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Role of Ettringite Formation in the Stabilization/Solidification of Sulphide-Bearing Mine Waste

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The **Perversity Principle** states that nature is hostile and life is a struggle against a malevolent enemy. From this, we get the impression just my luck when something goes bad. **Murphy's law** (*If something can go wrong, it will*) is thought of as an expression of the perversity principle. The perversity principle is no more true than the **Polyanna Principle** (*Everything will turn out all right*). What is true is that innumerable random things are happening and that only a few of them are favorable. In communication terms, the environment is noisy and very little of the noise is musical. Murphy's law is quite true, but not because something is trying to get you....

(Lawrence J. Kamm, Successful Engineering, p. 139, McGraw-Hill, New York, 1989)

Abstract

Disposal of acid generating sulphidic tailings is a major environmental problem facing the Canadian as well as the international mining and mineral industries. If the deposited tailings are not treated the sulphide minerals oxidise and create an acidic environment. The leachate from such a site is rich in soluble heavy metals and has the potential to contaminate the groundwater as well as the local surface watercourses. This thesis explores an alternative treatment method via ettringite formation, which stabilises and solidifies these highly reactive tailings.

Ettringite has the capacity of uptaking other metals into its structure by isomorphous substitution. Ettringite has also a negative surface charge, which makes it a good adsorbent for positively charged cations. Furthermore, the high pH solution required for ettringite formation will cause the precipitation of heavy metals from the solution. Therefore, ettringite in a lime-remediated sulphate rich acid mine drainage system could serve as a physical and chemical stabilization agent, which could also reduce the remediation costs over other commercially available stabilization technology.

In order to assess the feasibility of forming ettringite in sulphide rich tailings, a thermodynamic model was used to investigate the optimal geochemical parameters. The model predicts that ettringite is stable over a wide range of compositions and pH. Results presented in this thesis show that the sulphate content of the tailings samples could limit the precipitation of ettringite, and monosulphate could be the end-precipitate.

Long-term leachability and durability analysis showed that ettringite can be formed as a stable mineral in lime, fly ash, and aluminum rich sulphidic tailings samples. Ettringite formation reduced the leachability of the heavy metals and improved the geotechnical characteristics of the treated samples. Freeze and thaw analyses showed that formation of ettringite produce a low permeability and high strength tailings sample capable of withstanding harsh environmental fluctuations.

Résumé

Au Canada et à l'internationale, les industries minières et minérales souffrent d'un problème environnemental d'envergure produit par l'entreposage de résidus *sulfureux* qui libèrent une substance acide à grande échelle. Sans traitement, l'oxydation des minéraux à base de sulfures créent un environnement acide. Dans ces régions, la nappe phréatique et les bassins de drainage locaux risquent d'êtres contaminés par le lessivage d'une grand quantité de métaux solubles. Ce mémoire explore un traitement alternatif de l'acide lessivée en étudiant la formation de l'éttringite qui stabilise et solidifie les résidus hautement réactifs.

L'éttringite possède la capacité d'attirée d'autres métaux dans sa structure en raison d'une substitution *isomorphique*. De plus, l'éttringite possède une charge négative sur sa surface qui aide cette molécule à absorber facilement des cations. Vient s'ajouter le besoin d'une solution pH élevée pour la formation de l'éttringite. Ceci provoque la précipitation des lourds métaux dans la solution. Ceci dit, l'éttringite peut-être utilisée comme un agent stabilisateur dans un système d'entreposage d'acide riche en sulphates traités à la chaux. Cet agent peut ainsi réduire le coût du traitement du produit lessivé dans les mines.

Un modèle thermodynamique a été développé pour étudier les paramètres géochimiques optimaux. Ces paramètres ont servi à l'étude de faisabilité sur la formation de l'éttringite dans les rejets riches en *sulfures*. Le modèle thermodynamique démontre que l'éttringite est dans un état stable et ce, pour une grande gamme de compositions et de teneurs en pH. Dans ce mémoire, les résultats démontrent que la concentration de *sulfate* dans les échantillons de résidus peut limiter la réaction de précipitation de l'éttringite. Il est possible qu'un *monosulfate* soit le produit de la dernière phase de précipitation.

Une étude à long terme sur le lessivage et la durabilité a su démontrer que l'éttringite est formée comme minéral stable dans des échantillons de résidus riches en chaux, en escarbilles et en aluminium. L'éttringite réduit le lessivage des métaux lourds et améliore les caractéristiques géotechniques des échantillons. Une étude de comportement gel-dégel sur des échantillons de résidus, montre que la formation de l'éttringite produit un résidus de basse perméabilité et de haute résistance à des variations climatiques sévères.

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Chapter 1

Introduction

1.1 Acid Mine Drainage

Disposal of acid generating sulphidic mine tailings is a major world-wide environmental problem that adversely affects both surface and ground waters. It is caused by the oxidation and hydrolysis of metal sulphides (in particular pyrite) in water permeable strata, or in mined spoil dumped on the surface. This results in the formation of several soluble hydrous iron sulphates, the production of acidity and the subsequent leaching of metals. It is principally associated with the mining of sulphide ores, the most commonly associated minerals being sulphur, copper, zinc, silver, gold, lead and uranium (Hossein *et al.*, 1999; Gray, 1998). Acid mine drainage is a complex pollutant characterised in surface and ground waters by elevated concentrations of a wide variety of metals depending on the host rock geology .

Environmental management of acid generating tailings is a challenge facing the mining industry and government. In active mine sites, and some inactive sites, mining companies operate comprehensive systems to collect and treat effluents and seepage from tailings and waste rock impoundments. When well operated, these facilities are sufficient to prevent downstream impacts to the environment. Unfortunately, acid generation may persist for hundreds of years after mine closure, and the sludges from the treatment are themselves a waste product which need to be properly disposed of. The operation of these treatment facilities during post-closure stage of the mine life is clearly not desirable and runs counter to the principles and goals of sustainable development.

Environmental legislation, both in Canada and the United States, has added to a major risk and cost component to the mining company's business due to liabilities sustained from the contamination of the environment. Mining companies are therefore placing more emphasis on improving mine waste characterization and disposal technology in order to meet increasingly demanding environmental standards in a cost effective manner (California Mining Association 1992).

There are various disposal practices that are currently investigated for the long term containment of tailings and other reactive mine wastes. These practices include (i) dry cover (Yanful and St. Arnauld, 1991; Mohamed, 1997; Mohamed *et al.*, 1992 and 1993a); (ii) Water Cover (Mohamed et al., 1993b and 1994; St. Arnauld and Yanful, 1993; Amourgis, 1994); (iii) Vegetation; (iv) compost (Pierce, 1992), (v) biological treatment through use of sulphate reducing bacteria (Kim *et al.*, 1999), and (vi) acid neutralization which involves rising the pH of the pore waters by introducing lime to the system. This will result in changing the pH to a level where the solubility of most metals is at its lowest.

Another approach to the problem of acid generation would be the use of chemical fixation of sulphide bearing tailings to render them non-reactive. Stabilization/ solidification is a proven technology for the treatment of hazardous materials. Stabilization refers to those aspects of technology which result in rendering a waste less toxic through fixation of the contaminants that contain and/or by providing a stable chemical environment. Solidification is related to those operations which improve the physical and handling characteristics of the waste (Conner, 1990). This process typically involves the addition of binders and other chemical reagents to the contaminated material to physically solidify the waste and chemically bind the contaminant into a solid monolith.

Binder systems can be placed into two broad categories, inorganic and organic. While the organic binders have more specific applications and are generally expensive, the former, inorganic binders, such as cement and pozzolanic materials such as lime, fly ash, and slag are best suited for the application in the mining and mineral industry.

Lime treatment of acid generating tailings is the most common method of stabilization in Canada. In acid mine drainage systems,. pyrite oxidation produces a high concentration of sulphate. Lime treatments of tailings supply an elevated level of calcium in the system. Assuming that aluminum is available for the reaction, the system contains all the requirements for formation and precipitation of calcium sulphoaluminate hydrates. One of these minerals, ettringite $\{Ca_6[Al(OH)_6]_2(SO_4)_3 \bullet 26H_2O\}$, is responsible for retarding the hydration of tricalcium aluminates and binding aggregates in clasts in cements and concrete (Mehta and Monteiro, 1993). Ettringite consists of columns of $\{[Ca_6[Al(OH)_6]_2 \bullet 24H_2O]^{+6}\}$ which are basically lines of $[Al(OH)_6]^{-3}$ octahedra bonded with three Ca^{+2} ions. The coordination number of calcium is completed by water molecules. The sulphates are intercolumnar and can occur in four different positions. Three of these positions are occupied by sulphates and the remaining by two water molecules (Moore and Taylor, 1968,1970).

Ettringite has the capacity to uptake some of the metals of concern into its structure. The central Al^{+3} can be replaced by any trivalent cation of similar size through isomorphous substitution. Formation of ettringite may also be accompanied by the fixation of hazardous oxyanions such as arsenic, boron, chromium, molybdenum, selenium, and vanadium. Samples of substituted ettringites containing arsenic, boron, chromium, selenium and vanadium have been synthesized in laboratory studies (Hassett *et al.*, 1989). Also, the zeta potential, which is defined as the electric potential in the double layer at the interface between a particle which moves in an electric field and the surrounding liquid, of ettringite has been measured at the pH of 10.7 and gives a value of [-11.7 mV] (Chen and Mehta, 1982), making it a good adsorbent for a positively charged metal species. Moreover, in high pH regimes, dangling metal oxide bonds of phyllosilicates or multioxide feldspars, and ettringite surface sites are negatively charged. Cations can, therefore, be physically adsorbed. Possible surface complexation sites on ettringite include dangling metal oxide bonds at the adge of polyhedron. Formation of ettringite is also associated with a high pH condition in the solution, which will further lead to the precipitation of heavy metals from the solution (Mohamed *et al.*, 1995).

It is the goal of this study to employ stabilization/solidification technology by the means of ettringite formation. This will create a chemically neutral and physically stable solid material for mine tailings without any adverse environmental effect.

1.2 Statement of Work

Acid mine drainage is a natural phenomenon caused by the oxidation of metallic sulphides. The extent of mine tailings deposits in Canada is estimated to cover an area of land in excess of 15,000 hectares, with production of more than 500 million tonnes of waste every year in the form of tailings and waste rock.

During the active life of a mine, collection and treatment of acid generating tailings can be done in a comprehensive manner; however, concern arises after the closure of the mine as the acid generation can persist for hundreds of years. There are no proven technologies exist as yet to control and treat acid generating tailings in such a way to allow the mine operators to retire from the mine sites knowing that the environment will be protected. Amongst the technologies that have shown some promising results so far are water cover, organic cover, wetlands, impermeable soil covers, cementitious covers, bacterial inhibitation and alkaline treatment of sulphidic materials.

One possible solution for the disposal of acid generating mine tailings would be employing stabilization/solidification technology prier to final disposal. Stabilization and Solidification have been used for two to three decades as final treatment steps prior to land disposal of radioactive and chemically hazardous wastes. These technologies are also playing an increasingly important role for on-site or in-situ treatment and remediation of waste lagoons or contaminated soils. Stabilization refers to those aspects of technology which result in rendering a waste less toxic through fixation of the contaminants that contain and/or by providing a stable chemical environment. Solidification is related to those operations which improve the physical and handling characteristics of the waste (Conner, 1990). The ideal Stabilization/Solidification system would render all toxic materials in an industrial waste chemically non reactive and immobile. This immobilization could be obtained by encapsulating the contaminant or including the contaminant in a stable crystalline lattice. Employing this technology can potentially create an inert material which can be disposed of without any further monitoring.

Lime treatment of acid generating tailings is the most common method of stabilization in Canada. In acid mine drainage systems, pyrite oxidation produces a high concentration of sulphate. Lime treatments of tailings supply an elevated level of calcium in the system. Assuming that aluminum is available for the reaction, the system contains all the requirements for formation and precipitation of calcium sulphoaluminate hydrates. One of these minerals, ettringite, has the capacity of uptaking cations as well as anions into its crystal structure. The surface of this mineral is negatively charged which provides a suitable site for the positively charged metal ions adsorption. Moreover, the high pH induced environment required for the formation of ettringite will cause the precipitation of heavy metals.

It is the goal of this study to employ stabilization/solidification technology by the means of ettringite formation. This will create a chemically neutral and physically stable solid material for mine tailings without any adverse environmental effect. The chemically stable and physically durable material with structural integrity can be used in different applications in and around the mining facilities. However, since ettringite becomes unstable in an acidic environment it is imperative to determine its stability field in lime remediated sulphidic mine tailings.

1.3 Objectives of the Study

This research deals with the feasibility of stabilization and solidification of lime remediated sulfidic mine tailings through ettringite formation. The objectives of this research program are:

1) To evaluate the optimal thermodynamic conditions for ettringite formation;
2) To evaluate the role of tailings composition on ettringite formation and its chemical stability;
3) To evaluate the long-term geo-environmental aspects of the stabilized and solidified reactive tailings.

Therefore. proper binders and additives will be used to maximize the formation of ettringite in lime-remediated reactive mine tailings. The formation of ettringite will lead to neutralization. immobilization and encapsulation of the ions of concern in mine tailings.

The outcome of this research will contribute to create an economical and environmental acceptable solution to the historical problem of acid mine drainage.

1.4 Approach

The objectives of this research are implemented through experimental and theoretical studies. All the necessary details involved in the experimental studies will be explained in the corresponding chapters. The laboratory experimental studies include the following :

1) Conducting various physical and chemical experiments to determine the composition and physical properties of two sulphidic mine tailings to be used in this project. The experiments include water content determination, atterberg limits, particle size analysis, specific gravity, specific surface area, pH, redox potential, inorganic content, cation exchange capacity, and determination of optimum lime, fly ash, and aluminum content. Moreover, tailings samples' mineralogical composition will be determined using x-ray diffraction spectroscopy.

2) Application of stabilization/solidification principles to the tailings sample under investigation.

3) Conducting further chemical analysis to determine the chemical composition and chemical stability of the treated samples. Samples will be treated, cured and tested for pH analysis, and leachability studies. The leachability analysis will be based on toxicity characteristic leaching procedure and will be conducted on cured samples. X-ray diffraction analysis as well as scanning

electron microscopy coupled with energy dispersive X-ray microanalysis will be conducted to study the mineralogical composition of treated samples.

4) Conducting unconfined compressive strength, permeability, and freeze and thaw analysis on stabilized and solidified tailings sample to assess their mechanical integrity and stability. Samples will be treated in designated percentages and will be cured in humid room before being subjected to geotechnical analysis.

The theoretical study involves the application of an existing geochemical model developed by the department of Earth and Planetary Science at McGill University to the tailings sample under investigation.

1.5 Thesis Organization

The thesis consists of nine chapters, the content of which is as follows:

Chapter 1:	an introductory chapter to provide the necessary information on the background of the acidic drainage problem, structure of the research and its objectives, and approach of the present study.
Chapter 2:	review and summarize the published literature concerning acid mine drainage treatment, and the overall behavior of sulphide

minerals when exposed to air and humidity. Moreover, providing a comprehensive review of the stabilization and solidification technology as it applies to chemically unstable inorganic wastes.

Chapter 3:	describes the experimental methods, materials, and testing procedures employed to identify the physical and chemical characteristics of the tailings sample under investigation.
Chapter 4:	describes the thermodynamic model employed and the result of its application on tailings sample under investigation.
Chapter 5:	presents the results of laboratory optimization conducted on tailings sample to determine the optimal binder content required for formation and precipitation of ettringite as a stable mineral for stabilization and solidification of the tailings sample under investigation.
Chapter 6:	describes and presents the results of leachability analysis conducted on treated tailings samples. The results of x-ray diffraction analysis as well as scanning electron microscopy coupled with energy dispersive x-ray microanalysis is also presented to help to determine the extend of ettringite formation on the treated samples.
Chapter 7:	describes and presents the results of the geotechnical studies conducted on the treated tailings sample. These tests include

unconfined compressive analysis, permeability analysis, as well as freeze and thaw experiments.

Chapter 8: presents the results of the leachability analysis, x-ray diffraction, unconfined compressive analysis, permeability analysis, as well as freeze and thaw experiments conducted on another tailings sample stabilized and solidified based on the principle of the proposed treatment procedure. .

Chapter 9: provides the summaries and conclusions, suggestions for future research and the project's scientific contributions.

The major parts of the work described in chapters 4 and 5 are published in CIM Bulletin, Vol. 88, No. 995, in November/December 1995, and Vol. 92, No. 1029, April 1999.

Chapter 2

State-Of-The Art: Review of Acid Mine Drainage

2.1 Problem Identification

The disposal of tailings is a major environmental problem. It becomes more serious with the increasing exploration for metals and the working of lower-grade deposits. It is estimated that the Canadian mining industry produces in excess of 500 million tonnes of solid wastes each year. Wastewater associated with the mining and milling operations constitutes an equal quantity of liquid wastes. Quebec alone is estimated to have produced 102.1 million metric tons of tailings in 1990 (Intergovernmental, 1988; Rallon, 1989).

Surface disposal of mine waste material, as one of the most widely used method of tailings disposal in Canada, has been well documented (Hossein, 1991). The problem arises when acid producing tailings have to be disposed of. Most Canadian base metals, precious metals and uranium mines contain sulphide minerals, either in the ore or in the surrounding waste rock. Sulphide minerals, particularly pyrite and pyrrhotite, are unstable when exposed to oxygen and water, and begin to react immediately. This reaction yields sulphuric acid and causes the leaching of heavy metals, in concentrations toxic to aquatic life. As the reactions proceed, temperature and acidity rise which result in an increase rate of reaction. Several other factors which contribute to the rate of reaction are sulphide content, morphology, ferric iron concentration and bacterial population density (Moskalyk, 1995).

During the active life of a mine, collection and treatment of acidic water can be done in a comprehensive manner; but concerns arise after the closure of the site as the continuation of treatment can become a very expensive operation. Acid drainage from a reactive tailings site may contain very high concentrations of sulphate and ferrous iron, high concentrations of base metals such as lead, copper, nickel, zinc, or silver, and exhibit pH values below 7 (Filion et al., 1990). If acidic drainage is left uncontrolled and untreated, the drainage could contaminate groundwater and local watercourses, damaging the health of plants, wildlife, and fish.

One possible solution for the disposal of acid generating mine tailings would be employing stabilization/solidification technology prior to final disposal. Stabilization and Solidification have been used for two to three decades as final treatment steps prior to land disposal of radioactive and chemically hazardous wastes. These technologies are also playing an increasingly important role for on-site or in-situ treatment and remediation of waste lagoons or contaminated soils. Stabilization refers to those aspects of technology which result in rendering a waste less toxic through fixation of the contaminants that contain and/or by providing a stable chemical environment. Solidification is related to those operations which improve the physical and handling characteristics of the waste (Conner, 1990). The ideal Stabilization/Solidification system would render all toxic materials in an industrial waste chemically non reactive and immobile. This immobilization could be obtained by encapsulating the contaminant or including the contaminant in a stable crystalline lattice. Employing this technology can potentially create an inert material which can be disposed of without any further monitoring.

2.2 Acid Mine Research In Canada

Acid Mine Drainage (AMD) is the single largest impediment facing the Canadian mining industry today. Nearly 500,000,000 tons of tailings are deposited annually into tailings impoundment's covering roughly 15,000 hectares of Canadian wilderness. If the deposited tailings are not treated, the sulphide minerals oxidize and the heavy metal-rich leachates, often contaminate the surrounding environment. Nearly 60 Superfund sites in the U.S. can attest to the destructive potential of an abandoned mine site (Davis *et al.*, 1995).

To date, about 800 mining sites have been exploited or intensively explored in Quebec for metallic and non metallic minerals. At present, 61 sites are still active. Each year, these activities generate close to 100 million tons of waste rock and tailings that accumulate on 262 sites covering more than 12350 hectares. Among the

6400 hectares which are no longer active, restoration work has been conducted over 2000 hectares. Most of the land occupied by mining facilities has not been restored (Marcotte, 1995).

The theory of acid generation from sulphide minerals is well documented (Hossein, 1991) and factors found to influence their oxidation include sulphide content, morphology, ferric iron concentration, bacterial population density and gaseous oxygen (Siwik *et al.*, 1989). Pyrite and other sulphide minerals that undergo weathering produce acid solutions containing sulphate, iron and other dissolved metals. The complex series of chemical and biochemical reactions that result in the formation of acidic water can be represented by the following equations (Hossein, 1991).

$$FeS_2 + \tfrac{7}{2}O_2 + H_2O \rightarrow Fe^{+2} + 2SO_4^{-2} + 2H^+ \qquad (1)$$

$$Fe^{+2} + \tfrac{5}{2}H_2O + \tfrac{1}{2}O_2 \rightarrow Fe(OH)_3 + 2H^+ \qquad (2)$$

$$Fe^{+2} + \tfrac{1}{4}O_2 + H^+ \rightarrow Fe^{+3} + \tfrac{1}{2}H_2O \qquad (3)$$

$$FeS_2 + 14Fe^{+3} + 8H_2O \rightarrow 15Fe^{+2} + 2SO_4^{-2} + 16H^+ \qquad (4)$$

Metals and acid-forming ions are liberated during the initial stages of oxidation; these may combine with alkaline materials associated with the tailings, and settle out of solution as metal precipitates (Equations 1 and 2). With continued oxidation (Equation 3) and the lowering of solution pH, metallic precipitates may return to solution when available alkalinity in the waste is depleted. Liberated metal ions, particularly Fe in the ferric state, act as oxidizers which further react with sulphide materials and produce Fe^{+2} (Equation 4).

As the process continues and the pH of the solution drops below 2.5, the activity of Fe^{+3} is governed by the combined effect of bacterial oxidation of Fe^{+2},the reduction of Fe^{+3} by pyrite (Equation 4), and the associated formation of ferric sulphate and hydroxyl complex (Siwik *et al.*, 1989). If the reactions are allowed to proceed uncontrolled, the cycle will continue until the sulphide supply is depleted. The oxidation rate may increase 5 to 6 orders of magnitude due to the catalytic activity of *Thiobacillus ferrooxidans* (Ritcey, 1989).

2.3. Available Treatment Technologies

At the present time, most mining companies rely on lime treatment for neutralization of their acidic waters and for precipitation of soluble metals as hydroxides. However, there are some problems associated with this treatment technology, including the cost and the need for long term commitments. Also sludges, which are produced as a result of this treatment procedure, retain water and may occupy up to 40 times more volume than the treated waste. The long term stability of sludges has been questioned, and some provinces have classified them as hazardous waste materials (Dvorak *et al.*, 1991; MacDonald *et al.*, 1989).

No proven technologies exist as yet to control and treat AMD in such a way that would allow mine operators to retire from mine sites knowing that the environment will be protected. The key to prevent AMD appears to be the prevention of oxygen from coming into contact with sulphide-bearing waste materials. Technologies that have shown some promising results so far include water cover (Mohamed *et al.*, 1993b, 1994; St. Arnaud and Yanful, 1993, Amourgis, 1994), organic cover, wetlands, impermeable soil covers (Yanful and St. Arnaud, 1991; Mohamed *et al.*, 1992, 1993a), and cementitious covers over the waste containment area. The former method, water cover, by flooding the area which contains the sulphide waste materials, seems to be one of the most effective solution available today (Feasby *et al.*, 1991; Miller *et al.*, 1990; Filion *et al.*, 1989; and Environment Canada, 1987). In tailings, the primary mode of oxygen transport is diffusion through the pore spaces. The recognition of this process has led to the suggestion that materials with low diffusivities may be useful in limiting the rate of oxygen transfer from the atmosphere into the tailings and thereby decreasing the rate of oxidation and acid production (Nicholson *et al.*, 1991). Doepker (1991), and Doepker and Drake (1991) have suggested that sulphide minerals do not undergo any considerable amount of oxidation while in a saturated zone. The oxidation of sulphide tailings occurs in the unsaturated zone, requiring both water and atmospheric oxygen. Thereby, the very low diffusion rate of oxygen through water cover (2×10^{-9} m^2/s), and oxygen's low solubility (8.6 g/m^3 at 25°C), make water covers an effective way to prevent acid generation in sulphidic mine wastes. Therefore, a water cover on reactive wastes: 1) limits available oxygen and hence controls acid generation, 2) eliminates surface erosion by wind and water action, and 3) creates a reducing environment for bacterial reductions of nitrates and sulphates (Dave and Vivyurka, 1994). In an study by Ritcey (1991), he concluded that oxidation and therefore acid generation appears to be prohibited in low as well as high sulphide tailings, when deposited in a deep body of water. However, lysimeter tests have to be conducted under controlled, simulated weathering conditions to determine the effective depth of water cover in a particular sulphide concentration. At the same time he cautioned that subaqueous disposal of partly oxidized waste would result in release to the water of acidic reactions products that had accumulated on the mine waste surface.

For tailings that are not amenable to flooding, an alternative diffusion barrier is required and different materials have been suggested for this purpose. It has been suggested that effective porous granular covers can be designed to remain saturated above the water table by selective layering of materials. The contrast in the grain size between the cover and the underlying medium is the key factor that controls the moisture retention in these covers (Mohamed *et al.*, 1993a; Nicholson *et al.*, 1991; Yanful and Nicholson, 1991).

Other researchers such as Dvorak *et al.*, (1991) and Kuyucak *et al.* (1991), have examined the role of bacteria in suppressing the rate of acid production from sulphide tailings. It has been suggested that a group of anaerobic bacteria, that can convert the sulphate into hydrogen sulphide, can react with metal ions to form insoluble metal sulphide. The bicarbonate ions then can consume protons, thus raising the pH of acidic water. Microbiological processes may be an alternative to lime neutralization for treatment of acid mine drainage.

Amongst the bacterial inhibitation method of preventing acidic effluent generation is to inhibit *Thiobacillus* species which are responsible for metal sulphide oxidation (Ritcey, 1989). Anionic surfactants has been used successfully to inhibit thiobacillus ferrooxidans, an acidophile responsible for catalyzing iron and sulphur oxidation at pH values lower than 4.5. Tailings and waste rock environments are generally of neutral pH before oxidation begins. There is evidence that microorganisms are involved in the initial oxidation of tailings, even if this has not yet been clearly demonstrated (Stichbury *et al.*, 1995). There may be potential for preventing AMD by applying chemical inhibitors which inhibit neutrophilic thiobacillio, thereby decreasing the initial oxidation rate of the tailings significantly until a wet or dry cover can be applied.

One of the newly proposed techniques for treating reactive tailings is the inhibition of pyrite oxidation by surface treatment. In this technique the oxidation can be controlled using a coating agents which can be applied to the samples prior to the oxidation process. By this technique the sulphide waste is coated with ferric phosphate, a highly acid stable mineral, which is the main component of the coatings created on steel to prevent metal corrosion (Georgopoulou *et al.*, 1995). Iron sulphide waste will be treated with phosphate solution and upon oxidation the ferric ions released will react with the phosphate ions forming a passive coating on the sulphide mineral surfaces. Thus sulphide oxidation and acid production will stop. Acetyl acetone, humic acid, lignin, oxalic acid and sodium silicate are among other agents used for coating the sulphide minerals (Maki *et al.*, 1995).

Another approach to the problem of acid generation would be the use of chemical fixation of sulphide bearing tailings to render them non-reactive and immobile. This idea has been applied to uranium tailings in the past (Lakshmanan *et al.*, 1984; Haw *et al.*, 1983). But the high cost of application has prevented the base metal and gold mining industry from integrating this method of waste treatment into their operation.

Lime neutralization process is the most popular treatment available of acid generating tailings. Lime or hydrated lime, (CaO or $Ca(OH)_2$), is the most commonly used neutralizing agent for treating AMD because of their high reactivity, availability, and relatively low cost. The principal reaction in lime neutralization can be expressed as follows:

$$\mathbf{Ca(OH)_2 + Me2{+} /Me3{+} + H_2SO_4 \Leftrightarrow Me(OH)_2/Me(OH)_3 + CaSO_4 + H_2O} \tag{5}$$

In some cases, other alkaline chemical reagents such as NH_3, NaOH or $CaCO_3$ can be used. The mixture of metal hydroxide precipitates and gypsum ($CaSO_4$) is called "sludge" and is allowed to settle in ponds or in a solid/liquid (S/L) separation device (e.g. clarifier/thickner). The settled sludge is then disposed of in specifically-designed storage ponds. Hydroxide sludges are usually voluminous due to their gelatinous texture and, as a consequence, solid/liquid separation is difficult (Kuyucak *et al.*, 1995; Kuyucak, 1995). The annual volume of sludge production by the Canadian mineral industry is estimated at 140,000 dry tonnes/year (Fyson *et al.*, 1995).

The choice and cost of AMD treatment technologies depend upon site specific characteristics such as climate, geology, topography and proximity to population centres. Self-sustaining vegetative covers can be established on sites which contain sulphide waste material. Such covers improve aesthetics and help in controlling surface erosion. However, they help little in reducing either the oxidation of materials or the flow of water through the impoundment.

2.4. Stabilization/Solidification Technology

Stabilization/solidification is a proven technology for the treatment of hazardous wastes and hazardous waste sites. This technology has been used to minimize leaching of the resultant solid waste after disposal. Stabilization techniques attempt to reduce the solubility or chemical reactivity of a waste by changing its chemical state or by physical entrapment. This process usually involves adding materials that will ensure the hazardous constituents are maintained in their least mobile or toxic form. The addition of lime or sulphide to a metal hydroxide waste to precipitate the metal ions is an example of stabilization. Solidification refers to techniques that encapsulate the waste in a monolithic solid of high structural integrity. The monolith can encompass the entire waste disposal site, called a "monofill", or be as small as the contents of a steel drum. The contaminants do not necessary interact chemically with reagents. Instead, they are mechanically locked within the solidified matrix (Means *et al.*, 1995; Anderson, 1994; Environment Canada, 1991; Conner, 1990; U.S. EPA, 1989). Contaminant migration is restricted by vastly decreasing the surface area exposed to leaching and/or by isolating the contaminants from environmental influences within a relatively impervious capsule.

In the early days, many of the approaches used in solidifying or stabilizing hazardous industrial wastes originated in the area of radioactive waste management. The major goal in radioactive waste stabilization was the production of a solid material which would be suitable for transportation. Additionally, a great deal of work was done in developing solid materials that were suitable for long-term containment of radioactive wastes. The resulting processes were designed to produce a material that would (1) contain the waste in a nonleachable form, (2) be nondegradable, (3) reduce the potential for exposure to radiation and (4) be produced easily and nonexpensively. Solidification requirements in radioactive waste management area were satisfied by systems using cement mixtures, bituminous material, ureaformaldehyde resins or glass (Thompson, D.W., *et al.*, 1979)..

Industrial waste solidification differs from radioactive waste containment in that often in industrial processes very large volumes of waste are produced that have relatively low toxicity. The general emphasis in solidification of low toxicity industrial wastes is the production of a low cost material that as a result of cementing reactions has a decreased permeability and an increased shear strength. These sort of wastes have frequently been solidified by adding pozzolanic material such as fly ash, cement, lime and cement kiln dust.

Since the stabilization/solidification technology refers to the formation of a product which is resistant to the leaching in the environment, it is essential to understand the leaching process and the tests by which it is measured. Leaching can be defined as the process whereby water, or any other liquid, comes in contact with the waste material and dissolves part of it. The liquid is called the leachant and the contaminated liquid that has passed through the waste the leachate. The capacity of the waste material to leach is called the leachability. Therefore, leaching is a rate phenomenon and our interest, environmentally, is in the rate at which hazardous or other undesirable constituents are removed from the waste and passed into the environment via the leachate. The rate is usually measured and expressed, however, in terms of concentration of the constituent in the leachate (Conner, 1990). According to Environment Canada, compendium of waste leaching tests (EPS 3/HA/7, 1990), in porous wastes, leaching is initiated at the pore space, or at the particle interface. These wastes consist of individual particles with voids between them. If a porous waste is wet, there could be many different phases present: several solid phases, an aqueous phase, a nonaqueous phase liquid, and a gas phase. Before contact with a leachant, the waste is normally at or approaching a state of chemical equilibrium, contaminants are associated with specific phases. Contacting the solid phase with leachant disrupts this chemical equilibrium, initiating the leaching process. The new system may evolve towards a new equilibrium state if sufficient time is available, provided that the leachant is not renewed. For wastes that are initially dry, wetting initiates leaching by mobilizing those constituents that are easily dissolved or desorbed. At the pore scale, immobile constituents become mobile, as a result of complex combinations of chemical reactions, such as dissolution, desorption, and subsequent transport through the liquid film of immobile water that surrounds a particle of waste, by molecular diffusion.

The ultimate impact of leaching on the environment occurs when contaminants are transported away from the waste. If water flows within the solid waste, advective transport causes contaminants that have been mobilized by the reactions at the pore scale to flow through the waste at various velocity. The pore-water velocities vary considerably in both magnitude and direction because the pore water must travel a sinuous pathway (tortuosity) within the available pore spaces, termed effective porosity, which are connected in a nonuniform manner. The velocity variations at this scale result in individual elements of water moving faster or slower than the average velocity, which causes spreading (i.e. dilution) of the contaminant concentration with increasing distance from the source. If there is no flowing water within the porous waste soluble constituents may still be transported by molecular diffusion as a result of concentration gradients. Together, mechanical dispersion and diffusion constitute the lumped parameter known as hydrodynamic dispersion. Leaching, therefore, is the result of chemical reactions at the scale of individual particles, which acts to mobilize contaminants, coupled with transport processes that may be governed by advection, diffusion, or a combination of both, depending on the magnitude of leachant flow (EPS 3/HA/7, 1990). In an extensive study by Environment Canada (EPS 3/HA/9, 1991), it was shown that the hydraulic conductivity of a stabilized/solidified waste determines whether leaching will take place primarily by advection or molecular diffusion. The report refers to a work which was done by Shackelford in 1988, and concludes that for a hydraulic gradient around unity, diffusion can be neglected if the hydraulic conductivity is higher than 10^{-9} m/s. On the other hand, diffusion limits the rate of transport when hydraulic conductivity is lower than 10^{-9} m/s. When two materials with different hydraulic conductivities are involved (i.e., a solidified/stabilized waste and a surrounding soil), an analysis by Atkinson (1985), reveals that infiltrating rain water or groundwater flows mainly around or through the waste and may thus control the contaminant transport mechanism. According to the report by Environment Canada (EPS 3/HA/9, 1991), if the hydraulic conductivity of the stabilized/solidified waste is much lower, (e.g., two order of magnitude) than that of the surrounding material, water follows the path of least resistance by flowing mainly around the waste. In this case, leaching is limited by molecular diffusion in the connected porosity of the stabilized/solidified waste matrix (even if the hydraulic conductivity of the stabilized/solidified is higher than 10^{-9} m/s).

When contaminants reach the stabilized/solidified waste-surrounding material interface, they are carried away by the ground water. If, on the other hand, the hydraulic conductivity of the solidified waste is on the same order of magnitude or higher than that of the surrounding material, water flows through the waste. The pore water solution is thus displaced and leaching takes place largely by advection (EPS 3/HA/9, 1991).

There are several tests available for measurement of the leachability of the treated waste. In the United States, the environmental acceptability of a hazardous waste is based on the US EPA Extraction Procedure Toxicity (EPT) test and more recently, on the Toxicity Characteristics Leaching Procedure (TCLP) test. Other leaching procedures include the Multiple Extraction Procedure (MEP) and, the Oily Waste Extraction Procedure (OWEP) test (U.S. EPA, 1989). All of these tests create worst case scenarios, as their strength to leach out contaminants is much more than what could occur in nature. Most leach tests use a leachant to waste ratio of 20:1. Therefore, the maximum concentration of the constituents elements or compounds that can be attained in the leachate is only 5% of their concentration in the solid waste (Conner, 1990).

The leachability of a waste is a function of different variables and may give different results if one or more of these variables is changed. A list of the important factors that affect leachability are presented below (Conner, 1990):

- Surface area of the waste;
- Extraction vessel;
- Agitation technique and equipment;
- Nature of leachant;
- Ratio of leachant to waste;
- Number of elutions used;
- Time of contact;
- Temperature;
- pH adjustment;
- Separation of extract; and
- Analysis.

Stabilization/Solidification processes typically involve the addition of binders and other chemical reagents to the contaminated material to physically solidify the waste and chemically bind the contaminants into the monolith (Bishop, 1990). Binder systems can be placed into two broad categories, inorganic or organic. Most inorganic binder systems in use include varying combinations of hydraulic cements, lime, fly ash, pozzolans, gypsum and silicates. Organic binders used or experimented with include epoxy, polyesters, asphalt/bitumen, polyolefins (primarily polyethylene and polybutadiene) and urea formaldehyde. Combinations of inorganic and organic binder systems have also been used. These include diatomaceous earth with cement and polystyrene, polyurethane and cement, polymer gels with silicates, and lime cement with organic modified clays (Bishop, 1990; Cote, and Gilliam, 1989). Vitrification is another stabilization/solidification process which is relatively new and involves fusing of hazardous materials into a glass or synthetic silicate matrix. This has been done in-situ, by Geosafe Corporation of Kirkland, WA, and is a commonly used means of treating ash from a rotary kiln incinerator. In its in-situ application, electrodes are inserted into the ground around the contaminated site and an electric current is passed between them. The current melts the soil and organic compounds evaporate. The area being processed is shrouded with a hood which captures released organics and particulate air emissions for capture or further treatment (Weitzman, L., 1990). For treating ash from a rotary kiln incinerator, the incinerator is operated at a temperature high enough to melt the ash. After the molten ash is extinguished, it forms a rocklike slag which immobilizes metals in the waste. Overall, vitrification is considered a specialized technique for small scale applications involving extremely hazardous materials.

Organic stabilization/solidification, has been applied only to selected hazardous waste. Organic-based additives are normally hydrophobic. When used with aqueous waste streams, water is either evaporated in thermosetting processes or encapsulated within the polymer matrix in catalyst-based processes. Organic-based processes normally show very low leaching of contaminants since the matrices are impervious. However, there is usually no reaction between the waste constituents and the polymer. Since hazardous constituents are not destroyed or insolubilized, the long term stability of the waste form depends entirely on its physical integrity in the disposal environment. Organic-based processes are energy intensive, requiring high cost additives and sophisticated blending equipment. Their use has been practically limited to special types of high-hazard, low-volume wastes (Cote and Gilliam, 1989).

Inorganic-based systems all used some kind of hydraulic cement that allows the waste form to develop sufficient strength to be self supporting in a landfill. These processes create an alkaline environment suitable to the containment of several toxic metals. The additives, which are often themselves waste materials are inexpensive and can be blended with the waste using simple equipment. Cement-based processes have widely been used commercially for chemically hazardous wastes and low level radioactive wastes (Cote and Gilliam, 1989).

Stabilization/Solidification has considerable technical merit for the treatment of hazardous waste sites. Employing stabilization/solidification techniques, not only solidify the waste by chemical means, but also insolublize, immobilize, encapsulate, destroy, sorb, or otherwise interact with selected waste components. The purpose of these systems are to produce solids that are non hazardous, or less hazardous, than the original waste (Conner, 1990). While stabilization has been used for decades in geotechnical/civil construction, contaminated soil/waste stabilization or/and solidification is a relatively new technique. The typical goal of stabilization/solidification is to prevent or minimize the release of contaminant into the environment by (1) producing a solid, (2) improving handling characteristics, (3) decreasing surface area for contaminant transport, (4) limiting mobility of the contaminant when exposed to leaching fluids, or (5) chemically transforming or bonding the contaminant into a nontoxic form (Kleppe *et al.*, 1992).

A variety of stabilization/solidification technologies are available. However, the selection of a particular process is mainly dependent on the physical and chemical characteristics of the waste. Moreover, it is important to test the compatibility of the waste with the candidate fixation processes. Other considerations are pretreatment requirements, ease of operation, specifications of the finished product, cost of processing, and the location and method of disposal (O'Brien and Gere Engineers, 1988).

Inorganic-based solidification/stabilization systems are best suited for hazardous waste containing heavy metals and, is the dominant method of choice for the mining and mineral industry (except for the uranium mining); and therefore, it will be elaborated on further. As it was discussed earlier, the two principal types of inorganic binders are cement binders and pozzolanic binders (lime, kiln dust, flyash). A pozzolan is a material containing silica and alumina that has little or no cementitious value itself but, can react with lime or cement and water at ambient temperature to produce cementitious material (Means et al., 1995; U.S. EPA, 1989). Pozzolanic materials are plentiful, widely distributed in nature or are available as industrial by-products. The basic solidification reaction in pozzolanic systems requires polyvalent metal ions in stoichiometric excess, so calcium compounds such as lime is most commonly added as setting agent (Malone, G.A., and Lundquist, D.E., 1994).

2.4.1. Cement-Based Technique

Cement based techniques were the first developed stabilization and solidification methods and were a direct outgrowth of the use of cements to stabilize soils in various engineered fill applications. Use of cements to stabilize hazardous wastes at superfund sites in the United States dates from the earliest remedial actions conducted in the mid-1970s (Malone, G.A., and Lundquist, D.E., 1994).

Cement-based techniques generally use portland cement and sludge along with certain other additives including fly ash or other aggregates to form a monolithic rock-like mass. The basis for the success of this technique has been a reduction in the surface area-to-volume ratio and a decrease in permeability in the sludge mass (O'Brien and Gere Engineers, 1988). The cement-based techniques have proven successful on many sludges generated by the precipitation of heavy metals. The high pH of the cement mixture tends to keep the metals in the form of insoluble hydroxide or carbonate salts. Metal ions may also be taken up into the cement matrix (Jackman and Powell, 1991). Cocke and Mollah (1993) suggest that a waste ion may "chemisorb, precipitate, form a surface compound to any of several cement component surfaces, form inclusions or be chemically incorporated into the cement structures, or have simultaneous occurrence of several of these situations". Cement-based stabilization/solidification has been applied to plating wastes containing various metals such as cadmium, chromium, copper, lead, nickel, and zinc. Cement has also been used with complex wastes containing PCBs, oils and oil sludges; wastes containing vinyl chloride and ethylene dichloride; resins;

stabilized/solidified plastics; asbestos; sulphides; and other materials (U.S. EPA, 1989).

2.4.2. Lime-Based Technique

Lime-based stabilization of soil dates back to the construction of Roman roads. Lime and other pozzolans were used to improve the strength and durability of the soils. The mechanism for the soil stabilization process is facilitated in a high pH environment and occurs during the ionic substitution of calcium into the clay mineral lattice crystal structure. The soil lime reactions are complex and not completely understood. According to Chou (1987), an oversimplified qualitative view of some typical soil-lime reactions are:

$$\mathrm{Ca(OH)2} \rightarrow \mathrm{Ca}^{++} + 2(\mathrm{OH})^{-}$$

$$\mathrm{Ca}^{++} + 2(\mathrm{OH})^{-} + \mathrm{SiO2} \rightarrow \text{Calcium Silicate Hydrate (CSH)}$$

$$\mathrm{Ca}^{++} + 2(\mathrm{OH})^{-} + \mathrm{Al2O3} \rightarrow \text{Calcium Alumina Hydrate (CAH)}$$

Lime-based stabilization techniques generally depend on the reaction of lime with fine grained siliceous material and water to produce a hardened material. Hydrates of calcium silicates, calcium aluminates, or calcium aluminosilicates are formed by the reaction of calcium in lime with amorphous aluminosilicates. Eades (1962) suggested that the high pH causes silica from the clay minerals to dissolve and, in combination with Ca^{++} , form calcium silicate. Diamond, *et al.*, (1964) theorized that lime molecules are absorbed by clay surfaces and react with other clay surfaces to precipitate reaction products. These studies suggest that the clay lattice components are dissoloved from the clay structure and are precipitated as CSH and CAH. Jackman and Powell (1991) suggest that the pozzolanic products formed during the lime soil interaction has the capability to entrap the wastes.

Some of the most common additives used in lime-based stabilization processes are fly ash and cement-kiln dust and blast furnace slag.. All of these materials are waste products that have to be disposed of. Therefore, the fixation process can reduce the contamination potential of several wastes. Waste materials that have been stabilized/solidified with pozzolans include oil sludges, plating sludges containing various metals (aluminum, nickel, copper, lead, chromium, and arsenic) and waste acids (U.S. EPA., 1989).

Solidification/stabilization (S/S) is an economical process for the disposal of many types of hazardous wastes. the method involves mixing liquid or semisolid wastes with binders to produce a solid which is structurally sound and relatively impermeable. Binders often consist of ordinary portland cement or cement plus some pozzolanic materials (Means *et al.*, 1995). The primary concern in selecting stabilization and solidification technologies is assuring that the contaminants are sufficiently immobilized under all anticipated environmental conditions.

In order to further understand the mechanism of inorganic based stabilization/solidification systems and its application in mining and mineral industry, special attention must be given to cement and the mechanism of its hydration.

2.5. Cement

2.5.1. Cement Technology

Cement is a finely pulverized material which by itself is not a binder, but develops the binding property as a result of hydration (i.e., from chemical reactions between cement minerals and water). A cement is called hydraulic when the hydration products are stable in an aqueous environment. The most commonly used hydraulic cement is portland cement, which consists essentially of hydraulic calcium silicates (Mehta and Monteiro, 1993). Portland cement is produced by burning at high temperatures mixtures containing lime, alumina, iron, and silica in definite proportions.

When portland cement is dispersed in water, the calcium sulphate and the high temperature compounds of calcium tend to go into solution, and the liquid phase becomes rapidly saturated with various ionic species. As a result of combinations between calcium, sulphate, aluminate, and hydroxyl ions within a few minutes of cement hydration, first the needle-shaped crystals of a calcium sulphoaluminate hydrate called "ettringite" make their appearance. A few hours later large prismatic crystals of calcium hydroxide and very small fibrous crystals of calcium silicate hydrates begin to fill the empty space which formerly was occupied by water and the dissolving cement particles. After some days, depending on the alumina-to-sulphate ratio of the cement, ettringite may become unstable and decompose to form the monosulphate hydrate, which has hexagonal-plate morphology (Mehta and Monteiro, 1993; Neville, 1981).

Calcium sulphoaluminate compounds occupy 15 to 20 percent of the solids volume in the hydrated paste and therefore play only a minor role in the structural property relationship of portland cement. As it was already stated, during the early stages of hydration the sulphate/alumina ionic ratio of the solution phase generally favors the formation of trisulphate hydrate (ettringite), which forms needle-shaped prismatic crystals. In paste of ordinary portland cement, ettringite eventually transforms to the monosulphate hydrate which forms hexagonal-plate crystals (Mehta and Monteiro, 1993).

Anhydrous portland cement consists of angular particles typically in the size range of 1 to 50 µm. It is produced by pulverizing a clinker with a small amount of calcium sulphate. The chemical composition of the clinker minerals corresponds approximately to C_3S[1], C_2S, C_3A, and C_4AF.

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[1] C = CaO; S = SiO_2; A = Al_2O_3; F = Fe_2O_3;

2.5.2. Mechanism of Hydration

The actual mechanism of cement hydration is still a matter of debate in the field of cement chemistry. Two mechanisms for cement hydration has been proposed. According to the first theory, *through solution hydration*, anhydrous compounds are dissolved to their ionic constituents, formation of hydrates in the solution, and the eventual precipitation of the hydrates from supersaturated solution due to their low solubility. According to the second theory, called the *topochemical* or *solid state hydration*, the reactions take place directly at the surface of the anhydrous cement compounds without entering into the solution. However, from the electron microscope studies, it appears that the through solution mechanism is dominant in the early stages of cement hydration. At later ages when the ionic mobility in solution becomes restricted, the hydration of the residual cement particles may occur by topochemical reactions (Mehta and Monteiro, 1993).

Since portland cement is composed of a heterogeneous mixture of several compounds, the hydration process consists of simultaneously occurring reactions of the anhydrous compounds with water. However, all the compounds do not hydrate at the same rate. The aluminates are known to hydrate at a much faster rate than the silicates. From the stand point of cement stiffening, setting, and waste immobilization, the hydration of tricalcium aluminate (C_3A)in the presence of gypsum becomes important. According to Mehta and Monteiro (1993), since gypsum and alkalies go into solution quickly, the solubility of C_3A is depressed in the presence of hydroxyl, alkali, and sulphate ions. Depending on the concentration of aluminate and sulphate ions in the solution, the precipitating crystalline product is either the calcium aluminate trisulphate hydrate, called *ettringite*, or the calcium monosulphate hydrate. Ettringite is usually the first hydrate to crystallize because of the high sulphate to aluminate ratio in the solution phase during the first hour of the hydration. Later, after the depletion of sulphate in the solution when the aluminate concentration goes up due to renewed hydration of tricalcium aluminate, ettringite becomes unstable and is gradually converted into monosulphate.

There is another phenomenon related to the presence of sulphate containing compounds in cement which involves the formation of expansive products, known as sulphate attack. On hydration, portland cement with more than 5 percent potential tricalcium aluminate will contain most of the alumina in the form of monosulphate hydrate. In the presence of calcium hydroxide in portland cement pastes, when the cement paste comes into contact with sulphate ions, the alumina containing hydrates are converted to ettringite. There is a general agreement that the sulphate-related expansions in concrete are associated with ettringite; however, the mechanisms by which the ettringite formation causes expansion is still a subject of controversy (Cohen and Mather, 1991). Exertion of pressure by growing ettringite crystals, the crystal growth theory, and swelling due to adsorption of water in alkaline environment by poorly crystalline ettringite, the swelling theory, are two of the several hypotheses that are supported by most researchers (Mehta and Monteiro, 1993).

The crystal growth theory is based on the topochemical theory of ettringite formation and states that the expansive forces arise from the crystallization pressures of ettringite bound to the surface of C_3A clinker (Cohen, 1983). The amount of growth also depends on the number of nuclei sites per unit volume and the growth speed of the crystal. If the concentration of sulphates in the pore water are suddenly reduced ettringite converts back to monosulphate through metastable intermediates containing 3 to 1 sulphate and 32 to 18 water molecules. The expansion capacities of these metastable intermediates increase with more sulphates and water in the lattice. This is why the monosulphate is the least expandable of all the calcium sulphoaluminate hydrates and ettringite has the largest expansion capacities. The swelling theory is based on through-solution theory and explains the expansion by invoking the adsorption of water on high surface area ettringite. Adsorbed water increases the surface tension of ettringite particles, decreasing the interparticle Van der Waals forces and therefore, resulting in expansion (Cohen, 1983).

Both theories agree on the role of portlandite -$Ca(OH)_2$- in the solution. The absence of portlandite promotes the formation of large ettringite crystals which are nonexpansive. However, when portlandite is present, it limits the size of ettringite to a very small particles which are more susceptible to yield large expansive pressure (Deng and Tang, 1994). The two theories disagree, however on the rate of hydration of the ettringite in the presence and absence of lime. According to the first theory, hydration is more favorable and quicker in the presence of lime and the mode of formation of ettringite is topochemical; in the case where lime is absent the formation of ettringite is through solution. According to the second theory, ettringite always forms in a through solution mechanism, regardless of the presence or absence of lime. However, hydration of ettringite is smaller in the presence of lime.

2.5.3. Fly Ash

Fly ash is the finely divided residue that results from the combustion of ground or powdered coal. Fly ash is transported from the combustion chamber by exhaust gases and is usually collected by mechanical or electrostatic precipitators (Mehta, P.K., 1986). It is considered a waste itself, although it is increasingly being used in the concrete industry as a partial replacement for cement. Fly ash production in the United States was estimated to be 65 million tons per year in 1993, only 20 million tons of which were used as a substitute material in different projects. While its production is projected to double by the year 2005 (Khan and Sarker, 1993), the problem associated with the use or safe disposal of fly ash is intensifying. It is estimated that over a billion tons of fly ash has been stockpiled in the United States (McLaren and DiGioia, 1987).

Fly ash is a siliceous material which, in the presence of water, combines with lime to produce a cementitious material with excellent structural properties.

2.5.3.1 Composition

Fly ash is composed of particles that are predominantly amorphous and spherical in shape, whether solid or hollow (TRB, 1976). They range in diameter from 1-50 μm with surface areas of 4000-7000 cm^2/g. The size particles depends largely on the collection mechanism used; thus, electrostatic precipitators collect an ash that has much fine particles than one collected by a cyclone (Berry, E.E., 1976).

The composition of fly ash varies considerably depending on the nature of the coal burned and the power plant operational characteristics. Fly ash is designated as class F or class C depending on the parental coal source. Class F ash is derived from bituminous or anthracite coals. Class C ash comes from sub-bituminous or lignite coals predominantly mixed in the western United States. Type F fly ashes do not have pozzolanic reactivity while the type C ashes contain significant amount of CaO that gives a good pozzolanic characteristics (Usmen and Bowders. 1988). Table 2.1 provides the typical chemical composition of fly ash type C and F.

TABLE 2-1 TYPICAL CHEMICAL COMPOSITION OF FLY ASHES AND PORTLAND CEMENT (AFTER SMITH, 1993)

Compounds	**Fly Ash Class F**	**Fly Ash Class C**	**Portland Cement**
SiO_2	54.9	39.9	22.6
Al_2O_3	25.8	16.7	4.3
Fe_2O_3	6.9	5.8	2.4
CaO	8.7	24.3	64.4
MgO	1.8	4.6	2.1
SO_3	0.6	3.3	2.3

2.5.3.2. Pozzolanic Properties

By far the most important of the characteristics of fly ash is its pozzolanic properties. A pozzolan is defined as a "siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties" (ACI. 1985).

The lime-fly ash reaction (pozzolanic) is a slow process that takes place without any heat generation. When water and fly ash are mixed with lime, the silica and alumina will react with lime and the resulting product is tricalcium silicate and tricalcium aluminate. The presence of sulphates and sulphites in the fly ash will result in the formation of calcium aluminate trisulphate hydrate, ettringite (Conner.1990). The factors which affect these reactions are temperature, curing time. materials used and proportions. Barenberg (1974) suggests that for a given lime-fly ash mixture. increased quantities of pozzolanic materials are produced by extending the curing time and increasing the temperature.

According to Berry (1976). two successive stages of reactivity are taking place for pozzolanic reactions: (I) after the immediate mixing of fly ash with cement and water. the reaction seems to be controlled by the percentage of the amorphous particles present in the ash. as well as the reactive surfaces available for reaction with lime; (ii) after long curing periods, the reactivity becomes a function of the total SiO_2 and Al_2O_3 available in the ash.

2.5.3.3. Lime/Fly Ash Stabilization

Lime/fly ash combinations have been studied for some time. Without question, compositions including lime and fly ash have comprised the largest volumes of wastes treated in the United States. There seem to be two reasons behind mixing these two additives. The first one is to stabilize the fly ash itself, as it is considered a hazardous by-product of coal burning. The second one is to provide a binder within which other hazardous sludges and wastes could be stabilized. The range of applications of lime/fly ash extends from waste and soil stabilization to pavement construction. An example of the former case is the use of fly ash in the stabilization of tropical soils (Nicholson and Kashyap, 1993). A study was conducted on Hawaiian soils with high percentages of iron and aluminum. The stabilization process was attributed to two basic sets of reactions:

- Short term: This set included flocculation and agglomeration of clay particles due to iron exchange. The result was a reduction in swelling, shrinkage and plasticity;
- Long term: This set of reactions resulted in the binding of the soil particles together due to the formation of cementitious materials. The main factor behind these reactions was the presence of pozzolans provided by the fly ash.

Since the lime/fly ash treated soils gave higher strength values, the authors concluded that this method may provide a more cost effective treatment than the one with lime alone.

Not only soils, but wastes have also been stabilized using a lime/fly ash binder. Smith (1993), has done a comprehensive study on the utilization of these additives in industrial waste treatment. He states that fly ash and kiln dusts are the less expensive additives in stabilization, unlike portland cement and lime. Work in recent years has focused mainly on the application of lime and fly ash as a binder within which wastes and sludges have been solidified and stabilized. The main criterion for the success of the binder has been the amount of metals that could be leached from the end product. One such example has been the reduced leachability of metals from a combination of wastes (Hassett and Hassett, 1988). The authors concluded that the reduction in leachability was due to the formation of solid hydrated phases incorporating the trace metals and not just due to the rise in pH. Synthetic sludges have also been used with lime/fly ash binders. Roy and Eaton (1992) made a sludge with the metals nickel, chromium, cadmium and mercury, which were precipitated by lime addition. X-ray diffraction showed the formation of calcium hydroxide and calcium carbonate phases. The heavy metals were found to be in complex forms and were also seen on fly ash surfaces by energy dispersive x-ray spectroscopy (EDX). In another study by DebRoy and Dara (1994), synthetic sludge was made and three solidification procedures were followed:

- Fixation: The lime and fly ash were mixed and then the sludge was added to it. After the addition of water, the samples were compacted;
- Coating: Cubes were prepared according to the above procedure, then dipped into a 5% sodium silicate solution;

- Encapsulation: Cavities were made in the lime/fly ash mixtures molds and then the cavities were filled with hydroxide of the sludges.

After the initial curing and successive leaching of all the samples, the following conclusion regarding the effectiveness of the different methods were made:

Encapsulation > Coating > Fixation

Metal sludges are by no means the only type of waste to which lime/fly ash binders can be applied. Martin *et al.*, (1988), were able to apply it to a hydrocarbon sludge in a silty matrix. The binder was seen to effectively retard leachability due to physical micro encapsulation. Joshi *et al.*, (1989), studied the properties of Alberta fly ash, concentrating mainly on its physical characteristics. They reached the conclusion that the addition of lime decreased the conductivity of the mix, increased its strength and decreased the leaching of metals from the fly ash.

2.6. Ettringite

2.6.1. Ettringite; Definition and its Structure

Ettringite (Aft phase) is formed in limited amounts in portland cement pastes in the initial stage of hydration. It has the general formula (tricalcium)-*A*luminate *F*errite • *t*ri (sulphate, hydroxide, etc.) • (hydrate). The AFt designation was first suggested by Smolczyk in a 1961 publication in order to distinguish the high sulphate hydrate phases from the low sulphate phases, which are collectively termed Afm (*A*luminate *F*errite • mono) (Gougar, M.L.D. *et al.*, 1996). Ettringite occurs as a natural mineral along with others of similar structure and composition fitting into the ettringite groupe of minerals.

Ettringite, $\{Ca_6[Al(OH)_6]_2(SO_4)_3 \cdot 26H_2O\}$, is responsible for retarding the hydration of tricalcium aluminates and binding aggregates in clasts in cements and concrete (Mehta and Monteiro, 1993). Ettringite consists of columns of $\{[Ca_6[Al(OH)_6]_2 \cdot 24H_2O]^{+6}\}$ which are basically lines of $[Al(OH)_6]^{-3}$ octahedra bonded with three Ca^{+2} ions. The coordination number of calcium is completed by water molecules. The sulphates are intercolumnar and can occur in four different positions. Three of these positions are occupied by sulphates and the remaining by two water molecules (Moore and Taylor, 1968,1970).

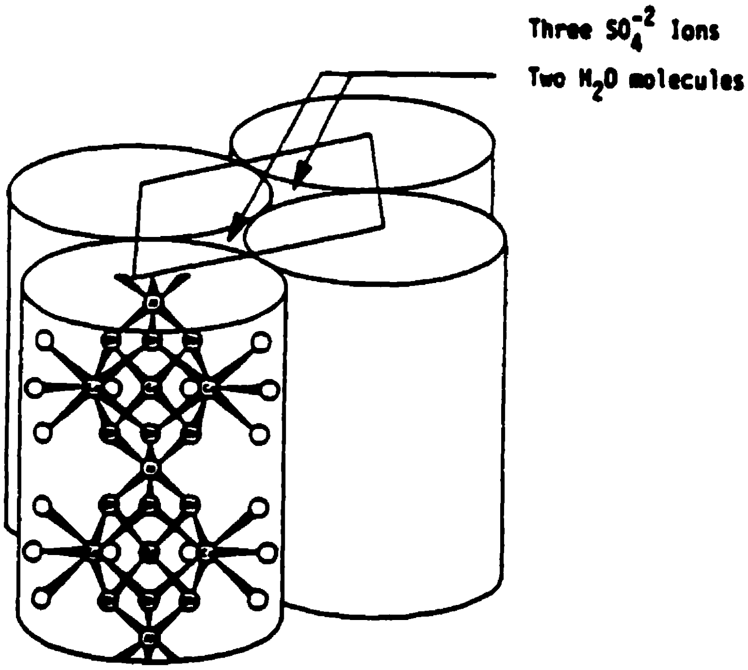
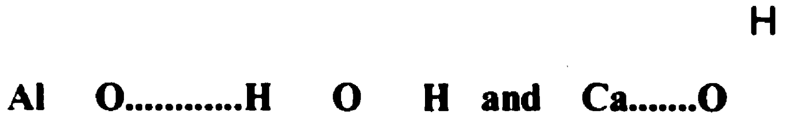


FIGURE 2- 1. CRYSTAL STRUCTURE OF ETTRINGITE, MODIFIED FROM MOORE AND TAYLOR, 1970

2.6.2. Ettringite Formation

The mechanism of ettringite formation is not a well resolved question. There are two different schools of thought existing on the mechanism of ettringite formation. They are the topochemical and the through solution mechanism (Cohen, 1983). But under which conditions one mechanism follows the other is not understood. Most of the studies of the mechanism of ettringite formation were focused to explain the expansion characteristics of expansive cements and lack a common opinion about the mechanism (Havlica and Sahu, 1992). The crystal of ettringite forms in-situ in pore solution with high hydroxyl ion concentration, and forms both in-situ and in bulk solution under conditions of low hydroxyl ion concentration (Deng and Teng, 1994). During the hydration of portland cement or super-sulfated cement, it may be assumed that, upon interaction of polar H_2O molecules and/or OH- ions with aluminates particles, intermediate components form on some surfacial regions of the grains.



$$\text{Al}\quad \text{O}\cdots\cdots\cdots\text{H}\quad \text{O}\quad \text{H}\quad \text{and}\quad \text{Ca}\cdots\cdots\overset{\qquad\text{H}}{\text{O}}$$

With the formation of these new bonds the original Ca--O and Al--O bonds will weaken, and eventually break down. The pieces broken down will exist mainly as Ca^{2+} and $Al(OH)^{4-}$ ions in pore solutions of cement pastes (Reardon, 1990). It is accepted that gypsum can readily dissolve into water, producing Ca^{2+} and SO_4^{2-} ions. OH- ions in pore solutions may come from the dissolution of either alkalies in clinkers or predominant clinker phases such as calcium aluminates and calcium silicates or both. When the pore solution is supersaturated with respect to ettringite crystals, the crystals will precipitate from the solution (Deng and Teng, 1994):

$$6Ca^{2+} + 2Al(OH)_4^{-} + 3SO_4^{2-} + 4OH^{-} + 26H_2O \rightarrow \{Ca_6[Al(OH)_6]_2 \bullet 24H_2O\}(SO_4)_3 + 2H_2O$$

2.6.3. Ettringite As An Agent For The Fixation Of Hazardous Waste Materials

The concept of fixing toxic inorganic and organic compounds into the crystalline structure of another mineral, by sorption into the crystal layers, adsorption on charged surfaces and replacement OH^- and H_2O groups is relatively new. By intelligently manipulating the chemical environment, it is possible to synthesize new classes of minerals that can be used for immobilizing and/or entrapping toxic substances. In some cases, there is a need to develop a new class of cement specifically for this purpose (Pollman, H., 1993). Ettringite, a hydrated mineral, has the potential for successful use for entrapping toxic wastes.

The ettringite structure is a very "forgiving" one. It can withstand some deviation in composition without a change in structure. Diodochic and/or isomorphic substitution of Ca^{2+} and Al^{3+} can occur in the crystal lattice. In the case of diodochic substitution, ions of similar sizes and charges substitute for each other;

and in the case of isomorphic substitution, ions of similar sizes but different charges substitute for each other. Structural Ca^{2+} can be replaced by other divalent metal cations like Zn^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+}, etc., and structural Al^{3+}, can be replaced by Cr^{3+}, Mn^{3+}, Ti^{3+}, Ti^{4+} . Si^{4+}, etc. (Vempati, R.K., *et al.*, 1996). The isomorphic substitution of ions will result in development of permanent structural charge. Hence, the ion-exchange capacity can be increased, which will result in additional fixation of metallic cations.

All crystal chemical substitutions in the mineral ettringite occur at the aluminum and sulphate sites. The aluminum site, in general, accommodates a variety of trivalent and tetravalent cations in a spectrum of proportions. Bensted and Varma (1971), have confirmed some of this mineral substitution by replacing Al_2O_3 with various sesquioxides of the first transitions. Also attempted in this study was a replacement of alumina with B_2O_3. In addition to those substitutions seen in the minerals, Bonen and Sarkar (1994), report Ni^{3+} and Co^{3+} replacing aluminum and Bensted and Varma (1972), make reference to an analogue of ettringite with Ti^{3+} in the aluminum site.

Although no calcium-site substitutions occur in the ettringite minerals, a number of reports suggest a variety of divalent cations will replace Ca^{2+}. An ettringite analogue with Sr^{2+} replacing Ca^{2+} is reported by Bensted and Varma (1972). Glasser (1993), suggests that Ba^{2+} and Pb^{2+}, among others, will generally replace calcium in cement hydrated phase. Bonen and Sarkar (1994), report the ettringite phase accommodating Cd^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} at the divalent metal site in the crystal structure.

Numerous studies conducted at the University of North Dakota as well as the State University of North Dakota has shown that formation of ettringite may be accompanied by the fixation of oxyanions in their structures. In a study by Hassett *et al.*, 1989, the oxyanions substituted ettringite were synthesized and their long term stability over wide pH ranges were determined. For this purpose the calcium, aluminum, and sulphates in the samples were leached and their content in the leachate were measured with the use of a inductively coupled argon plasma (ICAP) spectroscopy and ion chromatography. They concluded that the formation of ettringite could lead to the immobilization of elements such as arsenic, boron, chromium, molybdenum, selenium, and vanadium, while its stability decreases below the pH 10.

In another study by P. Kumarathasan et al (1990) the oxyanions substituted ettringite were leached over one thousand days. The results which showed between 76-96% of the trace elements of concern (As, B, Mo, Se, and V), were fixed in some solid phase or phases. Such results led them to the conclusion that solubility of these elements is being controlled by the formation of mineral ettringite. They also reported on previous works which has shown the substitution of borate, chromate, selenate, carbonate, nitrate, hydroxyl, and sulfite for sulphate in the structure of ettringite. In addition to the above mentioned elements, they suggested that other oxyanions which might substitute for sulphate are: MnO_4^- , WO_4^{2-} , PO_4^{3-} , SeO_3^{2-}, TeO_4^{2-}, SbO_4^{3-} , BiO_4^{3-} .

Examination of the ettringite group of minerals provides naturally occurring evidence of compositional change at these sites. When compared with ettringite $\{Ca_6[Al(OH)_6]_2(SO_4)_3\bullet 26H_2O\}$, the thaumasite mineral formula $\{Ca_6Si_2(OH)_{12}(SO_4)_2(CO_3)_2\bullet 24H_2O\}$, for example, shows aluminum replaced by the tetravalent cations, Si^{4+}, along with sulphates' partial replacement by another divalent anion, CO_3^{2-} (Gougar, M.L.D., et al., 1996). Table 2.2. provides a complete list of ettringite group of minerals. Study of these structures provides information on some natural and, therefore, stable ionic substitutions possible in the structure of ettringite.

TABLE 2- 2 STRUCTURE OF THE ETTRINGITE GROUP OF NATURAL MINERALS

Charlesite subgroup	
Bentorite	$Ca_6\ Cr_2(SO_4)_3(OH)_{12}\bullet 26H_2O$
Charlesite	$Ca_6(AlSi)_2(SO_4)_2\ [B(OH)_4]\ (OH,O)_{12}\bullet 26H_2$
Sturmanite	$Ca_6\ Fe_2(SO_4)_2\ [B(OH)_4]\ (OH)_{12}\bullet 26H_2O$
Ettringite subgroup	
Ettringite, syn	$Ca_6[Al(OH)_6]_2(SO_4)_3\bullet 26H_2O$
Thaumasite subgroup	
Jouravskite	$Ca_6Mn_2(OH)_{12}(SO_4)_2(SO_3)_2\bullet 24H_2O$
Thaumasite	$Ca_6Si_2(OH)_{12}(SO_4)_2(CO_3)_2\bullet 24H_2O$

Table 2.3 provides a summary of documented substitutions into the ettringite structure as reported by different authors.

Table 2- 3 Reported Waste Ion Substitutions in Ettringite Minerals and Synthetics

(After Gougar *et al.*, 1996)

(Ca2+) site	(Al3+) site	(SO$_4$2+) site	(OH-) site
Sr2+	Cr3+	B(OH)$_4$-	O2-
Ba2+	Si4+	CO$_3$2-	
Pb2+	Fe3+	Cl-	
Cd2+	Mn3+	OH-	
Co2+	Ni3+	CrO$_4$2-	
Ni2+	Co3+	AsO$_4$3-	
Zn2+	Ti3+	SeO$_4$2-	
Fe2+	Ti4+	VO$_4$3-	
		BrO$_3$-	
		NO$_3$-	
		MoO$_4$2-	
		ClO$_3$-	
		SO$_3$2-	
		IO$_3$-	

2.6.4. Mechanism of Waste Immobilization

Wastes containing toxic and often highly soluble sludges can be transformed by using cement based systems into solidified and stabilized materials (Conner, 1990). Depending on the application of various cements and cementitious materials different immobilization mechanisms can be predicted:

1. Precipitation at high pH-values of cement materials;
2. Sorption effects at high surface cement phases;
3. Crystallochemical incorporation into cement materials.

It is widely accepted that cement and pozzolan-based waste forms rely heavily on pH control for metal containment. The formation of insoluble heavy metal compounds during stabilization-induced high pH conditions, make it difficult for heavy metal species to remain in the solution. The hydroxides formed by many of the multivalent metals are characterized by decreasing solubility as the pH of the solution increases. Unfortunately, all metals do not reach minimum solubility at the same pH, so that optimum pH of the system must be a compromise. Solubility curves for various metal hydroxides, derived from several sources and here adapted from Conner (1990), is shown in the figure below:

A number of metal hydroxides such as arsenic and chromium, however, become increasingly soluble as the pH of the solution increases (Environment

Canada, 1987). Therefore, their immobilization is not readily explained in terms of hydroxide complexation mechanisms.

Another mechanism of immobilization is adsorption of metal oxides to the surface of cement based solidifying materials. At the solid surfaces of cement

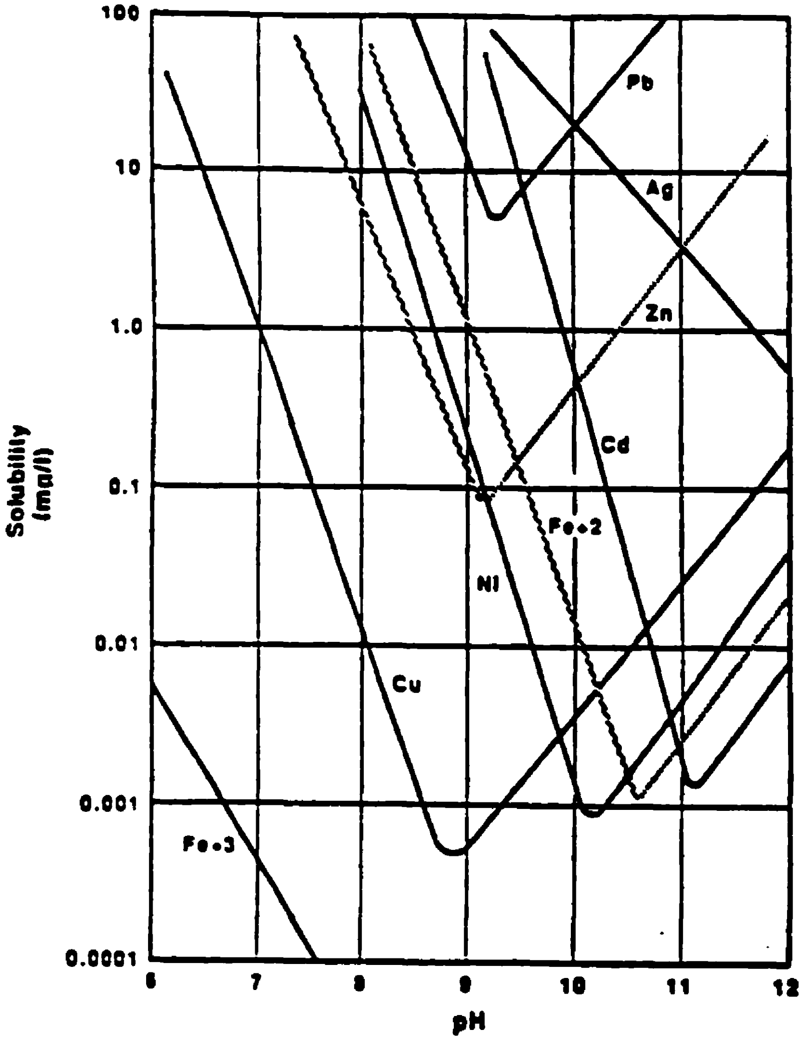


FIGURE 2-2 SOLUBILITIES OF METAL HYDROXIDES AS A FUNCTION OF PH (AFTER CONNER, 1990)

materials cohesive forces such as ionic, covalent and Van der Waals forces, are unbalanced. This situation gives rise to the phenomenon of adsorption. Adsorption occurs when a molecule or ion becomes attached to a surface. In surface layers of metal oxides, the metal ions have a reduced coordination number. In the presence of water, they develop a hydroxylated surface with a net negative charge at high pH. This cause the adsorption of cations to the surface of cement materials (Conner, 1990).

Glasser (1992) reported that in the progress of hydration a microporous matrix is built up and the tendency for leaching is decreasing. In another study by Amitava et al. (1992), waste materials from an electroplating plant were mixed with ordinary portland cement or lime and high calcium content fly ash. Sodium sulphate was added to the mixtures and its effect on the physical and chemical stability of the cementitious matrix was analyzed. The result of their investigation showed that upon the addition of sulphate to all the mixtures, ettringite was formed. The formation of mineral ettringite contributed to the reduction of elements of concern in the leachate from the matrixes. They concluded that physical encapsulation of the heavy metals in the matrix was the principal mechanism of immobilization. The result of this study revealed that the newly formed ettringite crystals contained significant amounts of Na, Cr and Ni.

Therefore, formation of ettringite in sulphate rich tailings could provide several stabilization possibilities: (I) incorporation into the crystal structure of ettringite; (ii) replacement of OH^- and H_2O groups in the crystal lattice of ettringite;

(iii) adsorption on charged surfaces and (iv) precipitation as insoluble metal-oxides and hydroxides because of alkaline nature of the composite waste mixture.

2.6.5. Ettringite in Lime-Remediated Mine Tailings

The formation of ettringite can be promoted in lime-remediated mine tailings. The acid generating mine tailings contain an important amount of sulphidic minerals which if left untreated could pose a serious environmental threat to surface and groundwater regime. The acidic environment is characterized, amongst others by an elevated amount of sulphate and ferric iron. Traditionally, mining companies in Canada rely on lime treatment of their acidic tailings which provides an alkaline environment with elevated level of calcium ion in solution. However, if sufficient amount of aluminum can also be provided in the solution, the system contains all the requirement for the precipitation of calcium sulphoaluminate hydroxide hydrate, ettringite. Formation of ettringite in lime remediated mine tailings can be associated with the fixation of heavy metals from the surrounding environment into and/or onto its crystal structure. Moreover, the high pH induced environment required for the formation of this mineral will cause the precipitation of heavy metals from the solution.

2.6.6. Ettringite Swelling and Expansion

It is generally believed that expansion of sulfoaluminate-type expansive cement is associated with the formation of ettringite. This phenomenon is called "sulfate attack" in the cement and concrete industry. Whereas researchers have yet to agree on the mechanism by which ettringite causes expansion, it is observed that ettringite is also the primary source of strength in many cements.

