad (1999). This last author even used partially immersed samples to enhance sulphate penetration.

3.8. ASSESSMENT OF TESTS FOR SULPHATE ATTACK

Tests currently in use are indirect in nature since they measure the results of the attack rather than the actual causes behind it. The unconfined compressive strength test (UCS), for example, is deemed by several authors to be inadequate in characterizing the degree of deterioration (Mehta 1997, Neville 1998, Jambor 1998; cited in Skalny et al 2002). According to Clifton et al (1999), deficiencies inherent in current tests include lengthy test periods and the insensitivity of the tools to the progression of attack. As for others, they enumerate the following points regarding current methods (Skalny and Pierce 1999):

- Lack of rapid test methods
- Test methods designed for mortars rather than concrete
- Reliance on oversimplified single measurements such as UCS

Others have been more vocal in sounding their concerns and have deemed current tests that evaluate the relative resistance to sulphate as unsatisfactory (Mehta and Gjörv 1974). One positive aspect of these concerns has been their discussion in ASTM E 632, entitled "Standard Practice for Developing Accelerated Tests to Aid Prediction of the Service Life of Building Components and Materials" (Clifton et al 1999). These authors restrict their observations to the method of immersion used in the tests. For a continuous immersion, they argue, the main factors to study are the concentration of sulphate in the solution and the amount of reactive material in the cement paste. Hence, in order to

accelerate the test, an increase in sulphate concentration would be needed. Another suggestion they make is to subject the samples to wet and dry cycles, but they touch on a very important fact when they look at partial immersion tests. It was noted in the previous section that Lagerblad (1999) used partially immersed samples to accelerate sulphate intake into the samples. Clifton et al (1999) are in agreement that partial immersion is a severe condition of both physical and chemical sulphate attack, citing as examples concrete elements placed directly on top of moist soil with their upper portions exposed to air. They lament the fact that a standard test for concrete that is partially immersed in a sulphate solution or one for wetting and drying cycles was not found during their research and at the time of writing.

3.9. CONCLUSIONS

The hydration of cement produces calcium hydroxide and a CSH gel that contributes significantly to strength development over time. Apart from this gel, ettringite forms in the initial stage and transforms to monosulphate within a short period of time. When hydrated concrete is exposed to sulphate-rich waters, monosulphate reverts back to ettringite and expansion could occur. In addition, due to the presence of excess sulphate, the CSH gel is decalcified and gypsum forms instead. The formation of ettringite and gypsum indicate the presence of sulphate attack according to most authors. Several researchers have experimented with ettringite quantification using a mixture of ethylene glycol and methanol to dissolve the mineral, which is the main product of sulphate attack.

Unfortunately, current ASTM tests have been deemed inadequate in assessing a binder's resistance to sulphate attack due to their focus on expansion mechanisms only. Researchers have called for new tests to be adopted that also shorten the amount of time needed for their performance. Several authors have developed an accelerated test in which samples are immersed in sodium sulphate solutions that are kept at constant pH levels through the addition of dilute sulphuric acid. Others have further increased the severity of the tests by the partial immersion of samples in the same solutions.

CHAPTER : 4 SULPHIDE MINERALS IN MINE BACKFILL

4.1. INTRODUCTION

Backfill preparation and placement is an integral part of a mining operation. Although its first use was in the 19th century, the incorporation of Portland cement took place in the 1950's with cemented tailings backfill starting in the 1970's (Hassani and Archibald 1998). The main purpose for backfill use at that time was to provide wall support and to dispose of the tailings, although the need for ground control and a working floor were other viable reasons (Hassani and Bois 1992). Due to the large amounts needed and the high cost of cement, the industry studied the potential of other binder alternatives such as pozzolans. At the same time, improvements were made in terms of using the full gradation of tailings in backfill operations in the form of paste, and these steps reduced cement consumption significantly. Apart from the useful engineering properties provided by backfill, an increasingly important factor was the environmental liability that large amounts of tailings would incur on a given operation. With the use of paste fill, through which the entire gradation of tailings can be sent back underground, operators could reduce the amount of waste that needs to be disposed of in an expensive surface impoundment.

4.2. MECHANICAL PROPERTIES

The properties of mine backfill are complex in that they are an overlap of several disciplines including soil mechanics, concrete technology, fluid mechanics, and process engineering (Kuganathan 2005). Added to this list is a preferred knowledge of chemistry and mineralogy where potentially detrimental reactions within the tailings are concerned. From a soil mechanics point of view, the properties of cohesionless soils are best suited to mine fill applications.

4.2.1. COMPRESSIVE STRENGTH

The two main mechanical properties required of backfill are compressive strength and permeability. The sought values for the former vary depending on application, and range from below 1 MPa after 28 days for cut-and-fill mining, and up to 5 MPa for delayed backfill in pillar recovery operations (Hassani and Archibald 1998). Clough et al (1989; cited in Potvin 2005) indicate that even when used as a bulking material without exposure to adjacent voids, a minimum UCS of 100 kPa is required of paste backfill in order to prevent liquefaction.

The primary function of backfill is provide stabilization through a lateral confinement pressure to rock walls and pillars that support the rock load mass (Archibald 1992; cited in Hassani and Archibald 1998), bearing in mind that compared to the rock mass, it is a relatively soft material. Potvin (2005) concurs that the main function of the fill is to occupy void space that – if left on its own – would otherwise collapse with time. It achieves this function by preserving some of the confining forces in the rockmass, and by limiting the amount of wall convergence. However, with the incorporation of classified tailings, cemented backfill has moved beyond its simple void-occupying function and has been used in recent years for artificial support that requires short curing times in order to facilitate a quick deployment of mine equipment. In methods that progress downwards, such as undercut-and-fill, the backfill may even act as a replacement roof (Potvin 2005).

Brady and Brown (1985; cited in Potvin 2005) define three types of mining methods; unsupported (caving) methods where voids are meant to be filled with caved in material, naturally supported methods where pillars are left in place to control stability, and artificially supported methods where fill is used in combination with pillars to limit void exposure. It is in this last category that mine backfill finds its most extensive application. The methodology of backfill operations, on the other hand, can be divided into cyclic and delayed ones. The first uses the fill as a platform for operations to take place on, and is employed in the case of cut-and-fill stoping with high strengths required as soon as possible for equipment traffic to take place. In the case of the second type, the end product must be a fill that can act as a freely standing wall. Many mining operations leave rock pillars in place to bear loads, and then return for their recovery once the primary phase is over. In these cases, backfilled areas of considerable height will be exposed and it is crucial that they remain free-standing throughout the operations. Based on the schedule of operations, a rapid gain in strength – similar to the first type – might not be expected from backfill used for such purposes but rather a gradual strength gain over time.

4.2.2. PERMEABILITY

Permeability, as the second important parameter, is used in stope dewatering with acceptable rates being above 100 mm/hr. This is especially important in slurry fill placements where it is crucial to eliminate extra water in order to avoid fill liquefaction problems, and to allow for high placement and curing rates (Falconbridge 1990; cited in Hassani and Archibald 1998). In the case of paste backfill, the problem of a decrease in permeability is compensated by the presence of cementitious binders that minimize liquefaction risks (Pierce 1997; cited in Hassani and Archibald 1998). However, the addition of cement reduces the percolation and drainage ability of the emplaced backfill. This is especially true for hydraulic fill where researchers have observed a 75% reduction in permeability with the addition of 4% cement by weight (Mitchell and Smith 1979; cited in Hassani and Archibald 1998). In order to obtain the best possible strength from backfill, adequate drainage must be allowed to take place whether binders are added to it or not.

Upon reviewing the basics of mine backfill, it can be said that since it resembles soil in many aspects, concepts inherent to soil mechanics can readily be applied to it as well. For example, backfill consists – as soil does – of two phases, viz. solids and void space. The voids, in their turn, can be filled with a gaseous (air) or liquid (water) phase. Moisture content, which is the percentage of the weight of water to the total weight, can vary from 15% to 22% in the case of slurry or high density backfill (Hassani and Archibald 1998). The importance of a high saturation percentage cannot be overstated since it assists in the drainage of extra transport water upon backfill placement. A 10%

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decrease in saturation would result in a 50% decrease in the percolation rate (Herget and de Korompay 1978; cited in Hassani and Archibald 1998). On a related note, void ratios range between 0.25 and 0.75 for slurry fills and between 0.50 and 0.85 for rock fills.

4.2.3. PARTICLE SIZE DISTRIBUTION

Particle size distribution and shape play major roles in backfill operations. The general shape of particles is angular due to the blasting and grinding processes, and the maximum size depends on the mode of transport. Where pipes are used, the general norm is to have the maximum particle size as 1/3 of the pipe diameter, while in the case of conveyors they could go up to 30 cm. The gradation used in backfill plays a major role in the permeability of the final product. An analysis of tailings from four gold mines showed that an increase in porosity would result in a better percolation rate, yet an increase in the concentration of particles less than 20 µm produced a significant decrease in the same rate. Other authors reached a similar conclusion in their studies (Liu 1983, Herget 1981; cited in Hassani and Archibald 1998). In the case of paste backfill, the entire spectrum of the particle size distribution can be used. An advantage of employing such techniques is to add compressive strength to the final backfill product, even though slimes and the finer portions have traditionally been eliminated to enhance drainage (Herget 1981; cited in Hassani and Archibald 1998).

4.2.4. FORMS OF FAILURE

A common form of failure in backfill is shear sliding in which a planar failure surface dips into the pillar being excavated. Cohesion along the plane of failure is a main factor in the resistance of backfill to slide, and cemented backfill would naturally be more resistant to such failure. Since the unconfined compressive strength is related to cohesion, it is the foremost parameter for testing in backfill used in pillar recovery operations. An assumed simplification proposed by Mitchell et al (1982; cited in Hassani and Archibald 1998) in which the factor of safety was set at unity was:

$$UCS = \gamma H / (H / L + 1)$$

In the formula above, the symbols stand for the following:

 $\gamma = \text{unit weight (kN/m^3)}$

H = height of exposed backfill (m)

L = strike length of backfilled stope (m)

Segregation is another phenomenon that could take place in backfill and result in the loss of cohesion and of binders. It occurs when the finer particles in hydraulic backfill settle at a slower rate than the coarser fraction due to the difference in mass. As decantation of the extra water takes place, the finer fraction still in suspension is typically washed out and stratification occurs that could result in areas of low binder content. These areas could eventually take on the role of planes of weakness along which failure could take place (Falconbridge 1990; cited in Hassani and Archibald 1998).

Liquefaction is a form of failure that could take place in saturated tailings at which point they would behave as a fluid with a mass greater than water. This is a risk in cases where unconsolidated fills are used and cannot occur where fills have developed a minimal internal cohesion (Falconbridge 1990; cited in Hassani and Archibald 1998). The same reference states that in the case of saturated unconsolidated tailings, loading caused by explosive charges within 15 m of the stope could trigger a liquefaction risk. Triaxial tests of various types remain the common testing method for liquefaction potential, and studies show that even at 30:1 tailings-to-cement ratios, this type of failure is unlikely to occur (Aref et al 1989; cited in Hassani and Archibald 1998).

4.2.5. STRENGTH GAINING METHODS

Due to the prime importance of mechanical properties in backfill operations, several methods have been attempted to increase or reinforce its strength. These include the use of fibre, mesh, and geotextile-sheet elements. Wittreich (1988; cited in Hassani and Archibald 1998) studied the use of steel and plastic fibres, concluding that they increased the strength of a 6% cemented backfill by up to 50%. The main reason was that

the fibres increased frictional resistance, maintaining a certain level of integrity even after fill failure.

A novel technique was recently developed that turned fine tailings into pellets, which were later used as coarse aggregates in backfill operations. The process is called cold bond tailings agglomeration (CBTA) and the author was able to create 19.1 mm pellets from sulphide-rich gold tailings with the addition of cement and fly ash (Amaratunga et al 1997; cited in Hassani and Archibald 1998). Paste backfill strength was observed to improve from 60% to 220% and the fine fraction of tailings was utilized instead of requiring surface disposal methods.

4.3. MINERALOGICAL PROPERTIES

Due to the highly variable nature of the local geology where mining operations take place, the mineralogical properties of backfill have attracted little attention in terms of research. The role of sulphides in relation to mining has been recognized due to their production of hydrogen sulphide gas that could cause underground fires. The oxidation of sulphide minerals is well known and was documented in the first chapter of this work. The various important factors in the oxidation rate are the type of sulphide mineral, the surface area, oxygen availability, temperature, pH values, and the mixture of different types of sulphides. This last factor has been studied by Anderson (1930; cited in Hassani and Archibald 1998) in which he found that mixing minerals such as sphalerite, galena, and covellite with pyrite increased their oxidation rates by 8 to 20 times.

Even though it could result in strength gain in non-cemented fills, sulphide oxidation produces the exact opposite effect in cemented ones, in addition to self-heating that could lead to self-combustion. The self-cementing action has been studied at the Horne, the Sullivan, and the Mattagami Mines in which pyrrhotite tailings were used with varying rates of success (Patton 1952, Iglesias 1966; cited in Hassani and Archibald 1998).
The deterioration caused by sulphates in concrete was reviewed in the second chapter of this work. It can be stated that similar reactions take place when sulphide minerals in backfill oxidize and produce sulphate, which reacts with the cement paste. The products of these reactions are the familiar ettringite, gypsum, and monosulphate noted in sulphate attack reactions in concrete. Hassani and Archibald (1998) list several studies conducted on this topic by different authors. Tests by Mitchell and Wong (1982) on slurry fill indicated that sulphide-bearing backfill rusted and lost strength when compared to the non-sulphide bearing one. Severe deterioration in the slurry fill of another mine showed the formation of gypsum (Archibald et al 1995). Another author reported the formation of ettringite in paste fill cured in a humid environment and used the width of the reaction rind at the surface of the samples to assess potential problems in the field (Pierce 1997).

The source of sulphate is not restricted to the oxidation of sulphides, though, due to the presence of large amounts of gypsum as a result of sulphide ore processing. In this regard, Archibald et al (1998; cited in Hassani and Archibald 1998) conducted tests on the Brunswick Mine paste fill and found that although no oxidation took place, a strength loss by a factor of 20 could be seen in the fill after 28 days of curing. Further studies by the same author indicated that a partial substitution of cement by ground waste glass could somewhat halt the deterioration process The concrete industry's own research has shown that certain pozzolans such as slag and fly ash could play similar roles in resisting sulphate attack.

As for the self-heating problem related to sulphides, it involves their spontaneous reaction to the point of combustion. Ninteman (1978; cited in Hassani and Archibald 1998) studied this feature and concluded that the problem could occur were the oxygen and moisture conditions ideal in the presence of large amounts of sulphides. Rosenblum and Spira (1995; cited in Hassani and Archibald 1998) further studied self-heating and concluded that pyrrhotite was the only mineral that exhibited this form of behaviour. Their recommendation was to dilute the reactive material with inert aggregates and to limit the supply of oxygen to the whole material, a condition that is readily found in paste fill due to its saturation.

4.4. COMPONENTS OF MINE BACKFILL

The main components of mine backfill are tailings or rock waste, binders (cement, fly ash, slag), sand, fine aggregates (where needed), and chemical additives (accelerators, retarders). The use of cementitious binders in mining applications is similar to those in civil engineering ones, and therefore the basics of cement hydration and the use of pozzolans are mostly the same. For example, most pozzolans contain little or no lime and cannot hydrate properly without its addition to the mix. In the following sections, the binder components used in backfill operations will be discussed in brief.

4.4.1. TAILINGS

Tailings are the product of crushing and grinding of the mined ore, with the processed ore generating revenue for the operation, and the tailings component incurring a cost in terms of its environmentally safe disposal in surface impoundments (Henderson and Revell 2005). It must be borne in mind that within backfill, tailings constitute the main component; therefore, a study of their properties is crucial in evaluating the final characteristics of the backfill product.

4.4.1.1 Size

The particle size distribution of tailings can range between fine sand and clay, with the grinding process being the main deciding factor. Well-graded tailings would have – as in the case of soils – a shallower plot in a size distribution curve, while poorly-graded ones would exhibit a rather steep curve. The size distribution curve of different types of tailings is presented in Figure 4-1 (Henderson and Revell 2005).



Figure 4-1 – Typical size distributions of mine backfill (Henderson and Revell 2005)

The importance of size distribution lies in its ability to determine several other properties of the final backfill, such as void ratio, flow properties, permeability and percolation rate, and the ease with which the fill can be pumped. Well-graded tailings, for example, exhibit lower void ratios due to the infilling action of the fines within the free spaces. Fines also have the ability to hold onto water and prevent settlement within the pipelines during transport. The main methods of determining particle size distribution are the traditional sieving and hydrometer analysis in addition to cyclone sizing, while newer methods include optical imaging using laser light (Kuganathan 2005). Soil mechanics guidelines specify particles less than 0.075 mm as fines but in fill technology, the useful cut-off size is either 10 μ m or 20 μ m in hydraulic and paste fill, respectively.

4.4.1.2 Particle shape

Apart from its size, the shape of a particle influences certain bulk properties as well. Flat particles would settle more slowly than rounded ones and could affect consolidation and drainage times. The smooth surfaces of mica minerals provide potential slippage planes on the microscopic level, since cement paste cannot penetrate in between to create a stronger bond.

4.4.1.3 Mineralogy

The mineralogy of tailings plays an important role not only in disposal methods, as discussed in the first chapter, but also in the backfill as reviewed in the preceding section. Apart from sulphide-related problems, clay minerals and sericite have been observed to retain water, resulting in a reduced strength due to an incomplete hydration of cement. As for sulphide oxidation, Henderson and Revell (2005) state that sulphate liberated during this reaction attacks the cement bonds after two months, which reduces the fill strength. Another concern is the heat generated from the oxidation reactions, which could result in spontaneous combustion, an example of which was an incident at the Brunswick Mine No. 12 due to pyrrhotite action. These authors recommend further research on oxidation within mine fill.

4.4.2. NATURAL SANDS

These are used either as the main source of fill materials in hydraulic fills or as a supplement to tailings in paste fills.

4.4.3. ROCK AND AGGREGATE

The source of rock and aggregates used in backfill could be waste from open cut operations, from underground development, or from specific quarries. In general, the inclusion of aggregates will contribute significantly to the UCS of the final product but care must be taken in order to assess several key parameters such as moisture content, grading, and attrition, which is the reduction of particle size due to breakage during transport or placement.

4.4.4. CEMENT

The chemistry of cement and its hydration process were covered in a previous chapter. As a revision, cement consists of four major phases; alite, belite, aluminate, and ferrite. Of these, the first one – also known as C_3S – is the most important in strength

development in the first 28 days of hydration, and comprises between 50% and 70% of the cement by weight. Henderson and Revell (2005) give the percentages for Australian cement as 60% C_3S , 15% C_2S , 8% C_3A , and 10% C_4AF . The relationship between binder content and backfill strength is not a simple one and tends to be site-specific. In general, though, 5% cement and 95% fill would combine to provide enough strength for a freestanding fill. Cement use constitutes an integral part of the mining industry, and the Ontario mining sector alone is known to consume approximately 6% of the cement produced annually in Canada (Hassani and Archibald 1998).

4.4.5. POZZOLANS

The definition of a pozzolan given by the ASTM is of a material that reacts with moisture and calcium hydroxide to form cementitious phases. The silicate phase in pozzolans such as fly ash is normally in the form of spherical amorphous particles that react with hydrated lime. It is the amorphous nature of these particles rather than their chemical composition that defines their reactivity. Whereas the hydration of cement produces lime and raises the pH, the pozzolans with cement, rather than lime, since the hydration of the former would result in free lime being generated in any case. The advantages of using pozzolans in backfill include economical ones due to their relatively lower costs, and chemical ones because of excess lime consumption that improves strength (Papadakis et al 1992; cited in Hassani and Archibald 1998).

4.4.5.1 Slag

Slag is produced from the processing of iron and steel, and is classified based on the type of cooling it undergoes. Air cooled slag used to be widespread in Canada but was discontinued due to its non-reactive nature. Foamed or expanded slag was similarly discontinued due to the production of hydrogen sulphide gas. Granulated slag is quenched by water jets and subsequent immersion in water. Pelletized slag is produced by throwing the particles up in the air after water spraying, which are dried by the time they land back on the ground. Currently, slag produced in northern Ontario is used primarily for mine backfill operations in that region.

The use of slags in mine backfill goes back to 1969 when Mount Isa Mine experimented with various alternative binders due to its remote location from cement producing plants (Thomas 1973; cited in Hassani and Archibald 1998). The author mentions that several mines have experimented with the production of their own slags for backfill in order to cut costs. Work was done in Finland (Nieminen and Seppänen 1983) and in Italy (Manca et al 1983) in this respect. In Canada, Falconbridge conducted tests on a nickel and copper slag, and found an optimum cement replacement at 50% (McGuire 1978). The St Lawrence Cement Company obtained a patent in 1975 for cement-slag binders to be used for tailings stabilization (Laneuville 1972). The Algoma Steel Corporation produced a ground granulated blast furnace slag in 1986 that was tested on tailings from several mines across the country (CANMET 1988). Falconbridge also conducted a comprehensive review of binder alternatives for hydraulic backfill and came up with a recipe that economized 64% on binder costs (Hopkins and Beaudry 1989).

4.4.5.2 Fly ash

Fly ash is produced in thermal power plants where various types of coal undergo combustion, and its average particle size ranges from 10 to 15 μ m. The lime-rich (15-30%) type C is produced when sub-bituminous or lignite coals are burnt whereas lime-poor (5% or less) type F is produced where bituminous coals are used. Most of the fly ash in Canada consists of this second type and its use has been approved in consolidated backfill after specific studies were undertaken regarding its toxicity effects when used near water sources (Yu and Counter 1988; cited in Hassani and Archibald 1998). The institutions and mines listed in the previous section also experimented with fly ash – in addition to slag – as a viable replacement alternative for cement, and obtained positive results in general.

4.4.5.3 Other pozzolans

Apart from the two main pozzolans – slag and fly ash – others have been used in mine backfill as alternatives. Silica fume, although used in the concrete industry, has not yet found it way into the mining one. Other alternatives, however, include clays, anhydrite, and even pyrrhotite, using the latter's natural self-cementing properties as a tool. In those cases, it was found, air circulation and drainage were needed to produce curing within a reasonable timeframe (Swain 1973; cited in Hassani and Archibald 1998). Calcined gypsum is another alternative that is relatively popular in Australian operations due to its availability and cheaper cost of production when compared to cement (Henderson and Revell 2005). Results obtained by Petrolito et al (1998) show that it can be used as a viable alternative to cement provided it is available in close proximity to the mining operation. Ordinary waste glass, when finely pulverized, provides a very good source of amorphous silica that combines with cement and lime to produce material with cementitious properties. It has been looked into as a potential material to be used in slurry and paste backfill (Archibald et al 1995, 1996 and 1997, cited in Hassani and Archibald 1998).

4.4.6. ADMIXTURES

Admixtures comprise materials added immediately before or during the mixing process in order to enhance the final properties of the concrete or backfill product. They include water reducers, retarders, accelerators, and various combinations of the above. In terms of properties being modified, the use of admixtures is employed to influence the rheology, hydration, or the durability of the product.

4.4.7. COST OF BINDERS

The main reason behind the research into alternative binders in mine backfill is to reduce the costs inherent in these operations. The price of cement is related to the availability of energy required to produce it; during the worldwide energy crisis of 1974-75, cement prices went up and prompted companies to look for alternative binders

(Nieminen and Seppänen 1983; cited in Hassani and Archibald 1998). DeGagné (1996) conducted a survey of binder costs at 22 mines in Canada, and these are presented in Table 4-1 below.

Binder	Average cost (\$/ton)	Cost range (\$/ton)	
Portland cement	100	90 to 150	
Slag	85	70 to 95	
Fly ash	60	3 to 105	
W aste glass	65	-1.25 to 93	

Table 4-1 – Comparison of binder costs (DeGagné 1996)

Another study by Hopkins and Beaudry (1989; cited in Hassani and Archibald 1998) compared the cost of binders for a stope with three alternatives; cement only, slag only, and a 50% replacement of cement by slag. Experiments showed that the combined binder would save at least \$50,000 for the said stope.

4.5. TYPES OF BACKFILL

Three types of mine backfill are used in the industry today; slurry or hydraulic fill, paste fill, and rock fill. Each of these methods has its positive and negative aspects and mine operators weigh in the various factors before making a final decision, which is based on site specific and operational requirements. In the following sections, the three types of mine backfill are discussed in detail.

4.5.1. SLURRY OR HYDRAULIC BACKFILL

The slurry type is also known as hydraulic backfill, and it utilizes classified tailings and sand in addition to the binders, with an average pulp density of less than 70%. It was developed in the 1940s and is the most widely used method in the industry today (Landriault 2001). It needs to be transported at relatively high velocities in order to maintain the solids in suspension. Due to the mode of transportation, drainage takes place upon placement and the extra water percolated from the stope needs to be returned to the surface. The classified tailings that form the basis of hydraulic fill are those that contain

less than 20% of 10 μ m particles, and that have percolation rates of 10 cm/hr or more. This is achieved by the use of techniques such as hydrocyclones, thickeners, separators, centrifuges, and filter dewatering devices. The material is also analyzed for the presence of sulphides due to their problematic effects especially in terms of self-heating and self-combustion, and the associated production of sulphide gas.

Great care must be taken with respect to the water level in the stope during the placement of the backfill since it could lead to segregation whereby the finer particles of binder form separate bands and deprive other sections of their cementitious properties (Landriault 2001). Prior to the placement of backfill, it is important for the stope to be prepared for the operation. This depends on the type of stope, which in turn is related to the mining method used. For example, cyclic stopes require an initial preparation followed by cyclic maintenance and adjustment, while non-cyclic ones need preparation only when the stope is completely depleted so as to receive the backfill in one continuous operation. The preparation itself consists of two tasks, viz., the installation of the stope and backfill dewatering system, and the installation of a bulkhead.

Hydraulic fill is typically used in the following mining methods:

- Cut-and-fill: uncemented, used to fill each lift as it is mined
- Drift-and-fill: cemented, used to maintain stable side exposures
- Post-pillar-cut-and-fill: uncemented, used as a working platform and to provide confinement to slender pillars
- Bench-stoping: cemented, used in primary benches and uncemented, where exposure is not required
- Sublevel open-stoping: cemented, used in primary stopes to ensure stable fill when adjacent pillars are mined

4.5.2. PASTE BACKFILL

Paste used in backfill generally consists of a mixture with high solids density and about 15% of particles being smaller than 45 µm. Whereas slurry backfill requires large volumes of water for transportation that need to be decanted or percolated out of the system once placement occurs, the water used in paste backfill lubricates the transport pipeline flow along with the fines particles. Upon placement, water is consumed by cement hydration or the interstitial spaces between the various sized particles, thus eliminating the need for drainage and its associated set-up. Properly prepared paste fill should therefore leave no bleed water (Potvin 2005). Some of the advantages of this type of backfill are the relatively high strengths achieved with comparable cement content due to the presence of fines, a larger usage of tailings materials that would have otherwise been placed in impoundments, a cleaner operation, no segregation inside the pipelines, and an earlier development of high compressive strengths. The disadvantages include the need for better dewatering facilities to produce the paste and higher pressures within the pipelines used for transport. Another point is that unlike hydraulic or rock fill, paste can never be placed underground without a binder due to risks associated with liquefaction (Landriault 2001).