As was discussed earlier, the origin of ettringite expansion is not yet fully understood. The numerous theories and models aimed at explaining the mechanism of formation of ettringite and expansion due to ettringite can be divided into two major groups: i) the crystal growth theory, and ii) the swelling theory (Deng and Tang, 1994; Mehta, 1983; Cohen, 1983). According to the first theory, expansion is caused by the growth of ettringite crystals which form on the surfaces of the expansive particles or in the solution. The growth of these crystals, commonly referred to as crystal growth, is responsible for the crystallization pressure and, hence, expansive force (Cohen, 1983). According to the second theory, expansion is caused by the swelling of the ettringite particles that are of colloidal size. These particles are commonly referred to as gel. This gel has a large specific surface area, takes up water to produce overall expansion by swelling. However, extensive research has shown that, regardless of the mechanism of expansion, ettringite growth and expansion depends on the concentration of hydroxyl ions in the pore solution (Deng and Tang, 1994; Wang *et al.*, 1986; Mehta, 1983). Mehta (1983), based on extensive experimental analysis has proposed to categorize ettringite crystals into two types: Type 1 ettringite crystals are large lath-like crystals, 10-100 µm long. They are typically formed under conditions of low hydroxyl ions concentration. Mehta (1983), has shown that cements containing considerable amount of large ettringite crystals manifest high strength but no expansion. This type of ettringite crystals are not expansive.

Type 2 ettringite crystals are small, rod-like crystals, typically 1-2 µm long, which are formed under conditions of high hydroxyl ions concentration. This condition exists, for instance, during the hydration of normal portland cements. From high magnification electron microscopic observations and surface area measurements by small angle diffraction study conducted by Mehta (1983), he concluded that the actual size of the ettringite crystals may even be considerably smaller than 1-2 µm. Since large amounts of these crystals are found in concrete deteriorated due to sulfate attack, it was proposed that this type of ettringite is expansive.

However, it is important to note that the question of ettringite expansion and swelling has been mostly addressed in the context of cement and concrete. Such environment is characterized by high hydroxyl ions concentration and ettringite formation is within a solid state. Ettringite crystals which are formed under this circumstances are small and are prone to expansion. On the other hand, in lime remediated mine tailings environment ettringite crystals are larger than those formed in portland cement environment and have no swelling or expansion characteristics. Furthermore, ettringite will be formed in a liquid state in mine tailings rather than in the solid state of cement and concrete environment. Such a condition will prevent ettringite expansion. Moreover, the expansion process of ettringite takes place, if any, during its formation process and not after it has been formed. Therefore, once the ettringite mineral has formed, its stability is related to the chemical characteristics of the surrounding environment, such as the availability of sulfate ions and pH condition. Hence, concern over ettringites' potential swelling and expansion has no effect on the adsorbed and/or absorbed ions from its structure.

2.7 General Remarks

From review of the existing literature, several comments can be made concerning the importance of new and innovative techniques to deal with the problem of acid mine drainage. Most researchers in the area of prevention and treatment of acid producing tailings have worked with the existing technologies and have tried to improve upon them. However, the natural constituents of reactive tailings have not been fully explored for immobilization and abatement of acidic drainage.

Ettringite utilization in terms of waste stabilization is a relatively new technology with great potential in stabilization and solidification of heavy metals and oxyanions in an alkaline environment. Acid producing tailings, on the other hand, has all the necessary constituents of ettringite formation, providing the pH of the medium is buffered and can resist acidification. If these conditions are met, it is believed that ettringite and ettringite substituted minerals can be formed in a stable form in potentially acid producing tailings. Formation of ettringite in these tailings will generate an inert material with reusability potential.

Chapter 3

Materials and Methods

The laboratory testing program is focused on physical and chemical characterization of the tailings samples selected for this study. The experimental procedures used for evaluation of the proposed treatment procedure, such as leachability, permeability, and unconfined compressive strength have been explained within the corresponding chapters.

3.1 Materials

Two sulfate rich mine tailings samples were obtained from two mine sites in Quebec. The first sample came from a copper, nickel, zinc, gold operation (labeled sample 1) and the second came from a copper, nickel, gold mine (labeled sample 2). Samples were received in sealed plastic containers and during the duration of the tests were kept in the humid room. Portion of the samples were air dried in order to conduct the initial physical and chemical analysis needed for identification of the samples. The air dried samples were gently crushed with a mortar and pestle and were kept in sealed glass container for further analysis.

3.2 Physical Characterization

All the following physical characteristics experiments are conducted according to ASTM standards testing procedures and various techniques reported by different researchers as described below. The selected analysis are conducted in triplicate and their average values are reported in Table 3.1.

TABLE 3.1 PHYSICAL ANALYSIS OF TAILINGS SAMPLE

Test	Sample 1	Sample 2
Moisture Content (%)	10.29	9.20
Specific Gravity	3.60	2.94
Specific Surface Area	10.62	12.76
Liquid Limit (L.L.)	18.23	19.06
Plastic Limit	Close to L.L.	Close to L.L.

3.2.1 Moisture Content

The measurement of the moisture content, both in the natural state and under certain defined test conditions, can provide an extremely useful methods of classifying cohesive soils and of assessing their engineering properties. Moisture content is defined as ratio of the mass of fluid in the sample to the mass of the solid particles as:

*Moisture Content (%) = Weight of pore fluid (g) * 100/Weight of Solid Particles (g)*

ASTM method D2216 were followed for determination of moisture content.

3.2.2 Specific Gravity

The specific gravity is defined as the ratio of a unit volume of material at a stated temperature to the mass, in air, of the same volume of distilled water at a stated temperature. Soil's specific gravity is in the range of 2.6 to 2.75. However, given the nature of the samples under investigation, it is expected that a higher specific gravity will be recorded for the mine tailings samples. ASTM method D854 was followed for measurement of specific gravity and their values are given in Table 3.1.

3.2.3 Liquid Limit and Plastic Limit

The liquid limit and the plastic limit together constitute the Atterberg limits of a given soil sample. There are two common methods for determining the liquid limit of a soil and both were considered for the tailings samples under investigation.

However, the method proposed by ASTM D4318 involving the use of the Casagrande apparatus proved difficult since the samples were rather silty. This property did not allow cutting a clean groove in the paste as outlined in the ASTM suggested method. Therefore, the cone-penetrometer method (British Standard BS 1377: part 2:1990:4:3) was employed (Head, 1992). The test was conducted in triplicate and the average values are given in Table 3.1. The test involved the use of a polisher stainless steel cone, 80 grams in weight, which falls freely for 5 seconds and penetrates the soil (tailings) sample contained in a special cylindrical cup. Tailings were mixed with varying amounts of distilled water, put in the steel cup and tested with the cone penetrometer. Four readings between 15 and 25 mm of penetration were taken for each tailings sample. The numbers were plotted against the respective moisture contents of that sample. The liquid limit of the tailings sample were determined by reading the moisture content for a penetration of 20 mm. The plastic limit was determined based on ASTM D 4318.

3.2.4 Grain Size Analysis

The purpose of particle size analysis of any soil is to determine the relative abundance of certain ranges of particle sizes. Determination of particle size analysis was done according to ASTM D421 and D422 testing procedures. Three Hundred gram of air dried sample was washed over a 200 mesh sieve. The residue was oven dried and later used for sieve analysis while the quantity which passed sieve # 200 was carefully collected, dried and were analysed for their grain size distribution, using a hydrometer. A mechanical shaker was used for 15 minutes in order to perform the sieve analysis. The results of tailings samples grain size analysis are given in Figures 3.1. The results presented in the figures below indicate that both samples contained between 3.5 (for sample 1) and 4.4 (for sample 2) of clay size particles. Most of the particle size distribution for both samples falls in medium to fine sand, with very limited amounts of silt and clay size particles. The Atterberg

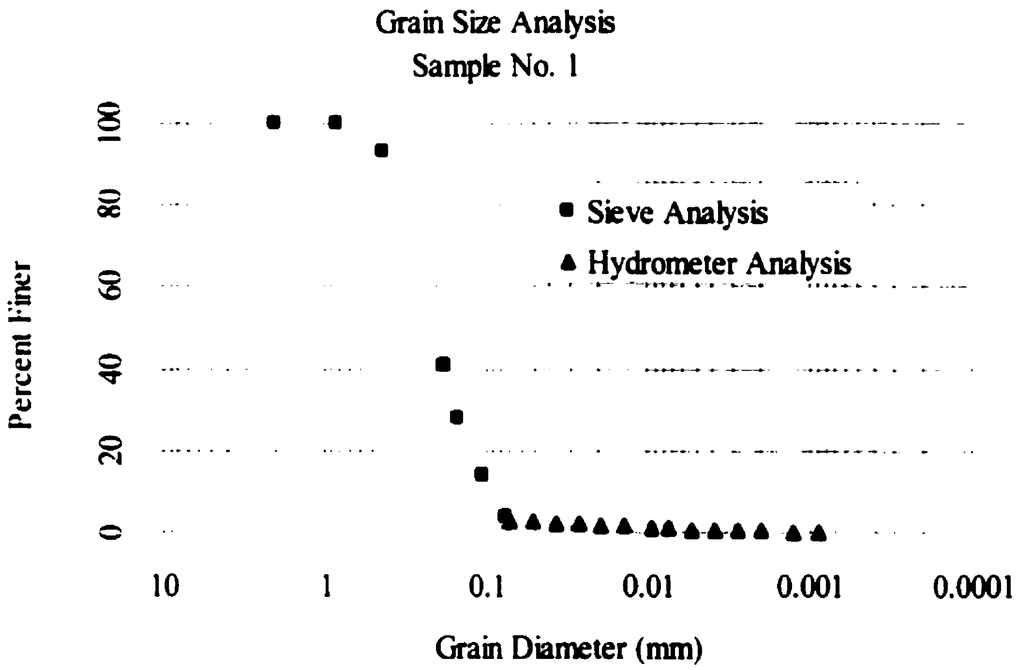


FIGURE 3.1 PARTICLE SIZE ANALYSIS OF TWO TAILINGS SAMPLES

limit tests conducted previously reveal that these tailings posses relatively low plasticity potentials.

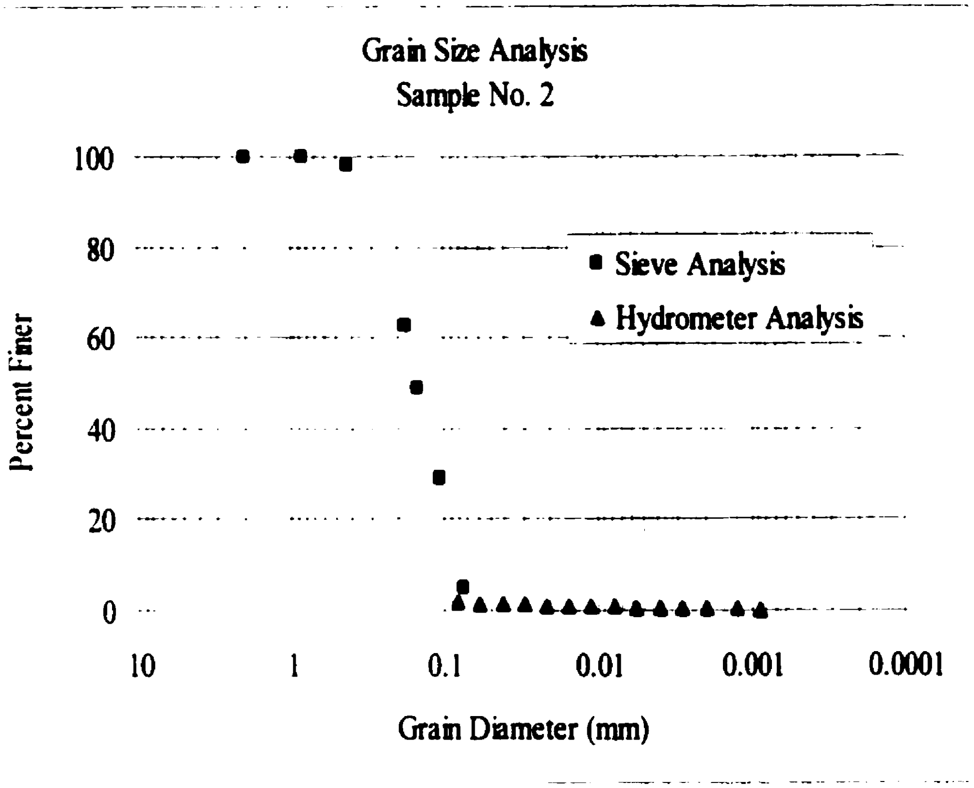


FIGURE 3.1 (CONTINUE) PARTICLE SIZE ANALYSIS OF TWO TAILINGS SAMPLES

3.2.5 Specific Surface Area

Specific surface area (SSA) is the ratio of the surface area of a media over its volume or mass. Usually the specific surface is an indication of the surface of ionic activity for a type of soil. Small particles tend to have larger specific surface area than larger particles. This is due to the relative size of the soil particle compared to its volume. Clays are very small particles and thus have larger specific surface area than other soil particles such as sand. A larger surface area is generally indicative of a more active site, be in terms of cation exchange capacity or water adsorption. Clay have a negatively charged surface due to isomorphous substitution and imperfections in the clay lattice. Isomorphous substitution occurs when one atom is replaced by another type of atom within the crystalline structure of the clay mineral. The overall effect of atomic substitution is to increase the negative charge on the particles (Holtz and Kovacs, 1981).

The ethylene glycol-monoethyl ether (EGME) method as described by Carter *et al.*, (1986) was used to determine the samples specific surface area. The experimental procedure used to determine the specific surface area consisted of measuring the adsorption of a specific cation or molecules on the surface of the soil particles. The table below is the result of the experiment to measure the SSA value:

TABLE 3.2. SPECIFIC SURFACE AREA MEASUREMENT

SAMPLE No.	SSArea (m^2/g) Trial 1	SSArea (m^2/g) Trial 2	Average (m^2/g)
Sample No. 1	**12.03**	**9.20**	**10.62**
Sample No. 2	**14.18**	**11.35**	**12.76**

3.3 Chemical Characteristics

3.3.1 pH and Redox Potential Measurements

Chemical experiments were performed on the tailings samples in order to better characterize their properties. Due to the focus of the project on stabilization of reactive tailings via the formation of ettringite, measurement of acidity and/or alkalinity of the samples are crucial. Therefore, pH and redox potential of the samples were measured in order to assess the properties of the samples.

pH measurement of 1:10 tailings - water extract was conducted according to ASTM method D4972 (Standard Test Method for pH of Soils). The redox potential was measured using the same extract solution and the results of the analysis are given in Table 3.3.

The redox potential of a galvanic cell depends on the activities (concentrations in infinitely dilute solutions) of the reduced chemical species and oxidized chemical species in a solution (Benefield, 1982). It is also known that redox potential readings are directly related to the pH of a solution. The measurement taken is the potential difference between the reference and indicator electrodes, which, in turn, depends on the activity of the hydrogen ion in the solution. Note that the redox potential of a solution is inversely proportional to its pH.

TABLE 3.3. PH AND REDOX POTENTIAL

Sample	**pH**	**Redox Potential (mv)**
Sample # 1	2.49	410
Sample # 2	3.26	255

3.3.2 Cation Exchange Capacity

Cation exchange capacity is defined as the exchange of cations in solutions for cations adsorbed to the negatively charged surface of a clay, organic colloids, or other negatively charged particles. The cation exchange capacity is the total of positively charged particles that a soil can adsorb at a given pH. The usual exchangeable cations that exist in a soil are as follows: Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}. The exchangeability of the ions is limited by the valence charge of the cation, the size of the cation (which is directly related to the hydrated radius) and the abundance of the cation in solution (Grim, 1968). The usual replacement order is as follows.

$$Na^{+} < Li^{+} < K^{+} < Mg^{+2} < Ca^{+2} < Cu^{+2} < Al^{+3} < Fe^{+3}$$

In general K^{+} will replace Na^{+} or Ca^{+2} will replace K^{+}. However, an ion with a higher replacement power can be replaced by an ion with low exchangeability by making that ion available in high concentrations. This process is used in the experimental procedure, where the silver ion is made available through a leaching solution containing high concentrations.

3.3.2.1 Experimental procedures

The method described by Chabra *et. al.*, (1975), employing silver-thiourea solution, was used to determine the tailings samples' cation exchange capacity. In general, the silver-thiourea solution is used to saturate the tailings samples. Due to the samples high preference for the silver-thiourea complex, it is adsorbed to the tailings particles while the other exchangeable ions are released into the solution. The concentrations of exchangeable ions, Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} and of silver are measure by atomic absorption spectroscopy. The difference in silver concentrations indicates the cation exchange capacity.

Due to the fact that the silver reagent solution is light sensitive, any step involving the silver reagent had to be done in the darkroom. Anhydrous thiourea in an amount of 7.5 g was dissolved in 250 ml of distilled water. After mixing 7.71 g of ammonium acetate to the mixture, the pH was measured and adjusted to 7, using NaOH if $pH > 7$, and acetic acid if $pH < 7$. The solution was transferred to a one-liter flask where 500 ml of 0.02 M $AgNO_3$ was slowly added. This solution was then diluted to one liter to finally give a solution 0.001 meq Ag/ml. The tailings samples were air dried and ground to pulverize the larger particles. Tailings samples of 0.5 g were weighed and placed in plastic centrifuge tubes. 40 ml of silver-thiourea reagent was also poured into each centrifuge tube. The tubes were then placed on the mechanical shaker for four hours, and then were immediately centrifuged and decanted. Atomic absorption spectroscopy was used to determine the concentration of each ion as previously mentioned.

$$\textit{Extractable Cations}\ (\text{meq/100g of tailings}) = \frac{[ion](meq/l) \times Vol.solution\,added \times 100}{SoilWeight(g)}$$

$$CEC(meq/100\,g\,of\,Soil) =$$

$$= \frac{\{[Ag^{+}]_{initial}(10\,meq/l) - [Ag^{+}]_{supernatant}(10\,meq/l)\} \times Vol.Solution\,added\,(ml) \times 100}{\{500 \times (SoilWeight(g))\}}$$

The results of cation exchange capacity measurement are given in Table 3.4.

TABLE 3.4 CATION EXCHANGE CAPACITY

Sample	**CEC Measured (meq/100g)**
Sample # 1	12.26
Sample # 2	13.71

3.3.3 Elemental Analysis

Tailings samples elemental composition was determined using two different techniques. A portion of air dried and slightly pulverized samples were submitted to school of Earth and Planetary Science at McGill University for elemental analysis using X-ray Fluorescence Analysis. The XRF is a useful technique in determining the total composition of a sample. The results of XRF analysis are given in Table 3.5.

As for the second method, to identify the soluble metal analysis in the samples, the acid digestion method involved the use of nitric (HNO_3) and hydrochloric (HCl) acids as the main reagents were used (U.S. EPA method 3050 ,1986). The testing procedures were as follows: 2 grams of each air-dried tailings samples were taken and transferred to a conical beaker. 10 ml of 1:1 nitric acid:water solution was added to the beakers and then were covered with a watch glass.

TABLE 3.5. THE XRF ANALYSIS OF TAILINGS SAMPLES

Element	Sample 1	Sample 2
Al_2O_3 (%)	6.6	14.77
Fe_2O_3 (%)	41.07	9.91
MgO (%)	1.31	4.81
CaO (%)	0	1.06
As (ppm)	93	112
Cd (ppm)	25	20
Cr (ppm)	0	15
Cu (ppm)	768	968
Pb (ppm)	115	216
Zn (ppm)	336	293

The slurry solutions were heated to 95°C and then refluxed for 20 minutes. After this period, 5 ml of concentrated nitric acid was added to each beaker and allowed to reflux for another 30 minutes. The solutions were then allowed to evaporate until the tailings samples were barely covered with liquid. The samples were allowed to cool down, after which 2 ml of distilled water and 3 ml of 30% hydrogen peroxide were added to each beaker. Subsequently, they were returned to hot plates for re-heating and to begin the peroxide reactions. After this step, 5 ml of concentrated hydrochloric acid and 10 ml of distilled water were added to the beakers and allowed to reflux for another 15 minutes. The slurries were then allowed to cool and diluted to 100 ml with distilled water. The new solution were allowed to sit for 30 minutes before 30 ml of each was transferred to a tube and centrifuged at 8000 rpm for 10 minutes to separate the supernatant from the solid particles. The former was analyzed for different elements using atomic absorption spectroscopy Perkin-Elmer 3500 machine. Sulfate content was measured using Dionex DX-100 Ion Chromatography. The results are given in Table 3.6.

TABLE 3.6. THE ELEMENTAL ANALYSIS OF TAILINGS SAMPLES

Element	Sample 1 (ppm)	Sample 2 (ppm)
Aluminum	206	130
Arsenic	23	4
Calcium	0	340
Cadmium	0	0
Chromium	0.5	0
Copper	17	15.4
Iron	3332	1800
Potassium	6	2
Magnesium	27	39
Manganese	5	11
Lead	34	0
Silicon	18	21
Sulfate	1626	1245
Zinc	25	65

3.4 Mineralogical Composition

In order to determine the mineralogical composition of the tailings samples under investigation, representative specimens were used for x-ray diffraction analysis. Air dried samples were pulverized to pass sieve number 200 and then the powder was subjected to X-ray diffraction analysis using Rigaku D/Max 2400 automated powder diffractometer. The X-ray diffraction pattern of both samples are given in Figure 3.2

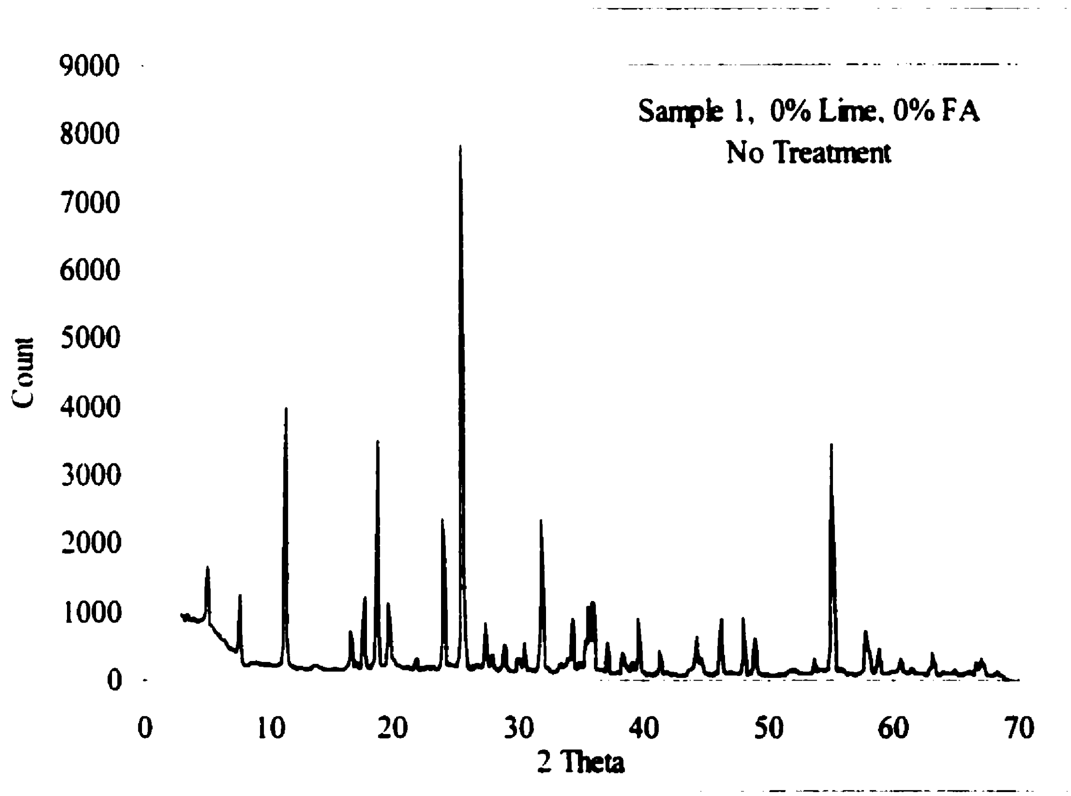


FIGURE 3.2 XRD DIFFRACTION PATTERNS OF TAILINGS SAMPLES (SAMPLE NO. 1)

The XRD analysis of sample 1 indicate that the mineralogical composition of this sample is mainly composed of pyrite, graphite, quartz, illite, clinochlore, thulium tellurate, nimite, copper sulfide, nickel sulfide, tin sulfide, strontium oxide and cobalt oxide.

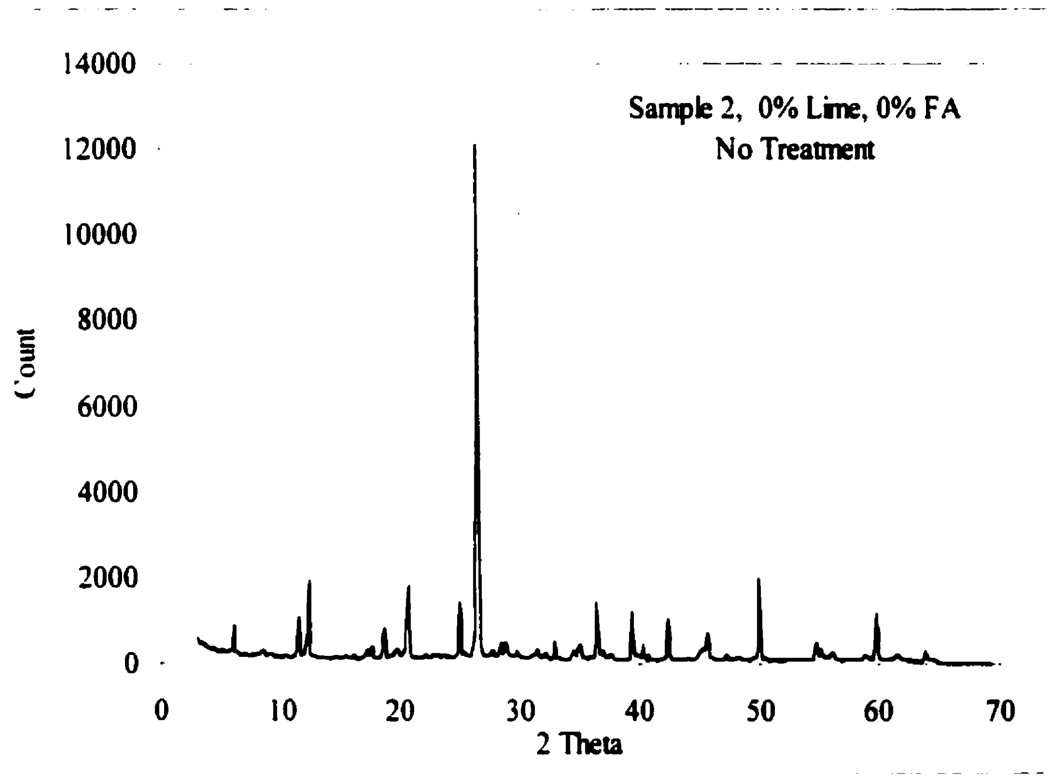


FIGURE 3.2 XRD DIFFRACTION PATTERN OF TAILINGS SAMPLES (SAMPLE NO. 2)

Sample two mainly consist of quartz, copper hydride, moganite, graphite, nimite, and iron phosphate.

3.5 Fly Ash Composition

The chemical composition of the fly ash used in this project is given in Table 3.7. The fly ash is type "C" and was supplied by CANMET research laboratory in Ottawa, Canada. The chemical composition of fly ash type "C" has been compared to that of ordinary portland cement type 10.

TABLE 3.7 CHEMICAL COMPOSITION OF CEMENT AND FLY ASH TYPE "C"

Element	Portlant Cement (% W/W) Lafarge type 10	Fly Ash (% W/W) type "C"
SiO_2	21.36	53.3
Al_2O_3	3.93	23.63
TiO_2	0.19	0.71
P_2O_5	0.21	0.12
Fe_2O_3	3.15	4.4
CaO	62.41	15.81
SrO	0.27	0.22
MgO	2.57	1.15
Na_2O	0.2	3.03
K_2O	0.8	0.42
SO_3	3.43	0.2
LOI	1.72	0.71

3.6 Project Related Experiments

All project related experiments, samples preparation, and curing methods are discussed in corresponding chapters.

Chapter 4

Thermodynamic Modeling

4.1 Introduction

Long-term batch leaching studies of composite waste compounds containing calcium, aluminum, and sulphate along with other heavy metals have shown the prominent formation of an ettringite structure phase, accompanied by reduction in solution concentration of potentially hazardous elements in leachates. Therefore, it is postulated that ettringite and ettringite like minerals have the potential of uptaking other metals (Solem, and McCarthy, 1992; Kumarathasan *et al.*, 1990). The immobilisation of heavy metals can take place in the form of isomorphous substitution: adsorbtion of positively charged metal species to negatively charged surface of ettringite; and precipitation of metals in high-induced pH environment necessary for ettringite formation and precipitation. Hence, ettringite, in a lime - remediated sulphate-aluminate rich acid mine drainage system, could therefore serve as a physical and chemical stabilizing agent (Mohamed *et al.*, 1995).

Study the optimisation process of forming and precipitating ettringite as a stable mineral in a acid producing tailings system rich in calcium, aluminum, and sulfides is essential to success of the project as well as to reduce the remediation costs over other commercially available stabilizing agents. Therefore, thermodynamic modeling was used to study the optimization process of ettringite formation in acid mine drainage system.

In order to evaluate the possibility of forming ettringite in mine tailings systems, the optimal geo-chemical parameters needed can be devised by thermodynamic models. Damidot and Glasser (1993a) have produced a three dimensional graph depicting the thresholds of the stability of common cement minerals in cement water system as shown in Figure 4.1. The range of calcium, aluminum and sulphate concentrations needed to precipitate ettringite in a system devoid of dissolved CO_2 is shown in Figure 4.1. It does not, however, depict the influence of pH on stability of minerals. For lime-remediated purposes, pH is a critical factor for insolubilizing heavy metals, and precipitating ettringite at the same time. Hence, the focus of this chapter is on the effect of pH on the stability of ettringite via thermodynamic modeling. Tailings samples from a Quebec mine were analyzed and the thermodynamic properties of their aqueous species were modelled.

The optimal geo-chemical parameters required to precipitate ettringite in the samples and the residual metal concentrations were calculated.

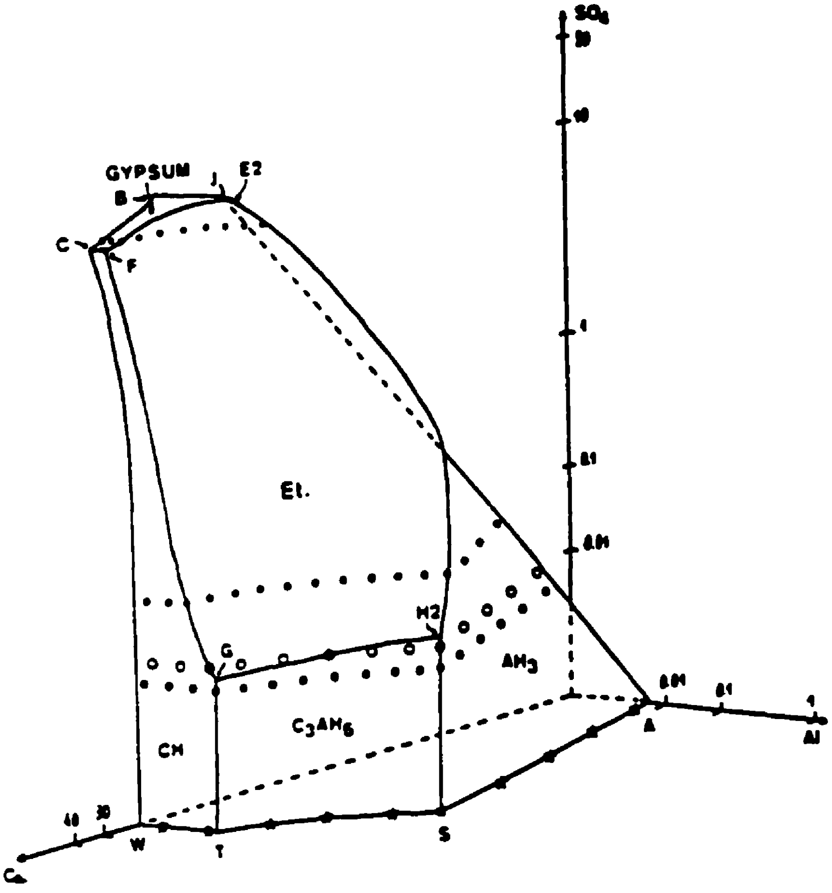


FIGURE 4. 1 THREE DIMENSIONAL REPRESENTATION OF THE $CaO-Al_2O_3-CaSO_4-H_2O$ SYSTEM. FROM DAMIDOT AND GLASSER (1993).

4.1.1 Properties of Ettringite in Cement Systems

Addition of gypsum in a cement mixture delays the binding properties of cements undergoing hydration. While this process is well-known throughout cement chemistry community, the actual mechanisms through which the delayed C_3A hydration of cements proceed is still a matter of debate. Sulphate-rich waters seeping through hardened cements induce further growth of ettringite and on a long term basis expansion of concrete. Once more, the mechanism involved responsible for the source of expansion are controversial in the field of cement chemistry.

4.1.1.1 Experimental Procedure: C_3A and Water

In the study of the stability of various calcium sulphoaluminate hydrates for different pH, Gabrisova *et al.* (1992), mixed tricalcium aluminate with water and observed the pH, pCa, and solid state changes. In a first instance, $2CaO.Al_2O_3.8H_20$ and $4CaO.Al_2O_3.19H_2O$ form both convert slowly to hydrogarnet ($3CaO.Al_2O_3.6H_2O$). The addition of sulphates in the solution at a pH greater than 10.7 induces the conversion of hydrogarnet to ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$). When sulphates deplete, ettringite converts to monosulphate ($3CaO.Al_2O_3.CaSO_4.18H_2O$). This experiment can be basically related to the role of sulphates in the delayed setting of cements. If sulphates are not available, hydrogarnet in the final hydration product of tricalcium aluminate and a "flash set" of the cement results (Mehta, 1986). By adding a small amount of gypsum, the setting time of concrete is delayed, whether ettringite is the cause of the delayed hydration of C_3A or is a by-product, is the centre of a lingering debate in the field of cement chemistry.

4.1.1.2 Experimental Procedure: C_3A-$CaSO_4.2H_2O$-H_2O

One of the most common experiments conducted in the field of cement chemistry makes use of a simplified cementitious system containing tricalcium aluminate and gypsum. Upon the addition of limited amounts of water, gypsum partly dissolves (solubility = 0.0022-0.00272 g/ml) and provides sulphate ions to the slurry. In a very similar experiment using hemihydrate ($CaSO_3.1/2H_2O$) Brown and LaCroix (1989) show that the growth of ettringite is delayed by a lag time during which hemihydrate converts to gypsum which in turn ultimately dissolves. Also, by adding $Ca(OH)_2$ (portlandite) to the solution, the rate of dissolution of gypsum is reduced due to the higher activity of calcium ions in the solution. In such conditions, the amount of sulphate ions available for the growth of ettringite is greatly reduced.

The hydration of calcium silicate produces a C-S-H gel (tobermortie) on the surface (Fu *et al.*, 1994). This gel serves as a sink for sulphates by adsorbing them and therefore increases the extent to which gypsum can dissolve. The gel with its adsorbed sulphates is called "phase X " (Fu *et al.* 1994), and acts as a kinetic barrier to the formation of ettringite by holding most of its constituents in a gel phase. The rate-determining step for the formation of ettringite is the diffusionally controlled desorption of the sulphate from phase X.

4.2 HYDRATION RETARDATION MECHANISMS

The actual mechanisms through which cement hydration is delayed are a matter of debate in the field of cement chemistry. There are two dominant theories, *topochemical* and *through solution* theories, which are both contradicting and controversial. Also, no one agrees on whether ettringite plays an important role in the delayed hydration or is just a by-product cementing grains and aggregates.

4.2.1 Topochemical Theory

Tricalcium aluminate clinkers react *topochemically* with $CaSO_4$, resulting in the formation of a film of ettringite on the surface. This film would serve as a physical barrier to the pore waters and therefore depress the solubility of C_3A. As the sulphate content decreases ettringite converts to monosulphate. This mineral still converts the unhydrated cement but has less expansive properties than ettringite. A renewed activity of cement hydration could be due to the disruption of the ettringite film by (1) crystallization pressures or (2) osmotic pressures arising from the difference of ion concentration between the film and the unhydrated cement, and the film and the pore waters.

Part of the reason why the debate has been lingering is caused by how the theory is interpreted. Some interpret the theory as a solid-solid phase transformations where the atoms of the cement lattice would migrate to the surface and reacting with sulphate and water. Solid-solid transformation is a process that can only occur at very high temperatures and pressures. The temperatures, at which cements hydrate, even if the heat liberated is large, do not allow this mechanism to proceed. In addition, the spacing groups of ettringite and C_3A are very different. The other, and more realistic, interpretation is the ettringite would preferentially form at the surface of cements since C_3A is the source of calcium and aluminum. Furthermore, aluminum surface sites could offer stable nucleation sites for etteringite.

4.2.2 Through-Solution Mechanism

In a series of experiments Mehta (1976) has proposed that ettringite forms indiscriminately through the solution and that the topochemical theory could be ruled out. Proponents of this theory contend that the depressed solubility of the C_3A is due to the presence of sulphates in the pore waters. Skalny and Tadros (1977), have shown that C_3A dissolves incongruently, leaving an aluminum-rich surface. Calcium would adsorb on the structure (but they did not say at what element) and therefore, minimize the reactivity of dissolution sites. In the presence of small amounts of gypsum, sulphates adsorb on the aluminum-rich surface and also reduce the number of dissolution sites.

4.2.3 A Compromise Between the Two Theories

In the C_3A-H_2SO_4-water system described above, Gabrisova *et al.* (1991) established the pH stability fields of the different hydration products of tricalcium aluminate. For pH greater than 10.7, ettringite is stable and forms long needles. For higher pH, ettringite forms smaller crystals with the formation of monosulphate favored. Havlica and Sahu (1992) proposed that if the pH at the cement/water interface is greater than 10.7, then ettringite forms on the surface. If the pH is less than 10.7, a liquid interface would form between the surface and the hydration products in the pore waters where pH is higher. Based on their calculations, they conclude that if the thickness of the liquid interlayer is more than 10 microns then the mechanism of ettringite formation is labeled as "through solution"; if it is 1.4 microns thick then the mechanism is "topochemical".

4.3 Sulphate Attack and Expansion

Seawater or sulphate-rich groundwater have deleterious effects on hardened cements. Sulphates promote the formation of ettringite, which could result in the expansion, and breakage of concrete structures. Two theories which explain the mechanism of growth and expansion are in conflict.

The *crystal growth theory* is based on the topochemical theory of ettringite formation and states that the expansive forces arise from crystallization pressures of ettringite bound to the surface of C_3A clinkers. The amount of growth also depends on the number of nuclei sites per unit volume and the growth speed of the crystal. If the concentration of sulphates in the pore waters is suddenly reduced ettringite converts back to monosulphate through metastable intermediates containing 3 to 1 sulphate and 32 to 18 water molecules. The expansion capacities of theses metastable intermediates increase with more sulphates and waters in the lattice. This is why monosulphate is the least expandable of all the calcium sulphoaluminate hydrates and ettringite has the largest expansion capacities.

The *swelling theory* is based on the through-solution theory, and explains the expansion by invoking the adsorption of water on high surface area ettringite. Adsorbed water increases the surface tension of ettringite particles, decreasing the interparticle Van der Waals forces and therefore, resulting in expansion.

Both theories agree on the role of portlandite in the solution. The absence of portlandite promotes the formation large ettringite crystals, C_3A, CSH_{12}, and gibbsite. Portlandite limits the size of ettringite to very small particles, which are more susceptible to yield large expansive pressure than larger crystals would. The two theories disagree, however on the rate of hydration of the ettringite in the presence and absence of lime. The first school contends that the presence of lime favours the hydration of ettringite and that the mechanism of ettringite formation is topochemical; in cases where lime is absent the formation of ettringite is always through solution and the hydration of the ettringite is reduced in the presence of lime.

4.4 Thermodynamic Approach to Expansion

In two recent papers, Ping and Beaudoin (1992a,b) developed an expression relating thermodynamic properties of cement hydrates and crystallization pressures. The formula is expressed for the following reaction where the reactants, R_n, with their respective stiochiometric coefficient y_n, form a solid S.

$$\gamma_1 R_1 + \gamma_2 R_2 + \ldots\ldots \gamma_N R_N = S \qquad (1)$$

The normalized free energy of the overall reaction is the sum of the chemical potentials for each reactant involved:

$$d\mu_s = \sum_{i=1}^{N} \gamma_i d\mu_i \qquad (2)$$

The relation G = H − TS is normalized into chemical potentials and expressed in terms of partial derivatives with respect to temperature and pressure:

$$d\mu_s = \left(\frac{\partial \mu_s}{\partial T}\right)_{P_s} dT + \left(\frac{\partial \mu_s}{\partial P_s}\right)_T dP_s \qquad (3)$$

This can be rewritten in terms of changing temperature and pressures and S_s is the entropy and V_s the volume of solid.

$$d\mu_s = -S_s dT + V_s dP_s \qquad (4)$$

The change of the chemical potential for each reactant for changing temperatures and pressures is expressed by the following where a_i is the activity:

$$d\mu_s = d\mu_i^{\circ}(T,P) + (R\ln a_i)dT + RTd\ln a_i \qquad (5)$$

Equation (2), (4), and (5) are rearranged in the following format:

$$V_s dP_s = \sum_{i=1}^{N}\gamma_i d\mu_i^{\circ}(T,P) + (S_s + R\sum_{i=1}^{N}\gamma_i \ln a_i)dT + RT\sum_{i=1}^{N}\gamma_i d\ln a_i \qquad (6)$$

At constant temperature, the formula is rearranged in terms of dP_s and the integral is taken: The sum of the natural log of the activity is converted to the

$$P_s - P_s^{\circ} = \frac{RT}{V_s}\sum_{i=1}^{N}\gamma_i \ln(\frac{a_i}{a_i^{\circ}}) \qquad (7)$$

solubility products of the solid, S, under atmospheric pressures, K_{sp}°, and pore water pressures, K_{sp}; Ω is referred to as the "solubility product ratio".

$$P_s - P_s^{\circ} = \frac{RT}{V_s}\ln(\frac{K_{sp}}{K_{sp}^{\circ}}) = \frac{RT}{V_s}\ln\Omega \qquad where\Omega = (\frac{K_{sp}}{K_{sp}^{\circ}}) \qquad (8)$$

P_c is the crystallization pressure:

$$P_c = P_s - P_s^{\circ} = \frac{RT}{V_s}\ln\Omega \qquad (9)$$

This is rearranged in terms of the molecular weight, M_s, and the density , ρ_s of the solid:

$$P_c = \frac{RT\rho_s}{M_s} \ln \Omega \qquad (10)$$

This simple algebraic expression implies that expansion is caused by crystallization pressures, which result from the conversion of free chemical energy to work. Two conditions are, however, essential for expansion to proceed: (1) confined crystal growth (pore water pressures greater than normal atmospheric pressures) and (2) $\Omega > 1$.

Expansion in cementitious system would therefore rely solely on the formation of any cement hydrates in a hardened cement. That is, the formation of ettringite, portlandite, monosulphate, or *any* other solid phases should result in expansive forces. The rationale behind this is simple: the precipitation of aqueous phases takes up volume. The explicit reason why ettringite plays a determining role in the expansion of cements is that its solubility product ratio, Ω is significantly larger than any other coexisting hydrates. Crystallography tells us that ettringite has a large lattice cell and that it can adsorb many water molecules, therefore resulting in expansion. The formation of portlandite, calcite or even barite (Ping and Beaudoin, 1992b), for example, do produce expansive pressures but these are not as large as those produced by the formation of ettringite. Coming back to the debate between the crystal growth and the swelling theories, the former agrees best with Ping and Beaudoin's (1992b) thermodynamics expression. In the presence of portlandite, the activity of calcium in pore waters is greatly increased and therefore the drive for the formation of ettringite is increased. The most logical explanation for expansion would therefore be related to the activity of the reactants. Also, the crystal growth theory is probably right by invoking the two mechanisms (topochemical and through solution) of ettringite growth in the presence and absence of portlandite (when portlandite is present, C_3A is not the only source of aluminum and calcium and ettringite can form anywhere). However, these processes should be definitely put aside when it comes to rationalizing expansion.

4.4.1 Thermodynamic Modeling

Thermodynamic models of cement systems using speciation programs is starting to make its way in the field of cement chemistry. The speciation of the system *before* and *after* precipitation of aqueous species has occurred is crucial in predicting the migration of contaminants. The idea is to devise the speciation of each element "nanoseconds" before the onset of precipitation. With this, using solubility curves for each element, the final concentrations of each element can be find. Then, and only then, one can qualitatively describe the decreased concentration of metals through adsorption and absorption by ettringite. In order to understand in microscopic details the contribution of ettringite in serving as sorptive agents, experimental studies describing thermodynamic properties are needed.

4.4.1.1. Aqueous Speciation

Most speciaton programs solve for the *activity* of dissolved species at equilibrium. The activity, a_i, is the product of the concentration, m_i, of a solute, i, by its activity coefficient, γ_i An activity coefficient is a fraction expressing the degree of non- ideality of a solution; when a solution is ideal, $\gamma = 1$ and the activity is equal to the molality. It is an expression that accounts for the effect of long range ion – ion interaction (repulsion and attraction). As the concentration of solutes increase in a solution, the solution becomes more and more non-ideal because water is taken up in order to solvate ions interact with each other. There are many equations used to calculate activity coefficients of a solution. The extended Debye-Hückel with the BI term is the most commonly used for solutions of ionic strengths, I, lower than 0.1. Ionic strength is calculated by:

$$I = \tfrac{1}{2}\sum_{i}^{n}(z_i^2 m_i)$$

Where z_i is the charge and m_i the molality of ion, i. Activity coefficients are then calculated with the extended Debye-Hückel:

$$\log\gamma_i = -Az^2\left(\frac{\sqrt{I}}{1+Ba\sqrt{I}} - 0.21\right) + BI$$

Where A = 0.5 and B = 0.33 at 25°C, 1 bar. The A term is a function of the dielectric constant of the water, ε, and the pressure and temperature. The B term equals 50.3 $(\varepsilon T)^{-1/2}$ and *a* is an adjustable parameter in angstrom corresponding to the size of the most common ion of the solution (usually, and preferentially, that of the electrolyte).

For highly concentrated solutions, the extended Debye–Hückel cannot be sued to calculate activity coefficients. The Pitzer equation is then used and is good for ionic strengths less than 6.0. This equation is essentially a Debye-Hückel term with additional empirical terms specific to the solution. The description of how the free energy of a solution is related to the activity, and how the Pitzer equation fits in are as follows:

$$\frac{\Delta G^{\circ}}{2.303RT} = \log K = \Big(\sum_{\text{products}} (\log m + \log \gamma)\Big) - \Big(\sum_{\text{reactants}} (\log m + \log \gamma)\Big)$$

Where the $\log\gamma$ terms is the energy due to the charge or polarity of a molecule. Charge and polarity create interactions with other molecules and so this energy is reaction energy of charged or polar molecule relative to an uncharged non-polar molecule.

$$G_i = G_i^{\circ} + 2.303RT \log m_i + 2.303RT \log \gamma_i$$

Now, we express the free energy due to a non-ideality by:

$$G_{i,xs} = 2.303RT \log \gamma_i$$

And generally the equation for a given solute becomes:

$$G_{i,xs} + (Debye - Huckel) + (solvent) + (ion - ioninteration)$$

The total free energy taken up by non-ideality is :

$$\frac{G_{total,xs}}{2.303\,RT} = n_w(f(I) + \sum_i \sum_j \lambda_{ij}(I) m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k)$$

Where n_w is the weight of water, m_i the molality of species *i* and f(I) a form of the Debye-Hückel which is only dependant on i. The variables λ_{ij} and μ_{ijk} and the second and third virial coefficient. They express the short-range interaction in water–dominated fluids. Specifically, λ_{ij} applies to the interaction of the ion pairs *i,j* and is a function of I; μ_{ijk} applies to the interaction of the ion triplets *i,j,k* and is independent of I. The λ and μ parameters have built in parameters which are specific to different electrolytes. They cannot, be extrapolated to other electrolyte compositions.

4.5 Materials and Methods

Acid digestions of three samples of the tailings from a Quebec mine were performed according to the U.S. EPA method 3050 (1986). The metals were analyzed by flame atomic absorption spectrometry. Determination of sulphate content was done using turbidimetric analysis. Sulphate analysis involved using buffer solution and barium chloride crystals to induce a barium sulphate precipitate. The results are shown in Table 4.1.

TABLE 4.1. AA RESULTS OF EPA ACID DIGESTION OF SAMPLES (IN LOG MOLALITY)
(B.D. = below detection limit)

Element	Sample I	Sample III	Sample IV
Al	-1.94	-2.12	-2.44
Si	-3.30	-3.19	-3.27
As	B.D.	-3.51	-4.09
Pb	-4.53	-3.78	-3.51
Mg	-1.97	-2.95	-2.32
Mn	-4.14	-4.04	-4.14
Zn	-3.19	-3.42	-3.73
Cd	B.D.	B.D.	B.D.
Cr	-5.02	-5.02	-5.24
Cu	-3.46	-3.57	-3.46
Fe	-1.57	-1.22	-1.09
K	-3.81	-2.94	-2.89

4.6 Application of Thermodynamic Modeling to Tailings Under Study

The speciation of 10 metals, carbonate and sulphate has been done for 74 aqueous species (Appendix 1). Also, 0.01 mol/L of lime has been added to the solution and the system is assumed to be closed and to have equilibrated with an atmospheric pCO_2 of 3.5. A computer program which was developed at McGill University, department of Earth and Planetary Science was used for thermodynamic modeling. Basically, the program solves the speciation at equilibrium using a Newton-Raphson iterative technique. The iterations are driven by the convergence of the ionic strength and the activity coefficients are calculated with the Debye-Hückel theory. The speciation of calcium, aluminum, sulphate and iron are shown in Figure 4.2 and represent the hypothetical speciation at equilibrium before the onset of precipitation.

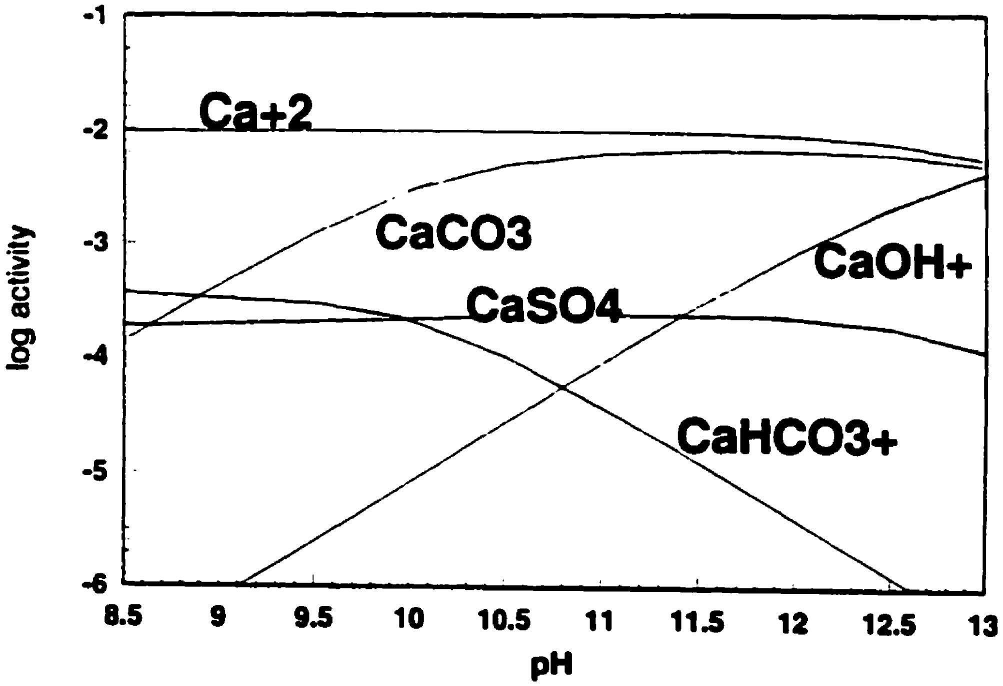


FIGURE 4.2. (a) SPECIATION OF CALCIUM, BEFORE THE ONSET OF PRECIPITATION

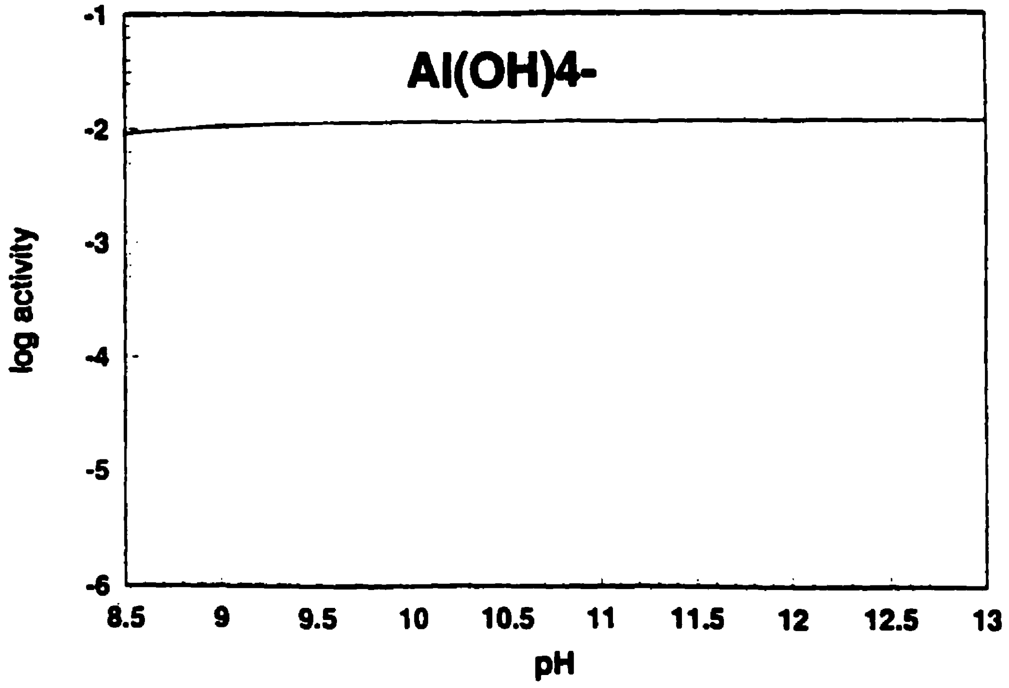


FIGURE 4.2. (b) SPECIATION OF ALUMINUM, BEFORE THE ONSET OF PRECIPITATION

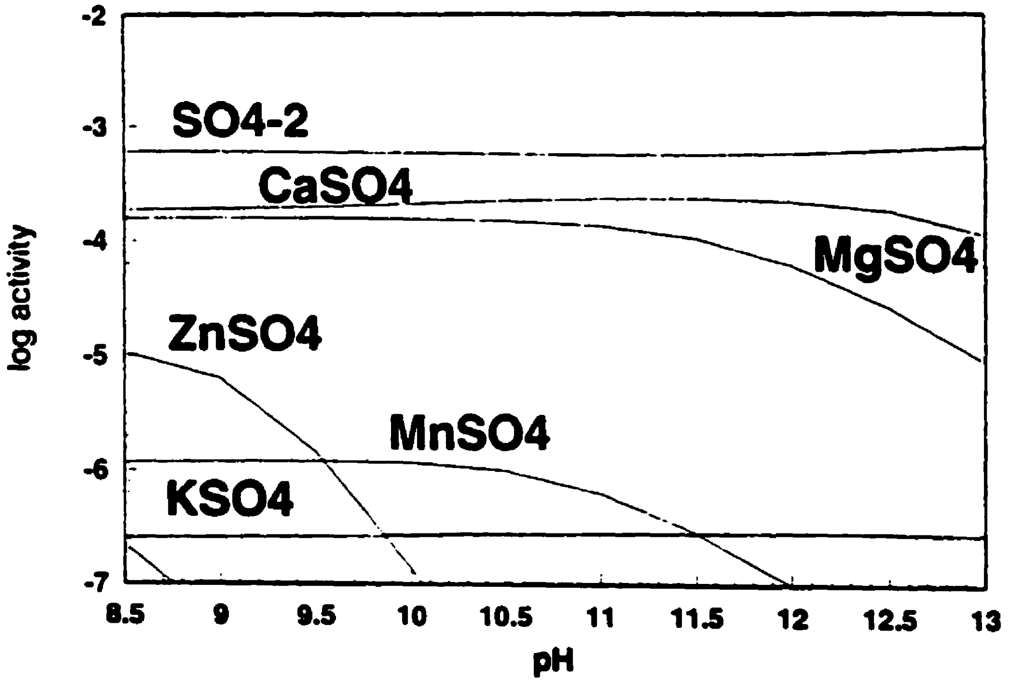


FIGURE 4.2. (c) SPECIATION OF SULFATE, BEFORE THE ONSET OF PRECIPITATION

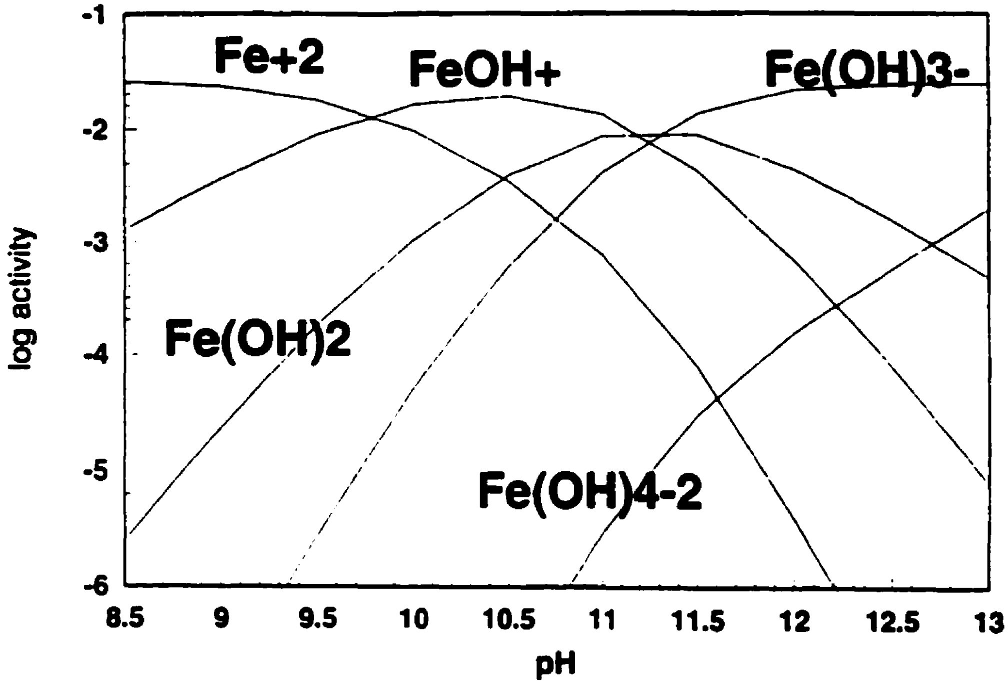


FIGURE 4.2. (d) SPECIATION OF IRON. BEFORE THE ONSET OF PRECIPITATION

Using these results. the pH-dependence on the stability fields of minerals with respect to a specific metal are devised by building activity ratio diagrams (Stumm and Morgan. 1981). This method consists of plotting the logarithm of the ratio of the activity of the minerals and the building cation versus pH. The solubility products of these minerals are given in the appendix. The stability field of aluminum-bearing minerals. for example. was found by plotting the activity ratios of kaolinite. gibbsite. ettringite. C_3AH_6. C_2AH_8, C_4AH_{13}, and monosulphate. The formation of ettringite is characterized by (Reardon, 1993):

$$Ca_6(Al(OH)_6)_2(SO_4)_3 \bullet 26H_2O \leftrightarrow 6Ca^{+2} + 2Al(OH)_4^- + 3SO_4^{-2} + 4OH^- + 26\ H_2O$$

$$\log K_{sp} = -43.13$$

This can be rewritten as:

$$K_{sp} = \frac{a_{Ca^{+2}}^{\ 6}\, a_{Al(OH)_4^-}^{\ 2}\, a_{SO_4^{-2}}^{\ 3}\, a_{OH^-}^{\ 4}\, a_{H_2O}^{\ 26}}{a_{ettringite}}$$

The activity ratio then becomes:

$$\log\left(\frac{a_{Ettringite}^{\ 1/6}}{a_{Ca^{+2}}}\right) = \frac{1}{6}43.13 + \frac{3}{6}\log a_{SO_4^{-2}} + \frac{2}{6}\log a_{Al(OH)_4^-} + \frac{4}{6}\log a_{OH^-} + \frac{26}{6}\log_{H_2O}$$

The data is then plotted for given $2Al(OH)_4^-$, SO_4^{-2}, and OH^- activities ($a_{water} = 1$). The mineral with the largest activity ratio is the one that precipitates, providing its saturation index also exceeds unity. The saturation indices of each mineral considered at pHs larger than 9 all exceeds unity. Figures 4.3 and 4.4 show the activity ratio diagrams for aluminum- and calcium-bearing minerals. The diagrams have been constructed with silica, aluminum and sulphate concentrations reflecting those of the tailings along with 0.01 mol/L of calcium. The activity ratio diagrams for aluminum-bearing minerals (Figure 4.3), a system containing 10^{-3} mol/L of sulphate, show that 0.01 mol/L calcium (Figure 4.3a) is needed to form ettringite at a pH of approximately 10.2. If the concentration of calcium was 10^{-4} mol/L (Figure 4.3b), then ettringite could only form above a pH of 12.4. Moreover, the depletion of sulphates narrows the stability field of ettringite to higher pHs. In the case of calcium-bearing minerals we find that at least 0.01 mol/L of aluminum and more than 10^{-3} mol/L of sulphate with 0.01 mol/L of calcium are needed to precipitate ettringite at pH larger than 11.4 (Figure 4.4a).

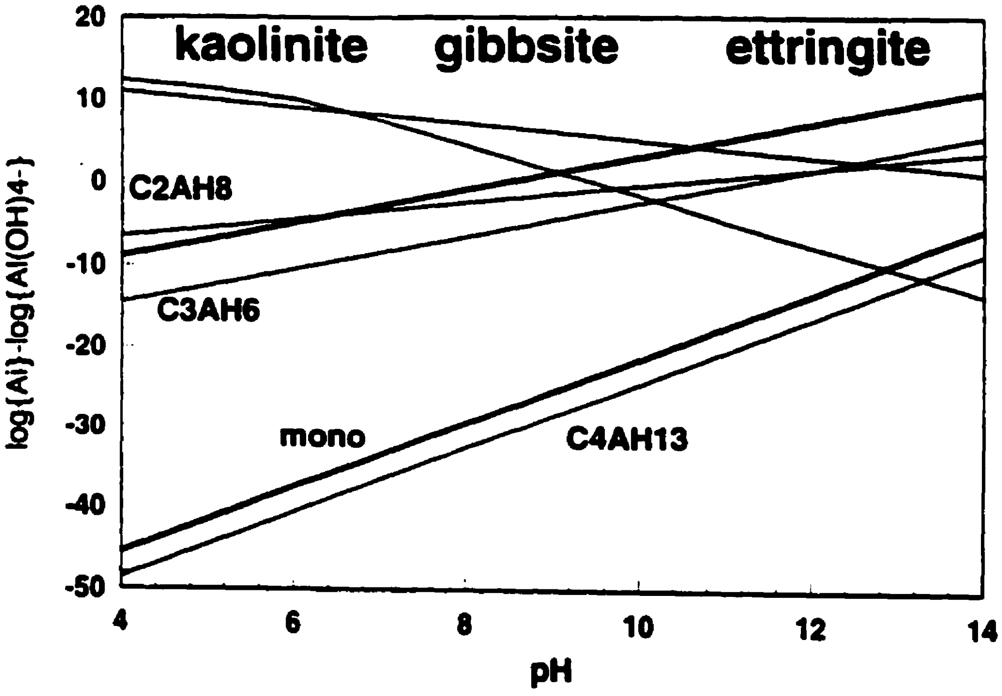


FIGURE 4.3. ACTIVITY RATIO DIAGRAM WITH RESPECT TO $AL(OH)_4^-$; (a) FOR $LOG[CA^{+2}]=$ $=-2M$, $\log[SO_4^{-2}]= -3M$

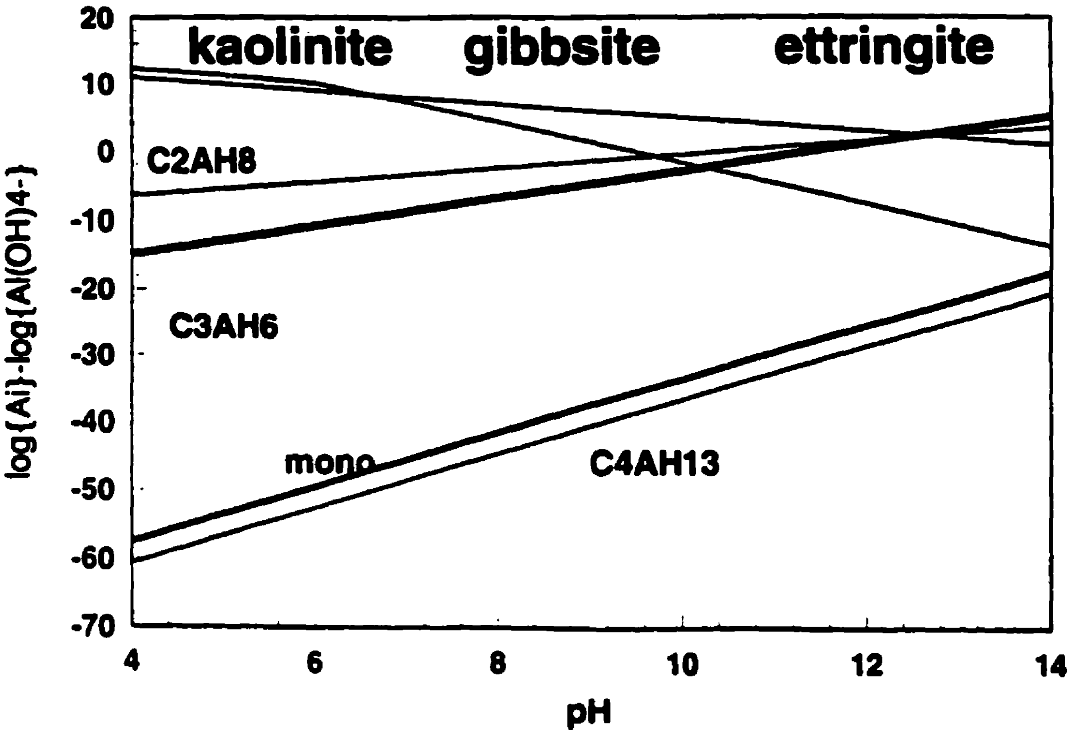


FIGURE 4.3. ACTIVITY RATIO DIAGRAM WITH RESPECT TO AL(OH)$_4^-$; (b) FOR LOG[CA^{+2}]=
= -4M, log[SO$_4^{-2}$]= -4M

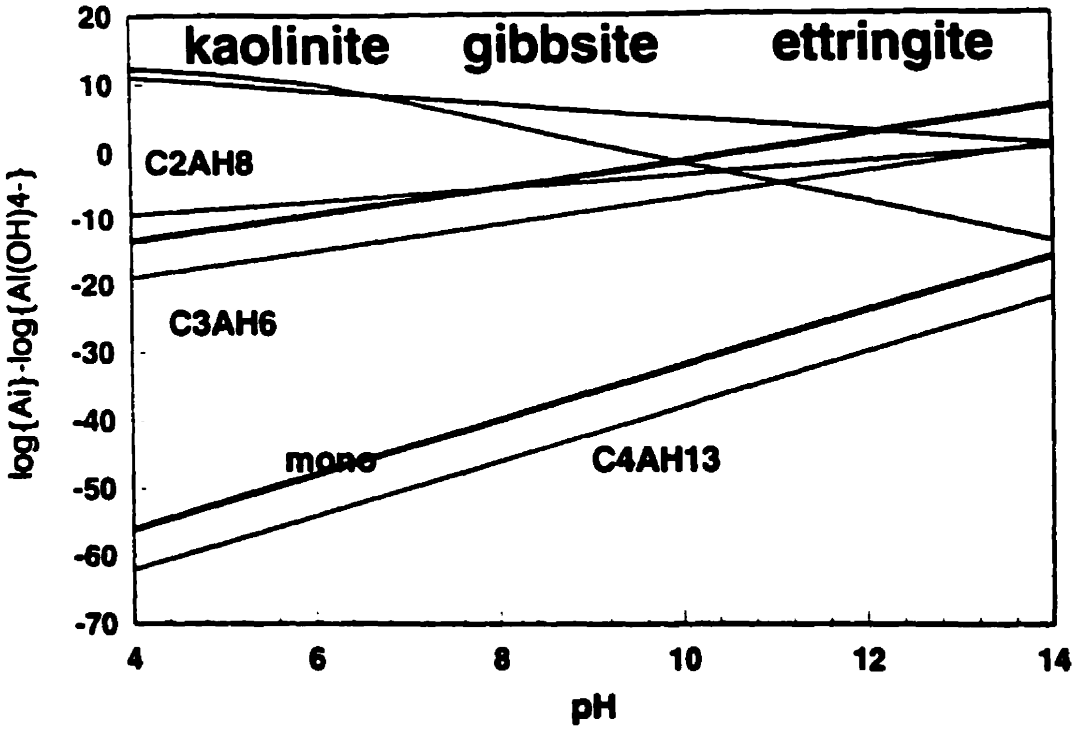


FIGURE 4. 3. ACTIVITY RATIO DIAGRAM WITH RESPECT TO AL(OH)$_4^-$; (c) FOR LOG[CA^{+2}]=
=-2M, log[SO$_4^{-2}$]= -6M

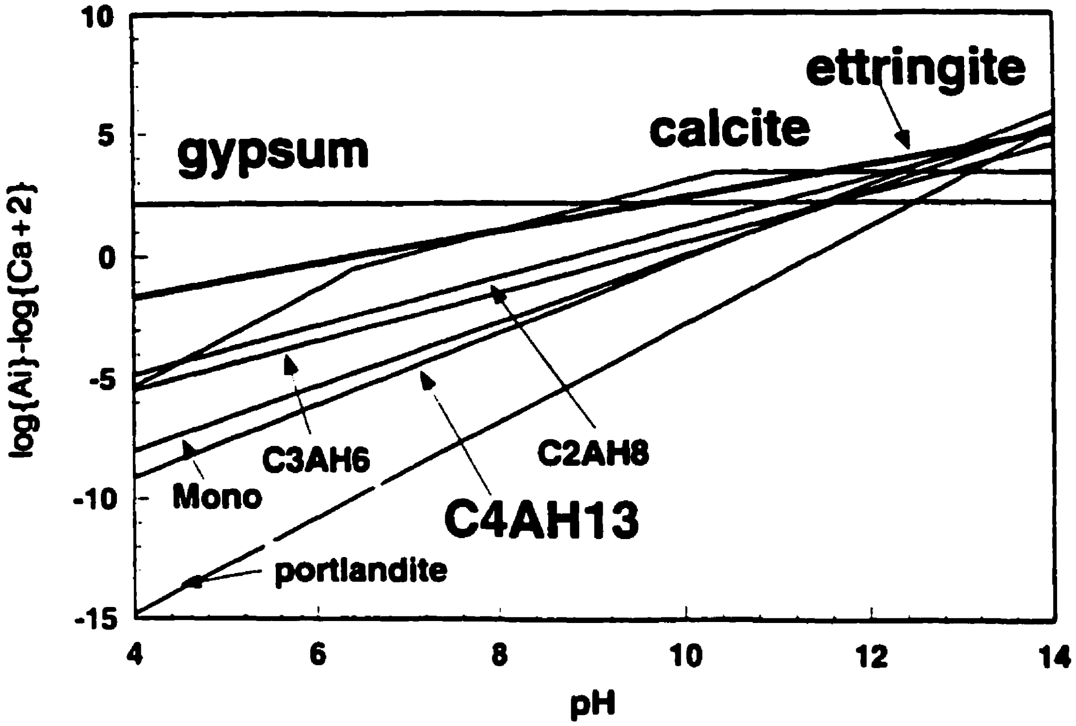


FIGURE 4.4 . ACTIVITY RATIO DIAGRAM WITH RESPECT TO CA^{+2}; (a) FOR $LOG[AL(OH)_4^{-1}]=$ =-2M, $\log[SO_4^{-2}]=$ -3M

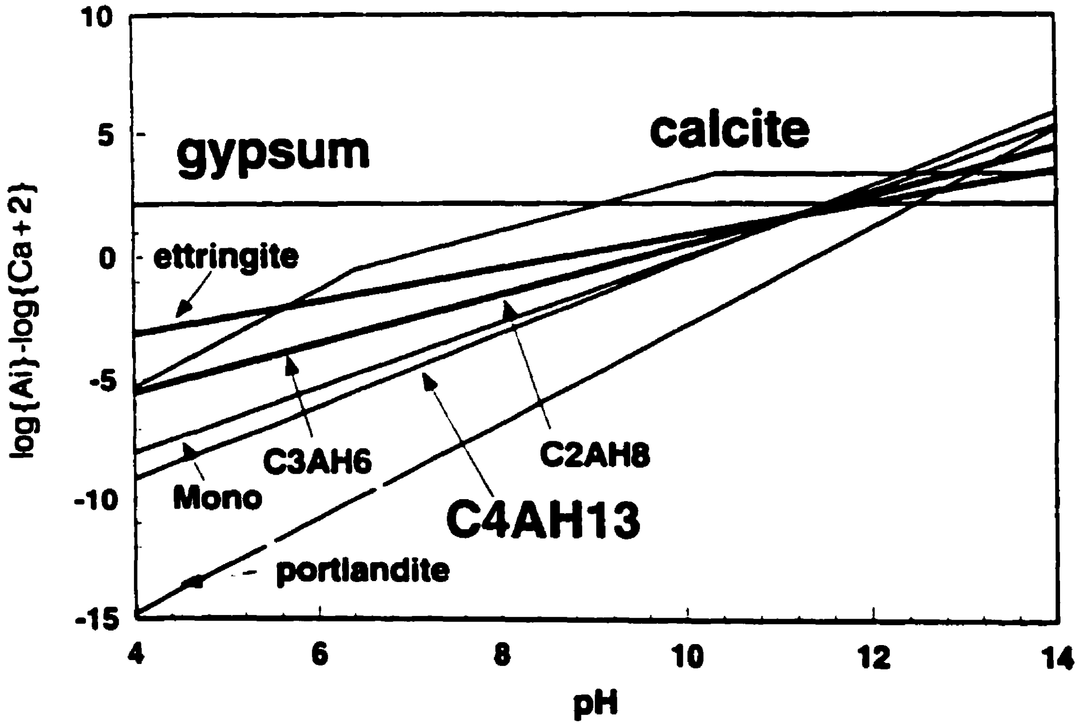


FIGURE 4.4. ACTIVITY RATIO DIAGRAM WITH RESPECT TO CA^{+2}; (b) FOR $LOG[AL(OH)_4^{-1}]=$ =-2M, $\log[SO_4^{-2}]=$ -6M

For lower sulphate concentrations, ettringite would no longer precipitate. Therefore, in a system containing 0.01 mol/L $Al(OH)_4^-$, 0.01 mol/L Ca^{+2}, and 0.001 mol/L SO_4^{-2} calcium and aluminum solubilities would allow ettringite to form at pHs larger than 11.6. Furthermore, if the dissolved CO_2 content decreases to values below the normal content of closed systems equilibrated with the atmosphere, the stability of calcite would decrease and ettringite would therefore, form down to pH of 10.2. While the graph suggests pH of 9.6, the activity ratio diagram for aluminum does not allow ettringite to form below a pH of 10.2.

From activity ratio diagrams, the solubility of calcium and aluminum for given constant calcium, aluminum and sulphate concentrations were devised (Figure 4.5). The method consists of calculating the activities of all the species of the cation-forming mineral from the solubility product of each minerals that have predicted of being formed. In the case of calcium, for example, the maximum amount of Ca^{+2} allowed by the solubility product of ettringite is:

$$a_{Ca^{+2}} = \left(\frac{10^{-43.13}}{(a_{SO_4^{-2}})^3 (a_{OH^-})^4 (a_{Al(OH)_4^-})^2 (a_{H_2O})^{26}}\right)^{1/6}$$

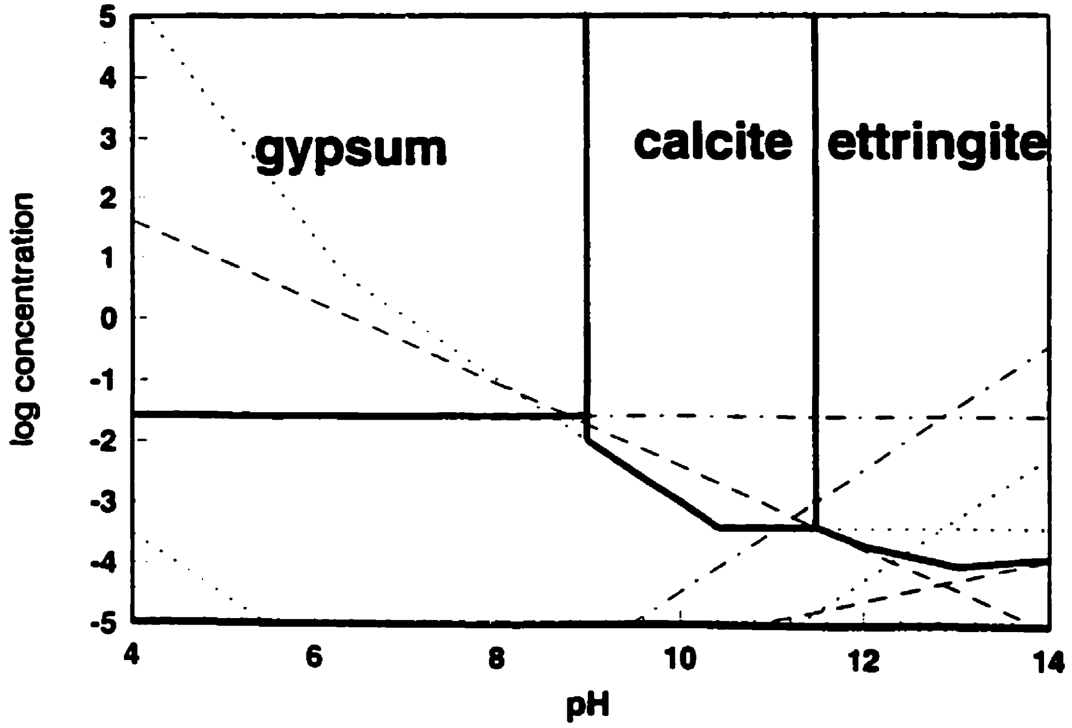


Figure 4.5. (a) Solubility of Calcium, WITH LOG[$Al(OH)_4^-$]=-2M, LOG[SO_4^{-2}]= -3M

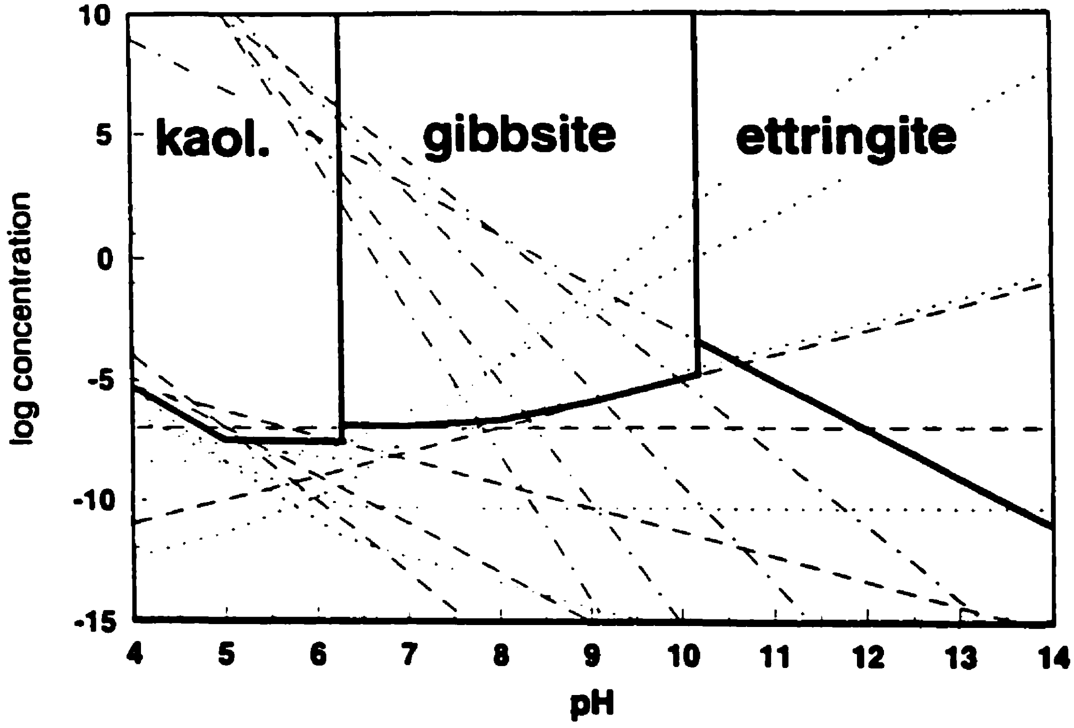


Figure 4.5. (b) Solubility of Aluminum, WITH LOG[Ca^{+2}]=-2M, LOG[SO_4^{-2}]= -3M

From the activity of Ca^{+2}, the activities of the other calcium species are calculated and the sum of the activities of all the species is the solubility of calcium with respect to ettringite. These calculations are performed also for calcite and gypsum. The outline of the solubility curve of a given mineral is then drawn according to pH range.

4.7 Fate of Residual Metals

With the solubility curves of each metal considered in the modeled (Baes and Mesmer, 1976; Stumm and Morgan, 1981; Figure 4.5), the percentages of metals removed from the solution by precipitation for each pH were calculated (Table 4.2). The residual metal concentrations are reentered in the computer program and a new speciation is calculated.

The most dominant species for each metals are $FeOH^+$, $Fe(OH)_2$, $Fe(OH)_3$, $ZnOH^+$, $Zn(OH)_3^-$, $Zn(OH)_4^{-2}$, Mn^{+2}, $MnOH^+$, $Pb(OH)_2$, $Pb(OH)_3^-$, $Cr(OH)_3$, $Cu(OH)_2$, $Cu(OH)_4^{-2}$, $Cu(OH)_3^-$, and $H_2SiO_4^{-2}$. The metals for which less than 95% of their initial content has been insolubilized at pH 12 include silica, arsenic, lead, manganese, zinc and chromium.

Table 4.2 Percent of metals removed by precipitation (B.D.= below detection limit)

pH	8	9	10	11	12	13
Si	0.00	0.00	0.00	0.00	0.00	sample I
	0.00	0.00	0.00	0.00	0.00	sample III
	0.00	0.00	0.00	0.00	0.00	sample IV
As	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.
	0.00	0.00	0.00	0.00	0.00	0.00
	0.00	0.00	0.00	0.00	0.00	0.00
Pb	0.00	0.00	0.00	0.00	0.00	0.00
	0.00	0.00	0.00	0.00	0.00	0.00
	0.00	0.00	0.00	0.00	0.00	0.00
Mg	90.6	99.0	99.9	99.9	100	100
	10.8	91.0	99.1	99.9	99.9	100
	79.1	97.9	99.7	99.9	100	100
Mn	0.00	0.00	0.00	55.3	95.5	99.4
	0.00	0.00	0.00	55.3	95.5	99.4
	0.00	0.00	0.00	64.5	96.4	99.5
Zn	95.1	99.7	99.7	99.6	95.1	0.00
	91.6	99.5	99.5	99.4	91.6	0.00
	83.0	99.1	99.1	98.9	83.0	0.00
Cr	86.8	96.9	0.00	0.00	0.00	0.00
	86.8	96.9	0.00	0.00	0.00	0.00
	78.1	94.5	0.00	0.00	0.00	0.00
Cu	100	100	100	100	99.9	97.1
	100	100	100	100	99.9	96.2
	100	100	100	100	99.9	97.1
Fe	100	100	100	100	100	100
	99.9	99.9	99.9	100	100	100
	99.9	100	100	100	100	100

In high pH regimes, dangling metal oxide bonds of phyllosilicates or multioxide feldspars, and ettringite surface sites are negatively charged. Cations can therefore, be physically adsorbed. Dissolved organic acids could also influence the partition of cations since metal organic complexes could compete with the surface-metal complexes. Providing that the solution is devoid of organic matter, the metals that could be adsorbed include iron, manganese and zinc. The dominant surface species of these metals are $>S\text{-}O\text{-}FeOH^{z+1}$, $>S\text{-}O\text{-}MN^{z+2}$, $>S\text{-}O\text{-}MnOH^{z+1}$, and $>S\text{-}O\text{-}ZnOH^{z+1}$, where $>S\text{-}O^{z}$ is the surface site. Also, due to steric effects, the stability of surface complex of the bare cations is larger than that of the hydroxylated metals. Since adsorbed metals can be treated as species, surface complexation reactions may be characterized thermodynamically and included in speciation programs. Amongst the zinc and iron species, $Fe(OH)_2$, $Fe(OH)_3^-$, $Zn(OH)_3^-$, and $Zn(OH)_4^{-2}$ are not expected to forming surface complexes. As for lead, chromium, silica and copper, $Pb(OH)_2$, $Pb(OH)_3^-$,$Cr(OH)_3$, $Cu(OH)_2$, $Cu(OH)_4^{-2}$, $Cu(OH)_3^-$, $As(OH)_4^-$, and $H_2SiO_4^{-2}$ remain in solution.

The residual metals that are of concern after lime has been added are therefore lead, chromium and arsenic. In fact, these metals should not have been partitioned. The formation of stable ettringite precipitates in these systems would therefore be necessary.

4.8 Stability of Ettringite Precipitates

With the use of the calcium and aluminum solubility curves, the molality of calcium, sulphate and aluminum ions lost in the crystallization of ettringite can be calculated. With 6 calcium ions, 2 alumina and 3 sulphates are consumed into the crystal lattice of ettringite. Sulphate concentrations in the tailings are ranging from $10^{-3.11}$ to $10^{-2.88}$ mol/L and are approximately one order of magnitude less than aluminum and calcium concentrations. The depletion of sulphate will therefore be limiting the extent to which ettringite precipitates. Through the consumption of 10^{-3} mol/L of sulphate, the minimum concentrations aluminum and calcium can reach through the precipitation of ettringite is therefore $10^{-2.13}$ mol/L (assuming an initial 0.01 mol/L concentration for both). These values are well above the maximum concentrations allowed by the solubility curves of aluminum and calcium. The fast depletion of sulphate relative to calcium and aluminum would probably drive ettringite to convert to monosulphate (Figure 4.4). For experimental purposes, it could thus be useful to add sodium sulphate to the solution, such that calcium, aluminum and sulphate reach stoichiometrically proportional concentrations. A significant quantity of ettringite could precipitate and hence mobilize the residual metals.

4.9 Conclusion

The results of the model should be used as a tool to understand the processes in lime-remediated mine tailings. It is possible to define the stability of each hydrates from the calculation of their equilibrium. Ettringite is stable on a wide range of composition and pH. However, the sulphate contents of the mine tailings limit the precipitation of ettringite, and monosulphate could be an end precipitate.

Thermodynamic modeling is a powerful tool to determine the variation of the system in presence of solution having known compositions. A knowledge of equilibrium diagram is important because it enables one to trace the kinetic path of the reaction and determines solution saturation of stable as well as unstable hydrates.

The reported method of calculation, which is described in this study, is the framework of the current research program on lime-remediated mine tailings. The experimental studies are focused on the importance of ettringite as sorptive agent.

Chapter 5

Laboratory Optimization of Ettringite Formation

5.1 INTRODUCTION

The experimental program were undertaken in order to evaluate the effect of calcium, aluminum and water variation on ettringite formation. Ettringite, $\{Ca_6[Al(OH)_6]_2(SO_4)_3 \bullet 26H_2O\}$, is responsible for retarding the hydration of tricalcium aluminates and binding aggregates in clasts in cements and concrete (Mehta and Monteiro, 1993). Ettringite consists of columns of $\{[Ca_6[Al(OH)_6]_2 \bullet 24H_2O]^{+6}\}$ which are basically lines of $[Al(OH)_6]^{-3}$ octahedra bonded with three Ca^{+2} ions. The coordination number of calcium is completed by water molecules. The sulphates are intercolumnar and can occur in four different positions. Three of these positions are occupied by sulphates and the remaining by two water molecules (Moore and Taylor, 1968,1970).

Ettringite can also be used as a means of stabilization of the sulphidic rich tailings. Ettringite, has the capacity to up take some of the metals of the concern into its structure. The central Al^{+3} can be replaced by any trivalent cation of similar size through isomorphous substitution. Formation of ettringite may also be accompanied by the fixation of hazardous oxyanions such as arsenic, boron, chromium, molybdenum, selenium, and vanadium. Samples of substituted ettringites containing arsenic, boron, chromium, selenium and vanadium have been synthesized in laboratory studies (Hassett *et al.*, 1989). Also, the zeta potential, which is defined as the electric potential in the double layer at the interface between a particle which moves in an electric field and the surrounding liquid, of ettringite has been measured at the pH of 10.7 and gives a value of [-11.7 mV] (Chen and Mehta, 1982), making it a good adsorbent for a positively charged metal species. Moreover, in high pH regimes, dangling metal oxide bonds of phyllosilicates or multioxide feldspars, and ettringite surface sites are negatively charged. Cations can, therefore, be physically adsorbed. Possible surface complexation sites on ettringite include dangling metal oxide bonds at the edge of polyhedron. Formation of ettringite is also associated with a high pH condition in the solution, which will further lead to the precipitation of heavy metals from the solution.

5.2 EXPERIMENTAL PROCEDURE

Laboratory experiments were set up in order to determine the optimum level of calcium and aluminum required to form and precipitate the mineral ettringite in oxidized mine tailings. A tailings sample with known amount of sulphate, high level of dissolved metal concentration and the pH of near 2 was mixed with different percentages of calcium and aluminum. The tailings sample was lightly pulverized before any mixing. Various water to solid ratios were used in order to obtain the maximum reactivity of the admixtures. The required amount of calcium and aluminum were obtained by mixing the tailings with predetermined amounts of quicklime, high calcium fly ash and an aluminum salt.

The formation of mineral ettringite requires a high pH environment where sufficient dissolved calcium, aluminum, and sulphate are present. In the previous studies (Mohamed et al., 1995; Solem and McCarthy, 1992; Kumarathasan et al., 1990; Hassett et al., 1989), it was shown that the required pH condition to optimize the formation of this mineral is between 11.5 and 12.5. Therefore, lime as a source of dissolved calcium, was added to the waste materials to elevate its pH to the optimum level. Moreover, based on the stoichiometry of the ettringite, sufficient amount of aluminum in the form of soluble aluminum nitrite was added to the samples.

The experimental program undertaken in this study consists of determination of optimum lime, water, and aluminum content. X-ray diffraction spectroscopy (XRD) were used to determine the extent of ettringite formation within the samples.

5.2.1 Optimum Lime Content

When a significant quantity of lime is added to a soil, the pH of the soil-lime mixture is elevated to approximately 12.4, the pH of saturated lime water. The solubility of silica and alumina, which might be naturally available in the waste compound, are greatly increased at elevated pH. Thus the conditions necessary for the formation of cementitious hydrates are provided. When the waste materials contain sulphate ions, as in the case of this study, it can combined with the alumina, and form a series of calcium-aluminate-sulphate hydrate compounds, leading ultimately to the formation of ettringite.

In order to establish the appropriate lime content and ensure a pH of 12.4 or near that level for sustaining the strength via pozzolanic reaction, a series of tests based on the method described by Eades and Grim (1966), were conducted. Samples of air dried tailings passing sieve no. 40 were used for this experiment. 20 grams of the sample were mixed with predetermined amount of lime and an equal amount of water to solid ratio (i.e., Ww/Ws = 100%; Ww = weight of water, and Ws = weight of solid). The samples were mixed for 48 hours using a table bench mixer and the pH of the slurry was recorded at the end of 24 and 48 hours and subsequently for several days thereafter. After establishing the optimum level of lime content, this amount was slightly increased and the effect of excess calcium on ettringite formation was studied. X-ray diffraction analysis was used to monitor the extent of ettringite formation on lime treated samples.

5.2.2 Optimum Water Content

In order to achieve the maximum reactivity of the admixtures, the amount of water added to the mixtures becomes crucial. Samples of the waste were lightly pulverized and then were mixed with different percentages of distilled water containing 225 mg/L of aluminum (calculated based on sulphate content of the sample and the stochiometry of ettringite). After mixing, the resulting low pH slurries were allowed to mellow for 24 hours at 20°C and 95% relative humidity. Then lime was added to the slurries in an attempt to raise the pH and provide the conditions needed for ettringite formation . The amount of lime added to all of these mixtures were kept to a optimum level which was determined from the previous experiment. These final mixes were allowed to cure and the formation of mineral ettringite was studied by X-ray diffraction analysis.

5.2.3 Optimum Aluminum Content

The formation of ettringite requires a sufficient amount of aluminum, calcium and sulphate ions in its structure. In order to further study the conditions required to optimize the formation of this mineral in mine tailings sample, different percentages of aluminum were added to the mixtures while the other variables were kept constant. The added aluminum was in the form of solid aluminum nitrite which was added to the water prior to the final mixing with the lightly pulverized waste materials. After the samples were allowed to mellow for 24 hours at 20°C and 95% relative humidity, lime was added to the slurries and the resultant mixtures were allowed to cure. The formation and disintegration of ettringite were further studied by X-ray diffraction analysis.

5.2.4 Optimum Fly Ash Content

Fly ash is the fine residue that results from the combustion of coal. It is usually collected by mechanical or electrostatic precipitators. Fly ash is considered a waste itself, although it is increasingly being used in concrete industry as a partial replacement for cement. The annual US production of fly ash is 50 million tons, 70% of which is land disposed (Maher *et al.*, 1993). The addition of fly ash to soils may change the following properties of the mixture: alteration in texture, bulk density, moisture holding capacity, pH, cation exchange capacity, hydraulic conductivity, cohesiveness and surface area (U.S. Department of Commerce, 1984). Moreover, due to its low cost, high alkalinity, and high metal adsorption capacity, fly ash can be an effective stabilizing agent (Roy and Eaton, 1992).

Fly ash possesses pozzolanic properties. A pozzolan is a "siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties. Fly Ash is typically classified by standards set by ASTM as class "F" or class "C" and the classification is generally based upon the parent coal source (ASTM C618, 1994). Class F fly ash is generated from the burning of bituminous or anthracite coals which are found in the eastern, mid-western and southern parts of the United States. Class C fly ash is generated from the burning of sub-bituminous or lignite coals of the type predominantly mined in the western United States (ACI 226.3R, 1987). Class C fly ash has generally a higher percentage of lime, than class F fly ash which tends to make it a better stabilizing agent for soil improvement. Its stabilization characteristics may be further improved upon the addition of lime (Nicholson and Kashyap, 1993). The principal active constituent of fly ash is silicious or aluminosilicate glass. The principal active constituent in class C fly ash is calcium alumino silicate glass (ACI 226.3R, 1987).Class C fly ash often react directly with water to form cementitious phases such as C-S-H (calcium-silicate-hydrate), calcium hydroxide, and ettringite.

The high calcium content of fly ash class C as well as its fine particles made it a suitable admixture to be used in conjunction with other additives in our experiments. The fly ash type C which was used in our experiment contained 13% by weight of calcium in the form of calcium oxide, and 53% by weight of silicon. Fly ash class C was added to the mixtures after the initial curing, which was the result of lime-waste pozzolanic reactions, had been taken place. Application of the fly ash to the mixtures would have help to reduce the moisture content and create a higher compressive strength in the admixture. Use of fly ash as a drying agent to facilitate compaction was one of the initial application for self-cementing ashes. Compaction of stabilized material during the fall or the spring is often hampered by the inability to reduce moisture contents to levels suitable for compaction. The addition of class C fly ash provides an immediate drying effect and allows final compaction to be completed within an hour or less (Fergoson, G., 1993).

Fly ash stabilize soil because of two basic sets of reactions: (1) Short term or immediate reactions and (2) Long term reactions. The immediate effect of the introduction of fly ash to the soil is to cause flocculation and agglomeration of the clay particles due to ion exchange at the surfaces of the soil particles. The result of these short-term reactions is to enhance workability and provide an immediate reduction in swell, shrinkage, and plasticity (Nicholson and Kashyap, 1993). The long term reactions are accomplished over a period of time (many weeks, months, or even years may be required for completion of these reactions) depending upon the rate of chemical breakdown and hydration of the silicates and aluminates. This results in further binding the soil grains together by the formation of cementitious materials (Usmen and Bowders, 1990).

Compressive strength of materials treated with class C ash is dependent upon moisture content at the time of compaction. A well-defined relationship exits between unconfined compressive strengths and moisture content, and this relationship being very similar to the moisture-density relationship established for a given compactive energy. Maximum strengths, however, have been observed at moisture contents ranging from 0 to 7 percent below the optimum moisture content for maximum density (Ferguson, 1993). The gain strength of lime-fly ash stabilized soil is primarily due to the formation of various calcium silicate hydrates (CSH) and calcium aluminate hydrates (CAH).

5.3 RESULTS AND DISCUSSION

5.3.1 Preliminary Tests

The experimental program undertaken in this study consists of laboratory characterization of a mine tailings sample with the following specifications:

TABLE 5.1: Test Results

Test	Magnitude
pH	2.49
Redox Potential (mv)	410
Moisture Content (field) (%)	10.29
Specific Gravity	3.60
Cation Exchange Capacity (meq/100g)	13.71
Specific Surface Area (m^2/g)	10.62
Liquid Limit (%)	18.23
Plastic Limit (%)	Close to L.L.

The soluble elemental analysis of the sample were performed based on acid digestion technique using nitric and hydrochloric acids and the results are shown in Table 5.2. The mineralogical composition of the sample was determined by using XRD analysis which revealed that the sample contains pyrite, graphite, quartz, illite, thulium tellurate, copper nickel tin sulphide, and stontium cobalt oxide.

The samples were air dried and lightly pulverized (passing sieve No. 40) before conducting any of the above mentioned tests. All of these experiments were conducted based on ASTM standards. All tests were performed on duplicate specimens to obtain average results.

TABLE 5.2: CHEMICAL ANALYSIS OF SAMPLE

Element	Concentration (ppm)
Aluminum	206
Arsenic	23
Calcium	0
Cadmium	0
Chromium	0.5
Copper	17
Iron	3332
Potassium	6
Magnesium	27
Manganese	5
Lead	34
Silicon	18
Sulphate	1626
Zinc	25

Since ettringite formation requires an alkaline environment, it is imperative to determine the availability of calcium, aluminum and sulphate within the waste material under the alkaline condition. Therefore, waste samples were leached with distilled water at pH of 12 which was set by the application of sodium hydroxide. Solid to water ratio of 1:20 was used in this leaching experiment and the samples were shaken for 24 hours. This method of leaching is based on Toxicity Characteristic Leaching Procedure (TCLP) test as described by U.S. EPA (1989). The results of the leaching test is tabulated below:

TABLE 5.3: LEACHING TEST RESULTS

Leaching of the Sample Under Alkaline Condition (pH 12)			
Waste Sample	Aluminum (ppm)	Calcium (ppm)	Sulphate (ppm)
	20	0	1200

Based on these results and the stochiometry of ettringite, which indicates that for every 3 moles of sulphate ion 2 moles of aluminum is needed, it was calculated that at least 225 ppm of aluminum is required to form ettringite in the mine tailings under investigation.

5.3.2 Optimum Lime Content

Addition of lime to raise the pH of the slurry is an effective technique to precipitate the soluble metals of concern as well as providing the necessary conditions needed to form ettringite. Lime in the form of quick lime was added in different percentages to the air dried and lightly pulverized waste material. Distilled water was added to this mixture with solid to water ratio of 1:5 and the resultant slurry was shaken with the use of a mechanical shaker for up to 48 hours. The results of these experiments are shown in Figures 1 and 2.

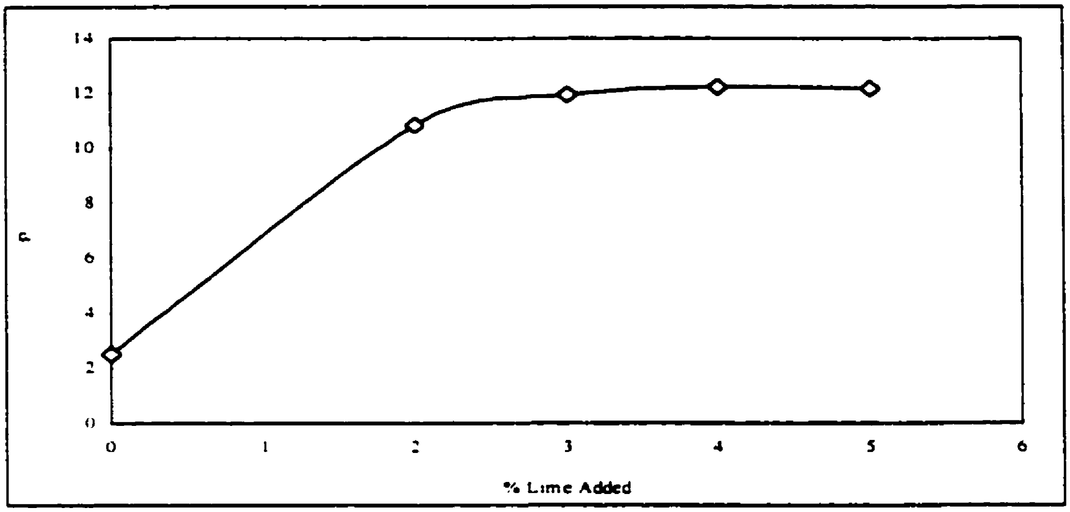


FIGURE 5.1. PH VARIATION VS. LIME CONTENT, DURATION 1 HOUR

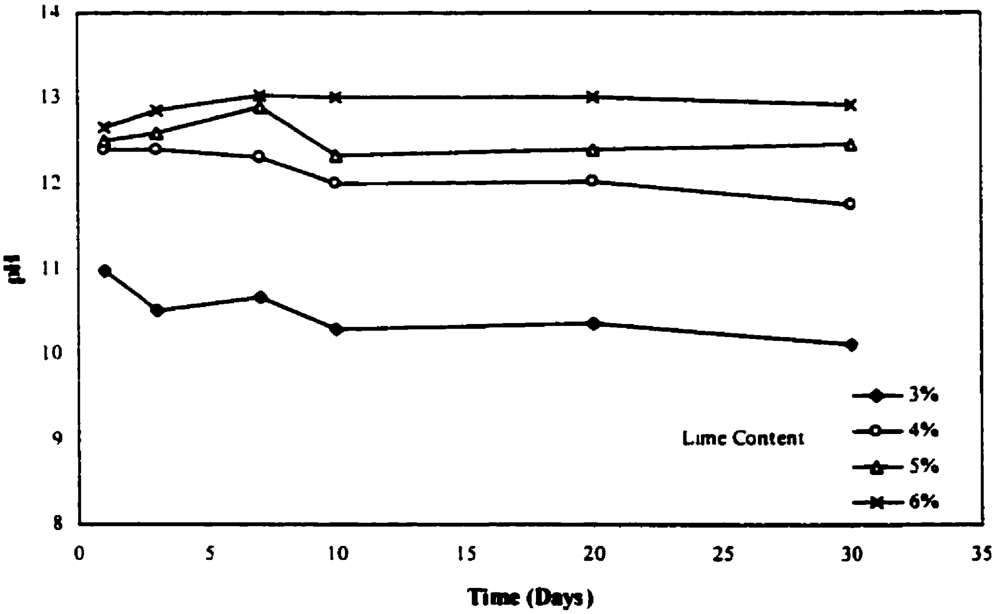


FIGURE 5.2. PH VARIATION VS. LIME CONTENT

The results obtained from these experiments indicate that addition of 4% lime to our waste is sufficient to raise the pH of the slurry to above 12. Attaining and maintaining such a high pH is necessary for ettringite formation (Mohamed *et al.*, 1995). However, it should be noted that the lime added merely raised the pH of the waste to the desired plateau; other variables such as reactivity of added lime with the waste materials and other additives were not taken into consideration. Defining the criteria needed to raise and maintain the high pH regime is an important factor for a system which relies heavily on pH of the system for its efficacy.

After determining that 4% lime is sufficient to raise the pH of the slurry to above 12, more experiments were undertaken to determine the effect of excess lime on the formation of mineral ettringite. However, since the waste sample lacked the proper aluminum content, 225 ppm of aluminum in the form of aluminum nitrite was added to the waste mixtures. This amount of aluminum was calculated based on the availability of sulphate in the waste sample and the stochiometry of the ettringite.

During this test, distilled water containing 225 ppm of aluminum nitrite with the solid to water ratio of 1:1 was added to the waste material. After mixing and allowing the resultant low pH slurry to mellow for 24 hours, different percentages of lime in the form of quick lime were added to the mixtures and the formation of ettringite was monitored using the X-ray diffraction analysis. Furthermore, the potential for formation and deterioration of ettringite was studied with respect to the formation of gypsum in the mine tailings. The high sulphate content and availability of calcium in such a system could lead to the formation of gypsum which will effect the stability of ettringite. Figures 5.3a and 5.3b show the extent to which ettringite and gypsum have been formed in these mixtures. The d-spacings, 0.763 nm and 0.972 nm were used for following the development of gypsum and ettringite, respectively.

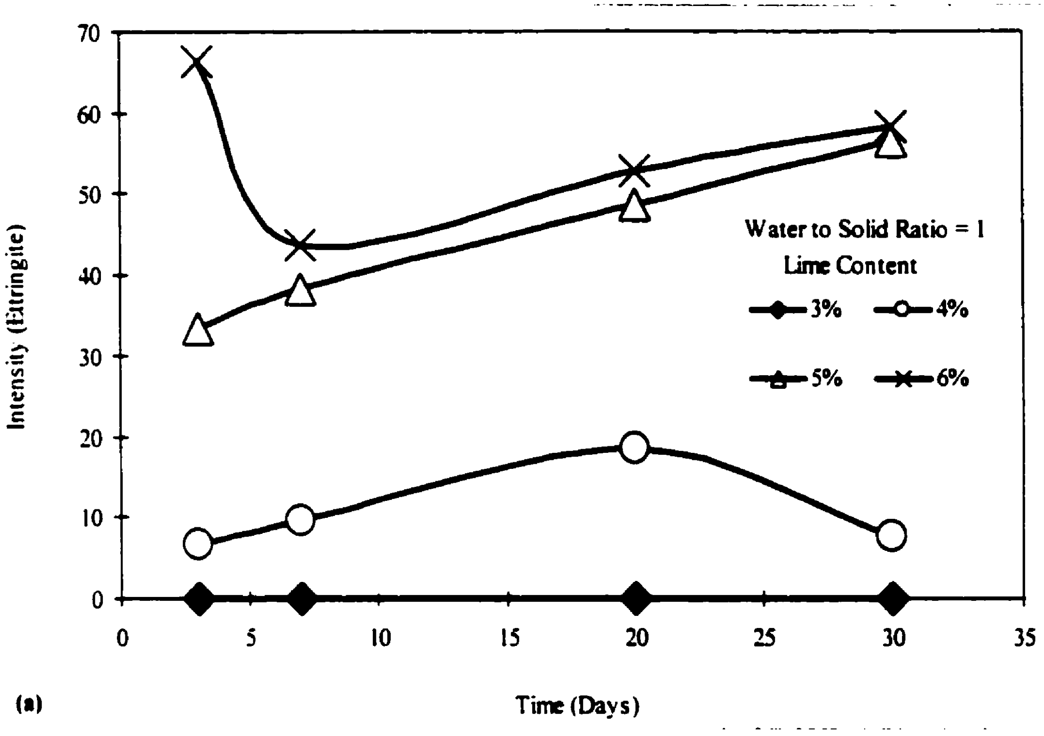


FIGURE 5.3.(a) EFFECT OF LIME CONTENT ON ETTRINGITE AND GYPSUM FORMATION

Figure 5.3a shows that 3 % lime is insufficient to create the conditions needed to form the mineral ettringite. This conclusion is evident from the pH conditions after the application of 3% lime as shown in Figure 5.2. From the geochemical modeling conducted previously (Mohamed *et al.*, 1995), it was shown that the pH conditions required to optimize the formation of ettringite is between 11.5 and 12.5.

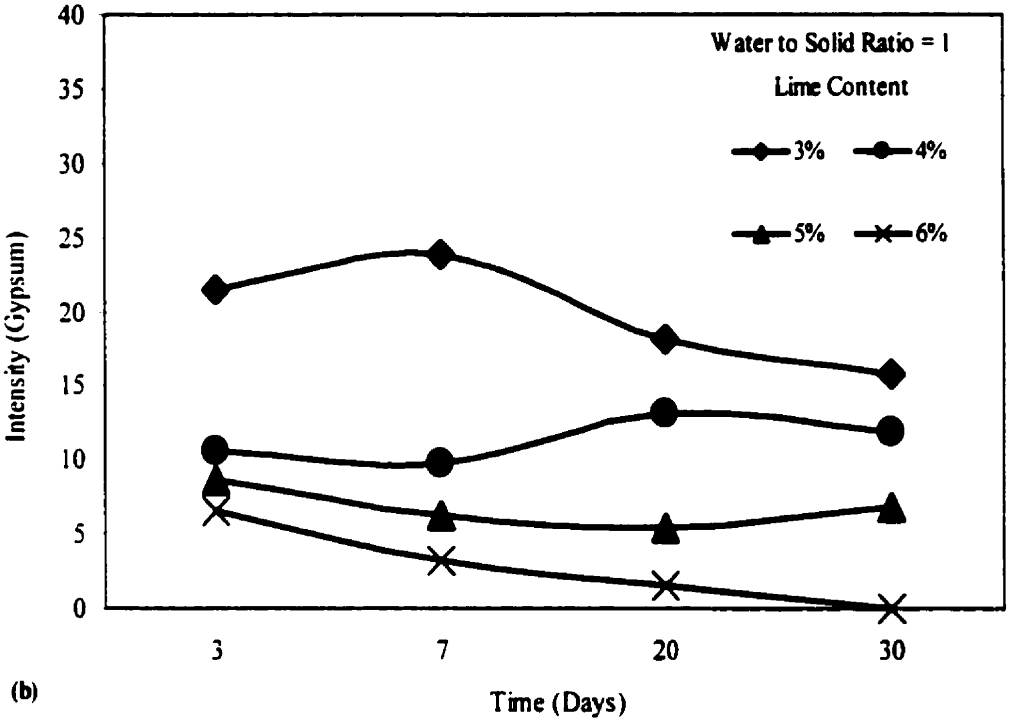


FIGURE 5.3.(b) EFFECT OF LIME CONTENT ON ETTRINGITE AND GYPSUM FORMATION

Application of 3% lime could not satisfy this requirement. However, the availability of sulphate within the tailings sample and the introduction of calcium in the form of added lime, has resulted in the formation of gypsum in the tailings sample (Fig. 5.3b). Ettringite was formed after the application of 4% lime. Although based on lime optimization experiment, such a reaction was expected, the XRD peak intensities of characteristics peaks for ettringite were very small while, a substantial amount of gypsum was still formed in the treated sample (Fig. 5.3a, &b). This might be the result of pH decline to around 10 in the sample. The reduction in pH causes a decrease in the magnitude of the mineral ettringite formed with 4% lime application.

Addition of aluminum compound to the system and the reaction between lime and the admixtures might have caused this reduction in pH.

Treatment of the tailings sample with 5% lime resulted in a much stronger XRD peak intensities for ettringite and a sharp decrease in the magnitude of the gypsum formed (Fig. 5.3a, &b). The pH of the treated samples with 5% lime were stable and remained around 12. Application of 6% lime also induced high XRD peak intensities for ettringite with low level of gypsum formation in the treated mine tailings samples. However, Figure 5.2 showed that the pH level of these samples were around 13. According to the study by Hampson and Bailey (1983), on the influence of pH on the microstructure and stability of the ettringite, it was reported that at such a high pH (about 12.5 and higher), the crystal structure of ettringite is disordered and the fiber length is reduced compared to that of ettringite formed at pH level between 11.5 and 12.

Therefore, while 4% lime could satisfy the pH requirement for the waste material, it seems that in the case of other additives, more lime was needed to rise the pH and to optimize the formation of the mineral ettringite. This is especially true as the age of the samples have increased. The reactivity of other additives in the waste samples caused a slight decrease in the pH of the mixtures with 4% lime. This in turn results in the fewer ettringite mineral in the samples.

5.3.3 Optimum Aluminum Content

Ettringite, which is a calcium aluminosulphate hydroxide hydrate compound, requires aluminum for its formation. In order to form this mineral in the lime remediated sulphidic mine tailings, the aluminum content of the samples were varied and the results were monitored by using the XRD analysis. From the stochiometry of the ettringite and with the given specification of the waste in this experiment (i.e., Ca and SO_4 content), it was calculated that about 225 ppm of aluminum is required to form this mineral in the system. Moreover, the potential of other trivalent cations already available in the waste matrix to replace the aluminum had to be investigated; and therefore, different amounts of aluminum in the form of soluble aluminum nitrite were added to the mixtures. As a result the final mixtures contained 110, 225, 350 and 500 ppm of aluminum. At the same time, all the above mentioned samples were also made with the addition of 20% of fly ash type C. Fly ash was added to the samples so that the effect of high calcium additives as well as its bounding capacity on the formation of mineral ettringite could be monitored. The effect of added aluminum on formation of ettringite and gypsum, has been compared and are shown in Figures 5.4 (a & b) and 5.5 (a & b).

The results indicate that ettringite formation in samples without the addition of fly ash was not significant (Fig. 5.4 a). Although limited amounts of ettringite were formed with the addition of 110 and 225 ppm of aluminum, they were completely disappeared after 28 days of curing. The pH of all these mixtures

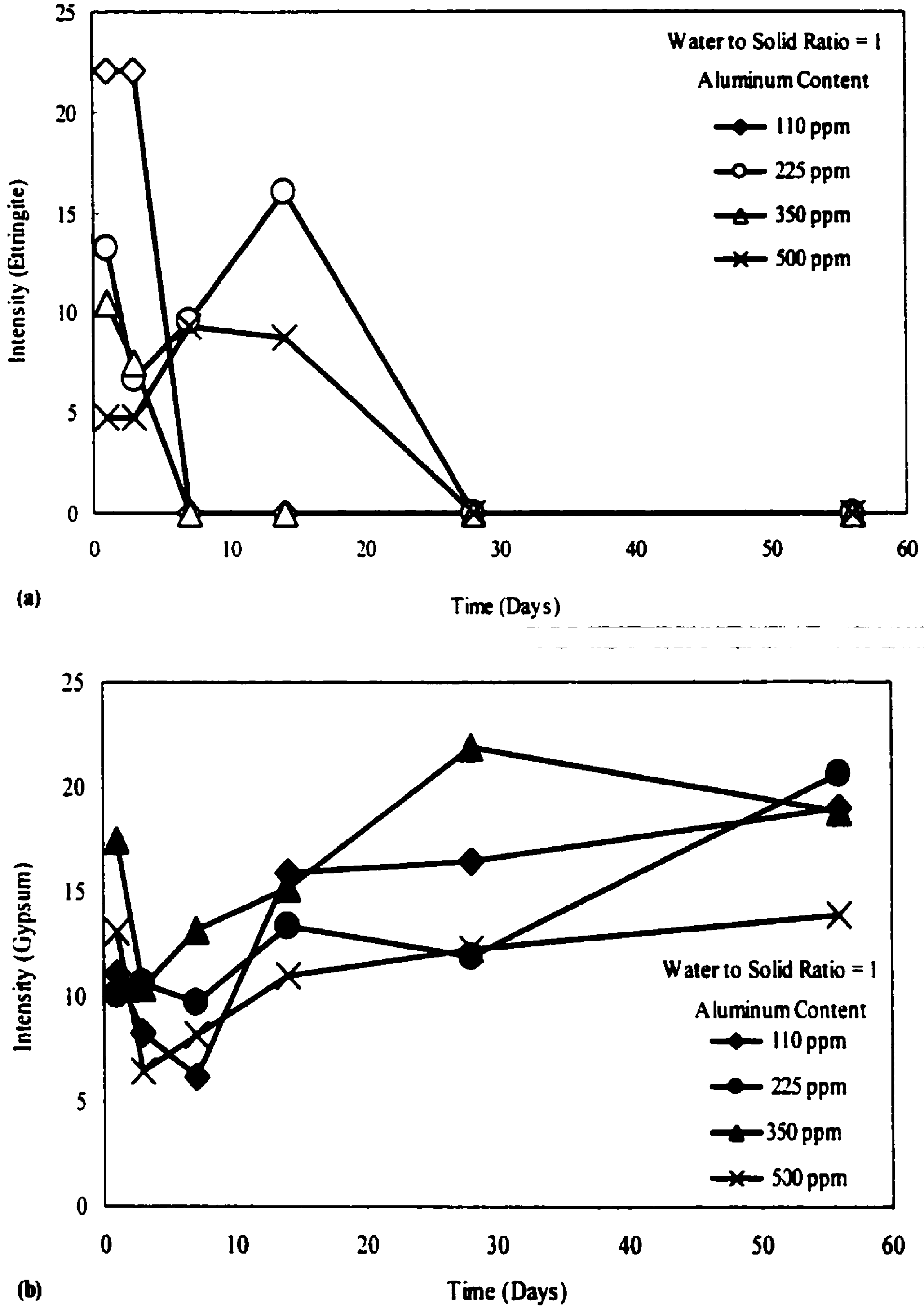
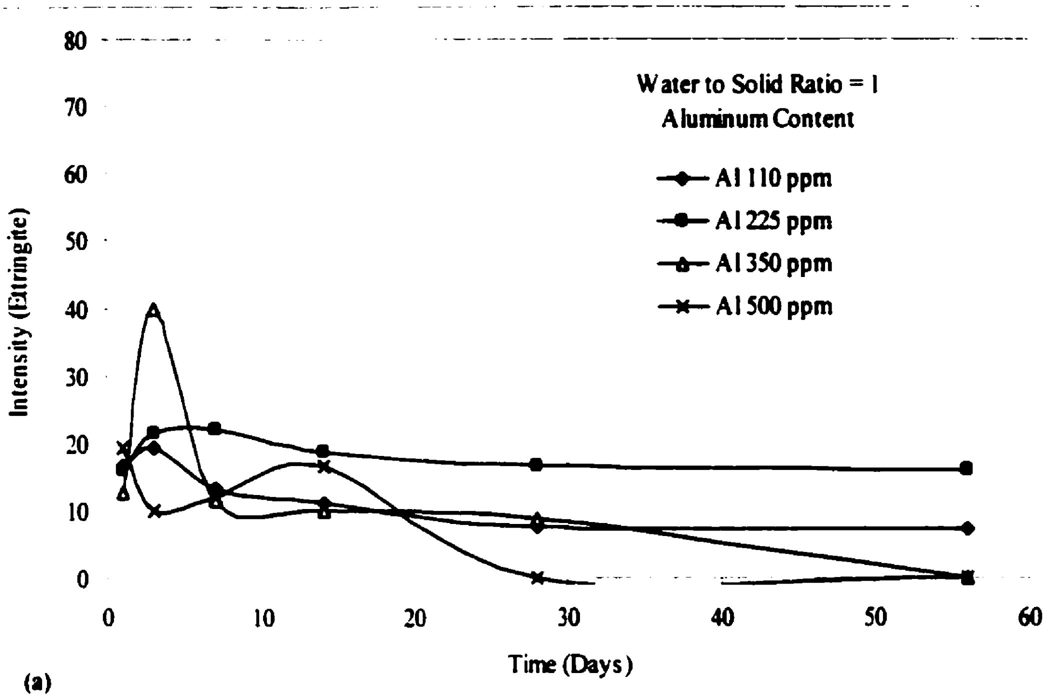
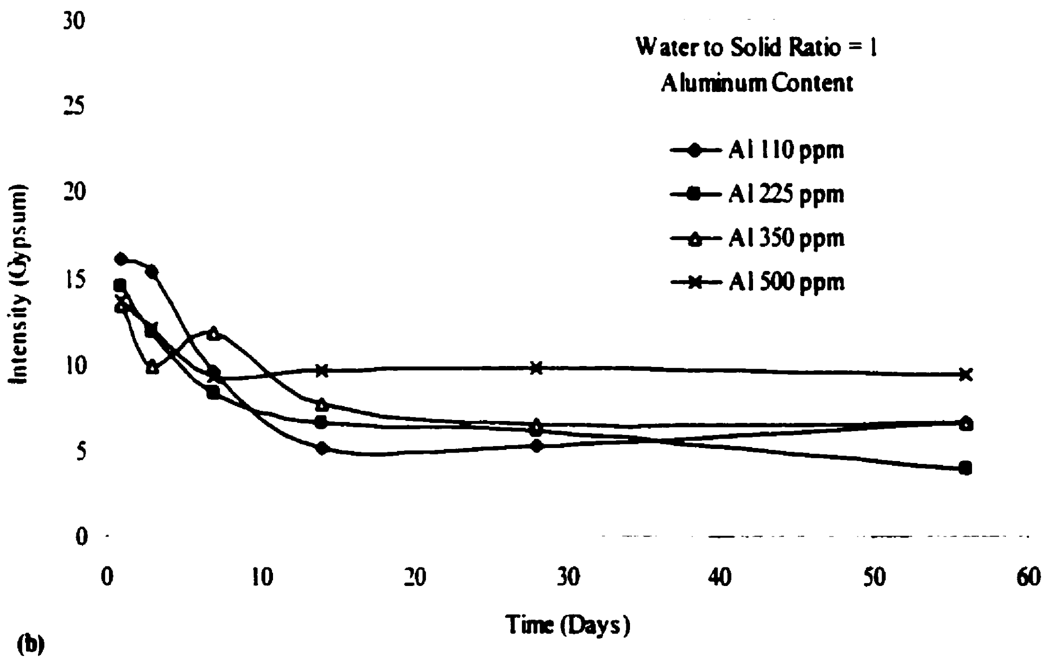


FIGURE 5.4 (a & b). THE EFFECT OF ALUMINUM VARIATION ON ETTRINGITE FORMATION; FLY ASH CONTENT 0%



(a)



(b)

FIGURE 5.5 (a & b) THE EFFECT OF ALUMINUM VARIATION ON ETTRINGITE FORMATION; FLY ASH CONTENT 20%

remained around 10.5, which is below the required pH for the formation of the ettringite. The disappearance of ettringite gives rise to the gypsum formation, while more of this mineral is formed with the higher availability of aluminum for reaction.

Samples with 20 percent fly ash produced stronger peaks for the mineral ettringite. This is again particularly true for the samples with smaller quantity of added aluminum. The pH of the samples with the addition of fly ash were higher (around 12) and showed less variations. This is the result of the high calcium content of the fly ash type C. However, addition of higher amount of aluminum (350 and 500 ppm), has resulted in the pH range of 9.5 to 10.5. This pH range is below the optimum condition for ettringite formation, and it is the result of added aluminum reactivity with the rest of the waste matrix. Since other cations can replaced the central Al^{+3} in the structure of ettringite (Mohamed *et. al.*, 1995), the high content of other cations in the waste materials, particularly iron, provided the necessary conditions required for the mineral ettringite to form with the addition of minimum aluminum. Therefore, more mineral ettringite has formed with the addition of 110 and 225 ppm of aluminum than when 350 and 500 ppm of aluminum were added. The added aluminum and its reactivity with the waste materials require more lime in order to elevate the pH of the matrix to the required level (above the pH of 12). Moreover, it is postulated that the presence of cations in the waste required the lesser amount of aluminum than its stochiometric level for ettringite formation. As it was expected, the higher formation of ettringite has also resulted in a decline in the amount of gypsum formed. Addition of 110 and 225 ppm of aluminum to the tailings samples reduced the gypsum formation significantly as less sulphate were remained in the sample for its formation. While the lesser amount of ettringite formed with the addition of 350 and 500 ppm of aluminum caused very little change in the amount of gypsum formed in the sample without any added fly ash. These conclusions can further be seen from Figure 5.5 (a & b).

Although it was expected that some ettringite to form while no fly ash was added to the system with 4% lime and 225 ppm of aluminum, no formed mineral was observed. This was attributed to low pH of the system which did not reached the required level to allow the ettringite to form. However, under the similar condition in the previous experiments, the pH was reached the required level. Therefore, the method of mixing could be a determining factor in the formation of mineral ettringite; while in order to ensure the stability of the pH range addition of 4% lime is not enough and slightly more calcium hydroxide should be added to the system.

5.3.4 Optimum Fly Ash Content

Sundance fly ash type C which contained 13% by weight of calcium in the form of calcium oxide, 53% by weight of silicon and 23% aluminum oxide was used as one of the admixtures in conjunctions with other additives in this experiment. The high calcium content of fly ash class C as well as its fine particles will enhance the optimization process for the mineral ettringite formation in the treated sulphide rich tailings sample, reduce the moisture content and create a higher compressive strength in the admixture.

Fly ash class C was added to the mixtures after the initial curing, which was the result of adding 225 ppm of aluminum in the form of aluminum nitrite, and 4% lime by dry weight of the tailings. In order to determine the maximum effectiveness of the added fly ash, the cured samples were mixed with 0% and 20% fly ash by weight of the dry tailings. The peak intensities for the formation of ettringite were monitored using XRD analysis and the results are presented in Figure 5.6.

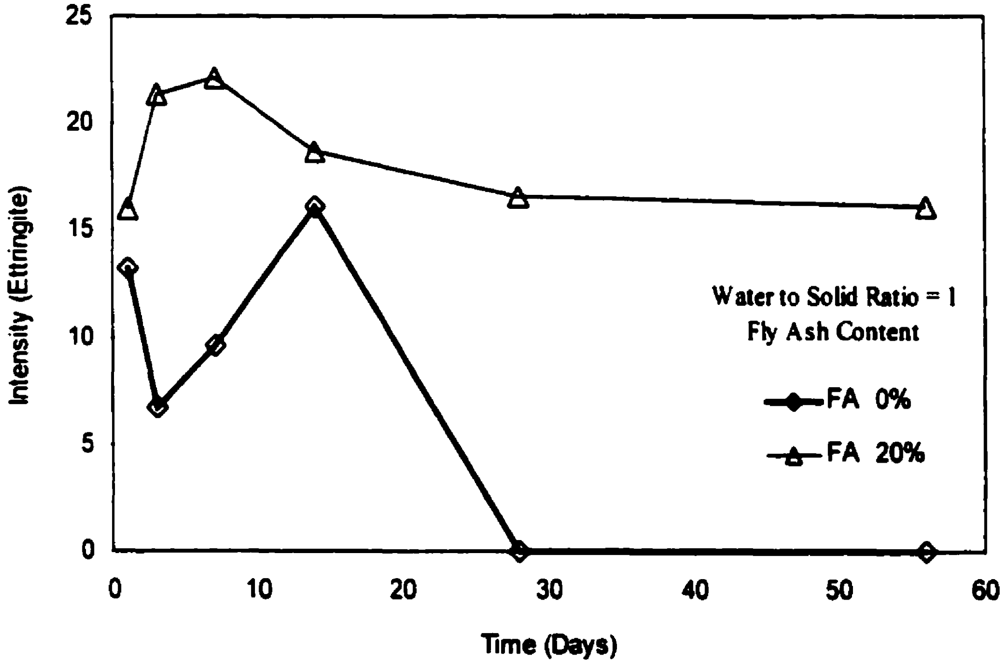


FIGURE 5.6. THE EFFECT OF FLY ASH CONTENT ON ETTRINGITE FORMATION

While some small amount of ettringite were formed in samples without any addition of fly ash, they were completely disintegrated after three weeks of curing. Ettringite peaks were observed with much stronger intensities in samples treated with 20% of fly ash which could be attributed to the high calcium, and aluminum content of the added fly ash. Moreover, the visual examination of these samples revealed that the treatment of samples with fly ash results in faster drying and better workability of the samples.

However, in the previous experiments, it was determined that 4% lime, which is the threshold of lime optimization for the sample under investigation, cannot elevate and maintain the required pH level for ettringite formation. The drop in the pH was attributed to the reactivity of additives such as fly ash and aluminum nitrite with the tailings, and formation of other compounds such as tricalcium silicate in the sample. Therefore, fly ash optimization experiment was repeated using 5% lime by dry weight of tailings. Under the new conditions, the pH was stabilized around 12 and remained as such throughout the length of the experiment.

Figure 5.7 represents the peak intensities at d space of 0.972 nm for the ettringite formed under the new condition. These samples were monitored for 28 days until a definitive pattern in the growth of ettringite were established. Samples were made without the addition of any fly ash, with 10% and with 20% fly ash. Figure 5.7 shows that the peak intensities of the ettringite became strongest with the addition of 10% fly ash. At the same time, the visual inspection of the treated samples indicate that those which were mixed with 10% fly ash were dried faster and had better workability conditions than those which were mixed with lesser or higher amounts of fly ash. The higher fly ash content has lead to the formation of other compounds such as calcium silicate hydrates in the samples. Therefore, from the results of this experiment, it was decided to use 10% fly ash as the optimum fly ash required to form the mineral ettringite in the tailings sample under investigation.

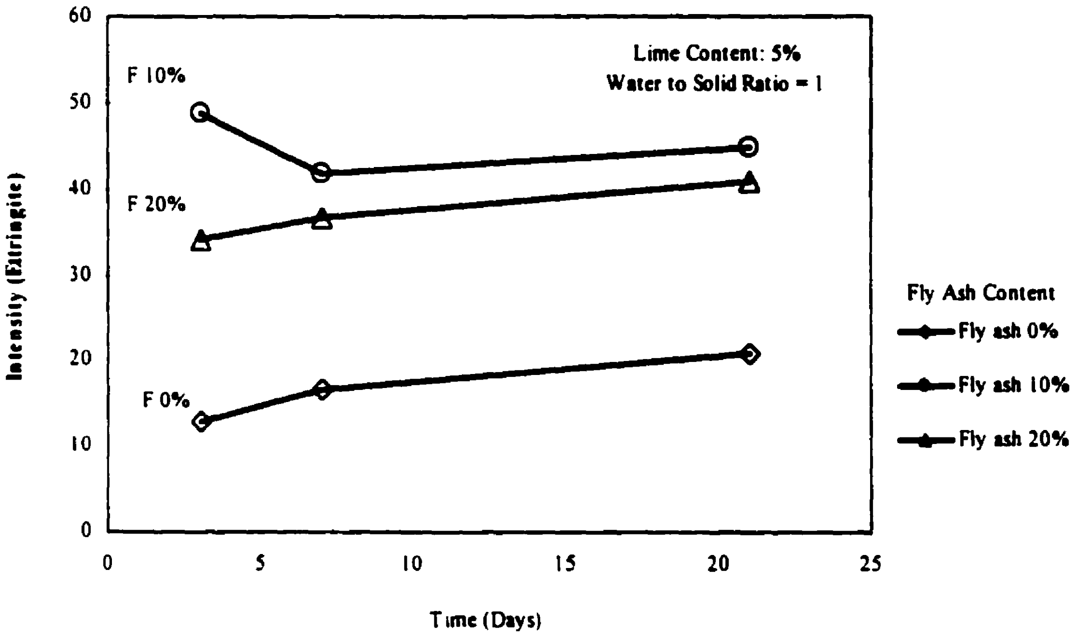


FIGURE 5.7. THE EFFECT OF FLY ASH CONTENT ON ETTRINGITE FORMATION

5.3.5 Optimum Water Content

The effect of water content and its relation to the degree of the reactivity of the additives in terms of the magnitude of the ettringite formation in the treated samples were monitored by using XRD analysis. Water to solid ratio of 0.4, 0.5, 0.7

and 0.9 were added to the samples. Figure 5.8 shows the extent of ettringite formation in samples treated with 4% lime and 225 ppm of aluminum. The results of this experiment indicates that as the water content increases, more reaction has taken place and more ettringite has formed in the waste matrix. However, the major draw back of increasing the water content beyond 50% is the formation of a slurry which has an extremely difficult workability characteristics. Addition of water content of 70% and 90% caused increase in the peak intensities of ettringite. But the resultant slurry had no workability characteristics and raised some concern about the ability to compact the treated waste materials.

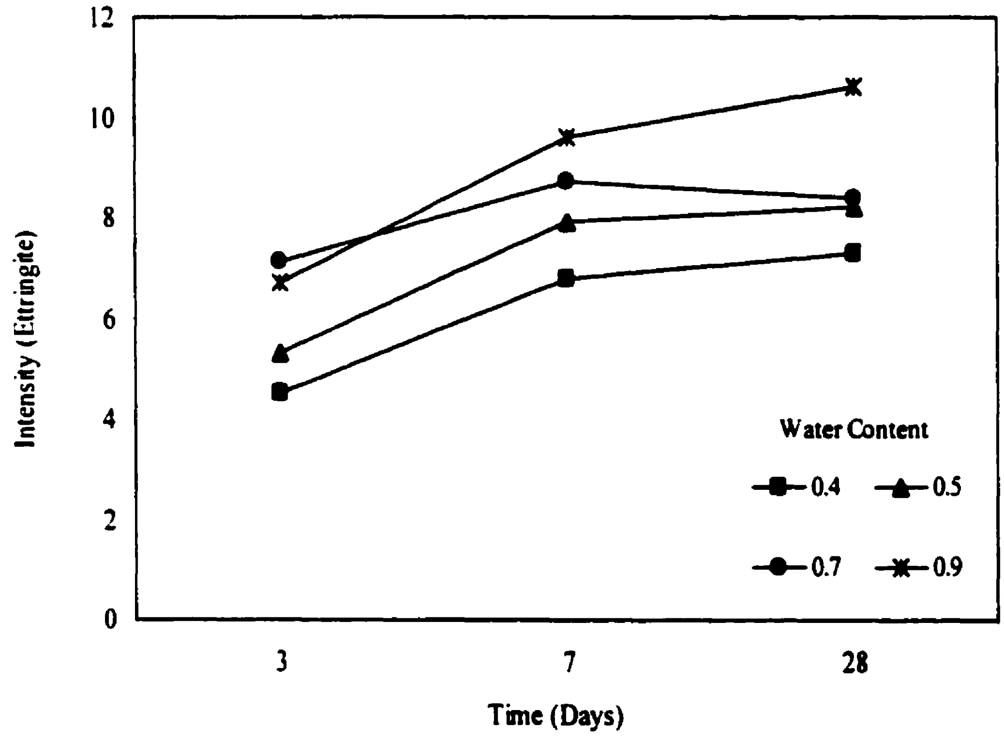


Figure 5.8. The effect of Water Content on Ettringite Formation

Therefore it was decided to choose 50% water content as the optimum condition to achieve the desired reactivity from the admixtures as well as creating a paste which upon its hardening could be compacted.

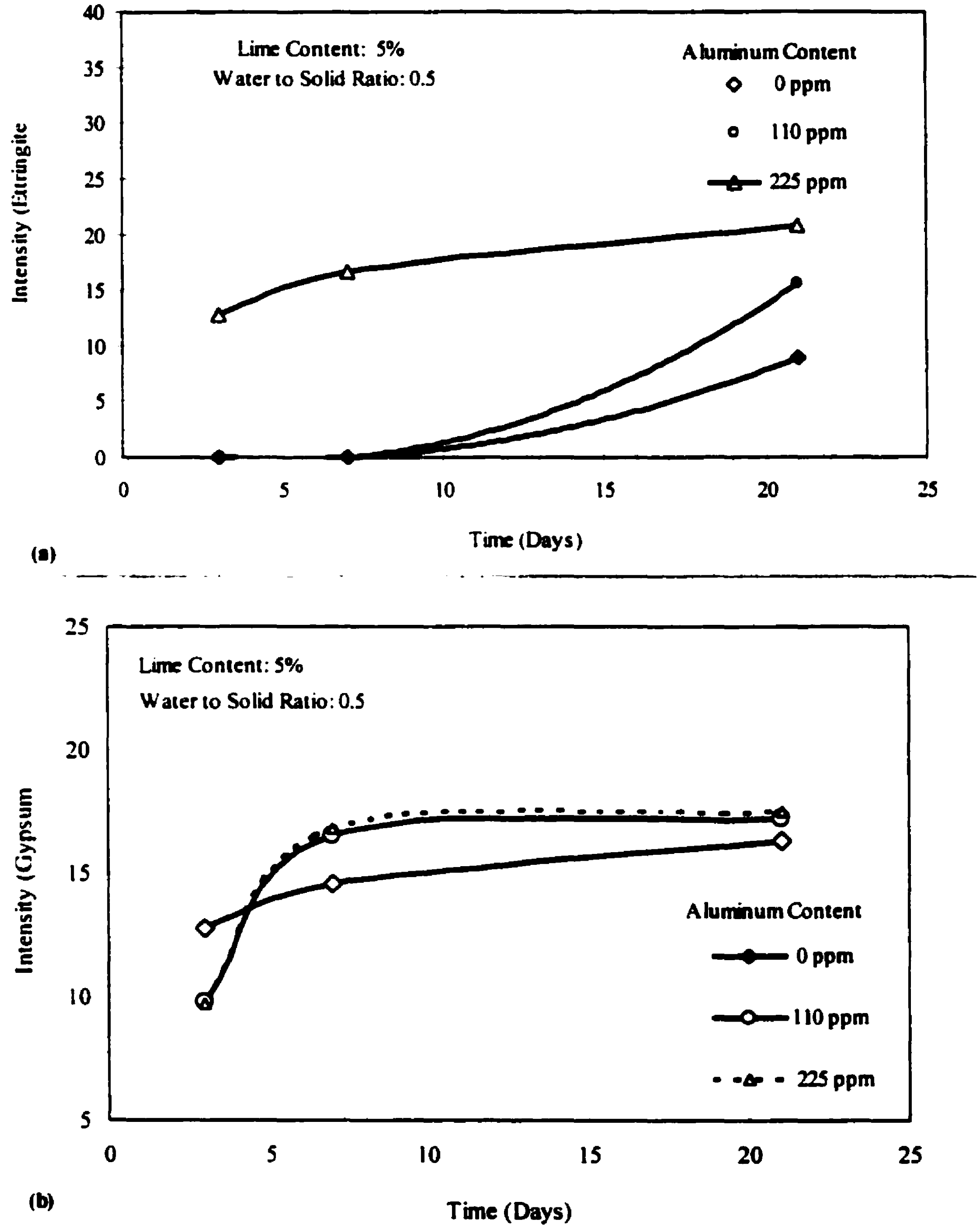
5.4 Optimization Based on Experimental Results

The thermodynamic modeling previously conducted by Mohamed *et. al.*, (1995), indicates that in the system containing 10^{-2} mol/L $Al(OH)^-_4$, 10^{-2} mol/L Ca^{2+} and 10^{-3} mol/L SO^{2-}_4, calcium and aluminum solubilities would allow ettringite $\{Ca_6Al_2(SO_4)_3(OH)_{12} \bullet 26H_2O\}$ to form at pHs larger than 11.6. Formation of ettringite in a lime-remediated sulphate rich mine tailings can reduce the heavy metals mobility from the tailings area to the surrounding environment. This could be achieve through isomorphous substitution of the heavy metals in the crystal structure of ettringite; by precipitation of heavy metals in high pH environment of ettringite formation, and by adsorption of positively charged heavy metals to its negatively charged surfaces. Therefore, formation of ettringite in a sulphate rich mine tailings could serve as a physical and chemical stabilization agent.

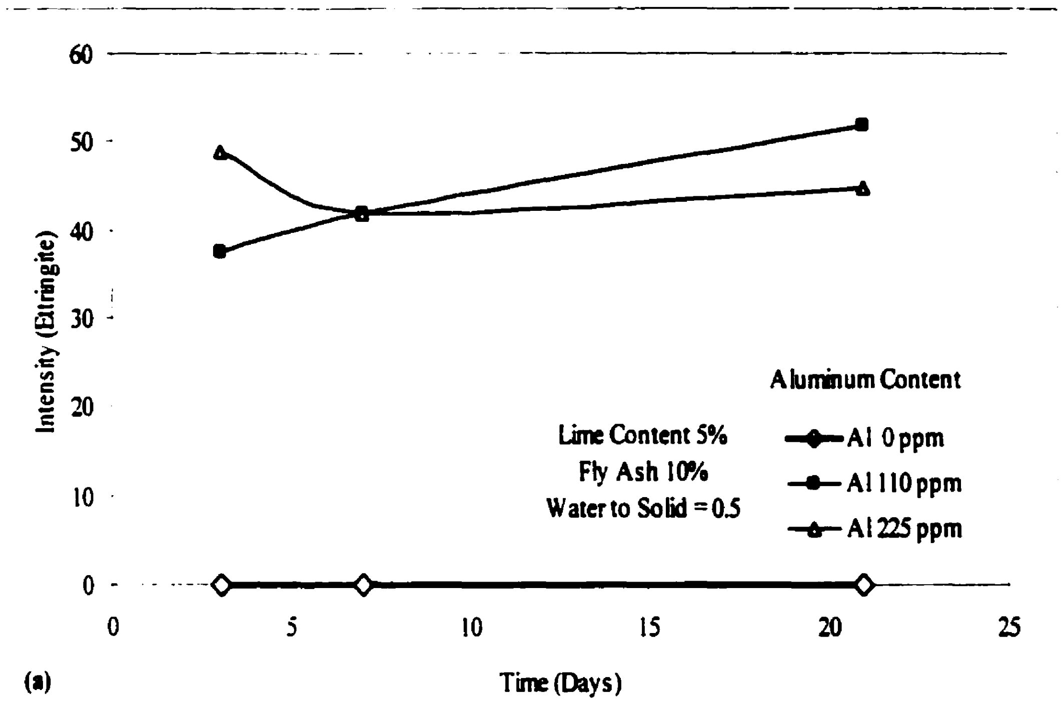
The previous experiments were based on optimizing the pH of the mine tailings by the application of 4% lime in the form of quick lime. However, the reactivity of other additives such as fly ash and aluminum with the mine tailings, caused a drop in the pH from the optimized level to around 10.5. The low pH condition caused fewer or complete disintegration of formed ettringite in the treated samples. Therefore, a complete set of new experiments were designed with the addition of 5% lime (instead of 4%), to the tailings sample under investigation. Under the new conditions, the pH was stabilized around 12 and remained as such throughout the length of the experiment. The water content of the new mixes were set up based on the previous water content optimization to 50%. Also, the new experiments were designed with the application of 10% fly ash to achieve the maximum reactivity as well as to improve the workability of the treated material. Moreover, in order to conclusively determine the threshold of the aluminum needed to form and precipitate ettringite in such a system, new experiments with different amount of added aluminum were set up. The aluminum was added in the form of aluminum nitrite in the designated amount to provide 110 and 225 ppm of soluble aluminum in the mixes. The aluminum was first mixed with the required water content (50% by weight) which was then added to the dry tailings. The resultant slurry was allowed to mellow and stabilize for 24 hours. Then, quick lime and fly ash type "C" were added to the slurry and the final mixes were cured at 20°C and 95% relative humidity. The following graphs were devised based on the variability of fly ash and aluminum content. The formation, growth and disintegration of ettringite were monitored with respect to formation of gypsum in the samples. The high sulphate content and availability of calcium in such a system could lead to the formation of gypsum which will effect the stability of ettringite in that system. The d-spacing, 0.763 nm and 0.972 nm were used for following the development of gypsum and ettringite.

No ettringite was formed within the first 7 days of curing in the system which contains 5% lime and zero or 110 ppm of aluminum, and no fly ash (Figure 5.9a). Increasing the aluminum content to 225 ppm, led to the formation of ettringite within the first 3 days of curing. After 7 days of curing, ettringite peaks could be detected on all three samples. However, the peaks were weak for the samples containing 0 or 110 ppm of aluminum. The gypsum were formed in all the three samples within the first 3 days of curing (Figure 5.9 b), and its peaks became stronger, regardless of aluminum content, as the age of the samples increased. Continues pyrite oxidation in the samples has led to the generation of more sulphate ions and subsequent formation of gypsum in the samples. The rate of ettringite formation in the sample made with 110 ppm of aluminum increased as the length of curing time was increased. Continues supply of sulphate in an alkaline environment rich in calcium and aluminum and other trivalent cations has resulted in delayed ettringite formation.

Addition of 10% fly ash type C to the tailings resulted in formation of ettringite in samples containing 110 and 225 ppm of aluminum; while ettringite peaks were completely undetected for samples without the addition of aluminum (Figures 5.10 a & b). The peak intensities of the formed ettringite in these samples were much stronger when compared with previous samples without any added fly ash. The formation of gypsum in all three samples were slightly reduced. This reduction in gypsum formation for samples which contained aluminum might be the result of increased formation of ettringite in the same samples; as sulphate content of the tailings sample were used for mineral ettringite to be formed.



Figures 5.9 (a&b). Optimization of Al Content for Ettringite Formation, Lime Content 5%



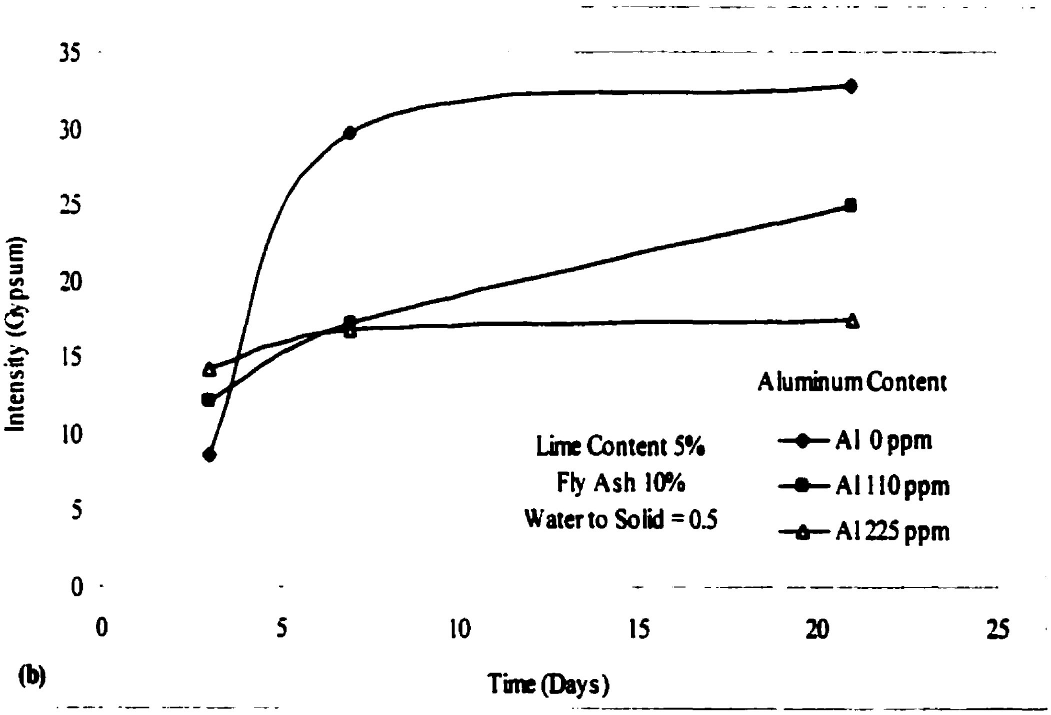


FIGURE 5.10 (a&b). OPTIMIZATION OF AL CONTENT FOR ETTRINGITE FORMATION; LIME CONTENT 5%

XRD analysis of samples which were made with 20% fly ash showed that ettringite has formed in all three samples containing 0, 110 or 225 ppm of aluminum (Figure 5.11 a & b). The peak intensities for ettringite formed with the addition of 110 and 225 ppm of aluminum were almost the same while the magnitude of gypsum formed in the samples has drastically reduced. The lowest amount of gypsum was recorded in the sample containing 225 ppm of aluminum which was almost reduced to 1/5 of the amount formed in the samples with 10% fly ash. The amount of gypsum formed in samples which contained 0 and 110 ppm of aluminum were also reduced to half. The sulphate ions in the samples have been incorporated into the structure of ettringite and thus are unavailable for reaction to form gypsum. Another reason for the reduction in the magnitude of gypsum could be the formation of tricalcium silicate in these samples. The excess amount of silicate in the added fly ash and availability of calcium leads to the formation of tricalcium silicate in these samples. According to the studies done by Fu *et. al.*, (1994) and Odler (1980), sulphate could be bound into the calcium silicate hydrate (C-S-H) gel structure and released at later ages. Secondary ettringite formation in hydrated portland cement has been reported in the past (Mehta *et. Al.*, 1979). The absorbed sulphate into the C-S-H gel will be released and provide the conditions needed for delayed ettringite formation in hydrated portland cement. Addition of fly ash with its high silicate content to the lime remediated sulphidic tailings, leads to the formation of C-S-H gel in the mixture. The calcium silicate hydrate gel works as a reservoir which sulphate and aluminate could sink into it (Taylor, 1993).