The main component of paste backfill is the full gradation of tailings generated from the mill but could also include sand and gravel. The dewatering techniques are similar to those used in slurry fill preparation but due to the higher solids content, certain modifications must be applied. Therefore, dewatering systems used in paste preparation include thickeners, filters, high density thickeners, cyclones, centrifuges, and the tailspiner, which is a special centrifuge for underground use. It enables the dewatering of hydraulic fill from 60% solids content to 76-84% solids content before mixing it with cement and placing it in the stope (Hassani and Bois 1992; cited in Hassani and Archibald 1998).

The transport mechanism of paste backfill in pipelines is that of a plug, which is applied to materials with higher than 50% solids content, and in which water and fines play the role of a lubricant around the main concentrated mixture (Verkerk and Marcus, 1988; cited in Hassani and Archibald 1998). Hence, they are transported at rates around 0.1 to 1.0 m/s as opposed to slurry fill that is transported at rates of 1.0 to 5.0 m/s. The inclusion of coarser particles has been observed to reduce pressure within the pipelines due to their overall lower surface areas, which tends to free more water to act as a lubricant around the central plug being transported. Interestingly, the presence of pyrite in the tailings has resulted in a higher flow resistance in steel pipes than in plastic ones, but the reasons are not yet completely understood (Landriault et al 1996; cited in Hassani and Archibald 1998).

The quality of paste backfill is measured by its strength and stiffness response. In order to enhance the strength parameters of the tailings used, alluvial sand is sometimes added to the mix, especially when its particle size ranges from fine to medium. From the economical point of view, when compared to slurry and rock fill methods, it can be seen that although paste systems require higher capital costs, they are more economical in the long run due to savings on binders, drainage, clean-up, and distribution costs associated with the other systems (Henderson et al 1997; cited in Hassani and Archibald 1998). A good example of savings on binders is illustrated by tests showing that a slurry fill with 70% solids content would require 9% cement to achieve a strength of 0.7 MPa after 28 days, while a blended paste fill (50% fine tailings and 50% sand) would require only 5% to attain the same strength (Brackebusch 1994; cited in Hassani and Archibald 1998). Another benefit of using paste fill is the reduction of dilution, which occurs when backfill components break and fall into stopes being mined, thus increasing the ratio of waste-to-ore recovery ratio. Henderson et al (1997) report that while a 10% dilution is found in slurry fill systems, paste backfill ones report figures less than 2%.

4.5.3. ROCK FILL

Rock fill consists of waste rock fragments that are mixed with binders either prior or subsequent to placement. Unconsolidated rock fill without binders is sometimes used in cases where the filled stope will not be exposed in the future and where only a passive wall support is needed. Since it exhibits higher strength values than equivalent slurry fills, cemented rock fill is used where large volumes and wall exposures with considerable heights are expected, cases in which the other types would not be economically viable. It is also placed in stopes where mining will take place either next to it or underneath it (Landriault 2001). There are generally four types of rock fill:

- RF: rock fill is made up of sized or unsized waste rock without the addition of binders
- CRF: consolidated rock fill is composed of sized rock fill mixed with 5-6% of cement, which is pumped at 50-60% pulp density, and the final product can provide active wall support
- CSRF: consolidated sand rock fill is the same as CRF with a 5-10% sand content to fill in the voids and provide a denser material
- CSWF: consolidated sand waste fill is used when rock waste is left in the stope after ore extraction, and a sand/cement slurry is poured in to provide consolidation

Many Canadian mines make extensive use of cemented rock fill with no tailings, especially in continuous retreat and pillarless mining operations. One of the reasons is that rock fill – when properly mixed and placed – provides a higher strength value than other types of fill, and it is therefore crucial to have control mechanisms in place in order to provide the highest possible quality of fill with minimal cost. Binder usage, excluding labour, comprises 80-90% of the operating cost of rock fill, and it is only logical that careful assessments are done in advance to optimize the operation. Although laboratory tests are the main evaluation tools, back analysis is also used in operational assessments. One of the disadvantages of this system is its being labour intensive and expensive in terms of operation and binder costs.

4.6. SULPHIDE-RICH TAILINGS IN BACKFILL

The use of sulphide-rich tailings in backfill was briefly alluded to in previous sections of this chapter where their undesirable effects were listed. In general, the study

of the chemical properties of tailings in relation to mine backfill is a relatively recent area of research. Ouellet and Hassani (2002) have conducted research on the chemistry of paste backfill in recent years. They studied the use of paste in backfill operations and discussed case studies where failure of the fill took place. Microscopic analysis indicated the presence of oxidation in the product with gypsum having formed instead of the usual portlandite expected from cement hydration. The authors went on to discuss the relevance of cement and concrete literature to the study of backfill based on the fact that the same materials were used in both cases, and they detailed the various factors and parameters that are crucial for mine backfill. Ouellet et al (1998) have also studied the physical properties of paste backfill in the laboratory as well as in-situ.

The issues specifically associated with sulphides in mine backfill were first brought up by Lukaszewski (1973) who studied the self-cementation of tailings containing pyrrhotite in its ranks. In other references (Lukaszewski 1969 and 1972), he studied the problems associated with sulphides, indicating that the factors involved were still not very well understood. A comprehensive research was conducted with respect to the different characteristics of backfill with high sulphur content by Benzaazoua et al (1999). The authors looked into the chemical processes that take place in backfill due to sulphide oxidation and the associated physical deterioration in strength. They designated the process as sulphate attack and studied the mineralogical changes in the backfill using SEM, detecting iron oxides and gypsum produced by oxidation. Their work confirmed the action of sulphate attack on backfill binders and the deterioration in strength that it caused.

Another study by Benzaazoua et al (2002) looked into the use of different binders in relation to backfill preparation. The authors investigated several types of cement, including the sulphate-resistant one, in addition to pozzolans such as fly ash and slag. The strengths attained by the various mixes gave the best results with the sulphate-resistant ones and the composition of the mixing water was observed to play a crucial role. In relation to controlling acid mine drainage, Bois et al (2005) looked into desulphurized tailings disposal, a process whereby the sulphides in the tailings are taken out using flotation. The interesting part of their work was the potential use of the desulphurized product as a component of paste backfill. Initial results indicated that after undergoing the process, backfill prepared with these tailings gave better strength results than the ones with a full sulphide component.

4.7. CONCLUSIONS

In conclusion, the different types of mine backfill and their usage were discussed in detail in this chapter. Based on developments in technology, the use of paste backfill was seen to be gaining popularity due to its greater use of the tailings gradation and the minimal volume of water that needs to be recycled. However, the work of several authors indicated that the presence of sulphides in tailings could cause certain problems in the final backfill product. They looked into the chemical aspects of oxidation in relation to its reaction with concrete and concluded that sulphate attack could take place in mine backfill in the same manner as it does in concrete. Other authors studied the mineralogical changes associated with backfill incorporating sulphides and noted the presence of ettringite, gypsum, and iron oxides in addition to the absence of normal cement hydration products such as portlandite.

CHAPTER: 5 EXPERIMENTAL PROCEDURE

5.1. INTRODUCTION

In the preceding chapters, a detailed review was conducted on the geochemistry of sulphide-rich tailings, the issue of sulphate attack in concrete, and the use of different types of backfill in mine operations. The objective of this research project was to study the problem of sulphate attack in mine backfill due to the prevalence of sulphide minerals like pyrite in the tailings component. It was noted that sulphide oxidation could lead not only to a sulphate type of attack in backfill, but to an acid type as well. Based on the fact that currently available sulphate attack tests have been deemed inadequate to simulate field conditions, and that even in cases where they do, no direct quantitative measurement is possible, an attempt was made to develop a test method that could meet both these requirements.

5.2. MATERIALS

The materials used in the course of the experimental phase can be divided into three groups; laboratory grade chemicals, cementitious binders obtained from Lafarge, and lab hardware in which the tests were conducted.

5.2.1. CHEMICALS AND SOLUTIONS

Chemicals obtained from commercial suppliers were of laboratory grade quality, and they are listed below with a summary of their role in the experimental phase, whether on their own or in a solution.

5.2.1.1 Deionized water

Laboratory grade deionized water was obtained from a Barnstead Reverse Osmosis System in the Materials Engineering department. Unless otherwise stated, water mentioned in this thesis refers to the deionized type. It constituted the most crucial component of the tests, as it was used for washing, dilution, leaching, and mineral formation.

5.2.1.2 Nitric acid

The nitric acid used was from EMD Chemicals with a normality of 15.7N, and was used primarily in the second stage of the washing process at a 10% dilution with water. It was also used in concentrated form to preserve leach samples.

5.2.1.3 Tricalcium aluminate

The tricalcium aluminate was obtained from A&C American Chemicals, and it was used in the preparation of ettringite in combination with gypsum using Method 2 proposed by Odler and Abdul-Maula (1984) as outlined in upcoming sections.

5.2.1.4 Gypsum

The gypsum used was obtained from A&C American Chemicals in the form of CaSO₄.2H₂O with a molecular weight of 172.17 and a purity of 98-101%.

5.2.1.5 Aluminum sulphate

The aluminum sulphate used was obtained from Fisher Scientific in the form of ACS-certified $Al_2(SO_4)_3.18H_2O$ with a molecular weight of 666.42. It was used in the preparation of ettringite using Method 3 proposed by Odler and Abdul-Maula (1984).

5.2.1.6 Lime

Hydrated lime with a molecular weight of 74.10 was obtained from Aldrich as an ACS reagent with a 95+% purity, and was used in the preparation of ettringite using Method 3.

5.2.1.7 Ethylene glycol

The ethylene glycol [HOCH₂CH₂OH] used was of laboratory grade obtained from EMD Chemicals with a molecular weight of 62.07, and a minimum purity of 99%. It was the main leach component used in combination with methanol for ettringite and gypsum extraction. The ratio used in the tests was either a 3:1 combination of ethylene glycol and methanol, which is abbreviated as EGM 31, or a 1:3 mix abbreviated as EGM 13.

5.2.1.8 Methanol

The methanol [CH₃OH] used was of laboratory grade obtained from EMD Chemicals with a molecular weight of 32.04, and a minimum purity of 99.8%. It was used in combination with ethylene glycol for ettringite and gypsum extraction.

5.2.1.9 Acetone

The acetone [CH₃COCH₃] used was of laboratory grade obtained from Fisher Scientific, with a molecular weight of 58.08. It was used during the grinding process of binder cubes in order to stop the hydration process and to dry the sample.

5.2.1.10 Sodium sulphate

Granular anhydrous sodium sulphate [Na₂SO₄] was used primarily in the preparation of a 4% solution by weight in water for simulating sulphate attack at neutral pH conditions. It was of laboratory grade and obtained from EMD Chemicals with a molecular weight of 142.04 and a purity of 99%.

5.2.1.11 Sulphuric acid

A 36.8N laboratory grade sulphuric acid obtained from Fisher Scientific was used primarily as an acid attack solution at 2% by volume in water. It was of reagent quality, with a molecular weight of 98.075.

5.2.2. CEMENTITIOUS BINDERS

The cementitious binders were all obtained from Lafarge, and included ordinary Portland cement, slag, and fly ash. Their chemical and phase composition as provided by the supplier is given in Table 5-1 below.

Component	Cement	Slag	Fly ash
SiO ₂	20.1	36.1	36.9
Al ₂ O ₃	4.6	10.4	18.3
Fe ₂ O ₃	2.8	0.7	4.6
CaO	64.2	37.1	19.9
MgO	2.3	13.2	4.6
SO3	2.5	3.4	2.8
Free lime	1.1		
C ₃ S	58		
C ₃ A	8		

Table 5-1 – Chemical composition of cementitious binders (in %)

5.2.3. LABORATORY HARDWARE

Laboratory hardware refers to the tools and consumables used in the experimental phase, and they are listed below:

- Horizontal shaker: used for mineral formation and leach tests
- Vacuum pump: used for filtration
- AND electronic balance with a maximum weight of 1000 g and an accuracy of 0.01 g used for large quantities
- Sartorius BP 110S electronic balance with a maximum weight of 110 g and an accuracy of 0.1 mg used for small quantities
- Mini ice-cube trays used as moulds for preparing samples with various binder combinations

- Filter holders and 5.5 cm diameter glass microfiber filters with pores of 0.45 μm
- Pipettes (0.50 to 5.00 ml and 20 to 200 µm) and pipette tips
- Glass pipettes (10 ml and 25 ml) and controller
- Nalgene bottles (60 ml) for extraction
- Nalgene bottles (1 litre) for sulphate attack tests
- Centrifuge tubes (50 ml) for storing leach solutions
- Test tubes (10 ml) for dilutions
- Glass volumetric and vacuum flasks
- Polypropylene wash bottles for water, 10% HNO₃, acetone, and EGM solutions
- Two sets of ceramic mortar and pestle for grinding
- Stainless steel trays for partial immersion sulphate attack tests

5.3. INSTRUMENTATION

Analysis for various solid and liquid samples was conducted with a variety of instruments in different departments. They are briefly described below with a short mention of their role in the experimental phase.

5.3.1. X-RAY DIFFRACTION

XRD was conducted in the Materials Engineering department with a Philips PW-1710 diffractometer with a copper tube anode, which was run at 40 kV and 20 mA from a 2 θ angle of 5° to 40° with a step size of 0.01 2 θ and a scan step time of 0.5 seconds. XRD was used to identify crystalline phases in ettringite samples and the cementitious binders prior to and after their being subjected to sulphate or acid attack.

5.3.2. ATOMIC ABSORPTION

Atomic absorption was conducted briefly on leach samples to measure aluminum concentrations. The instrument was a Varian AA240FS fast sequential atomic absorption spectrometer in the Materials Engineering department. Its application was discontinued due to its inability to detect aluminum below a concentration of 10 ppm, and the role was taken up by an inductively-coupled plasma optical emission spectrometer (ICP-OES).

5.3.3. ION CHROMATOGRAPHY

Ion chromatography was conducted using a Dionex DX-100 ion chromatograph in the Materials Engineering department. Its primary function was to measure sulphate $[SO_4^{2^-}]$ concentrations in leach solutions. Although successful, the required 15-minute elution time per sample and the fact that it could only measure the element in sulphate form did not suit well with the objectives of the experiment. Its use was eventually discontinued in favour of the ICP-OES.

5.3.4. ICP-OES

The instrument adopted was a Thermo TraceScan ICP-OES in the Chemical Engineering department and it was used for measuring aluminum and sulphur concentrations simultaneously in leach solutions. Fresh standards for both elements were prepared using a 10% EGM 31 (diluted in water) solution to better correlate with the samples being tested.

5.4. METHODOLOGY

The methodology followed during the course of the research project was broadly divided into two phases. Phase I comprised ettringite preparation using two methods

outlined by Odler and Abdul-Maula (1984) and Lafarge Canada (1995), and leach tests on ettringite, gypsum, Portland cement, slag, and fly ash using water, EGM 31, and EGM 13 as the extracting solutions. In addition, these components were characterized using XRD analysis. Phase II comprised the preparation of four binders using Portland cement, slag, and fly ash in different combinations, their curing at 50°C for 7 days, and their immersion in solutions simulating sulphate and acid attack. Subsequent to immersion, and based on the results of Phase I, they were leached with the EGM 31 solution in order to quantify the amount of ettringite and gypsum formed. The details of these experiments are covered in the following sections.

Regardless of the experimental phase being conducted, certain procedures were followed at all times to ensure lab safety and a high quality in all segments of the research project, the details of which are given in the paragraphs below.

5.4.1. WASHING PROCEDURE

New centrifuge tubes and reaction bottles delivered in a sealed package were used during the different parts of the experimental phase to ensure quality results. New leach bottles and filter holders were used for the first tests but were subsequently washed prior to use in others due to economical reasons. Similarly, wash bottles, glassware, and mortar and pestles were all washed prior to each use, and dried with laboratory grade paper towels. All washing of lab equipment consisted of the following three steps:

- Detergent and tap water wash to take out particulate matter, followed by rinsing
- Rinsing with 10% nitric acid solution to dissolve and leach out chemical impurities
- Rinsing thrice with deionized water to get rid of nitric acid droplets

5.4.2. WEIGHING AND VOLUME MEASUREMENT

Two balances were used in the weighing of different samples. The first one was an AND FP-6200 electronic balance with a maximum weight of 1000 g and an accuracy of 0.01 g, and it was used for bulk measurements such as ettringite preparation during Phase I or binder combinations in Phase II when weights in excess of 500 g were involved. The second balance was a Sartorius BP 110S with a maximum weight of 110 g and an accuracy of 0.1 mg, and it was used for all other applications such as weighing of cured samples to be used with leach solutions.

Regarding large volumetric measurements, all solutions and mixtures were prepared with specific calibrated flasks to ensure high quality results. This was applied in the preparation of EGM 31, sulphate and acid attack, and nitric acid solutions. In those cases where small volumes were involved, calibrates pipettes with tips or controllers were used, such as in the case of preparing 1:10 dilutions of sample leachates.

5.4.3. QUALITY ASSURANCE – QUALITY CONTROL

Due to the desired accuracy and precision in the research project, the quantitative segments of Phases I and II were conducted in triplicate. For example, initial leach tests on ettringite and gypsum used three points per sample per weight-to-volume ratio. In a similar manner, subsequent tests on cured binders used three cubes per binder per period of curing. The reported values in the coming sections are therefore the average of the triplicate values. Furthermore, chemical analysis was also conducted on a blank control to ensure that no contamination had taken place during the various stages of sample preparation.

5.4.4. SAMPLE ACIDIFICATION AND STORAGE

Leach samples using water, EGM 31, or EGM 13 solutions were immediately acidified with 1-2% (by volume) concentrated nitric acid, and stored in a fridge at 4°C to preserve them until such time as elemental analysis could be conducted. The procedure is an international standard for preserving metals in solutions (SMO 1992, Reeve 2002).

5.4.5. FUMEHOOD

All procedures involving the use of chemicals such as acids or organics and the preparation of solutions were conducted under a fume-hood to ensure proper ventilation and to prevent the inhalation of harmful gases. In addition, the containers of samples undergoing sulphate attack solutions were stored under the fume-hood during the entire period of experimentation.

5.4.6. PH MEASUREMENT

The pH of sulphate attack solutions during Phase II was monitored using a Multiline P4 meter with a SenTix 41 probe for pH and temperature (accuracy of 0.01 ± 1 digit). In order to ensure quality, the meter was calibrated with standard solutions of pH 7 and 10 on a weekly basis.

5.5. PHASE I – TESTS ON MINERALS

Phase I of the research project comprised the formation of ettringite using two methods outlined by Odler and Abdul-Maula (1984) and Lafarge Canada (1995). The objective of this phase was to conduct leach tests on the two types of ettringite formed, in addition to gypsum, tricalcium aluminate, aluminum sulphate, Portland cement, slag, and fly ash. The leach solutions used were water (as a control), EGM 31 (3:1 combination of ethylene glycol and methanol) and EGM 13 (1:3 combination of the same), and the purpose was to verify that the EGM leach method reported by several researchers (Odler and Abdul-Maula 1984, Uchikawa and Uchida 1974, and Bernier et al 1999) was able to completely and exclusively dissolve ettringite but not the other phases in hydrated cement pastes.

As specified in this method, the leaching procedure would be followed by the measurement of aluminum extracted and the subsequent calculation of ettringite from stoichiometry. In addition, the optimum ratio of ettringite to leach solution in the literature was set to be 20 mg to 200 to 300 ml without specifying the effect of other

ratios on the results. A second purpose, therefore, was to investigate the relationship between the ettringite-to-solution ratio and the final readings. A third objective was to determine the amount of gypsum that different solutions were able to dissolve to study the potential of using sulphur measurement – in addition to that of aluminum – for a simultaneous determination of gypsum and ettringite amounts. In connection with this last objective, tricalcium aluminate, aluminum sulphate, Portland cement, slag, and fly ash were all leached to determine their solubility in EGM 31 at different ratios in order to check for any aluminum or sulphur readings that could originate from the non-reacted portions of these components in the cured samples.

5.5.1. GYPSUM LEACHING

Since it is the second mineral formed by sulphate attack, gypsum was leached in addition to ettringite to better understand its contribution to solutions when extracted alongside the main mineral. Based on the work of Odler and Abdul-Maula (1984), the EGM solution is observed to also extract gypsum, though not completely. Their reported value was 69.6% dissolution in EGM 31 when extracted for 30 minutes at a weight of 200 mg in 300 ml solution. The objective of gypsum leaching was, therefore, to confirm this result at a weight-to-volume ratio of 0.67, and to verify its dissolution percentage at other ratios, for different times of extraction, and in different solutions. The ultimate goal was to see if the sulphate measurement could help in determining the amount of gypsum in the mix after ettringite was assessed from the aluminum values. A rapid simultaneous determination of both ettringite and gypsum in sulphate attack samples would be a powerful tool in evaluating the resistance of different binders. Gypsum leaching was conducted in several batches to test the different variables involved, the details of which are given in the sections below. Characterization was also done with XRD in order to provide a basis of comparison with the hydrated binders in Phase II.

5.5.1.1 Batch 1

The first batch of leach tests on gypsum was conducted using the EGM 31 and 13 solutions. The samples were weighed on the Sartorius balance and put into 50 ml tubes

along with 20 ml of solution using a glass pipette and its controller. A weight-to-volume ratio of 1 was used in this initial batch, and the details are given in Table 5-2 below.

 Table 5-2 – Details of Batch 1 tests on gypsum

Sample ID	Wt (g)	Nt (g) Vol (l)		W:V	Extract
G 1:10	0.0192	0.02	EGM 13	0.9617	2 hrs
G 1:100	0.0206	0.02	EGM 31	1.0317	2 hrs

The tubes were agitated on the horizontal shaker for 2 hours before they were centrifuged for 10 minutes. Dilutions of 1:100 were initially made by adding 101 μ m solution to 10 ml water but 1:10 dilutions were also prepared by mixing 0.5 ml of sample with 4.5 ml water. No acidification was done due to its interference with the IC, which was used for sulphate measurement.

5.5.1.2 Batch 2

A second batch of tests was performed on gypsum using EGM 31 and 13. Its purpose was to verify the dissolution rate at various weight-to-volume ratios. The samples were weighed on the Sartorius balance, the details of which are given in Table 5-3 below, and 20 ml was added to the tubes using a glass pipette and its controller.

Sample ID	Wt (g)	Vol (I)	Leach	W:V	Extract
G 1-3	0.0113	0.02	EGM 13	0.57	2 hrs
G 4-6	0.0208	0.02	EGM 13	1.04	2 hrs
G 7-9	0.0303	0.02	EGM 13	1.52	2 hrs
G 10-12	0.0099	0.02	EGM 31	0.50	2 hrs
G 13-15	0.0200	0.02	EGM 31	1.00	2 hrs
G 16-18	0.0300	0.02	EGM 31	1.50	2 hrs

Table 5-3 – Details of Batch 2 tests on gypsum

Extraction was done on the horizontal shaker for 1 hour, followed by 10 minutes of centrifugation. Dilutions of 1:10 were prepared by mixing 1 ml of sample with 9 ml of water, and sulphate analysis was conducted by IC.

5.5.1.3 Batch 3

A third batch of tests was performed on gypsum using EGM 31 and 13, and the purpose was to assess its dissolution using ICP-OES for the first time instead of the IC, which took 15 minutes per sample for analysis. Furthermore, this technique was able to analyze the total sulphur content instead of only the sulphate anion $[SO_4^{2^-}]$. Samples were weighed on the Sartorius balance and placed into 50 ml tubes for an intended weight-to-volume ratio of 1, and their numbers presented in Table 5-4 below.

Table 5-4 – Details of Batch 3 tests on gypsum

Sample ID	Wt (g)	Vol (I)	Leach	W:V	Extract
G 13	0.0200	0.02	EGM 13	1.00	1 hr
G 31	0.0215	0.02	EGM 31	1.07	1 hr

A 20 ml solution was added to each tube using a glass pipette and its controller, and they were agitated on the horizontal shaker for 1 hour. The supernatants were separated by 10 minutes of centrifugation, and 1:10 dilutions were prepared by mixing 1 ml of sample with 9 ml of water. Analysis was conducted by ICP-OES.

5.5.1.4 Batch 4

The fourth batch of tests was done simply to verify the dissolution of gypsum in EGM 31, 13, and water at a weight-to-volume ratio of 1. Samples were weighed on the Sartorius balance (see Table 5-5), placed in 50 ml tubes, and 20 ml solution was added with the glass pipette and its controller.

Table 5-5 –	Details of	of Batch 4	tests on	gypsum
1 4010 0 0	2 counts v	or Batten i		5 , P , a , b

Sample ID	Wt (g)	Vol (I) Leach		W:V	Extract
G 13	0.0214	0.02	EGM 13	1.07	1 hr
G 31	0.0205	0.02	EGM 31	1.02	1 hr
G W	0.0201	0.02	Water	1.01	1 hr

After 1 hour of extraction on the shaker, the tubes were centrifuged for 10 minutes, and dilutions of 1:10 were prepared by mixing 1 ml sample with 9 ml of water.

The samples were acidified with $200 \,\mu m$ nitric acid in this case as it did not interfere with the ICP instrument, with which they were analyzed.

5.5.1.5 Batch 5

The fifth batch of tests on gypsum was conducted in order to assess its dissolution at three weight-to-volume ratios with the ICP-OES technique, using EGM 31 and water as the leach solutions. Samples were weighed on the Sartorius balance and placed into new 60 ml Nalgene bottles to which 50 ml of solution was added with a glass pipette and its controller (Table 5-6).

Sample ID	Wt (g)	Vol (I) Leach		W:V	Extract
G 31	0.0253	0.05	EGM 31	0.51	1 hr
G 31	0.0500	0.05	EGM 31	1.00	1 hr
G 31	0.1247	0.05	EGM 31	2.49	1 hr
G DI	0.0254	0.05	Water	0.51	1 hr
G DI	0.0498	0.05	Water	1.00	1 hr
G DI	0.1247	0.05	Water	2.49	1 hr

Table 5-6 – Details of Batch 5 tests on gypsum

This was the first time that these small bottles were used for leaching gypsum, and they would become the standard from this point onwards due to their relatively small size and ability to hold 50 ml solution with room for liquid circulation. Extraction was done on the horizontal shaker for 1 hour after which the liquid portion was separated directly into a 50 ml tube with a 0.45 μ m glass microfiber filter paper using a technique explained in more detail in Section 5.5.3.8 below. This was the first time that filtration, instead of centrifugation, was used for gypsum extraction and it was important to establish its dissolution fundamentals with this technique, seeing that it would be the adopted one for experiments in Phase II.

5.5.1.6 Batch 6

The sixth and final batch of tests on gypsum was conducted to evaluate its dissolution in EGM 31 at variable weight-to-volume ratios. The samples were weighed

with the Sartorius balance and placed into 60 ml bottles to which 50 ml solution was added using a calibrated volumetric tube (Table 5-7).