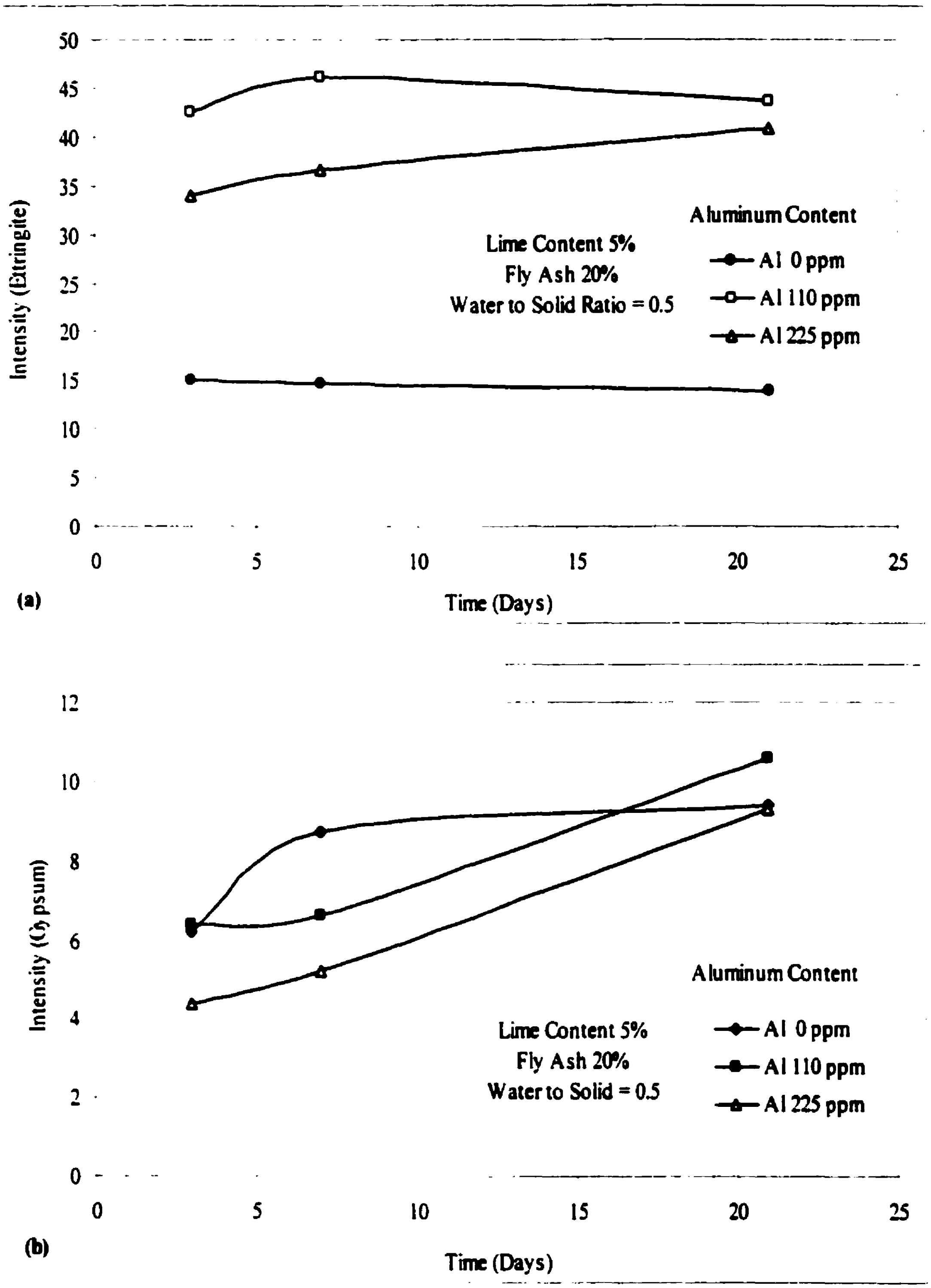


FIGURE 5.11 (a&b). OPTIMIZATION OF AL CONTENT FOR ETTRINGITE FORMATION; LIME CONTENT 5%

Therefore, addition of 5% lime, 10% fly ash class "C", with the application of at least 110 ppm of aluminum are the necessary elements in our system for the formation of ettringite.

5.5 CONCLUSIONS

Tailings sample with high sulphate content were treated with the application of lime and aluminum nitrate and the possibility of forming ettringite were studied. From the preliminary experiments regarding the optimum lime content it was concluded that about 4% lime is required to elevate the pH of the waste slurry to the pH of saturated lime water; the optimum pH condition to form and precipitate ettringite. This was the minimum lime needed to elevate the pH to desired plateau. However, the application of other admixtures such as aluminum nitrate, which is essential for the formation of ettringite, further reduces the pH of the slurry, and therefore, more lime is needed to elevate the pH to the required level. Further experiments has shown that 5 percent lime is sufficient to provide the adequate conditions for the formation and precipitation of the mineral ettringite.

Optimum water content experiments were performed based on the magnitude of water required to cause the maximum reactivity of the admixtures as well as providing the possibility of compacting the resultant slurry. The experiments show that as the water content increases, the magnitude of the formed ettringite is increased. However, water content more than 50 percent by weight of the dry waste creates a slurry which is very difficult to compact. Therefore, since one of our objectives has been the possibility of compacting the resultant slurry, it was concluded that water to dry waste ratio of 0.5 to be used for achieving the required reactivity from the admixtures as well as creating a slurry which is easily compactable. Moreover, high calcium content fly ash was added to the samples to facilitate its compaction. The experimental results indicated that more ettringite was formed with the addition of 10% fly ash to the samples. At the same time, samples were dried faster and showed better workability characteristics with the addition of 20% fly ash.

The XRD analysis of the samples indicate that the formation of mineral ettringite is optimized when up to 225 ppm of aluminum has been added to the tailings sample under investigation. However, because of high cation content of the tailings itself as well as the addition of fly ash, the aluminum content was reduced to 110 ppm and still a substantial amount of ettringite was observed in the resultant mixtures. Formation of ettringite with lower aluminum content than its stochiometric requirement (225 ppm), is the result of other cations replacement for the aluminum in the structure of ettringite.

Chapter 6

Leachability Analysis of the Treated Sample

6.1 Introduction

Generation of acidic effluents from sulphide rich tailings has been one of the major environmental concerns among the Canadian base metals, precious metals and uranium mining industry. When sulphide minerals, particularly pyrite and pyrrhotite are exposed to oxygen and water, they begin to react almost immediately. This reaction yields sulphuric acid and causes the leaching of heavy metals, in concentrations toxic to aquatic life. Therefore, preventing and/or retrofying the existing acid producing tailings sites is a challenge facing the Canadian mining industry. Mining companies are emphasizing on improving mine waste characterization and disposal technology in order to meet increasingly demanding environmental standards in a cost effective manner.

No proven technologies exist as yet to control and treat acid mine drainage in such a way that would allow mine operators to retire from mine sites knowing that the environment will be protected. However, there are several disposal practices that are currently being investigated for the long-term containment of tailings and other reactive mine wastes. The key to prevent acid mine drainage appears to be the prevention of oxygen from coming into contact with acid producing materials. Amongst the technologies that are currently investigated one can name water cover, dry cover, vegetation, compost and acid neutralization which involves rising the pH of the pore waters by introducing a caustic agent, such as lime to the system. This will result in changing the pH to a level where the solubility of most metals is at its lowest.

Lime neutralization process is the most common treatment available of acid generating tailings. Lime or hydrated lime, (CaO or $Ca(OH)_2$), is the most commonly used neutralizing agent for treating acid mine drainage, because of their high reactivity, availability, and relatively low cost. In some cases, other alkaline chemical reagents such as NH_3, $NaOH$ or $CaCO_3$ can be used. The mixture of metal hydroxide precipitates and gypsum ($CaSO_4$) is called "sludge" and is allowed to settle in ponds or in a solid/liquid (S/L) separation device (e.g. clarifier/thickener). The settled sludge is then disposed of in specifically-designed storage ponds. Hydroxide sludges are usually voluminous due to their gelatinous texture and, as a consequence, solid/liquid separation is difficult (Kuyucak *et al.*, 1995; Kuyucak, 1995). The annual volume of sludge production by the Canadian mineral industry is estimated at 140,000 dry tonnes/year (Fyson *et al.*, 1995).

Chemical admixtures, such as lime, for waste stabilization/solidification is not a new technology. Lime based stabilization of wastes have been widely applied to inorganic wastes in the past. Employing lime based stabilization technique has several advantages over other commercially available stabilization agents which makes this type of treatment the method of choice for mining and mineral industry. These advantages can be summarized as follows:

- The additives such as fly ash and slag are generally very inexpensive and widely available,
- The equipment required for processing is usually simple to operate,
- The chemistry of the pozzolanic reactions are relatively known.

However, the main disadvantage associated with this technique of waste immobilization is the increase in the weight and bulk of the waste sludge (Thompson *et al.*, 1979). Substituting or combining some industrial wastes or by-products with self-cementing and/or pozzolanic properties, such as fly ash and slag, with lime not only enhance the structural integrity of the resultant solid, but also reduce the cost of treatment. Addition of pure lime to the waste stream does not form a solid matrix. It will however, rise the pH and help to precipitate many of the metals of concern from the solution. At the same time, if lime is mixed with some iron and aluminum bearing minerals, such as fly ash, it will form a crude form of cement. Therefore, addition of fly ash and/or slag to lime, create a mixture which can react with the tailings in a manner analogous to portland cement.

The lime/fly ash mixture probably has been used most extensively in the United States, in terms of total volume of waste treated (Means *et al.*, 1995, Conner, 1990). The hydration reaction of the additives with the waste provide the necessary means to increase soluble ionic concentrations. When lime and other additives ionize in water, the dissolved concentrations of calcium and hydroxide ions are increased because calcium hydroxide is released from the added lime. The increase in hydroxide ions produced by hydration also increases the pH of the solution and lead to the precipitation of metals from the solution (Merritt *et al.*, 1992). However, the main hydration product of lime/fly ash and lime/slag mixture is the formation of calcium silicate hydrate gel. Providing that the waste material of concern contains sulphate, calcium aluminate sulphate hydrate, ettringite, will also form within the pozzolanic reactions. Both of these minerals are known to have the capabilities of incorporating trivalent and divalent cations and anions into their crystal structure. Ettringite acts as a host to a number of waste ions through crystal chemical substitution both in the column and channel sections of its structure. A summary of these substitutions is provided in Table 6.1. Semi-crystalline calcium silicate hydrate gel isolates ions and salts of the waste species through a variety of mechanisms, including sorption, admixing of other phases, and substitution at interlayer sites (Gougar, et al., 1996).

In acid mine drainage systems, pyrite oxidation produces important amounts of sulphate. Providing that lime based stabilization of these tailings can provide aluminum, the system has all the requirement to form and precipitate calcium trisulphoaluminate hydrates. Formation of ettringite in lime based stabilization of acid generating tailings can lead to: (I) incorporation of ions of concern into its crystal structure, (ii) replacement of OH^- and H_2O groups in the crystal lattice of ettringite, (iii) adsorption on negatively charged surfaces of ettringite and (iv) precipitation as insoluble metal-oxides and hydroxides because of alkaline nature of the composite mixture. In addition, formation of calcium silicate hydrate from the pozzolanic reactions with the fly ash in such a system will provide strength. A wide range of raw materials, including industrial wastes by-products, can be employed for the formulation of ettringite-based stabilization systems. Materials such as coal fly ash, blast furnace slag and bauxite wastes can be used in addition to commercial lime, limestone and alumina.

In order to evaluate the effectiveness of the proposed ettringite-based stabilization of lime remediated mine tailings, several samples were prepared and leached with different solvents. The leaching test is the primary and most widely used indicator of

TABLE 6. 1 REPORTED WASTE ION SUBSTITUTIONS IN ETTRINGITE MINERALS AND SYNTHETICS

$(Ca^{+2})^{VIII}$ site	$(Al^{+3})^{VI}$ site	(SO_4^{-2}) site	(OH^{-1}) site
Sr^{+2}	Cr^{+3}	$B(OH)_4^{-1}$	O^{-2}
Ba^{+2}	Si^{+4}	CO_3^{-2}	
Pb^{+2}	Fe^{+3}	Cl^{-1}	
Cd^{+2}	Mn^{+3}	OH^{-1}	
Co^{+2}	Ni^{+3}	CrO_4^{-2}	
Ni^{+2}	Co^{+3}	AsO_4^{-3}	
Zn^{+2}	Ti^{+3}	SeO_4^{-2}	
		VO_4^{-3}	
		BrO_3^{-1}	
		NO_3^{-1}	
		MoO_4^{-2}	
		ClO_3^{-1}	
		SO_3^{-2}	
		IO_3^{-1}	

(AFTER GOUGAR *ET AL.*, (1996))

chemical stability and thereby the potential environmental effects of the treated waste. Reduction in the short and long term leachability of the waste is one of the key parameters for evaluating the effectiveness of a particular stabilization process. Leaching can be defined as the process by which a component of waste is removed mechanically or chemically into solution from the solidified matrix by the passage of the solvent such as water (Environment Canada, 1990 and Poon, 1989). In general, a leaching test involves contacting a waste material with a liquid to determine which components in the waste dissolve in the liquid. The liquid, prior to contact with the waste, is called the leachant; after contact, it is called the leachate (Figure 6.1).

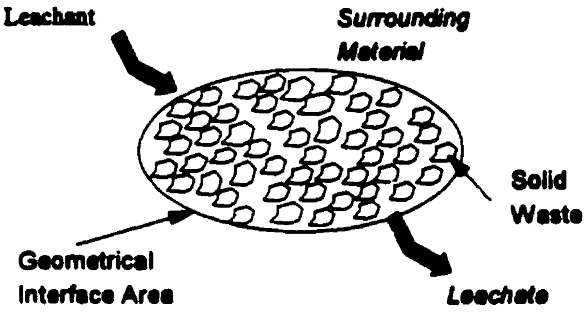


Figure 6.1 Waste Leaching System, (after Environment Canada, 1990)

6.2 Overview of Leaching Mechanisms and Leach Test

In the field, leaching of hazardous constituents from stabilized/solidified wastes is a function of both the intrinsic properties of the waste form and the hydrologic and geochemical properties of the site (U.S. EPA, 1989). Although laboratory physical and chemical tests can be used to define the waste form's natural properties, the controlled conditions of the laboratory environment are usually not equivalent to changing field conditions. At best, laboratory leaching data can simulate the behavior of waste forms under "ideal" or worst-case field conditions.

The main leaching mechanisms can be summarized as follows:

- Chemical composition of waste and leaching medium;
- Physical and engineering properties (e.g., particle size, porosity, hydraulic conductivity) of the waste and surrounding materials;

- Hydraulic gradient across the waste.

The chemistry of the waste and the leaching solution defines the type and kinetics of the chemical reactions the mobilize or demobilize contaminants in the stabilized/ solidified waste. Reactions that can mobilize contaminants adsorbed or precipitated within the waste form include dissolution and desorption. Under nonequilibrium conditions, these reactions compete with demobilizing reactions such as precipitation and adsorption. Nonequilibrium conditions generally develop when a stabilize/solidified waste is contacted by a leaching solution and can result in a net transfer, or leaching, of contaminants into the leaching solution (U.S. EPA, 1989).

The physical and engineering properties of the waste material, and the hydraulic gradient determine how a leaching solution contacts the waste materials. The hydraulic gradient, together with effective porosities and permeabilities, governs the velocity and quantity of the leaching solution migrating through the waste form.

Depending on the physical and chemical properties of the waste and leaching solution, the kinetics of contaminant transport in a porous medium are controlled by advective or dispersive mechanisms. Advective refers to the hydraulic flow duo to hydraulic gradient. Dispersion refers to the transport of contaminants via mechanical mixing in the pore solution and molecular diffusion (Yong *et al.*, 1992, U.S. EPA, 1989). Due to the low permeabilities of most stabilized/solidified wastes, the rate of contaminant transport for adsorbed or chemically bonded constituents is generally considered to be controlled by molecular diffusion rather than advection or dispersion (U.S. EPA, 1989).

6.3 Leaching Tests

Numerous laboratory leaching procedures have been developed to assess waste leachability. For the purpose of discussion, leaching tests will be separated into two broad categories on the basis whether or not the leachant is renewed:

(i) Extraction tests (no leachant renewal);

(ii) Dynamic tests (leachant renewal).

6.3.1 Extraction Tests

Extraction (or batch extraction) tests refer to a leaching test that generally involves agitation of pulverized waste forms in a leaching solution. In these tests a specific amount of leachant is contacted with a specific amount of waste for a certain length of time, without leachant renewal. The leaching solution may be acidic or neutral. Extraction tests may involve one-time or multiple extractions. The underlying assumption is that a steady-state condition is achieved by the end of extraction test (i.e., the concentrations of constituents in the leachate become constant by the end of the test). Therefore, extraction tests are generally used to determine the maximum, or saturated, leachate concentrations under a given set of test conditions.

Nonagitated extraction tests are also performed to study the physical mechanisms that are rate limiting in leaching. The underlying assumption behind a nonagitated extraction tests is that the physical integrity of the waste matrix affects the amount of contaminants that are leached during the test. Therefore, the nonagitated tests can be performed on ground or monolithic waste. The disadvantage of running a nonagitated test is that a much longer contact time is required to reach the steady-state conditions that is in an agitated test. The nonrenewality of the leachant in extraction tests results in maximum leachate concentrations (Environment Canada, 1990, U.S. EPA, 1989).

6.3.2 Dynamic Tests

In dynamic leach tests, the leaching solution is periodically replaced with new solution; therefore, this test simulates the leaching of a monolithic waste form under nonequilibrium conditions in which maximum saturation limits are not obtained and leaching rates are high. Dynamic leach tests are nonagitated and the renewal of the leachant provides the driving force for leaching.

Dynamic leach tests provide information about the kinetics of contaminant mobilization. Information is generated as a function of time, and attempts are often made to preserve the waste form's structural integrity. Results of dynamic leach tests are generally expressed in terms of a flux or mass transfer parameter (i.e., leaching rate), whereas data from extraction tests are expressed in terms of leachate concentration or cumulative fraction of total mass leached. Another important difference between extraction tests and dynamic tests is that extraction tests are short-term tests lasting from hours to days, whereas leach tests generally take from weeks to years. Due to the crushed nature of the waste and the larger amount of surface area available for leaching, extraction tests (although short term) are used to simulate "worst-case" scenarios for leaching conditions. The nonagitated monolithic leach tests are often used to simulate leaching under "well-managed", short-term scenarios in which the waste form is intact (Environment Canada, 1990, U.S. EPA, 1989).

The column leach test is another type of dynamic laboratory leaching test. This test involves placing pulverized waste in a column, where it continuously contacts with a leaching solution at a specified rate. The leaching solution is generally pumped through the waste in an upflow column setup. Column tests are considered to be more representative of field leaching conditions than batch extraction tests because of the continuos flux of the leaching solution through the waste. This test is not often used, however, because of problems with the reproducibility of the test results. These problem include channeling effects, nonuniform packing of the wastes, biological growth, and clogging of the column (Cote and Constable, 1982).

6.4 Controlling Factors for Leaching Tests

There are several factors which can significantly effect the leaching behavior of a sample. These factors can be summarized as follows:

- Sample preparation;
- Leachant composition;
- Method of contact;
- Liquid to solid ratio;
- Contact time;
- Temperature;
- Leachate separation.

Compacting the sample, particle size reduction for maximum surface area exposure, curing and liquid/solid separation are among the factors related to sample preparation. At the same time the release of contaminants from a waste in any leaching test can be strongly influenced by the leachant composition, especially at high liquid-to-solid ratios, or with the use of an aggressive solution. Chemical properties of the leachant that influence contaminant mobilization are given in Table 6.2.

TABLE 6.2 IMPORTANT FACTORS OF LEACHING COMPOSITION.

Factor	Release Mechanism Affected
pH	Dissolution/precipitation of metals, speciation of inorganic species; adsorption/desorption of organics
Eh, redox potential	Oxidation/reduction of inorganic species
Ionic strength	Ionic exchange of metals, speciation chemistry, and solubility products
Chelating and complexing agents	Metal solubility
Buffering capacity	All above properties

(AFTER ENVIRONMENT CANADA, 1990).

Since a leaching test is primarily a system to study the transfer of contaminants from a waste to a liquid, therefore, method of contact between the waste and the leachant becomes an important factor in leaching behavior of a sample. Liquid-to-solid ratio (i.e., amount of leachant in contact with the waste to the amount of waste being leached) depends on the objective of the leaching test, the solubility of species of interest, and the analytical constraints. Contact time which is the total amount of time that a leachant is in contact with a waste sample before the attainment of steady-state conditions will influence the amount of contaminants released. In extraction tests, the contact time is equivalent to the duration of the test; whereas in dynamic tests, it is a function of the flow rate, or the number of elutions, in addition to the test duration. Temperature and the method of leachate separation are other factors that greatly influence the rate of leaching from a waste sample. Amount of available surface area and the rate of diffusion of metals through the leachant are also important factors controlling the leaching of the solidified waste. Leaching is a process in which the contaminants in the solid phase are transferred to liquid phase in contact with it. Therefore, the area of the interface between the solid and the liquid in the pores is very important. A more detailed explanation of the above mentioned factors are given in a publication by Environment Canada, report number EPS 3/HA/7 (Environment Canada, 1990).

Sample porosity and pore size distribution is another important factor in determining the degree of leaching that will occur in a solidified waste. The pozzolanic reactions create a calcium-silicate-hydrate (C-S-H) gel that hardens into thin, densely packed, silicate fibrils which grow and interlace. As the water in the mix reacts with the lime and fly ash, small pores, often of capillary size, are left behind. The amount and size distribution of these pores is dependent on such factors as the water/cement ratio (excess water will produce a higher porosity) and the rate of reaction.

6.5 Leaching Test Procedure

Over the years many different tests have been developed to assess and to evaluate the performance of various stabilization/solidification methods. The environmental acceptability of a hazardous waste for land disposal in the United States and in Canada is now largely based on the results obtained from running the U.S. Environmental Protection Agency Toxicity Characteristic Leaching Procedure (TCLP) test. In the TCLP test, the test is contacted with a leachant which is determined by the type of the waste being tested for 18 to 24 hours, after which the leachate is analyzed for specific metals and organics which may have leached (U.S. EPA, Method 1311, 1990). In TCLP test which is a single step batch extraction test, waste samples are prepared by crushing the wastes to pass through a 9.5-mm screen, and liquids are separated from the solid phase by filtration through a 0.6 to 0.8 μm borosilicate glass fiber filter. Two choices of buffered acidic leaching solutions are offered under TCLP, depending on the alkalinity and the buffering capacity of the wastes. Both are acetate buffer solutions. Solution No. 1 has a pH of about 5; solution No. 2 has a pH of about 3. The leaching solution is added to the waste with the liquid to solid ratio of 20:1, and the sample is agitated for 18 hours. The leaching solution is then filtered and analyzed. The pollutant concentrations in the final leachate are used by the U.S. EPA as the current regulatory benchmark to determine the hazardous potential of a waste for land disposal purposes.

TCLP test and the modified TCLP test with different leachant solutions were used to evaluate the effectiveness of the proposed technology. The heavy metal leachability in the treated samples was evaluated using TCLP leaching procedure with buffered acetic acid solutions, sulphuric acid, acid rain simulated and groundwater simulated solutions as extract. It is believed that exposure of the remediated samples to the harsh and aggressive conditions of the TCLP test and its modified form can provide a good understanding of the long term effectiveness of the treatment technology. The mechanisms responsible for the heavy metal mobility reduction were also investigated using several supplementary experimental tools, including x-ray diffraction, and scanning electron microscopy with energy dispersive x-ray.

6.6 Experimental Procedures

In order to evaluate the effectiveness of lime fly ash treatment of acid producing tailings, and study the role of ettringite formation in immobilization of metals of concern, laboratory leaching program based on the principal of toxicity characteristics leaching procedure (TCLP) were set up. The TCLP test is a single step batch extraction test since during the experiment a suspension consisting of acetic acid solution and pulverized solid is mixed in a container. The pollutant concentrations in the final leachate (extract) are used by the U.S. EPA and Environment Canada as the current regulatory benchmark to determine the hazardous potential of a waste for land disposal purposes.

A sample of acid producing tailings from a northern Quebec mine were treated with different percentages of lime and high calcium fly ash (class C) in order to raise the pH and provide the conditions needed to form and precipitate ettringite. The treated samples were leached with the buffered acetic acid solution based on the principal of TCLP. The specimen preparation involved dry mixing of all constituents in designated percentages, followed by addition of water and curing under standard condition (25 degree Celsius temperature, and 95% humidity). The amount of water added to the solid mixes were such that as to obtain the minimum amount of moisture that would saturate the waste completely (according to ASTM C-128) plus water to binder ratio of 0.3 by weight for the pozzolanic reactions to proceed. By the term "binder" it is meant the sum of the weights of lime and fly ash added to the dry waste. Water to binder ratio was chosen based on principles of cement hydrology and pozzolanic reactions (Shi and Day, 1995; Mehta and Monteiro, 1993; Alasali and Malhotra, 1991).

Prior to any treatment of the specimens, acid digestion of the tailings sample was performed according to the U.S. EPA method 3050 (1986). The elemental analysis of acid digested tailings sample is given in Table 6.3. Sulphate content was determined by ion chromatography and the optimum lime content was determined based on method proposed by Eades and Grim (1966). The optimum lime content is defined as the minimum percentage of lime, CaO, that needed to rise the pH of the specimen to 12. A complete description of the test procedures and waste characterization is provided in Chapter 3.

TABLE 6.3 ELEMENTAL ANALYSIS OF UNTREATED SAMPLE

Element	Tailings Sample (ppm)
Al	206
As	23
Ca	0
Cd	0
Cr	0.5
Cu	17
Fe	3332
K	6
Mg	27
Mn	5
Pb	34
Si	18
Zn	25

Since the pH stability field for the formation of ettringite is around 12, the binder ratio was designed such that the minimum amount of lime required to reach such pH, would be the upper limit of lime addition. Therefore, one sample would have this amount of lime without addition of any other binder (i.e., fly ash), as the added lime would be enough to obtain the required pH. Another set of specimens would receive lime in an amount that is 1% less than the optimum lime content of the waste. This decrease in lime content would be compensated by the addition of 0, 10, 15 and 20% by weight (relative to waste) of fly ash type C. The third set of specimens received lime in an amount 2% less than the optimum lime content in order to reach the pH of 12, and again the deficiency in lime was compensated by the addition of 0, 10, 15 and 20% by weight of fly ash. The same analogy was followed for the subsequent specimens and one sample received no additives at all to be used as the control specimen.

The samples were initially dry mixed and the required water content to surface saturate the samples were added and then the resultant low pH slurries were allowed to mellow in closed plastic containers for 24 hours at 25°C and 95% relative humidity. Subsequently, binders in the form of lime and fly ash type C in designated percentages plus water to binder ratio of 0.3 were added to the samples and resultant paste were thoroughly mixed and allowed to cure at 25°C and 95% relative humidity.

The cured samples were leached using two acetic acid solutions, using TCLP leaching procedure. The extraction experiment was conducted by adding 40 ml of leachant to 2 ml of slurry and mixed for 18 hours in a screw-cap plastic container held on an end-over-end shaker at a speed of 30 rpm. The resultant slurry suspension were then filtered using 0.8 μm borosilicate glass fiber filter and then the metal concentration in the solution were determined using Perkin-Elmer 2100 atomic absorption spectroscopy system. All standards contained similar matrix to that of the analyte.

6.7 Results and Discussion

Numerous batch tests have been performed on stabilized/solidified wastes in an attempt to assess the potential of ettringite formation and to elucidate the metals binding mechanisms. The first leaching test consists of the United States E P A, TCLP test. Samples of treated waste with different combination of lime and fly ash class "C" were subjected to TCLP leaching procedure. Concentration of elements of concern in the TCLP extract, following different curing time are given in Figures 6.2 to 6.7, as a function of the amount of lime (% by total weight of waste) added in each specimen. Concentration of iron, magnesium, copper and zinc in TCLP extract were monitored for 360 days. Calcium, aluminum and sulphate concentrations were also monitored in order to assess the formation of ettringite in the samples.

The high pH environment created as a result of lime addition to the samples reduced the solubility of Fe, Mg, Cu and Zn. The solubility of all the elements were the lowest after the addition of 5% lime to the samples. That is, 5% is the minimum lime content for which treatment was most effective in terms of harsh TCLP leaching procedure. This conclusion was further evident from the results of long term pH analysis of samples which was discussed in chapter 5. Samples which contained less than 5% lime, had a tendency to lower their pH, and subsequently releasing more of soluble metals to the leachant. Addition of fly ash to the samples, did not reduced the solubility of elements significantly. However, in the case of Cu and Zn, fly ash addition was more effective. Such results can be explained if the effect of lime and fly ash content on the pH of the respective mixes is considered. The pH values obtained as a result of lime and fly ash addition is plotted as part of Figures 6.2 through 6.7. These figures indicate that when 5% or more lime is added to the samples, pH of near 11 or higher is attained. Addition of 10, 15 and 20% fly ash has further stabilized the pH value over the period of 360 days. However, the difference in pH value obtained after the addition of 15% or 20% fly ash is not so significant to justify the higher consumption of fly ash. This could be attributed to the solubility of fly ash in the sample. After the addition of 10% fly ash to the samples, tailings mixes were saturated with respect to fly ash content. Increasing the fly ash from 10% to 15% and 20% has not altered the characteristics of the mixes significantly.

The pH diagram in Figure 6.2 shows that addition of fly ash to the samples containing 4 and 5 percent lime did not change the pH significantly. After one day of curing, samples containing fly ash had the same pH as the sample without addition of fly ash. The rate of pH increase is very sharp up to the 4% lime addition to the mixes, while the rate of pH change stabilizes for the samples with 4 and 5 percent lime. This trend is the same during the 360 days of curing. However, after 140 days of curing, the pH of all the mixes were slightly decreased (Figure 6.6). This is an indication of oxidation process, which is taking place in the samples. The oxidation process and the decline in the pH were further evident after 360 days of curing (Figure 6.7). It is interesting to note that all the samples were cured at 25°C and 95% relative humidity which provides the ideal environment for the oxidation of the reactive tailing. However, it is interesting to note that samples containing 5% lime and fly ash, maintained the pH condition of near 11 even after 360 days of curing. Therefore, fly ash addition has helped to stabilize the pH condition and reduced or slowed the oxidation process in the samples.

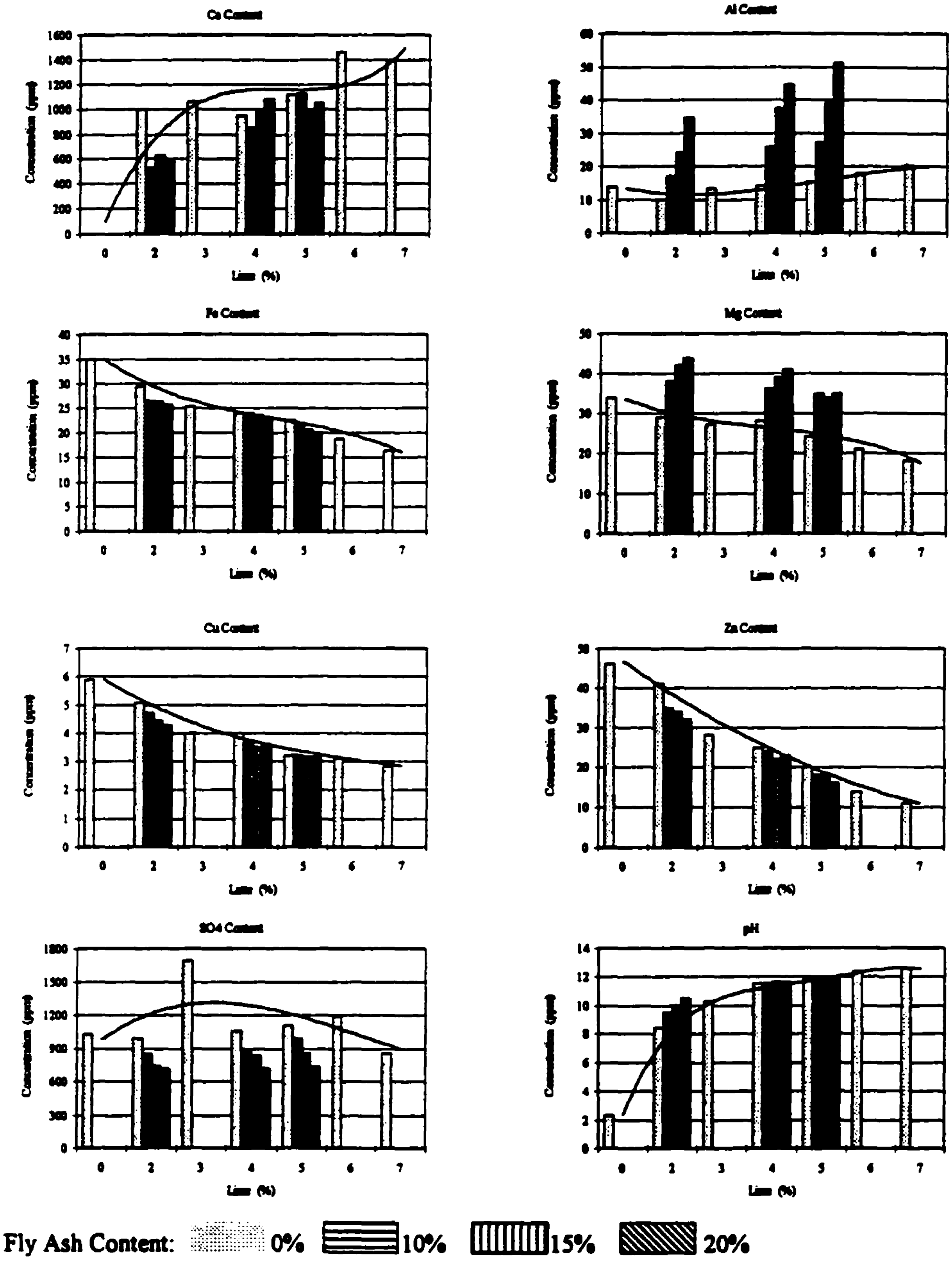


FIGURE 6.2: ELEMENTS CONCENTRATION VS. LIME CONTENT; DURATION 1 DAY.

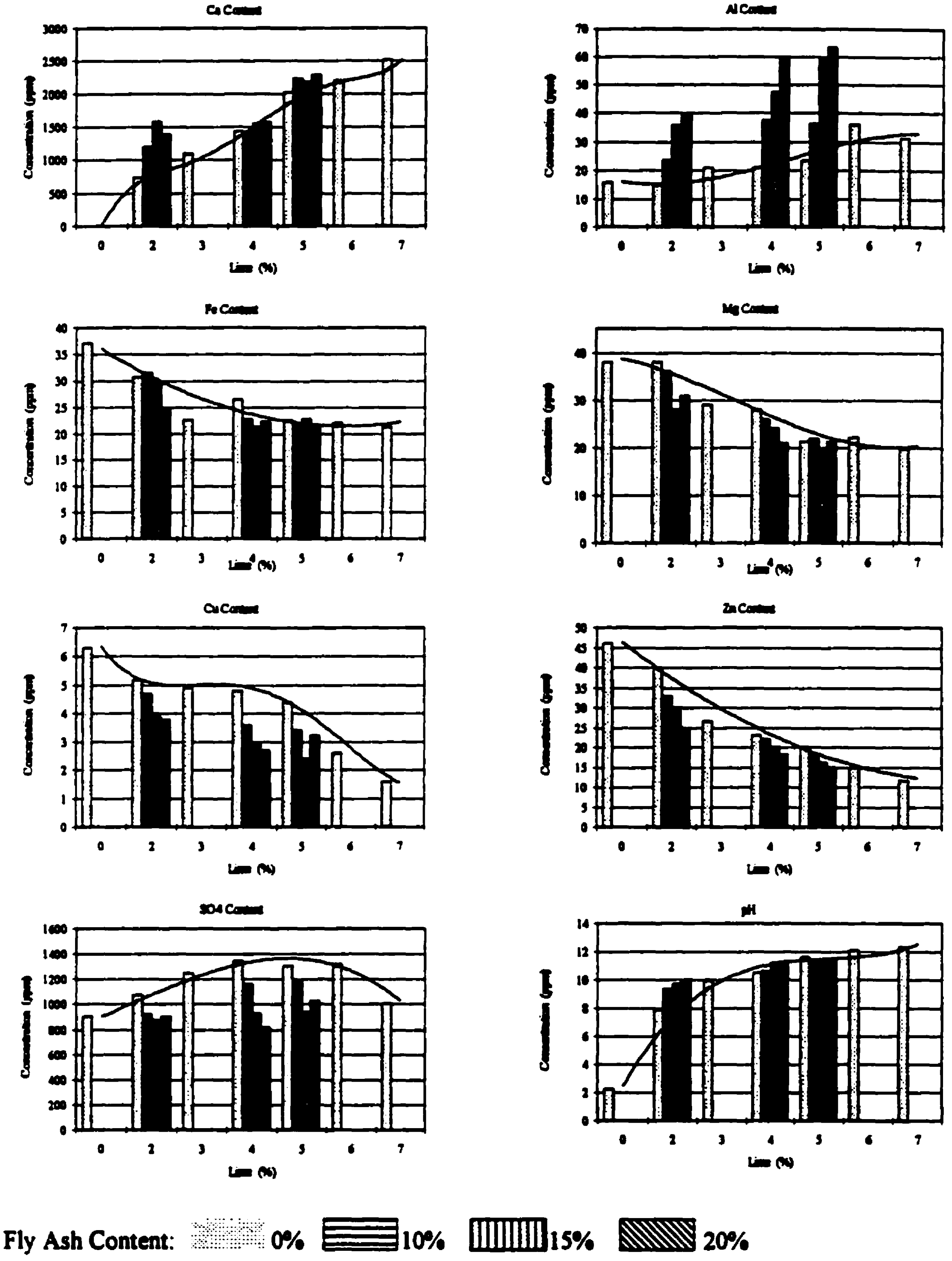


FIGURE 6.3: ELEMENTS CONCENTRATION VS. LIME CONTENT; DURATION 14 DAYS.

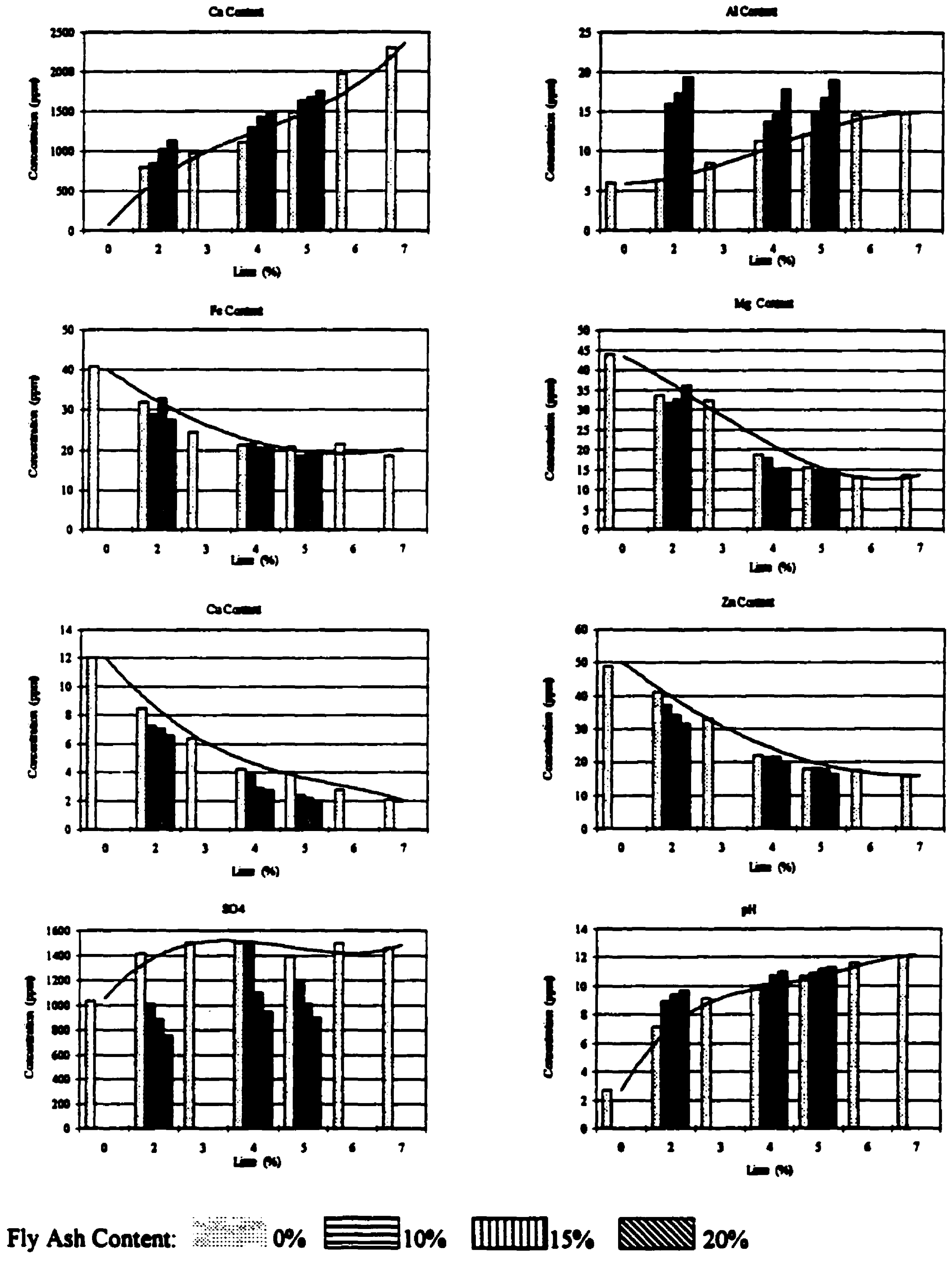


FIGURE 6.4: ELEMENTS CONCENTRATION VS. LIME CONTENT; DURATION 35 DAYS.

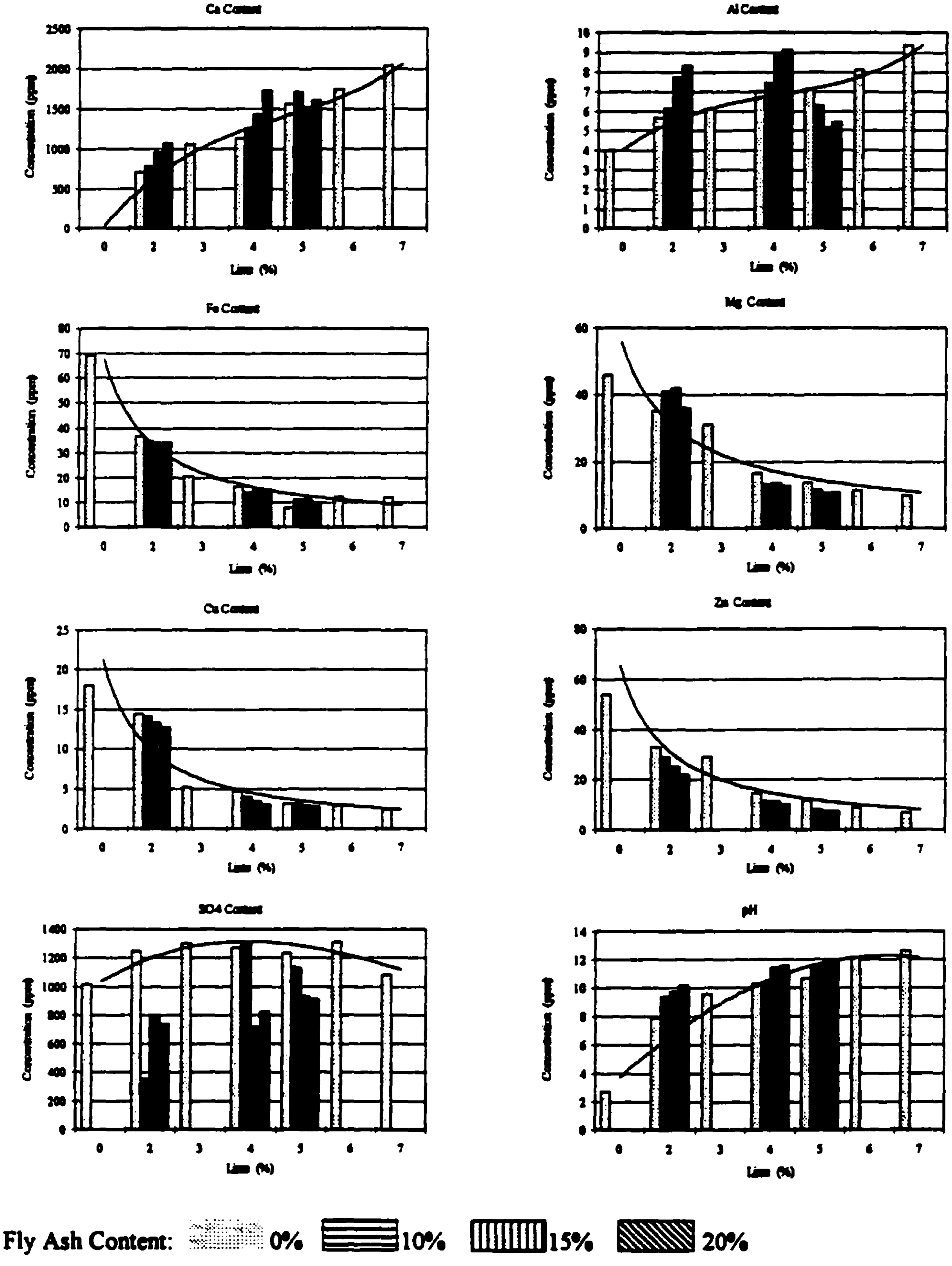


FIGURE 6.5: ELEMENTS CONCENTRATION VS. LIME CONTENT; DURATION 70 DAYS.

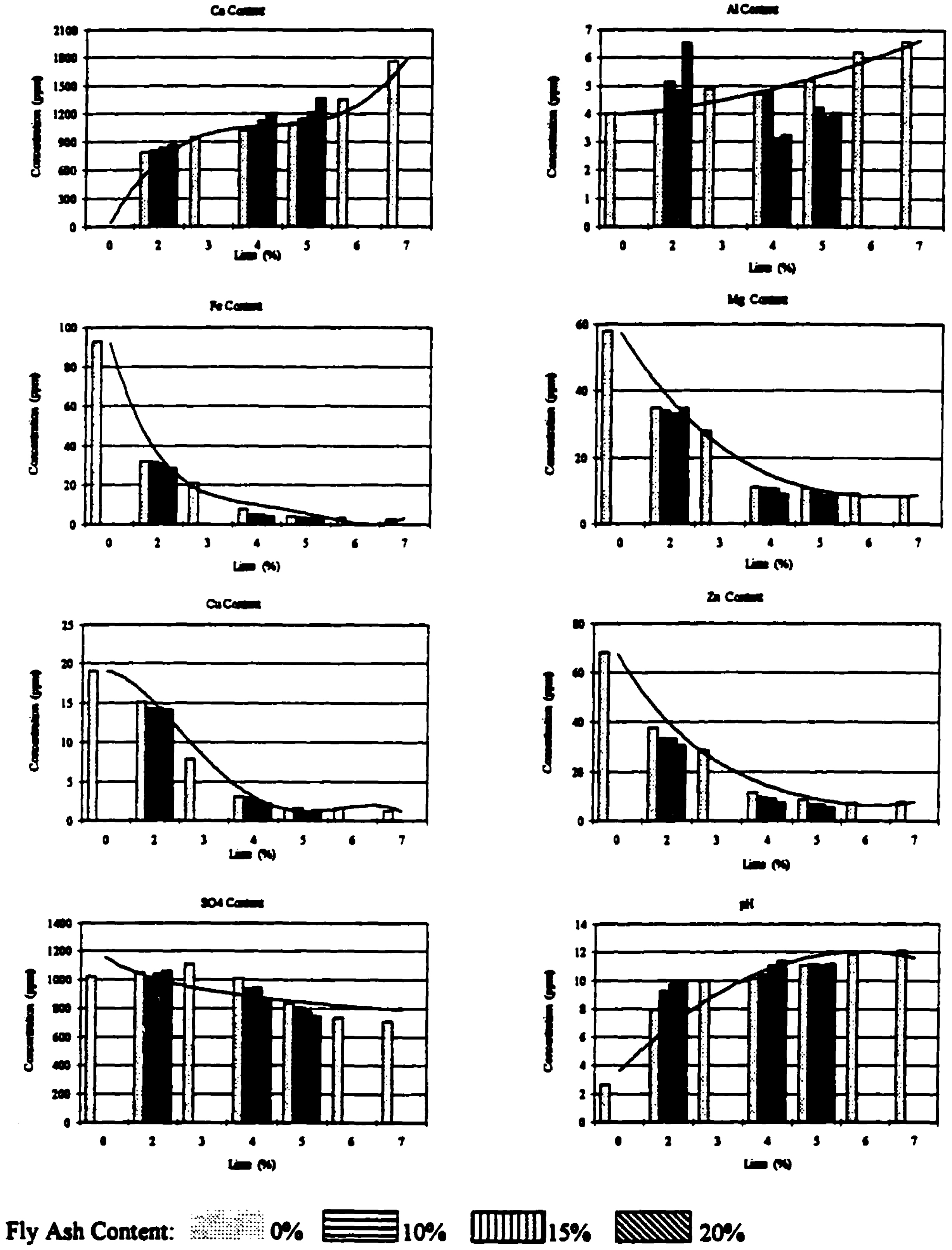


FIGURE 6.6: ELEMENTS CONCENTRATION VS. LIME CONTENT; DURATION 140 DAYS.

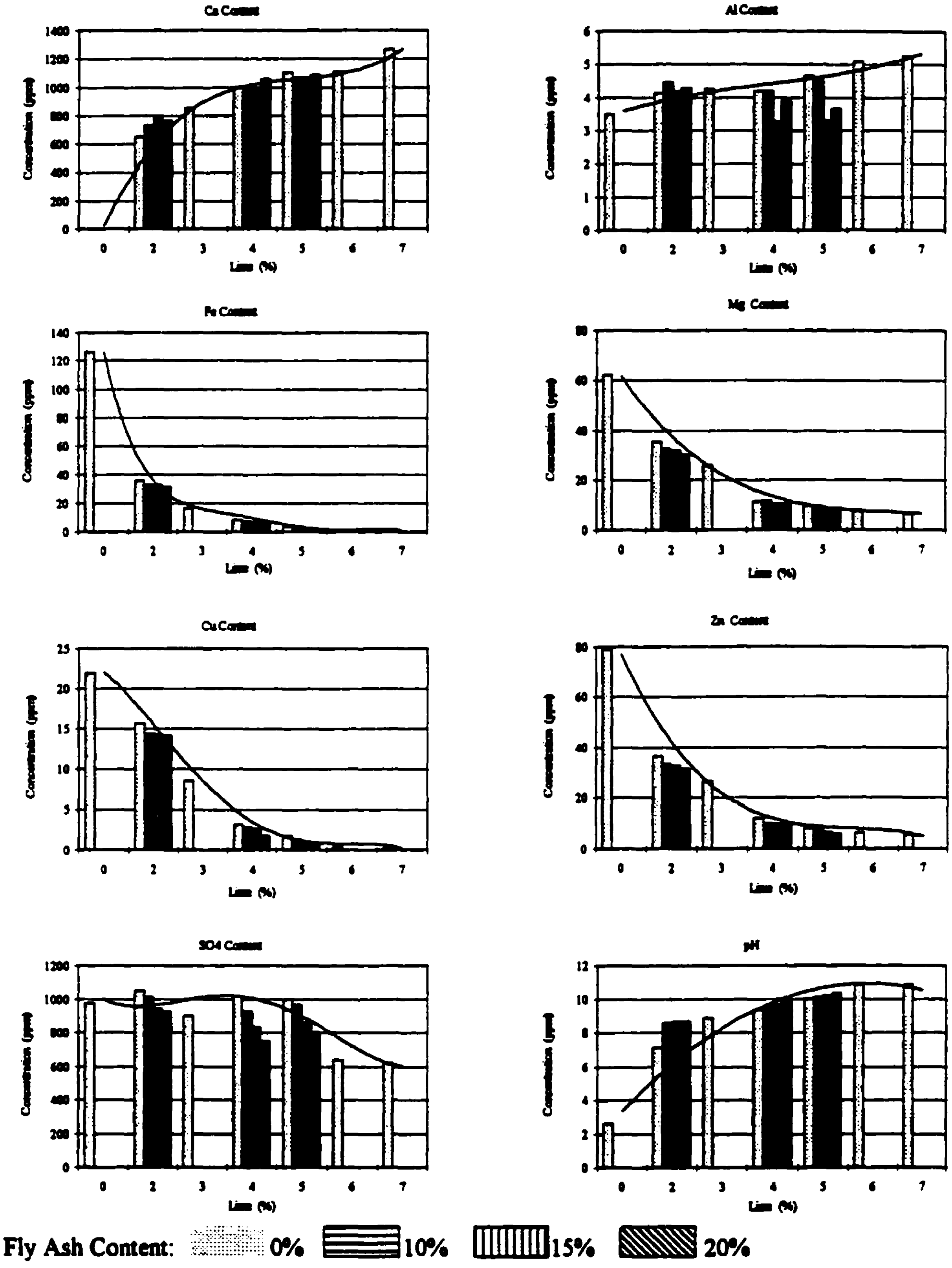


Figure 6.7: Elements Concentration vs. Lime Content; Duration 360 Days.

The iron content was drastically reduced after 360 days of curing. The greatest rate of iron solubility was observed after 35 days of curing and its solubility had reached its equilibrium within the 140 days of curing. Iron solubility was not effected upon the application of 2% and 3% lime and its amount in the solution remained almost constant throughout the 360 days of measurement. Magnesium content, on the other hand, was initially increased upon the addition of fly ash to the samples. While the application of 5% lime in conjunction with 10 to 20% fly ash reduced the solubility of magnesium to one forth of its original concentration after 360 days of curing.

Copper and zinc have behaved very similar throughout the treatment period. This is particularly true with the application of 4 to 5% lime as well as fly ash to the samples. The magnitude of the metal content in the harsh TCLP solution were gradually reduced with the higher lime and fly ash content in the solution and a steady state equilibrium had been achieved after 140 days of curing.

In discussing the solubility of metals from a waste matrix with respect to the pH condition, only one mechanism that could be responsible for immobilization of metals is considered, that is the precipitation. However, as it was discussed in chapter 2, there are three distinct mechanisms that could be responsible for the entrapment of the metal species in the stabilized waste matrix. First the formation of insoluble metal compounds during stabilization-induced high pH conditions. The second possible mechanism is incorporation of the metal species into crystal structure of the cementitious compounds such as ettringite. The third possible mechanism is that due to the excessive formation of high surface area cementitious compounds, the metal species are trapped (adsorbed) in a low permeability matrix. In order to further elucidate these possibilities, and particularly study the role of ettringite in immobilization of metals of concern in mine tailings, further attention has to be given to calcium, aluminum and sulphate content (the principal constituents of ettringite) of the samples under study.

As discussed previously, addition of 5% lime particularly when it was accompanied by certain amounts of fly ash has provided an important amount of calcium in the solution. Although, the calcium presence in the solution has decreased over the period of 360 days, its solubility remained high enough to provide the necessary conditions for ettringite formation. The decrease in calcium concentration could be due to the formation of ettringite or calcite in the samples.

Aluminum concentration in the samples without any additives were quite low, while its concentration increased with the addition of fly ash (Figures 6.2 to 6.7). As it was expected, the solubility of aluminum was highest in high pH environment as the aluminum solubility is highest in pH of near 12. However, even with the addition of fly ash, the availability of aluminum was below the threshold of the amounts needed for ettringite formation. The thresholds of different compounds needed to form and precipitate the ettringite in the tailings sample under investigation were established in chapter 5, and it was concluded that based on the availability of calcium and sulphate, much more aluminum is needed to form the ettringite. This conclusion justifies the use of additives rich in aluminum such as fly ash as well as the possibilities of incorporating other waste materials and by-products rich in aluminum such as bauxite to optimize the formation of ettringite in our samples.

While addition of 10, 15 and 20% fly ash increased the availability of soluble aluminum in the samples, the highest amount of aluminum was recorded when 4 to 5% lime was also added to the samples. As it was stated earlier, this could be attributed to the high pH environment of those samples. Although the addition of fly ash to the samples provided up to 5 times more aluminum than those samples without any fly ash, this amount is still below the threshold of aluminum requirement (as established in chapter 5) for ettringite formation in the samples under investigation. Moreover, after 14 days of curing, the aluminum content of the samples decreased significantly. The reduction of aluminum content is attributed to the formation of ettringite and ettringite like minerals in the treated samples.

The sulphate content in the leachate remained very much the same throughout the experiment, while this amount was lower than the total soluble sulphate in the sample (1600 ppm, table 5.2). However, over the period of 360 days, and particularly with the addition of fly ash to the system, sulphate leachability was slightly decreased. Such behavior was tentatively attributed to the presence of ettringite in the system which contained fly ash. As it was discussed before, addition of fly ash to such a system not only tend to stabilize the pH condition to a desired plateau (near 12), but it also provided more aluminum to the system which depends on it for the formation of ettringite.

In the previous chapter, the optimum condition for the formation of ettringite in tailings samples under investigation was established. The high sulphate and its low aluminum content of the tailings samples required that a source of aluminum which could also help to elevate the pH of the mixtures be employed. A suitable additive which could satisfy both requirements is fly ash class C. However, since one of the major goals in any remedial project is to reduce the cost of treatment, the high consumption of lime and fly ash is not desirable. Therefore, based on experiments conducted previously (chapter 5; availability of aluminum and stabilization of pH condition), as well as the results of leaching studies, it was concluded that 10% fly ash can provide the appropriate conditions needed for stabilization to take place and ettringite to be formed in the samples. The higher application of fly ash (more than 10%) tends to remain as unreactive in the solution.

The metals concentration extracted using different percentages of lime with 10% and 20% fly ash content are compared in Figure 6.8. The pH of extraction solution for samples received no lime were around 2.5. When 5% lime with 10% fly ash was added to the mixes the pH of extraction solution was increased to near 12 which is approximately the pH of a saturated $Ca(OH)_2$ solution. The calcium and aluminum content of extraction solution were highest with the addition of 5% lime over the 360 days of testing. A closer examination of Figure 6.8 shows that all the elements of concern have reached their solubility equilibrium after 140 days of curing and increasing the fly ash content from 10% to 20% has not affected the solubility of elements of concern significantly.

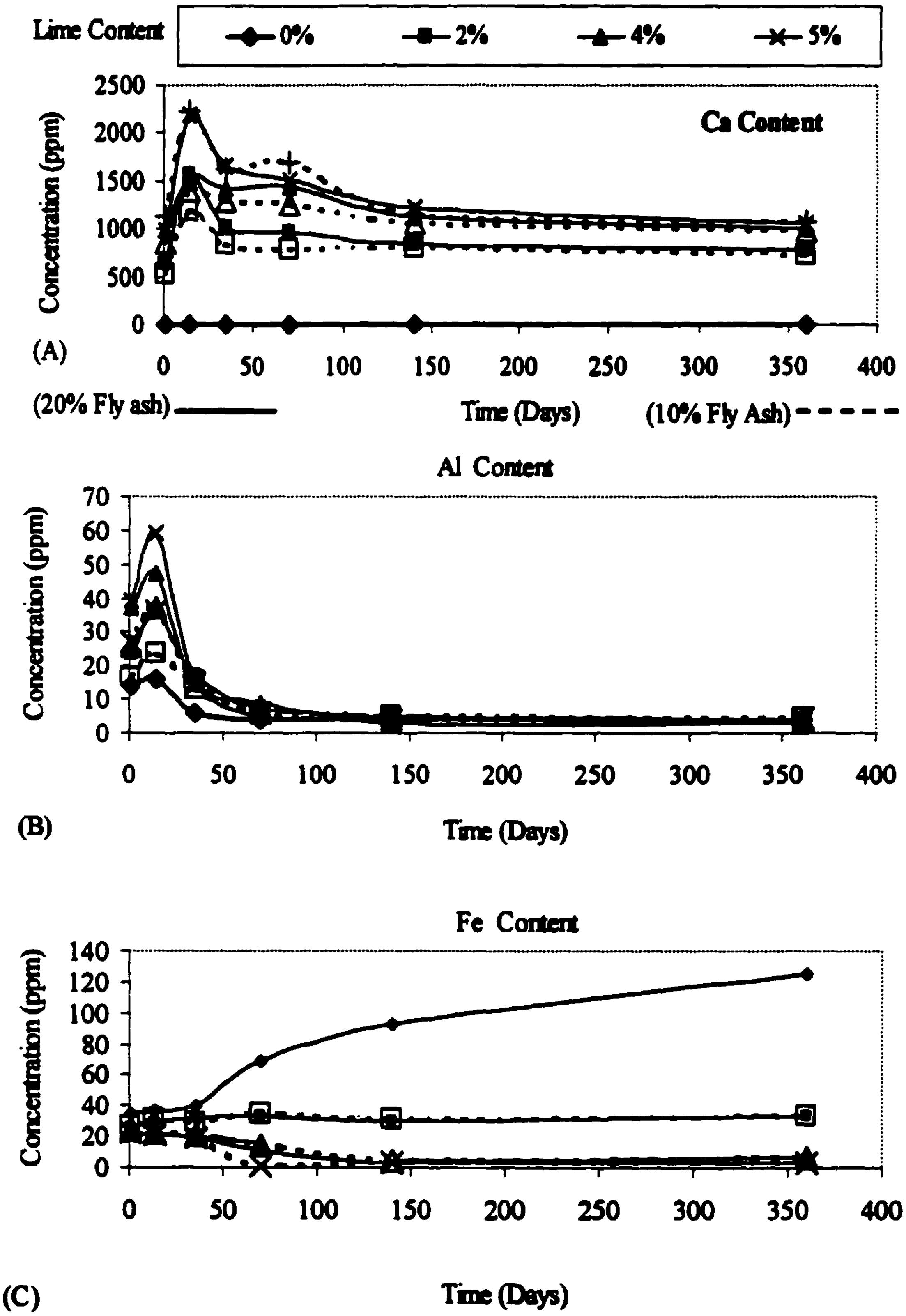


FIGURE 6.8. ELEMENTS CONCENTRATION VS. TIME; (FLY ASH CONTENT 10% AND 20%)

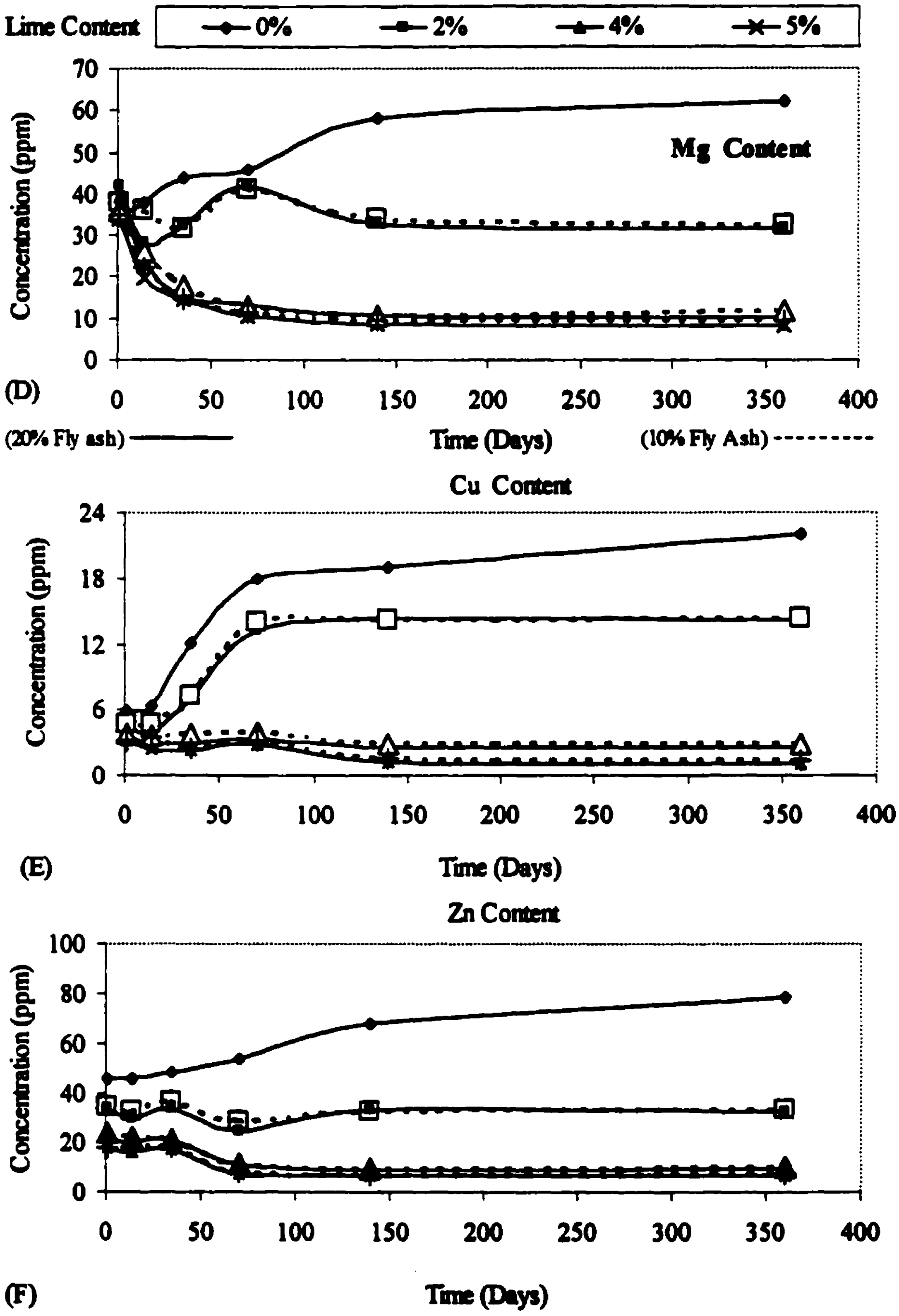


FIGURE 6.8 (CONTINUE) ELEMENTS CONCENTRATION VS. TIME; (FLY ASH CONTENT 10% AND 20%)

The effect of 10% and 20% fly ash and different percentages of lime on iron content is shown as part of Figure 6.8. This figure indicates that the solubility of iron has significantly decreased after the addition of 5% lime. The iron content of the leachate was stabilized after 140 days of curing and has shown a decrease of about 99.9% compare to the total soluble iron content of untreated samples. Similar results (though with not the same level of leachability reduction) were recorded for magnesium, copper and zinc. Application of 5% lime to the samples has resulted in the appearance of the highest quantity of aluminum and calcium in the solution. While 5% lime provides the sufficient quantity of calcium for calcium hydrate reactions to take place in the samples, the quantity of aluminum released in the samples has not elevated significantly.

The effects of 5% lime and 10% fly ash addition on the metal leachability of the tailings sample, as determined using TCLP method, is shown in Figure 6.9. The results show the decrease in the metal concentration while the calcium and aluminum content are elevated and sulphate content is stabilized. This figure shows that the application of 5% lime and 10% fly ash has effectively stabilized the elements of concern over the 360 days period. Figure 6.9. represents the best results which were obtained from the leachability study.

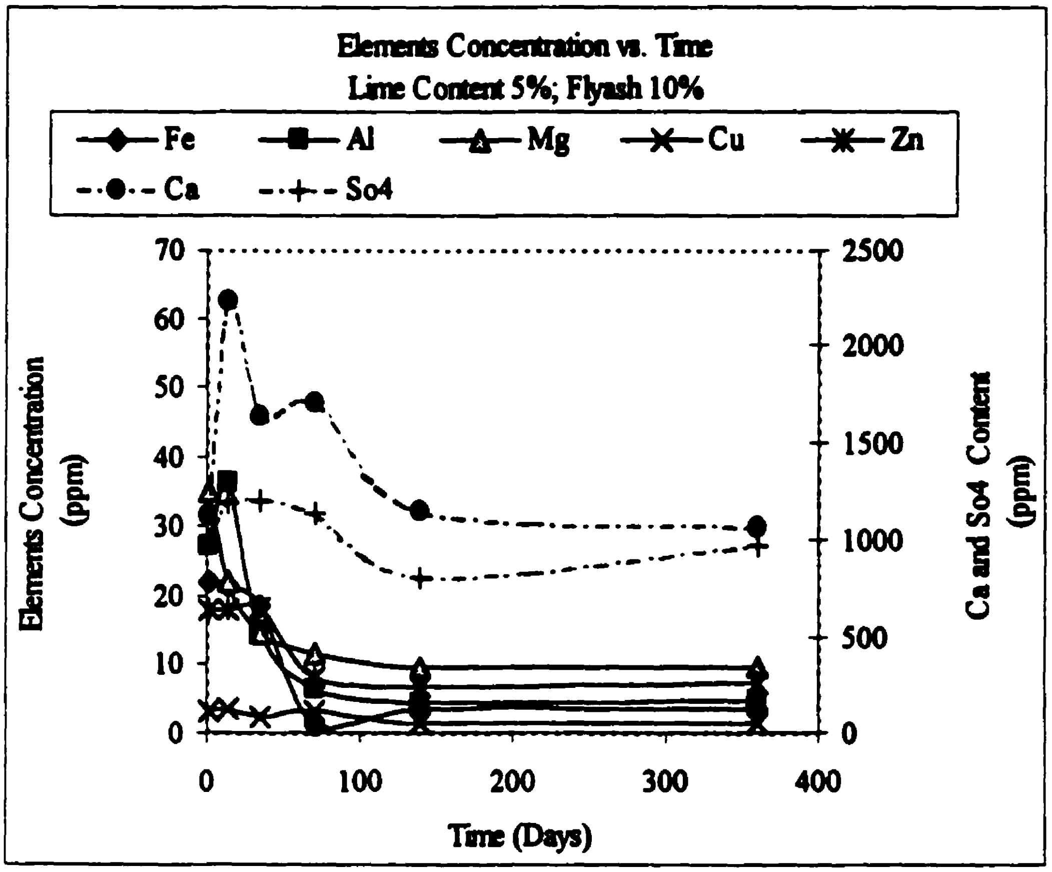


FIGURE 6.9. ELEMENTS CONCENTRATION VS. TIME; LIME CONTENT 5%, FLY ASH CONTENT 10%

6.8 X-ray Diffraction Analysis

In order to establish whether the pozzolanic reactions have occurred in the lime, and/or lime plus fly ash treated mixes, samples cured for 28 days were analyzed using X-ray diffraction techniques. Figure 6.10 represents the XRD patterns of the lime treated as well as untreated samples. The XRD patterns indicate that only after the addition

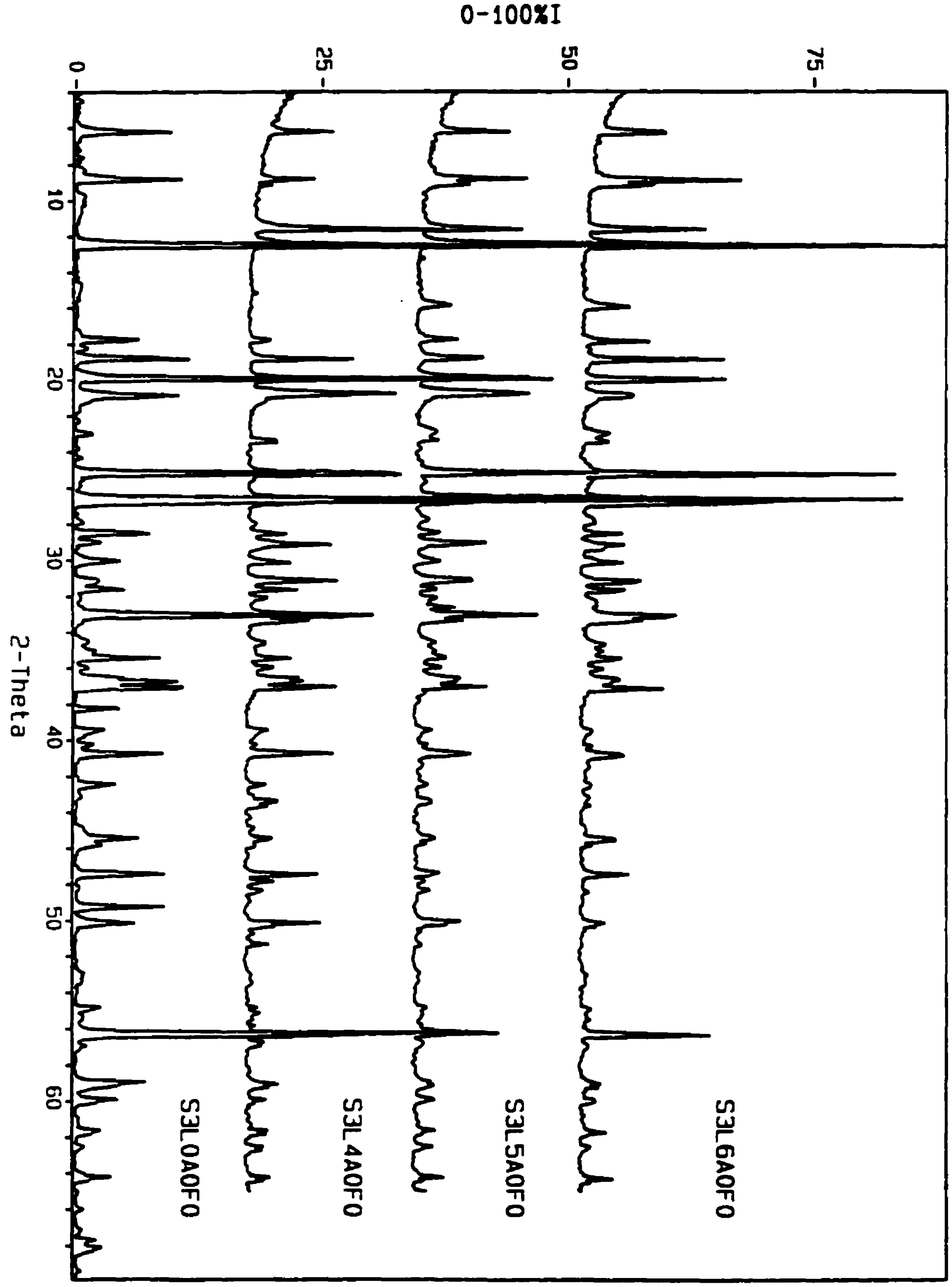


FIGURE 6.10 THE X-RAY DIFFRACTION ANALYSIS OF LIME TREATED SAMPLES

of 4% lime to the samples, ettringite peaks in the mixes were observed. As the amount of lime in the mixes increased, stronger ettringite peaks in the XRD pattern were detected. Addition of 4% lime has caused the formation of gypsum in the sample. Gypsum had been formed as a result of reaction between the added calcium hydroxide and the sulfate ions in the sample. However, the increase in the amount of lime from 4 to 5 and 6% has resulted in decrease in the gypsum content while more ettringite has formed in the samples. As it is shown in Figure 6.10, the increase in lime content and the subsequent increase in the amount of calcium added to the samples, has resulted in an increase in the quantity of calcium silicate hydrate, ettringite and reduction of gypsum content of the mixes. These findings are more clearly shown in Figure 6.11, which compares the formation of ettringite with gypsum and calcium silicate hydrate in the mixes under the same conditions.