Sample ID	Wt (g)	Vol (l)	Vol (I) Leach		Extract
G 31	0.0253	0.05	EGM 31	0.51	1 hr
G 31	0.0500	0.05	EGM 31	1.00	1 hr
G 31	0.1247	0.05	EGM 31	2.49	1 hr
G DI	0.0254	0.05	Water	0.51	1 hr
G DI	0.0498	0.05	Water	1.00	1 hr
G DI	0.1247	0.05	Water	2.49	1 hr

Table 5-7 – Details of Batch 6 tests on gypsum

They were placed on the horizontal shaker for 1 hour and filtered on 0.45 μ m glass microfiber filter papers and into 50 ml tubes. Dilutions of 1:10 were made by mixing 0.5 ml of solution with 4.5 ml water, and they were acidified with 100 μ m acid.

5.5.2. ETTRINGITE FORMATION

Ettringite was formed using two different methods presented by Odler and Abdul-Maula (1984) and confirmed by Lafarge Canada (1995). These two were chosen out of four methods outlined in their work due to the relatively short period of time required, and the simplicity of the preparation techniques. Based on the nomenclature used in the article, these methods were designated as 2 and 3 and the products were similarly labelled as Ettringite 2 and Ettringite 3, respectively. For quality purposes, each type of ettringite was formed three times using different weights and volumes, and the labels were further modified to read Ettringite 2A, 2B, 2C and Ettringite 3A, 3B, and 3C.

5.5.2.1 Ettringite 2

Ettringite was initially formed using Method 2 by adding 2.70 g of C_3A and 5.17 g of gypsum (weighed on the AND balance) into a 1-liter Nalgene jar. The two powders were mixed thoroughly before 500 ml water was slowly added to them. The jar was capped and placed on a rotary mixer for 72 hours to provide constant agitation. After the required time had elapsed, the solution was filtered on a 0.45 μ m glass microfiber filter

paper using a vacuum pump and a flask. The filtered cake was moved into a ceramic mortar and ground lightly in acetone to stop the reactions. It was allowed to dry under the fume-hood for a few days, and the powder was placed in a 60 ml polypropylene bottle. The minerals present in the product were verified using XRD, and it was labelled Ettringite 2A.

A second batch was prepared using 5.40 g of C_3A and 10.35 g of gypsum (weighed on the AND balance) in 1 litre of water in a Nalgene jar. The solution was agitated on a horizontal shaker for 72 hours (Figure 5-1) before being filtered on a 0.45 µm glass microfiber filter paper using a vacuum pump and a flask. The resultant cake was drenched in acetone and placed under a vacuumed desiccator for two months to dry. It was then crushed lightly and placed in capped bottles for storage. The product was analyzed using XRD, and it was labelled Ettringite 2B.



Figure 5-1 – Ettringite formation on the horizontal shaker

A third and final batch was prepared using 2.7017 g of C_3A and 5.1650 g of gypsum (weighed on the Sartorius balance) in 250 ml water in a Nalgene jar. The solution was shaken horizontally for 72 hours and filtered on a 0.45 µm glass microfiber filter paper. It was then drenched in acetone and put under the fume-hood to dry for a few days. No XRD analysis was conducted on this sample due to the repetitiveness of the formation process and the verifications obtained from the previous two attempts. The batch was designated as Ettringite 2C.

5.5.2.2 Ettringite 3

An initial batch of ettringite was formed using Method 3 by combining 4.45 g of lime with 6.68 g of aluminum sulphate (weighed on the AND balance) in a Nalgene jar. The powders were well mixed in dry form before 500 ml water was added. The solution was placed on a rotary shaker for 48 hours to complete the reaction. It was then filtered on a 0.45 μ m glass microfiber filter paper with a vacuum pump and flask. The cake was put in a ceramic bowl and drenched in acetone before being allowed to dry under the fume-hood for a few days. The dried cake was placed in a 60 ml polypropylene bottle and labelled Ettringite 3A, and its contents were verified with XRD analysis.

A second batch of Ettringite 3 was produced by mixing 8.90 g of lime with 13.35 g of aluminum sulphate (weighed on the AND balance) in a Nalgene jar, to which 1 litre of water was added. The solution was placed on a horizontal shaker for 48 hours before being filtered on a 0.45 µm glass microfiber filter paper with a vacuum pump and flask. The product was drenched in acetone and left to dry under a vacuumed desiccator for two months. It was then allowed to dry under the fume-hood for a few days since it was still somewhat moist after coming out of the desiccator. After being lightly crushed, it was stored in a bottle, labelled Ettringite 3B, and analyzed by XRD.

A final batch was prepared by mixing 2.2217 g of lime with 3.3317 g of C_3A (weighed on the Sartorius balance) and 250 ml water. The solution was horizontally shaken for 48 hours, and filtered on a 0.45 µm glass microfiber filter paper. It was then drenched in acetone and put under the fume-hood for a few days to dry. The powder was stored in a bottle and labelled Ettringite 3C, and no XRD analysis was conducted on it.

5.5.3. ETTRINGITE LEACHING

The ettringite produced by Methods 2 and 3 on different occasions were leached several times using water, EGM 31, and EGM 13 as the extracting solutions. The leaching was conducted for 1 or 2 hours on a horizontal shaker at different weight-to-volume ratios, and using varying weights and extracting vessels. The purpose of these

tests was to confirm the amount of ettringite formed in the six batches outlined above, and to assess the role of extraction time and ratio on the results. The leach tests were carried out in several batches and these are listed below with their specific conditions. It should be noted that the tables given in this chapter present the average values obtained from testing the batches in triplicate, and that this method of presentation has been adopted to circumvent lengthy tabulations and to present the crucial numbers in a concise manner.

5.5.3.1 Batch 1

The first batch of leach tests was conducted on samples of Ettringite 2B and 3B using a 3:1 proportion of ethylene glycol and methanol. The samples were weighed on the Sartorius electronic balance and placed in a 50 ml centrifuge tube, to which 40 ml of EGM 31 was added with a glass pipette and its controller. The details are presented in Table 5-8 and include the weight-to-volume ratio for each sample.

Sample ID	Туре	Wt (g)	Vol (I)	Leach	W:V	Extract
Ett 20.2	2B	0.1997	0.04	EGM 31	4.99	2 hrs
Ett 2 0.5	2B	0.5015	0.04	EGM 31	12.54	2 hrs
Ett 2 1.0	2B	0.9992	0.04	EGM 31	24.98	2 hrs
Ett 3 0.2	3B	0.2014	0.04	EGM 31	5.03	2 hrs
Ett 3 0.5	3B	0.5004	0.04	EGM 31	12.51	2 hrs
Ett 3 1.0	3B	0.9988	0.04	EGM 31	24.97	2 hrs

Table 5-8 – Details of Batch 1 tests on ettringite

The tubes were placed on a horizontal shaker for 2 hours and the liquid was separated by centrifugation for 10 minutes. The supernatants were stored in new tubes and two different sets of dilutions of 1:10 were prepared by mixing 2 ml of sample with 18 ml of water and 1 ml of sample with 9 ml of water, respectively, with the aid of pipettes. The reason for this duplication was that the first dilution was acidified with 200 µm nitric acid to preserve the metal component for analysis on the AA spectrometer. The second dilution was for sulphate analysis on the IC, and no acidification could be done lest it damaged the machine. In addition, dilutions of 1:100 were prepared from the 1:10 dilutions for the 0.5 g and 1 g samples in case the latter proved to be too concentrated for

the instruments to measure. All samples were analyzed on the AA spectrometer for aluminum content and for sulphate on the IC after freshly prepared standards for both were analyzed by the respective instruments.

5.5.3.2 Batch 2

A second batch of leach tests was conducted on ettringite samples 2A and 3A using EGM 31 and EGM 13 solutions. Samples were weighed on the Sartorius electronic balance and placed into 50 ml centrifuge tubes with 20 ml of solution placed with a glass pipette and a controller. The weight-to-volume ratio for all samples was kept at 1 and the objective was to study the difference between the EGM 13 and 31 solutions on the extraction of ettringite. Sample details are given in Table 5-9 below.

Table 5-9 – Details of Batch 2 tests on ettrin	gite
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Sample ID	Туре	Wt (g)	Vol (l)	Leach	W:V	Extract
Ett II 1:10	2A	0.0212	0.02	EGM 13	1.06	2 hrs
Ett II 1:10	2A	0.0199	0.02	EGM 31	0.99	2 hrs
Ett III 1:10	3A	0.0209	0.02	EGM 13	1.04	2 hrs
Ett III 1:10	3A	0.0200	0.02	EGM 31	1.00	2 hrs

The tubes were placed on a horizontal shaker for 2 hours after which they were centrifuged for 10 minutes. Dilutions of 1:10 were prepared by adding 0.5 ml of the sample to 4.5 ml water, and of 1:100 by adding 101 μ m of supernatant to 10 ml solution. They were analyzed for aluminum and sulphate using the AA and IC, respectively.

5.5.3.3 Batch 3

A third batch of tests was conducted on Ettringite 2C and 3C using EGM 13 and 31 solutions. Samples were weighed on the Sartorius balance and placed into 50 ml tubes to which 20 ml of solution was added with a glass pipette and its controller. The details are given in Table 5-10 below.

Sample ID	Туре	Wt (g)	Vol (I)	Leach	W:V	Extract
Ett2 1:10	2C	0.0102	0.02	EGM 13	0.51	2 hrs
Ett2 1:10	2C	0.0201	0.02	EGM 13	1.00	2 hrs
Ett2 1:10	2C	0.0302	0.02	EGM 13	1.51	2 hrs
Ett2 1:10	2C	0.0101	0.02	EGM 31	0.50	2 hrs
Ett2 1:10	2C	0.0202	0.02	EGM 31	1.01	2 hrs
Ett2 1:10	2C	0.0305	0.02	EGM 31	1.52	2 hrs
Ett3 1:10	3C	0.0106	0.02	EGM 13	0.53	2 hrs
Ett3 1:10	3C	0.0202	0.02	EGM 13	1.01	2 hrs
Ett3 1:10	3C	0.0305	0.02	EGM 13	1.53	2 hrs
Ett3 1:10	3C	0.0105	0.02	EGM 31	0.53	2 hrs
Ett3 1:10	3C	0.0204	0.02	EGM 31	1.02	2 hrs
Ett3 1:10	3C	0.0308	0.02	EGM 31	1.54	2 hrs

Table 5-10 – Details of Batch 3 tests on ettringite

After 2 hours of extraction, the solutions were centrifuged for 10 minutes and dilutions of 1:10 were prepared by adding 1 ml of solution to 9 ml of water. These samples were analyzed for aluminum using the AA spectrometer and for sulphate using the IC, with acidification done after the IC analysis using 200 μ m of nitric acid. It was the last batch where separate instruments were used to measure the amount of aluminum and sulphur. Due to the inability of the AA spectrometer in detecting aluminum concentrations below 10 ppm in the 1:10 dilutions or in measuring the original solutions due to their concentrated organic content, it was decided to use an ICP-OES from this point onwards to simultaneously measure the aluminum and total sulphur – and not just sulphate – contents in the samples.

5.5.3.4 Batch 4

The fourth batch of tests was conducted on Ettringite 2B and 3B samples using EGM 31 and 13 as the leach solutions. The main objective of this batch was to test the new ICP-OES technique and its ability to replace the combined AA and IC analysis that had been used so far. A second objective was to attempt the reduction of the extraction time from 2 hours to 1 hour. Samples were weighed on the Sartorius balance and placed into 50 ml tubes to which 20 ml of EGM 31 or 13 solutions was added using a pipette and controller. Only a weight-to-volume ratio of 1 was used in this batch, and the sample details are presented in Table 5-11 below.

Sample ID	Туре	Wt (g)	Vol (l)	Leach	W:V	Extract
Ett 2 1:10	2B	0.0205	0.02	EGM 13	1.02	1 hr
Ett 2 1:10	2B	0.0208	0.02	EGM 31	1.04	1 hr
Ett 3 1:10	3B	0.0209	0.02	EGM 13	1.04	1 hr
Ett 3 1:10	3B	0.0197	0.02	EGM 31	0.98	1 hr

Table 5-11 – Details of Batch 4 tests on ettringite

They were then extracted for 1 hour on the horizontal shaker and separated from the solids by centrifuging for 10 minutes. Dilutions of 1:10 were prepared by mixing 1 ml of solution with 9 ml of water, and the samples were tested for aluminum and sulphur using the ICP-OES without acidification. Samples from batch 3 were also tested with the machine for comparison purposes.

5.5.3.5 Batch 5

The fifth batch of tests was done on all ettringite samples comprising 2A, 2B, 2C, 3A, 3B, and 3C in order to determine the percentage of the mineral in each one. The results of previous batches had indicated that although the same technique was used for their formation, the amount of ettringite yield within a given method was different based on whether it was designated as A, B, or C. Another purpose of this test was to determine the ability of water – in addition to EGM 31 and 13 – to dissolve the ettringite samples formed in the laboratory knowing that this mineral's reported K_{sp} value in the literature is -44.9 \pm 0.32 (Perkins and Palmer 1999), which translates into a solubility of 0.31 g/l in water. For this purpose, only a weight-to-volume ratio of 1 was used in this batch.

Samples were weighed on the Sartorius balance and placed into 50 ml tubes with 20 ml of leach solution introduced by pipette and controller. The details are presented in Table 5-12 below. They were extracted on the horizontal shaker for 1 hour and were then separated using the centrifuge for 10 minutes. Dilutions of 1:10 were prepared by mixing 1 ml of solution with 9 ml of water, and they were acidified with 200 µm nitric acid. The aluminum and sulphur contents were measured with the ICP-OES.

Sample ID	Туре	Wt (g)	Vol (I)	Leach	W:V	Extract
Ett2A 13	2A	0.0206	0.02	EGM 13	1.03	1 hr
Ett2A 31	2A	0.0206	0.02	EGM 31	1.03	1 hr
Ett2A water	2A	0.0207	0.02	Water	1.03	1 hr
Ett2B 13	2B	0.0198	0.02	EGM 13	0.99	1 hr
Ett2B 31	2B	0.0209	0.02	EGM 31	1.04	1 hr
Ett2B water	2B	0.0203	0.02	Water	1.02	1 hr
Ett2C 13	2C	0.0197	0.02	EGM 13	0.98	1 hr
Ett2C 31	2C	0.0201	0.02	EGM 31	1.01	1 hr
Ett2C water	2C	0.0198	0.02	Water	0.99	1 hr
Ett3A 13	3A	0.0202	0.02	EGM 13	1.01	1 hr
Ett3A 31	3A	0.0205	0.02	EGM 31	1.02	1 hr
Ett3A water	3A	0.0202	0.02	Water	1.01	1 hr
Ett3B 13	3B	0.0200	0.02	EGM 13	1.00	1 hr
Ett3B 31	3B	0.0204	0.02	EGM 31	1.02	1 hr
Ett3B water	3B	0.0201	0.02	Water	1.01	1 hr
Ett3C 13	3C	0.0197	0.02	EGM 13	0.99	1 hr
Ett3C 31	3C	0.0204	0.02	EGM 31	1.02	1 hr
Ett3C water	3C	0.0202	0.02	Water	1.01	1 hr

Table 5-12 – Details of Batch 5 tests on ettringite

5.5.3.6 Batch 6

A sixth batch of leach tests was conducted on Ettringite 2B and 3B, seeing that they comprised the best readings amongst the three sets formed, with water, EGM 31 and 13 as the leach solutions. Furthermore, in order to check for potential errors on samples of smaller weight, the extraction vessels used in this batch were larger 250 ml bottles. In keeping the same ratios, a larger weight would be needed with an increase in volume and a check for errors due to smaller weights would be possible. The samples were weighed on the Sartorius balance and placed into the bottles with 50 ml of solution, the details of which are give in Table 5-13.

Extraction was done on a horizontal shaker for 1 hour and supernatant separation was achieved with 0.45 μ m glass microfiber filter papers. From this point onwards, filtration was used as the principle method of supernatant separation due to its superiority to centrifugation in terms of time required, effectiveness, and practicality. The centrifuge available was designed for holding 50 ml tubes only, thus limiting the volume of leach solutions and affecting the weight of the sample due to weight-to-volume requirements.

After the filtration process, 1:10 dilutions were prepared by mixing 1 ml of solution with 9 ml of water, and they were acidified with 200 µm nitric acid.

Sample ID	Туре	Wt (g)	Vol (l)	Leach	W:V	Extract
E2B 13 1	2B	0.0049	0.05	EGM 13	0.10	1 hr
E2B 13 2	2B	0.0151	0.05	EGM 13	0.30	1 hr
E2B 13 3	2B	0.0250	0.05	EGM 13	0.50	1 hr
E2B 13 4	2B	0.0357	0.05	EGM 13	0.71	1 hr
E2B 31 1	2B	0.0059	0.05	EGM 31	0.12	1 hr
E2B 31 2	2B	0.0150	0.05	EGM 31	0.30	1 hr
E2B 31 3	2B	0.0246	0.05	EGM 31	0.49	1 hr
E2B 31 4	2B	0.0347	0.05	EGM 31	0.69	1 hr
E2B W 1	2B	0.0055	0.05	Water	0.11	1 hr
E2B W 2	2B	0.0145	0.05	Water	0.29	1 hr
E2B W 3	2B	0.0258	0.05	Water	0.52	1 hr
E2B W 4	2B	0.0346	0.05	Water	0.69	1 hr
E3B 13 1	3B	0.0058	0.05	EGM 13	0.12	1 hr
E3B 13 2	3B	0.0154	0.05	EGM 13	0.31	1 hr
E3B 13 3	3B	0.0245	0.05	EGM 13	0.49	1 hr
E3B 13 4	3B	0.0350	0.05	EGM 13	0.70	1 hr
E3B 31 1	3B	0.0047	0.05	EGM 31	0.09	1 hr
E3B 31 2	3B	0.0157	0.05	EGM 31	0.31	1 hr
E3B 31 3	3B	0.0251	0.05	EGM 31	0.50	1 hr
E3B 31 4	3B	0.0354	0.05	EGM 31	0.71	1 hr
E3B W 1	3B	0.0050	0.05	Water	0.10	1 hr
E3B W 2	3B	0.0151	0.05	Water	0.30	1 hr
E3B W 3	3B	0.0246	0.05	Water	0.49	1 hr
E3B W 4	3B	0.0356	0.05	Water	0.71	1 hr

Table 5-13 – Details of Batch 6 tests on ettringite

5.5.3.7 Batch 7

Based on the results of the sixth batch, it was decided to establish the behaviour of ettringite dissolution in water. Therefore, a seventh batch of tests was done on ettringite 2A, 2B, 3A and 3B using large samples weights and liquid volumes in order to minimize the errors inherent in the use of smaller values. Samples were weighed on the Sartorius balance and placed into 250 ml bottles to which 200 ml of water was added. The details are presented in Table 5-14 below. The bottles were placed on the horizontal shaker for 1 hour and the supernatant was extracted using 0.45 µm glass microfiber filter papers. A 50 ml portion of each sample was stored in tubes and acidified with 1 ml nitric acid, and they were analyzed for aluminum and sulphur with the ICP-OES.
Sample ID	Туре	Wt (g)	Vol (l)	Leach	W:V	Extract
E2A 0.075	2A	0.0750	0.20	Water	0.38	1 hr
E2A 0.125	2A	0.1244	0.20	Water	0.62	1 hr
E2A 0.140	2A	0.1407	0.20	Water	0.70	1 hr
E2A 0.150	2A	0.1506	0.20	Water	0.75	1 hr
E2A 0.160	2A	0.1606	0.20	Water	0.80	1 hr
E2A 0.200	2A	0.2009	0.20	Water	1.00	1 hr
E2A 0.250	2A	0.2504	0.20	Water	1.25	1 hr
E2A 0.300	2A	0.3003	0.20	Water	1.50	1 hr
E3A 0.025	3A	0.0255	0.20	Water	0.13	1 hr
E3A 0.050	3A	0.0494	0.20	Water	0.25	1 hr
E3A 0.070	3A	0.0700	0.20	Water	0.35	1 hr
E3A 0.075	3A	0.0755	0.20	Water	0.38	1 hr
E3A 0.080	3A	0.0796	0.20	Water	0.40	1 hr
E3A 0.100	3A	0.1010	0.20	Water	0.51	1 hr
E3A 0.150	3A	0.1506	0.20	Water	0.75	1 hr
E3A 0.200	3A	0.2015	0.20	Water	1.01	1 hr
E2B 0.075	2B	0.0756	0.20	Water	0.38	1 hr
E2B 0.150	2B	0.1503	0.20	Water	0.75	1 hr
E2B 0.165	2B	0.1665	0.20	Water	0.83	1 hr
E2B 0.175	2B	0.1742	0.20	Water	0.87	1 hr
E2B 0.185	2B	0.1848	0.20	Water	0.92	1 hr
E2B 0.225	2B	0.2254	0.20	Water	1.13	1 hr
E2B 0.250	2B	0.2499	0.20	Water	1.25	1 hr
E2B 0.300	2B	0.2999	0.20	Water	1.50	1 hr
E3B 0.010	3B	0.0098	0.20	Water	0.05	1 hr
E3B 0.025	3B	0.0259	0.20	Water	0.13	1 hr
E3B 0.050	3B	0.0504	0.20	Water	0.25	1 hr
E3B 0.075	3B	0.0744	0.20	Water	0.37	1 hr
E3B 0.100	3B	0.1007	0.20	Water	0.50	1 hr
E3B 0.120	3B	0.1207	0.20	Water	0.60	1 hr
E3B 0.125	3B	0.1267	0.20	Water	0.63	1 hr
E3B 0.130	3B	0.1308	0.20	Water	0.65	1 hr
E3B 0.150	3B	0.1522	0.20	Water	0.76	1 hr
E3B 0.175	3B	0.1750	0.20	Water	0.88	1 hr
E3B 0.200	3B	0.2002	0.20	Water	1.00	1 hr

Table 5-14 - Details of Batch 7 tests on ettringite

5.5.3.8 Batch 8

The eighth batch of leach tests concentrated on Ettringite 3B as it proved to have the highest yield of the mineral amongst the Method 3 samples. EGM 31 and water were used as the leach solutions based on the results of the former batches in which the further use of EGM 13 was not deemed to be of further interest. The samples were weighed on the Sartorius balance and placed into 250 ml bottles to which 50 ml of solution was added, the details of which are given in Table 5-15 below.

Sample ID	Туре	Wt (g)	Vol (I)	Leach	W:V	Extract
E3B W	3B	0.0049	0.05	Water	0.10	1 hr
E3B W	3B	0.0152	0.05	Water	0.30	1 hr
E3B W	3B	0.0306	0.05	Water	0.61	1 hr
E3B W	3B	0.0504	0.05	Water	1.01	1 hr
E3B W	3B	0.1246	0.05	Water	2.49	1 hr
E3B W	3B	0.2500	0.05	Water	5.00	1 hr
E3B 31	3B	0.0052	0.05	EGM 31	0.10	1 hr
E3B 31	3B	0.0156	0.05	EGM 31	0.31	1 hr
E3B 31	3B	0.0306	0.05	EGM 31	0.61	1 hr
E3B 31	3B	0.0501	0.05	EGM 31	1.00	1 hr
E3B 31	3B	0.1251	0.05	EGM 31	2.50	1 hr
E3B 31	3B	0.2504	0.05	EGM 31	5.01	1 hr

Table 5-15 - Details of Batch 8 tests on ettringite

The samples were extracted for 1 hour on the horizontal shaker. Returning back to 50 ml solutions was deemed necessary because of the large volumes required for 200 ml ones, especially in light of the upcoming Phase II experiments where a greater number of samples were expected to be used. In addition, a pragmatic method of filtration was developed that could be used with 50 ml solutions in which the tube was placed in a flask and the entire leach solution could be directly filtered on a 0.45 μ m glass microfiber filter paper and into the tube rather than into the flask first (Figure 5-2).



Figure 5-2 – Direct filtration into 50 ml tube

This step shortened the operational time for filtration significantly, and allowed for a higher quality supernatant to be produced with minimal risk of outside contamination. Dilutions of 1:10 were prepared by mixing 1 ml of sample with 9 ml of water using a pipette, and they were acidified with 200 μ m of nitric acid, while the water-extracted originals were also acidified with 1 ml of the same in case they were required for measurement due to small amounts of aluminum or sulphur in the dilutions.

5.5.3.9 Batch 9

A ninth and final batch of leach tests focussed on Ettringite 2B in the same way Batch 8 focussed on Ettringite 3B. The samples were weighed on the Sartorius balance (details in Table 5-10 below) and placed into new 60 ml Nalgene bottles, to which 50 ml of EGM 31 and water were added with a glass pipette and its controller. This was the first use of these 60 ml bottles, which took less space on the shaker, could contain 50 ml of solution, and could have room for its circulation during the leaching procedure. From this point onwards, they replaced the 50 ml tubes and 250 ml bottles hitherto used.

Sample ID	Туре	Wt (g)	Vol (I)	Leach	W:V	Extract
E2B W	2B	0.0057	0.05	Water	0.11	1 hr
E2B W	2B	0.0150	0.05	Water	0.30	1 hr
E2B W	2B	0.0302	0.05	Water	0.60	1 hr
E2B W	2B	0.0504	0.05	Water	1.01	1 hr
E2B W	2B	0.1249	0.05	Water	2.50	1 hr
E2B W	2B	0.2503	0.05	Water	5.01	1 hr
E2B 31	2B	0.0053	0.05	EGM 31	0.11	1 hr
E2B 31	2B	0.0150	0.05	EGM 31	0.30	1 hr
E2B 31	2B	0.0298	0.05	EGM 31	0.60	1 hr
E2B 31	2B	0.0495	0.05	EGM 31	0.99	1 hr
E2B 31	2B	0.1248	0.05	EGM 31	2.50	1 hr
E2B 31	2B	0.2500	0.05	EGM 31	5.00	1 hr

Table 5-16 - Details of Batch 9 tests on ettringite

They were extracted for 1 hour on the horizontal shaker (Figure 5-3), and filtered into 50 ml tubes using the filtration technique outlined above. Dilutions of 1:10 were prepared by mixing 1 ml of sample with 9 ml of water, and acidified with 200 μ m of nitric acid. The water-extracted originals were also acidified with 1 ml in case they were needed during measurement due to very low values of aluminum or sulphur in the dilutions.



Figure 5-3 – Extraction of ettringite samples in 60 ml Nalgene bottles on shaker

5.5.4. LEACHING OF OTHER MATERIALS

In addition to ettringite and gypsum, several other materials used in Phase I or to be used in Phase II were leached with water and the EGM 31 and 13 solutions. The reason for their extraction was to assess the amount of aluminum or sulphur emanating from them so as to serve as a background against which higher values could be assessed. For example, it was important to verify the aluminum content coming from non-hydrated slag and fly ash in order to take those numbers into consideration when analyzing the results from cement and fly ash binders. Similarly, it was important to know whether aluminum sulphate was soluble in EGM 31 in order to put the results of Ettringite 3 dissolution into perspective should there be any of the original non-reacted component left during the preparation process. No XRD was done on tricalcium aluminate or aluminum sulphate but the location and relative intensities of their primary peaks were retrieved from the databases available in the XRD laboratory for comparison purposes.

5.5.4.1 Batch 1

Leach tests on ettringite-forming chemicals were done on aluminum sulphate and tricalcium aluminate with water, EGM 31 and 13 as the extracting solutions, and at a weight-to-volume ratio of 1. Samples were weighed on the Sartorius balance (see Table

5-17), placed into 50 ml tubes, and 20 ml solution was added with the glass pipette and its controller.

Sample ID	Wt (g)	Vol (I)	Leach	W:V	Extract
C3A 13	0.0203	0.02	EGM 13	1.01	1 hr
C3A 31	0.0194	0.02	EGM 31	0.97	1 hr
C3A Water	0.0207	0.02	Water	1.04	1 hr
AIS 13	0.0207	0.02	EGM 13	1.04	1 hr
AIS 31	0.0199	0.02	EGM 31	0.99	1 hr
AIS Water	0.0202	0.02	Water	1.01	1 hr

Table 5-17 – Details of batch tests on chemicals

After 1 hour of extraction, the tubes were centrifuged for 10 minutes and dilutions of 1:10 were prepared by mixing 1 ml sample with 9 ml of water. The samples were acidified with 200 μ m nitric acid and analyzed with the ICP machine.

5.5.4.2 Batch 2

Another batch of tests was done on non-hydrated cement, slag, and fly ash using EGM 31 as the sole leach solution, and at a weight-to-volume ratio of only 1. They were weighed with the Sartorius balance and placed into 60 ml bottles to which 50 ml solution was added using a calibrated volumetric tube (Table 5-18).

Sample ID	Wt (g)	Vol (l)	Leach	W:V	Extract
C 1 1/10	0.0058	0.05	EGM 31	0.12	1 hr
C 2 1/10	0.0506	0.05	EGM 31	1.01	1 hr
S 1 1/10	0.0057	0.05	EGM 31	0.11	1 hr
S 2 1/10	0.0512	0.05	EGM 31	1.02	1 hr
F 1 1/10	0.0052	0.05	EGM 31	0.10	1 hr
F 2 1/10	0.0514	0.05	EGM 31	1.03	1 hr

Table 5-18 – Details of batch tests on cementitious binders

The bottles were then placed on the horizontal shaker for 1 hour and filtered on 0.45 μ m glass microfiber filter papers and into 50 ml tubes. Dilutions of 1:10 were made by mixing 0.5 ml of solution with 4.5 ml water, and they were acidified with 100 μ m nitric acid before being analyzed with the ICP-OES.

5.6. PHASE II – TESTS ON BINDERS

Upon terminating the tests on minerals and based on the evaluation of the results, a number of conclusions were drawn as to the final testing procedure to be adopted for Phase II, which comprised tests on backfill binders. Among these was the decision to use 1 hour of extraction as a standard protocol, followed by direct filtration of the supernatant into a 50 ml centrifuge tube, preparation of a single dilution of 1:10, its acidification by 200 μ m of nitric acid, and analysis by the ICP method. As for the weight-to-volume ratios to be used, it was decided to have a total of six points including three numbers less than 1, 1, and two above it. EGM 31 was the only leach solution that was used based on the results of Phase I tests on minerals.

5.6.1. PREPARATION OF BINDERS

The backfill binders used in Phase II of this project were based on the ones normally used in Canadian mines. Table 5-19 below lists a number of mines along with the details of the binders used in those operations.

Mine	Method	Fill	Binder	Ratio	Amount
Aur Louvicourt	Longhole open	Paste	Slag:cement	80:20	4.5%, 2%
Barrick Bousquet	Open stoping	CRF	Cement:fly ash	50:50	4%,7%
Breakwater Langlois	Longhole	Paste	Cement		3-6.5%
Breakwater	Transverse	Paste	Cement:fly ash	50:50	2-5%
Bouchard-Hebert	blasthole				
Cambior Doyon	various	CRF	Cement:fly ash	50:50	2%
		Paste	Cement		2.1%
Inco Birchtree	Slot & slash	CRF	Cement:fly ash	30:70	3.5%
Inco Frood	Vertical retreat	Cemented tails	Slag:cement	90:10	3-4%

Table 5-19 - Binders used in several Canadian mines (Mining Sourcebook 2003)

Based on the data given above, four binders were decided upon, which were cement-slag [PS], cement-fly ash type C [PF], cement-only [PC], and a combination of cement, slag, and fly ash [PSF]. The proportions used in each of these are given in Table 5-20. A water-to-binder ratio of 0.5 was adopted based on the literature due to the inherent high permeability, which would increase the rate of sulphate attack for the purposes of this study.

Binder ID	Acronym	Cement (g)	Slag (g)	Fly ash (g)	Water (ml)
1	PS	250.3	250.0		250
2	PF	250.0		250.0	250
3	PC	500.0			250
4	PSF	125.0	125.0	250.0	250

Table 5-20 – Phase II binders and their proportions

The dry components for a given binder were mixed by hand in a glass bowl with a stainless steel whisk and water was added slowly to it while mixing. Since it was not a variable in the research, the time of mixing was kept at 3 minutes while the paste was stirred constantly but gently to provide a uniform product. After the required time, the paste was poured into two plastic mini ice-cube trays measuring 12.1 mm per cube for a total of eight trays for four binders. The trays were tapped gently on the sides in order to rid them of air bubbles. They were then placed in plastic bags and left in the humid room for initial drying.

5.6.2. CURING PROCESS

Following the procedure outlined by Mehta and Gjörv (1974) and Monteiro et al (2000), an accelerated curing process was adopted for all the binders alike. The trays were left in the humid room for 4 hours, after which they were removed from the plastic bags and wrapped in clean laboratory paper towels drenched in water. They were then placed in aluminum trays and stored in an oven at 50°C for 20 hours. On the following day, the trays were taken out of the oven, and the solidified cubes were demoulded. The towels were drenched with water again and wrapped around the cubes before returning them to the oven (Figure 5-4).

Subsequently, and on each day, the cubes were removed and the towels were drenched in water anew, wrapped around them, and they were returned back to the oven. The process continued for 7 days as per the referenced procedures so that the hydration process was complete for cement and the pozzolans as stated by Mehta and Gjörv (1974). After the elapsed time, a number of cubes were set aside for testing and the rest were placed in marked plastic bags, sealed tight, and returned to the humid room for storage.



Figure 5-4 – Oven curing of cubes wrapped in wet towels

5.6.3. SULPHATE AND ACID ATTACK TESTS

Immediately after the 7 days of curing, a number of samples from each binder were subjected to sulphate and acid attack tests using two solutions and two modes of immersion, which are presented in detail below.

5.6.3.1 Full immersion in a 4% Na₂SO₄ solution

The first solution used was based on the procedure outlined by Monteiro et al (2000) and Mehta and Gjörv (1974) where a 4% by weight sodium sulphate solution (NS) is used. In order to use an adequate volume of solution, several references were consulted but no agreement appeared amongst the authors. Hence, Brown (1991) recommended the use of a volume of solution three times that of the number of cubes to be immersed, while Mehta and Gjörv (1974) adopted a volume at a rate of 25 ml per square centimetre of surface area exposed. Monteiro et al (2000), on the other hand, implemented the use of a 19-litre tank in which 108 cubes were immersed, which translated into an approximate ratio of 175 ml solution per cube. Although most of the ratios used were feasible, the last one was the most voluminous and was therefore unpractical. However, it also provided the highest ratio of volume per cube and was thus seen to promote acceleration in the rate of attack. Hence, in the experiments with sodium sulphate, the highest possible ratio was

adopted that could be practically implemented, and it was decided to use 800 ml of solution for 15 cubes, which would be the equivalent of about 50 ml per cube. Therefore, 32 g of anhydrous sodium sulphate was weighed using the AND balance and placed in a Nalgene jar to which 800 ml water was added. The solution was shaken until the salt dissolved completely, after which the cubes were immersed and the jar was left open under the fume-hood. Separate jars were used for each type of binder tested (Figure 5-5).





The procedure outlined by the aforementioned references called for an automatic titrating machine for controlling the pH of the solutions. The purpose of the control is to accelerate the attack process as lime dissolution from the cubes would otherwise raise the pH to alkaline conditions and stabilize it at that level. A 0.1N sulphuric acid solution is recommended for providing a constant pH of 6 to 7, but due to the large volumes required to make the changes in pH, and the limitations of a 1 litre jar almost filled to capacity, a more concentrated 1N solution (prepared by mixing 28 ml of acid with water for a total of 100 ml solution) was used instead. An aliquot of a few millilitres of the 1N solution was added daily to the jars using a pipette while the pH was monitored so as to bring it down from typical values of 10.30 to between 6.7 and 7.2. A magnetic stirrer was used to keep the solution moving while the pH was read and acid added (Figure 5-6).



Figure 5-6 – Monitoring of pH for samples fully immersed in NS

When the level of solution in the jars dropped due to evaporation, water was added to prevent the cubes from being exposed to air. The testing period lasted 28 days and the solutions for each jar were made afresh after 14 days of curing. Three cubes per sample were taken out for testing after 14 and 28 days of immersion. It should be noted that only the cement-slag [PS] and cement-fly ash [PF] binders were tested with full immersion in sodium sulphate.

5.6.3.2 Partial immersion in 4% Na₂SO₄ solution

The literature on sulphate attack tests was reviewed in Chapter 3 and several references were made to the use of partial immersion tests for attack (Lagerblad 1999) or the lack of a standardized procedure for it (Clifton et al 1999). In order to test the results of partial immersion compared to the full one, a stainless steel tray was filled with 4% sodium sulphate solution prepared by dissolving 38.50 g of anhydrous sodium sulphate in 960 ml water. Twelve cubes per binder sample were placed in the tray and in addition to the cement-slag and cement-fly ash binders, cement-only [PC] and cement-slag-fly ash [PSF] ones were also tested in the partial immersion procedure to provide a comparison with the main binders. In addition, the total volume used was designed to provide half the amount of solution per cube as was allocated in the full immersion test, at a rate of about

25 ml per cube. The tray was placed under the fume-hood and the cubes were seen to be partially exposed to air while remaining within the solution, which was the main purpose of the test (Figure 5-7).





Unlike the full immersion version, the pH of the test with partial immersion could not be controlled by adding aliquots of 1N sulphuric acid due to the impracticality of stirring the whole solution in a wide tray with minimal vertical dimensions. Furthermore, due to the partial exposure of the samples, the test solution was observed to evaporate in the space of a few days. Hence, this characteristic was employed as a quantitative guideline for the solutions used for the partial immersion test. In addition to the initial volume, the sodium sulphate solution was renewed twice using the same amount of solution prepared for the first immersion. In total, three 960 ml solutions of 4% sodium sulphate were used on Days 1, 3, and 5 of the test schedule, with each one requiring two days for complete evaporation.

5.6.3.3 Full immersion in a 2% H₂SO₄ solution

In the first three chapters, a review of the literature clarified the fact that whereas sulphate attack could take place in both concrete structures and mine backfill, the use of sulphide-rich tailings in the latter could produce an acid attack as well. Therefore, it was deemed necessary to subject the two main binders to a simulation of acid attack that would resemble conditions found in a mine backfill environment, if not in severity then at least in the nature of the acid. The oxidation of pyrite in tailings was reviewed at length in the first chapter, and the main detrimental product formed was observed to be sulphuric acid. Therefore, this was chosen as the testing acid for the binders and a concentration of 2% by volume (HS) was adopted. Li and Zhao (2003) report its use as part of Chinese Standard GJ-82-85 on testing for durability of concrete. In that procedure, mortar cubes cured for three days in the humid room are immersed in the solution and tested after 7, 28, 56, 112, and 350 days of immersion by comparing the weight and compressive strength of the samples to others immersed in water. The procedure was modified slightly to compare with the 4% sodium sulphate solution used. Hence, 15 cubes from each of the cement-slag and cement-fly ash binders were immersed in separate jars of 800 ml of 2% sulphuric acid (prepared with mixing 16 ml of acid with water for a total volume of 800 ml) solution to provide a ratio of about 50 ml per cube. Due to the extremely acidic nature of the solution - at a pH less than unity - and its persistence over a long period of time, there was no need for pH adjustments with aliquots of sulphuric acid. However, a fresh solution was prepared after 14 days of curing and water was added whenever the amount of evaporation threatened to partially expose the cubes.

5.6.3.4 Partial immersion in 2% H₂SO₄ solution

Similar to the sodium sulphate solution, the acid one was also tested in terms of partial immersion. A stainless steel tray was used to contain 960 ml of 2% sulphuric acid (prepared by mixing 19.2 ml of acid with water for a total volume of 960 ml) solution in which a total of 36 cubes were partially immersed, with 12 cubes from each of the four binders. The solution was left to evaporate with renewals taking place on Days 3 and 5, in addition to the initial volume used, similar to the procedure used in the sodium sulphate partial immersion test. The tray was placed under the fume-hood and monitored on a daily basis. An interesting feature in the partial immersion test with sulphuric acid was the immediate reaction of the cubes upon placement in the tray and their lateral movement to agglomerate together. In order to prevent confusion about the nature of samples due to this action, plastic barriers were placed between the samples from each of the binders as seen in the tray in the back of Figure 5-7.

5.6.4. QUALITATIVE ANALYSIS – XRD

Based on the results of the Phase I procedure on minerals, a qualitative analysis of the binders was undertaken with the XRD. In order to provide a basis for comparison, the original components of the binders – cement, slag, and fly ash – were analyzed using the same settings as the ones for pure minerals. During the curing period, cubes from each of the four binders were taken after 3 and 7 days for analysis by XRD. They were ground to a fine powder in acetone in a ceramic mortar and pestle to halt all hydration reactions, and stored in small plastic boxes until tested (Figure 5-8).



Figure 5-8 – Grinding a cube in excess acetone

The purpose of the XRD analysis after 3 days was to monitor any potential development of primary ettringite, and the 7-day tests were used to assess the quality of the final product prior to immersion in the sulphate and acid attack solutions. XRD analysis was also conducted on the samples undergoing attack. Hence, they were removed from each of the testing solution jars and ground in the manner described above. From the full immersion tests, samples were tested after 14 and 28 days and the results were compared to the ones after 7 days of curing in the oven. Samples from the partial immersion tests were tested after 5 and 8 days of immersion in order to compare the results to the original ones after 7 days of curing, as well as to one another to trace the development of the attack process after two and three solution renewals.

5.6.5. QUANTITATIVE ANALYSIS – EGM 31

Based on the extensive leach testing on minerals in Phase I and the study of five variables, viz., the time of extraction, the weight-to-volume ratio, the leach solution, the method of separating the supernatant, and the instruments used for analysis, a unified procedure was developed for the leach tests conducted in Phase II. Samples from the cement-slag and cement-fly ash binders were tested – as with XRD analysis – after 3 and 7 days of curing to trace the development of any primary ettringite formation so as not to confuse its presence with the mineral formed due to either sulphate or acid attack. Once the full and partial immersion tests with the two types of solutions were underway, samples were taken after 14 and 28 days for the former, and after 8 days for the latter. For the partial immersion tests, samples from all four binders were leached to compare the results amongst themselves and also to the full immersion ones where applicable. Due to the demanding nature of the leach tests, they were conducted only at the end of the partial immersion tests and not during the intervals in between, which was monitored by XRD only. The grinding process was the same for the leach samples as it was for the XRD ones.

The testing procedure comprised leaching three cubes per binder sample per day of testing with the EGM 31 solution at weight-to-volume ratios of 0.1, 0.3, 0.6, 1.0, 2.5, and 5.0. Samples were weighed on the Sartorius electronic balance and placed into 60 ml Nalgene bottles to which a leach solution of 50 ml was added using a volumetric tube. Extraction was done on a horizontal shaker for 1 hour, and the supernatants were separated by filtering on 0.45 µm glass microfiber filter papers and directly into a 50 ml tube using the technique detailed previously. Dilutions of 1:10 were prepared by mixing 0.5 ml of the sample with 4.5 ml of water with a calibrated pipette, and they were acidified with 200 µm nitric acid. Both the original and diluted solutions were stored in a fridge until after testing in case they were needed for a second round of measurements. Aluminum and sulphur were analyzed by ICP-OES after the instrument was calibrated with freshly prepared standards for both elements at 1 ppm, 10 ppm, and 100 ppm concentrations. As part of the quality check of the readings, the standards themselves

were analyzed after every 10 samples to check for instrument drifts, and to correct subsequent readings accordingly.

5.7. CONCLUSION

As outlined in this chapter, the experimental part of the research project was divided into two phases. In the initial one, ettringite was formed using two methods outlined by Odler and Abdul-Maula (1984) and Lafarge (1995). In addition to these, gypsum and other components such as aluminum sulphate and tricalcium aluminate were tested in a qualitative manner using XRD analysis. A detailed and extensive quantitative procedure followed in which all the components were leached with water, EGM 31, and EGM 13 solutions for different periods of time, at various weight-to-volume ratios, and with two methods of supernatant separation. The main parameters measured were Al and S, using three different pieces of instrumentation.

The second part of the experimental section was designed based on the results of Phase I. Four binder combinations including cement-slag, cement-fly ash, cement-only, and cement-slag-fly ash were prepared at a water-to-binder ratio of 0.5, cast in 12.1 mm ice-cube trays, and cured for 7 days in an oven at 50°C wrapped in towels drenched in water on a daily basis. Samples from the cement-slag and cement-fly ash mixes were then fully immersed in solutions of 4% sodium sulphate constantly kept at a pH of 7 with 1N acid additions, and of 2% sulphuric acid. In addition, samples from all four binders were partially immersed in the same two solutions for a total of 8 days to compare with their fully immersed counterparts. Qualitative XRD analysis and quantitative ettringite and gypsum evaluations with an EGM 31 solution were conducted on fully immersed cubes after 14 and 28 days, and on partially immersed ones after 8 days. The leached samples were analyzed for aluminum and sulphur with the ICP-OES technique, and the amount of minerals formed was calculated from its stoichiometry.

CHAPTER : 6 RESULTS AND DISCUSSION

6.1. INTRODUCTION

In the preceding chapter, the materials and methodology used in the research project were presented in detail, in addition to the rationale behind their adoption. In this chapter, the results are given in tabular and graphical form and are discussed at length. The outline follows that of the preceding chapter in general, with additional subdivisions where needed so as to better orient the reader and keep the logical alignment established.

6.2. PHASE I RESULTS – MINERALS

The objective of ettringite formation was to assess the amount of the mineral produced using two different methods of preparation as outlined in Odler and Abdul-Maula (1984) and Lafarge (1995). Formation took place on three different occasions and the main purpose for the repetition was to test the accuracy of the method in producing a similar product at all times. In order to study the impact of the drying method, the initial and final batches were air-dried under the fume-hood while the second batch was initially dried in a desiccator, followed by air-drying under the fume-hood. As an introduction to a discussion of the ettringite results, those of gypsum are presented first due to this mineral's availability in pure form and the more straightforward nature of its analysis.

6.2.1. GYPSUM CHARACTERIZATION

The characterization of gypsum was done by XRD analysis and leach tests using different parameters and techniques. Its discussion prior to that of ettringite samples is necessary in order to better evaluate their results due to the fact that ettringite contains three sulphates in its molecular formula, which creates a common ion with the sulphate coming from gypsum dissolution in water. In addition, the tests and analysis of gypsum were simpler because laboratory-grade samples free from major impurities were available for testing, and it did not need preparation from primary reagents. A last point is the fact that along with ettringite, gypsum itself is one of the principle products of sulphate attack and therefore merits separate characterization.

6.2.1.1 Qualitative analysis – XRD



Gypsum was analyzed by XRD and its plot is given in Figure 6-1 below.

Figure 6-1 – XRD plot for gypsum

The plot is clear and shows the main mineral peaks in the scanned range at 11.650°, 20.737°, 23.391°, 28.871°, 31.027°, and 33.280°. It can be seen that no major impurities are present that are detectable through the XRD technique.

6.2.1.2 Quantitative analysis – EGM 31

The solubility of gypsum in water is reported to be 15.2 mmol/l or 1.46 g $SO_4^{2^2/l}$ at 20°C (Skalny et al 2002), which translates to approximately 2.62 g/l. Other authors (Sokolovich and Evdokimova 1997) give a different value of 7.8 x 10⁻³ mol/l, which is equivalent to 1.34 g/l, at almost half the amount above. Deutsch (1997) provides a more detailed table in which gypsum solubility is 1.46 g/l at 10°C and moves up to 1.57 g/l at 25°C. A maximum value of 1.92 g/l is reached at 75°C, which is not applicable for the

tests conducted in this project. Through simple calculations, the solubility of the mineral in 20 ml and 50 ml solutions is equivalent to 0.05 g and 0.13 g, respectively, for the first reference cited above and 0.03 g and 0.07 g, respectively, for the second one. These numbers will be useful further on in this section when gypsum dissolution in water is discussed. The first two batches of leach tests on gypsum were conducted after an extraction of 2 hours at various weight-to-volume ratios, and the samples were analyzed by IC. The measured sulphate was recalculated as sulphur using gypsum stoichiometry, and the results of these tests are presented in Tables 6-1 and 6-2 below.

Table 6-1 – Results of Batch 1 tests on gypsum – IC/centrifuge

Sample ID	W:V	Leach	SO4 (g)	S (g)	Gyp (g)	Gyp (%)
G 1:10	0.9617	EGM 13	0.0007	0.0002	0.0012	6.47
G 1:100	1.0317	EGM 31	0.0045	0.0015	0.0082	39.61

Sample ID	W:V	Leach	SO4 (g)	S (g)	Gyp (g)	Gyp (%)
G 1-3	0.57	EGM 13	0.0009	0.0003	0.0015	13.53
G 4-6	1.04	EGM 13	0.0009	0.0003	0.0016	7.69
G 7-9	1.52	EGM 13	0.0009	0.0003	0.0016	5.25
G 10-12	0.50	EGM 31	0.0037	0.0012	0.0067	67.56
G 13-15	1.00	EGM 31	0.0062	0.0021	0.0112	55.87
G 16-18	1.50	EGM 31	0.0092	0.0031	0.0164	54.64

Table 6-2 – Results of Batch 2 tests on gypsum – IC/centrifuge

The results indicate similar numbers in the case of EGM 13 extraction, which is around 7% gypsum dissolution at a ratio of 1. Nearly twice the amount of gypsum can be dissolved in the same matrix when this ratio is halved, and somewhat less soluble behaviour is manifested when the ratio is raised to 1.5. In general, the maximum dissolution in the range tested is below 15%. In the case of EGM 31, however, certain inconsistencies are seen in that the values obtained for a ratio of 1 differ by about 15%. One possible explanation is the use of an older centrifuge for the separation of the supernatant in the two cases. Another reason could be experimental error due to the use of a 1:100 dilution prepared from the 1:10 one in the former case whereas a 1:10 dilution was used for the second. The consistent part is the drop in the ability of EGM 31 to dissolve gypsum when the weight-to-volume ratio is raised, which is similar to the

behaviour of EGM 13. The difference is more dramatic when the ratio goes up from 0.5 to 1.0 than it is when raised from unity to 1.5.

The use of the IC for sulphate analysis was discontinued after the second batch of tests on gypsum due to its limitation on several fronts. Firstly, the time required for the sulphate anion to elute was minimum 15 minutes, which required several days of testing for a sizeable batch of samples. This was not deemed efficient in terms of both time and resources and an alternative was sought. Secondly, no acidification could be done on solutions tested by IC as it would damage the instrument, which required a second set of dilutions prepared exclusively for this purpose when ettringite samples were tested. Thirdly, due to the absence of preservatives, the samples required testing within a few days of extraction, creating scheduling and logistical problems. The third batch of tests on gypsum was therefore analyzed by the ICP technique and the results are presented in Table 6-3.

Table 6-3 – Results of Batch 3 tests on gypsum – ICP/centrifuge

Sample ID	W:V	Leach	S (g)	Gyp (g)	Gyp (%)
G 13	1.00	EGM 13	0.0004	0.0020	10.02
G 31	1.07	EGM 31	0.0020	0.0109	50.63

The results of the ICP analysis were very similar to the ones obtained through the IC one, bearing in mind that for Batch 3, an extraction time of 1 hour was used instead of the 2 hours in the former ones. At a weight-to-volume ratio of 1, EGM 13 was able to dissolve 10% gypsum, and this is not too far from the 7.69% value obtained previously. In addition, the use of nitric acid for preservation ensured the absence of any precipitates pending analysis. The result of leaching by EGM 31 was also similar to previous readings and 51% gypsum was extracted at a ratio of 1, compared to 56% obtained from 2 hours of extraction.

Table 6-4 – Results of Batch 4 tests on gypsum – ICP/centrifuge

Sample ID	W:V Leach		S (g)	Gyp (g)	Gyp (%)
G 13	1.07	EGM 13	0.0019	0.0024	11.04
G 31	1.02	EGM 31	0.0032	0.0104	50.96
G W	1.01	Water	0.0030	0.0172	85.29

With a difference of 2% and 5% for EGM 13 and 31, respectively, it was decided to adopt an extraction time of 1 hour for all upcoming tests. In order to confirm the validity of these results and to establish the dissolution of the mineral in water, a fourth batch of tests was undertaken, the results of which are give in Table 6-4 and conform to those in Table 6-3 quite well. In the case of EGM 13, 11% of the mineral is dissolved compared to 10% in the former case. For EGM 31, the solubility stands at 51% compared to about the same value obtained previously. Dissolution in water is the new data obtained in this batch, and shows 85% for the mineral at a ratio of 1. Bearing in mind that 20 ml of water was used, and using the literature values referenced above, up to 0.05 g gypsum should have been dissolved in the solution and a 100% rate should have been observed. The rates given in reference books are usually average values and individual samples show variations around those values.

The fifth batch was conducted with the purpose of concentrating the study on dissolution with water and EGM 31, seeing that EGM 13 was not very useful in ettringite extraction and could serve no further purpose. An important factor that needed further investigation was the various weight-to-volume ratios and their effect on the percentage of gypsum dissolved. Another new method used in this batch was the employment of filters for supernatant separation instead of centrifugation, which proved to be more effective in the solid component removal process. The initial analysis ran into technical difficulties due to sulphur remnants in the instrument tubing that gave very high readings. The problem was solved by analyzing the same samples a few days later, and the results of this second round are presented in Table 6-5.

Sample ID	W:V	Leach	S (g)	Gyp (g)	Gyp (%)
G 31	0.51	EGM 31	0.0029	0.0157	62.27
G 31	1.00	EGM 31	0.0048	0.0258	51.59
G 31	2.49	EGM 31	0.0082	0.0441	35.40
G DI	0.51	Water	0.0045	0.0240	94.63
G DI	1.00	Water	0.0081	0.0435	87.34
G DI	2.49	Water	0.0169	0.0908	72.83

Table 6-5 – Results of Batch 5 tests on gypsum – ICP/filter

A comparison between the results of batches 4 and 5 at a ratio of 1 confirms the quality of the work done. The dissolution of 52% gypsum closely agrees with the 51% obtained previously for EGM 31, as does the 87% value with the former 85% for water. In addition, the solubility of gypsum at various weight-to-volume ratios can be traced in both solutions. Whereas it decreases by a value of 20% between 0.5 and 2.5 for water, the ability of EGM 31 in dissolving gypsum diminishes from 63% to almost half of that value within the same range. Needless to say, these are important numbers to consider when analyzing the results of mixed samples.