As the magnitude of the added lime increases, the ettringite and calcium silicate hydrate peaks are become stronger while the gypsum peaks show a significant decline. The result of the leachability study confirms these findings. While the addition of 4% lime causes the increase in the calcium content of the samples, gypsum is formed and the elemental analysis of the samples (from leachability study) did not show a significant decrease in the amount of iron, magnesium, copper and zinc. However, further increase in the amount of lime, stabilizes the pH of the samples and forms more ettringite and calcium silicate hydrate, which decreases the amount of gypsum in the samples. Addition of 5% lime to the mixes caused a substantial decrease in the magnitude of the iron, magnesium, copper and zinc, which

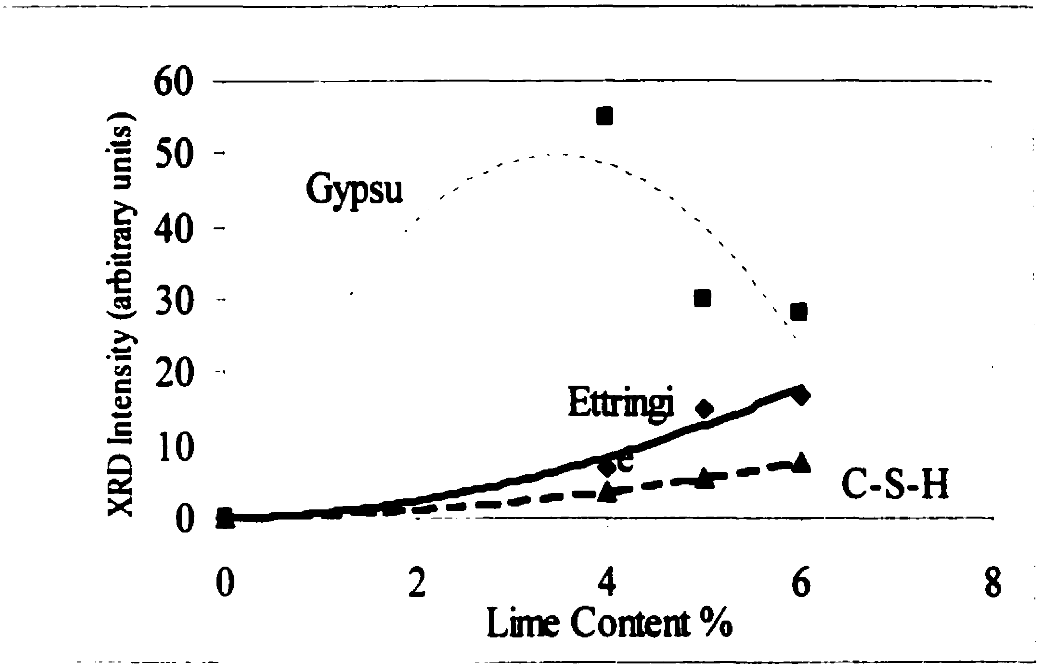


FIGURE 6.11: EFFECT OF LIME ON ETTRINGITE, GYPSUM AND PORTLANDITE FORMATION

were leached from the mixes. These results can be correlated to the formation of ettringite mineral in the mixes. Several other studies by other researchers have concluded that the present of metal oxides or hydroxides such as zinc and iron can promote the formation of ettringite in the proper environment (Vempati *et al.*, 1995; Trussell, S. and Spence, R.D., 1994; Poon *et al.*, 1986; Tashiro *et al.*, 1979). Increasing the lime content of the mixes from 5% to 6% resulted in stronger peak intensities for ettringite mineral and decline in the intensities of the peaks corresponding to gypsum. However, the differences between the intensities of the X-ray diffraction patterns of 5% and 6% lime is not as substantial as the difference in the patterns of 4% and 5% lime. Therefore, it is concluded that 5% lime is the optimum lime content to form and precipitate ettringite in the samples.

In order to investigate the effect of fly ash addition to the mixes, samples with 4% lime and different percentages of fly ash were prepared. Fly ash class C in the amount of 10 and 20% were added to the mixes and its effect on the peak intensities of ettringite, gypsum and calcium silicate hydrate were investigated. Figure 6.12 represents the XRD pattern of these mixes.

As it was anticipated, due to the rich calcium, silicate and aluminum content of the fly ash, its addition has resulted in the formation of stronger peak intensities for the ettringite and calcium silicate hydrate, while has caused an adverse affect on the gypsum in the samples. This observation is clearly shown in Figure 6.13.

As the fly ash is being added to the mixes, stronger ettringite peaks are appeared in the XRD pattern, while a constant reduction in the magnitude of gypsum is noticeable. The XRD intensities of characteristics peaks for ettringite which are shown in Figure 6.13 indicate that the rate of growth for ettringite is higher with 10% fly ash addition than with 20% fly ash. The slope of the curve becomes almost flat as the solubility of the fly ash has reached its maximum capacity with the addition of 10% fly ash.

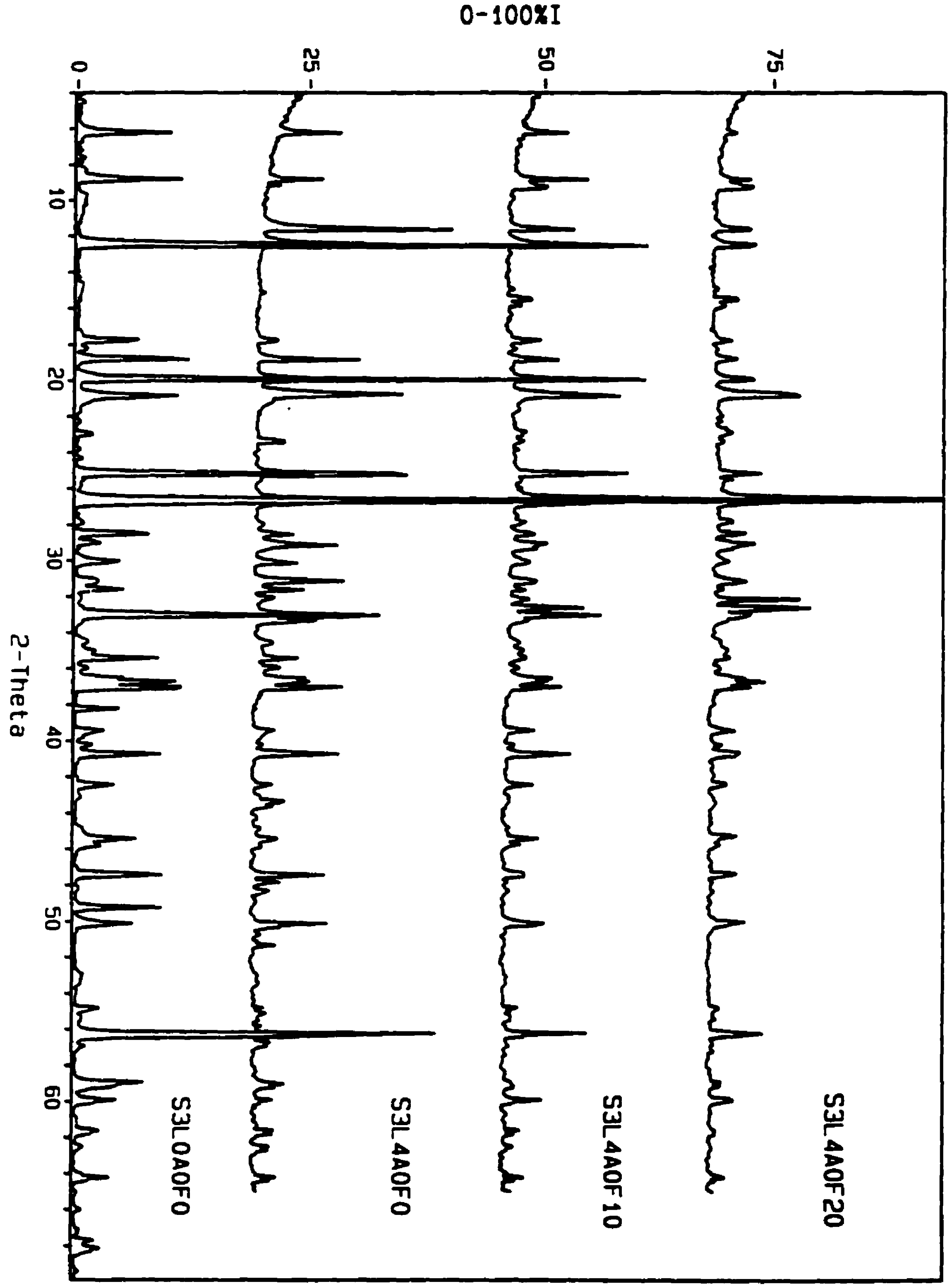


FIGURE 6.12 THE X-RAY DIFFRACTION ANALYSIS OF LIME AND FLY ASH TREATED SAMPLES

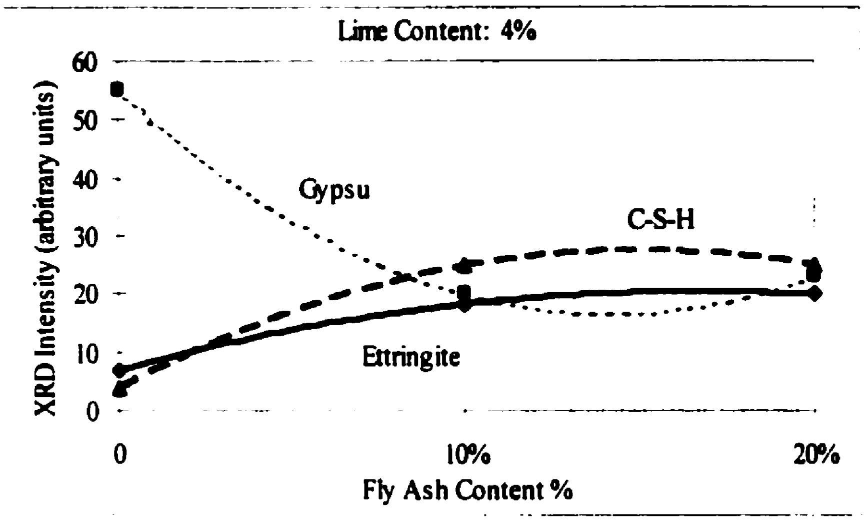


FIGURE 6.13: EFFECT OF FLY ASH ON ETTRINGITE, GYPSUM AND PORTLANDITE FORMATION

Once again, the formation of ettringite and calcium silicate hydrate are analogous in their growth patterns. The higher availability of calcium and aluminum as a result of fly ash addition resulted in the stability of the pH and higher formation of minerals ettringite and calcium silicate hydrate.

Figure 6.14 shows the XRD pattern of the samples treated with 5% lime and 0, 10 and 20% fly ash. Addition of 5% lime without the application of fly ash has led to the formation of gypsum and ettringite in the samples. However, the peak intensities of gypsum in this case are lower than in the case of 4% lime and no fly ash. Lower gypsum in the case 5% lime can be correlated to the formation of ettringite in the same sample. As the excess amount of lime (from 4% to 5%) has stabilized the

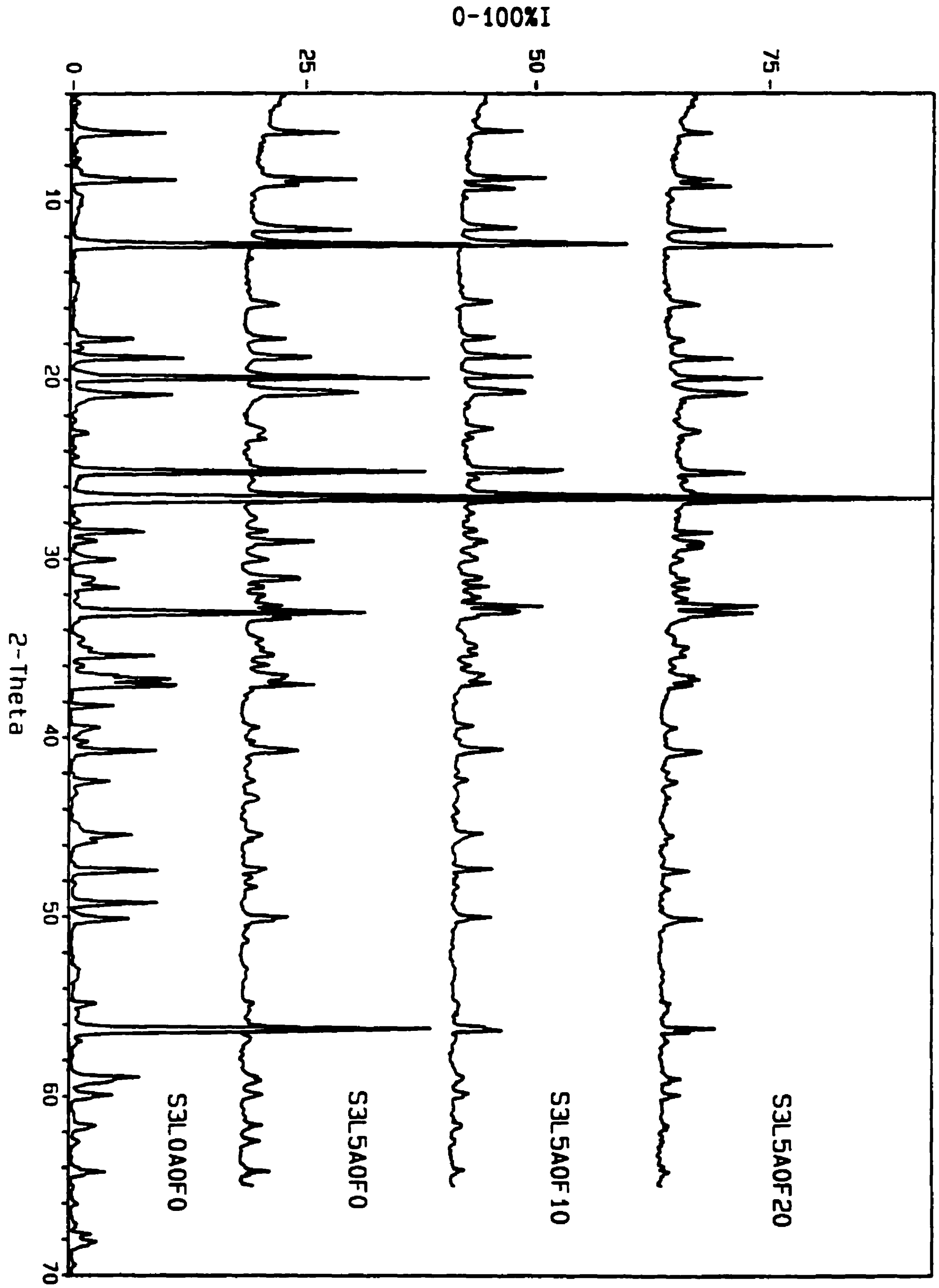


FIGURE 6.14 THE X-RAY DIFFRACTION ANALYSIS OF 5% LIME AND FLY ASH TREATED SAMPLES

pH of the sample to near 11.5, ettringite has formed. As it was expected, increase in the lime content to 5% and addition of 20% fly ash has resulted in a significant increase in quantity of calcium silicate hydrate present in the samples. Once more, this observation is shown in Figure 6.15.

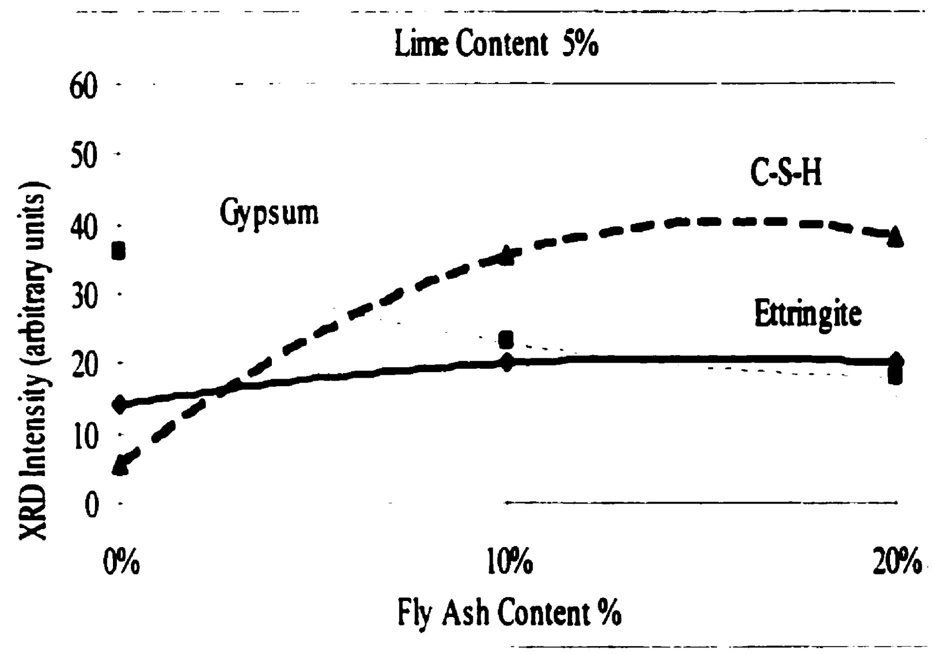


FIGURE 6.15: EFFECT OF FLY ASH ON ETTRINGITE, GYPSUM AND PORTLANDITE FORMATION

Figure 6.16 (a, b, and c) represents the XRD patterns of lime treated samples for 3, 28, and 75 days of curing. A sample was treated with 4% lime, as the principal binding agent, and the XRD pattern of ettringite from the onset of its complete transformation (in 75 days of curing time) was followed. Addition of 4% lime after 3 days of curing has led to the formation of gypsum (Figure 6.16, a).

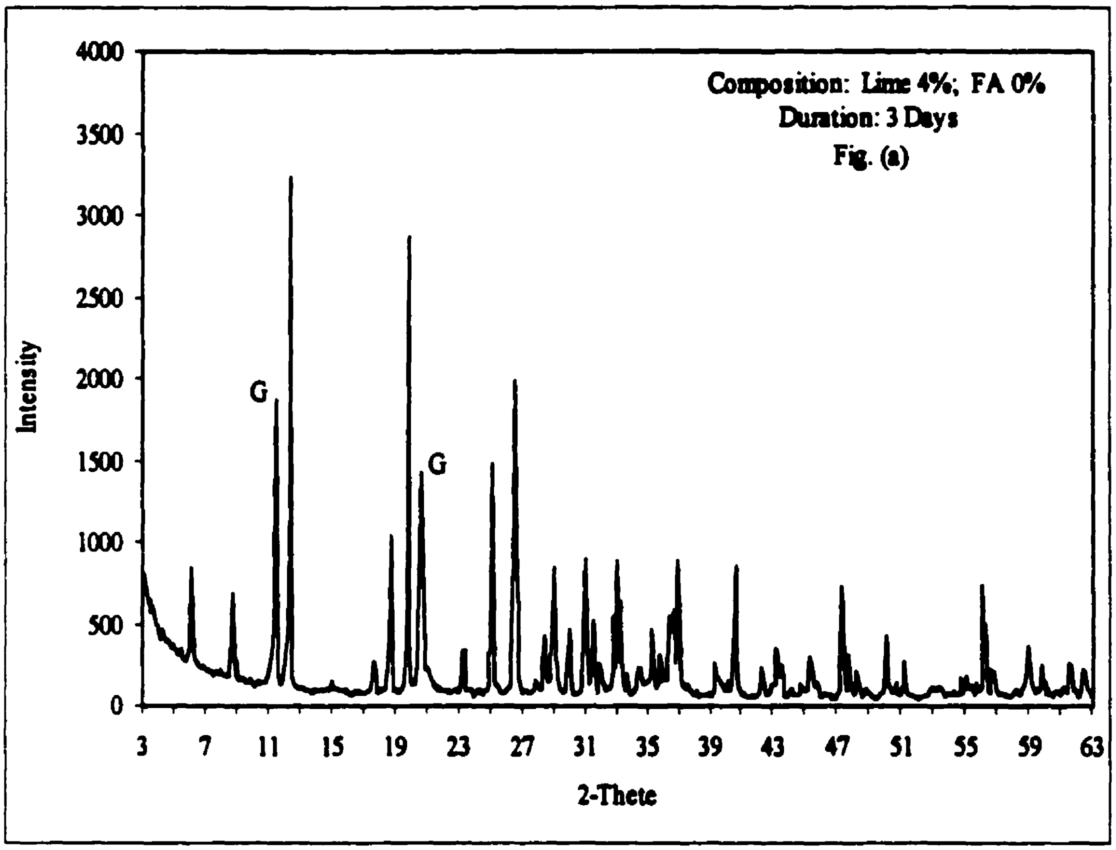


FIGURE 6.16 (a) X-RAY DIFFRACTION ANALYSIS OF 4% LIME TREATED SAMPLE (G = GYPSUM)

After 28 days of curing, the ettringite peaks were observed (Figure 6.16, b), while at the same time, more gypsum has also formed in the samples. Figure 6.16 (c) represent the XRD pattern of 4% lime treated sample after 75 days of curing.

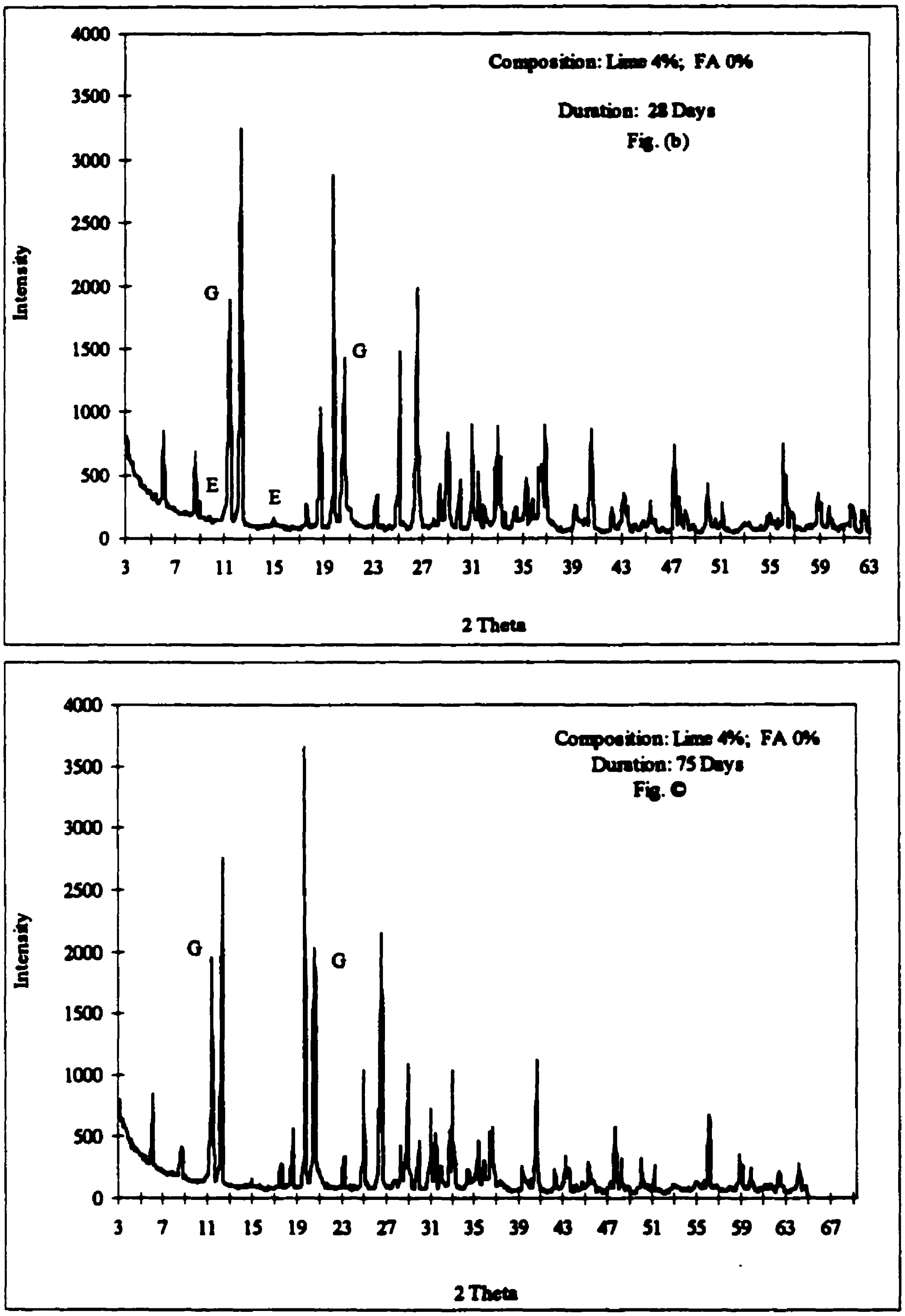


FIGURE 6.16 (b, c) X-RAY DIFFRACTION ANALYSIS OF 4% LIME TREATED SAMPLE (G = GYPSUM ; E = ETTRINGITE)

It is clearly evident that all the ettringite formed in the sample had completely disintegrated. The pH analysis of the sample also revealed that the pH of the sample were below the required pH condition for ettringite formation (above 10.5). The higher gypsum formation after 28 days and 75 days also suggests that all the ettringites have transformed or disintegrated. The release of the sulfate ions from the ettringite formation has provided the necessary condition for the higher formation of gypsum in these samples.

Samples treated with a combination of lime and fly ash as their binding agents are shown in Figure 6.17. Addition of 4% lime and 10% fly ash class "C" to these samples has resulted in the formation of ettringite and calcium silicate hydrate after 3 days of curing (Figure 6.17, a). Peak intensities of ettringite and calcium silicate hydrate continue to grow after 28 days and 75 days of curing (Figure 6.17, b, and c). Gypsum formation is also evident in all of these samples. After 180 days of curing (Figure 6.17, d) ettringite and calcium silicate hydrate peaks have diminished while gypsum peaks have increased. The pH of the samples after 75 days of curing has reduced. These were all the indication of more oxidation in the samples and disintegration of ettringite which was continued up to 365 days of curing (Figure 6.17, e), while more gypsum had formed in the samples. The peak intensities of gypsum remained almost constant for the first 180 days of curing and began to increase between 180 days and 365 days of curing. This behavior is tentatively attributed to the disintegration or transformation of ettringite into mono-sulfate and the release of sulfate ions into the samples. The available free lime in the samples and

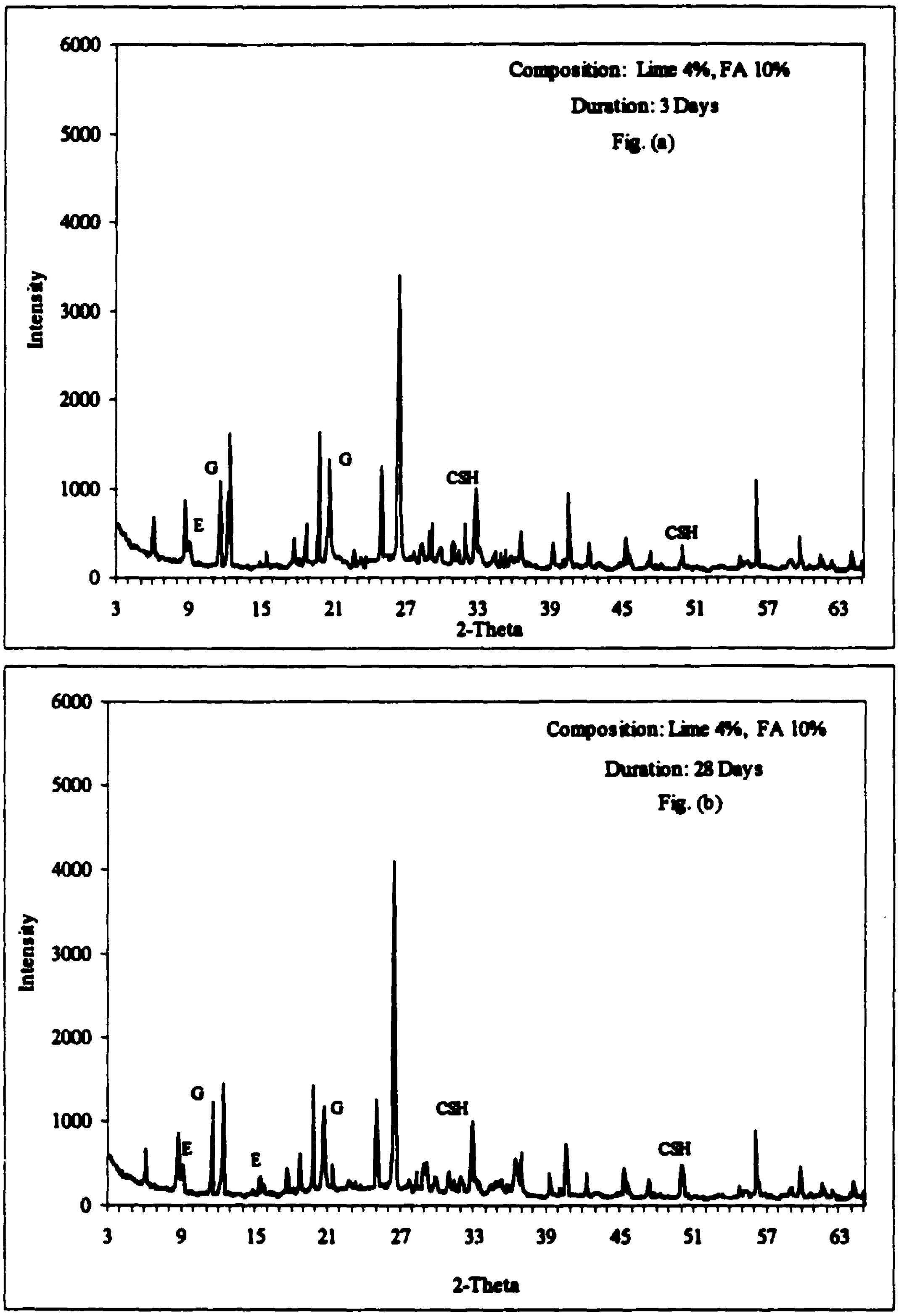


FIGURE 6.17 (a, b) X-RAY DIFFRACTION ANALYSIS OF 4% LIME, 10% FLY ASH TREATED SAMPLE (G = GYPSUM; E = ETTRINGITE; CSH = CALCIUM SILICATE HYDRATE)

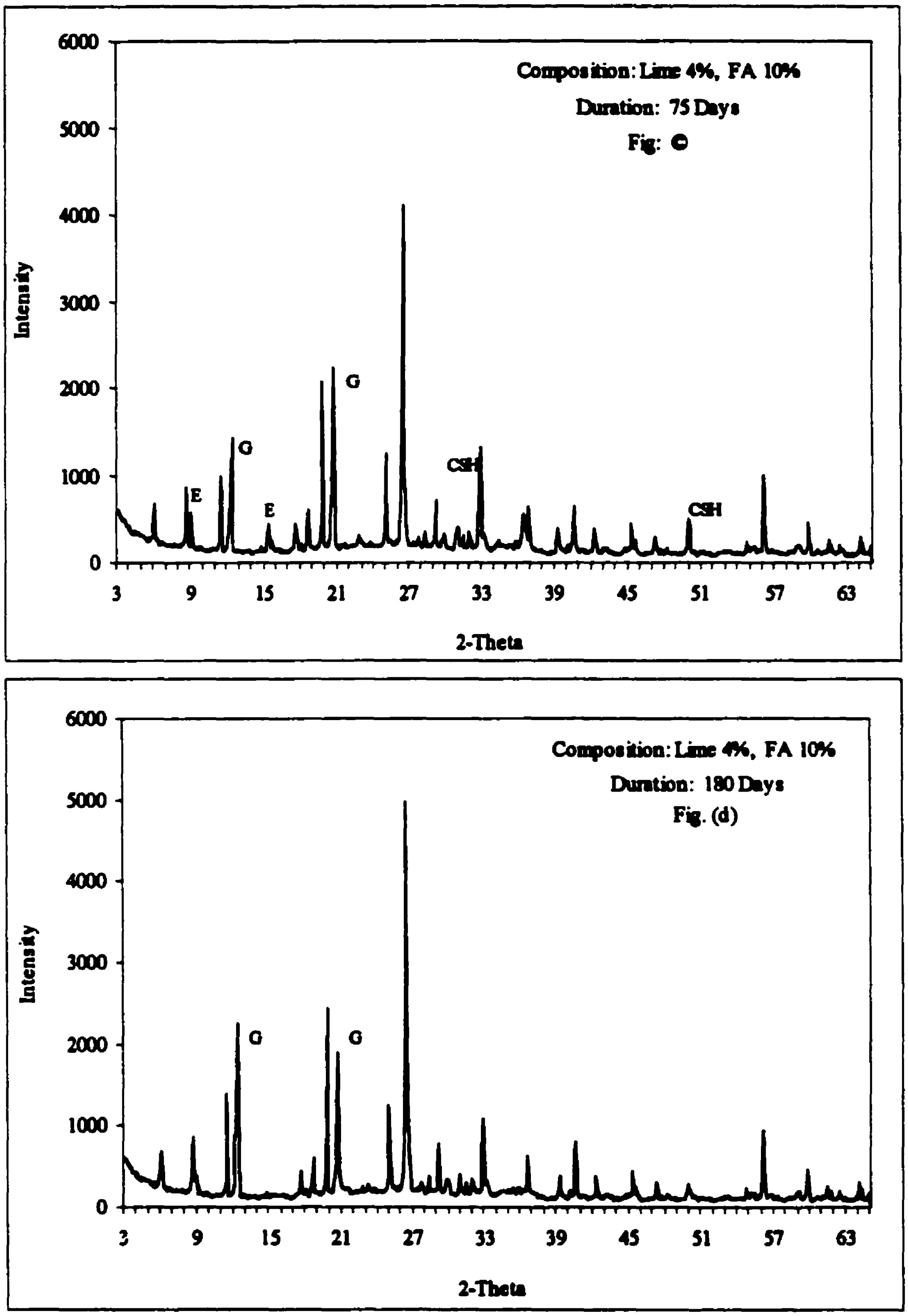


Figure 6.17 (c, d) X-ray Diffraction Analysis of 4% Lime, 10% Fly ash Treated Sample (G = Gypsum ; E = Ettringite; CSH = Calcium Silicate Hydrate)

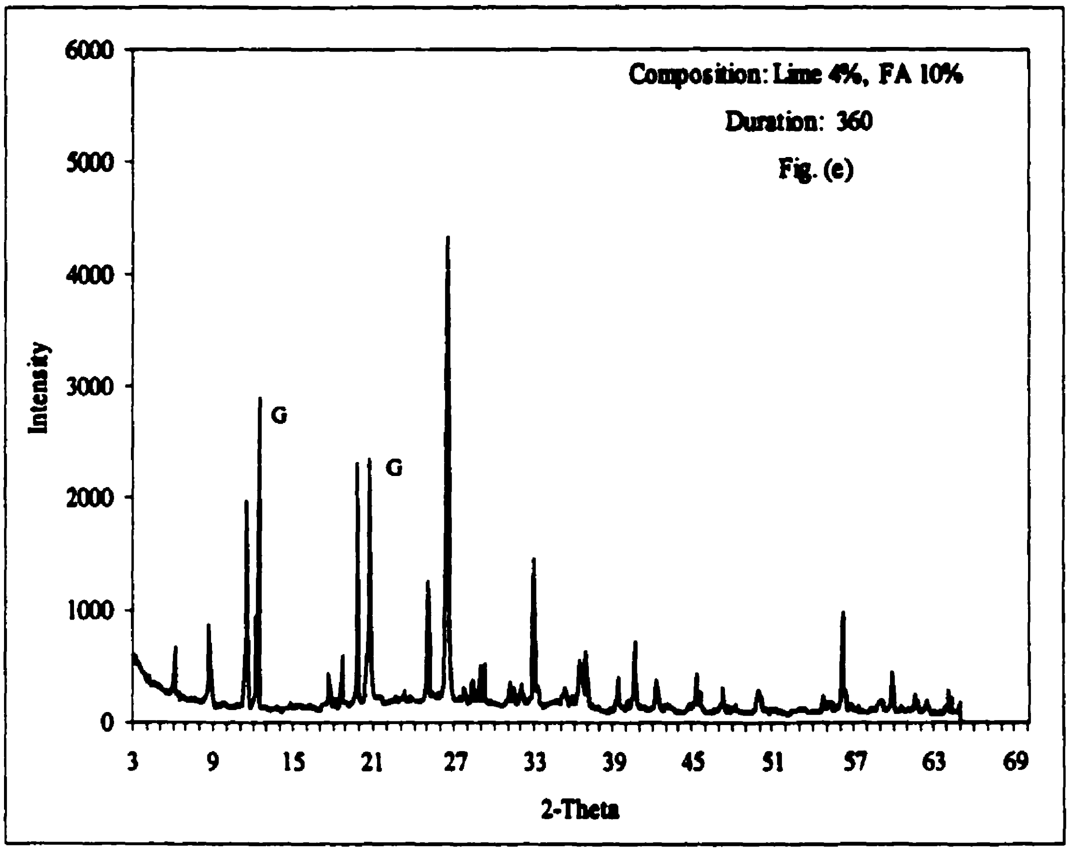


Figure 6.17 (e) X-ray Diffraction Analysis of 4% Lime, 10% Fly Ash Treated Sample (G = Gypsum; E = Ettringite; CSH = Calcium Silicate Hydrate)

the accessibility of sulfate ions have caused the formation of more gypsum in the samples.

Increasing the fly ash content from 10% to 20% and its effect on the formation and disintegration of ettringite and calcium silicate hydrate was studied for the period of 360 days (Figure 6.18 a, b, c, d and e). The XRD pattern for ettringite formation is the same as for samples which were made with 4% lime and 10% fly ash. The higher fly ash content of these samples resulted in a slight increase in the amount of calcium silicate hydrate, while no significant changes in the magnitude of gypsum or ettringite was recorded. This could partly be due to the fact that the matrix was over saturated with the addition of 20% fly ash and most of the added fly ash might have remained unreacted. This conclusion was further reinforced by the result of the leachability study, as the increase in the amount of fly ash from 10% to 20% has not significantly reduced the mobility of the ions under study.

Ettringite and calcium silicate hydrate were observed after 3 days of curing (Figure 6.18, a). Gypsum content remained the same as for the samples containing 4% lime and 10% fly ash (Figure 6.18, a). Ettringite and calcium silicate hydrate continue to grow within the 75 days of curing (Figure 6.18, b and c). Once more, further curing led to the complete disintegration of ettringite.

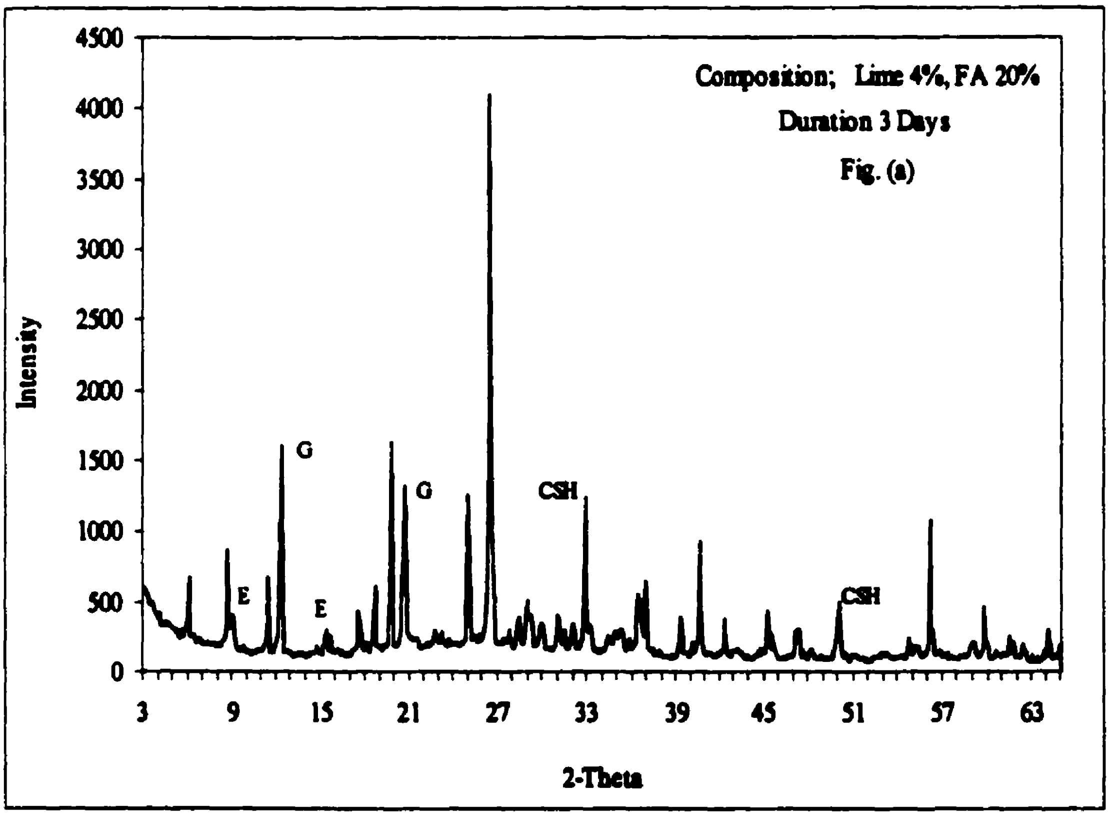


FIGURE 6.18 (a) X-RAY DIFFRACTION ANALYSIS OF 4% LIME, 20% FLY ASH TREATED SAMPLE (G = GYPSUM; E = ETTRINGITE; CSH = CALCIUM SILICATE HYDRATE)

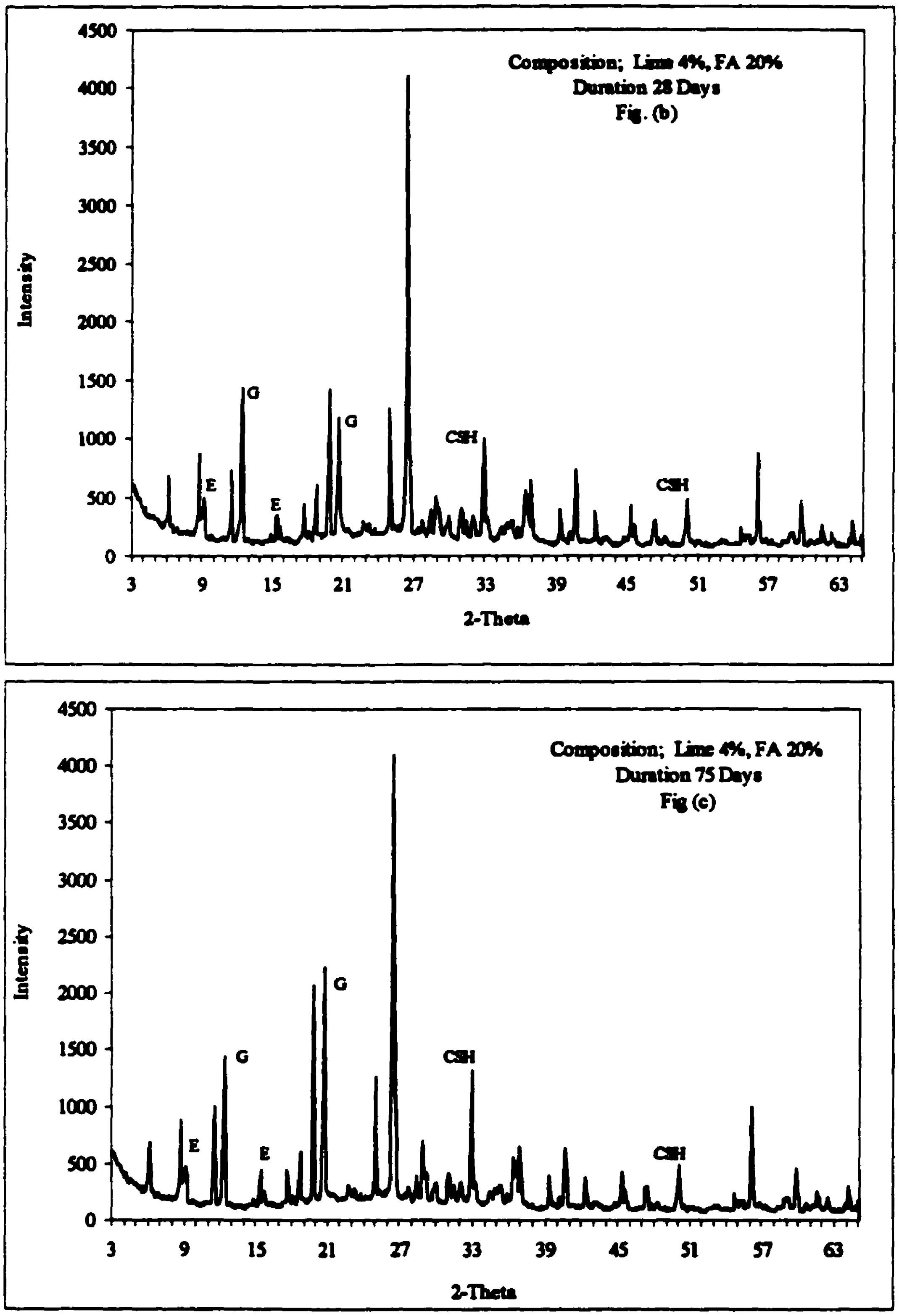


FIGURE 6.18 (b, c) X-RAY DIFFRACTION ANALYSIS OF 4% LIME, 20% FLY ASH TREATED SAMPLE (G = GYPSUM; E = ETTRINGITE; CSH = CALCIUM SILICATE HYDRATE)

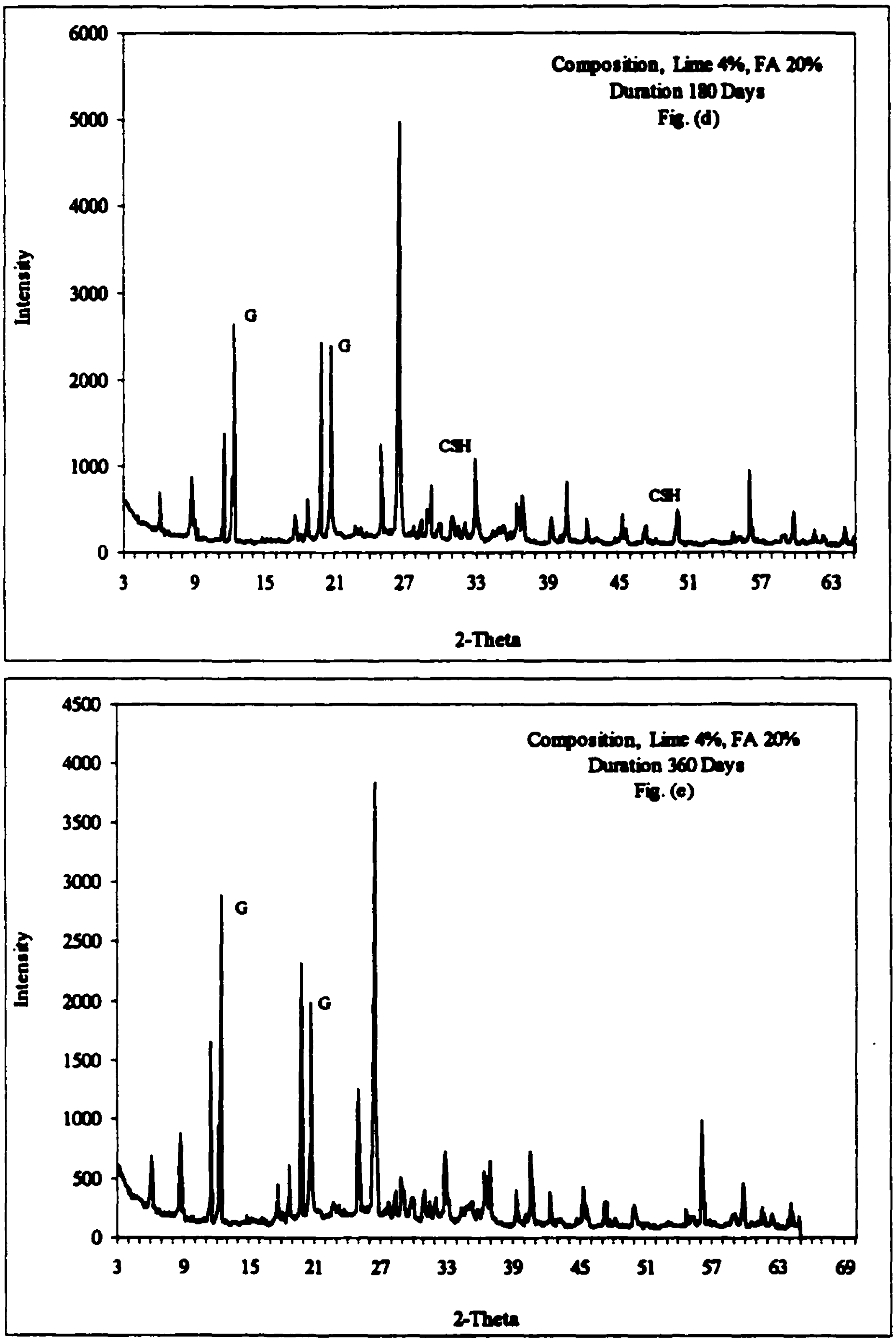


Figure 6.18 (d, e) X-ray Diffraction Analysis of 4% Lime, 20% fly ash Treated Sample (G = Gypsum; E = Ettringite; CSH = Calcium Silicate Hydrate)

The pH of the samples were below the threshold requirements of ettringite formation and the availability of sulfate and calcium caused the higher presence of gypsum in the samples cured for 180 days (Figure 6.18, d). As a result of further oxidation and drop in the pH of the samples, no ettringite was observed in the samples after 360 days of curing (Figure 6.18, e).

Since achieving and maintaining a high pH condition is necessary for stability of ettringite, and as a result of optimization experiments conducted previously, it was decided to elevate the pH of the samples by increasing the lime content. New samples were made with the addition of 5% lime as the principal binding agent and the XRD pattern for the formation of ettringite was studied over the period of 360 days (Figure 6.19, a, b, c, d, and e). Application of 5% lime to these samples has resulted in formation of significant amount of ettringite within the first 3 days of curing (Figure 6.19, a). The XRD peak intensities of ettringite and calcium silicate hydrate continue to grow up to 75 days of curing (Figure 6.19, b and c) and tend to stabilize afterwards (Figure 6.19, d and e). However, a slight reduction in the magnitude of ettringite was observed after 360 days of curing. The gypsum content of the samples remained the same throughout the experiment. Application of 5% lime has also caused more gismondine to appear in these samples. Moreover, some calcium hydroxide (portlandite) which were still unreacted in the samples were detected in the X-ray diffraction analysis.

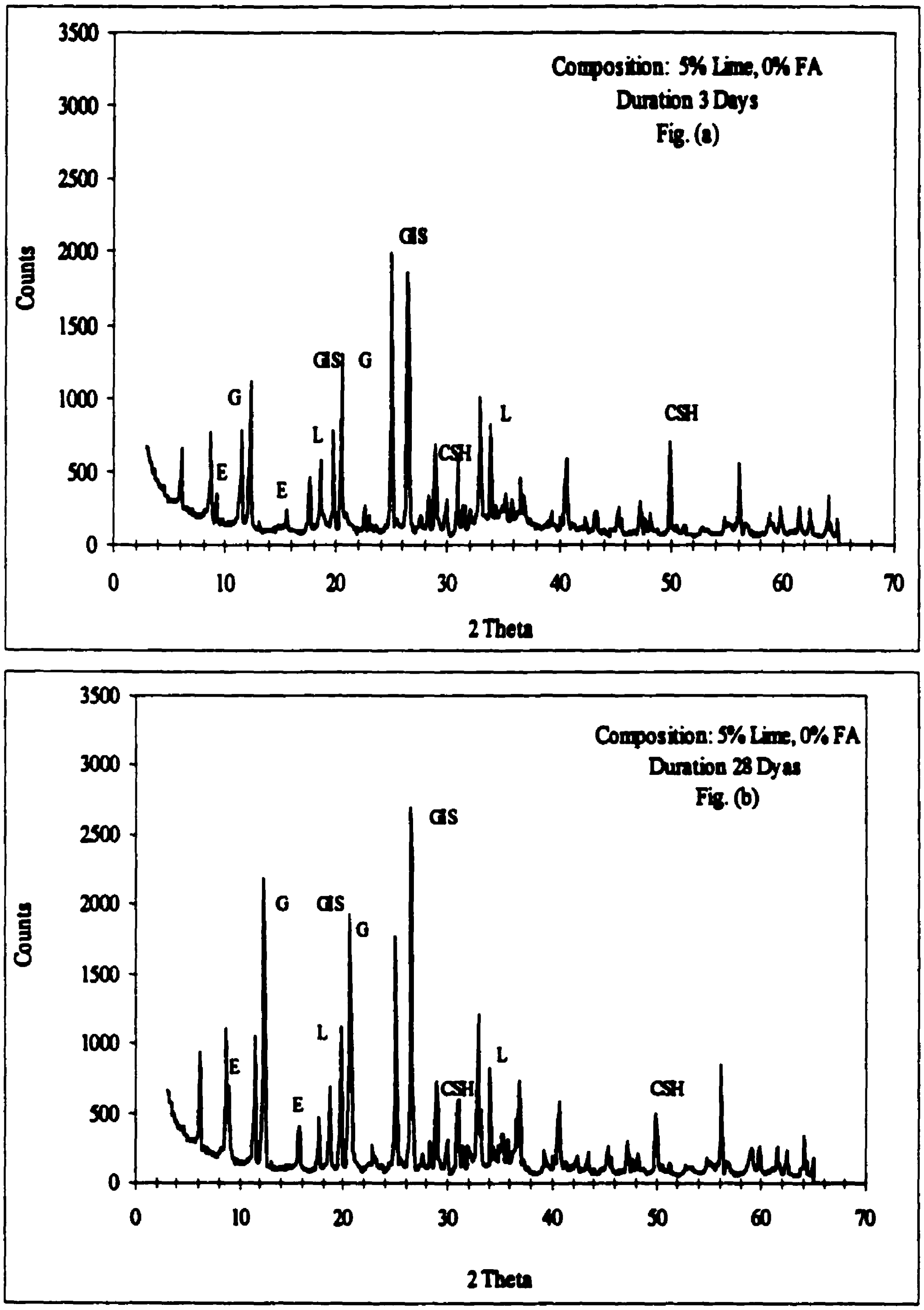


Figure 6.19 (a, b) X-ray Diffraction Analysis of 5% Lime Treated Sample (G = GYPSUM ; E = ETTRINGITE; CSH = CALCIUM SILICATE HYDRATE; L = LIME; GIS = GISMONDINE)

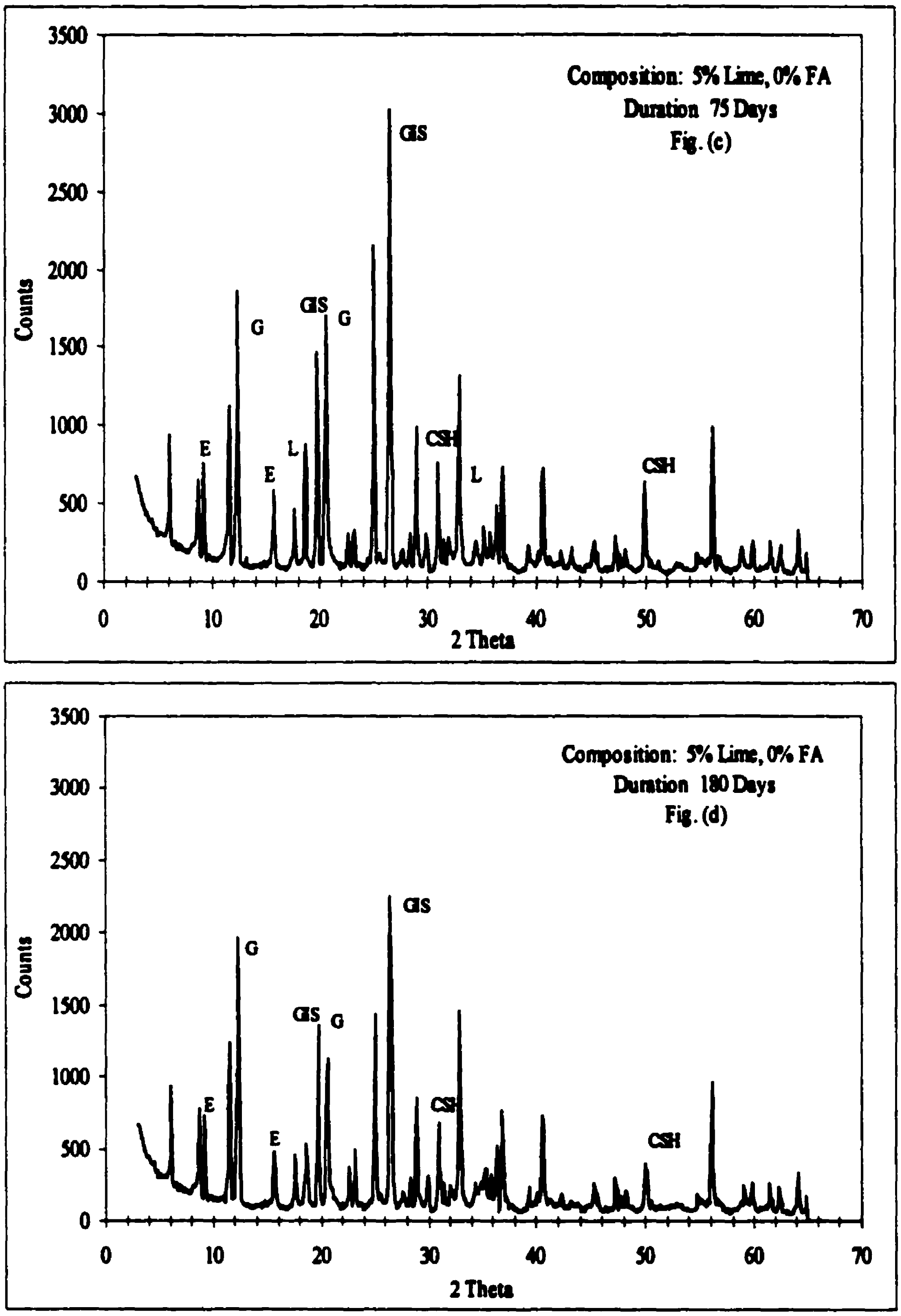


Figure 6.19 (c, d) X-ray Diffraction Analysis of 5% Lime Treated Sample (G = Gypsum ; E = Ettringite; CSH = Calcium Silicate Hydrate; L = Lime; GIS = Gismondine)

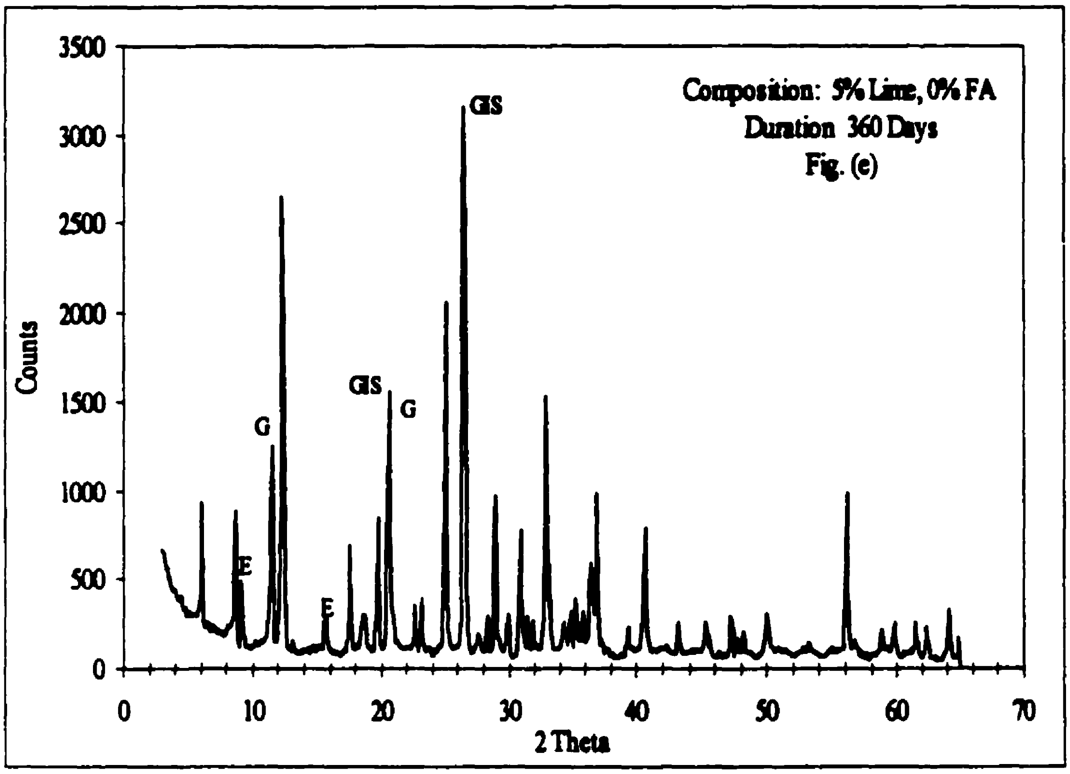


Figure 6.19 (e) X-ray Diffraction Analysis of 5% Lime Treated Sample (G = Gypsum ; E = Ettringite; CSH = Calcium Silicate Hydrate; L = Lime; GIS = Gismondine)

The optimization experiments conducted previously revealed that in order to maintain the high pH environment in this harsh and potentially acidic condition, application of 10% fly ash is essential. Therefore, samples were prepared with the addition of 5% lime as well as 10% fly ash (Figure 6.20, a, b, c, d, and e) and the ettringite formation was monitored for a period of 360 days. As it was anticipated, the high ettringite peak intensities were detected within the first 3 days of curing (Figure 6.20, a). Moreover, application of fly ash has led to the formation of calcium silicate hydrate in these samples. Once more, calcium hydroxide as well as gismondine were also detected in these samples.

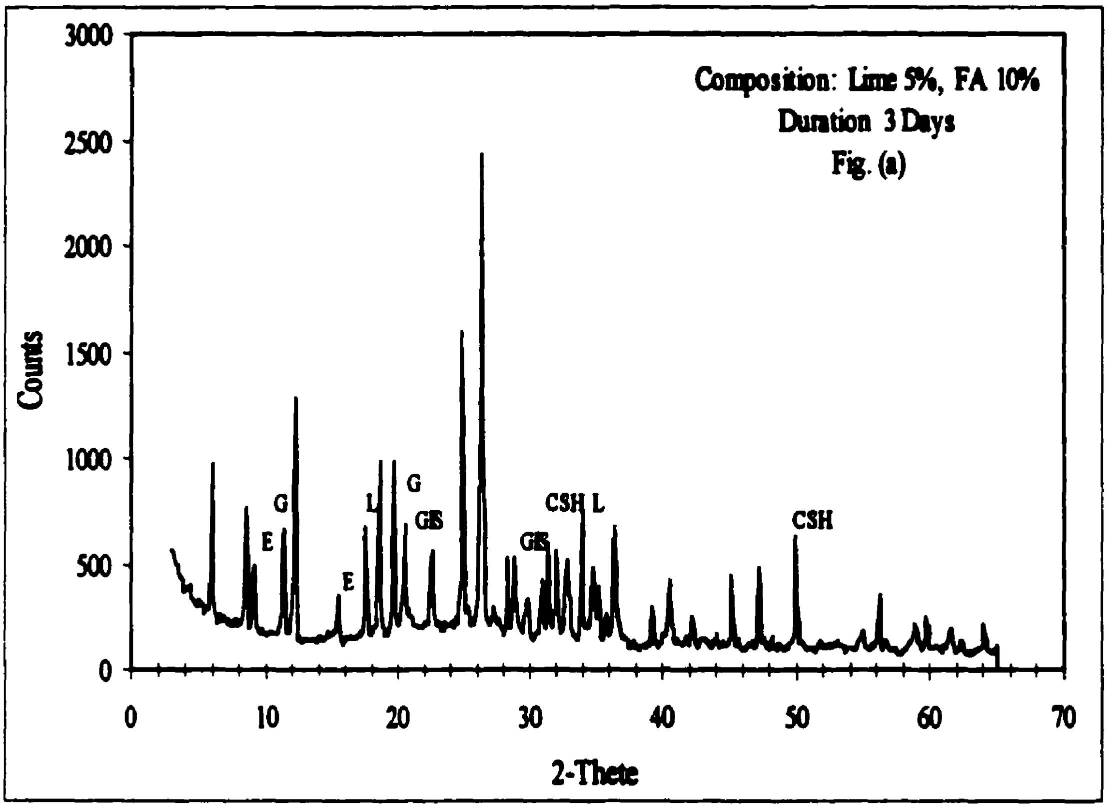


Figure 6.20 (a) X-ray Diffraction Analysis of 5% Lime, 10% F.A. Treated Sample (G = GYPSUM; E = ETTRINGITE; CSH = CALCIUM SILICATE HYDRATE; L = LIME; GIS = GISMONDINE)

Ettringite and calcium silicate hydrate which were formed in these samples continued to increase up to 180 days of curing and remained fairly constant between 180 days and 360 days of curing (Figure 6.20, b, c, d and e). Continued growth of ettringite (formation of secondary ettringite) could be attributed to the high pH of the mixture as well as to the higher availability of calcium silicate hydrate as a result of fly ash addition. As it was stated in chapter 4, calcium silicate hydrate (C-S-H) has the ability to adsorb and desorbe sulfate ions from and into the solution.

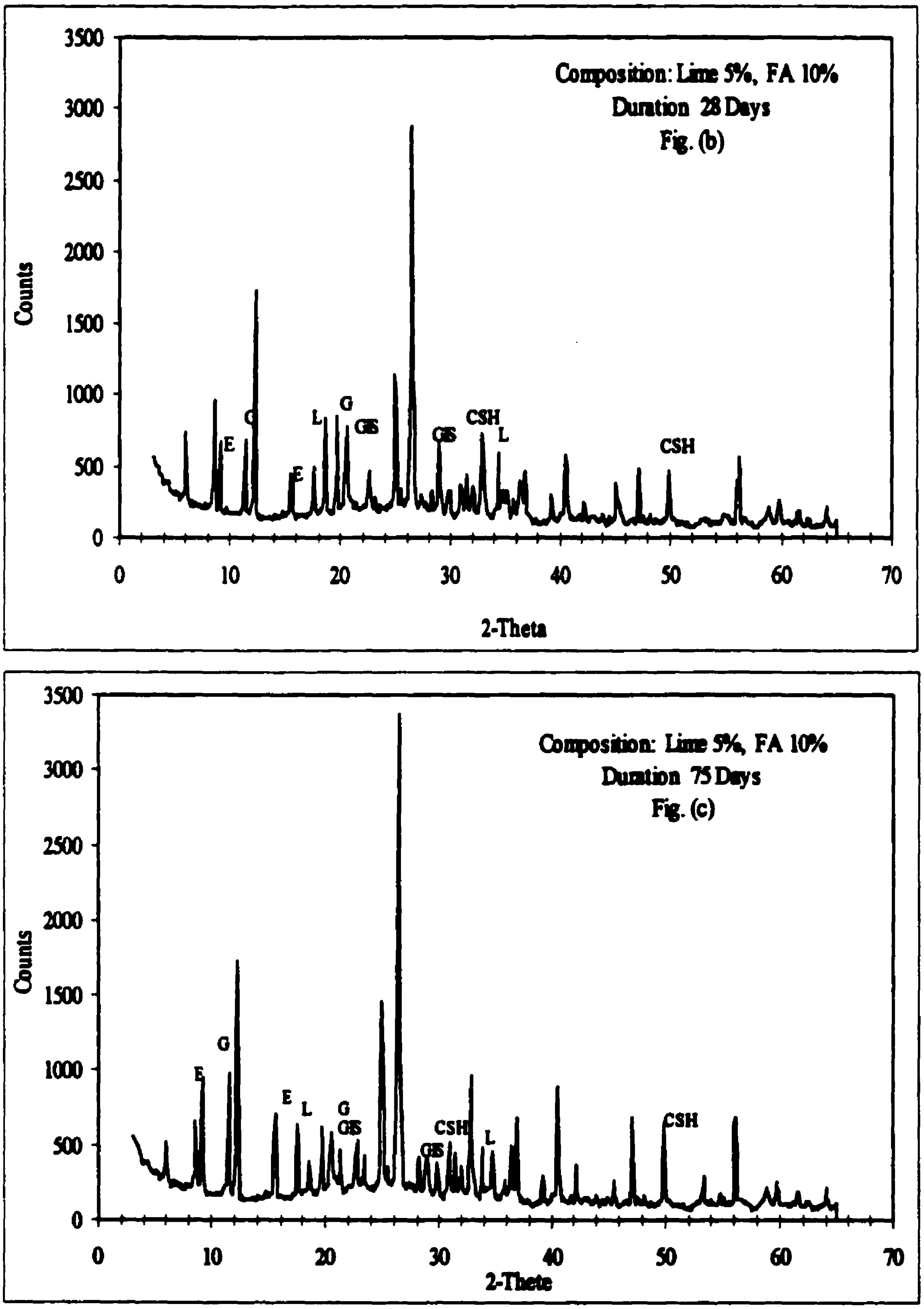


Figure 6.20 (b, c) X-ray Diffraction Analysis of 5% Lime, 10% F.A. Treated Sample (G = Gypsum ; E = Ettringite; CSH = Calcium Silicate Hydrate; L = Lime; GIS = Gismondine)

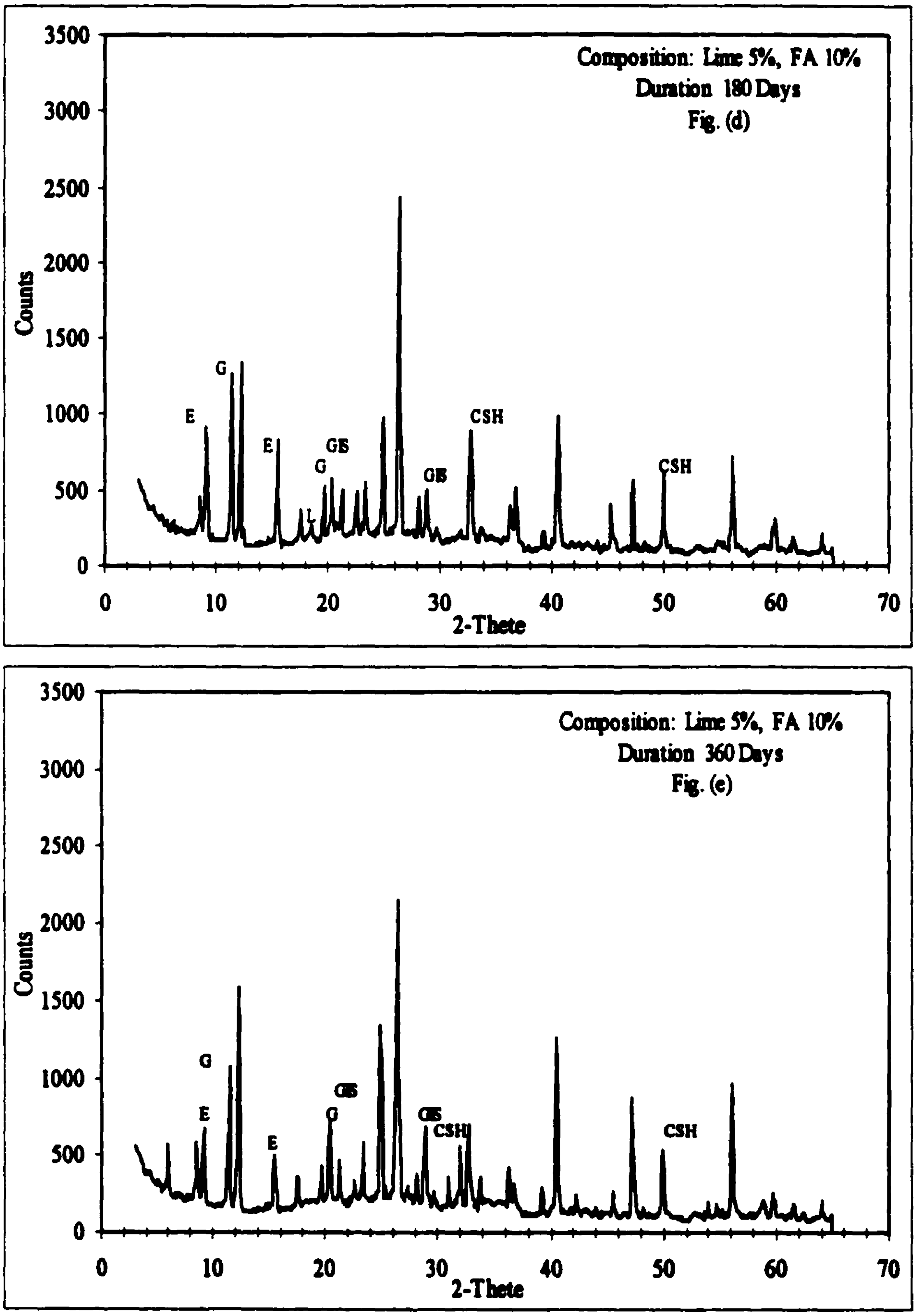


Figure 6.20 (d, e) X-ray Diffraction Analysis of 5% Lime, 10% F.A. Treated Sample (G = Gypsum ; E = Ettringite; CSH = Calcium Silicate Hydrate; L = Lime; GIS = Gismondine)

Such phenomenon was first reported by Lerch *et al.*, (1929) and later was confirmed by Kalousek and Adams (1951). These researchers have postulated that the sulfate ions could be bound into the C-S-H gel structure to form a new phase called "phase X". Copeland *et al.*, (1967) reported that sulfate combined with C-S-H gel to form "phase X" at early ages and then sulfate ions were released at later ages. This phenomenon could cause the formation of secondary ettringite in the samples under investigation.

Another conclusion drawn from the optimization experiments which were conducted previously revealed that addition of aluminum is crucial to the formation and precipitation of ettringite as a stable mineral in the sample under study. Therefore, new experiments were set up to study the effect of aluminum addition to the stability of ettringite in the samples. It is postulated that availability of aluminum in the mixtures will elevate the formation of ettringite while reduces the potential of gypsum formation. Hence, formation of primary ettringite as well as "phase X" will reduce the sulfate ions availability and therefor, reduce the magnitude of gypsum formation in the samples. Reduction in gypsum content of the sample will create a more chemically stable matrix which will resist the change of its pH. Stability and maintenance of high pH is crucial to stability of ettringite in the treated samples.

Based on the optimization experiments conducted previously, samples were prepared with the addition of 110 ppm of soluble aluminum, 5% lime in the form of quick lime and 10% fly ash type "C". As it was explained previously, 110 ppm of aluminum is half of the stochiometric amounts of aluminum needed to form and precipitate ettringite in the sample under study. It is believed that the deficiency of the aluminum needed to form ettringite will be compensated by the other divalent and trivalent cations present in the sample. The tailings sample, lime and fly ash were dry mixed while aluminum was added to the water and then added to the dry mixture. Once more, the water to solid ratio was 0.5, based on the results of comprehensive optimization study which was carried out previously. Samples were mixed for 10 minutes by hand and were stored in plastic containers in 25°C and 90% relative humidity. By using X-ray diffraction technology (XRD), the formation of ettringite in these samples were monitored for the period of 660 days. Surface metal analysis was also carried out with a scanning electron microscopy (SEM) coupled with an energy dispersion system (SEM/EDS).

In order to further evaluate the effectiveness of treatment reagents on stability of ettringite and its role in immobilization of metals of concern, laboratory leaching program with 4 different leachants based on the principals of toxicity characteristics leaching procedure (TCLP) test were set up. The newly mixed samples were leached using simulated ground water (pH 5.5), simulated acid rain (pH 4.2), sulfuric acid solution (pH 2.5) and acetic acid solution (pH 2.88).

6.9 Results and Discussion of Optimization Experiments

6.9.1. X-ray Diffraction Analysis

Samples which were treated with 5% lime and 10% fly ash type C (by the weight of dry waste) and addition of 110 ppm aluminum were hydrated at 25°C and 95% relative humidity for 3, 28, 90, 180, 365, and 660 days. These samples were made with water to solid ratio of 0.5, which was the optimum value to ensure good workability and sufficient hydration. Samples were taken at pre-fixed hydration times and were dried in a laboratory oven at 40°C, ground and then subjected to X-ray diffraction analysis.

The XRD pattern of the sample hydrated for only 3 days is shown in Figure 6.21 (a). Addition of aluminum to this sample has resulted in formation of equal amount of ettringite compared to the sample cured for 28 days and no aluminum addition. Moreover, the gypsum content of the sample made with the addition of aluminum has been reduced significantly when compared with the same sample without any aluminum additives in its structure. Formation of gypsum is not favorable as far as the durability of the sample is concerned. Furthermore, its formation and leads to the reduction of pH which will disintegrate ettringite. Calcium silicate hydrate and unreacted lime are also detectable in the XRD pattern presented in Figure 6.21 (a).