A final batch of testing on gypsum was conducted simply as part of a larger group of samples being tested, and the only leach solution used was EGM 31 over a wider range of weight-to-volume ratios. The results of the final batch are given in Table 6-6.

Sample ID	W:V	Leach	S (g)	Gyp (g)	Gyp (%)
G 1 1/10	0.11	EGM 31	0.0009	0.0050	95.08
G 2 1/10	0.30	EGM 31	0.0023	0.0123	82.31
G 3 1/10	0.62	EGM 31	0.0030	0.0162	52.55
G 4 1/10	1.01	EGM 31	0.0041	0.0222	44.18
G 5 1/10	2.51	EGM 31	0.0081	0.0434	34.58
G 6 1/10	5.01	EGM 31	0.0110	0.0588	23.48

Table 6-6 - Results of Batch 6 tests on gypsum - ICP/filter

The numbers are in close agreement to the ones obtained previously, with the weight-to-volume ratio of 1 value at 44% varying slightly from the 52% of the previous run. At the minimal ratio of 0.1, gypsum is almost completely dissolved in EGM 31 while the value for 2.5 agrees well with the 35.5% obtained previously. It must be stressed that the variations are more frequent in the smaller ratios due to the weight of sample used and the greater effect of weight variations on the outcome at those numbers.

6.2.1.3 Derivation of solubility curves – Water and EGM 31

The results of all leach tests conducted have been plotted in Figure 6-2 as gypsum dissolved against the weight-to-volume ratios for water and EGM 31. The EGM 13 solution results have not been plotted due to its minimal extraction of the mineral. Furthermore, only results obtained from filtered samples analyzed by the ICP have been

used due to their superior quality over the other methods. It can be observed that whereas the water solubility follows an almost linear to a very gently polynomial trend until a ratio of 2.5, the solubility in EGM 31 describes a polynomial one until the same ratio and even beyond. The latter reaches a maximum value at around 5 and its continuation would either remain on that plateau or dip downward at higher ratios. The curve is important in its description of gypsum solubility in the EGM 31 solution, and proves that water can dissolve more gypsum than the organic solution at a given ratio within the range tested.



Figure 6-2 – Gypsum dissolution (g/l) in water and EGM 31

The same information is plotted as percentage of gypsum dissolved in the solutions in Figure 6-3. In this case, the curves for both solutions are similar in nature and follow an exponential trend. Water is seen to dissolve around twice the amount of gypsum at a given ratio than its organic counterpart. The importance of the EGM 31 curve cannot be overstated in that apart from describing the mineral dissolution behaviour, it provides an important assessment tool for mixed samples where gypsum constitutes a certain percentage.



Figure 6-3 – Gypsum dissolved in water and EGM 31 (%)





A note of comparison can be made with the 69.6% dissolution rate given by Odler and Abdul-Maula (1984) for gypsum at a ratio of 0.67. Based on Figure 6-3, the value obtained in these experiments yielded approximately 52%, which is somewhat lower than their number. However, the time of extraction used by these authors was 30 minutes

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compared to the 1 hour used in these tests. A final set of gypsum solubility curves is presented in Figure 6-4 where the percentages of the mineral extracted by water and EGM 31 are plotted in terms of sulphur percentage with respect to the sample weight.

In summary, the ability of three leach solutions – water, EGM 13, and EGM 31 – in dissolving gypsum was studied in the six batches of tests run for the mineral. EGM 13 was discontinued as a testing solution in part because of its inability to dissolve gypsum in appreciable quantities. The results from water leaching served as a comparison to the ones from EGM 31, which was the main target of investigation. The values for this latter solution were confirmed under various testing parameters including two liquid separation techniques and two different extraction periods. This phase concluded with the establishment of solubility curves for gypsum, which served as the benchmark against which the results of ettringite dissolution in Phase I and binder extraction in Phase II were assessed.

6.2.2. ETTRINGITE 2 CHARACTERIZATION

Ettringite 2 was prepared in the laboratory and was characterized by XRD and extraction with water, EGM 13 and 31 solutions, the results of which are covered in the sections below.

6.2.2.1 XRD analysis

Ettringite 2A and 2B were analyzed using XRD and their plots are given in Figure 6-5 below. The main ettringite peaks are given at 2θ values of 9.016°, 15.533°, 22.962°, 32.054°, and 34.882° in the scanned range of 5° to 40°. Gypsum is plotted for comparison purposes with its maximum peaks in the same range given at 11.650°, 20.737°, 23.391°, 28.871°, 31.027°, and 33.280°.



Figure 6-5 – XRD plot for Ettringite 2A and 2B

Although XRD analysis cannot be directly used for quantitative analysis – unless a specialized technique like Rietveld refinement or Debye-Scherrer is employed – it can nevertheless be used for a qualitative or semi-quantitative evaluation based on the relative intensity of the maximum peaks. Based on such an assessment, it can be clearly seen that a significant portion of the formed product in both Ettringite 2A and 2B is gypsum. The intensities of the four major peaks in the mineral between 10° and 30° 20 are clearly reflected in the plots for the ettringite samples. Although the first three of the ettringite peaks can be seen as well between 9° and 23°, they are much less intense than the gypsum ones.

The presence of gypsum in the final product is not surprising seeing that it was one of the components used in the formation process alongside tricalcium aluminate, which does not appear at all in the plot at its main peak at 33.169°. The significance of the matter lies in the seemingly larger amounts of gypsum when compared to ettringite. Hence, it can be deduced that the formation of ettringite with Method 2 was successful in essence but produced a larger proportion of gypsum than expected. Since the molecular formula of ettringite contains sulphate, this is an important factor to consider when analyzing the results of Ettringite 2 dissolution in water as the presence of gypsum would create a common ion effect and could limit its dissolution if the maximum allowable limit for gypsum solubility is reached. It is not known whether a similar phenomenon takes place in the organic EGM solutions.

6.2.2.2 Leaching tests – previous work

The qualitative evaluation of Ettringite 2 samples by XRD was complimented by a quantitative assessment in the form of leach tests. As outlined in the preceding chapter, a large number of tests were conducted on ettringite so as to determine the exact amount of its dissolution in three matrices, viz., EGM 13, 31, and water. The method derives from the work of Uchikawa and Uchida (1974), Odler and Abdul-Maula (1984), and Bernier et al (1999). The authors of the first work conducted a detailed study on the solubility of ettringite with various proportions of ethylene glycol and methanol, in which they estimated ettringite based on the calcium, aluminum, and sulphur contents of the leached solutions. Their recommendation was to use aluminum as the most reliable datum because sulphur and calcium had higher affinities to ethylene glycol. In addition, calcium from lime and sulphur from gypsum in hydrated cement pastes were seen to interfere with ettringite estimation when these elements were used.

Their mode of preparation for ettringite was similar to the ones used in this project, and they reported minimal results in aluminum extraction from hydrated C₃S, Al(OH)₃ gel, and calcium aluminate hydrate, which are phases that are usually present in hydrated cement alongside ettringite. Based on their plots, ettringite is extracted at almost 100% when EGM 31 is used and the time of extraction is not a major contributing factor. Estimates from their graphs give a 91.5% dissolution rate of ettringite after 1 hour, and 95% after 2 hours. On the other hand, EGM 11 gives 70.5% and 74% and EGM 13 gives 38.5% and 44% after 1 hour and 2 hours, respectively. As for the weight-to-volume ratio, the authors used 0.2 g ettringite with 200 ml solution, which gives a ratio of 1 when volume is converted to litres. Estimates of aluminum and the equivalent ettringite are presented in Table 6-7 based on the graphs of these authors.

		Al2O3 (mg)		Ettringite %			
Ex hrs	13 EGM 11 EGM		31 EGM	13 EGM	11 EGM	31 EGM	
1	6.29	11.43	14.86	38.69	70.34	91.44	
2	7.14	12.00	15.43	43.96	73.86	94.96	
3	8.00	13.14	15.14	49.24	80.89	93.20	
4	9.43	13.43	15.14	58.03	82.65	93.20	
5	10.00	13.71	15.43	61.55	84.41	94.96	

Table 6-7 – Aluminum and ettringite extraction (from Uchikawa and Uchida 1974)

Uchikawa and Uchida (1974) tested the solutions on hardened cement pastes as well and found a very good correlation between estimates based on the aluminum content and the actual amounts of ettringite. However, their recommendation is puzzling based on their experimental process in that EGM 13 – and not EGM 31 – is presented as the best solution. It can be suggested that a simple typographical mistake must have occurred. The work of Odler and Abdul-Maula (1984) closely follows the former one in methodology, where the authors worked with four types of ettringite and five types of monosulphate. In their research, they used a single extraction solution in the procedure. By a remarkable coincidence, they add to the confusion introduced by the first authors by alternating references to EGM 13 and 31 in their paper. Ettringite is removed from monosulphate by an EGM 31 solution (p 134 of their work), a table of solubility values in an EGM 13 solution is referred to (p 136), the said table is presented with EGM 31 in its title (p 138), and finally the recommendation is made to use EGM 13 and the aluminum content to determine the amount of ettringite (p 140)!

Bernier et al (1999) were the latest in the series of authors who used the EGM technique to quantify ettringite in relation to paste backfill operation. Their main concern was the loss of strength observed after 90 to 120 days of curing. In order to study the effects of different binders on the strength of backfill, they investigated the potential of an internal sulphate attack using the EGM technique. Their samples were made with 95% tailings and 5% of binders using various combinations of cement, fly ash, and two types of slag. It is the first work that studied the potential of ettringite formation in relation to mine backfill in which an attempt was made to quantify the mineral, and their tests took 360 days to complete. The authors used EGM 13 for their analysis and 2.2% ettringite

in hydrated sulphate-resistant cement. For paste backfill samples, and after obtaining maximum values of 0.30% with cement after 28 days of curing, ettringite decreased to 0.07% after 90 days, which was interpreted as the gradual transformation of the trisulphate mineral into its monosulphate counterpart. However, a sudden increase to 0.23% after 120 days of curing was interpreted as delayed ettringite formation (DEF), which was accompanied by a decrease in UCS strength. Mortar bar expansion tests were also conducted on the pastes but showed no appreciable expansion (<0.04%), which confirmed observations from many authors that the presence of ettringite need not necessarily imply expansion.

6.2.2.3 Leaching tests – current work

Based on the above, the initial leach tests on the ettringite samples formed for the project used both EGM 31 and 13 solutions in order to establish their relative abilities to dissolve the mineral. Water was used as well due to the highly insoluble nature of ettringite in that medium as reported in the literature. In addition, and based on the XRD results, gypsum dissolution in these solvents was studied in combination with ettringite. Due to the mixed nature of the formed ettringite, the first task was to assess its quantity in Ettringite 2 samples so as to have a basis for comparison with the results obtained from previous works. The results of the first three batch tests done on Ettringite 2 samples are presented in Table 6-8 through 6-10, and the analytical procedure used comprised 2 hours of leaching, followed by centrifugation and analysis with AA and IC.

Table 6-8 – Results of Batch 1 tests on Ettringite 2B – AAIC/centrifuge

Sample ID	W:V	Leach	Al (g)	SO4 (g)	S (g)	Ett (g)	Ett (%)	S (%)
Ett 20.2	4.99	EGM 31	0.0019	0.0203	0.0068	0.0449	22.47	3.40
Ett 2 0.5	12.54	EGM 31	0.0041	0.0341	0.0114	0.0958	19.10	2.27
Ett 2 1.0	24.98	EGM 31	0.0076	0.0435	0.0145	0.1765	17.67	1.45

Table 6-9 - Results of Batch 2 tests on Ettringite 2A - AAIC/centrifuge

Sample ID	W:V	Leach	AI (g)	SO4 (g)	S (g)	Ett (g)	Ett (%)	S (%)
Ett II 1:10	1.06	EGM 13	-0.0001	0.0007	0.0002	-0.0017	-7.95	1.12
Ett II 1:10	0.99	EGM 31	0.0000	0.0023	0.0008	-0.0001	-0.30	3.84

Sample ID	W:V	Leach	Al (g)	SO4 (g)	S (g)	Ett (g)	Ett (%)	S (%)
Ett2 1:10	0.51	EGM 13	-0.0002	0.0003	0.0001	-0.0037	-35.95	0.96
Ett2 1:10	1.00	EGM 13	-0.0001	0.0004	0.0001	-0.0027	-13.64	0.71
Ett2 1:10	1.51	EGM 13	-0.0001	0.0006	0.0002	-0.0017	-5.71	0.63
Ett2 1:10	0.50	EGM 31	-0.0001	0.0008	0.0003	-0.0028	-28.26	2.58
Ett2 1:10	1.01	EGM 31	-0.0001	0.0012	0.0004	-0.0014	-7.12	2.04
Ett2 1:10	1.52	EGM 31	0.0000	0.0017	0.0006	0.0001	0.47	1.82

Table 6-10 – Results of Batch 3 tests on Ettringite 2C – AAIC/centrifuge

The tables show that at high weight-to-volume ratios, Ettringite 2B dissolves in the EGM 31 solution readily and can be estimated at around 22.5%. As the sample weight increases, the solubility of the mineral clearly diminishes although at a relatively gentle slope. A 5-fold increase in the weight decreases the reading by a 5% value as can be seen from Table 6-8. The following two tables show negative values for ettringite, which should not be taken at face value. The analytical technique for aluminum used in the tests was the AA method, and it was not able to read element concentrations less than 10 ppm in the diluted solutions. It was in such cases that negative readings were obtained, indicating a concentration less than the capabilities of the instrument, which would translate into an impossibly small amount of ettringite at a weight-to-volume ratio of 1 if Ettringite 2 samples comprised around 25% of the mineral. Since the original leach solutions could not be used because of the organics, and smaller weight-to-volume ratios needed to be looked into, the analytical method was changed to the ICP technique.

Sample ID W:V Leach Al (q) S (g) Ett (g) Ett (%) S (%) Ett2 1:10 0.51 EGM 13 0.0001 0.0002 0.0014 13.49 1.50 Ett2 1:10 1.00 EGM 13 0.0001 0.0002 0.0026 13.07 1.19 Ett2 1:10 1.51 EGM 13 0.0039 12.90 0.0002 0.0002 0.68 Ett2 1:10 0.50 EGM 31 0.0001 0.0001 0.0017 16.86 1.41 Ett2 1:10 1.01 EGM 31 0.0001 0.0002 0.0033 16.55 1.22 Ett2 1:10 1.52 EGM 31 0.0002 0.0004 0.0055 17.91 1.18

Table 6-11 – Results of Batch 3 tests on Ettringite 2C – ICP/centrifuge

Table 6-11 above presents the same samples in Table 6-10 except for the fact that the analysis for both aluminum and sulphur was done by ICP. The advantages of the new technique are immediately apparent and its ability to read concentrations down to the 1 ppm level in the 1:10 dilutions proves to be invaluable. The ettringite yield in sample 2C

can be estimated at 17% from the EGM 31 solutions with no major differences between the three weight-to-volume ratios used. On the other hand, the more dilute form of the mix – EGM 13 – gives the mineral percentage at around 13%. Considering the large difference in the concentration of ethylene glycol in EGM 13 and 31 - 25% and 75% - it is noteworthy that the difference in the dissolved ettringite is only about 4%. The explanation lies in the fact that the total amount of ettringite is low enough even at 20%, and therefore the difference in concentration of the leach solution does not have a greater impact on its dissolution.

With the more reliable data obtained through the ICP technique, an adjustment to the methodology was attempted by reducing the leach time from 2 hours to 1 hour. The justification for this step could be seen from the work of Uchikawa and Uchida (1974) as presented in Table 6-7 where the difference in the percentage of ettringite dissolved by an added hour of extraction was around 3% in EGM 31 and around 5% in EGM 13. This was the main reasoning behind the Batch 4 tests conducted on Ettringite 2B, in addition to testing the capabilities of the ICP machine with freshly prepared solutions. Ettringite 2C samples tested (Tables 6-10 and 6-11) had originally been prepared for analysis with the AA and IC instruments a few weeks before being tested with the ICP. Once the ability of the latter was confirmed and its advantage over the combined AA and IC method proven, a more ambitious testing program was undertaken, which was the dissolution of Ettringite 2A, 2B, and 2C in EGM 13, 31, and water at a weight-to-volume ratio of 1. The results of the resulting Batch 4 and 5 tests are given in Tables 6-12 and 6-13, respectively.

Sample ID	W:V	Leach	AI (g)	S (g)	Ett (g)	Ett (%)	S (%)
Ett 2 1:10	1.02	EGM 13	0.0001	0.0002	0.0029	14.45	0.88
Ett 2 1:10	1.04	EGM 31	0.0002	0.0008	0.0038	18.15	3.78

Table 6-12 – Results of Batch 4 tests on Ettringite 2B – ICP/centrifuge

When the results of Table 6-12 are compared to those of Table 6-8, it can be seen that the difference between the two is relatively small. An estimate of 22.5% ettringite can be deduced from the latter while about 18% is given by the former. Considering the different ratios and instruments used in the two sets, a slightly less than 5% variation can

be accepted. As for the difference between the EGM 31 and 13 values in Table 6-12, they are less than 4%, which was the same difference obtained in the case of Ettringite 2C in Table 6-11. No previous leaching with EGM 13 was done on Ettringite 2B to compare to, but the values in Table 6-12 are remarkably close to those for Ettringite 2C.

Sample ID	W:V	Leach	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
Ett2A 13	1.03	EGM 13	0.0001	0.0003	0.0023	11.22	1.33
Ett2A 31	1.03	EGM 31	0.0001	0.0006	0.0024	11.78	2.85
Ett2A water	1.03	Water	0.0001	0.0010	0.0033	16.01	4.78
Ett2B 13	0.99	EGM 13	0.0001	0.0004	0.0028	14.32	1.92
Ett2B 31	1.04	EGM 31	0.0002	0.0008	0.0039	18.65	3.72
Ett2B water	1.02	Water	0.0001	0.0013	0.0027	13.42	6.29
Ett2C 13	0.98	EGM 13	0.0001	0.0003	0.0020	9.98	1.29
Ett2C 31	1.01	EGM 31	0.0001	0.0005	0.0023	11.58	2.41
Ett2C water	0.99	Water	0.0001	0.0013	0.0021	10.67	6.55

Table 6-13 – Results of Batch 5 tests on Ettringite 2A, 2B, and 2C - ICP/centrifuge

Table 6-13 presents an entire batch of tests on the three formations of Ettringite 2 using the same analytical technique, thus providing a solid basis of comparison amongst them. Sample 2A shows interesting results in that it yields higher percentages of ettringite in water than in any of the EGM solutions. It is intuitive to expect maximum dissolution to take place in the EGM 31 solution as it is the most concentrated one amongst the three, and ettringite does not readily dissolve in water. By comparing the EGM 31 results, Ettringite 2A has a 12% yield of the mineral, compared to 19% for 2B and 12% for 2C. Hence, the maximum yield is given by 2B, which was dried for a few months in a desiccator. Except for 2A, the other samples exhibit maximum dissolution in EGM 31, followed by either EGM 13 or water. In all cases, however, differences between the minimum and maximum values do not exceed 5%. One of the better correlations is the result for 2B obtained in this batch with those in the previous one where the differences in each of EGM 13 and 31 do not exceed 0.5%.

The experiments conducted so far concentrated on a weight-to-volume ratio of 1. Given the low solubility of ettringite in water and the existence of a K_{sp} value to serve as a benchmark, an investigation into the lower ranges of that ratio was needed in order to verify the true amount of ettringite present in the formed samples. Seeing that no hard data was available for the EGM solutions, the water approach was more promising. The

 K_{sp} value given by Perkins and Palmer (1999) is -44.9 and translates into 0.3148 g/l. However, the same authors admit that the value for ettringite ranges from -35 to -45; an average value of -40 would yield a solubility of 0.6678 g/l, which is greater than double the amount for a K_{sp} of -44.9. While the former would allow a maximum amount of 0.0155 g to be dissolved in 50 ml water, the latter value would accept 0.0344 g of the mineral. It meant that at ratios less than 0.3, all the ettringite present in the sample would dissolve in the first case and the same would take place in the second case for ratios less than 0.7. The next batch was designed to look into ettringite dissolution for 2B – as it yielded the maximum mineral amongst the three – in all three solvents at ratios less than 1 based on these solubility estimations, and the results are given in Table 6-14 below.

Sample ID	W:V	Leach	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
E2B 13 1	0.10	EGM 13	0.0000	0.0003	0.0010	21.13	5.43
E2B 13 2	0.30	EGM 13	0.0001	0.0004	0.0022	14.41	2.57
E2B 13 3	0.50	EGM 13	0.0001	0.0005	0.0032	12.96	1.94
E2B 13 4	0.71	EGM 13	0.0002	0.0005	0.0056	15.62	1.46
E2B 31 1	0.12	EGM 31	0.0000	0.0003	0.0006	9.95	4.72
E2B 31 2	0.30	EGM 31	0.0000	0.0007	0.0010	6.81	4.40
E2B 31 3	0.49	EGM 31	0.0001	0.0010	0.0020	8.22	4.24
E2B 31 4	0.69	EGM 31	0.0001	0.0016	0.0032	9.13	4.54
E2B W 1	0.11	Water	0.0000	0.0004	0.0003	6.14	7.72
E2B W 2	0.29	Water	0.0001	0.0012	0.0027	18.82	7.96
E2B W 3	0.52	Water	0.0003	0.0023	0.0060	23.38	9.02
E2B W 4	0.69	Water	0.0004	0.0030	0.0082	23.81	8.63

Table 6-14 - Results of Batch 6 tests on Ettringite 2B - ICP/filter

The leach volume used in Batch 6 was 50 ml and from the solubility values given above, it can be calculated that the maximum amount of ettringite dissolved in 50 ml of water is 0.0344 g using a K_{sp} value of -40 (0.67 g/l) and 0.0155 g using -44.9 (0.31 g/l). The values in Table 6-14 are well below those numbers and it can safely be assumed that all the ettringite available has been dissolved barring any effects of the common sulphate ion emanating from gypsum. The results obtained for EGM 31 and 13, however, were unexpected as the more dilute of the two solutions extracted much more of the mineral than the concentrated one. The difference between the two was large and consistent enough so as not to be the result of experimental errors. When compared to former tests, it can be seen that the EGM 13 results are in line with the values in Tables 6-12 and 6-13.

Hence, it is the EGM 31 outcomes that are at variance with former values, which predict an 18% extraction for a weight-to-volume ratio of 1. However, even with this discrepancy, it can be seen that the different ratios did not affect the percentage of ettringite extraction in EGM 31 solutions within this batch.

Sample ID	W:V	Leach	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
E2A 0.075	0.38	Water	0.0010	0.0050	0.0223	29.68	6.63
E2A 0.125	0.62	Water	0.0016	0.0084	0.0364	29.26	6.78
E2A 0.140	0.70	Water	0.0019	0.0096	0.0441	31.34	6.83
E2A 0.150	0.75	Water	0.0019	0.0102	0.0447	29.67	6.75
E2A 0.160	0.80	Water	0.0021	0.0110	0.0483	30.11	6.85
E2A 0.200	1.00	Water	0.0027	0.0127	0.0618	30.77	6.31
E2A 0.250	1.25	Water	0.0027	0.0173	0.0638	25.49	6.92
E2A 0.300	1.50	Water	0.0028	0.0192	0.0656	21.85	6.40
E2B 0.075	0.38	Water	0.0009	0.0094	0.0206	27.24	12.42
E2B 0.150	0.75	Water	0.0019	0.0182	0.0453	30.11	12.09
E2B 0.165	0.83	Water	0.0021	0.0195	0.0493	29.58	11.72
E2B 0.175	0.87	Water	0.0023	0.0228	0.0529	30.34	13.10
E2B 0.185	0.92	Water	0.0026	0.0254	0.0605	32.74	13.73
E2B 0.225	1.13	Water	0.0033	0.0299	0.0767	34.02	13.25
E2B 0.250	1.25	Water	0.0036	0.0295	0.0826	33.06	11.82
E2B 0.300	1.50	Water	0.0044	0.0396	0.1014	33.81	13.20

Table 6-15 - Results of Batch 7 tests on Ettringite 2A and 2B - ICP/filter

Due to data being available from the literature for water solubility, Ettringite 2A and 2B underwent the next batch of tests with this medium as the sole leach solution at a wide range of weight-to-volume ratios. From the results in Table 6-15 above, consistent values are observed for both samples with the former at around 30% up to a ratio of 1, and the latter at slightly higher overall values at around 32%. These numbers are deemed to be quite reliable due to the fact that the volume of water used was 200 ml, which required larger weights, thus decreasing the risk of using unrepresentative samples at lower ratios.

The results of the final batch of tests for Ettringite 2B are presented in Table 6-16 below. The solutions used were 50 ml and the analysis had to be repeated due to errors in the sulphate readings, and experimental errors are detected once again in the lower range of ratios. Although slightly lower values are observed in water, the EGM 31 readings were consistent with former ones.

Sample ID	W:V	Leach	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
E2B W	0.11	Water	0.0000	0.0009	0.0005	9.39	15.40
E2B W	0.30	Water	0.0001	0.0027	0.0027	18.21	18.26
E2B W	0.60	Water	0.0003	0.0059	0.0064	21.33	19.49
E2B W	1.01	Water	0.0005	0.0103	0.0122	24.31	20.41
E2B W	2.50	Water	0.0003	0.0084	0.0072	5.75	6.75
E2B W	5.01	Water	0.0003	0.0168	0.0062	2.48	6.71
E2B 31	0.11	EGM 31	0.0000	0.0012	0.0011	21.93	24.83
E2B 31	0.30	EGM 31	0.0001	0.0019	0.0012	8.27	12.44
E2B 31	0.60	EGM 31	0.0001	0.0024	0.0035	11.67	7.98
E2B 31	0.99	EGM 31	0.0003	0.0034	0.0075	15.16	6.77
E2B 31	2.50	EGM 31	0.0010	0.0056	0.0228	18.23	4.52
E2B 31	5.00	EGM 31	0.0018	0.0062	0.0412	16.46	2.48

Table 6-16 - Results of Batch 9 tests on Ettringite 2B - ICP/filter

6.2.2.4 Derivation of solubility curves – Water and EGM 31

The derivation of solubility curves for gypsum in water and EGM 31 solutions was outlined in a previous section, and the reasons for disregarding the EGM 13 results were stated. Using the same process, and relying on results obtained by filtration and ICP analysis only, the first parameter to look into was the dissolution for ettringite in both solutions. Based on the tables in the previous section, samples 2A and 2B were the only ones tested in both solutions within ranges sufficient enough to merit a graphical study. It must be kept in mind that whereas the leaching of gypsum was simpler, the ettringite samples were mixtures of two minerals in unknown percentages. Hence, the first priority of the graphical study was to determine the amount of ettringite in the samples prepared by Method 2.