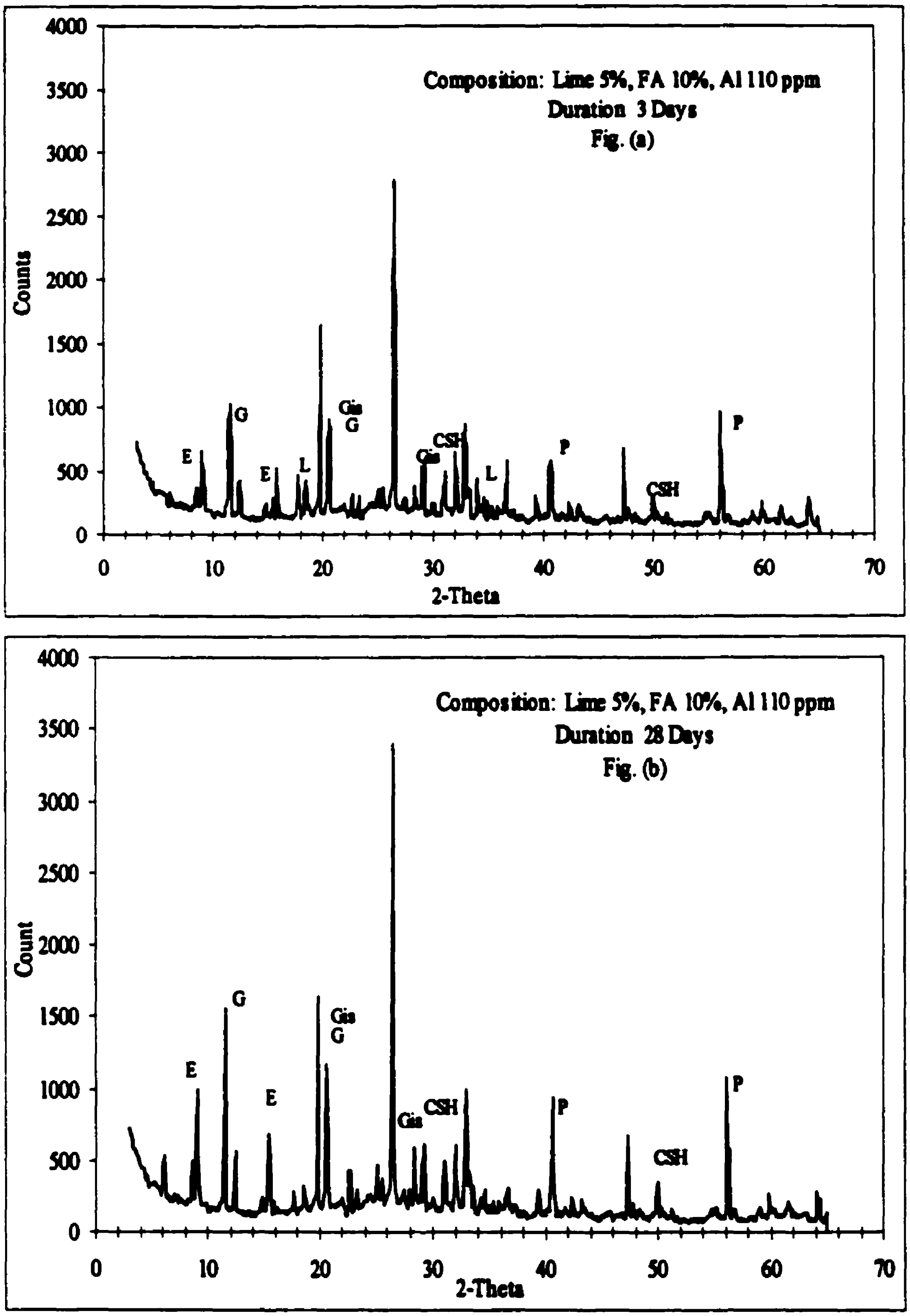


Figure 6.21 (a, b) X-ray Diffraction Analysis of 5% Lime, 10% F.A. & 110 ppm Al. Treated Sample (G = GYPSUM ; E = ETTRINGITE; CSH = CALCIUM SILICATE HYDRATE; L = LIME; GIS = GISMONDINE; P = PYRITE)

Samples which were cured for 28 days have higher ettringite content, calcium silicate hydrate, and lower aluminum oxide content compared to 3 days cured sample (Figure 6.21, b). The gypsum content in these samples has also increased. Moreover, Gismondine have also been detected in these samples. As the curing age of the samples has increased, ettringite peaks have shown a steady growth while gypsum's growth has been hindered. Pyrite peaks were remained constant while after 365 days of curing, were slightly reduced. This is attributed to the oxidation process of pyrite. The sulfate released as a result of pyrite oxidation has been mostly consumed by ettringite, gypsum and "phase X" of the calcium silicate hydrate formed in these samples. Another interesting observation is related to disappearance of lime as well as any trace of the aluminum oxide in these samples. All these observations are shown in Figure 6.21 (c, d, and e).

In order to further evaluate the stability of the ettringite in these samples, some of the columns treated with these reagents were cured up to 660 days. Figure 6.21 (f) represent the XRD pattern of this sample. The ettringite peak intensity remained constant compared to the samples cured for 360 days. Gypsum, and pyrite peaks have shown reduction in their intensity which is attributed to slow rate of reaction in the samples. As the reaction rate has been slowed down, but not halted, less and less sulfate is present for reaction. However, slow rate of reaction continues to supply sulfate which prevents the complete conversion of ettringite to monosulfate. Formation and stability of ettringite in a system rich in internal source

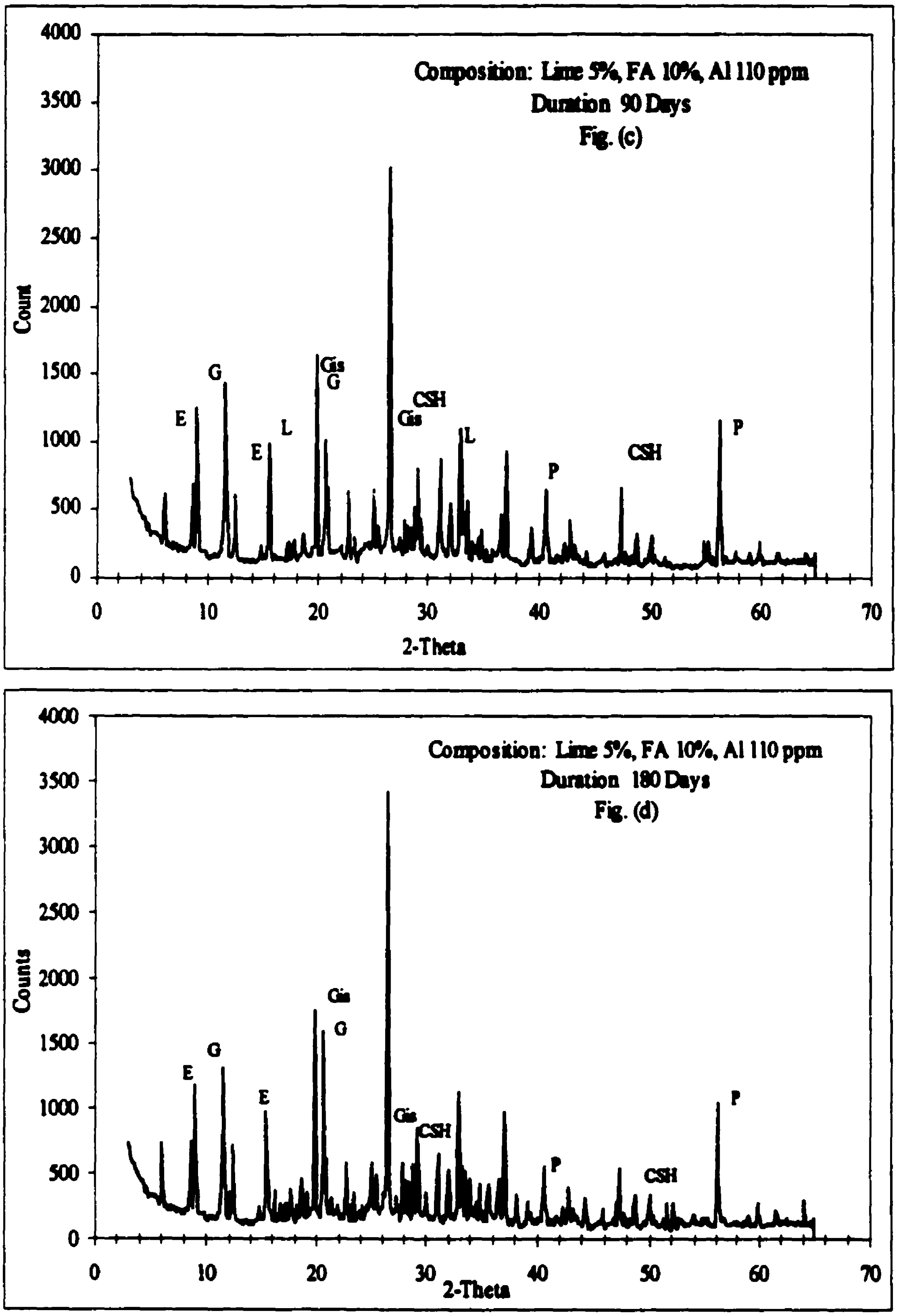


Figure 6.21 (c, d) X-ray Diffraction Analysis of 5% Lime, 10% F.A. & 110 ppm Al. Treated Sample (G = Gypsum ; E = Ettringite; CSH = Calcium Silicate Hydrate; L = Lime; GIS = Gismondine; P = Pyrite)

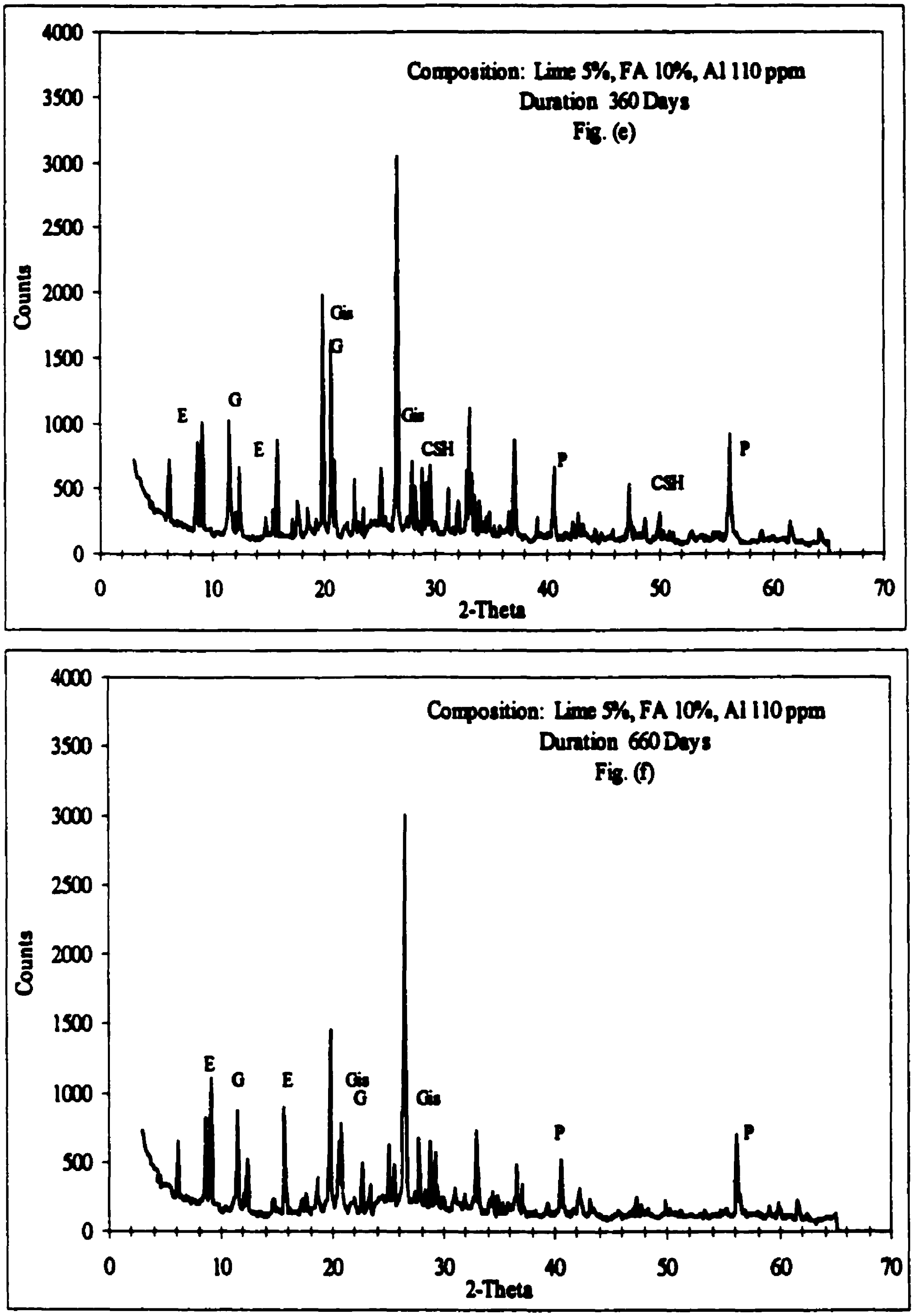


Figure 6.21 (e, f) X-ray Diffraction Analysis of 5% Lime, 10% F.A. & 110 ppm Al. Treated Sample (G = Gypsum ; E = Ettringite; CSH = Calcium Silicate Hydrate; L = Lime; GIS = Gismondine; P = Pyrite)

of sulfite, and metal ions such as iron and zinc which are known to have retarding effect on the formation of ettringite is an indication of chemical stability of the treated matrix. It is postulated that the source of sulfate could be the result of pyrite oxidation as well as desorption of sulfate from the surface of calcium silicate hydrate gel (phase X). Moreover, the availability of gismondine (calcium aluminate silicate oxide) in the samples after 660 days of hydration is another indication of chemical stability of the treated matrix.

6.9.2 Leachability Analysis

Treated samples with 5% lime, 110 ppm of aluminum and 10% fly ash type "C" were subjected to different leaching tests, each test follow TCLP leaching procedure. The leachants for this part of the experiments were simulated groundwater (GW), acid rain (AR), sulfuric acid solution (Modified TCLP), and 0.1 molar acetic acid solution (TCLP). The pH of the groundwater was adjusted between 5.3 and 5.5 using sodium hydroxide solution or nitric acid solution. The solution was doped with 500 ppm of calcium, iron, sulfide and magnesium. The acid rain solution had the pH of 4.5 using sulfuric acid solution. The sulfuric acid solution had a pH of 2.5 and acetic acid solution was adjusted to pH of 2.88 according to TCLP testing protocols. Samples were grinded, and pulverized to expose the largest surface area and were mixed with the leachant in polyethylene bottles. Extraction was carried out at 20:1 liquid to solid ratio over 18 hours of vigorous shaking. The leachate solutions were analyzed by Atomic Absorption Spectroscopy for the metal concentrations.

It is generally assumed that the metal leaching rates would increase as particle size decrease due to an increase in available surface area for leaching. As it was discussed earlier, metals binding mechanism could be locked in the pores of matrix, adsorbed onto the pore walls, or chemically complexed with paste constitutes. Since one of the binding mechanisms for metals of concern is the sorption, increase surface area which is the characteristics of smaller particles cause greater sorption and thus lowering the metal leaching concentration. On the other hand, larger particles can resist the variation of the pH since smaller surface area is exposed for alkalinity to leach out. However, grinding and pulverization are exposing the largest surface area which is believed to be the more dominant mode in effecting the leaching characteristics of the samples. Hence, the results obtained could be interpreted as the worst case scenario for leaching in simulated conditions.

The results of the leaching experiments show that the solidified and stabilized matrices have remained insoluble when were leached with groundwater and acid rain water, as shown in Figures 6.22 and 6.23 respectively. While less than 1.5 ppm of iron was leached out of the samples, all other metals of concern such as copper, magnesium, and zinc remained insoluble within the solidified and stabilized matrices. It is, therefore, environmentally remarkable that the maximum amount of iron released during 660 days of curing is less than 0.06% of its original concentration and no other elements leached, considering the matrix complete disaggregation.

The pH of the samples remained above 10 during the 660 days of curing for both leachants while it was slightly reduced in the case of acid rain. The quantity of calcium and sulfate leached out of the samples were remained low and were

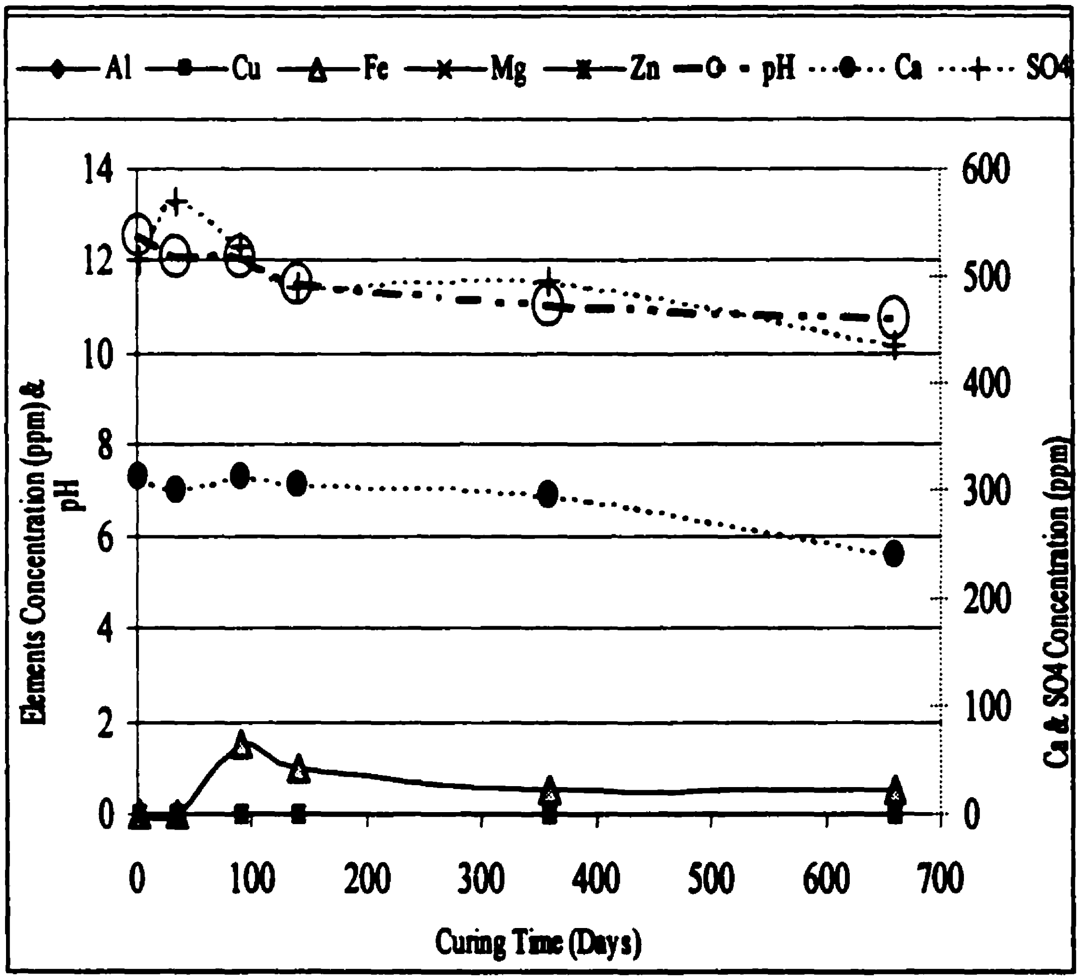


FIGURE 6.22. GROUNDWATER LEACHABILITY TEST RESULTS

comparable for both groundwater and acid rain leachants. The sulfate content was slightly reduced while calcium content remained constant throughout the curing and testing periods. Therefore, in the case of leaching with groundwater and acid rain, which can be considered as the most probable case scenario for deposited tailings in their natural environment, the treatment with lime, fly ash and added aluminum has stopped the release of metals completely.

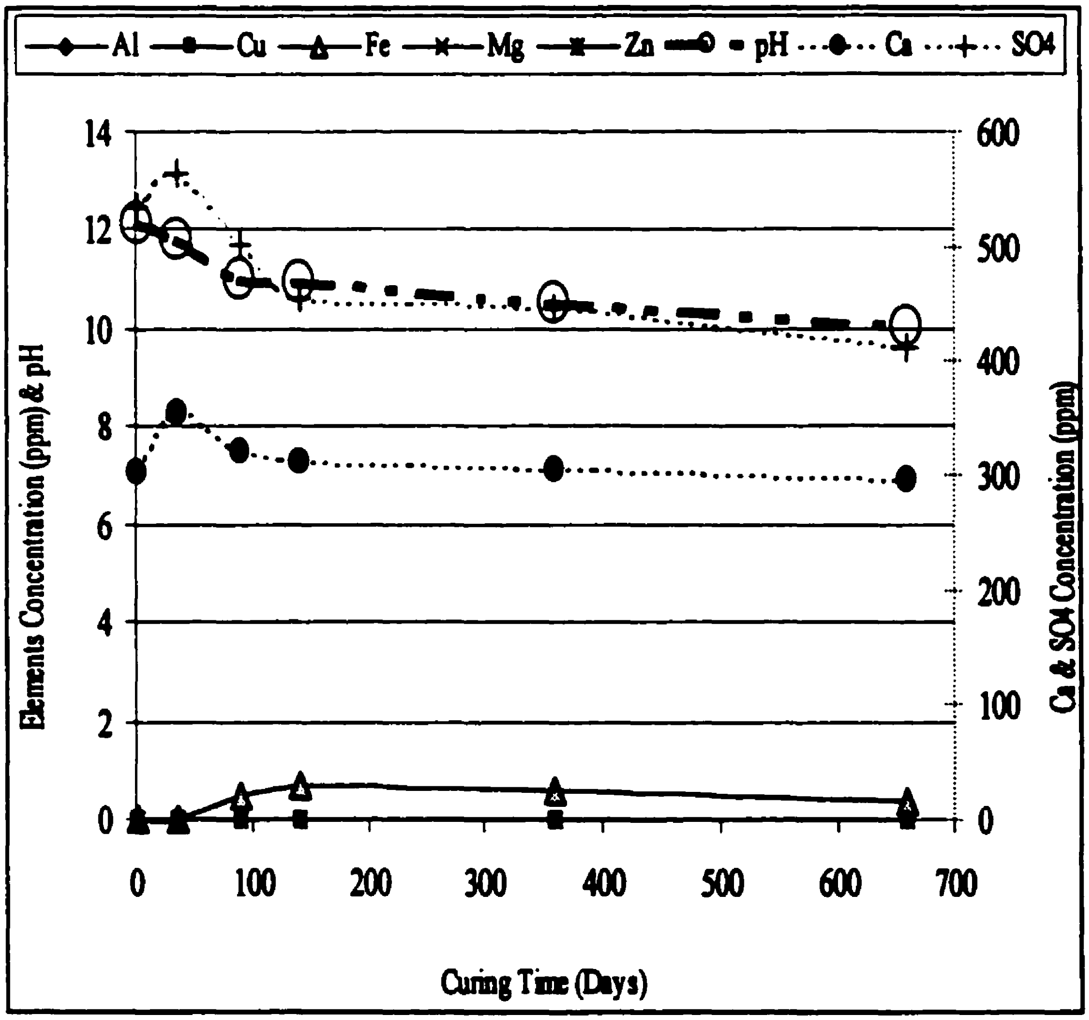


FIGURE 6.23. ACID RAIN LEACHABILITY TEST RESULTS

The results of leaching of the samples with sulfuric acid (Modified TCLP) and acetate acid are shown in Figures 6.24 and 6.25 respectively. By using both of these leachants, much more aluminum was leached out of the samples within the first day of hydration. However, the aluminum content drastically reduced as the hydration continued. Considering the results of X-ray diffraction done on the same samples, (Figures 6.21 a, and b), disappearance of aluminum was accompanied by the formation of ettringite and ettringite like minerals in the sample. After 90 days of hydration, the leachability of all the elements of concern have reached their equilibrium and remained as such throughout the 660 days of curing and testing period. Comparison between groundwater and acid rain leachability with modified and unmodified TCLP leaching show that magnesium is more susceptible to pH change as the lower pH leachants have cause more magnesium to leach out of the treated matrixes.

As it was expected, leaching with sulfuric acid (MTCLP) and acetic acid (TCLP) caused that the samples pH drop to 5 and 4 respectively. Such low pH environment has consequently led to release of more calcium and sulfate ions into the solution. The excess amount of calcium and sulfate might have come from partial disintegration of calcium aluminate sulfate compounds, such as ettringite in the solution.

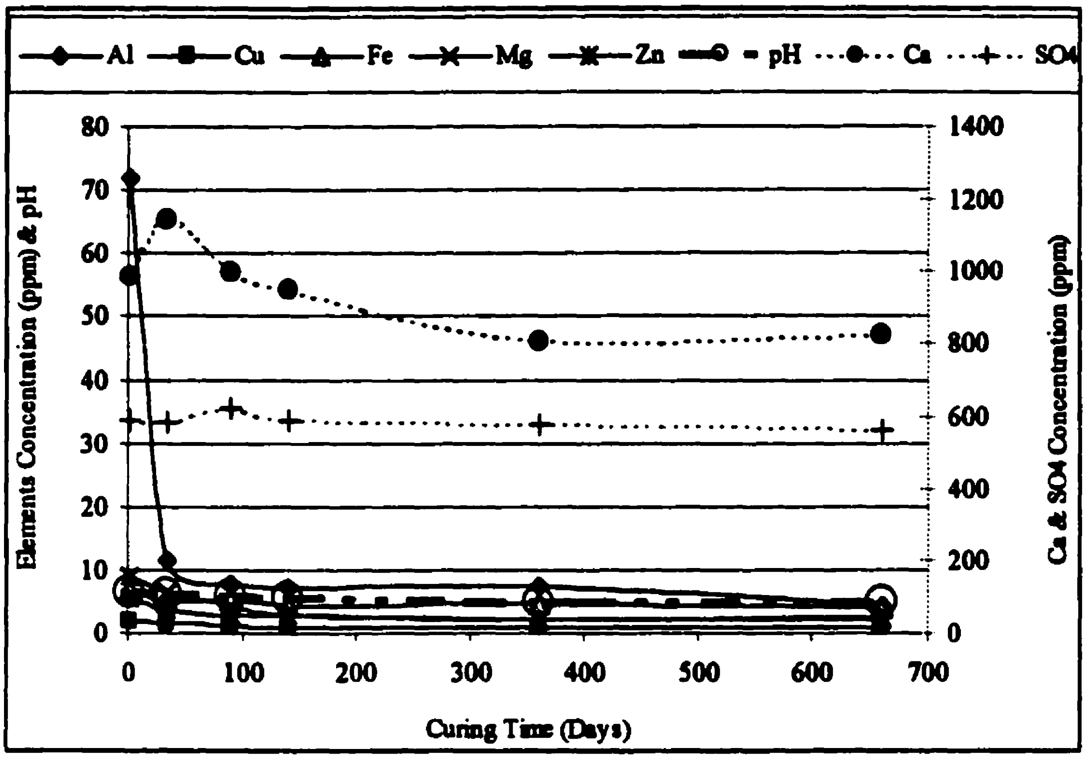


FIGURE 6.24. MODIFIED TCLP LEACHING TEST RESULTS

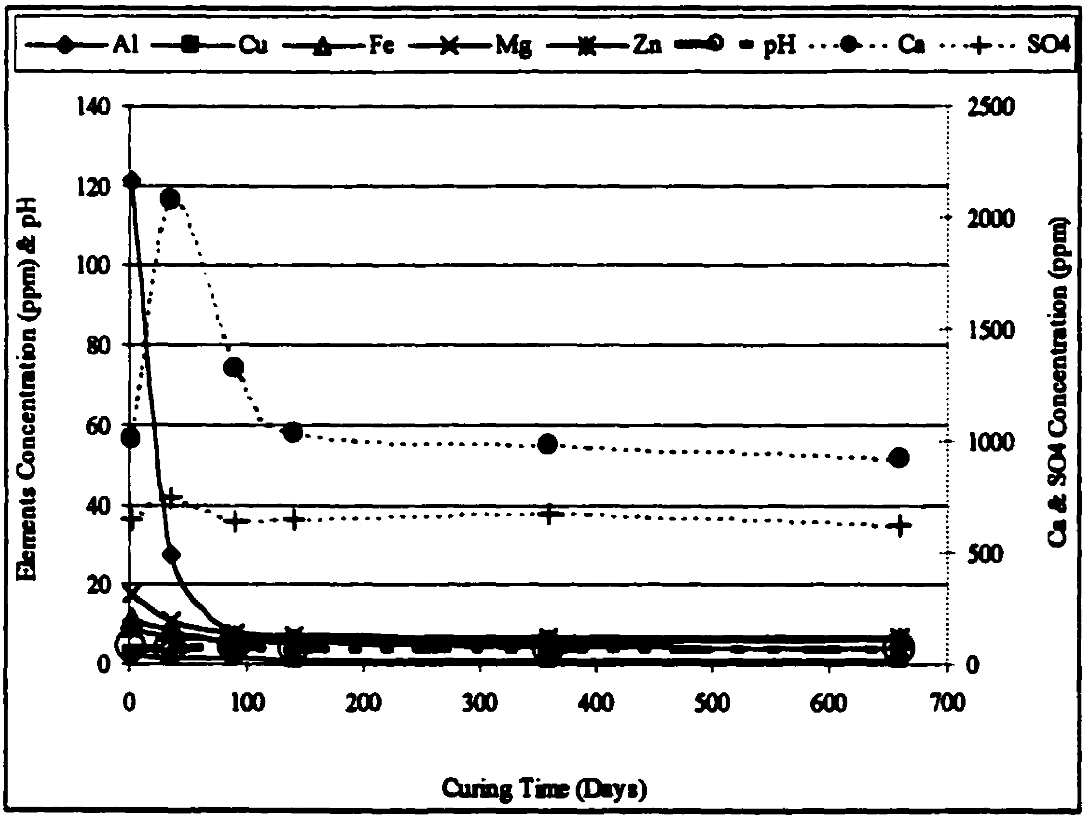
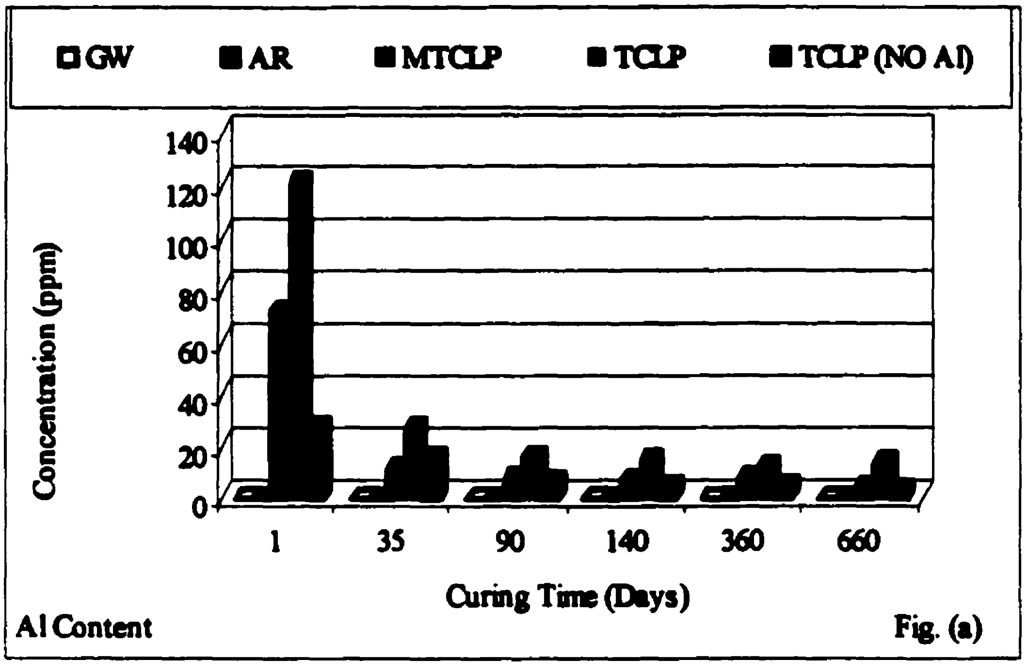


FIGURE 6.25. ACETATE ACID (TCLP) LEACHING TEST RESULTS

Figure 6.26 represents the elemental behavior under different leaching medium. Because of the addition of aluminum to the samples, leaching with sulfuric and acetic acids has caused some considerable quantity of aluminum (up to 120 ppm) to leach out of the samples within the first day of hydration (Figure 6.26. a). However, as the hydration time increased, aluminum was totally consumed by the formation of other aluminum bearing minerals, such as ettringite and gismondine, and its availability decreased significantly.

The leachability of copper with different leachants is shown in Figure 6.26 (b). Treatment of the sample with the added aluminum has led to formation of more ettringite and ettringite like minerals in the sample, which cause reduction in the solubility of copper. Moreover, the increase in hydration time has not effected the leachability of copper and it has remained insoluble. On the other hand, for the samples treated without any aluminum addition, longer hydration had led to release of more copper in the solution. Magnesium and zinc leachability have also followed the same trend as the copper regarding their leachability behavior. Treatment of the samples with combination of lime, fly ash and aluminum has led to higher insolubility in the samples as less of elements are leached out. Samples that were treated with lime and fly ash alone and without any aluminum have released more of elements when leached with acetate acid, particularly in longer curing period. Continued curing of the samples up to 660 days caused more oxidation to take place in the samples without aluminum addition. This is evident from the leaching of more iron ions along with other elements from the samples; while aluminum addition has



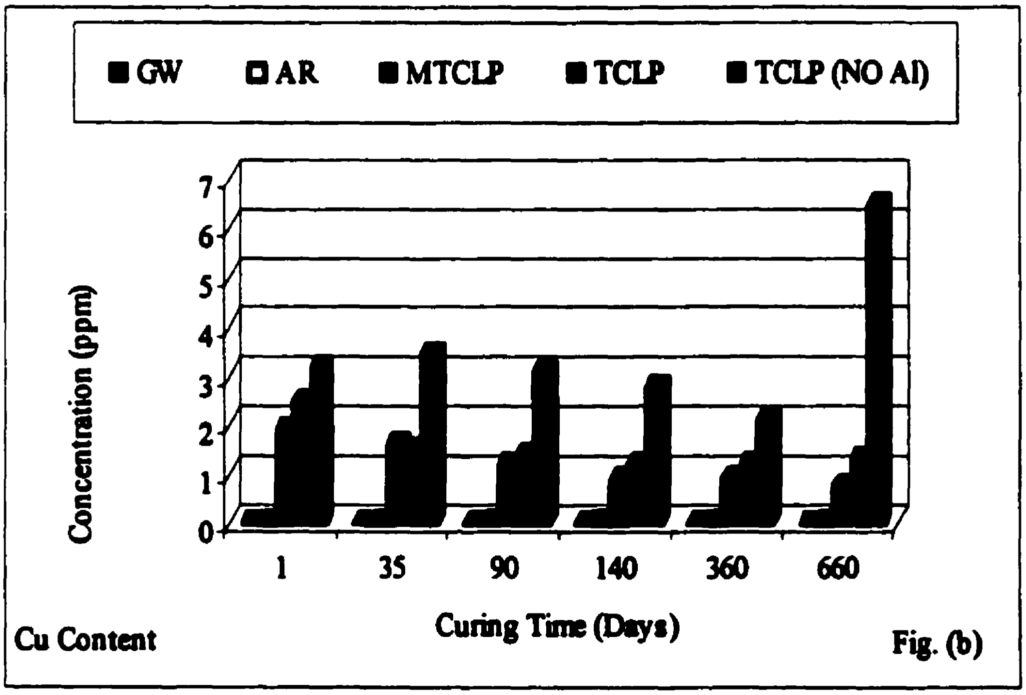
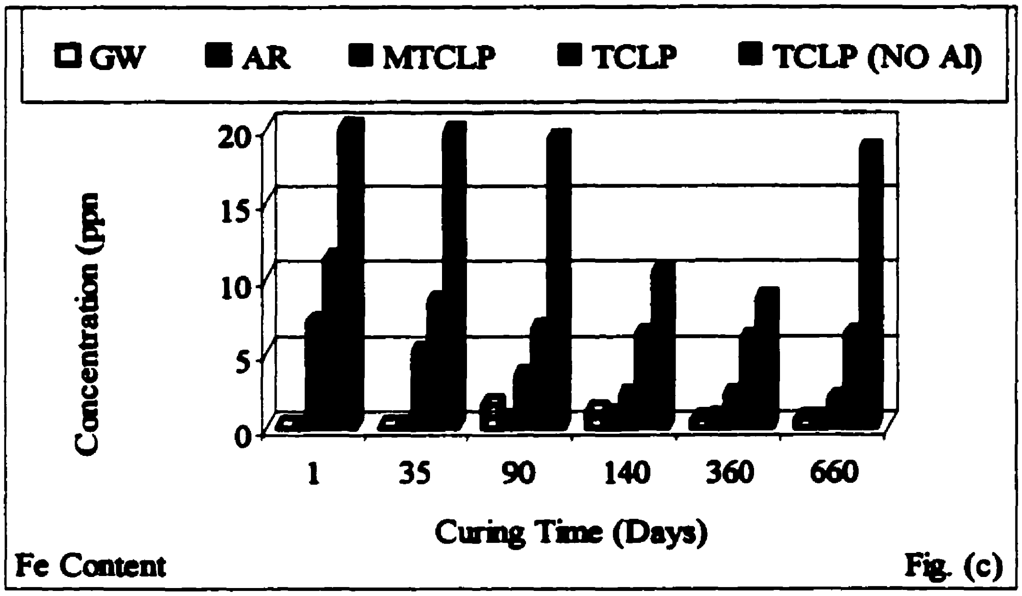


FIGURE 6.26. (a, b) ALUMINUM AND COPPER LEACHABILITY

created more stable environment with lower leachability rate for elements of concern and lower oxidation rate in the sample (Figure 6.26, c, d, e, f, and g).

The pH of the samples treated with combination of lime, fly ash and aluminum has remained above 10 when leached with groundwater and acid rain within the 660 days of curing period. Exposing these samples to sulfuric acid or acetate acid has caused reduction in their pH which consequently led to release of more metals from their structure. On the other hand, the sulfate content of the samples remained constant with respect to leachant throughout the hydration period (Figure 6.26 h). This is despite of the fact that oxidation of pyritic samples should produce more sulfate ions, however, formation of calcium sulfate and calcium aluminate sulfate compounds consumes the excess sulfate generated in the treated samples. Moreover, the application of lime and fly ash reduces the permeability and voids ratio of the samples, which could have a negative effect on oxidation of these samples.

Overall, as already mentioned, the leachability results show that application of lime, fly ash and aluminum has been successful to create a chemically stable matrix which has resisted the leachability of elements of concern from its structure. The X-ray diffraction analysis of the same samples revealed that such treatment procedure has led to formation of ettringite and ettringite like minerals in the samples. The high pH environment combined with the formation of calcium aluminate sulfate compounds have led to the elimination or drastic reduction of heavy metals leachability from these otherwise highly acidic and reactive tailings. Therefore, the immobilization of heavy metals in the lime, fly ash and aluminum treated samples can be attributed to all three separate but interrelated mechanisms of immobilization:



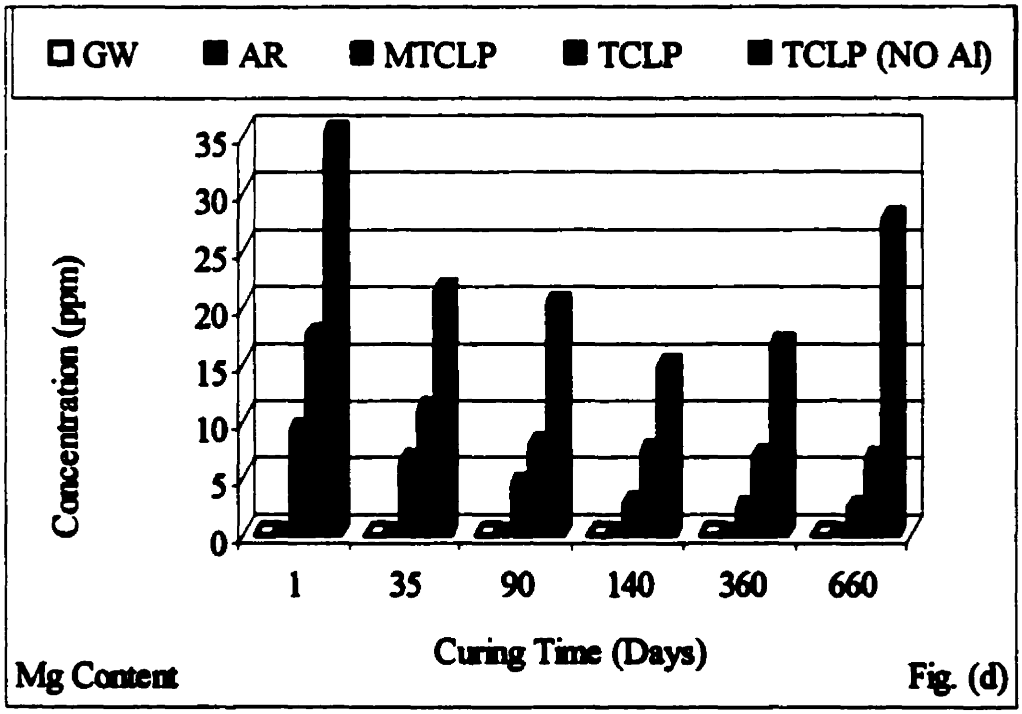
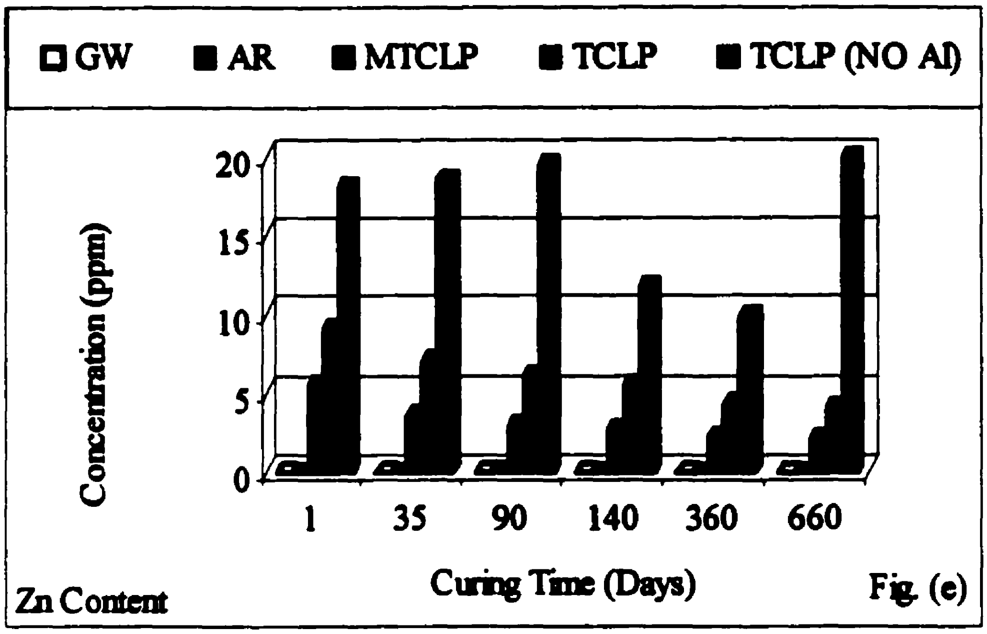


FIGURE 6.26. (c, d) IRON AND MAGNESIUM LEACHABILITY



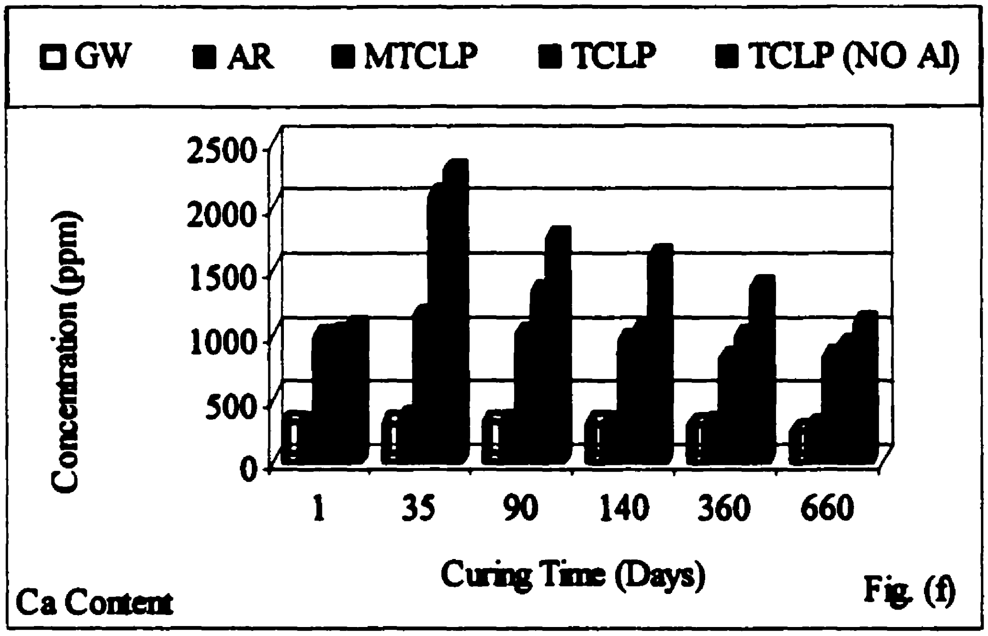
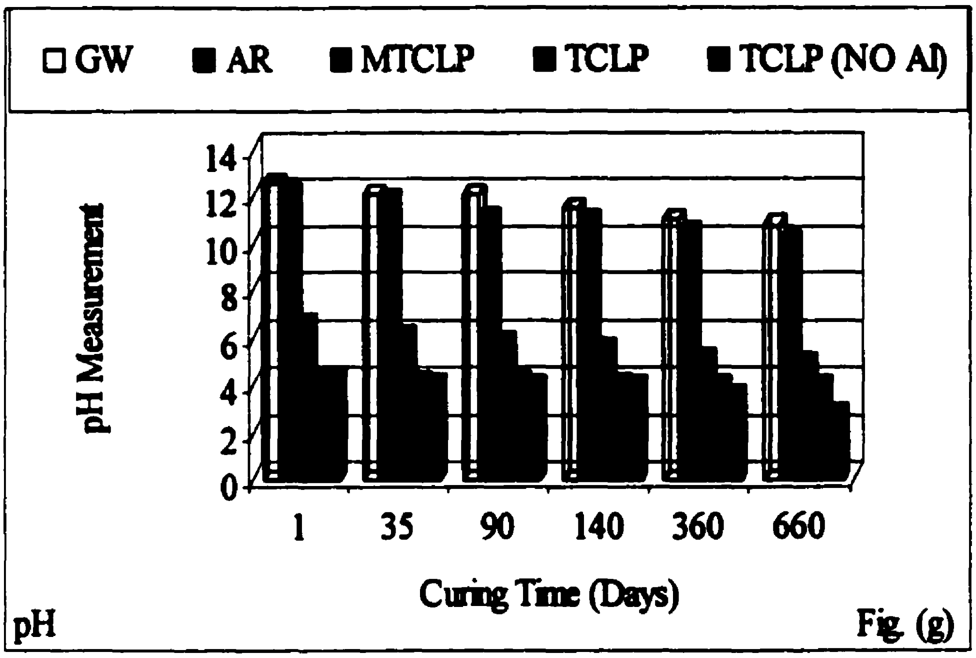


FIGURE 6.26. (e,f) ZINC AND CALCIUM LEACHABILITY



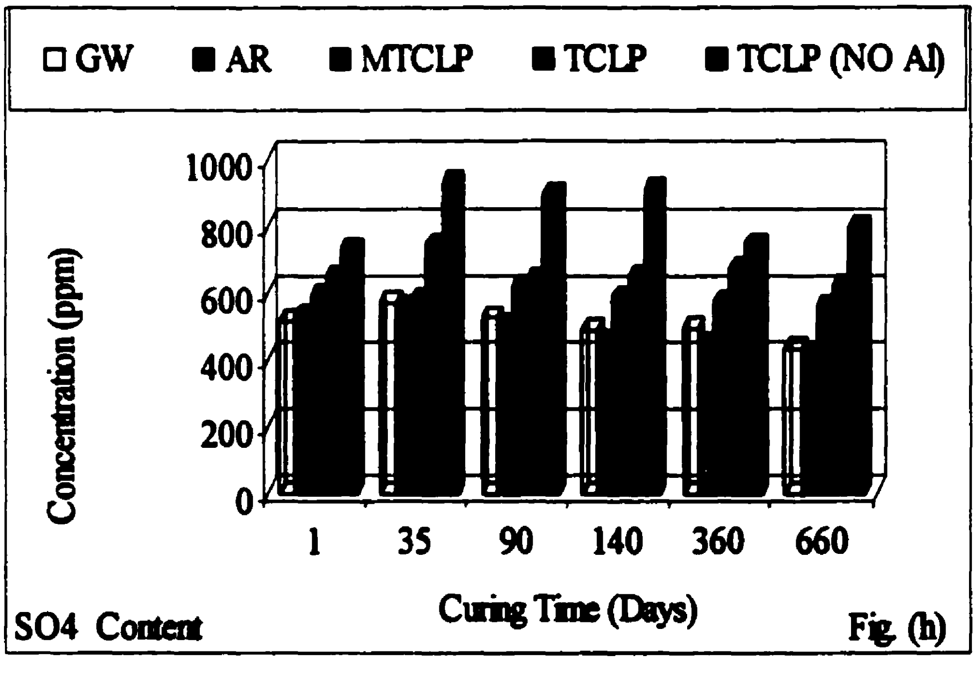


FIGURE 6.26. (g, h) PH MEASUREMENT AND SULFATE LEACHABILITY

sorption to negatively charged surface of calcium aluminate sulfate minerals, precipitation of the metals as hydroxides in the high pH environment as well as the inclusion through isomorphous substitution of heavy metals into the reaction products (such as ettringite).

Overall, the extraction experiment confirmed this theory that upon availability of aluminum, ettringite and ettringite like minerals could be formed in sulfidic tailings as a stable mineral which could prevent the mobilization of heavy metals from otherwise these highly reactive tailings. The results also suggest that the TCLP test (using acetate acid as leachant) will generally overestimate the leachability characteristics of heavy metals from treated tailings. This is due to the fact that pH of the TCLP equilibrium solution is usually much lower than what tailings experience in natural environments and they contain no organic compounds.

6.10 Scanning Electron Microscopy (SEM)

In order to further investigate the formation of ettringite in samples under study, Scanning Electron Microscopy (SEM) coupled with a Tracor Northern Energy-Dispersive X-ray Spectrometer for elemental analysis (EDS) were carried out on lime and fly ash treated samples. The surface of the cured samples were coated with gold and examined using JOEL-840A Scanning Electron Microscopy. The microstructures of the specimen which were treated with 4% lime and 10% fly ash type "C" are given in Figure 6.27. (a,b,c and d) for 3, 28, 90, and 180 days of hydration respectively. Curing the samples for 3 days has resulted in formation of needle like ettringite which are about 5 μm long and 0.5 μm wide (Figure 6.27, a). At the same time, the gypsum mineral which appeared in the form of rods are also clearly visible in the SEM micrographs.

FIGURE 6.27 (a) SEM MICROGRAPH OF THE 4% LIME, 10% F.A. TREATED SAMPLE (3 DAYS)

The EDS analysis of the samples are shown in Figures 6.28 and 6.29. The elemental analysis of the needle shape minerals indicate that they have formed with combination of aluminum, sulfur, and calcium (ettringite).

FIGURE 6.27. (b) SEM MICROGRAPH OF THE 4% LIME, 10% F.A. TREATED SAMPLE
(28 DAYS)

FIGURE 6.27. (c) SEM MICROGRAPH OF THE 4% LIME, 10% F.A. TREATED SAMPLE
(90 DAYS)

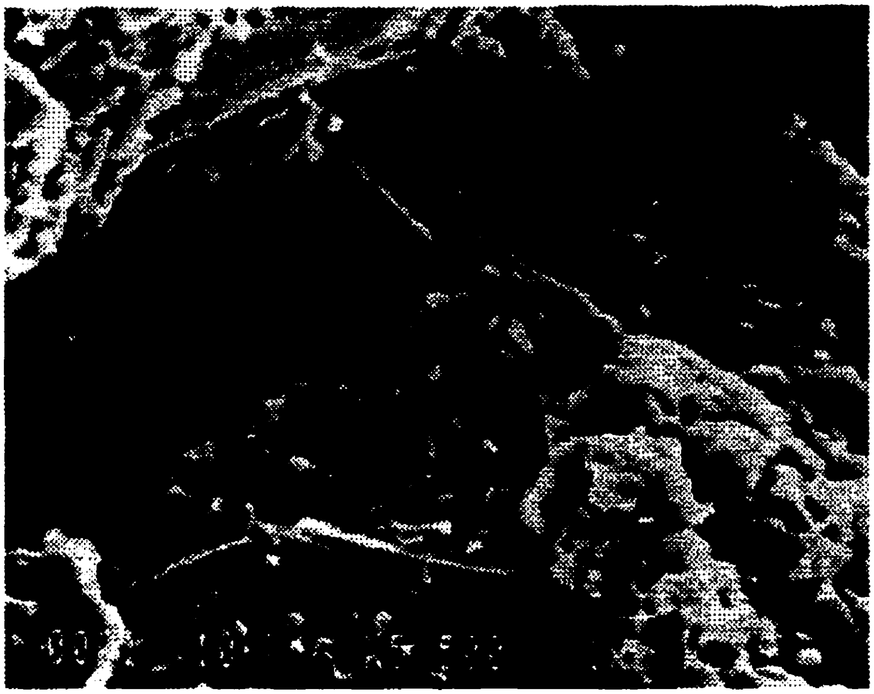


Figure 6.27. (d) SEM Micrograph of the 4% lime, 10% F.A. Treated Sample (180 Days)

This analysis is shown in Figure 6.28. The EDS analysis of rod shape mineral indicates that it has formed mainly from calcium and sulfur (gypsum). This observation is shown in Figure 6.29.

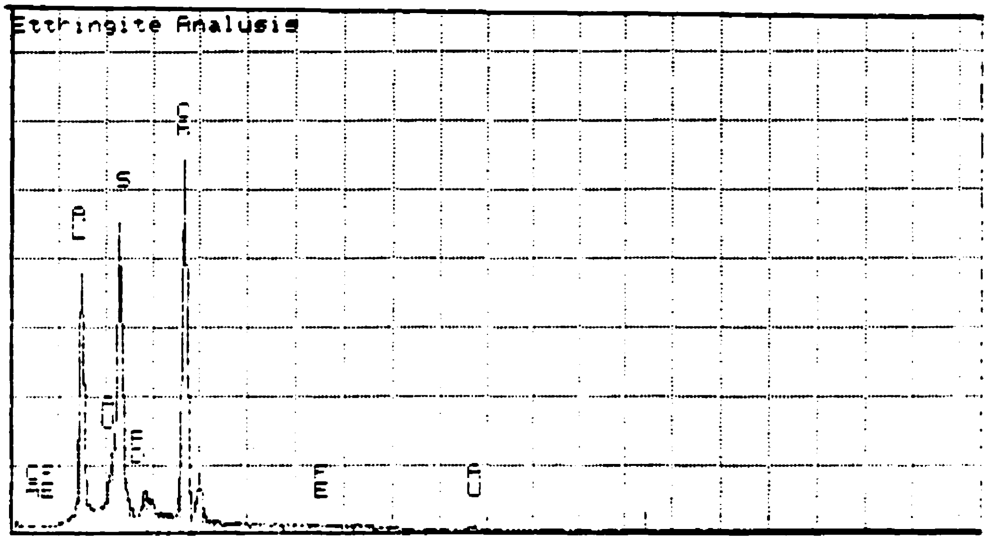


FIGURE 6.28. THE EDS ANALYSIS OF THE 3 DAYS CURED SAMPLES (NEEDLE TYPE LATHS)

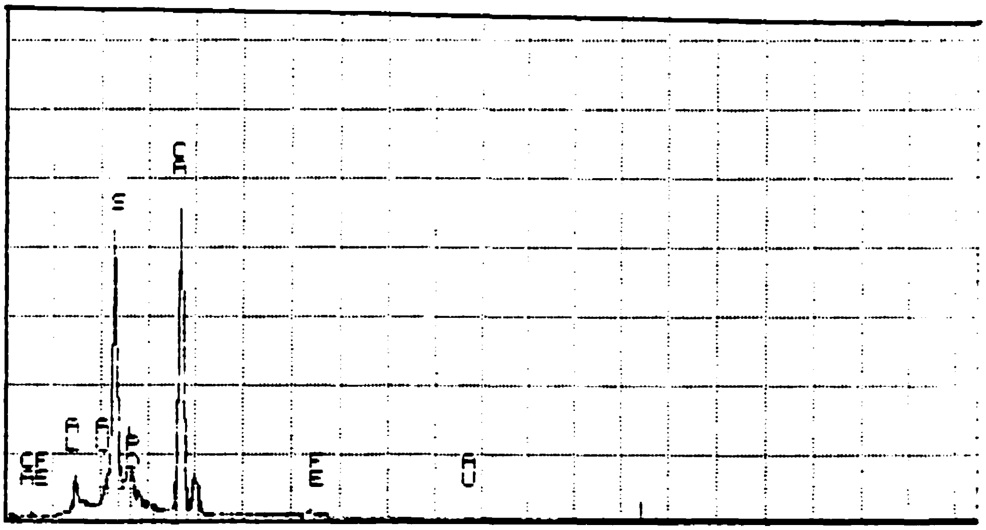


FIGURE 6.29. THE EDS ANALYSIS OF THE 3 DAYS CURED SAMPLES (ROD TYPE LATHS)

Continued curing of the samples to 28 days resulted in coarser grains ettringite laths which were 7 to 8 μm long and 1 to 2 μm wide. Also they were randomly oriented plates forming a fairly dense mosaic texture (Figure 6.27, b). At 90 days, the ettringite laths were coarser (6 μm long and 2 μm wide) and less abundance. Continued hydration to 180 days resulted in disappearance of ettringite laths and (needle and platy forms) appearance of gypsum rods which dominated the structure. The microstructures of 90, and 180 days hydrated samples are shown in Figures 6.27, c and d respectively.

The microstructure of the samples made with 5% lime and 10% fly ash type "C" are given in Figure 6.30(a, b, c, d and e). The needle type ettringite crystals are clearly visible in hydrated samples for the whole curing period. The ettringite laths are 10 μm long and 0.5 to 1 μm wide between 3 days to 180 days of hydration (Figures 6.30, a, b, c). The laths are randomly oriented but form a fairly tight structure. Figure 6.30, d shows the microstructure of the 180 days cured sample. The ettringite laths have reduced in size while gypsum rod lattices are clearly visible.

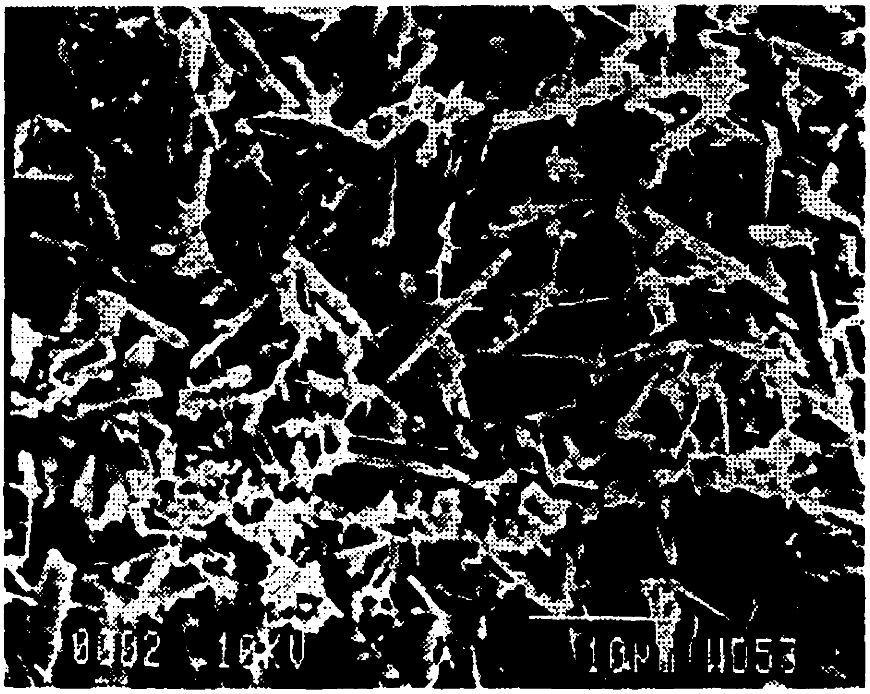


FIGURE 6.30. (a) SEM MICROGRAPH OF THE 5% LIME, 10% F.A. TREATED SAMPLE (3DAYS)

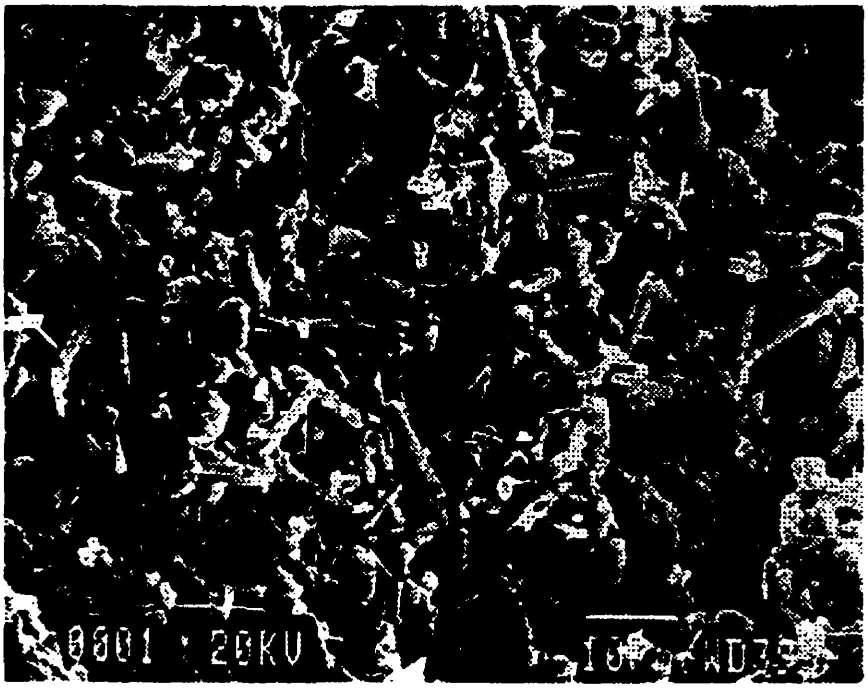


FIGURE 6.30. (b) SEM MICROGRAPH OF THE 5% LIME, 10% F.A. TREATED SAMPLE (28 DAYS)

FIGURE 6.30. (c) SEM MICROGRAPH OF THE 5% LIME, 10% F.A. TREATED SAMPLE (90 Days)

FIGURE 6.30. (d) SEM MICROGRAPH OF THE 5% LIME, 10% F.A. TREATED SAMPLE (180 DAYS)

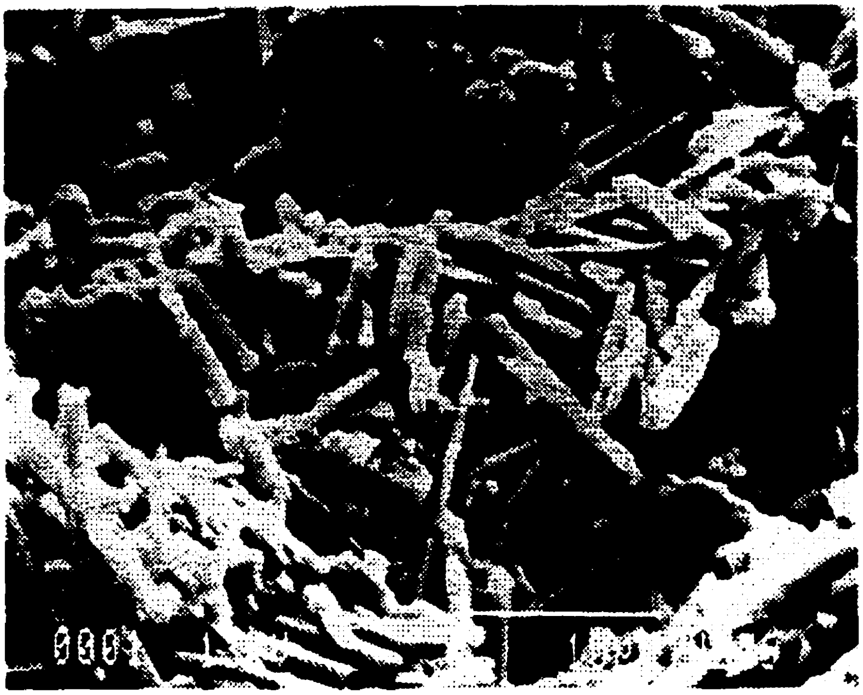


FIGURE 6.30. (e) SEM MICROGRAPH OF THE 5% LIME, 10% F.A. TREATED SAMPLE (360 DAYS)

In Figures 6.30, e and f, the microstructure of the treated sample for 360 days is given. The ettringite laths have reduced in size to about 4μm long and 1μm wide and are arranged in a subparallel fashion over gypsum rods. These figures are the indication of excessive oxidation in the sample which has led to deterioration of ettringite and formation of gypsum in long term hydration.

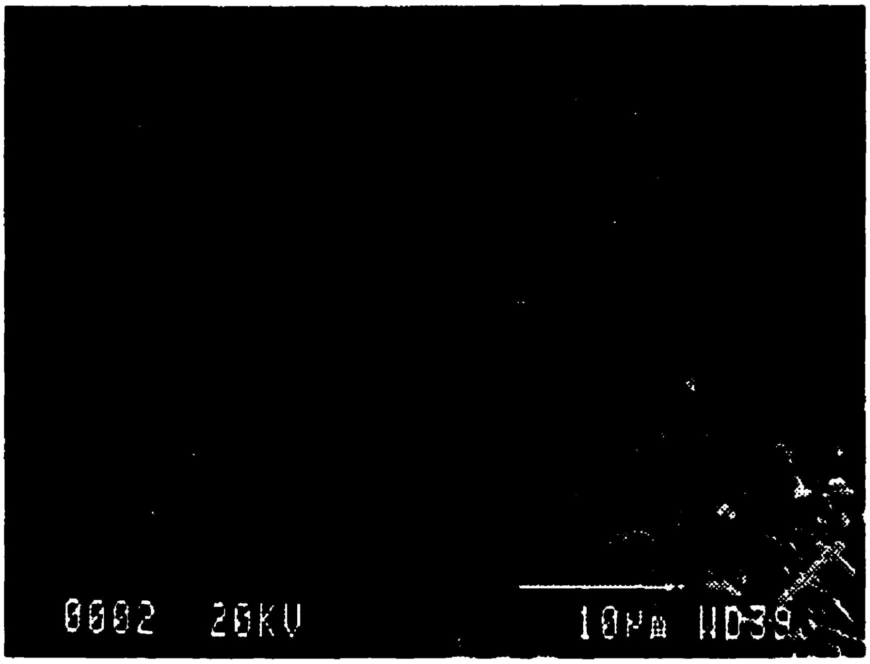


FIGURE 6.30. (f) SEM MICROGRAPH OF THE 5% LIME, 10% F.A. TREATED SAMPLE (360 DAYS)

Based on the results of the optimization study, samples which were made with the addition of aluminum and were treated with combination of lime and fly ash type "C" were analysed with the scanning electron microscopy. The microstructure of the treated samples are shown in Figures 6.31 (a, b, c, d, and f). The ettringite laths are visible after 3 days of hydration (Figure 6.31, a). They are generally 6 to 7 µm long and about 0.5 µm wide. The ettringite has formed an open lattice structure and gypsum rods are also present in the hydrated samples. When the sample is hydrated for 28 days, the microstructure is markedly different as can be seen in Figure 6.31, b. The ettringite laths are very coarse at 10 µm long and 1 µm wide. The ettringite fibers appear to have formed a mat, which is very dense. Similar structures are observed after 90 and 180 days of hydration. Moreover, in 180 days hydrated samples, the ettringite laths also appeared in the form of randomly oriented plates.

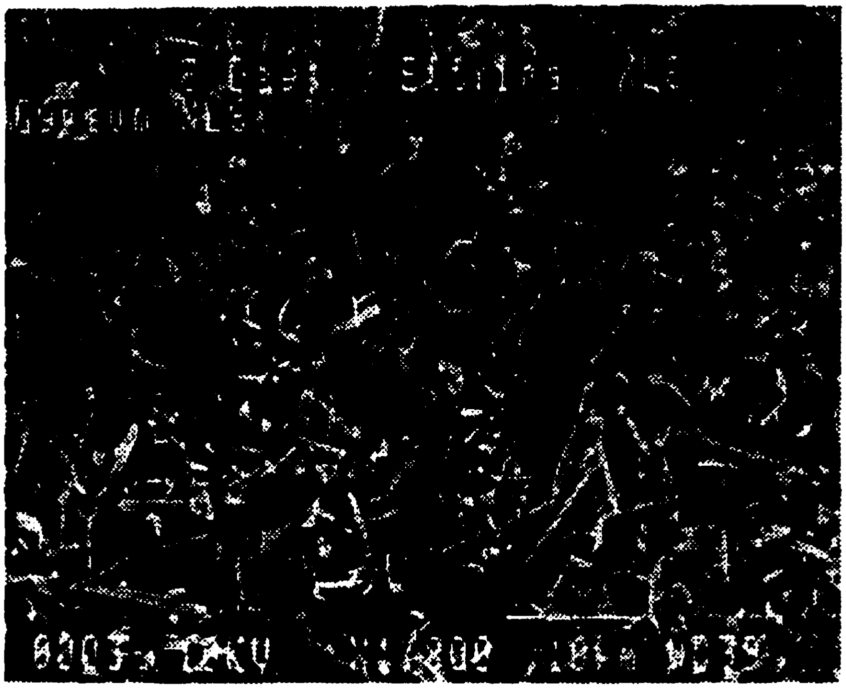


FIGURE 6.31. (a) SEM MICROGRAPH OF THE 5% LIME, 10% F.A., 110 PPM AL TREATED SAMPLE (3 DAYS)

FIGURE 6.31. (b) SEM MICROGRAPH OF THE 5% LIME, 10% F.A., 110 PPM AL TREATED SAMPLE (28 DAYS)

Figure 6.31. (c) SEM Micrograph of the 5% Lime, 10% F.A., 110 ppm Al Treated Sample (90 Days)

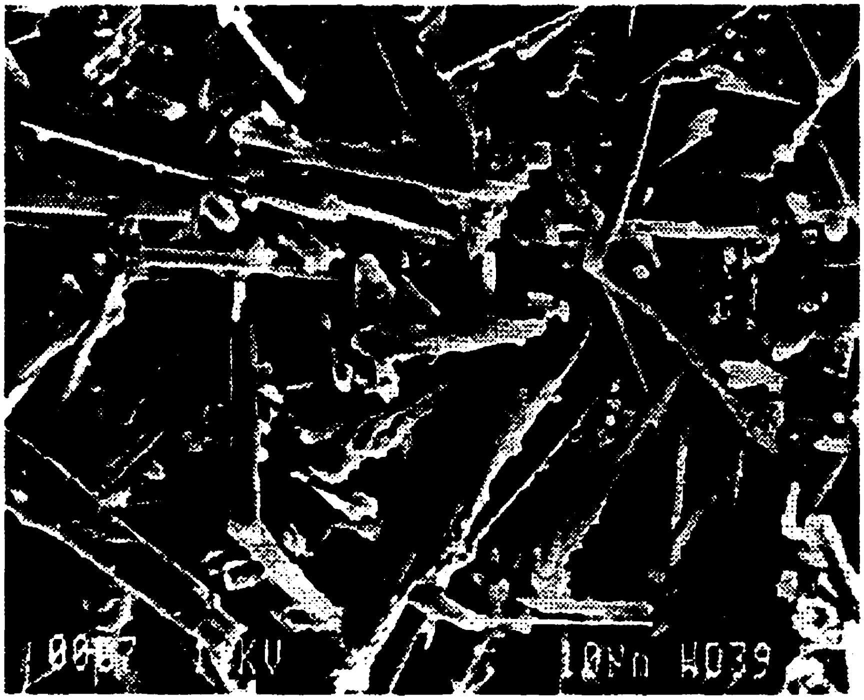


Figure 6.31. (d) SEM Micrograph of the 5% Lime, 10% F.A., 110 ppm Al Treated Sample (180 Days)

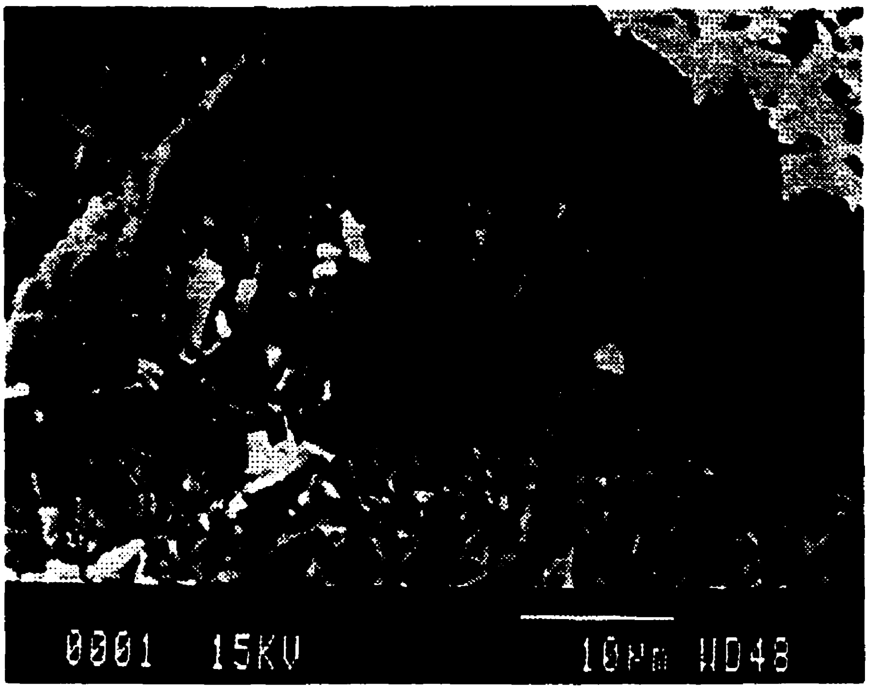


FIGURE 6.31. (e) SEM MICROGRAPH OF THE 5% LIME, 10% F.A., 110 PPM AL TREATED SAMPLE (360 DAYS)

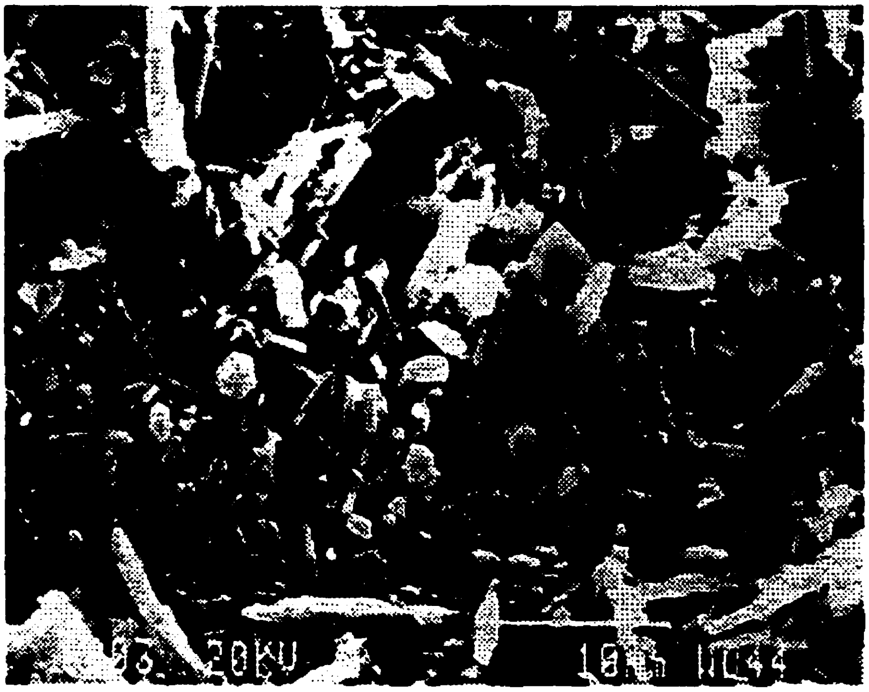


FIGURE 6.31. (f) SEM MICROGRAPH OF THE 5% LIME, 10% F.A., 110 PPM AL TREATED SAMPLE (660 DAYS)

The microstructure of the hydrated sample for 360 days appears the same as the sample hydrated for 180 days. However, some gypsum rods have also are visible in the microstructure (Figure 6.31, e).