Figures 6-6 and 6-7 below plot the dissolution of Ettringite 2 samples in water and the EGM 31 solution, respectively. In the first case, 2A and three different tests on 2B are presented as ettringite dissolved against the weight-to-volume ratio used. An immediate pattern can be discerned in terms of mineral solubility in water, which is an increase in its concentration until about 0.5 g/l after which a sharp drop can be seen to about 0.15 g/l, where the curve seems to stabilize. The increase takes place until a ratio of 1.5 is reached and it is not known whether the rise continues slightly before it goes down towards a ratio of 2.5.



Figure 6-6 – Ettringite 2 solubility in water



Figure 6-7 – Ettringite 2 solubility in EGM 31

If the last point is taken at 1.5, the solubility in water can be given as 0.51 g/l, which translates into a K_{sp} of -42. The value obtained is higher than the 0.31 g/l given by Perkins and Palmer (1999) but is below the average number they cite from the literature, which is 0.67 g/l. In simple terms, it means that as long as the amount of ettringite remains below this threshold, the mineral can be dissolved in its entirety in water. Hence, any percentage values obtained for it within the range would be the actual amount of ettringite present in the sample tested. While several values were available from the literature for dissolution in water, none were given for its solubility in EGM 31. Although Uchikawa and Uchida (1974) did provide an approximation, their value was valid only for a weight-to-volume ratio of 1 and they recommended its adoption without explaining if any discrepancies would arise if different ratios were used. Similarly, Odler and Abdul-Maula (1984) gave a value of 98.4% for a ratio of 0.67 without further clarification regarding other numbers. In addition, both of these references experimented with pure ettringite whereas in the tests outlined above, the products were a mixture of the mineral with gypsum. Therefore, it was crucial to study the behaviour of the mix in the EGM 31 solution.

Figure 6-7 above plots the same data as in the previous graph except for the fact that the solution used was the organic one. It can immediately be observed that where ettringite dissolution is concerned, EGM 31 is superior to water over the tested range in that no solubility limit is reached and that a linear relation exists between the amount of ettringite in the sample and the portion that is dissolved. This is crucial information since it allows for higher weight-to-volume ratios to be used in the tests without concern for an upper ceiling that should not be crossed. The use of larger amounts would naturally be more representative of the sample being tested, and would decrease the effect of errors in weighing or analysis. Since the trend is linear in the graph, the amount of ettringite dissolved in 1 g of sample can be read from the slope of the line. Hence, an initial estimate of the overall amount of ettringite dissolved in the 2B samples is 16.49%.

Figure 6-8 presents Ettringite 2 dissolution in water for the range within which the relationship with respect to the weight-to-volume ratio is linear. Trials 1 and 3 for sample 2B give identical lines while trial 2 is slightly higher than the two. On the other hand,
sample 2A remains identical to trial 2 values until a ratio of 1 where the curve reaches a plateau. The reason is because the maximum amount of ettringite available in the sample has been reached and increasing the weight will not provide any further mineral for dissolution. Using the same technique as in EGM 31, the amount of ettringite can be read from the slope of the lines and this gives about 23% for Ettringite 2B and 32.5% for 2A.



Figure 6-8 – Ettringite 2 solubility in water (W:V 0.1 to 1.5)

The data is plotted as percentage of ettringite in the samples in Figure 6-9 and 6-10 for water and EGM 31, respectively. Two trials of Ettringite 2B provide a maximum number of 25% in the first plot, while the third trial and sample 2A give a higher amount at around 30%. This translates into 70-75% gypsum in Ettringite 2 samples, which means that the formation of the mineral was not very successful using the method suggested. The data in the graph shows a good consistency with an average value of 25-30% of ettringite in these samples. By lowering the weight-to-volume ratio sufficiently, it was possible to dissolve all the ettringite present and these were the values obtained. On the other hand, Figure 6-10 gives the amount of the mineral dissolved in the EGM 31 solution. No data is available for sample 2A but Ettringite 2B shows a maximum value of around 18.25% at a ratio of 2.5.



Figure 6-9 – Ettringite 2 percentage in water



Figure 6-10 – Ettringite 2 percentage in EGM 31

This is close to the percentage dissolved in water but is less than that value. One explanation can be that EGM 31 cannot completely dissolve this type of the mineral except for about 75% of its amount. Another possibility is the unknown effect of gypsum on ettringite solubility in EGM 31. Whereas mineral dissolution in water is well known,

and the effect of common ions is an established fact in chemistry, the solubility of these two minerals and the effect of a common ion in an organic solvent are less clear. The 75% extraction rate of EGM 31 is lower than the 91% reported by Uchikawa and Uchida (1974) at a weight-to-volume ratio of 1 or the 98.4% dissolution presented by Odler and Abdul-Maula (1984) at a ratio of 0.67.

As explained in the preceding paragraph, a final factor that must be weighed in with respect to the amount of ettringite dissolved is the gypsum content and the effect of having sulphur originating from two different sources in the solution. Figure 6-11 plots the sulphur percentage obtained from Ettringite 2 and compares it with the same data from pure gypsum. It is obvious that the two plots are strikingly similar in trend, and it proves the fact that the percentage of gypsum must be high enough in the sample to be comparable to that of the pure mineral. It remains to be seen whether any numerical calculations can be obtained from the plots.



Figure 6-11 – Ettringite 2 sulphur percentage in EGM 31

The initial value obtained at a weight-to-volume ratio of 0.1 shows a higher amount of gypsum in Ettringite 2 than in the pure mineral, thus indicating the deficiencies inherent in using a very small amount of sample. However, when the other values are compared to that of pure gypsum, amounts of 81.15% to 82.26% of the mineral are calculated for ratios 0.3, 0.6, and 1. These are very close to the 75% gypsum estimate obtained previously by deducting the amount of ettringite present from the total amount of sample. The method provides 70% and 57% of the mineral at weight-to-volume ratios of 2.5 and 5, respectively. Although an estimate, it can be concluded that where gypsum is present substantially, the sulphur percentage value can be used as a second method of calculating the amounts of the two minerals in a mixed sample.

6.2.3. ETTRINGITE 3 CHARACTERIZATION

Ettringite 3 was prepared in the laboratory as outlined in Chapter 5 and it was characterized by the same techniques as gypsum and Ettringite 2, which were XRD and dissolution in water, EGM 13 and 31 solutions.

6.2.3.1 XRD analysis

XRD was conducted on samples of Ettringite 3A and 3B and their plots are given in Figure 6-12 below. As in the case of Ettringite 2, the gypsum plot has been added to the ones for Ettringite 3A and 3B for comparison purposes. However, the trend seen in the mineral obtained from the previous method is reversed. While the peaks of gypsum dominated the XRD plot in the former case, the ettringite peaks at 20 values of 9.016°, 15.533°, 22.962°, 32.054°, and 34.882° within the scanned range of 5° to 40° are in clear dominance in the samples here. It must be noted that only the main peaks of the mineral have been labelled in the figure below, and some of the other peaks are secondary ones.

The main gypsum peak can be detected with difficulty at 11.650° while the one at 20.737° is somewhat clearer. It is obvious that a small percentage of gypsum does exist with the ettringite, thus resulting in a second mixed sample, but the latter mineral is the quantitatively dominant one. Since the XRD provides semi-quantitative analysis at best, the dissolution techniques used for Ettringite 2 were employed for a quantitative evaluation of Ettringite 3.



Figure 6-12 – XRD plot for Ettringite 3A and 3B

6.2.3.2 Leaching tests – current work

The leach test results from previous work were covered in Section 6.2.2.2 above, and need not be repeated here. The tests were performed on Ettringite 3 using EGM 13, 31, and water as the solutions, and followed the same procedure as those of Ettringite 2. The results from the first three batches on Ettringite 3A, 3B, and 3C are given in Tables 6-17 through 6-19 below.

Table 6-17 – Results of Batch 1 tests on Ettringite 3B – AAIC/centrifuge

Sample ID	W:V	Leach	Al (g)	SO4 (g)	S (g)	Ett (g)	Ett (%)	S (%)
Ett 30.2	5.03	EGM 31	0.0068	0.0241	0.0080	0.1575	78.19	3.99
Ett 3 0.5	12.51	EGM 31	0.0151	0.0441	0.0147	0.3522	70.38	2.94
Ett 3 1.0	24.97	EGM 31		0.0644	0.0215	0.0000		2.15

Table 6-18 – Results of Batch 2 tests on Ettringite 3A – AAIC/centrifuge

Sample ID	W:V	Leach	Al (g)	SO4 (g)	S (g)	Ett (g)	Ett (%)	S (%)
Ett III 1:10	1.04	EGM 13	0.0001	0.0009	0.0003	0.0022	10.66	1.40
Ett III 1:10	1.00	EGM 31	0.0004	0.0028	0.0009	0.0084	41.82	4.61

Sample ID	W:V	Leach	Al (g)	SO4 (g)	S (g)	Ett (g)	Ett (%)	S (%)
Ett3 1:10	0.53	EGM 13	-0.0002	0.0007	0.0002	-0.0035	-33.63	2.19
Ett3 1:10	1.01	EGM 13	-0.0002	0.0008	0.0003	-0.0036	-17.74	1.33
Ett3 1:10	1.53	EGM 13	-0.0002	0.0009	0.0003	-0.0038	-12.53	0.94
Ett3 1:10	0.53	EGM 31	-0.0001	0.0018	0.0006	-0.0012	-11.44	5.81
Ett3 1:10	1.02	EGM 31	0.0001	0.0035	0.0012	0.0020	10.18	5.67
Ett3 1:10	1.54	EGM 31	0.0001	0.0050	0.0017	0.0031	10.21	5.42

Table 6-19 – Results of Batch 3 tests on Ettringite 3C – AAIC/centrifuge

The results in Table 6-17 show the relatively high percentage of ettringite formed in sample 3B. Even at higher weight-to-volume ratios such as 12.5, a 70% extraction with EGM 31 took place. At a ratio of 5, the value was around 78%, and if it is assumed that the entire sample was ettringite, the concentrated EGM solution was able to dissolve 78% of that amount. This is very close to the maximum dissolution of 75% that was observed for the same solution in Ettringite 2B. The following batches tested Ettringite 3A and 3C and the same analytical techniques were used as in the previous batch, albeit at different weight-to-volume ratios. Sample 3A provided 42% dissolution with EGM 31 and although lower than the 3B content, it was nevertheless superior to the Ettringite 2 samples. The negative readings obtained for the EGM 13 solution for sample 3C with the AA instrument proved again that a new analytical technique was in need due to the spectrometer's inability to detect aluminum levels lower than 10 ppm in the dilutions.

Sample ID	W:V	Leach	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
Ett3 1:10	0.53	EGM 13	0.0001	0.0002	0.0013	11.94	1.68
Ett3 1:10	1.01	EGM 13	0.0001	0.0001	0.0013	6.68	0.73
Ett3 1:10	1.53	EGM 13	0.0001	0.0002	0.0012	3.96	0.60
Ett3 1:10	0.53	EGM 31	0.0002	0.0005	0.0037	35.62	4.60
Ett3 1:10	1.02	EGM 31	0.0003	0.0010	0.0073	36.07	4.68
Ett3 1:10	1.54	EGM 31	0.0004	0.0015	0.0082	26.61	4.71

Table 6-20 – Results of Batch 3 tests on Ettringite 3C – ICP/centrifuge

With the change in analytical technique, the samples from Batch 3 were tested with the ICP in order to compare them with the former readings obtained with the AA (Table 6-20). The first observation was that the amount of ettringite leached was closer to the 30-35% range than the 10% values indicated previously. That the fault lay with the method of analysis was clear from the readings for sulphur. Although slightly lower with

the ICP than with the IC, the percentage of sulphur read remained relatively close to the previous values. The ICP analysis was conducted on the samples a few weeks after they were extracted, as opposed to the AA one that was done in the following days, and a 1% drift in the EGM 31 solution is not unusual. The differences between the EGM 13 sulphur percentages are even less.

Batch 4 was conducted in part to test the ICP instrument with fresh samples, and also in order to verify the percentage of ettringite in sample 3B as it proved the best in mineral yield based on the results of the first three batches. The numbers are given in Table 6-21 below, and show a remarkable 90% extraction with EGM 31 while EGM 13 could dissolve slightly more than 50%. The high extraction rate was in line with the first tests if an allowance were made for the lower weight-to-volume ratio used here.

Table 6-21 - Results of Batch 4 tests on Ettringite 3B - ICP/centrifuge

Sample ID	W:V	Leach	AI (g)	S (g)	Ett (g)	Ett (%)	S (%)
Ett 3 1:10	1.04	EGM 13	0.0005	0.0003	0.0111	53.34	1.29
Ett 3 1:10	0.98	EGM 31	0.0008	0.0010	0.0178	90.47	5.04

In order to conduct an evaluation on the three ettringite samples, the tests of Batch 5 were undertaken using three types of leach solutions and the results are given in Table 6-22. EGM 31 proved to be superior to both EGM 13 and water in dissolving ettringite and gave values of 42%, 63%, and 11% for samples 3A, 3B, and 3C, respectively. The percentage of Ettringite 3B in EGM 31 was somewhat lower than the previous 90% obtained as was the one in EGM 13 with a 30% extraction compared to the previous 53%. The differences were in stark contrast to the same set of tests conducted on Ettringite 2B where Batch 4 values served as a confirmation for the ones in Batch 3. Since the same ratios, volumes, and period of extraction were used, the error must derive from an experimental one with the solution used or the inefficiency of the centrifuge system in separating the solids from the supernatant. One source of consistency, though, was the amount of sulphur in that it matched the previous results well.

Sample ID	W:V	Leach	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
Ett3A 13	1.01	EGM 13	0.0003	0.0003	0.0058	28.97	1.56
Ett3A 31	1.02	EGM 31	0.0004	0.0007	0.0087	42.32	3.45
Ett3A water	1.01	Water	0.0003	0.0010	0.0069	34.05	5.02
Ett3B 13	1.00	EGM 13	0.0003	0.0003	0.0060	29.80	1.63
Ett3B 31	1.02	EGM 31	0.0005	0.0010	0.0128	62.71	4.89
Ett3B water	1.01	Water	0.0002	0.0007	0.0048	23.95	3.38
Ett3C 13	0.99	EGM 13	0.0000	0.0003	0.0005	2.32	1.35
Ett3C 31	1.02	EGM 31	0.0001	0.0009	0.0022	10.76	4.34
Ett3C water	1.01	Water	0.0001	0.0012	0.0014	6.81	6.02

Table 6-22 – Results of Batch 5 tests on Ettringite 3A, 3B, and 3C – ICP/centrifuge

The values for the other samples were quite far from previous results even when the same instrument was used. For example, sample 3C yielded around 30% ettringite with EGM 31 in a second analysis of Batch 3 but only 11% in Batch 4. The rate of dissolution in EGM 13 showed less discrepancy with 7% and 2% for the two batches, respectively. In the case of sample 3A, the only result that could be taken as reference was from Batch 2 analyzed with the AA instrument. The 11% and 42% in EGM 13 and 31 were inconsistent with the 29% and 42% values, respectively, obtained in Batch 4. Once again, the results for sulphur were relatively harmonious with previous assessments. Compared to the 0.73% and 4.68% for EGM 13 and 31 at a ratio of 1, the new tests gave 1.35% and 4.34% for Ettringite 2C, which were somewhat consistent. As for Ettringite 2B, 1.63% and 4.89% were obtained for EGM 13 and 31 at a ratio of 1, compared to the previous values of 1.29% and 5.04%. Based on the consistency of sulphur but not aluminum readings, the experimental process cannot be at fault. One possible explanation could be instrument malfunction for aluminum measurement similar to the one affecting sulphur analysis in a previous batch. The new leach solution used in this series was water but due to the lack of previous data, no assessment could be made on the results, except that they were closer to the EGM 13 ones for ettringite dissolution, but nearer to the EGM 31 values in terms of sulphur.

Based on the inconsistent results for ettringite dissolution percentage obtained during Batch 5, further testing was needed to establish the amount of mineral present in the samples. The sample of choice was Ettringite 3B due to its high mineral content, and it was leached with EGM 13, 31, and water at ratios inferior to unity in order to maximize the dissolution of ettringite. In addition, filtration was used for the first time to separate the solid part from the supernatant due to the aforementioned inconsistencies with the centrifuge system. Analysis was conducted with the ICP instrument and the results are presented in Table 6-23.

Sample ID	W:V	Leach	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
E3B 13 1	0.12	EGM 13	0.0001	0.0003	0.0025	43.75	5.71
E3B 13 2	0.31	EGM 13	0.0003	0.0004	0.0071	46.25	2.57
E3B 13 3	0.49	EGM 13	0.0003	0.0004	0.0076	31.15	1.55
E3B 13 4	0.70	EGM 13	0.0006	0.0005	0.0133	37.96	1.48
E3B 31 1	0.09	EGM 31	0.0001	0.0003	0.0013	27.41	5.42
E3B 31 2	0.31	EGM 31	0.0004	0.0008	0.0095	60.25	4.85
E3B 31 3	0.50	EGM 31	0.0006	0.0008	0.0142	56.57	3.10
E3B 31 4	0.71	EGM 31	0.0010	0.0012	0.0223	63.10	3.46
E3B W 1	0.10	Water	0.0001	0.0002	0.0017	34.30	4.44
E3B W 2	0.30	Water	0.0003	0.0007	0.0064	42.59	4.43
E3B W 3	0.49	Water	0.0005	0.0012	0.0117	47.36	4.98
E3B W 4	0.71	Water	0.0005	0.0013	0.0117	32.84	3.52

Table 6-23 – Results of Batch 6 tests on Ettringite 3B – ICP/filter

The values for ettringite dissolution showed a remarkable consistency with those from Batch 5, with the maximum amount not exceeding the 63% threshold for EGM 31. The results for EGM 13 were the more interesting in that they provided around 45% ettringite at the lower weight-to-volume ratios but quickly diminished to the mid-30% range just before reaching unity, which complimented the previous result of 30% at a ratio of 1. The values for water exhibited the same behaviour with a start around 42% followed by a dip back to 33% at a ratio of 0.71, which was consistent with the 24% at unity. The sulphur values fell in pattern as well with no appreciable differences observed. Hence, it can be concluded that the readings in Batch 4 were the exception rather than the rule and due to an experimental error, they showed higher values of the mineral than was dissolved.

The next step was to study the dissolution in water in a wide-spanning range in order to establish the solubility value for Ettringite 3 in this medium. The samples used were Ettringite 3A and 3B and the different ratios and their results are presented in Table 6-24. The amount of ettringite extracted in sample 3A showed an average of 75% up to a weight-to-volume ratio of 0.5, after which the expected dip was observed until 61% at 1.

Sample ID	W:V	Leach	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
E3A 0.025	0.13	Water	0.0008	0.0025	0.0192	75.30	9.74
E3A 0.050	0.25	Water	0.0015	0.0050	0.0344	69.57	10.15
E3A 0.070	0.35	Water	0.0024	0.0072	0.0567	81.00	10.35
E3A 0.075	0.38	Water	0.0024	0.0074	0.0555	73.47	9.76
E3A 0.080	0.40	Water	0.0025	0.0078	0.0584	73.38	9.85
E3A 0.100	0.51	Water	0.0032	0.0106	0.0745	73.76	10.48
E3A 0.150	0.75	Water	0.0040	0.0127	0.0922	61.22	8.41
E3A 0.200	1.01	Water	0.0052	0.0169	0.1220	60.56	8.36
E3B 0.010	0.05	Water	0.0003	0.0008	0.0070	71.51	7.94
E3B 0.025	0.13	Water	0.0009	0.0022	0.0218	84.31	8.51
E3B 0.050	0.25	Water	0.0018	0.0043	0.0415	82.33	8.47
E3B 0.075	0.37	Water	0.0023	0.0056	0.0543	73.02	7.49
E3B 0.100	0.50	Water	0.0037	0.0078	0.0860	85.38	7.79
E3B 0.120	0.60	Water	0.0042	0.0095	0.0976	80.90	7.85
E3B 0.125	0.63	Water	0.0041	0.0090	0.0948	74.82	7.12
E3B 0.130	0.65	Water	0.0041	0.0098	0.0947	72.37	7.47
E3B 0.150	0.76	Water	0.0044	0.0107	0.1033	67.87	7.00
E3B 0.175	0.88	Water	0.0053	0.0114	0.1231	70.33	6.49
E3B 0.200	1.00	Water	0.0049	0.0118	0.1131	56.50	5.90

Table 6-24 – Results of Batch 7 tests on Ettringite 3A and 3B – ICP/filter

For Ettringite 3B, the value was around 83% until a ratio of 0.65 when the decrease started and ended with about 57% at 1. The consistency of the readings around an average value at lower ratios could be used for an initial evaluation of ettringite content and values of 75% and 80% for samples 3A and 3B, respectively, would constitute acceptable estimates.

Sample ID	W:V	Leach	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
E3B W	0.10	Water	0.0001	0.0004	0.0025	50.35	7.79
E3B W	0.30	Water	0.0004	0.0012	0.0092	60.38	7.71
E3B W	0.61	Water	0.0007	0.0021	0.0173	56.43	6.97
E3B W	1.01	Water	0.0010	0.0034	0.0230	45.59	6.71
E3B W	2.49	Water	0.0009	0.0043	0.0211	16.90	3.46
E3B W	5.00	Water	0.0008	0.0067	0.0193	7.72	2.70
E3B 31	0.10	EGM 31	0.0001	0.0003	0.0015	29.30	6.29
E3B 31	0.31	EGM 31	0.0004	0.0008	0.0098	62.99	5.25
E3B 31	0.61	EGM 31	0.0011	0.0014	0.0249	81.39	4.53
E3B 31	1.00	EGM 31	0.0018	0.0021	0.0408	81.58	4.15
E3B 31	2.50	EGM 31	0.0043	0.0040	0.0998	79.72	3.22
E3B 31	5.01	EGM 31	0.0081	0.0068	0 1875	74 87	2 72

Table 6-25 – Results of Batch 8 tests on Ettringite 3B – ICP/filter

With the information gathered from Batch 7 tests, a final assessment was done on Ettringite 3B samples due to their highest concentration of the mineral amongst the three. EGM 31 and water were used as the solutions and the results are given in Table 6-25. The results for water dissolution are much lower than those of the previous batch, and show a decrease of 20% in the 0.3 to 0.6 ratio range. Once again, the sulphur results remain consistent with minor differences only. The variation in water dissolution values seems to be the norm for Ettringite 3B, with 24% in Batch 5, 57% in Batch 7, and 46% in Batch 8 for a weight-to-volume ratio of 1. A possible explanation could be that due to its high ettringite percentage, even small differences in the sampling process produced large discrepancies. This was not the same for Ettringite 2B where the average amount of the mineral did not exceed 35%.

6.2.3.3 Derivation of solubility curves – Water and EGM 31

Using the same technique as in the discussion of Ettringite 2 results, the readings for Ettringite 3 samples were plotted in terms of mineral dissolved, having been converted to g/l for consistency. Figure 6-13 gives the results for the water extractions while Figure 6-14 describes the ones for EGM 31. Regarding the dissolution in water, it follows the same trend as in Ettringite 2 except that the exact location of the peak cannot be determined due to the large gap between ratios of 1 and 2.5. The highest values plotted read 0.62 g/l, which is quite close to the 0.51 g/l for the former sample, and can be converted to a K_{sp} value of -40. Once again, the dissolution in EGM 31 is seen to be a linear affair from a ratio of 0.1 until at least 5 with a best fit curve shown based on the 3B samples. This demonstrates for the second time that the use of the organic solution is superior to water in terms of the stability provided in the readings.



Figure 6-13 – Ettringite 3 solubility in water



Figure 6-14 – Ettringite 3 solubility in EGM 31

With the same rate of dissolution for higher weight-to-volume ratios, larger samples could be used in order to minimize experimental errors and their effects on the final readings. Using the method of assessing the amount of ettringite dissolved from the slope of the line, it could be calculated that EGM 31 indicated the presence of around 75.5% of the mineral in sample 3B. For the amount derived through water dissolution, the lower ratios must be consulted, and these are presented in Figure 6-15 below. In this case, the trends are slightly more complex than the Ettringite 2 ones for the same region, and they can be observed to be polynomial in nature rather than linear. However, if linear approximations are taken, values of 65-70% can be obtained from the slopes. In order to verify the numbers, the percentages of ettringite in both solutions are plotted in Figures 6-16 and 6-17.



Figure 6-15 – Ettringite 3 solubility in water (W:V 0.1 to 1.5)



Figure 6-16 – Ettringite 3 percentage in water





It can immediately be observed that Ettringite 3 provided a much higher yield of the mineral than its previous counterpart. The percentage given by water dissolution was about 75% for sample 3A, but the numbers for the three trials on sample 3B were different from each other. The first trial gave quite low percentages at 50%, and the third

one was somewhat higher at about 60%. The second trial, which had the most readings, provided an average of 80-85%, meaning that only 15-20% of the sample was made up of gypsum. As for the EGM 31 solution, it remained characteristically stable at around 80% for the third trial. It must be pointed out that unlike the Ettringite 2 samples both solutions gave around the same values for Ettringite 3 ones.

Therefore, the amount extracted by EGM 31 for this type of mineral was the same as the one leached by water, thus proving that the organic solution could dissolve almost 100% of the ettringite in the sample. These were slightly higher than the values given by previous authors such as Uchikawa and Uchida (1974) who have 91.44%, and Odler and Abdul-Maula (1984) who suggested a rate of 97.8% for Method 3. One advantage of the current work over previous ones was the wide range of weight-to-volume ratios tested for the mineral and the associated increase in the level of confidence. When a value of 80% ettringite could be plotted from a ratio of 0.61 to 2.5, and similar numbers are derived from water extraction, the conclusion is that the EGM 31 solution is able to dissolve the entire ettringite component in a given sample even when its weight is 2.5 times the volume used when expressed in litres.

As with Ettringite 2, a final word must be said about the sulphur percentage in the sample. Figure 6-18 below plots the amount of sulphur dissolved against the ratios, and compares it with the one obtained from pure gypsum. Unlike the former sample, the trend line for Ettringite 3 does not follow the one for gypsum, and it is observed to be rather flat in the lower ranges of the weight-to-volume ratio axis. This is undoubtedly due to the presence of large amounts of ettringite in the sample, with the majority of sulphur originating from there rather than the calcium sulphate mineral. A separate analysis of plots at various proportions of ettringite and gypsum proved this point and showed that the shape of the gypsum trend line is followed until a 50:50 combination of the minerals. Once ettringite starts to dominate, a flatter curve is observed at low ratio values, and therefore the sulphur percentage value can no longer be directly used with respect to gypsum to calculate the amount of the mineral present.



Figure 6-18 – Ettringite 3 sulphur percentage in EGM 31

6.3. PHASE II RESULTS – BINDERS

The objective of the experimental procedure adopted in Phase II of the project was to quantitatively evaluate the formation of ettringite and/or gypsum in four binder samples undergoing sulphate and acid attack. The tests followed the procedure suggested by Mehta and Gjörv (1974) and Monteiro et al (2000) for a full immersion test of sample cubes in a 4% by weight solution of sodium sulphate (NS) kept at a constant pH of 6-7 with aliquots of 1N sulphuric acid. A ratio of around 50 ml per sample cube was adopted for this test based on the work of several authors, as explained previously in Chapter 5. Acid attack was simulated by adopting a 2% by volume sulphuric acid (HS) solution used in Chinese Standard GJ-82-85 for the durability of concrete, and the same ratio of solution-to-cube was adopted as for the sodium sulphate test. Full immersion tests with the two solutions were conducted on the cement-slag and cement-fly ash binders for a period of 28 days. In addition, partial immersion tests were done with the same solutions for all four binders for a period of 8 days. The results of the qualitative and quantitative tests on the binders are presented in the coming sections.