The microstructure of the sample hydrated for 660 days is given in Figure 6.31, f. Ettringite crystals have appeared in needle type laths as well as hexagonal form. Ettringite laths have reduced in size (about 7 to 8 μm long) while some gypsum crystals are also present in the microstructure. The ettringite laths are oriented randomly and are densely packed in an open network.

6.11 Conclusion

Samples of the tailings under study were treated with combination of lime and fly ash type "C". The success of the treatment was evaluated based on results of leachability combined with x-ray diffraction and scanning electron microscopy. The preliminary investigation showed that 5% lime as well as 10% fly ash is the threshold of the treatment agents needed to prevent oxidation and form ettringite as a stabilization technique in these samples. However, long term hydration resulted in lowering the pH of the samples and consequently, destruction and deterioration of the ettringite formed in the samples and release of the stabilized metals of the concern into the solution.

In order to facilitate and enhance the formation of ettringite, as a means of stabilization agent in the tailings under investigation, aluminum in less than its stochiometric quantity was added to the samples and formation of ettringite was monitored over a period of 660 days. As in the previous experiments, the success of the treatment techniques was evaluated by the means of leachability, x-ray diffraction technology combined with scanning electron microscopy. The results of the experiments indicate that upon availability of aluminum for reaction, ettringite and ettringite like minerals could be formed and precipitate as a stable mineral in these samples. Moreover, the high pH environment of the samples as a result of lime and fly ash addition combined with the stabilization effect of ettringite reduced the solubility of the metals of concern significantly.

The X-ray diffraction analysis as well as the microstructure figures obtained by using scanning electron microscopy proved that ettringite remained as a stable mineral in these samples within the 660 days hydration period.

Based on the obtained results it can be concluded that the proposed lime-fly ash and aluminum based treatment technique is effective in significantly reducing heavy metal leachability for the waste form tested. In addition, the results presented here formed the basis for the development of an experimental protocol to be used for testing the effectiveness of a given remediation technology or for the preliminary design of a given remediation technology. The approach is developed for the lime-fly ash based considered in the present study, but can be easily extended to a wide array of in-situ remediation schemes.

Chapter 7

Geotechnical Analysis

7.1 Introduction

Numerous investigators have performed research in the area of Acid Mine Drainage (AMD) and heavy metal stabilization (Kuyucak et al., 1995; Hedin, and Watzlaf, 1994; Kepler, and McCleary, 1994; Hossein, 1991) by means of chemical admixtures, but the bulk of the studies performed seem to be concentrating on the use of lime as the chemical additives. Moreover, previous research does not consider the reuse potential of the stabilized tailings, as it concentrates more on the reduced leachability of heavy metals as a result of treatment. Therefore, development of a treatment procedure capable of reducing the leachability of heavy metal and other environmental concerns as well as producing an inert material with reuse potential is of great interest to the mining industry.

In the context of the present study, it is proposed to use lime, fly ash as well as aluminum in the presence of sulphate compounds to enhance and promote the formation of mineral ettringite as means of solidification/stabilization of other wise reactive tailings. However, ettringite is generally believed to be expansive with deteriorating consequences, which could cause physical and chemical instability. Occurrence of expansion in ettringite not only could result in structural instability, but it could also lead to release of absorbed and/or adsorbed metals from its structure. Moreover, disintegration of ettringite could result in release of excess sulphate ions into the surrounding environment and lowering of the pH. In a low pH condition, the solubility of heavy metals, which were otherwise precipitated, will increase with potentially harmful effect to the surrounding environment. Therefore, study the factors that could induce or prevent ettringite expansion is crucial to success of the present study.

The phenomenon of expansion in cementitious mortars is known as sulphate attack in concrete industry. Expansion and loss of structural integrity can take place in two forms; expansion due to the formation of ettringite, and/or loss of strength through softening that has been attributed to gypsum formation. Depending on sulphate concentration, the corrosive mechanism of concrete is divided into two parts (Cohen and Mather 1991). At low concentrations, (approximately 830 mg/L of SO_3 — this limit changes with the change in aluminum availability in the sample) mechanism causing change is controlled by ettringite formation. When SO_3 concentration attains a higher value, the mechanism is dominated by gypsum formation.

Gypsum formation is not generally believed to cause expansion, but softening and mushiness in the sample, while expansion and subsequent microcracking are generally attributed to ettringite formation. However, it has been suggested that not all types of ettringite are expansive (Mehta, 1983). The large lath-like crystals of ettringite (about 10 μm), which form in the lower pH range of ettringite (around 10.5 to 11.5) and under conditions of low hydroxyl ions concentration, are not expansive. On the other hand, the small rod-like crystals of ettringite, typically 1-2 μm long, which forms under condition of higher pH (usually around 12 and higher) and high hydroxyl ions concentration, are expansive. Moreover, addition of natural pozzolans such as fly ash can further stabilize the physical and mechanical structure of the treated mortars.

According to Mehta (1986 a), the technical significance of the use of fly ash is derived mainly from three features of the pozzolanic reaction. First, the reaction is slow; second, the reaction is lime consuming instead of lime producing; and third, the reaction products are very efficient in filling up large capillary space. The second and third features of pozzolans are responsible for the capacity of fly ash to improve the sulphate attack resistance of mortars. Addition of fly ash to cement in the case of internal sulphate attack was addressed in another study by Ouyang *et al.* (1988). After conducting research on expansion and subsequent loss of strength due to ettringite formation in the cement mortar, the authors concluded that substitution of cement with fly ash greatly reduces expansion. Mehta (1986 b), considered both the chemistry and mineralogy of fly ash to explain the effect of fly ash to sulphate resistance of cement paste. He attributed the sulphate resistance of the class "C" fly ash/cement mixture to their tendency to form ettringite prior to excess sulphate exposure; ettringite remains stable in presence of additional sulphate ions.

In the event of reusing the stabilized tailings, the strength of compacted treated specimens is an important property to assess its recycling potential. Special emphasis should also be given on controlling possible material deterioration due to freezing/thawing or wetting/drying processes on a seasonable basis. This deterioration results in loss of specimen's structural integrity or visual cracking due to existence of high swelling potential. Furthermore, permeability of the treated samples is also measured to examine the effect of proposed treatment procedure on porosity of the specimens.

7.2 Experimental Procedure

7.2.1 Unconfined Compression Strength Test

Addition of lime, and fly ash type "C" to sulfide content tailings is expected to enhance its cohesive properties, and thus increase its compressive strength. The development and maintenance of high strength and stiffness is achieved by elimination of large pores, by bonding particles and aggregates together, by maintenance of flocculent particle arrangements, and by prevention of swelling. Moreover, upon addition of aluminum, ettringite will form in the treated tailings which will further enhance the strength properties of the treated sample. Based on this analogy, the unconfined compression test was used to measure the change in the treated tailings strength and to assess its reusability.

Unconfined compressive strength (UCS) test refers to the sample's resistance to compression with increasing strain, measured under unconsolidated, undrained condition. In this study, the unconfined compression tests were performed in accordance with the ASTM D2166 procedure, test method for unconfined compressive strength of cohesive soil. For ASTM D2166, the U.S. EPA generally considers a stabilized material as satisfactory if it has a UCS of at least 50 psi; however, the minimum required strength should be determined from the design loads to which the material may be subjected. Also, the UCS for cohesive soil is defined as the load per unit area at which an unconfined prismatic or cylindrical specimen of soil will fail in a simple compression test.

In order to measure the compressive strength of the treated samples, cylindrical specimens (with a diameter of 30 mm and a height of 60 mm; Figures 7.1 and 7.2) were prepared at solid to water ratio of 0.5. Samples were dry mixed and water was added and allowed to mellow and cure for 24 hours at 90% relative humidity and 25°C temperature before being compacted in specifically designed

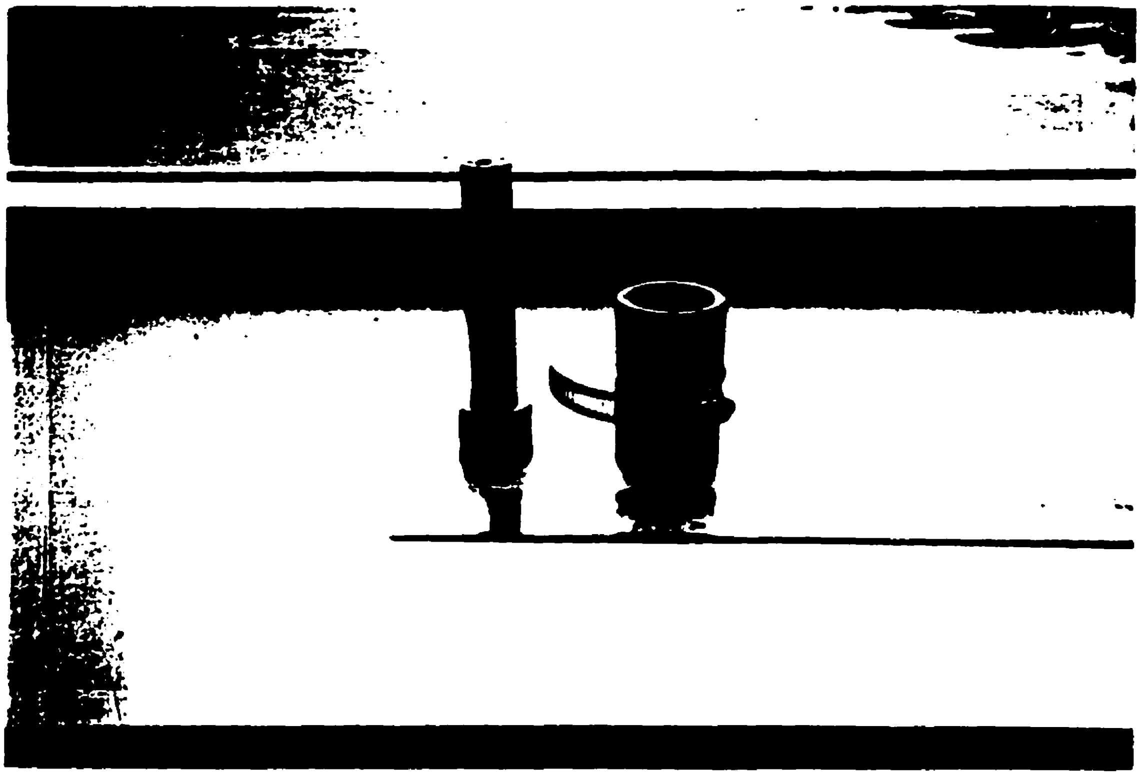


FIGURE 7.1 PHOTOGRAPH OF THE COMPACTION MOLD AND ITS ROD

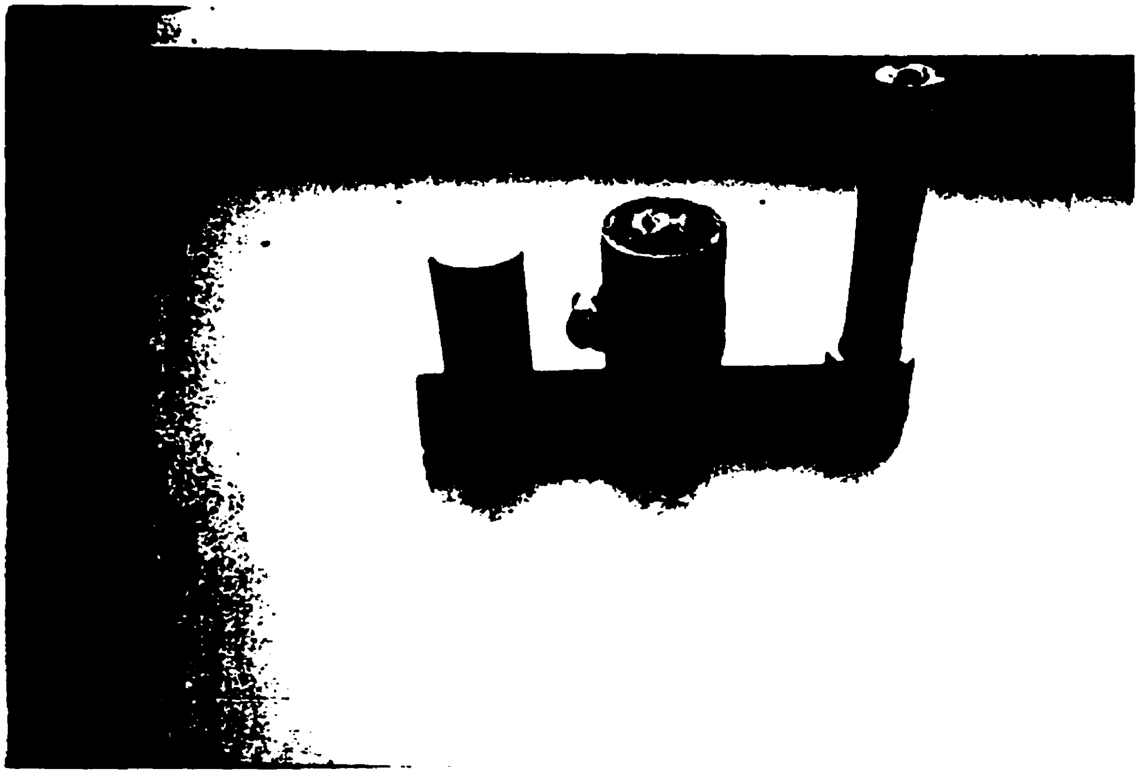


FIGURE 7.2 PHOTOGRAPH OF THE COMPACTED SAMPLE IN THE MOLD AND OUT OF THE MOLD

molds. The compacted samples were wrapped in plastic sheet and subsequently were stored in humid room until the testing schedules. Samples were tested after 1 day, 28 days, 140 days and 360 days of curing. The loading rate was 0.5-1.5 mm/min., so that the maximum loading time did not exceed 15 minutes. The resulting stress and strain were then measured. For each applied load, an axial unit strain (ϵ) was computed by dividing the specimen's change in length ΔL, by its initial length L0, according to the equation:

$$\epsilon = \Delta L / L0$$

The value of ΔL is given by the deformation dial reading, the cross-sectional area will increase slightly from the initial area (A0) to (A) which can be computed by equation

$$A = A0/(1-\epsilon)$$

Each applied axial load P was determined by multiplying the proving ring dial reading by the proving ring calibration factor. The compressive stress (σc) was computed using the following equation:

$$\sigma c = P/A$$

The experiments were conducted in triplicate to ensure the reliability of the test results.

7.2.2 Permeability (hydraulic conductivity) Test

The permeability of a stabilized waste is an important factor, as it indicates the ability of a material to permit the passage of water and to limit the loss of contaminant from the stabilized waste to the environment. Addition of lime and fly ash to fine grained soil type material will improve its plasticity, workability, and volume change characteristics. Furthermore, most of these materials will also exhibit improved strength, stress-strain, and fatigue characteristics, and develop lower values of hydraulic conductivity. The reduction in permeability and the value of hydraulic conductivity is achieved through modification of pore size and pore size distribution as a result of pozzolanic activity.

There are two types of laboratory tests for measurement of soil permeability: Constant Head and Falling Head Methods. The constant head method is used for soils of high permeability (such as sands), while the falling head method is used for soils of intermediate and low permeability (such clays and silts). The falling head test, whether carried out in a standard permeameter cell or in a sample tube, can be performed either on an undisturbed or recompacted material. The constant head permeameter on the other hand can be carried out only on recompacted soil, but it is possible to apply a known constant axial stress to the sample during the test, if necessary. (Head, 1992). However, it is important to note that the laboratory permeability measurement and actual or field permeability value could be one to two order of magnitudes different from each other, since the initial and boundary conditions in the laboratory are not generally similar to those surrounding the field problem being studied. Therefore, laboratory measurement of permeability is only an indication of the permeability that is expected in the field.

There are several factors that can influence the value of permeability measured in the laboratory, such as: sample particle size, void ratio, the geometry of the flow channels, compaction method, degree of saturation, sample hydraulic gradient, and the viscosity and the density of the permeant (Yong *et al.*, 1992).

Samples were premixed with water and were allowed to mellow for 24 hours before be compacted into the modified permeameter cell with a diameter of 30 mm and a length of 60 mm (Figure 7.3).

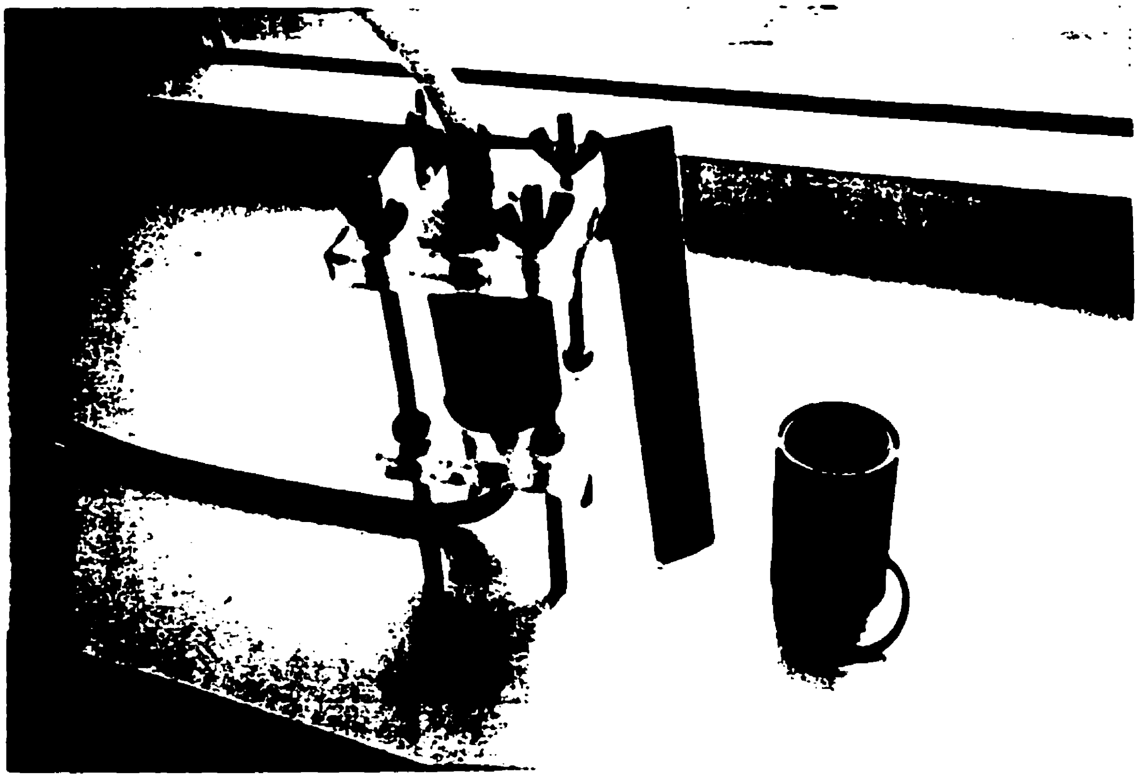


FIGURE 7.3: PHOTOGRAPH OF THE MODIFIED PERMEAMETER

The treated samples were cured in the humidity room at 90% relative humidity and 25°C temperature for 28 days before being tested for their permeability using falling head test method. Prior to the test, the permeameter was placed in a sink in which the water was about 2 inches above the cover of the permeameter while the outlet was opened so that the water could back up through the specimen. This procedure was done to insure the saturation of the sample and elimination of entrapped air. When the water in the plastic inlet tube on the top of the mold reached equilibrium with the water in the sink (allowing for capillary rise in the tube), the sample was assumed to be saturated.

The coefficient of permeability was computed using the equation:

$$\mathbf{K = (2.3\ aL)/At)^{*}log\ (h1/h2)}$$

where k = coefficient of permeability, cm/s
a = area of standpipe, cm^2
A = area of the specimen, cm^2
L = length of the specimen, cm
h1 = hydraulic head at beginning of the test, cm
h2 = hydraulic head at end of the test, cm
t = total time for water in the standpipe to drop from h1.

The permeability was corrected by multiplying the computed value by the ratio of viscosity of water at the test temperature to the water at 20 °C. The experiment was conducted in duplicate to increase the reliability of the test results.

7.2.3 Freeze and Thaw Test

The durability of a treated sample is usually evaluated by its resistance to repeated freeze/thaw cycles. It is suggested that freezing and thawing breaks down the natural bonds of the hydration products by pore-ice formation (Leroueil *et al.* 1991). Laboratory investigations have also shown that freeze-thaw can increase the hydraulic conductivity of compacted fine-grained soils by one or two orders of magnitude (Othman 1992; Chamberlain *et al.* 1990). These studies have shown that ice lenses formed during freeze-thaw result in a network of cracks. When the soil temperature drops below 0°C, ice crystals nucleate in the center of large pores. When water changes to ice, its volume increases about 9% due to the opening of the lattice of its hexagonal crystal structure. As the ice crystals grow, they interfere with each other and soil particles. Thus, ice exerts pressure on the surrounding soil and causes it to move, rearrange, and consolidate (Alkire and Morrison 1982). Moreover, the cyclic freezing and thawing by the ice crystal formation causes mechanical stresses, which results in the formation of planes of weakness in the aggregates and as a consequence, damage to the structural integrity of the treated samples may result. However, addition of fly ash type "C" to the tailings is expected to improve tailings plasticity, and volume change characteristics. Furthermore, addition of fly ash will improve the flocculation of tailings particles' arrangement and it will reduces its permeability and porosity. Therefore, the overall results of the proposed treatment procedure are to lower values of hydraulic conductivity and prevent or reduce the penetration of moisture into the treated mortar.

In order to perform the freeze and thaw tests on the treated tailings samples, eight compacted and 28 days cured specimens were subjected to repeated freeze and thaw conditions. Each cycle induces 24 hours freeze at -10°C and 24 hours thaw at 25°C. Samples were thawed in a constant temperature and relative humidity room. Overall, 4 specimens were subjected to 6 sets of freeze/thaw cycles and the other 4 to 12 set of freeze/thaw cycles before the samples being tested for their unconfined compressive strength as well as permeability measurement according to the procedures described previously.

7.3 Results and Discussion

7.3.1 Unconfined Compressive Strength Test Results

The strength of compacted specimens is an important property for assessing the success of stabilization and solidification and potential reusability of the treated tailings. Improvement in physical and mechanical characteristics of the treated tailings will enhance its handling and disposal capabilities in tailings pond or as aggregates in related applications. Development of sufficient strength in treated tailings will allow its use (as an inert material) for embankments, retaining walls, or other applications which require a certain level of shear strength.

A total number of 57 cylinders were made and tested to determine the unconfined compressive strength of the samples and to establish a general trend for the gain in strength with different treatment additives. The specimen preparation for the unconfined compressive strength experiments involved mixing of all constituents in designated percentages, followed by the addition of water with the water to solid ratio of 0.5, mellowing and compaction in modified molds. The molds for this experiment were designed as 30 mm in diameter and 60 mm in length.

In order to examine the gain and/or loss of strength in these samples, control cylinders were made and compacted without addition of any treatment agent. Moreover, 12 cylinders were compacted with the addition of 5% lime as the treatment agent. Furthermore, in order to examine the effect of fly ash to the strength of the samples, 12 cylinders were compacted with the addition of 5% lime plus 10% fly ash type "C". Finally, based on the results of the optimization experiments conducted previously, 21 cylinders were made with the addition of 5% lime plus 10% fly ash type "C" as well as 110 ppm of aluminum. The aluminum was added in an attempt to promote the formation of ettringite in the samples and study its effect on the strength of the treated specimens. Most of the specimens were tested for curing periods of 1, 7, 14, and 28 days. However, in order to study the long-term effect of ettringite on the strength of the treated samples, the aluminum

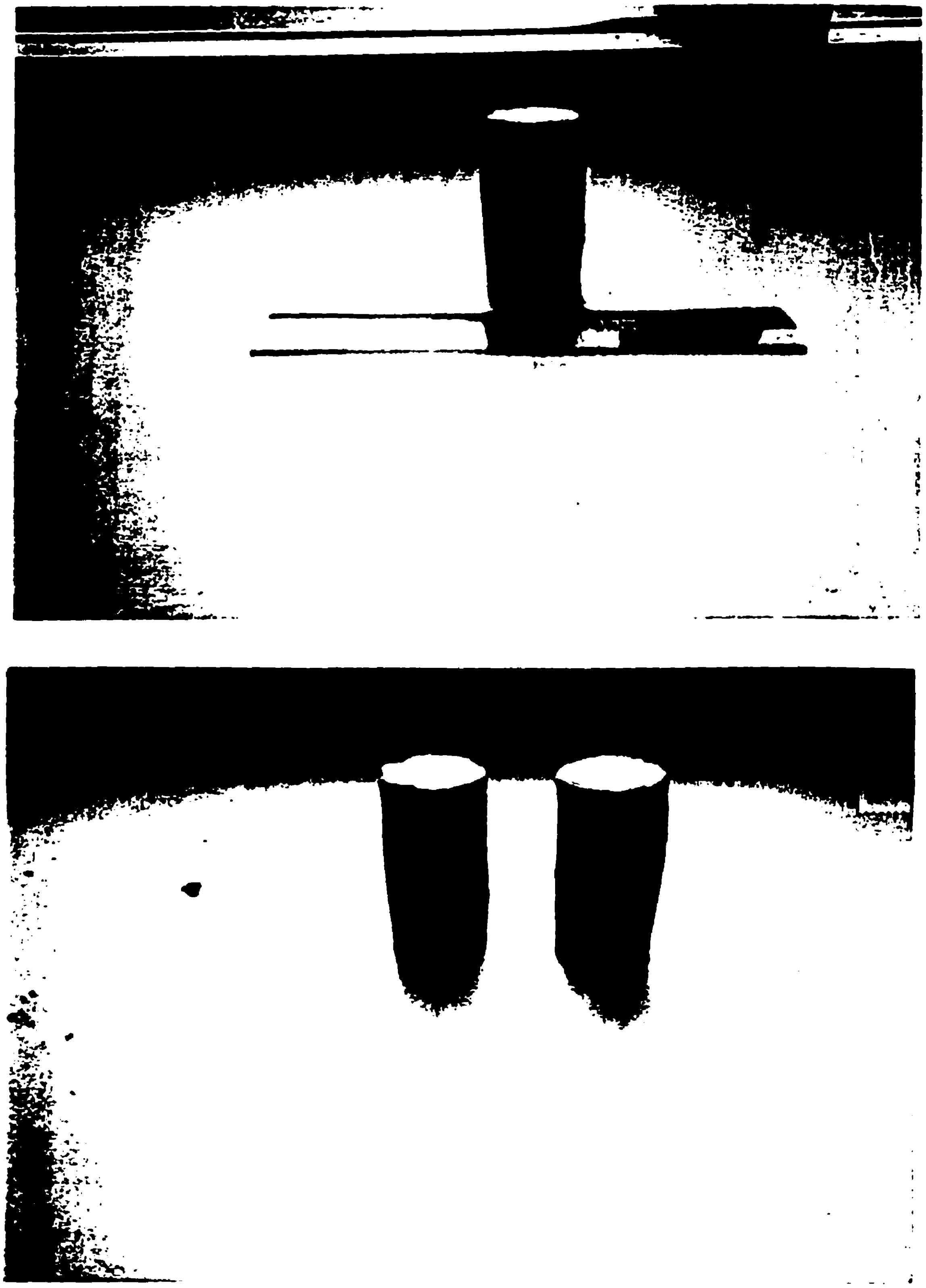


Figure 7.4: Photograph of the specimens after unconfined compressive strength experiment

treated specimens were further cured and tested after 90 days, 140 days and 360 days of hydration.

The results for the unconfined compressive strength test performed on all the samples up to 28 days of curing are shown in Figure 7.5. The control sample, which was made without any additives, failed to gain any strength during the hydration period. Addition of 5% lime to the tailings sample, which is the threshold of lime needed to stabilize the pH of the sample to near 11, resulted in gain of moderate strength after 7 days of hydration. These samples reached an unconfined compressive strength of 137 kPa between 7 days and 14 days of hydration. However, further curing led to disintegration and loss of strength in these samples.

The result of X-ray diffraction analysis performed on 28 days cured lime treated sample (Figure 7.6) showed the presence of gypsum crystals in these samples. Therefore, it is postulated that addition of lime alone could not instigate enough pozzolanic activities to generate a substantial amount of strength in the samples.

Application of 5% lime plus 10% fly ash type "C" has generated higher strength in the samples than those which were treated with lime alone (Figure 7.5). Within the first day of treatment, 90 kPa of strength was measured in these samples. Generation of high early strength in these samples is attributed to activation of lime's pozzolanic properties in the presence of fly ash type "C".

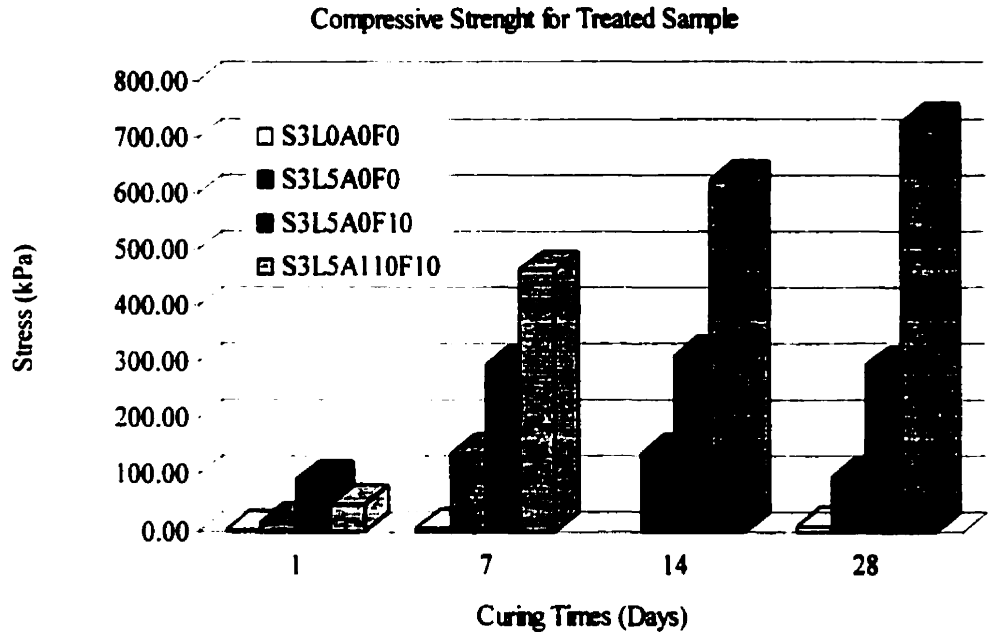


FIGURE 7.5 UNCONFINED COMPRESSIVE STRENGTH OF THE SAMPLES

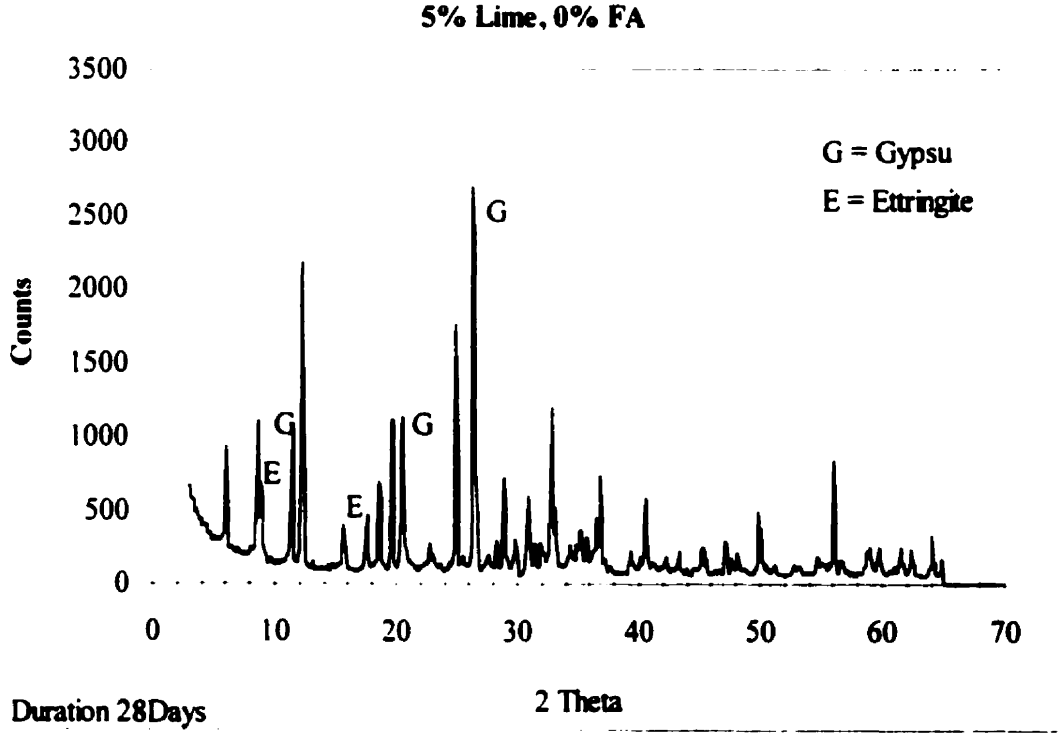


FIGURE 7.6 X-RAY DIFFRACTION ANALYSIS OF 5% LIME TREATED SAMPLE

The strength of these samples increased to 300 kPa after 7 days of hydration and almost remained the same until 28 days of curing. The X-ray diffraction analysis of lime and fly ash treated sample is shown in Figure 7.7. Upon application of fly ash type "C" to lime treated samples, stronger peak intensities for ettringite is observed. Moreover, there is an slight reduction in the peak intensities of gypsum for samples treated with the combination of lime and fly ash as compared with those treated with lime alone.

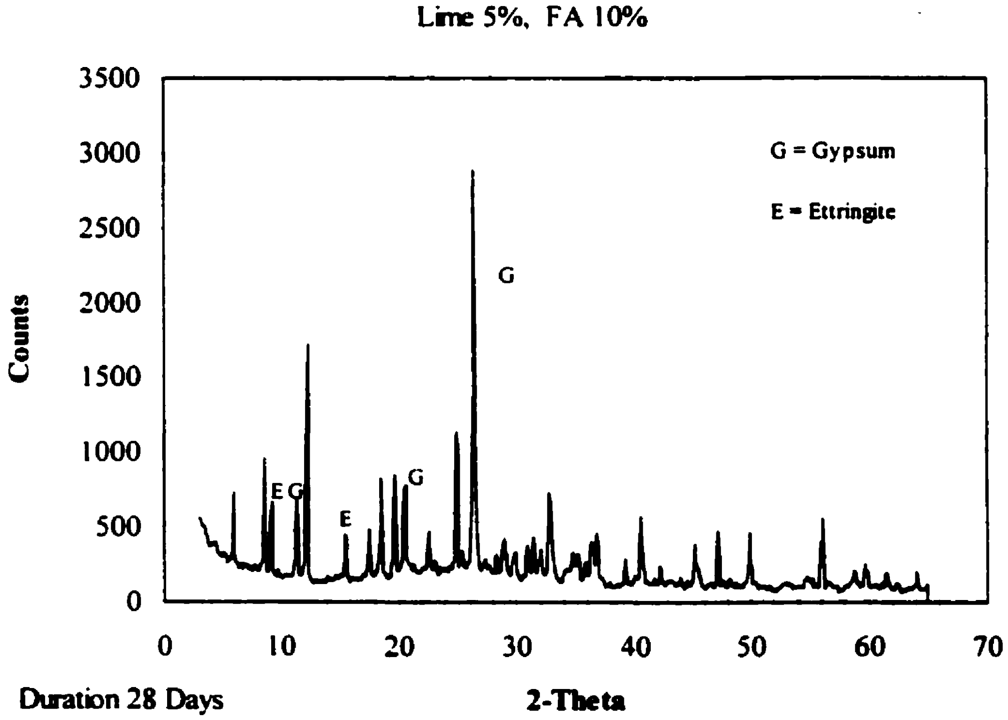


FIGURE 7.7. THE X-RAY DIFFRACTION ANALYSIS OF LIME, AND FLY ASH CLASS "C" TREATED SAMPLE.

However, the higher unconfined compressive strength of these samples is not only attributed to the formation of ettringite and reduction of gypsum, but also to the higher pozzolanic properties of lime and fly ash combination. As it was stated before, application of lime and fly ash type "C" have resulted in elimination of large pores, creation of bonding between particles and aggregates, and maintenance of flocculent particle arrangements, which contributes to the higher strength of the samples. Moreover, high silicon content of the fly ash results in the formation of calcium silicate hydrate, which also contributes to generation of high strength in these samples.

Samples treated with the application of aluminum as well as lime and fly ash have gained more than 700 kPa after 28 days of hydration (Figure 7.5). This amount of strength is recommended by U.S. EPA (1989), as the minimum strength required for reusability of treated waste material. Since aluminum has a retardation effect on the lime and fly ash pozzolanic reactions, samples treated with aluminum did not gain any significant strength until 7 days of hydration. However, after 7 days of curing, about 460 kPa of strength were generated in these samples and they continued to gain strength up to 28 days of hydration. X-ray diffraction analysis of 28 days cured sample, shown in Figure 7.8, indicates strong formation of ettringite in the sample.

Addition of aluminum has resulted in formation of primarily ettringite in the samples. Therefore, the high strength generated is mainly attributed to the formation of ettringite as well as other pozzolanic products, such as calcium silicate hydrate, in the sample.

Figure 7.9 shows the long-term unconfined compressive analysis of the aluminum, lime, and fly ash treated sample. The strength in the sample reached nearly 1000 kPa after 90 days of hydration and it continued to gain strength until 140 days of curing. The rate of strength gain in the samples became almost flat after 90 days of hydration as more than 90% of the samples strength was reached within the first 90 days of hydration.

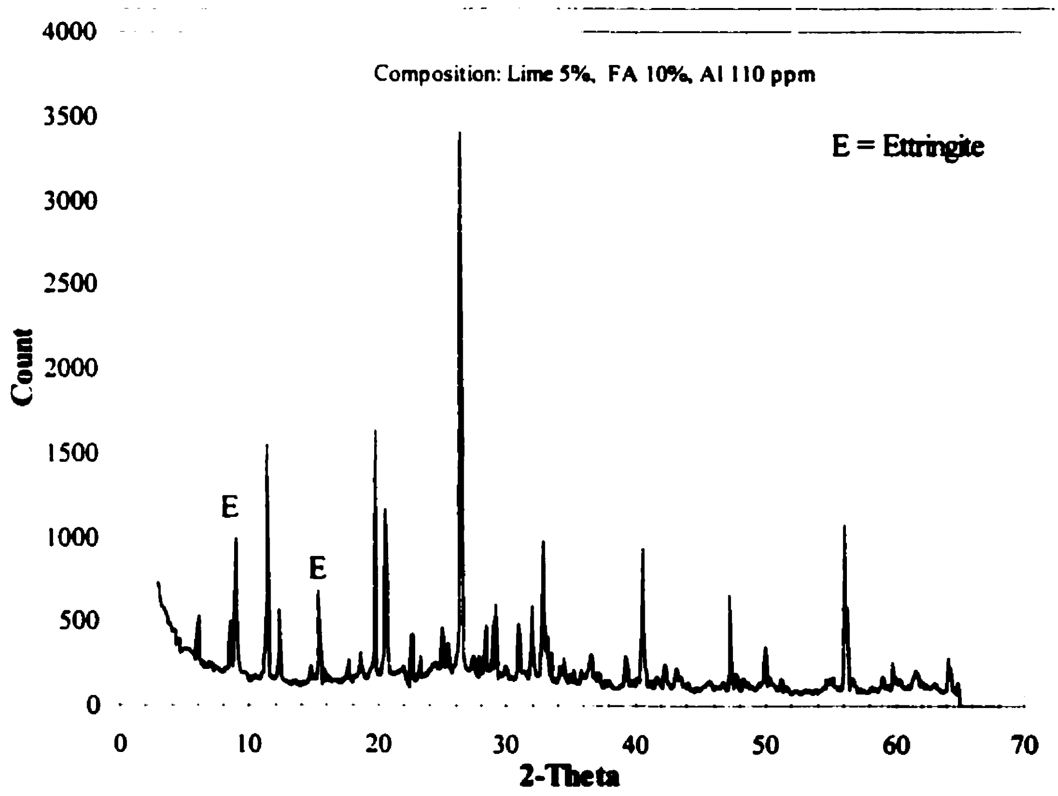


FIGURE 7.8. THE X-RAY DIFFRACTION ANALYSIS OF ALUMINUM, LIME, AND FLY ASH CLASS "C" TREATED SAMPLE.

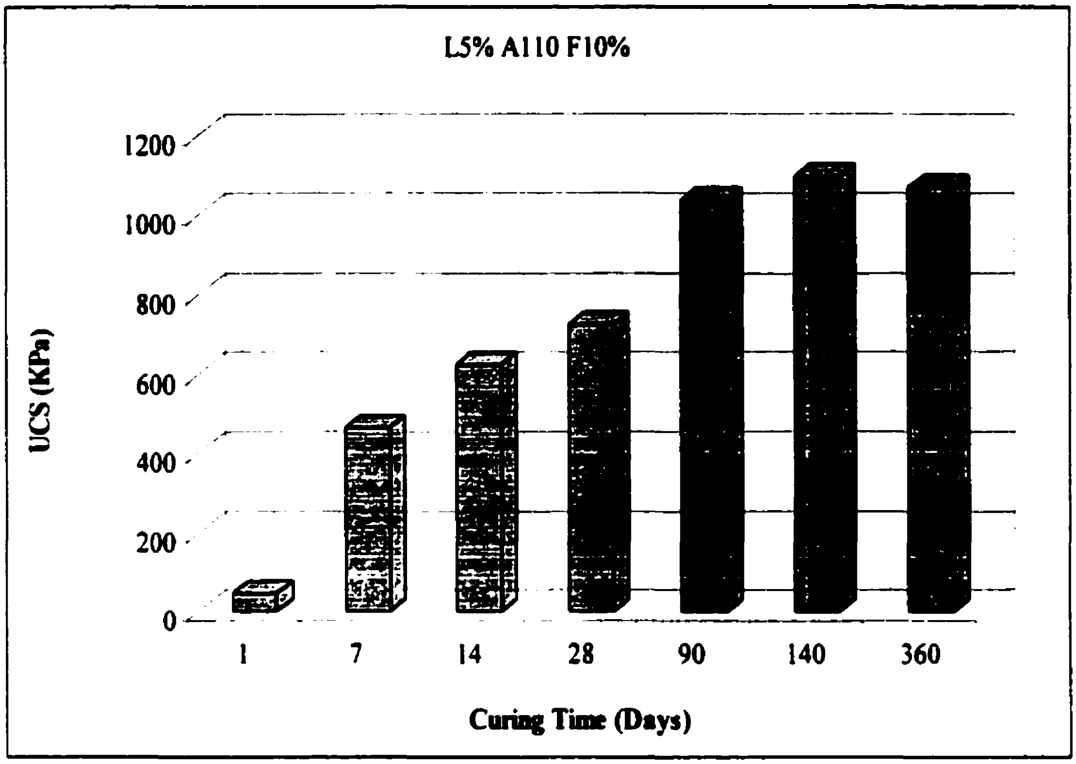


FIGURE 7.9 UNCONFINED COMPRESSIVE STRENGTH OF THE ALUMINUM, LIME, AND FLY ASH TREATED SAMPLE

The strength of the sample remained more than 1000 kPa after 360 days of hydration. Application of fly ash is responsible for the generation of latent strength and slow pozzolanic reactions in these samples. Moreover, formation of ettringite as a stable mineral prevents the acidification of the specimen - as a result of excess free sulphate availability - and provides high strength in the sample. Maintaining such a high strength is good indication of physical stability and success of the proposed treatment techniques.

Moreover, owing to this high strength, treated tailings can potentially used in a variety of mine structural fill application. The formation of a monolithic solid also results in a significant reduction of the contact area between the solid and any leachant, and therefore, reduces the inherent leachability of the stabilized tailings. Furthermore, the treated tailings can be potentially used in landfill liner or top cover applications due to its low permeability.

7.3.2 Permeability Analysis Test Results

The permeability of a solidified and stabilized waste (tailings) to leaching fluid encounter in a disposal facility is one of the most important properties of the solidified material in a governing two interrelated properties, namely, durability and leachability. Durability, addresses the long-term stability of the treated material and leachability refers to the amount of pollutant released over time.

Permeability (often referred to as hydraulic conductivity) has been defined as the measure of fluids passing through the tortuous pore structure of the waste or the treated waste (Means *et al.*, 1995). As it was stated before, the permeability of a stabilized waste is an important factor, as it indicates the ability of a material to permit the passage of water and to limit the loss of contamination from the stabilized waste to the environment. Permeability is examined in conjunction with leach test results to evaluate the potential of the stabilized waste to release contaminants into the environment.

The relevance of permeability measurements can be understood by comparing them with natural materials. Sand, a highly permeable material, has a hydraulic conductivity on the order of 10^{-2} cm/s. Clay, a material that is used to line lagoons and surface impoundments, can have hydraulic conductivity on the order of 10^{-6} cm/s or less and is considered relatively impermeable. Thus, stabilized tailings with a permeability similar to clay is desirable because it will not permit the free passage of water through the stabilized tailings. By slowing the contact of fluid with the tailings, it reduces the possible transport of contaminants out of the stabilized tailings. Typical hydraulic conductivities for stabilized waste range from 10^{-4} cm/s to 10^{-8} cm/s. Hydraulic conductivities of less than 10^{-5} cm/s are recommended for stabilized waste destined for land disposal by United State environmental protection agency (U.S. EPA 1989). Reduction of permeability of the aluminum, lime, and fly ash treated tailings to 10^{-5} cm/s is considered the success criteria for the proposed treatment procedure.

Falling head permeability tests have been conducted on the aluminum, lime, and fly ash treated tailings. Water with the water to solid ratio of 0.5 was added to the treated specimens and then were allowed to mellow for 24 hours in 95% relative humidity and 25°C temperature. The 24 hours cured samples were compacted in the modified molds (30 mm in diameter and 60 mm in length; Figure 7.3) and were cured in control humidity and temperature condition for 28 days before be subjected to permeability analysis. Prior to conducting the experiment, samples were fully saturated by back-suction technique. Experiments were conducted in duplicate to ensure the reliability of the test results.

The results of the permeability test as depicted in Figure 7.10 point to several changes concerning the hydraulic conductivity of the treated specimens. In general, the untreated sample has a magnitude of hydraulic conductivity of 3.5E10^{-4} cm/s after 28 days of curing in humid room and in constant temperature (25°C). Addition of 5% lime to this sample has resulted in lowering the permeability to 2.5E10^{-4} cm/s after 28 days of curing. Therefore, the permeability of the lime treated sample is still more than the minimum permeability of 10^{-5} cm/s recommended for the success of the treatment procedure.

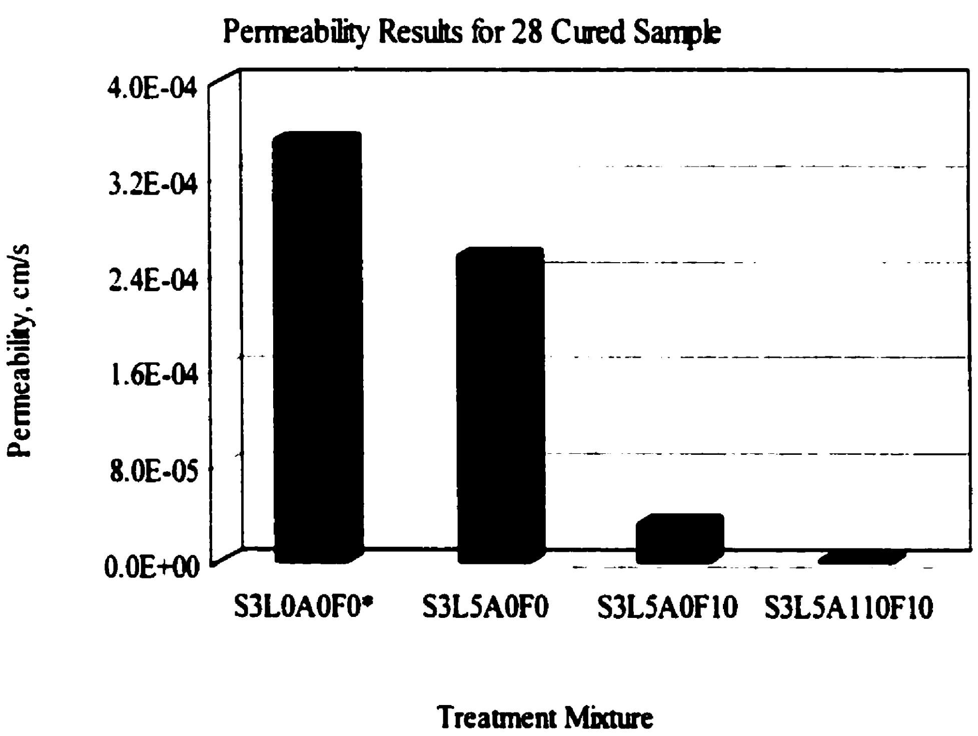


FIGURE 7.10 PERMEABILITY OF THE 28 DAYS TREATED SPECIMENS

Application of 10% fly ash type "C" in conjunction with 5% lime have reduced the permeability of the treated specimens to $3.2E10^{-5}$ cm/s after 28 days of curing. Such a low permeability is the result of modification of pore size and pore size distribution of the samples, which are the characteristics of the fly ash treated tailings. Moreover, addition of lime and fly ash to the tailings sample have resulted in elimination of large pores, increasing the bonding particles and the maintenance of the particles arrangements.

Addition of aluminum to lime and fly ash treated samples has resulted in formation of ettringite and further reduction of the permeability in the samples. The hydraulic conductivity of the aluminum treated specimens was reduced to $1.96E10^{-6}$ cm/s after 28 days of curing. Therefore, in addition to the beneficial properties of lime and fly ash type "C" treatment of the tailings, formation of ettringite in these samples has helped to produce an inert material with much lower value of hydraulic conductivity. Hence, it is postulated that ettringite crystals have formed and filled the capillary pores of the cylindrical specimens and have further reduced their permeability. According to the United States environmental protection agency, the permeability of stabilized/solidified materials should be two orders of magnitude below that of the surrounding materials (U.S. EPA, 1989). Therefore, from the results of the permeability study, the aluminum, lime and fly ash treated tailings have reached an acceptable permeability value range for safe disposal in the environment.

In order to better understand and delineate the relationship between permeability and other physical properties of the sample, a relationship was developed between the strength of the material and the corresponding permeability as shown in Figure 7.11.

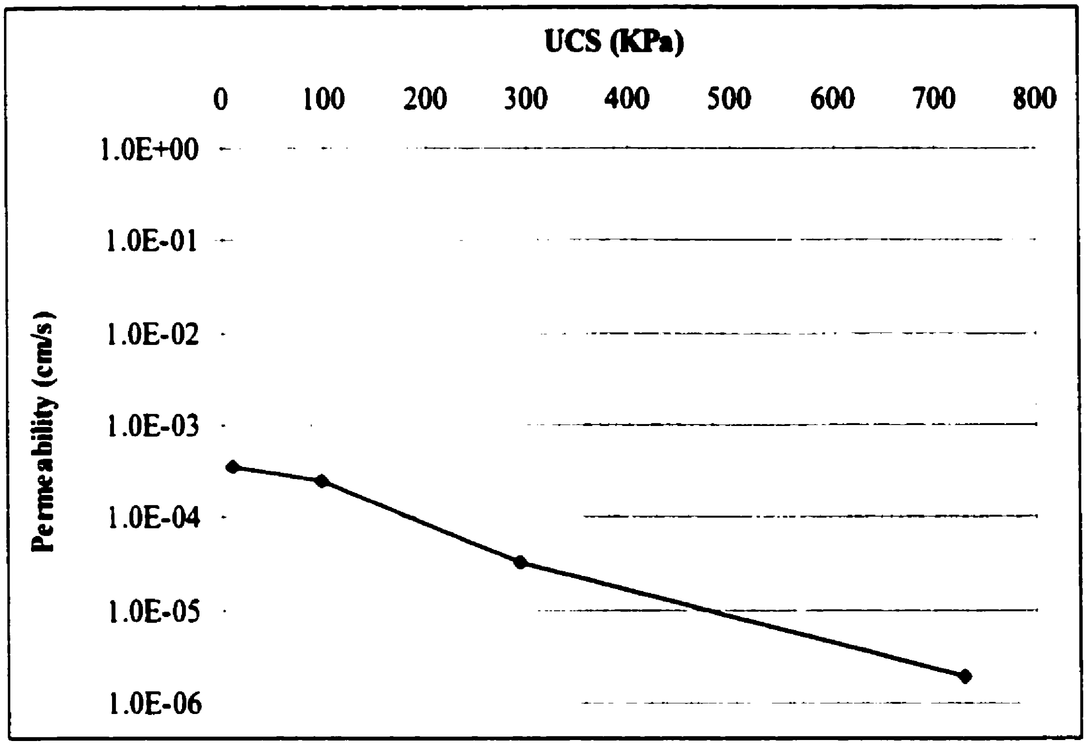


FIGURE 7.11 RELATION BETWEEN SAMPLES STRENGTH AND ITS PERMEABILITY

In Figure 7.11, the strength of the material and the corresponding permeability are plotted on a semilogarithmic chart. As the strength of the material is increasing, its permeability value has decreased. Therefore, formation of ettringite in the aluminum, lime, and fly ash treated samples not only increased its unconfined compressive strength properties, but by achieving it so, it has also reduced its value of hydraulic conductivity.

7.3.3 Freeze and Thaw Experimental Test Results

In cold climates, repeated cycles of freezing and thawing can cause physical deterioration of an exposed solidified waste product, thereby increasing contact with groundwater. According to United States environmental protection agency (U.S. EPA, 1989), durability testing evaluates the resistance of a stabilized/solidified waste mixture to degradation due to external environmental stresses. The test are designed to mimic natural conditions by stressing the sample through freezing/thawing, and wetting/drying. The stabilized/solidified specimens undergo repeated cycling during testing. Unconfined compressive strength, permeability, or other performance based tests may be conducted on the solidified/stabilized samples after each cycle to determine how the physical properties of the solidified/stabilized waste change as a result of simulated climatic stresses. The number of cycles a material can withstand without failing can be used to judge the mechanical integrity of the material.

Eight stabilized and solidified samples, treated with combination of lime, fly ash, and aluminum as well as four untreated samples to be used as controls, were subjected to repeated cycling of freeze and thaw in our laboratory. Samples were cured for 28 day in 95% humidity and 25°C temperature before being subjected to freeze and thaw cycling. Six samples were subjected to 6 cycles of freeze and thaw and the other 6 to 12 cycles before being tested for unconfined compressive strength as well as permeability measurement. The results of the experiments are shown in Figures 7.12 and 7.13.

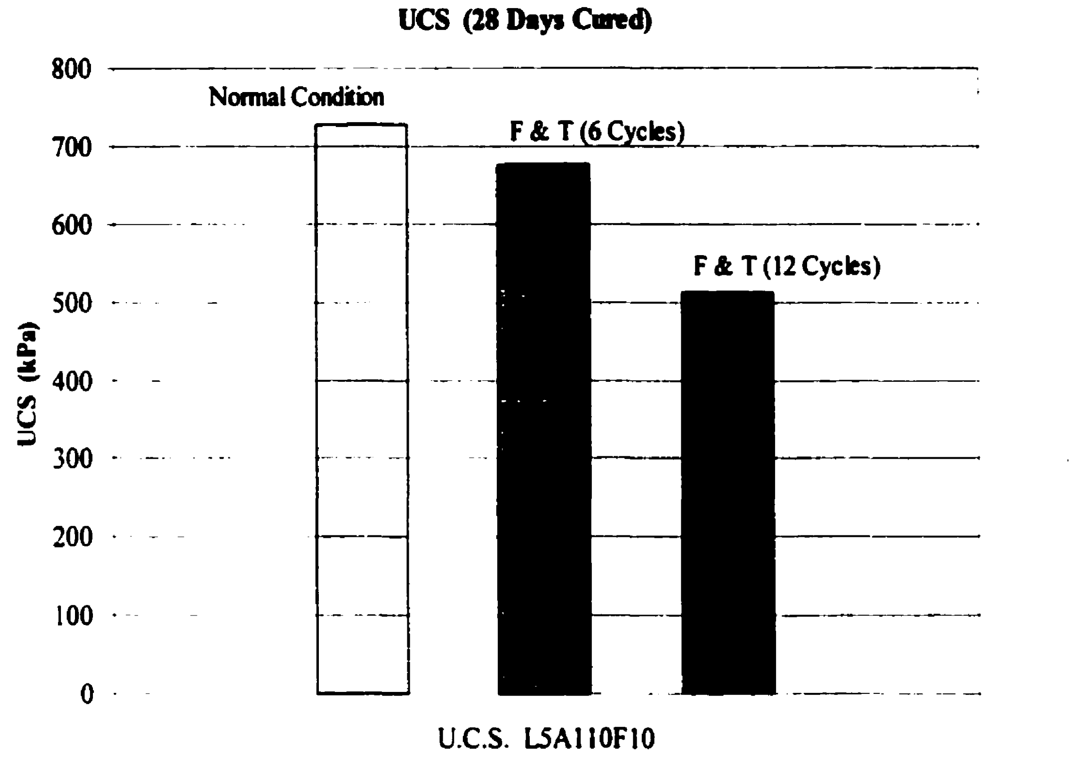


FIGURE 7.12 COMPRESSIVE STRENGTH OF FREEZE AND THAW SAMPLES

The 28 Days cured and treated sample hydrated under normal condition reached a magnitude of 730 kPa without being subjected to the harsh and deteriorating effect of freeze and thaw cycling. As shown in Figure 7.12, subjecting the samples to 6 cycles of freeze and thawing resulted in negligible loss of strength in the treated specimens. Samples did not show any visual sign of deterioration and no vertical expansion was measured in these specimens. In another words, the treatment procedure used to solidify and stabilized the tailings sample was capable of stabilizing the specimens and resist any physical and mechanical disintegration after 6 sets of freeze/thaw cycles. However, the untreated specimens showed significant deterioration after the second sets of freeze/thaw cycles and finally disintegrated.

Samples which were subjected to 12 cycles of freezing and thawing showed almost 30% reduction in the magnitude of their unconfined compressive strength, while they maintained their structural integrity during the repeated freeze/thaw cycles. The reduction in the strength of these samples is attributed to high tailings moisture suction developed in the freezing zone. This will cause an increase in the effective stress in the region immediately below the freezing front and the formation of segregated ice lenses. Such behavior could result in shrinkage of the tailings structure, formation of cracks, and a change in the pore size characteristics of the unfrozen section immediately below the ice lenses.

The results of permeability studies conducted on these samples are shown in Figure 7.13. It was expected that freezing and thawing cycles would have resulted in increase in permeability of samples by particle reorientation, and reduction of particle spacing due to thinning of water films around the tailings particles. However, the results of the permeability tests, as depicted in Figure 7.13, indicate that samples survived the 12 cycles of freezing and thawing and generally performed very well. The low permeability change in the samples, even after 12 sets of freeze/thaw cycles, is mainly attributed to the pozzolanic properties of lime and fly ash which have resulted in the particles arrangement, and lower void ratio in the samples. Moreover, formation of ettringite as a result of aluminum addition, has resulted in reduction of capillary spaces in the samples. The fine, needle shape ettringite crystals

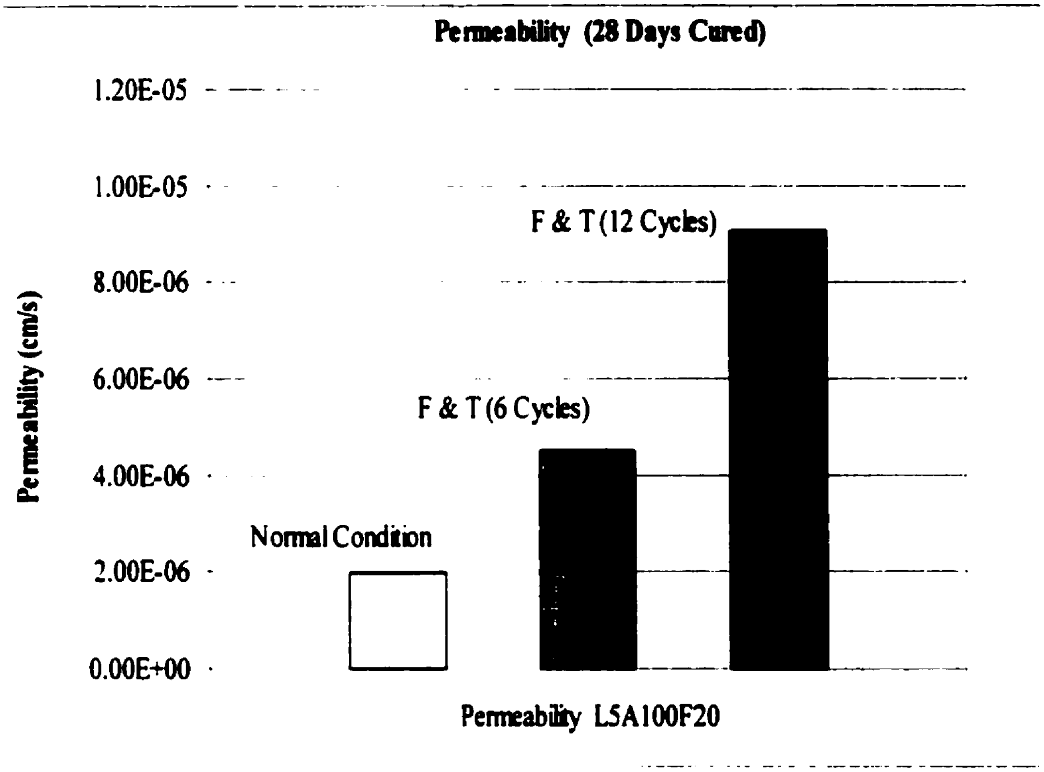


FIGURE 7.13 PERMEABILITY RESULTS OF FREEZE AND THAW SAMPLES

prevent the penetration of water in the capillary zones which could otherwise, become frozen and increase in volume, and cause internal stress during freezing.

Based on Figures 7.12 and 7.13, the durability of the treated samples, proved that the proposed treatment procedure is an effective method to maintain the physical integrity of the stabilized tailings under extreme environmental fluctuations.

Therefore, it is anticipated that freeze/thaw cycles will cause slight deterioration in the upper few inches of the surface of the treated tailings.

7.4 Conclusion

Application of lime, fly ash type “C”, and aluminium to high sulfide content tailings have resulted in formation of a solid monolith capable of producing more than 1000 kPa unconfined compressive strength in the samples. The treated monolith was exposed to 12 sets of freeze and thaw cycles and it preserved its structural integrity. Development and maintenance of high strength and stiffness in these samples are attributed to pozzolanic properties of lime and fly ash specifically in an environment rich in aluminium and sulfide compounds.

Application of lime and fly ash type “C” to high sulfide content tailings have improved its plasticity, workability, and volume stability. Moreover, upon addition of aluminium to lime and fly ash in a sulfide rich environment, ettringite, calcium sulfo-aluminate hydrate, has also formed in these samples. Formation of ettringite has further contributed to high strength and stiffness of the treated tailings. Furthermore, the needle type ettringite crystal formed as a result of excess aluminium addition to samples blocked the capillary spaces of the tailings, and therefore, reduced the permeability of the treated samples. Application of 5% lime, 10% fly ash type "C" in combination with 110 ppm aluminium, designated percentages of treatment agents based on optimisation experiments conducted previously for tailings samples under investigation, reduced tailings permeability to 1.96E-06 cm/s. According to published report by United States environmental protection agency, 1.0E-05 cm/s is the maximum permeability allowed to render a waste stabilised and impermeable. The permeability of the treated tailings samples remained below the recommended permeability even after exposing the treated samples to 12 sets of freeze and thaw cycles.

Overall, based on the results of the geotechnical analysis, treatment of high sulfide content tailings with lime and fly ash, combined with availability of aluminum for reactions, is a successful method of solidifying these highly reactive tailings. The pozzolanic properties of lime and fly ash coupled with the possibilities of ettringite formation in the samples will lead to generation of a solidify monolith capable of withstanding harsh environmental fluctuations.

Chapter 8

Application of Proposed Treatment Technology To Another Tailings Sample

8.1 Introduction

Ettringite, calcium sulphualuminate hydrate, which can be formed in lime-remediated sulfidic mine tailings, can be used as a stabilization/solidification technology in acid mine drainage systems. Ettringite which forms in limited amounts in portland cement pastes in the initial stage of hydration, is also responsible for retarding the hydration of tricalcium aluminates and binding aggregates in clasts in cements and concrete (Mehta and Monteiro, 1993). However, ettringite structure is a very 'forgiving' one. It can withstand modest deviation in its composition without a change in structure. This compositional change occurs on the crystal chemical level in the form of ionic substitution. The ions available for substitution in the ettringite structure are Ca^{+2}, Al^{+3}, SO_4^{-2} and OH^-. Formation of ettringite may also be accompanied by the fixation of hazardous oxyanions such as arsenic, boron, chromium, molybdenum, selenium, and vanadium. Samples of substituted ettringite containing arsenic, boron, chromium, selenium, and vanadium have been synthesized in laboratory studies (Hassett *et al.*, 1989). Also, the zeta potential of ettringite, which is defined as the electric potential in the double layer at the interface between a particle that moves in an electric field and the surrounding liquid, has been measured at the pH of 10.7 and gives a value of [-11.7 mV](Chen and Mehta, 1982). This makes ettringite a good adsorbent for positively charged metal species. Moreover, formation of ettringite is associated with a high pH condition, which will further lead to the precipitation of heavy metals from the solution.

In order to further evaluate the success of the proposed treatment technology to stabilize and solidify the acid producing tailings by means of ettringite formation, another tailings sample from a mine in the province of Quebec was subjected to treatment and subsequent evaluation. Tailings sample was initially subjected to physical and chemical analysis and the optimized condition for the formation and precipitation of ettringite within the sample was established. The optimized sample was subsequently subjected to chemical, mineralogical and physical analysis to evaluate the stability of the treatment procedure.

8.2 Materials and Methods

The initial physical and chemical characteristics of the new tailings sample were evaluated through standard laboratory investigation. The physical characteristics of the tailings sample were established by the use of ASTM standard methods as described in chapter 3. The results of these analyses are given in Table 8.1.

TABLE 8. 1 PHYSICO-CHEMICAL ANALYSIS OF NEW TAILINGS SAMPLE (SAMPLE 2)

Test	Magnitude
pH	2.55
Moisture Content (%)	9.20
Specific Gravity	2.94
Cation Exchange Capacity (meq/100g)	12.26
Specific Surface Area (m2/g)	11.25
Liquid Limit (%)	19.06
Plastic Limit (%)	Close to L.L.

This sample has slightly higher pH and lower redox potential than previously tested and treated sample (Sample # 1; pH of 2.49 and redox potential of 410 mV, compare to current sample # 2; pH of 3.26 and redox value of 255 mV). It can be seen that higher pH of sample #2 results in lower redox potential which is an indication of ratio of activity between oxidizing and reducing agents. The pH and redox were measured using the electrical probe and based on ASTM standard D4972-89. Its moisture content was determined to be around 9.2% by following the ASTM method D2216-89. Determination of specific gravity was done based on ASTM method D854-83. The value of the specific gravity was recorded as 2.94, which was in the expected range given that the sample under investigation is tailings. The liquid limit was determined by using Cone-Penetrometer method (British Standard BS 1377: Part 2: 1990: 4:3) since the ASTM D418-84 involving the use of the Casagrande apparatus proved to be a difficult one given the silty nature of the tailings sample under investigation. The specific surface area was determined by using Ethylene Glycol Monoethyl Ether (EGME) reagent. The water retention capacity and exchangeable cations have been shown to be highly correlated with the surface area. The term "specific surface" refers to area per unit weight of soil or sample and is usually expressed in square meters per gram (Heilman, *et al.*, 1965). The cation exchange capacity of a sample is defined as the exchange of cations in solution for cations adsorbed to the negatively charged surface of the particle. The cation exchange capacity is the total of positively charged particles that a soil can adsorbed at a given pH (Grim, 1968). The cation exchange capacity was measured by using a silver-thiourea solution. All the methodologies and proper standards used to determine these parameters are given in chapter 3.

Moreover, Since the success of the proposed treatment procedure will be assessed mainly on the result of the leachability analysis to determine whether the metals of concern have been insoluble or not, acid digestion of untreated tailings sample was performed according to the U.S. EPA method 3050 (1986). Sulfate content was determined using a DIONEX DX-100 Ion Chromatograph machine. The results of the acid digestion and ion chromatography analysis are given in Table 8.2.

TABLE 8.2 SOLUBLE CHEMICAL ANALYSIS OF NEW TAILINGS SAMPLE (SAMPLE 2)

Element	Concentration (ppm)
Aluminum	130
Arsenic	4
Calcium	340
Cadmium	0
Chromium	0
Copper	15.40
Iron	1800
Potassium	2
Magnesium	39
Manganese	11
Lead	0
Silicon	21
Sulfate	1245
Zinc	65

Upon completion of elemental analysis and physical/chemical characterization of untreated sample, the tailings was subjected to the treatment procedure based on the result of optimization experiments conducted previously. The procedures for these experiments have been explained in chapter 5. The optimization experiments revealed that 4% lime is the optimum lime is required to rise the pH of the sample to 12 and maintaining it in that level. Moreover, 10% fly ash type "C" as well as 110 ppm of aluminum is needed to provide necessary conditions for the formation and precipitation of ettringite in the sample under investigation. Such quantity of the additives is considered the minimum requirement in order to maintain the ideal conditions for ettringite formation as a stable mineral. All the experiments were performed based on optimization experiments described in chapter 5. The water to solid ratio of the sample was 0.5. All experiments were duplicated to ensure the reliability of test results.

The samples were initially dry mixed and the required water content which contained 110 ppm of aluminum was added while the resultant low pH slurries were allowed to mellow in closed plastic containers for 24 hours at 25°C and 95% relative humidity. Subsequently, binders in the form of 4% lime and 10% fly ash type "C" were added to the samples and the resultant paste were thoroughly mixed and allowed to cure under the previously described condition. Some samples were compacted in modified molds designed for this project (as described in chapter 7) for unconfined compressive strength as well as permeability and freeze and thaw experiments.

The cured samples were subjected to leaching test according to TCLP leaching procedure (explained in chapter 6) using 4 different leachants. The extraction experiment was conducted by adding 40 ml of leachant to 2 ml of slurry and mixed for 18 hours in a screw-cap plastic container held on an end-over-end shaker at a speed of 30 rpm. The resultant slurry suspensions were then filtered using 0.8μm borosilicate glass fiber filter and then the metal concentration in the solution were determined using Perkin-Elmer 2100 atomic absorption spectroscopy system. All standards contained similar matrix to that of the analyte. Part of each treated and cured sample was also used for mineralogical analysis using powder diffraction analysis with a Rigako 2400 X-ray diffractometer.

The criteria to assess the success of the proposed treatment technology is mainly based on the result of leachability analysis. Through leachability test results coupled with X-ray diffraction analysis we can determine if the ettringite has been formed in the sample and if the formation of ettringite has contributed to immobilization of heavy metals from the treated sample. Moreover, geotechnical analysis such as unconfined compressive strength, permeability as well as freeze and thaw will be performed to assess the reusability of the treated sample.

8.3 X-ray Diffraction Analysis

In order to establish whether the pozzolanic reactions have occurred in the treated samples and monitor the growth of ettringite in the specimens under investigation, the cured samples were subjected to powder X-ray diffraction analysis. Samples, which were cured for 3 days, 28 days, 90 days, 360 days and finally 660 days, were analysed for their mineralogical constituents. The X-ray analysis of untreated as well as treated samples are shown in Figure 8.1 and 8.2 (a, b, c, d, and e).