6.3.1. CURING PROCESS

Curing was done at 50°C in a laboratory oven at an accelerated pace designed to correspond to the regular 28 days required by concrete standards. The method was based on the work of several authors (Mehta 1975, Mehta and Gjörv 1974, and Monteiro et al 2000) who confirmed that the rapid curing pace at an elevated temperature would guarantee maximum hydration especially from blended binders using slag and fly ash. These would normally require much longer periods than the 28 days needed for pure cement to undergo the better part of their hydration. The curing process was assessed using XRD and dissolution tests with EGM 31, followed by an analysis of the ettringite and gypsum formed by measuring the aluminum and sulphur concentrations with the ICP instrument. These tests were conducted after 3 and 7 days of curing.

6.3.1.1 Qualitative analysis – XRD

The results of the XRD analysis on the unhydrated components of the different binders are given in Figure 6-19 below. The intensity of the peaks for the various materials has been modified so as to better fit in the graph.



Figure 6-19 - XRD analysis of binder components

From the plot, it can be seen that both slag and fly ash comprise amorphous contents, characterized by the gentle humps that appear in the graphs between 20° and 35°. Slag is entirely composed of this amorphous material since it lacks any actual peaks. A comparison with several other slag samples verified the existence of the characteristic hump in all of them between the aforementioned angles. This is not surprising because the process of preparing slag is geared towards fast quenching and the production of amorphous phases, which give the material its pozzolanic properties. Fly ash is characterized by a gentler hump indicating the presence of glassy microspheres, which has been widely reported in the literature. In addition, it exhibits a single characteristic peak at 26.5°, which is indicative of mullite, a key component of fly ash. The cement signature lies within the two sets of clinker peaks between 28.8° and 29.8°, and 31.3° and 35.5° for the range scanned by the XRD.

Figures 6-20 and 6-21 present the XRD plots of the four binders after 3 and 7 days of curing in the oven. The first observation is the relative decrease or absence of the portlandite, the calcium hydroxide mineral produced as a result of cement hydration – in addition to the CSH gel – and the main peaks for the mineral lie at 18° and 34°.



Figure 6-20 - XRD analysis of the four binders - 3 days of curing

This is readily observed in the mixed binders as opposed to cement after 3 days of curing. The peaks are very pronounced in the cement-only binder but are less so in the others, and are minimal in the cement-slag-fly ash one, which is not surprising since the cement content in this binder is at a minimum. A second observation pertains to the characteristic fly ash peak at 26.5° in that it is lower in the binder with all three components than in the cement-fly ash one, even though the amount of ash used was the same for both types at 50% by weight. This is indicative of a higher amount of fly ash reacting with the other components in Binder 4. Clinker peaks appear to be the same for cement-slag and cement-fly ash binders and the lower peaks in Binder 4 are due to the lower cement content. A final feature in the two binders containing fly ash – Binders 2 and 4 – is the small peak that appears at 10°. Analysis shows that this belongs to jaffeite, which is simply the hydrated form of C₃S, and its maximum peak is at 10.206°. That it appears in only the two binders could be due to its origin in the fly ash segment.



Figure 6-21 - XRD analysis of the four binders - 7 days of curing

After 7 days of curing, no major changes are seen in the binders, except for the decrease in intensity for some of the essential peaks. Hence, the portlandite peaks at 18° and 34°, the fly ash peak at 26.5°, and raw clinker peaks all show a retreat indicating

further reactions during the hydration process. The jaffeite peak at 10° is replaced by a gentle hump in the cement-slag-fly ash binder, indicating its possible transformation into an amorphous equivalent such as hydrated gel.

6.3.1.2 Quantitative analysis – EGM 31

The results of leach tests are presented in Tables 6-26 and 6-27 for cement-slag samples after 3 and 7 days of curing, respectively. It can be observed that the amount of ettringite after 3 and 7 days of curing is minimal at only 2% for a weight-to-volume ratio of 5. The high amount indicated at the lower end of the 7-day old cubes is most likely due to experimental errors caused by the very small amounts of samples used. This is further indicated by the negative values for the first two ratios for most of the readings. The error does not originate from the instrument but rather from the very low amount of aluminum in the 1:10 dilution of the sample in question.

Sample ID	Wt (g)	Vol (I)	W:V	AI (g)	S (g)	Ett (g)	Ett (%)	S (%)
PS 1/10	0.0050	0.05	0.10	0.0000	0.0000	-0.0001	-1.67	0.72
PS 1/10	0.0154	0.05	0.31	0.0000	0.0003	-0.0002	-1.14	1.71
PS 1/10	0.0303	0.05	0.61	0.0000	0.0000	0.0002	0.56	0.06
PS 1/10	0.0501	0.05	1.00	0.0000	0.0000	0.0003	0.66	0.06
PS 1/10	0.1249	0.05	2.50	0.0001	0.0002	0.0023	1.81	0.18
PS 1/10	0.2503	0.05	5.01	0.0002	0.0005	0.0047	1.89	0.18

Table 6-26 - Results of leach tests on PS binder - 3 days of curing

Table 6-27 – Results of leach tests on PS binder – 7 days of curing

Sample ID	Wt (g)	Vol (I)	W:V	AI (g)	S (g)	Ett (g)	Ett (%)	S (%)
PS 1/10	0.0052	0.05	0.10	0.0000	0.0003	0.0003	5.64	5.39
PS 1/10	0.0152	0.05	0.30	0.0000	0.0002	-0.0003	-2.01	1.56
PS 1/10	0.0300	0.05	0.60	0.0000	0.0003	0.0002	0.83	1.04
PS 1/10	0.0505	0.05	1.01	0.0000	0.0007	0.0003	0.53	1.37
PS 1/10	0.1249	0.05	2.50	0.0001	0.0008	0.0015	1.21	0.63
PS 1/10	0.2505	0.05	5.01	0.0002	0.0013	0.0047	1.86	0.52

The lowest concentration of standards used for ICP calibration was 1 ppm and the aluminum content at that ratio was below that value, in which case a negative reading was registered, similar to the lower-than-10 ppm values measured on the AA machine in

Phase I. The 2% ettringite detected in the samples is most probably the primary mineral formed due to cement hydration and this number can be taken as a benchmark against which future results are compared. As for the amount of sulphur present, it can be observed that it is minimal after both 3 and 7 days of curing, indicating that no appreciable amounts of either ettringite or gypsum are present in the samples prior to immersion in the attack solutions. The maximum numbers are around 1.4% of sulphur compared to the weight of the sample. Along with the ettringite values, the sulphur amount could act as a baseline against which future readings can be compared.

The results for the cement-fly ash binder are given in Tables 6-28 and 6-29 for 3 and 7 days of curing in the oven, respectively. Elevated amounts of ettringite are observed in the latter samples compared to the former ones, indicating the formation of primary ettringite due to hydration. The information is useful in that it provides a look into the hydration of cements incorporating fly ash. Whereas no increase was observed in the first binder, the higher amounts of ettringite in the second indicate that this binder requires a longer period to fully hydrate. At the highest weight-to-volume ratio used, comparable amounts of ettringite are observed to have been dissolved in the 3-day and 7-day cured samples.

Sample ID	Wt (g)	Vol (I)	W:V	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
PF 1/10	0.0052	0.05	0.10	0.0000	0.0002	-0.0001	-1.83	4.21
PF 1/10	0.0153	0.05	0.31	0.0000	0.0002	-0.0003	-1.68	1.56
PF 1/10	0.0303	0.05	0.61	0.0000	0.0003	0.0000	-0.01	1.11
PF 1/10	0.0505	0.05	1.01	0.0000	0.0003	0.0001	0.15	0.52
PF 1/10	0.1250	0.05	2.50	0.0001	0.0003	0.0017	1.37	0.22
PF 1/10	0.2502	0.05	5.00	0.0001	0.0004	0.0031	1.25	0.15

Table 6-28 – Results of leach tests on PF binder – 3 days of curing

Table 6-29 - Results of leach tests on PF binder - 7 days of curing

Sample ID	Wt (g)	Vol (I)	W:V	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
PF 1/10	0.0053	0.05	0.11	0.0000	0.0005	0.0004	7.20	9.42
PF 1/10	0.0154	0.05	0.31	0.0000	0.0005	0.0003	1.94	3.35
PF 1/10	0.0303	0.05	0.61	0.0000	0.0005	0.0005	1.72	1.79
PF 1/10	0.0501	0.05	1.00	0.0001	0.0006	0.0012	2.34	1.12
PF 1/10	0.1247	0.05	2.49	0.0003	0.0009	0.0061	4.91	0.71
PF 1/10	0.2505	0.05	5.01	0.0002	0.0011	0.0049	1.95	0.42

Figures 6-22 and 6-23 plot the numbers into similar graphs that were done for gypsum and ettringite in Phase I. Based on the stable range of solubility values for EGM 31, the slopes of the dissolution lines can be used to estimate the amount of the mineral formed in the two binders. In the first one, ettringite remains almost constant at 1.75% and does not change dramatically between 3 and 7 days of curing. In the cement-fly ash binder, however, it makes up 1.2% of the sample after 3 days but increases to around 2% after 7 days of curing. This could be a result of the slower hydration of second binder when compared to first one. Nevertheless, it proves the effectiveness of the method in giving a quantitative assessment of the mineral at variable ratios.

When the sulphur amounts are reviewed, it can be observed once again that their percentage compared to the weight of the sample is minimal even after 7 days of curing. This indicates – as was the case for the first binder – that minimal amounts of ettringite or gypsum have formed as a result of hydration in the oven. The 1.1% sulphur values, in addition to the primary ettringite amounts, act as a baseline against which future readings of the element can be compared in order to assess the percentage of secondary phases of the two minerals formed due to attack.



Figure 6-22 – Ettringite percentage in PS binder



Figure 6-23 – Ettringite percentage in PF binder

6.3.2. FULL IMMERSION TESTS

The process for testing the samples by full immersion in two attack solutions was outlined in Chapter 5. Cubes from the cement-slag and cement-fly ash binders were analyzed qualitatively after 14 and 28 days of immersion with XRD, and quantitatively by leaching with the EGM 31 solution in the same manner as the oven-cured samples. In addition, a visual assessment was conducted on the samples due to their exhibiting the typical characteristics of attack described in the literature.

6.3.2.1 Visual assessment

A visual assessment was carried out on the samples after 14 and 28 days of immersion and prior to their crushing for XRD and leach analysis. Photos of the cement-slag binder are presented in Figure 6-24 for samples immersed for 14 days in sodium sulphate (NS) and sulphuric acid (HS) solutions. No major visual observations could be noted in terms of damage except for the fact that a white material – possibly gypsum – covered the cubes immersed in sulphuric acid.



Figure 6-24 – PS binder cubes fully immersed in NS (left) and HS (right) – 14d

Once crushing was undertaken, however, a reaction rim was observed in the cubes that had been immersed in acid (Figure 6-25). Measurement with a ruler gave its thickness at around 1-2 mm, which is about 17% of the original thickness of the cube. No such rims were observed in the samples immersed in the sodium sulphate solution.



Figure 6-25 – PS binder cube showing reaction rim – fully immersed in HS – 14d

Photos of the cement-fly ash binders are given in Figure 6-26 for the sulphate and acid solutions. No visual differences were observed between samples immersed in the two solutions as had been the case for the first binder. Upon crushing the cubes, a similar reaction rim was seen, however, in the samples immersed in the acid solution. It was somewhat thicker than the one in the cement-slag binder and was accompanied by yellow-brown staining at the border between the core and the outer rim (Figure 6-27).



Figure 6-26 – PF binder cubes fully immersed in NS (left) and HS (right) – 14d





After 28 days of curing, both binders in the two solutions – except cement-slag in the sodium sulphate solution – showed marked signs of further deterioration in terms of their visual assessment. This was not very apparent in the case of the cement-slag binder undergoing sulphate attack, and no visual differentiation could be made between the 14day and 28-day samples of this type. However, in samples of the same binder that had been subjected to acid attack, the difference was markedly obvious (Figure 6-28). The faces of the cube samples seemed to be coming off the inner core in a geometric manner. Comparing the features of the cubes to their 14-day counterparts, it was obvious that the deterioration process had accelerated in the last two weeks of the testing period. When crushed, the cubes did not exhibit any reaction rims that were seen after 14 days of immersion, and the entire cube now seemed to be affected (Figure 6-29).



Figure 6-28 – PS binder cubes fully immersed in NS (left) and HS (right) – 28d



Figure 6-29 – PS binder cube transformed into gypsum – fully immersed in HS – 28d

The cement-fly ash binder showed similar signs of damage not only in its samples that had been immersed in acid, but also in the ones attacked by sodium sulphate. If the photo in Figure 6-30 is compared to its 14-day counterpart, it can be seen that the binder exhibited disintegration. No discoloration or other features could be discerned between samples of different age except for the physical disintegration of some of the cubes. In the case of samples that had been placed in acid, they did not show any of the whitening caused by gypsum as in the cement-slag samples but exhibited slight cracking. However, when crushed, a small inner core of yellowish-brown colour could be clearly discerned in some cubes, which constituted a small percentage of the entire cube (Figure 6-31). It was obvious that the reaction had progressed during the interval between 14 and 28 days.



Figure 6-30 – PF binder cubes fully immersed in NS (left) and HS (right) – 28d



Figure 6-31 - PF binder cube showing reaction rim - fully immersed in HS - 28d

6.3.2.2 Qualitative analysis – XRD

The results of the qualitative analysis on the two binders after 14 days of immersion in sulphate and acid attack solutions are shown in Figures 6-32 and 6-33, respectively. Apart from the peaks of the original binder components, the ettringite ones can be seen in both binders that had been immersed in the sodium sulphate solution. Moreover, the relative intensity of the peaks with respect to the others in the plot clearly demonstrates the appreciable quantity of ettringite that was formed in the sulphate attack process. On the other hand, no peaks could be detected that signalled the presence of gypsum in these samples.



Figure 6-32 - XRD analysis of PS and PF binders fully immersed in NS - 14d

The plots for the binder cubes immersed in the sulphuric acid solution presented the exact opposite scenario to those in the sodium sulphate one. In this case, both binders were overwhelmed in terms of the intensity of gypsum peaks seen in Figure 6-33 below, and the original component peaks had all but disappeared. Moreover, in the cement-slag binder, a small peak at around 9° was detected, which could be indicative of ettringite present. If so, then the mineral would be located deep within the core of the sample as it is not stable in acidic environments such as the one into which the cubes were immersed.



Figure 6-33 - XRD analysis of PS and PF binders fully immersed in HS - 14d

The results of the XRD analysis on the binders after 28 days of immersion are given in Figures 6-34 and 6-35. Comparing them with the 14-day readings, the increase in the amount of ettringite and gypsum formed can be clearly discerned. In the first figure, both binders show enrichment in ettringite content, with the cement-fly ash binder's allocation surpassing that of the cement-slag one. The acid solution, on the other hand, marks an extensive accumulation of gypsum in both binders to the extent that hardly any of the original components appear in either sample. This is in line with the visual assessment given in the preceding section, where the 28-day cubes from both binders showed more deterioration than their 14-day counterparts.



Figure 6-34 – XRD analysis of PS and PF binders fully immersed in NS – 28d



Figure 6-35 - XRD analysis of PS and PF binders fully immersed in HS - 28d

These plots were helpful in demonstrating qualitatively that ettringite and gypsum were the main products of sulphate and acid attack, respectively, and that their amounts were in significant enough quantities for the XRD technique to be able to detect their presence. It remained for the EGM 31 leach procedure to verify if these minerals could be quantified for a better assessment of the extent of the attack.

6.3.2.3 Quantitative analysis – EGM 31

The results of the quantitative leach tests on the cement-slag binder for 14 and 28 days of immersion are given in Tables 6-30 and 6-31, respectively, for the sodium sulphate solution. It must be noted that based on the 14-day results and the continuous errors in reading concentrations in the lower weight-to-volume ratios, the 28-day tests were conducted only on the upper three ratios for all samples, viz., 1, 2.5, and 5. The amount of ettringite leached in the EGM 31 solution fluctuated slightly in the lower ratios for the 14-day samples but stabilized around 5.5% afterwards. The amount dissolved was higher than the 2% ettringite detected in the oven-cured cubes and it was quite obvious that its formation was due to sulphate attack and not simply binder hydration. The results corresponded well with the qualitative XRD analysis and complemented it by providing a numerical assessment of the extent of the attack as mirrored by ettringite formation.

Sample ID	Wt (g)	Vol (I)	W:V	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
PS NS 1/10	0.0047	0.05	0.09	0.0000	0.0012	0.0004	9.80	25.21
PS NS 1/10	0.0149	0.05	0.30	0.0000	0.0015	0.0003	2.30	10.38
PS NS 1/10	0.0296	0.05	0.59	0.0001	0.0015	0.0016	5.50	5.09
PS NS 1/10	0.0506	0.05	1.01	0.0001	0.0014	0.0028	5.44	2.70
PS NS 1/10	0.1248	0.05	2.50	0.0003	0.0019	0.0074	5.96	1.53
PS NS 1/10	0.2496	0.05	4.99	0.0006	0.0029	0.0148	5.92	1.17

Table 6-30 - Results of leach tests on PS binder - fully immersed in NS - 14d

Table 6-31 - Results of leach tests on PS binder - fully immersed in NS - 28d

Sample ID	Wt (g)	Vol (I)	W:V	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
PS NS 1 1/10	0.0500	0.05	1.00	0.0002	0.0005	0.0036	7.30	1.10
PS NS 2 1/10	0.1244	0.05	2.49	0.0003	0.0009	0.0077	6.18	0.70
PS NS 3 1/10	0.2505	0.05	5.01	0.0006	0.0016	0.0145	5.81	0.64

The amount of ettringite remained almost constant after 28 days of immersion, with only the sample at a weight-to-volume ratio of 1 showing a slight increase in the mineral. The XRD results indicated a higher level of ettringite presence in the 28-day samples but the quantitative analysis did not show a dramatic increase. As for the sulphur content, a comparison of the results showed that a slight increase was registered in its amount after 14 days of curing but they went down to below 1% after 28 days. The fluctuation did not follow the ettringite trend, and it could be concluded that the sulphur content read did not originate in the mineral but from another source. One potential source could be the sodium sulphate salt that might have adsorbed to the sample cubes.

On the other hand, the results of the sodium sulphate attack solution on the cement-fly ash binder for 14 days and 28 days are given in Tables 6-32 and 6-33 below. It can be observed that around 7.7% ettringite was formed after 14 days of attack and this remained more or less constant after 28 days, with a slight decrease in the readings. When compared to the first binder, the numbers for the second one were higher after 14 days, and it would seem that the former combination was more resistant to attack. However, after 28 days in the solution, the amount of ettringite formed became remarkably comparable between the two binders with no clear winner emerging.

Sample ID	Wt (g)	Vol (I)	W:V	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
PF NS 1/10	0.0045	0.05	0.09	0.0000	0.0002	-0.0002	-4.11	5.53
PF NS 1/10	0.0150	0.05	0.30	0.0000	0.0002	0.0011	7.09	1.25
PF NS 1/10	0.0300	0.05	0.60	0.0001	0.0002	0.0023	7.69	0.70
PF NS 1/10	0.0501	0.05	1.00	0.0002	0.0002	0.0038	7.66	0.41
PF NS 1/10	0.1248	0.05	2.50	0.0004	0.0007	0.0100	8.05	0.58
PF NS 1/10	0.2500	0.05	5.00	0.0008	0.0014	0.0190	7.60	0.56

Table 6-32 - Results of leach tests on PF binder - fully immersed in NS - 14d

Table 6-33 – Results of leach tests on PF binder - fully immersed in NS – 28d

Sample ID	Wt (g)	Vol (I)	W:V	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
PF NS 1 1/10	0.0502	0.05	1.00	0.0002	0.0005	0.0036	7.27	1.09
PF NS 2 1/10	0.1253	0.05	2.51	0.0003	0.0009	0.0077	6.14	0.70
PF NS 3 1/10	0.2507	0.05	5.01	0.0006	0.0016	0.0145	5.80	0.64

When the sulphur content is assessed in the second binder, almost the same trend could be noted that was present in the first one. In this case, however, the amount of sulphur never exceeded 1% at the higher weight-to-volume ratios even though a substantial amount of ettringite had formed due to attack. It can therefore be deduced that the element did not originate from the mineral in question but could have come from the original components of the binder or from sodium sulphate adsorbed onto the cubes.

In order to assess the values graphically, the data obtained from the EGM 31 leach tests is plotted in Figures 6-36 and 6-37 for the cement-slag and cement-fly ash binders, respectively. For the cement-slag binder, it showed the increase in ettringite after 14 days when compared to the 7-day cured sample, and this was seen in the change in slope of the line. It was clear, however, that after 28 days of immersion, the ettringite amount did not change much and the two lines almost coincided.



Figure 6-36 – Ettringite percentage in fully immersed PS binder – 14 and 28 days



Figure 6-37 – Ettringite percentage in fully immersed PF binder – 14 and 28 days

The consistent factor was that the sulphate attack reactions that took place during the 28 days of immersion could be quantitatively assessed when compared to the amount of ettringite formed due to hydration in the 7-day cured samples. The slopes of the trend lines show this comparison visually and the ratio of their slopes with the initial line shows an almost threefold increase in the amount of ettringite formed due to sulphate attack.

The trend lines for the cement-fly ash binder show similar results in Figure 6-37. Compared to the initial 7-day amount of ettringite, the 14-day samples exhibited a significant rise in the mineral content at about 7.7% based on the slope of the line. After 28 days, however, the same amount could be detected as in the cement-slag binder since the amount of ettringite went down to around 6%. The variation between the two intervals was noteworthy because it took place in both binders, and could be attributed to adjustments in the chemical equilibrium of the mineral within the new settings or its gradual transformation to monosulphate. What is certain, though, is that the results confirmed the qualitative assessment conducted by XRD, and provided a set of solid quantitative data to complement it. Hence, it can be concluded that the EGM 31 method of dissolving ettringite was successful in its numerical evaluation of the extent of sulphate attack acting on the cement-slag and cement-fly ash binders.

Tables 6-34 and 6-35 present data obtained for the cement-slag binder undergoing acid attack. As hinted at through the XRD analysis, no ettringite could be detected in the samples except minor quantities of around 2% that were already present in the 7-day cured samples. The reason for the absence of the mineral was simply due to the very low pH regime under which the samples were attacked. Ettringite requires minimum pH of 11 to form and exist and the 2% acid solution was at the opposite end of this condition. Another possible observation is that due the penetrating action of acid, the small amount of primary ettringite present was dissolved and that is why not much of it could be detected after 28 days of curing.

Sample ID	Wt (g)	Vol (I)	W:V	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
PS HS 1/10	0.0049	0.05	0.10	0.0000	0.0012	-0.0002	-2.91	25.01
PS HS 1/10	0.0151	0.05	0.30	0.0000	0.0015	-0.0003	-1.71	10.21
PS HS 1/10	0.0304	0.05	0.61	0.0000	0.0023	0.0009	2.91	7.64
PS HS 1/10	0.0499	0.05	1.00	0.0001	0.0031	0.0015	3.08	6.29
PS HS 1/10	0.1250	0.05	2.50	0.0001	0.0058	0.0035	2.78	4.60
PS HS 1/10	0.2504	0.05	5.01	0.0003	0.0085	0.0064	2.57	3.40

Table 6-34 – Results of leach tests on PS binder - fully immersed in HS – 14d

Table 6-35 - Results of leach tests on PS binder - fully immersed in HS - 28d

Sample ID	Wt (g)	Vol (I)	W:V	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
PS HS 1 1/10	0.0501	0.05	1.00	0.0000	0.0026	0.0003	0.61	5.27
PS HS 2 1/10	0.1257	0.05	2.51	0.0000	0.0050	0.0008	0.66	3.94
PS HS 3 1/10	0.2506	0.05	5.01	0.0000	0.0116	0.0008	0.31	4.64

On the other hand, the amount of sulphur registered a substantial increase from the amounts detected in the 7-day samples. The results were not surprising based on the fact that the XRD analysis showed the presence of substantial amounts of gypsum, and the sulphur extracted was undoubtedly an indication of the mineral dissolved. While the results of the oven-cured samples gave an average of 1% sulphur per weight, the 14-day samples give at least 5% and it remained around the 4% mark after 28 days of acid attack. The results for the cement-fly ash binder were not different from the first one, and Tables 6-36 and 6-37 give those numbers.

Sample ID	Wt (g)	Vol (I)	W:V	AI (g)	S (g)	Ett (g)	Ett (%)	S (%)
PF HS 1/10	0.0050	0.05	0.10	0.0000	0.0006	-0.0005	-11.12	11.62
PF HS 1/10	0.0151	0.05	0.30	0.0000	0.0010	-0.0002	-1.54	6.47
PF HS 1/10	0.0302	0.05	0.60	0.0000	0.0019	0.0006	1.91	6.30
PF HS 1/10	0.0497	0.05	0.99	0.0000	0.0026	0.0008	1.58	5.28
PF HS 1/10	0.1251	0.05	2.50	0.0001	0.0055	0.0032	2.54	4.36
PF HS 1/10	0.2505	0.05	5.01	0.0001	0.0091	0.0030	1.22	3.62

Table 6-36 - Results of leach tests on PF binder - fully immersed in HS - 14d

Table 6-37 – Results of leach tests on PF binder - fully immersed in HS – 28d

Sample ID	Wt (g)	Vol (I)	W:V	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
PF HS 1 1/10	0.0503	0.05	1.01	0.0000	0.0026	0.0003	0.60	5.25
PF HS 2 1/10	0.1242	0.05	2.48	0.0000	0.0050	0.0008	0.67	3.99
PF HS 3 1/10	0.2498	0.05	5.00	0.0000	0.0116	0.0008	0.31	4.66

The tables show an absence of any additional ettringite in the cubes apart from the original 7-day cured values. After 28 days of curing, the same trend could be seen as in the first binder where the small amounts of the mineral were dissolved due to the penetrating action of the acid solution. In addition, they proved the increase in the amount of sulphur extracted from around 1.5% to at least 5.5% after 14 days, which remained around the 4% mark after 28 days of attack. This was in line with the very high relative intensity of the gypsum peaks in the XRD plots. Figures 6-38 and 6-39 provided the visual assessment of the data tabulated above, along with the solubility curve for pure gypsum in the organic solution for comparison.

From the first figure, it can be observed that the data for the 14-day cement-slag samples followed the same pattern as the one for pure gypsum in the amount of sulphur extracted from the samples as a percentage of the total weight. It is also noted that the amounts were much higher than the initial 7-day cured values, and were therefore due to gypsum formation and not initial hydration. Furthermore, at weight-to-volume ratios of 1 and higher, the curves remained generally apart and ran parallel to each other. Based on this, an estimate of the total amount of gypsum could be made in the samples attacked by sulphuric acid by comparing the percentage of sulphur dissolved to that of pure gypsum, similar to the technique used in Phase I for Ettringite 2 and 3. Based on that, the amount

of gypsum present was calculated at around 74% after 14 days of immersion, and 63% after 28 days.



Figure 6-38 – Gypsum percentage in fully immersed PS binder – 14 and 28 days

Although these numbers seem to indicate that the amount of gypsum has decreased from 14 to 28 days of attack, the difference could be attributed to variations in the reading of sulphur with the ICP. It was mentioned in a previous section that a drift took place with the instrument in its measurement of sulphur and the readings for the element were corrected throughout the tables presented in this work. The method of correction applied was based on the reading of the standards at regular intervals. However, it is possible that certain variations remained in spite of the rigorous correction attempts at correcting this drift. Even with the variations, though, the general trend of the data is obvious and the results for sulphur should be allowed a broader fluctuation range than the aluminum ones. With the use of a newer ICP instrument, it is possible to use the sulphur readings to estimate the amount of gypsum formed due to acid attack.


Figure 6-39 – Gypsum percentage in fully immersed PF binder – 14 and 28 days

Figure 6-39 provides the same data in graphical form for the cement-fly ash binder, along with the gypsum curve for comparison purposes. The similar trends of the 14-day and 28-day sulphur values with those of gypsum dissolved in the same solution are apparent, in addition to the nearly total absence of any readings on the 7-day cured samples. As was done in the case of the cement-slag binder, and based on the same technique, the amount of gypsum in both the 14-day and 28-day cement-fly ash samples could be estimated at 64%. This is slightly different than the qualitative values in the XRD plots, which registered a slight increase in the amount of gypsum in the 28-day samples. Once again, the need for better instrumentation can be cited for the slight discrepancy in the quantitative values of samples cured for different periods but it is possible to see the trend followed by the results when compared to pure gypsum.

6.3.3. PARTIAL IMMERSION TESTS

The partial immersion tests were described in terms of methodology in Chapter 5, in which samples from four binders were placed in sulphate and acid attack solutions, with the difference being that the samples were partially exposed to the atmosphere. This resulted in a faster rate of reaction with the solutions than the fully immersed ones, and complete evaporation required the replenishment of the attack solutions after two to three days of partial immersion. In total, three volumes of each solution were added to the trays over a period of 8 days and the samples were compared to each other in terms of visual assessment, qualitative XRD analysis, and quantitative measurement with the EGM 31 solution.

6.3.3.1 Visual assessment

A visual assessment of the samples was carried out after each evaporation cycle for the solutions, which took place after 2, 5, and 8 days of partial immersion. The photos are presented in Figures 6-40 and 6-41 for the sulphate attack solution for cement-slag and cement-fly ash, and cement-only and cement-slag-fly ash binders, respectively. It can be observed that no major changes could be discerned amongst the four binders and that no physical damage could be detected. The only visual trait was an accumulation of white salt on the cubes, which was confirmed to be sodium sulphate upon XRD analysis. This was in line with the literature review where salt accumulation was seen to be categorized as physical attack by certain authors. The condition persisted after 5 and 8 days of attack and no changes could be noted except for further salt accumulation.



Figure 6-40 – PS and PF binders partially immersed in NS – 2d



Figure 6-41 – PC and PSF binders partially immersed in NS – 2d

The situation was different for the samples partially immersed in sulphuric acid because they showed marked signs of visual deterioration after each period of solution renewal. Figures 6-42 and 6-43 present the photos for the initial two binders and the two additional ones, respectively. The cement-slag binder showed the start of cracking along the edges that had been observed in its 14-day full immersion counterpart, in addition to the accumulation of a translucent white mineral on top of the cubes. The cement-fly ash binder showed a yellowish-brown accumulation at the top, which was reminiscent of the colour in the reaction core observed during the crushing process of the 14-day samples.



Figure 6-42 – PS and PF binders partially immersed in HS – 2d

In Figure 6-43, the same situation could be seen for the cement-only and cementslag-fly ash samples. In the former, the translucent white mineral was apparent while the yellow-brown version encircled the upper portion of the latter samples. The distinct colour seemed to be due to the presence of fly ash since only those samples in which it was used were affected. The characteristic colour, whether as a mineral accumulation or as part of a reaction rim within the cubes, was probably due to the presence of iron in the fly ash.



Figure 6-43 – PC and PSF binders partially immersed in HS – 2d

After a renewal of three solutions, the damage on the binders became visually apparent and was far greater than the initial effect after only 2 days. The cement-slag and cement-fly ash binders are shown in Figure 6-44 and the other two ones are presented in Figure 6-45. The cracking along the edges of the cement-slag binder was complete after 8 days of partial immersion and although the cement-fly ash one showed less damage, more salt and mineral accumulation could be observed in the latter.



Figure 6-44 – PS and PF binders partially immersed in HS – 8d



Figure 6-45 – PC and PSF binders partially immersed in HS – 8d

In Figure 6-45, the cement-only binder showed that it was very poor in its resistance to acid attack when no other additives are used in combination with it. Surprisingly, the combined binder of cement, slag, and fly ash showed the least damage on a visual level. It could be that the fly ash acted as a resisting agent against acid attack due to the fact that amongst the four binder samples, the ones incorporating it showed lesser visual damage than the others.

6.3.3.2 Qualitative analysis – XRD

The results of a qualitative analysis on the four binders are given in Figure 6-46 after 8 days of partial immersion in sodium sulphate. The plots provide an excellent tool of comparison amongst the four binders, and the formation of ettringite can be detected in all of them. If relative intensities are used as a semi-quantitative guideline, it can be concluded that the amount of ettringite formed in the binders was minimum in the combined binder of cement, slag, and fly ash. The relative abundance of the mineral in the other three binders seemed to be comparable.



Figure 6-46 – All binders partially immersed in NS – 8d

In the case of acid attack, the comparative XRD plots are given in Figure 6-47 below. The analysis showed the prevalence of gypsum in all the binders and the characteristic peaks of the mineral started to emerge dominantly in the plots. Once again, a semi-quantitative analysis showed that the amount of gypsum formed is proportionally higher in the cement-slag and cement-fly ash binders than in the others. Surprisingly, the cement-only binder showed minimal effects of gypsum formation, although its samples showed a very severe physical deterioration.



Figure 6-47 – All binders partially immersed in HS – 8d

6.3.3.3 Quantitative analysis – EGM 31

The results of the quantitative analysis for the partially immersed samples are given in Tables 6-38 through 6-41 for the sulphate attack solution. In all binder samples, the amount of ettringite was observed to be less than 6%. However, differences could be seen amongst the different binders in terms of the quantity of the mineral formed. The amount of ettringite was highest in the cement-only binder with a 5.5% value at a weight-to-volume ratio of 1. This was followed by the cement-slag binder, the cement-fly ash

one, and the binder incorporating all the ingredients. These results were significant in that they matched with the qualitative analysis of the binders done with XRD where the fourth binder showed the least intense peaks of the mineral. Therefore, as in the full immersion tests, the EGM 31 solution was able to provide a quantitative assessment of sulphate attack experienced by four different binders at a very accelerated rate. As in the case of ettringite samples, the EGM 31 solution remained a powerful tool in the quantification of the mineral.

Table 6-38 - Results of leach tests on PS binder - partially immersed in NS - 8d

Sample ID	Wt (g)	Vol (I)	W:V	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
NS 1 1/10	0.0501	0.05	1.00	0.0001	0.0002	0.0025	5.05	0.49
NS 2 1/10	0.1247	0.05	2.49	0.0002	0.0009	0.0054	4.35	0.70
NS 3 1/10	0.2489	0.05	4.98	0.0004	0.0018	0.0103	4.12	0.71

Table 6-39 – Resu	lts of leach tests on	PF binder - partial	y immersed in NS – 8d
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Sample ID	Wt (g)	Vol (I)	W:V	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
NS 1 1/10	0.0511	0.05	1.02	0.0001	0.0002	0.0022	4.26	0.45
NS 2 1/10	0.1257	0.05	2.51	0.0001	0.0008	0.0033	2.66	0.60
NS 3 1/10	0.2495	0.05	4.99	0.0003	0.0014	0.0065	2.59	0.55

Table 6-40 - Results of leach tests on PC binder - partially immersed in NS - 8d

Sample ID	Wt (g)	Vol (I)	W:V	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
NS 1 1/10	0.0508	0.05	1.02	0.0001	0.0003	0.0028	5.52	0.58
NS 2 1/10	0.1247	0.05	2.49	0.0003	0.0009	0.0072	5.79	0.74
NS 3 1/10	0.2506	0.05	5.01	0.0006	0.0018	0.0137	5.46	0.70

Table 6-41 - Results of leach tests on PSF binder - partially immersed in NS - 8d

Sample ID	Wt (g)	Vol (I)	W:V	AI (g)	S (g)	Ett (g)	Ett (%)	S (%)
NS 1 1/10	0.0496	0.05	0.99	0.0001	0.0005	0.0017	3.45	0.93
NS 2 1/10	0.1243	0.05	2.49	0.0002	0.0012	0.0045	3.60	1.00
NS 3 1/10	0.2504	0.05	5.01	0.0004	0.0023	0.0082	3.29	0.93

With respect to a comparison between the fully and partially immersed samples of cement-slag and cement-fly ash, the results were once again revealing. The 5% ettringite formed in the former upon 8 days of partial immersion was only slightly behind the 7.3% in the fully immersed one after 28 days at a weight-to-volume ratio of 1. This confirmed

the XRD analysis and gave solid proof as to the relative damage exerted by a partial immersion when compared to a full one. The numbers followed a similar trend in the case of the cement-fly ash binder where the 4.25% of ettringite in partially immersed cubes was in close proximity to the 7.25% of their fully immersed counterparts.

The results for the partially immersed samples in an acid attack solution are given in Tables 6-42 through 6-45. A surprising piece of information in all these tables was the amount of aluminum present in the solution, and the equivalent amounts of ettringite that they could be translated into. The XRD analysis showed the definite absence of the mineral in all samples, and it cannot be that such high levels of ettringite could exist in the samples without being detected by the qualitative technique that was able to analyze much lower amounts.

Table 6-42 - Results of leach tests on PS binder - partially immersed in HS - 8d

Sample ID	Wt (g)	Vol (I)	W:V	AI (g)	S (g)	Ett (g)	Ett (%)	S (%)
HS 1 1/10	0.0498	0.05	1.00	0.0003	0.0026	0.0079	15.96	5.30
HS 2 1/10	0.1255	0.05	2.51	0.0009	0.0066	0.0207	16.53	5.24
HS 3 1/10	0.2515	0.05	5.03	0.0016	0.0122	0.0375	14.92	4.87

Table 6-43 - Results of leach tests on PF binder - partially immersed in HS - 8d

Sample ID	Wt (g)	Vol (I)	W:V	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
HS 1 1/10	0.0507	0.05	1.01	0.0006	0.0021	0.0143	28.15	4.13
HS 2 1/10	0.1249	0.05	2.50	0.0015	0.0057	0.0356	28.50	4.53
HS 3 1/10	0.2503	0.05	5.01	0.0030	0.0107	0.0687	27.43	4.29

Table 6-44 - Results of leach tests on PC binder - partially immersed in HS - 8d

Sample ID	Wt (g)	Vol (l)	W:V	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
HS 1 1/10	0.0504	0.05	1.01	0.0003	0.0018	0.0069	13.65	3.48
HS 2 1/10	0.1251	0.05	2.50	0.0007	0.0045	0.0174	13.94	3.60
HS 3 1/10	0.2492	0.05	4.98	0.0015	0.0092	0.0348	13.98	3.69

Table 6-45 – Results of leach tests on PSF binder - partially immersed in HS – 8d

Sample ID	Wt (g)	Vol (I)	W:V	Al (g)	S (g)	Ett (g)	Ett (%)	S (%)
HS 1 1/10	0.0500	0.05	1.00	0.0006	0.0029	0.0133	26.54	5.84
HS 2 1/10	0.1253	0.05	2.51	0.0015	0.0075	0.0339	27.07	5.98
HS 3 1/10	0.2499	0.05	5.00	0.0031	0.0150	0.0729	29.19	6.02

A different explanation must therefore be sought on the basis that no aluminum was observed in samples that were fully immersed in the acid solution, which eliminates the possibility of an acid extraction of the element from the original binder components. The sole variable that remains was the use of stainless steel trays in the partial immersion tests. Although these should not be affected by a 2% acid solution, it could be that they reacted with it in some way and released the aluminum that was adsorbed or absorbed by the cubes. This would explain for the element's abundance in the solution and its absence in the form of ettringite in the XRD plots.

The data from the binders in the sulphate attack solution is plotted in Figure 6-48 below, and it shows graphically the relative abundance of secondary ettringite formed in the four different combinations used. The linearity of the relationship between the amount of mineral formed and the weight-to-volume ratio range used was once again confirmed, and the usefulness of this method for the quantification of ettringite was highlighted. Apart from the slight difference in the amount of ettringite formed in the cement-fly ash binder at a ratio of 1, the rest of the data fitted in the trends remarkably well.



Figure 6-48 – Ettringite percentage in partially immersed binders – 8 days

On the other hand, the amount of sulphur present in the binders immersed in the acid solution is plotted in Figure 6-49 below. An immediate observation about the points in the graph is the consistency of sulphur dissolved within a given combination and at different weight-to-volume ratios. The gypsum curve clearly exhibits a decreasing trend in the amount of sulphur dissolved as the ratio increases, and the consistency in the readings from the binder samples must be attributed to the relatively low amounts of the mineral compared to a pure gypsum samples. Based on the comparison technique explained previously, the amount of gypsum present in the binders could be calculated at around 71% for the combined binder, 65% for the cement-slag one, 51% for the cement-fly ash one, and 42% for the cement-only one. Caution is urged, though, in using these numbers due to the problem encountered in the aluminum readings from HS solution tray. It could be that the sulphur read had also been affected by the possible reaction of acid with the stainless steel tray, and the results presented above are only given with this cautionary note attached.



Figure 6-49 – Gypsum percentage in partially immersed binders – 8 days

6.3.4. FULL AND PARTIAL IMMERSION TESTS - COMPARISONS

Two of the binders tested were subjected to both sulphate and acid attack using different techniques of immersion in the solutions, viz., partial and full. It is essential, therefore, to make a brief comparison note between the two conditions in order to assess the effects of the manner of immersion – if any – on the final results. A comparison of the visual effects can be made by referring to the relevant sections above, and there is no need for a repetition of the photos here. Therefore, only the qualitative XRD and the quantitative EGM 31 results will be presented in this section.

6.3.4.1 Qualitative analysis – XRD

When the intensities of the cement-slag and cement-fly ash binders are compared to their fully immersed counterparts in the same solutions, it can be observed that the amounts of ettringite formed in the sodium sulphate solution are comparable. In Figure 6-50, the plot for cement-slag for 28 days of full immersion is compared to 8 days of partial immersion in the same solution.



Figure 6-50 - XRD of PS binder immersed in NS - 8d partial and 28d full

It can be noted that the amount of ettringite formed in the latter case was not much less than the value in the former one. If this was the case, then an even more accelerated test than the one proposed by Mehta and Gjörv (1974) could be designed that incurs an equal amount of damage in only 8 days instead of 28. Without numbers, though, no final judgement can be passed and it remains for the EGM 31 leach test to provide the data required.



Figure 6-51 - XRD of PF binder immersed in NS - 8d partial and 28d full

In the case of the cement-fly ash binder, a similar pattern can be seen in Figure 6-51 where the data of 28 days of full immersion is compared to those of 8 days of partial immersion. Although the relative intensity of the ettringite peak was stronger in the 28day sample, the 8-day one showed a value readily approaching it. The results were quite encouraging in terms of the ability of the partial immersion test to match the effects – albeit in part – of the full immersion one. The use of the leach test with EGM 31 is required to conduct a quantitative analysis of the patterns seen with the XRD technique.



Figure 6-52 – XRD of PS binder immersed in HS – 8d partial and 28d full





The pattern of comparable results between partial and full immersion was repeated for both binders when they are immersed in the acid attack solution. Figures 6-52 and 6-53 plot the data for cement-slag and cement-fly ash binders, respectively, of the fully immersed 28-day samples and the partially immersed 8-day ones. In both cases, the

amount of gypsum formed was observed to be superior in the full immersion tests, although the others were not lagging far behind. As before, no ettringite was detected in any of the acid attack solutions due to the extremely low pH regime of the solution. Comparing the two binders on a semi-quantitative basis, it initially seemed that the amount of gypsum formed in the cement-slag one was slightly less than the value in the cement-fly ash one. The task of quantitative comparisons is once again left to the EGM 31 solution.

6.3.4.2 Quantitative analysis – EGM 31

The results of the quantitative analysis for the fully and partially immersed samples were tabulated previously in their respective sections, and need not be repeated here. The data for the cement-slag binder has been plotted in Figure 6-54 to compare the amount of ettringite formed after 28 days of full immersion to the amount after 8 days of partial immersion. Using the slope of the line, it can be observed that the former value is about 6% compared to 4.2% for the latter.



Figure 6-54 – Ettringite percentage in PS binder – 8d partial and 28d full

The implications of these values are quite substantial in two respects. Firstly, a quantitative comparison is made between the partial and full immersion techniques as to the amount of damage they can inflict on the same binder based on the manner of the immersion, viz., 6% ettringite in the former and 4.2% in the latter. Secondly, they allow a conclusion to be reached about the potency of the two techniques that could have far-reaching consequences. The formation of 4.2% ettringite after 8 days represents roughly 70% of the amount formed after 28 days. If a partial immersion technique can inflict 70% of the damage on the binder after one third of the period compared to the full immersion, then the latter can be successfully replaced by a new procedure that would reduce the test period required by two thirds. When a proven accelerated procedure is combined with the quantitative assessment capabilities of the EGM 31 solution, the emergence of a new integrated procedure for evaluating binder durability can become a reality.



Figure 6-55 – Ettringite percentage in PF binder – 8d partial and 28d full

A similar plot is prepared in Figure 6-55 above for the cement-fly ash binder. It can be observed yet again that the total amount of ettringite formed after 28 days of full immersion was around 6% while after 8 days of partial immersion, the same value stood at 2.7%. Two observations can be made regarding these results, similar to the case for the cement-slag binder. Firstly, the amount of damage after 8 days of partial immersion is

45% of the same after 28 days of full immersion. Secondly, this value is markedly different than the first binder where the amount of ettringite formed was 70% of the full immersion amount. The conclusion derived presents another milestone in understanding the ability of the new accelerated technique since it can clearly be observed that not all binders are damaged equally or at the same rate.

The amounts of ettringite formed in both cement-slag and cement-fly ash binders were equal after 28 days of full immersion, and it can easily be concluded that they are equal in terms of durability. However, the partial immersion results cast a new light on their resistance to attack by differentiating between the two. While it could be that after a certain period of time, the amount of ettringite formed would eventually be the same, the speed at which that amount is attained is markedly different for the two binders. Predicting the speed with which a given binder will deteriorate when under sulphate attack has far-reaching implications for planning and scheduling mining operations.



Figure 6-56 – Gypsum percentage in PS binder – 8d partial and 28d full

Figures 6-56 and 6-57 plot the data for the two binders when they are immersed in the acid attack solution. The amount of gypsum is calculated from the comparative technique outlined previously. Although the numbers are quite similar for the full and partial immersion samples, no definite comparison can be made due to the uncertainty of the values from the latter technique. In the case of the cement-slag binder, the amount of gypsum is almost the same and if proven, this would be a remarkable achievement. The sulphate attack solution could provide 70% of the ettringite in the partial immersion test, and it would be immensely significant if the acid solution were able to provide 100% of the amount of damage in 8 days instead of 28. For the cement-fly ash binder, the numbers fluctuate and are lower for partial immersion at a weight-to-volume ratio of 1 but the trend is reversed at 2.5, and finally the values become the same at 5. Once again, the need for more reliable data is required to make a final judgement, and this could come from a more reliable instrument for sulphur measurement and a change in the types of tray used in the partial immersion tests.



Figure 6-57 – Gypsum percentage in PF binder – 8d partial and 28d full

6.3.5. CONCLUSIONS

In conclusion, it can be said that the results of the experimental phase were largely satisfactory. Using a combination of water and EGM 31 solutions, the dissolution trends of gypsum and two types of ettringite – which were actually combinations of gypsum and

ettringite – were determined in Phase I of the project. In Phase II, two binders were fully immersed in sulphate and acid attack solutions for 28 days, and four binders – including the first two – were partially immersed in the same solutions. A combination of visual assessments, qualitative XRD analysis, and quantitative analysis with EGM 31 was conducted on all of these samples. The organic solution proved invaluable in assessing the amount of secondary ettringite and gypsum formed as a result of sulphate and acid attack, respectively. The partial immersion technique revealed its capability in inflicting a substantial percentage of damage compared to the full immersion one in only one third of the period required for the latter. Furthermore, it was able to provide the relative rates of sulphate attack in two of the binders. When combined with the quantitative EGM 31 analysis, it presents an integrated accelerated sulphate attack test that could eventually replace the currently available tests that have been deemed to be inadequate by several authors.

CHAPTER: 7 CONCLUSIONS AND RECOMMENDATIONS

7.1. INTRODUCTION

The different phases of the research project undertaken were covered in Chapters 5 and 6, with a detailed discussion of the results and a series of comparative analyses. In this final chapter, the different conclusions reached at are summarized from the various segments. In addition, a statement is made about the originality of the research done, and a final section is set aside for recommendations regarding future work.

7.2. CONCLUSIONS

The main aim of this research project was two-fold; the establishment of the solubility behaviour of gypsum and ettringite in an EGM 31 leach solution at different weight-to-volume ratios, and its potential use in quantifying the amount of these minerals formed in four different binders (cement-slag, cement-fly ash, cement-only, and cement-slag-fly ash) due to sulphate and acid attack, respectively.

In Phase I, ettringite was formed using two methods and was dissolved in EGM 31 and water, in addition to pure gypsum dissolved separately. It was observed that whereas the amount of gypsum solubility in water was superior to that in the organic solution, the trends followed with the variation of weight-to-volume ratios were of the same nature and decreased with increasing gypsum content. For ettringite, however, the water solubility curves proved to be limited in usefulness in that they quickly reached a maximum peak and subsequently dropped to very low levels. The EGM 31 solution, on the other hand, was observed to be very consistent in the weight-to-volume ratio range of 0.1 to 5 and was able to dissolve nearly 75% of the mineral in Ettringite 2 samples and 100% in Ettringite 3 ones. The difference is probably due to the crystal structure of ettringite formed by the two methods, and the amount of the mineral in samples 2 and 3 was measured to be about 25% and 85%, respectively, with the rest of the samples

consisting of gypsum. Qualitative XRD analysis confirmed the relative abundance indicated by the EGM 31 leach test.

In Phase II, four binders commonly used in mine backfill operations in Canada were subjected to an accelerated curing procedure for 7 days at 50°C. The primary binders, which consisted of cement-slag and cement-fly ash combinations, were subjected to sulphate and acid attack by full immersion for 28 days in 4% sodium sulphate and 2% sulphuric acid solutions, respectively. In addition, all four samples were subjected to the same forms of attack in a partially immersed environment for 8 days. Qualitative tests with XRD analysis and quantitative ones with the EGM 31 solution were conducted after the oven-curing process, after 14 and 28 days for the fully immersed samples, and after 8 days for the partially immersed ones. The results of the two types of immersion were consistent and showed that the cement-slag-fly ash combination was the most resistant to sulphate attack due to the minimum amount of ettringite formed whereas the cement-only one showed the least amount of gypsum formed in the acid attack sloution. Furthermore, the partially immersed samples undergoing accelerated attack showed – after only 8 days – an amount of damage comparable to their fully immersed counterparts after 28 days.

7.3. STATEMENT OF ORIGINALITY

The originality of the research project conducted lies in more than one aspect, and it can be summarized in the following points:

- Development of solubility curves for ettringite and gypsum in water and EGM 31: this was done in Phase I of the project and reasserted the curves for water solubility for two types of ettringite and gypsum. However, the main contribution comes from the development of solubility curves for these minerals at various weight-to-volume ratios in the EGM 31 solution, which has not been done previously.

- Development of a quantitative testing procedure for accelerated attack: this was done in Phase II by the combination of accelerated curing, accelerated sulphate/acid attack tests, and the quantitative analysis using the solubility curves in EGM 31 that were developed in Phase I.
- Development of a highly accelerated attack testing procedure: this was done in Phase II of the project where the accelerated attack procedure developed by several authors previously was increased even more in terms of speed by the use of partially immersed samples, thus reducing the overall period of testing to 15 days only (including curing period).
- Testing of mine backfill binders for resistance to sulphate and acid attack: this was done in Phase II where binders used in mine backfill operations were tested quantitatively as to their relative resistance to these types of attack for the first time, based on the fact that they would be mixed with tailings containing large amounts of pyrite and other sulphides.

7.4. RECOMMENDATIONS FOR FUTURE WORK

The research conducted during the course of this project has by no means reached completion in all the various disciplines that it comprised. In the need for limiting time and resources, several aspects of the work started here were left for future researchers to carry on. Another important point to be made is that its main objective was to establish the fundamentals of the EGM 31 dissolution technique for the quantification of ettringite and gypsum due to the paucity of available data on the topic. This is why nearly half of the work done (Phase I) in the experimental section was geared towards this end. The lack of a partially immersed test in the field of sulphate or acid attack provided the second main objective of the work and the target towards which Phase II was directed. In both these cases, since the basic fundamentals needed to be established, tests were limited

to minerals and unmixed binder samples only, without the presence of tailings as would be the case in a realistic scenario. Without the basic essentials, mixed samples would have created havoc with the data output and it would have been almost impossible to determine where aluminum and sulphur originated from. Once the fundamentals are established, though, the testing of more complex samples can proceed.

Based on the discussion above, the following recommendations can be made in order for a more comprehensive study of the topics that were touched upon in this work:

- In focusing on the chemical aspects of the sulphate and acid attack processes, no physical tests were conducted on the binders. Hence, future work can focus on unconfined compressive strength testing in combination with the chemical parameters of sulphate and acid attack.
- The attack solutions employed were standard ones recommended by international guidelines, and these are meant to provide a worstcase scenario that might not necessarily occur in the field. One realistic innovation would be to use mine water from oxidized tailings as the main attack solution, which is renewed on a frequent basis.
- The binders in this project were tested alone, and not when combined with tailings as would be the case in a mine backfill environment. Future testing could focus on actual backfill samples for their resistance to attack.
- The usefulness of the partially immersed technique in determining the rate of attack in different binders was noted. When combined with the actual rate of oxidation from various sulphide minerals, a prediction tool can be prepared for evaluating the durability of binders in terms of the time required for failure to take place.

 Previous work has been conducted on backfill that incorporated sodium silicate as part of the binder (Razavi 2007). It would be interesting to assess the resistance of such binders to both sulphate and acid attack based on the fact that silicates would not combine with sulphate as readily as aluminates, and would probably be more resistant to acidity.

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