The XRD pattern of treated samples indicate that ettringite has been formed within the first 3 days of hydration (Figure 8.2, a), and its peak intensities continued to grow up to 90 days of curing (Figure 8.2, b, c). In X-ray diffraction analysis of 3 days cured samples, other pozzolanic minerals such as calcium aluminate hydrate, calcium silicate hydrate as well as gypsum and some unreacted lime were also detected. However, continued curing of the samples to 28 days and 90 days has

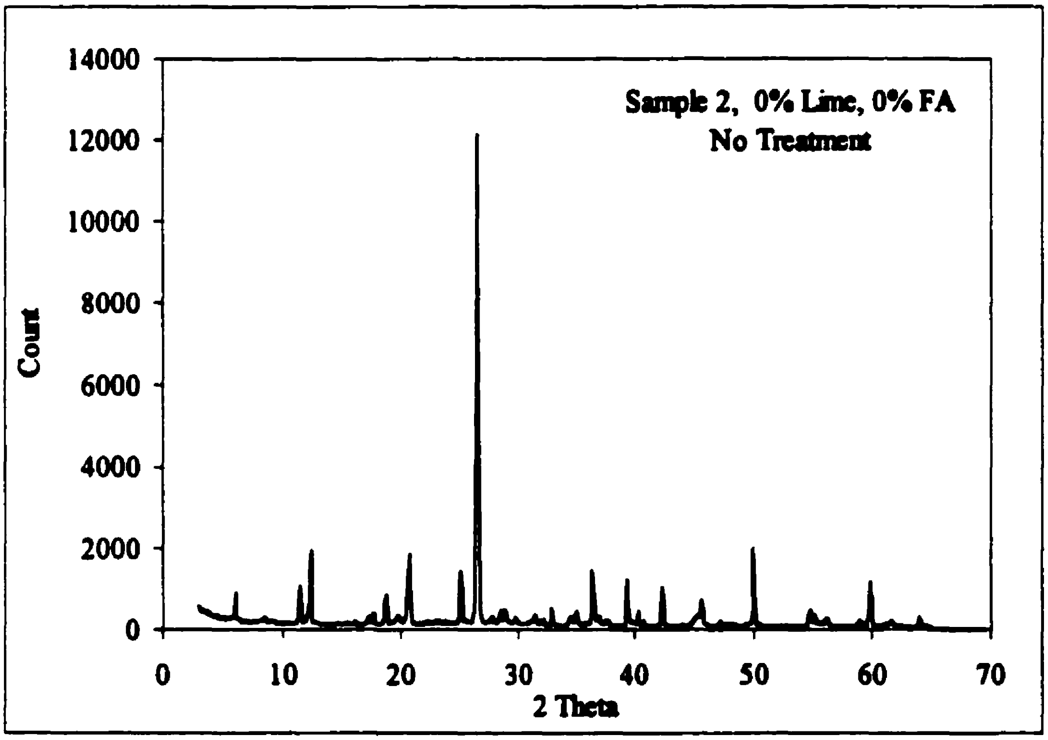


FIGURE 8.1 X-RAY DIFFRACTION ANALYSIS OF SAMPLE 2 (UNTREATED)

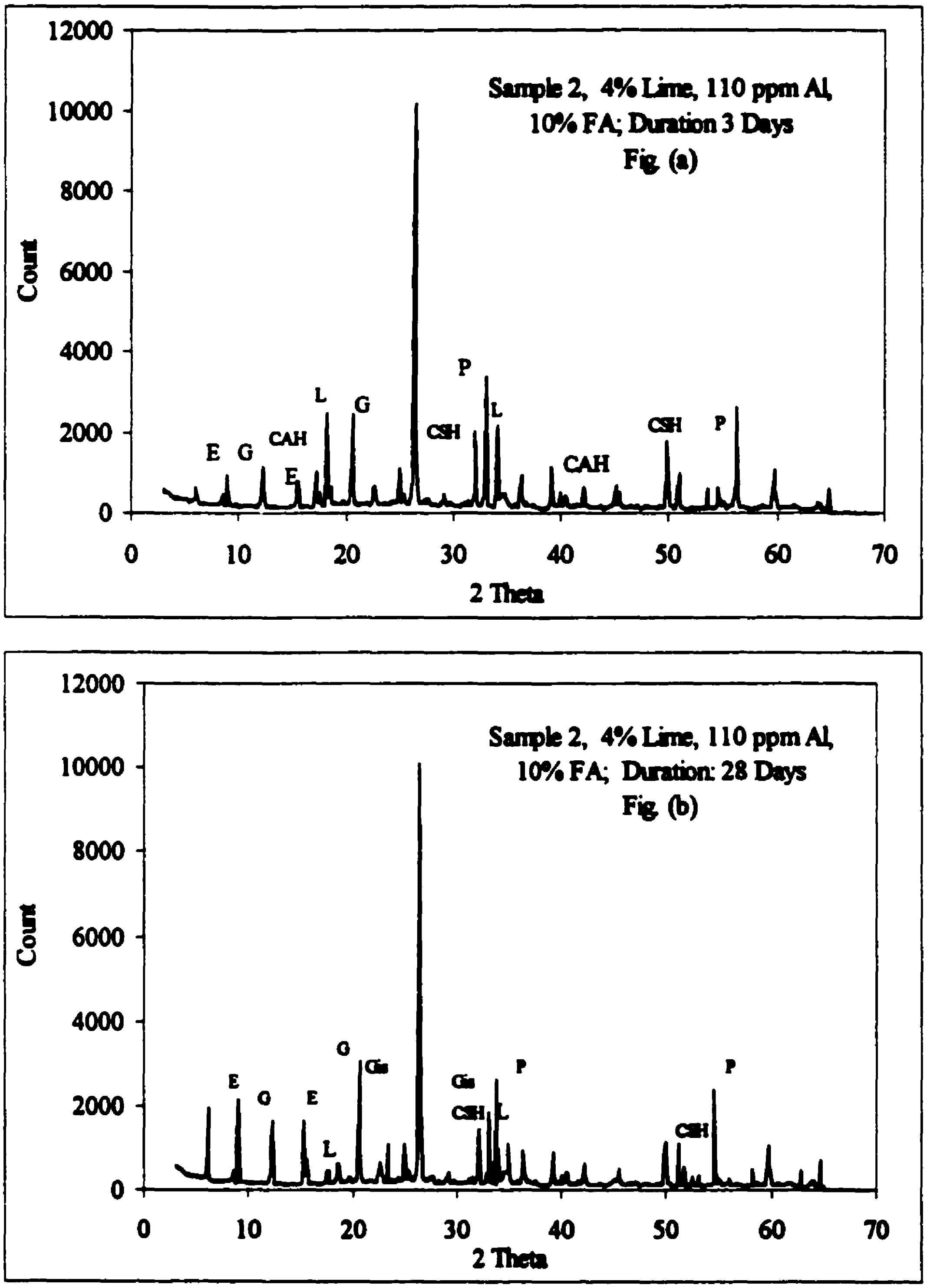


Figure 8.2 (a,b) X-Ray Diffraction Analysis of Treated Sample (E = Ettringite; G = Gypsum; L = Lime; CSH = Calcium Silicate Hydrate; CAH = Calcium Aluminate Hydrate; Gis = Gismondine; P = Pyrite)

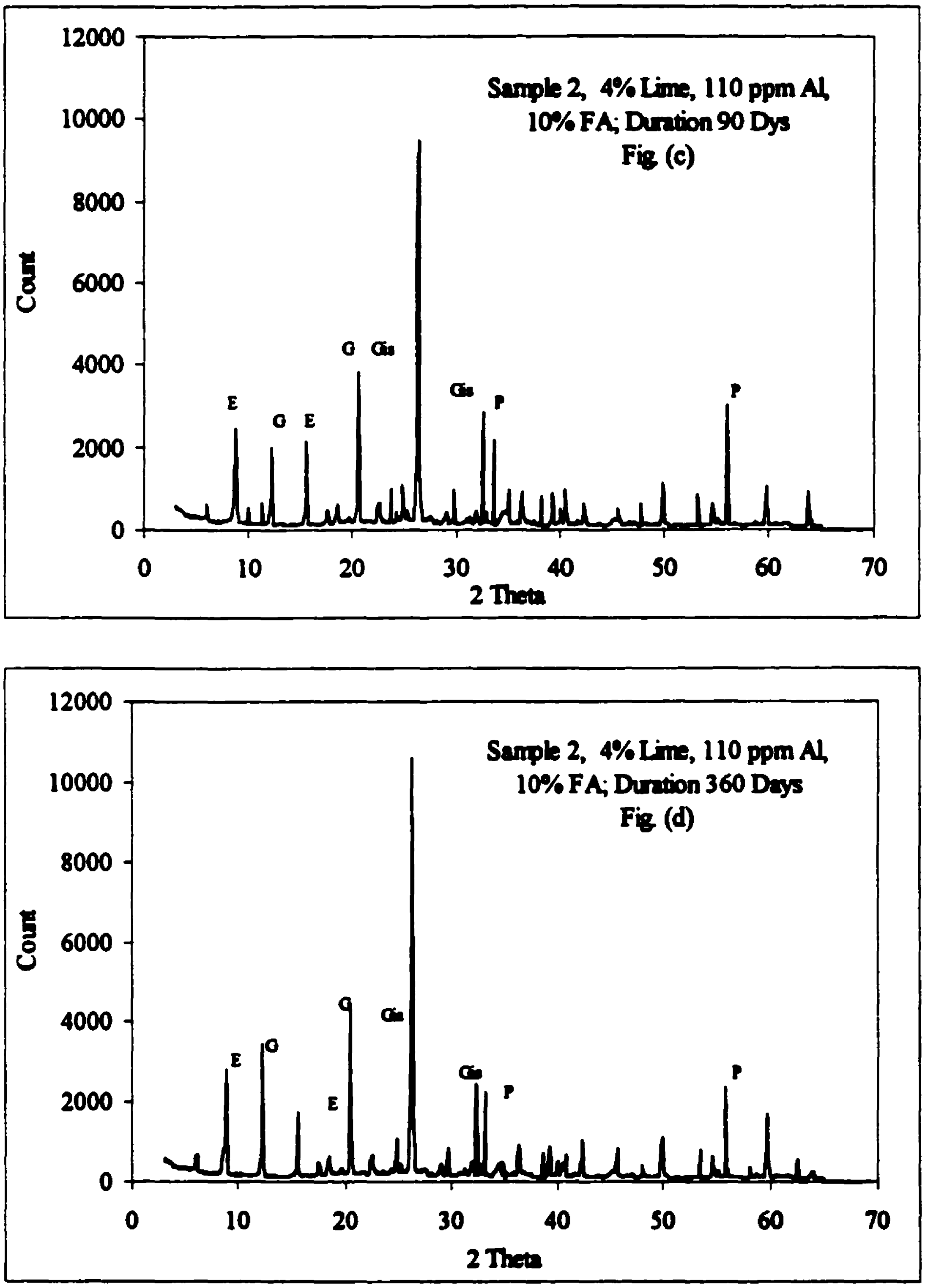


Figure 8.2 (c,d) X-Ray Diffraction Analysis of Treated Sample (E = Ettringite; G = Gypsum; L = Lime; CSH = Calcium Silicate Hydrate; CAH = Calcium Aluminate Hydrate; Gis = Gismondine; P = Pyrite)

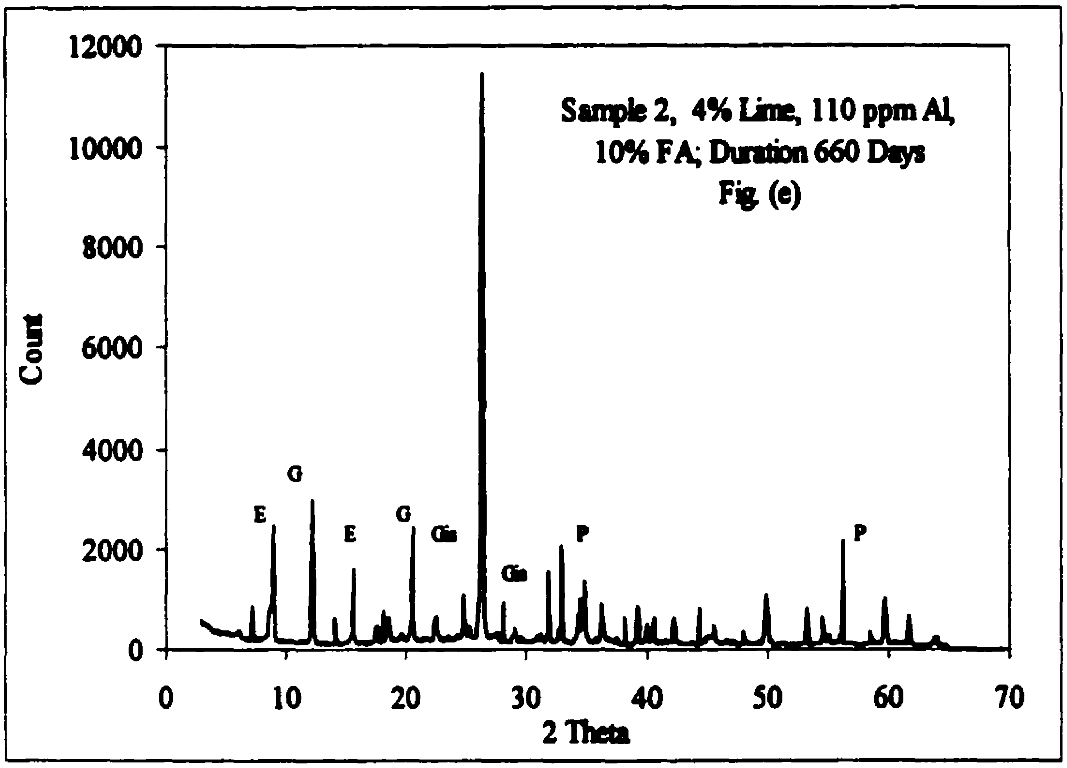


Figure 8.2 (e) X-Ray Diffraction Analysis of Treated Sample (E = Ettringite; G = Gypsum; L = Lime; CSH = Calcium Silicate Hydrate; CAH = Calcium Aluminate Hydrate; Gis = Gismondine; P = Pyrite)

resulted in complete consumption or deterioration of lime as well as calcium silicate hydrate and calcium aluminate hydrate. This observation is analogues to the growth of ettringite as well as gypsum and formation of gismondine in the sample after 90 days of hydration. Addition of lime, fly ash type "C", and aluminum resulted in appearance of these pozzolanic reactions in the sample while continued curing has led to their destruction and formation of more stable mineral such as ettringite and gismondine. The silicate ions might have been consumed in the formation of gismondine ($Ca\ Al_2\ Si_2\ O_8 \cdot 4H_2O$) and ettringite like minerals such as thaumasite ($CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$). Thaumasite has a mineral structure similar to ettringite, which could not be clearly distinguished from the X-ray diffraction pattern of ettringite. Long term hydration of the samples under ideal conditions (i.e., treated with 4% lime, 10% fly ash, and 110 ppm of aluminum and cured in 25°C and 95% relative humidity) are shown in Figures 8.2 (d, e). Ettringite mineral, gypsum, and gismondine are still visible after 660 days of hydration. It is important to note that gypsum peak intensities have not grown within the 660 days of hydration which could have otherwise detrimental effect on success of the treatment procedure. Pyrite peak intensities have also remained almost constant throughout the 660 days of hydration, which could be the result of slow rate of reaction in the sample as a consequence of pozzolanic reactions.

8.4 Leachability Analysis

Treated samples with 4% lime, 10% fly ash type "C" and 110 ppm of aluminum were subjected to different leaching tests, each test follow TCLP leaching procedure. The leachants for this part of the experiment were the same as the leachants used previously and were described in chapter 6, section 6.9.2. The leachants were simulated groundwater (GW) with a pH of 5.5; acid rain (AR) with a pH of 4.5 which contained sulfuric acid; a sulfuric acid solution with a pH of 2.5 (Modified TCLP); and acetic acid solution (TCLP) with pH of 2.88. Samples were grind, and pulverized and then were mixed with the leachant in polyethylene bottles. Extraction was carried out at 20:1 liquid to solid ratio over 18 hours of vigorous shaking. The leachate was extracted and analyzed using atomic absorption spectroscopy for metal concentration.

The results of the leaching experiment were similar to those of sample 1 analyzed previously in chapter 6. The leaching of the sample with groundwater is shown in Figure 8.3. All of the elements of concern have been successfully immobilized within the solidified matrix. The pH has remained around 11 even after 660 days of hydration.

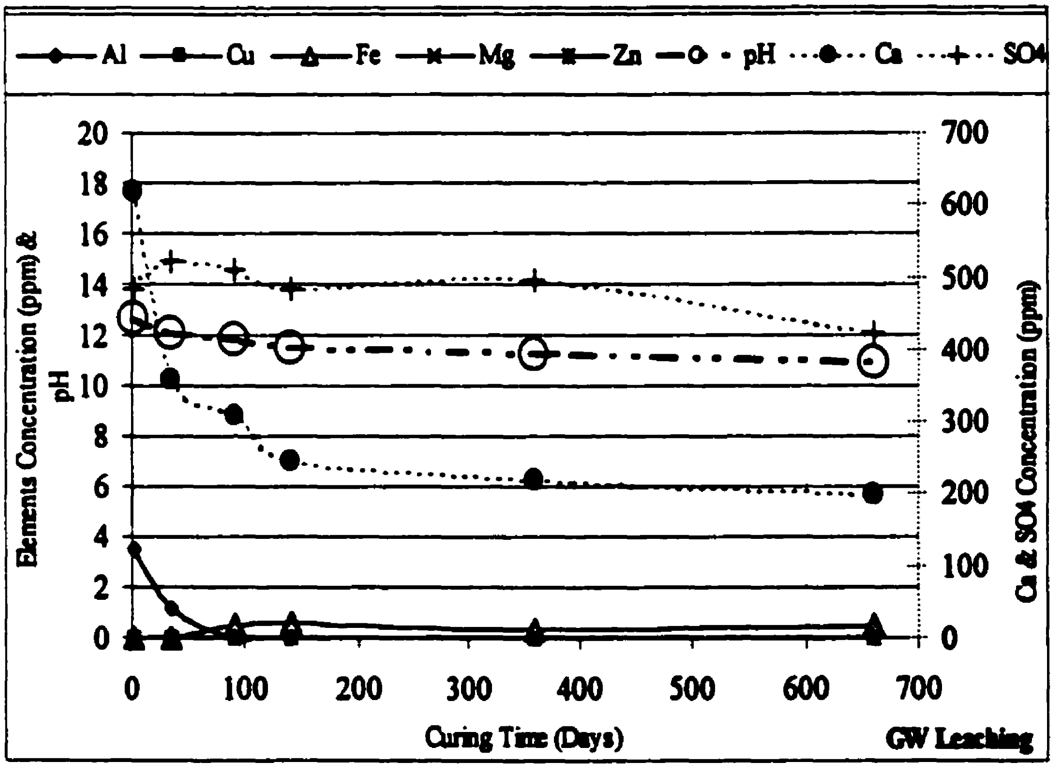


FIGURE 8.3 GROUNDWATER LEACHABILITY TEST RESULTS

The sulfate content has remained constant which is an indication of slow oxidizing reaction, most probably as a result of pozzolanic activity of lime and fly ash addition to the sample. Iron content has increased in the sample after 90 days of hydration (below 1 ppm) but its availability was drastically reduced by further hydration. Such phenomenon is potentially attributed to fixation of iron within the structure of ettringite mineral.

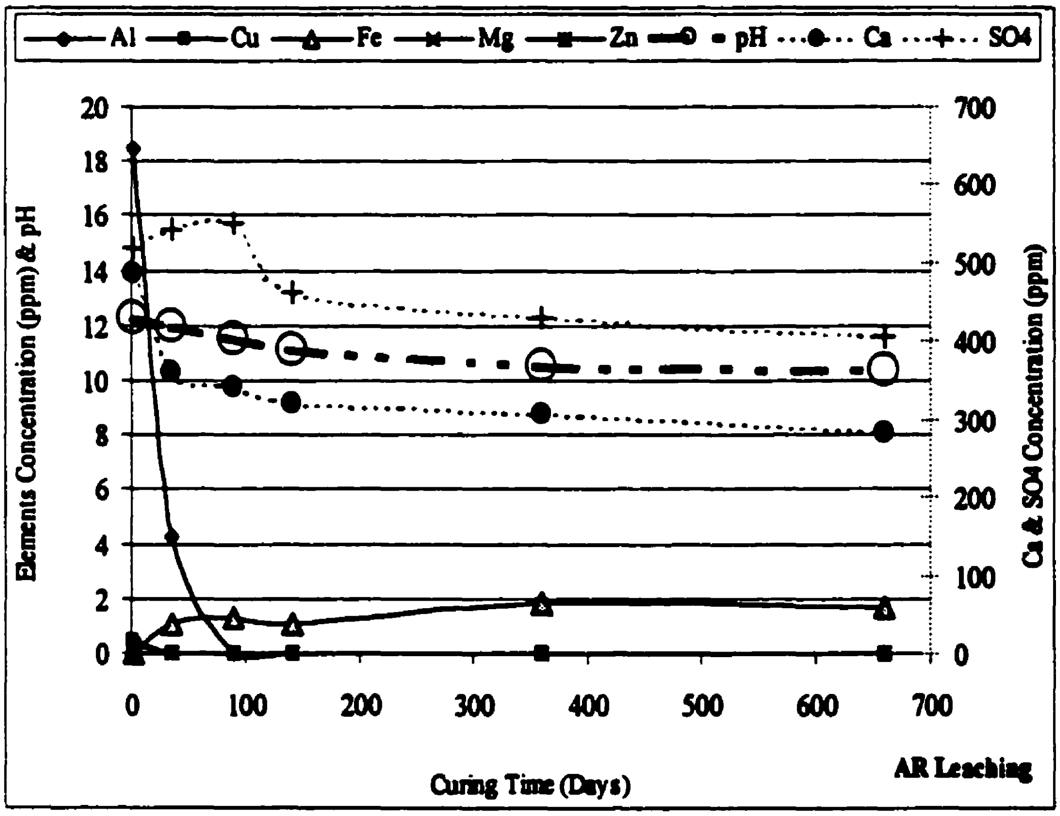


FIGURE 8.4. ACID RAIN LEACHABILITY TEST RESULTS

The result of leachability analysis using acid rain simulated leachant is shown in Figure 8.4. Within the first 3 days of hydration, about 18.5 ppm of aluminum were leached out of the solution. However, continued hydration of the samples led to total disappearance of aluminum from the leached solution. It is postulated that formation of stronger ettringite, which was detected in X-ray diffraction pattern, is responsible for the disappearance of aluminum from the solution. All the other elements remained insoluble within the solidified matrix. pH of the samples remained above 10 after 660 days of hydration. The sulfate content measured throughout the experiment remained constant during the hydration period and was comparable with the quantity leached out with the groundwater as the leachant. The longer hydration period in the case of acid rain as the leachant has resulted in solubility of 1.8 ppm of iron in the sample. However, comparing this quantity with total iron in the sample (1800 ppm), one can consider this result as total success in terms of iron immobilization.

The results of leachability with sulfuric acid solution (Modified TCLP) and acetic acid solution are shown in Figures 8.5 and 8.6. Using these two harsh and strong leachants have resulted in higher leaching of aluminum within the first 3 days of hydration. However, continues hydration of the samples and formation of ettringite has resulted in disappearance of aluminum from the solution. All other elements have remained with very low solubility in the stabilized matrices. The pH of the samples have dropped significantly when they are exposed to these leachants while the leachability of all the metals of concern have remained constant during the 660 days of hydration.

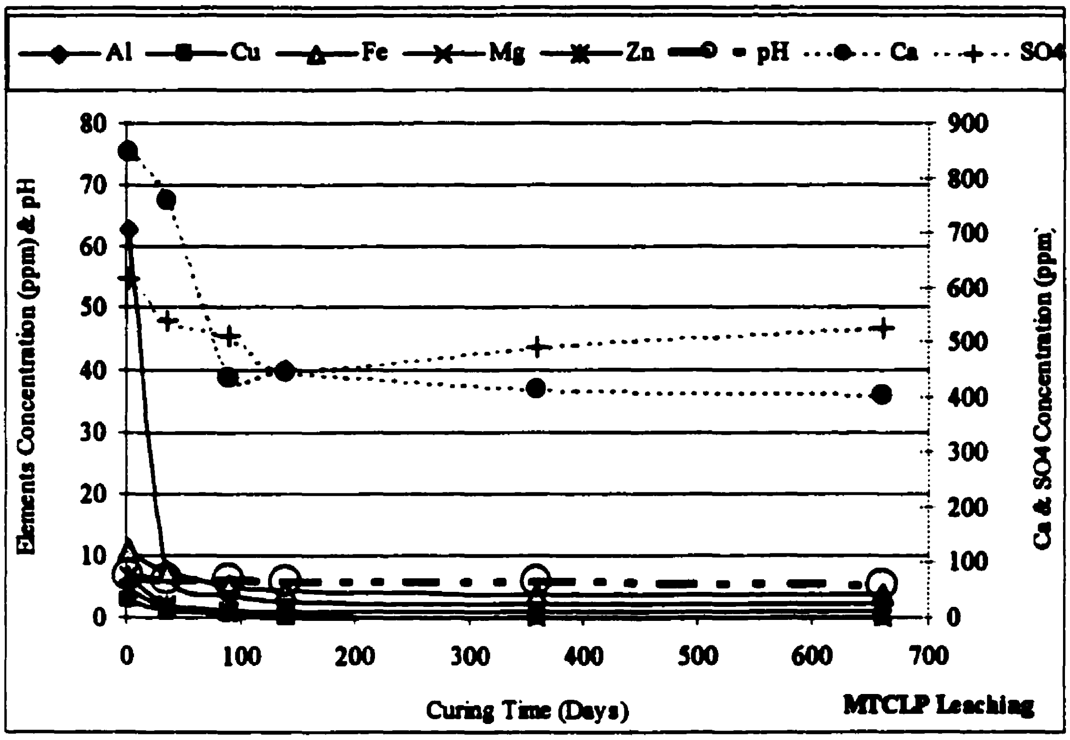


FIGURE 8.5 MODIFIED TCLP LEACHABILITY TEST RESULTS

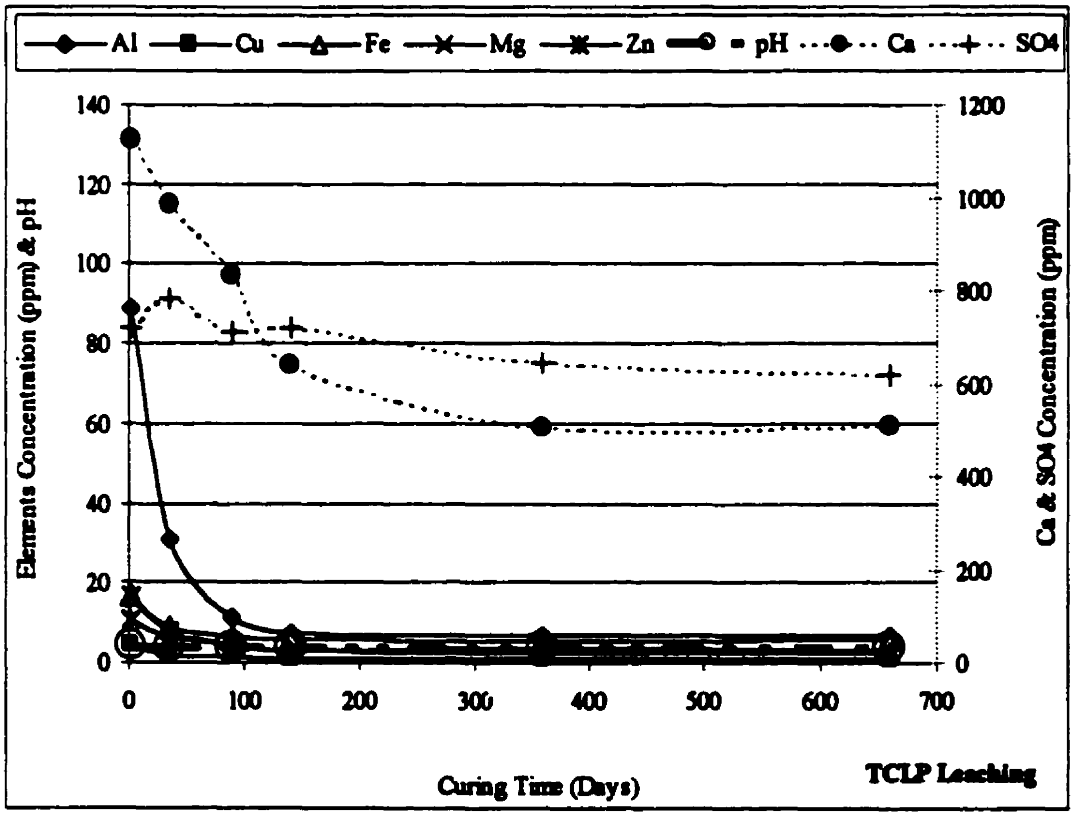


FIGURE 8.6 ACETIC ACID (TCLP) LEACHABILITY TEST RESULTS

The elemental analysis of the samples are given in Figure 8.7 (a, b, c, d, e, and f). The aluminum leachability is highest after 3 days of hydration when leached with acetic acid solution (Figure 8.7, a). However, its quantity reduces and diminishes with further hydration of the sample and formation of ettringite.

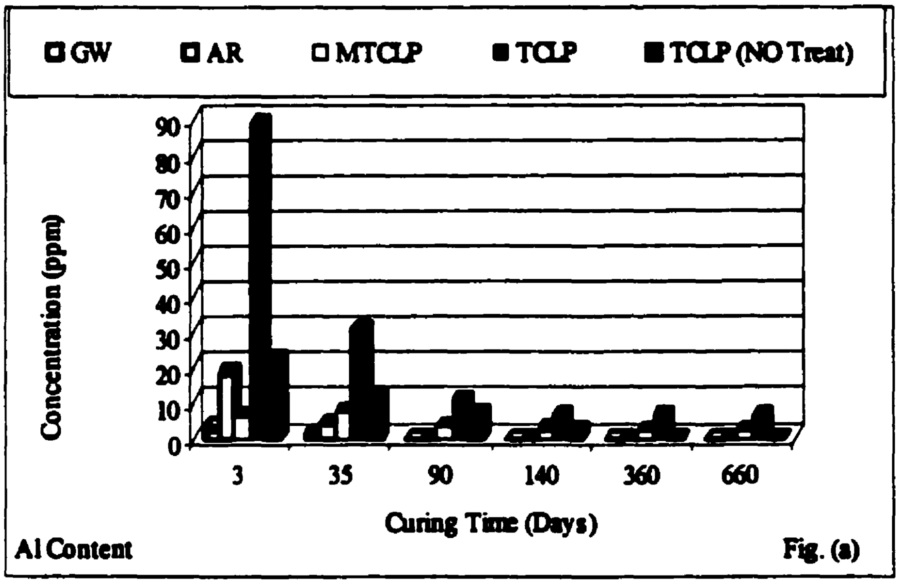


FIGURE 8.7 (a) ALUMINUM LEACHABILITY

In the case of copper, (Figure 8.7, b), hydration of the sample without any treatment has led to reduction of pH (Figure 8.7, g), and increase in copper solubility. However, treatment of the sample with 4% lime, 10% fly ash and 110 ppm of aluminum has successfully immobilized the copper in the solution. The same trend is repeated for the leachability of Iron, Magnesium, and zinc (Figure 8.7, c, d, and e). While the untreated samples have oxidized and had a significant drop in their pH value, metals have become soluble and their value has risen in the leachability

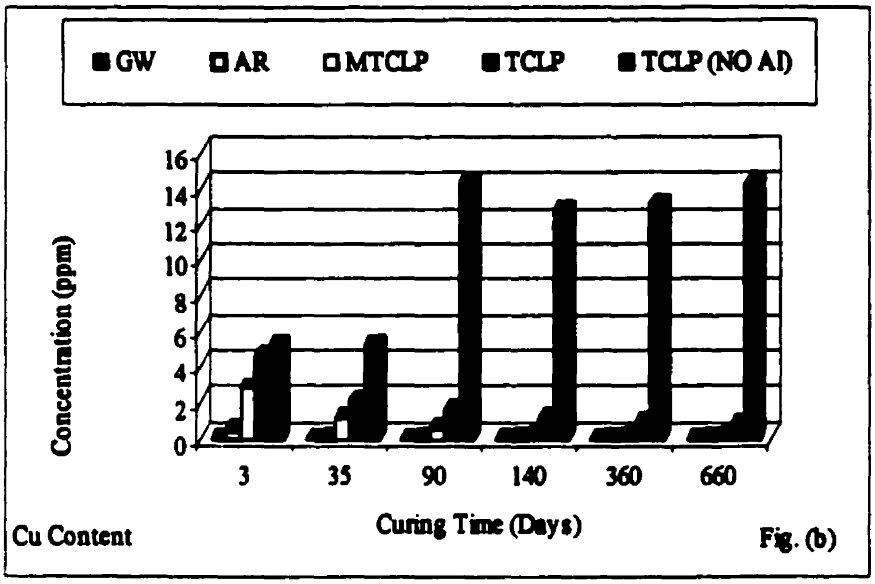


FIGURE 8.7 (b) COPPER LEACHABILITY

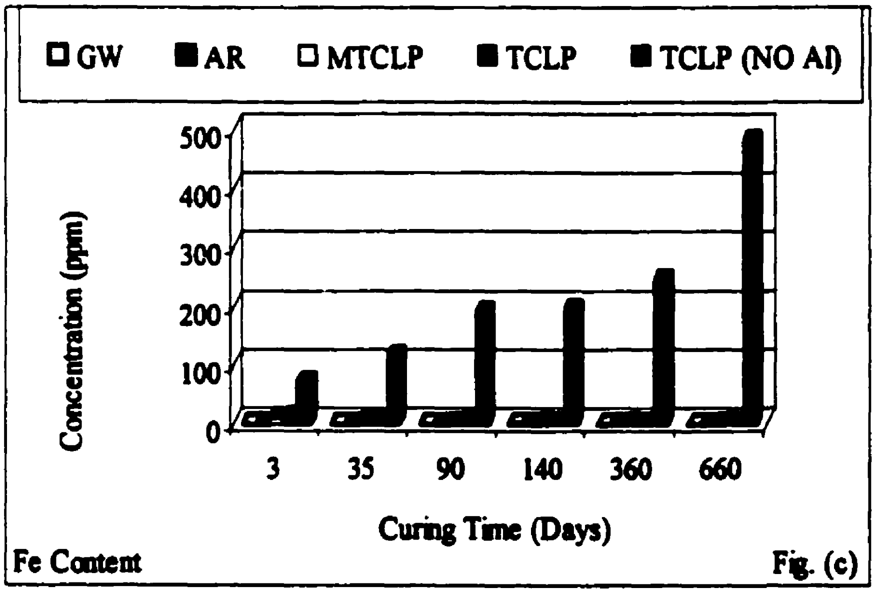


FIGURE 8.7 (c) IRON LEACHABILITY

measurement. The treatment of the samples, on the other hand, has successfully immobilized the ions and stabilized the samples.

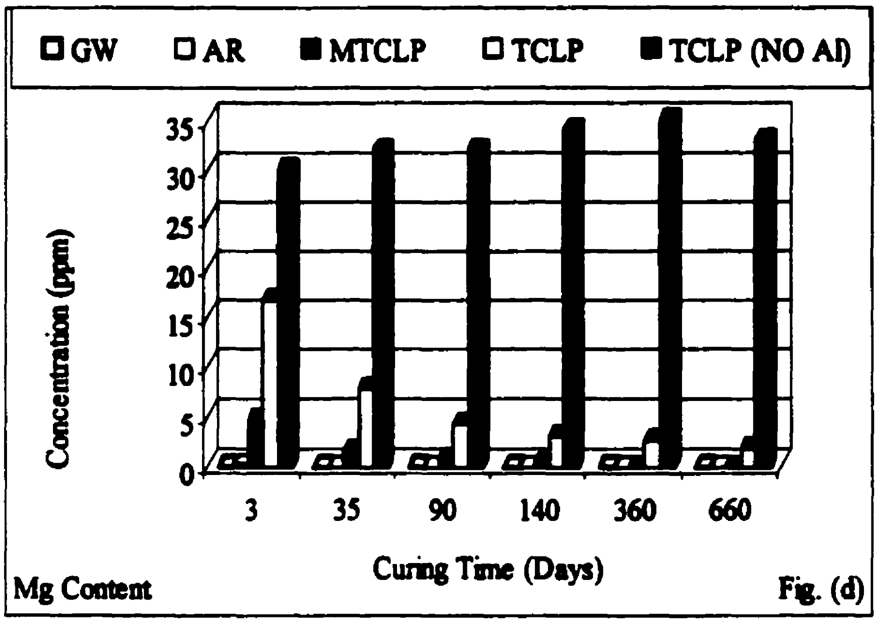


FIGURE 8.7 (d) MAGNESIUM LEACHABILITY

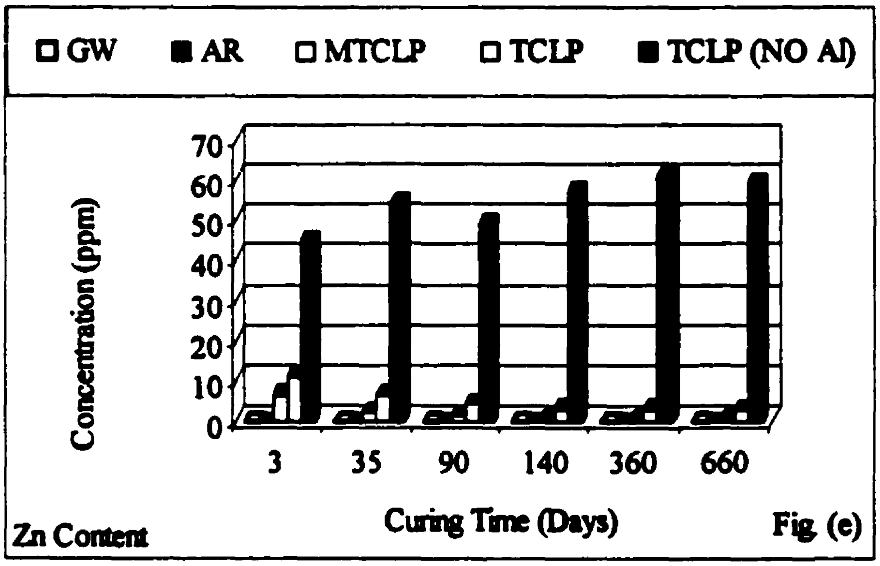


FIGURE 8.7 (e) ZINC LEACHABILITY

Calcium leachability has been the same as aluminum as the treated samples had more calcium in their mineralogical composition and more calcium has been solubilized when treated samples were leached compare to untreated samples.

However, longer curing of the samples has led to consumption of calcium in pozzolanic reactions and to buffer the pH of the mixture to around 10. The leachability of calcium and samples pH values have shown in Figure 8.7 (f, and g). The sulfate content of the treated samples have also remained fairly constant

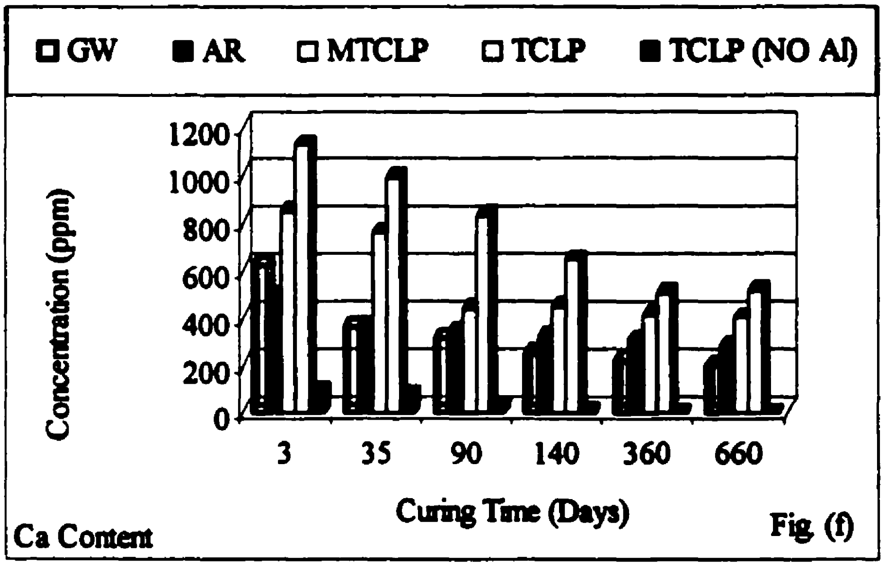


FIGURE 8.7 (f) CALCIUM LEACHABILITY

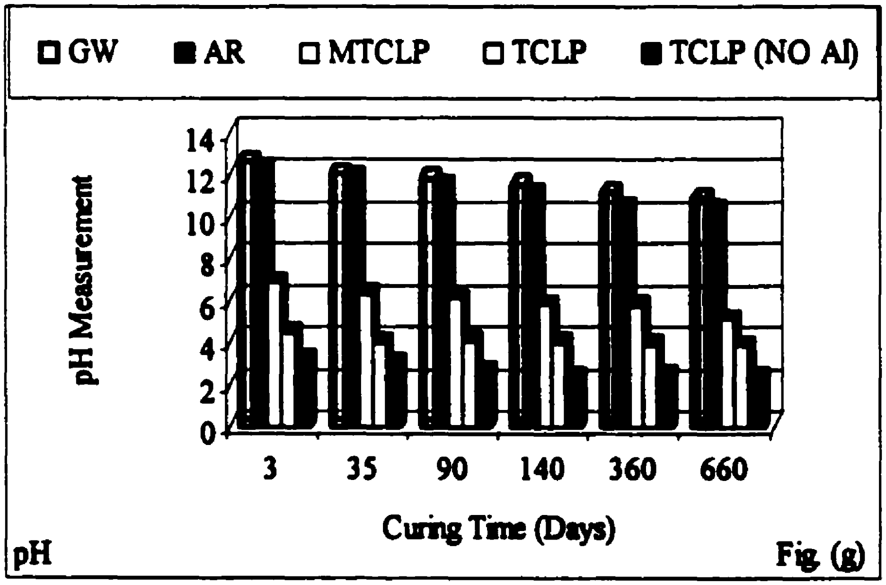


FIGURE 8.7 (g) PH MEASUREMENT OF THE SAMPLES

throughout of the hydration period as the oxidation rate has been slowed considerably, while the untreated samples have oxidized and produced significant quantity of sulfate during the hydration period (Figure 8.7, h).

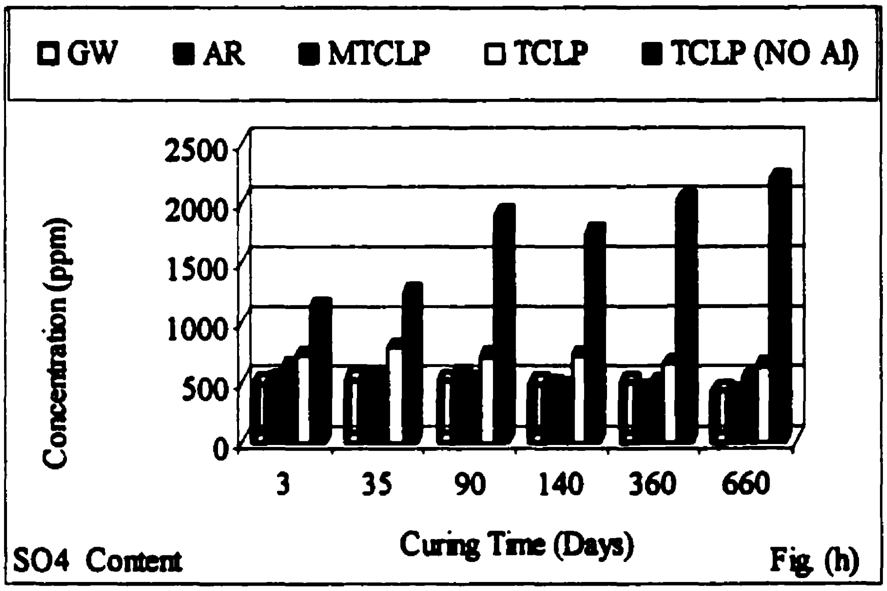


FIGURE 8.7 (h) SULFATE LEACHABILITY

8.5 Geotechnical Studies

Solidification/stabilization is a process involving chemical reactions and results in notable changes in the physical and chemical properties of the treated samples. As such, certain properties whereby the success or failure of the process is evaluated are of great interest. In the previous section, the leachability of the treated samples was evaluated. Moreover, physical stability and durability of the treated samples need to be evaluated to determine the reusability potential of the treated specimens. Therefore, geotechnical analysis such as measurement of unconfined compressive strength, permeability, and freeze and thaw were performed on the lime, fly ash and aluminum treated samples. Determination of physical stability and integrity of a treatment system which relies on ettringite formation for its efficacy is very important, particularly since ettringite is known to be expansive with deteriorating consequences under certain conditions. Physical instability of the treated samples could lead to release of absorbed and/or adsorbed metals from its structure.

In this study, the unconfined compressive strength experiment was performed in accordance with the ASTM D2166 procedure. Sample preparation, compaction and curing procedure were exactly the same as procedure followed for sample number 1, described in chapter 7. Treated samples were compacted in cylindrical molds (with a diameter of 30 mm and a height of 60 mm, shown in Figures 7.1 and 7.2). Samples were dry mixed and water containing the required aluminum content for the formation of ettringite were added to the samples with the water to solid ratio of 0.5. The compacted molds were cured in 25°C and 95% relative humidity. Samples were tested after 1 day, 28 days, 90 days, 140 days and 360 days of hydration. All the experiments were conducted in triplicate to increase the accuracy of the test results. Moreover, the compacted samples were subjected to falling head permeability analysis after 28 days of hydration. Prior to conducting the permeability analysis, the permeameter was placed in a sink in which the water was about 2 inches above the cover of the permeameter while the outlet was opened so that the water could back up through the specimen. This procedure was done to insure the saturation of the sample and elimination of the entrapped air.

Amongst the different experiments to assess the physical integrity of the treated specimen, freeze and thaw analysis is of a great importance since its simulate the long term behavior of the specimens under natural environmental conditions. Sample's strength and permeability can greatly be effected after repeated exposure of the specimen to freezing and thawing cycles. The cycling freezing and thawing causes mechanical stresses by the ice crystal formation in the samples. This could result in the formation of planes of weakness in the aggregates and as a consequence, damages the structural integrity of the treated specimens.

In order to perform the freeze and thaw experiments on the treated tailings samples, the 28 days compacted and cured specimens under previously described conditions were subjected to two sets of freezing and thawing. The first set consisted of 6 cycles and the second set of 12 cycles of repeated freeze and thaw conditions. Each cycle induces 24 hours freeze at -10°C and 24 hours thaw at 25°C. Samples were thawed in a constant temperature and relative humidity room. The unconfined compressive strength and permeability analyses were conducted on samples after completion of 6 and 12 freeze and thaw cycles.

8.5.1 Unconfined Compressive Strength Analysis

The results of the unconfined compressive strength for the treated as well as untreated samples are shown in Figure 8.8. Samples which were compacted without addition of treatment agent failed to get any strength during the 28 days hydration period. While application of 4% lime, 10% fly ash and 110 ppm of aluminum to this sample has resulted in considerable gain of strength within the first 28 days of hydration. Curing the sample for 28 days has generated more than 800 kPa of strength in the sample. The X-ray analysis of this sample (Figure 8.2, b) showed that ettringite and calcium silicate hydrate has been formed in this sample. Both of these minerals along with other pozzolanic properties of lime and fly ash could have contributed to the strength of the specimen.

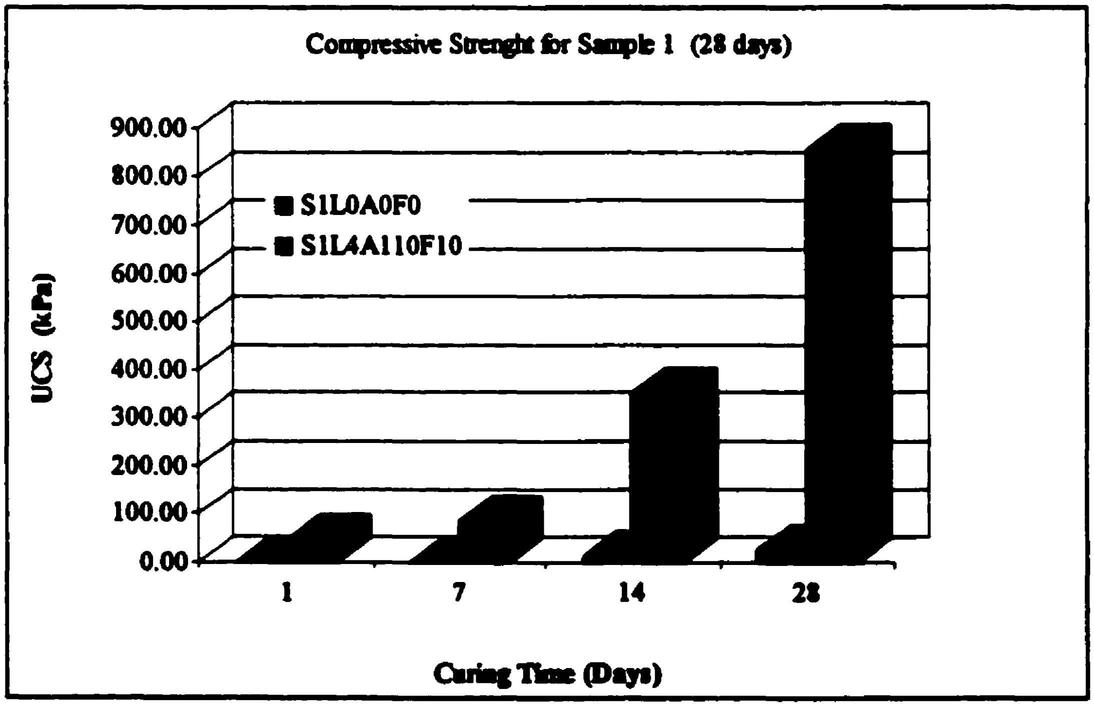


FIGURE 8.8 UNCONFINED COMPRESSIVE STRENGTH OF THE TREATED AND UNTREATED SAMPLES

In order to assess the long term strength of the sample under investigation, samples which were cured for 28 days, 90 days, 140 days and 360 days were subjected to unconfined compressive strength analysis (Figure 8.9).

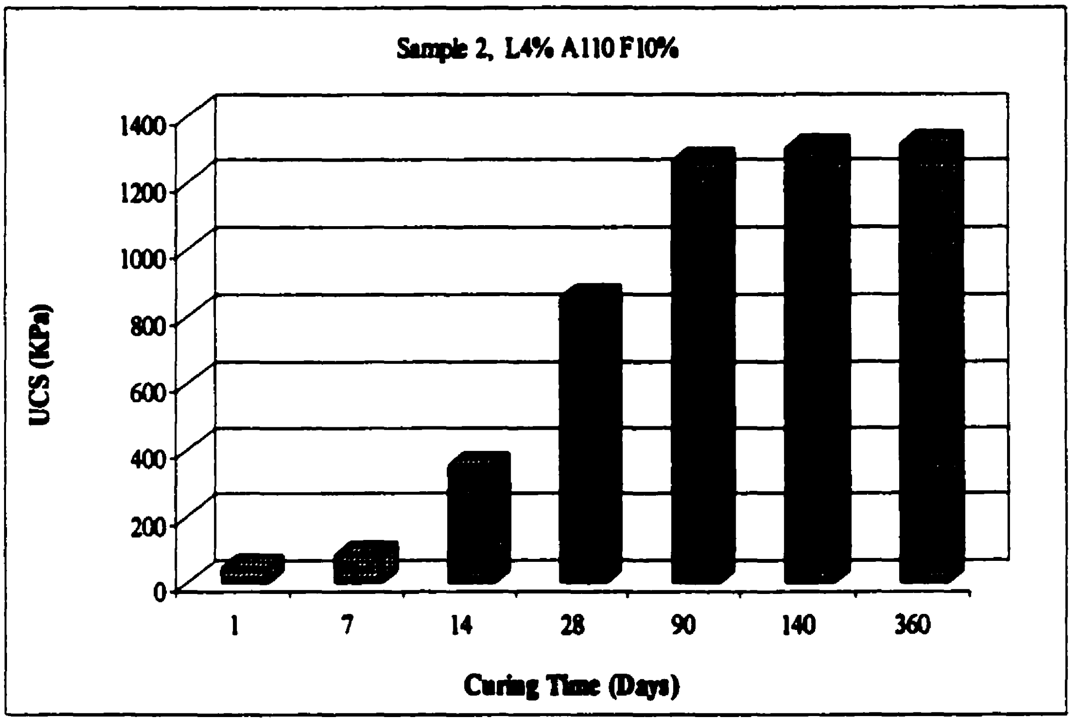


FIGURE 8.9 UNCONFINED COMPRESSIVE STRENGTH OF ALUMINUM, LIME AND FLY ASH TREATED SAMPLE

Application of the proposed treatment procedure has led to generation of more than 1200 kPa of strength after 90 days of hydration. The strength of the treated specimen remained constant up to 360 days of curing without any sign of deterioration. The strength of the specimen is correlated to the presence of ettringite in this sample. The X-ray diffraction analysis of the same samples (Figure 8.2) showed the presence of ettringite in the specimen. Achieving and maintaining such a strength in a sample which is potentially acid producing with detrimental physical and chemical consequences is a remarkable success.

8.5.2 Permeability Analysis

Reduction of permeability is an important factor to assess the success of stabilization and solidification for a treated waste sample. Reduction of permeability reduces and limits the contact of fluid with the tailings sample and the possible transport of contaminants out of stabilized matrix. The previous tailings sample under investigation, reached a permeability value of 10^{-6} cm/s after the application of treatment procedure. Based on regulations of Environment Canada and U.S. EPA, reduction of permeability for a stabilized waste typically range from 10^{-4} to 10^{-8} cm/s and hydraulic conductivities of less than 10^{-5} cm/s are recommended for stabilized waste destined for land disposal (U.S. EPA, 1989). Therefore, for the aluminum, lime, and fly ash treated tailings, permeability value of 10^{-5} cm/s is considered the success criteria for the proposed treatment procedure.

The result of the permeability analysis is shown in Figure 8.10. The untreated sample has a permeability value of 3.6E-4 cm/s. Application of treatment binders to this tailings sample has reduce its permeability to 1.16E-6 cm/s. Achieving such a low permeability is attributed to the modification of pore size and pore size distribution of the samples, which are the characteristics of the lime and fly ash treated tailings sample. Moreover, elimination of large pores, increasing the bonding particles and the maintenance of the particle arrangements as a result of the treatment with lime and fly ash have contributed to the reduction of permeability. Furthermore, it is postulated that ettringite crystals have filled the capillary pores of the cylindrical specimens and have further reduced their permeability.

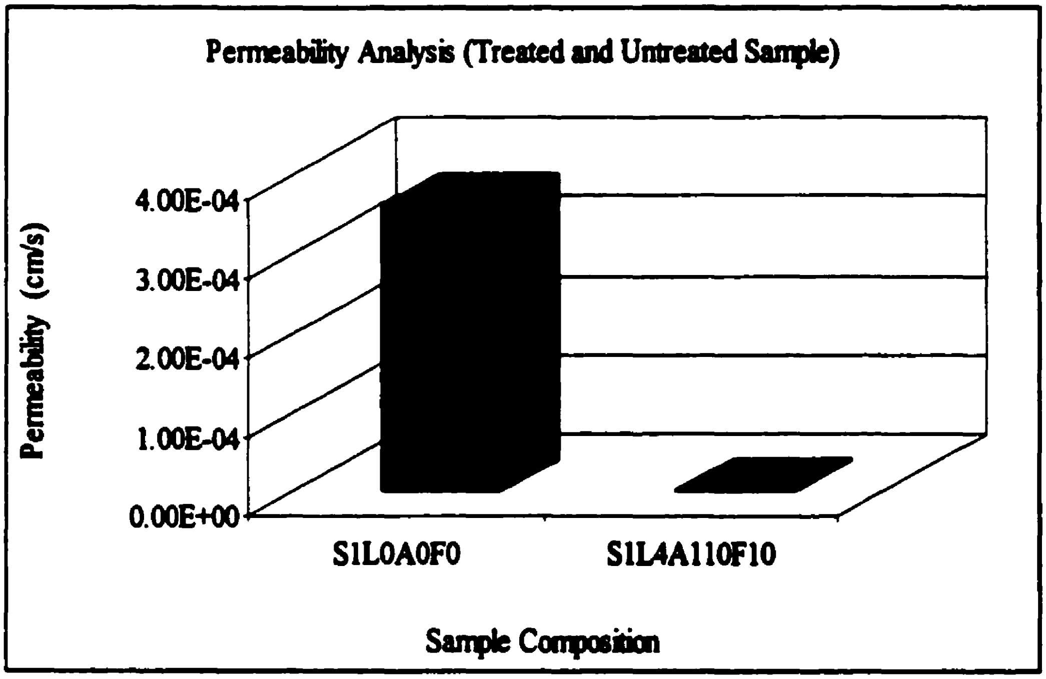


FIGURE 8.10 PERMEABILITY ANALYSIS OF 28 DAYS CURED SAMPLES

The results of the permeability analysis show that application of the proposed treatment procedure has reduced the permeability of the stabilized waste by 2 order of magnitude. Such a low permeability is an indication for safe disposal of tailings samples in the environment.

8.5.3 Freeze and Thaw Analysis

According to U.S. EPA (1989), durability testing evaluates the resistance of a stabilized/solidified waster to degradation due to external environmental stresses. This test is important since it mimics the natural conditions by stressing the samples through freezing/thawing. Unconfined compressive strength, permeability and other performance based tests may be conducted on the stabilized/solidified waste samples in order to determine how the physical properties of the treated waste has changed as a result of simulated climatic stresses. The number of cycles a material can withstand without failing can be used to judge the mechanical integrity of the material.

The treated and 28 days cured samples were subjected to 2 sets of freeze and thaw cycles. The first set consisted of 6 cycles and the second set consisted of 12 cycles of repeated freezing and thawing according to the procedure described previously (chapter 7). Samples after completion of each set were subjected to unconfined compressive strength and permeability analysis. The results of the experiments are shown in Figures 8.11 and 8.12.

Normal hydration of samples and their treatment with lime, fly ash and aluminum generated 855 kPa of strength after 28 days of curing. Samples which were subjected to 6 sets of freeze and thaw, after their initial 28 days hydration, generated 674 kPa strength; while 543 kPa of compressive strength was recorded for the sample which was subjected to 12 sets of freeze and thaw cycles. However, the untreated sample was totally disintegrated after one set of freeze and thaw cycling.

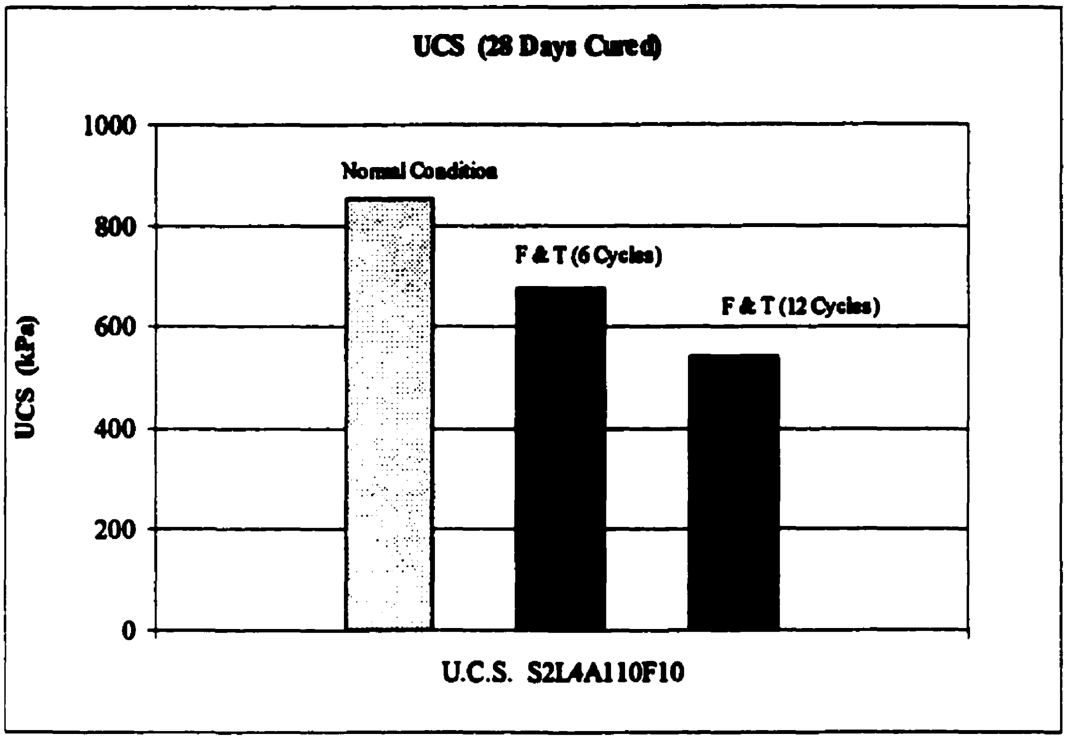


FIGURE 8.11 COMPRESSIVE STRENGTH OF FREEZE AND THAW SAMPLES

The reduction of strength in the treated samples is attributed to high tailings moisture suction which has been developed in the freezing zones. This could have caused an increase in the effective stress in the region immediately below the freezing front and the formation of segregated ice lenses. Such behavior could result in shrinkage of the tailings structure, formation of cracks, and a change in the pore size characteristics of the unfrozen section immediately below the ice lenses. However, no visible sign of stress or cracking were detected in the treated samples. It is postulated that pozzolanic properties of lime and fly ash and availability of ettringite crystals have prevented excessive shrinkage of the treated tailings samples.

The results of permeability analysis conducted on lime, fly ash and aluminum treated samples are shown in Figure 8.12. As the behavior of other treated tailings sample under the similar conditions showed, the freezing and thawing of the specimens did not deteriorate their structural integrity and the reduction of the permeability even after 12 cycles of freeze and thaw was not so significant. The low permeability increase in the sample after 12 sets of freeze and thaw cycles is mainly attributed to the pozzolanic properties of lime and fly ash which have resulted in the particle arrangement, and lower void ratio in the samples. As it was stated earlier, it is postulated that ettringite mineral could have blocked the capillary spaces in the samples and have resulted in significant reduction in their magnitude. The fine needle shape ettringite crystals prevent the penetration of water in the capillary zones which could have otherwise, become frozen and increase in volume, and therefore, cause internal stress during freezing.

Based on the results of durability analysis, the proposed treatment procedure is an effective method to maintain the physical integrity of the stabilized tailings and can prevent deterioration of the treated sample even under extreme environmental fluctuation. This is an important consideration given the harsh and rapid climatic changes in Canadian weather system.

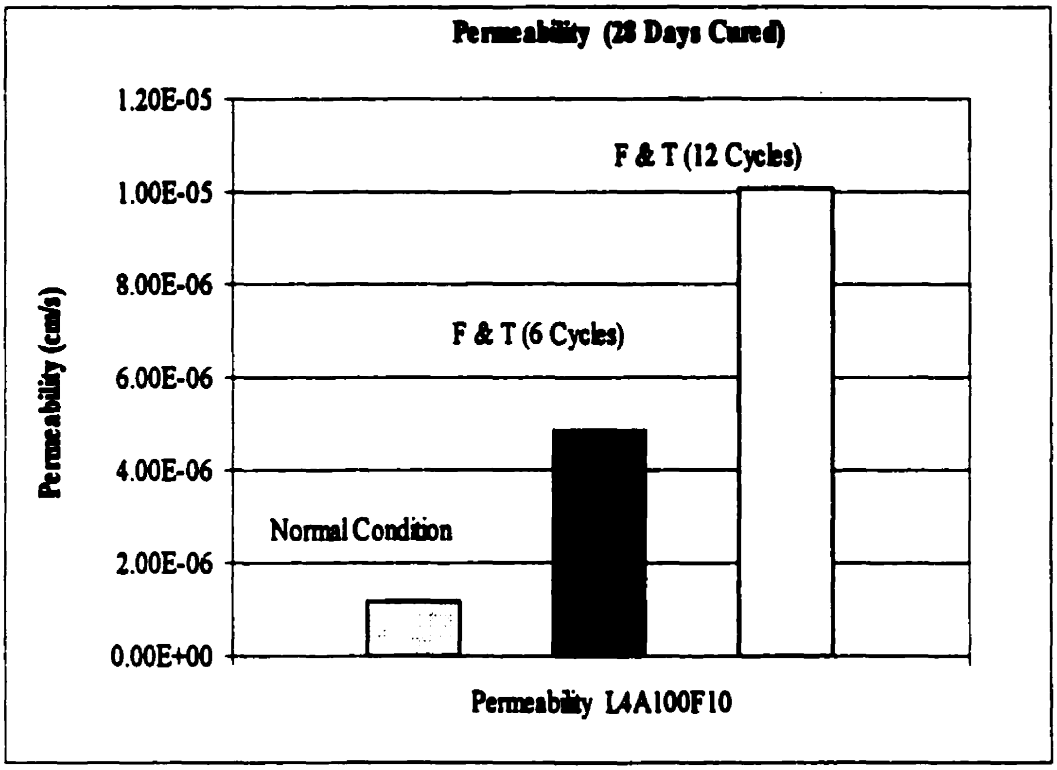


FIGURE 8.12 PERMEABILITY RESULTS OF FREEZE AND THAW SAMPLES

8.6 Conclusion

Results of the optimization experiment showed that application of 4% lime, 10% fly ash type "C", and 110 ppm of aluminum is necessary to form ettringite as a means of solidification/stabilization for the tailings samples under investigation. Leachability analysis showed that samples have been chemically stabilized after application of treatment procedure. The physical integrity of the samples were further evaluated by conducting unconfined compressive strength, permeability and freeze and thaw experiments. The X-ray diffraction analysis of the samples showed that ettringite mineral has been formed as a result of pozzolanic reactions between lime, fly ash, and water in the samples. Formation of ettringite has been accompanied by reduction of metals leachability and permeability of the samples. Based on the result of X-ray diffraction analysis, ettringite is the most dominant mineral formed in this sample as a result of pozzolanic reactions. Therefore, the physical and chemical stability of the treated sample is mainly attributed to ettringite formation and its capacity to immobilize other cations and anions in the sample. More over, formation of ettringite has been accompanied by higher strength and reduction of pore size distribution in the sample. Durability analysis of the treated samples revealed that extreme environmental fluctuation could not alter the physical integrity of the treated sample. Fine needle type crystals of ettringite are known to contribute to the strength of cement mortars as well as being able to block the capillary spaces in the sample, and therefore, prevent the water penetration into the capillary zone. Such phenomenon could be responsible for increase in durability of the treated matrices.

Chapter 9

Summary and Conclusion

Acid mine drainage is a natural phenomenon caused by the oxidation of metallic sulphides. The sulphides of primary concern are pyrite and pyrrhotite as they are among the most common minerals found in mining and mineral processing waste. Underground metal sulphides, in their natural crystalline form, are relatively stable but when mined and milled, they become exposed to oxygen and water, causing the mineral to oxidize. In the absence of calcareous materials, the oxidation of sulphide minerals produces sulphuric acid and liberates heavy metals. Such phenomenon has the potential for serious environmental degradation which could also be extremely expensive to remediated for the mining industry.

Lime treatment of sulphidic tailings is the most common method of treatment for acid producing tailings in Canada. Application of lime will increase the pH of the slurry which will cause the precipitation of the soluble metals. Moreover, its application to fine grained tailings sample will improve plasticity, workability, and volume change characteristics of the mixture. Strength of the lime treated tailings sample is expected to improve due to the formation of cementitious hydrates, bonding aggregated and particles together, and maintenance of flocculent particle arrangements. Furthermore, the permeability of lime treated tailings sample is expected to be reduced due to modification of pore size and pore size distribution within the sample structure. In conjunction with the application of lime, fly ash type "C', which is rich in calcium, was added to the tailings sample. Application of fly ash to the mixtures will provide a source of calcium, silicon, and aluminum to the tailings sample. Moreover, its application will enhance the workability and cause reduction in swell, shrinkage, and plasticity characteristics of the tailings samples as well as reduce the moisture content and create a higher compressive strength in the mixture.

In lime-remediated mine tailings, whereby aluminum can be released and the pH is elevated, the system could have all the requirements needed to precipitate calcium sulphoaluminate hydrates. One of these minerals, ettringite, has the capacity to uptake some of the metals of concern into its structure. Moreover, its surface is negatively charged which makes it a good adsorbent for positively charged metal species. Formation of ettringite is also associated with a high pH condition in the solution, which will further lead to the precipitation of heavy metals from the solution.

This research work investigated the feasibility of using ettringite based stabilization/solidification technology to prevent the acid mine drainage generation from other wise highly reactive-sulphidic mine tailings. Since generation of acidic effluent can pose a serious threat to the surface and ground water, special emphasis on environmental impacts associated with its application in tailings was undertaken. The environmental study focused on leachability potential of the metals of concern to the surrounding environment. Moreover, the metals retention characteristics and their immobilization technology were investigated. Furthermore, the geotechnical aspects of the stabilized tailings were investigated to assess the reusability of the treated tailings materials.

The required physical and chemical analysis was attained by an extensive laboratory testing program. In addition, a theoretical analysis was performed to evaluate the stability field of ettringite and ettringite like minerals in lime remediated sulphidic mine tailings. Observations and conclusions of this study are presented in the next section, followed by suggestions for further studies, and contribution to knowledge.

9.1 Summary and Concluding Remarks

9.1.1 Thermodynamic/Laboratory Optimization Aspects

Two acid producing tailings samples were obtained from two different mine sites in Quebec, Canada, and were subjected to different experiments to determine their chemical and physical characteristics. These tailings samples were sandy, silty in nature with high concentrations of pyrite, copper and zinc.

In order to evaluate the feasibility of forming ettringite, as the dominant method of stabilization/solidification, in sulphidic mine tailings systems, the optimal geochemical parameters needed to precipitate this mineral as a stable form was devised using a thermodynamic model. The model predicts that an optimal stability field for ettringite in mine tailings samples containing 10^{-3} mol/L of SO_4^{-2}, 10^{-2} mol/L of $Al(OH)_4^-$ requires at least 10^{-2} mol/L of Ca^{+2} and a pH around 11.5. The model predict that ettringite is stable over a wide range of composition and pH. However, the sulphate content of the tailings samples could limit the precipitation of ettringite and monosulphate could be the end-precipitate.

Based on the conclusions of the theoretical study, laboratory experimental program was undertaken to determine the threshold of lime, fly ash type "C", and an aluminum nitrate compound needed to promote the formation of ettringite and ettringite like minerals as the dominant method of stabilization for the tailings sample under investigation. Attaining and maintaining a high pH environment is crucial for ettringite based stabilization system. Moreover, the experimental program showed that the high metallic content of the tailings samples could partially replace the required trivalent aluminum from the ettringite structure and reduce the required stochiometric amounts of aluminum needed to form ettringite.

Optimum water content experiments were performed based on the magnitude of water required to cause the maximum reactivity of the admixtures as well as providing the possibility of compacting the resultant slurry. The experiments show that as the water content increases, the magnitude of the formed ettringite is increased. However, water content more than 50 percent by weight of the dry waste creates slurry which is very difficult to compact. Therefore, since one of the objectives has been the possibility of compacting the resultant slurry for its reusability, it was concluded that water to dry waste ratio of 0.5 to be used for achieving the required reactivity from the admixtures as well as creating slurry which is easily compactable.

9.1.2 Geochemical/Geoenvironmental Aspects

The leachability analysis conducted on lime, fly ash, and aluminum treated samples showed that all the metals of concern have been successfully immobilized. The success of the proposed treatment methodology was evaluated with leachability analysis, using four different leachants. The results of the experiments indicate that upon availability of aluminum for reactions, ettringite and ettringite like minerals could be formed and precipitate as a stable mineral in lime remediated sulphidic tailings. Moreover, the high pH environment of the samples as a result of lime and fly ash addition combined with the stabilization effect of ettringite reduced the solubility of the metals of concern significantly. Hence, from the results of all the leaching tests carried out, it appears that the matrix under investigation owes its stabilizing properties not only to physical factors, but also to chemical ones. In this respect, the formation of partially substituted ettringite has played an important role.

The X-ray diffraction analysis as well as the microstructure figures obtained by using scanning electron microscopy confirmed the formation of ettringite in the treated samples. Ettringite peak intensities were monitored over a long period of time in the treated samples. It was concluded that ettringite formation is the result of the pozzolanic reactions between lime, fly ash, and aluminum treated samples. Formation of ettringite was accompanied by the reduction in the magnitude of the gypsum in the samples. In lime-remediated tailings, formation of gypsum is not favorable as far as the chemical fixation and the durability of the samples are concern. Moreover, the results of the chemical analysis revealed that the treated samples' oxidation rate has been slowed down significantly. The surface chemical composition and X-ray diffraction patterns of the treated samples suggested that ettringite is the only stable mineral formed as a result of the pozzolanic reactions. Therefore, it was concluded that formation of ettringite was partly responsible for the immobilization of metals from the treated tailings samples.

Based on the obtained results it can be concluded that the proposed lime-fly ash and aluminum based treatment technique is effective in significantly reducing heavy metal leachability for the waste form tested. In addition, the results presented here formed the basis for the development of an experimental protocol to be used for testing the effectiveness of a given remediation technology or for the preliminary design of a given remediation technology. The approach is developed for the lime-fly ash based considered in the present study, but can be easily extended to a wide array of in-situ remediation schemes.

9.1.3 Geotechnical Aspects

The unconfined compressive strength test results revealed a significant increase in the strength performance of the tested treated tailings samples. Application of lime, fly ash type "C", and aluminium to high sulphide content tailings has resulted in formation of a solid monolith capable of producing more than 1000 kPa unconfined compressive strength in the samples. The treated monolith was exposed to 12 sets of freeze and thaw cycles and it preserved its structural integrity. Development and maintenance of high strength and stiffness in these samples are attributed to formation of ettringite as a result of the pozzolanic properties of lime and fly ash specifically in an environment rich in aluminium and sulphide compounds. Therefore, formation of ettringite leads to creation of a more resilient and stronger tailings sample.

Permeability of the treated tailings were measured and compared to those for untreated samples. Application of the treatment agents to the tailings sample reduces its permeability to around 1.00E-06 cm/s. According to published report by United States Environmental Protection Agency, 1.00E-05 cm/s is the maximum permeability allowed to render a waste stabilised and impermeable. The permeability of the treated tailings samples remained below the recommended permeability even after exposing the treated samples to 12 sets of freeze and thaw cycles. Low permeability of the treated samples was also an indication of non-expansively of the ettringite crystals in the treated samples.

Overall, based on the results of the geo-environmental analysis, treatment of high sulphide content tailings with lime and fly ash, combined with availability of aluminum for reactions, is a successful method of solidifying these highly reactive tailings. The pozzolanic properties of lime and fly ash coupled with the possibilities of ettringite formation in the samples will lead to generation of a solidify monolith capable of withstanding harsh environmental fluctuations.

9.2 Economics Impact Evaluation

Today's environmental constraints demand that a reactive tailings basin be designed with consideration of the long term as the cost of abandonment and reclamation is a major portion of the life cycle cost of any waste facility (Knapp, R., and Welch, D., 1991). Treatment of acidic effluent, sludge management and close-out costs can be much greater than the initial construction and operating costs for a waste management facility. Therefore, consideration must be undertaken during the active life of the mine as to the proper procedure required for mine closure.

Very little is known about the technical or economic effectiveness of managing acid-producing waste at mines as the procedure has rarely been attempted on a large scale. The cost of doing so is very high and a long time period is required to measure the effectiveness. Although the problems involved are the focus of considerable research, there do not appear to be any simple solution.

The cost of stabilizing reactive tailings is highly site specific, and thus will vary greatly from site to site. Acid neutralization capacity of the host rock, topography and morphology of the disposal area, availability of the treatment agents can all have significant effect on overall cost and liabilities of the mining operations. Moreover, for precious metal rock piles, more stringent containment requirements, which involve the introduction of liner systems would dramatically increase the waste management costs. There is an order-of-magnitude spread between the lowest and the highest costs impact the financial rate of return of the mining project. Cost increases may, in fact be as large as a reasonable profit margin (Hutchison, I.P., and Ellison, R.D., 1992).

Ettringite formation in sulfidic mine tailings is a viable solution for stabilization/solidification of reactive tailings. This treatment method can be applied to an ongoing tailings disposal facility or can be used to form an inert capping agent to prevent the oxidation of deposited tailings and waste rock.. The operating cost of this treatment technology is mostly devised of the price for the binders used to form and precipitate ettringite. The binder are a source of aluminum as well as an alkaline agent rich in calcium such as lime, limestone, and fly ash type "C". The source of treatment agents as well as their availability at the treatment site can greatly influence the cost of this stabilization/solidification technology. In the laboratory optimization study, calcium needed to form and precipitate ettringite was provided through the application of hydrated lime. Fly ash type "C" as a source for calcium, aluminum, and silicate was also added to the tailings to reduce the required quantity of calcium and aluminum needed as well as to enhance the treated samples workability, plasticity, and reduce their permeability. Additional aluminum was provided through the application of aluminum nitrite to the samples. The required aluminum to form ettringite can be provided from different sources such as natural clay, bauxite, other waste byproduct which contain aluminum or from a chemical source. Depending on the source of aluminum and its availability at the site, the cost of this treatment technology can be influenced.

Under the applied laboratory conditions, the cost of this treatment technology has been estimated to be between $16 to $17 per metric ton of tailings. This is based on the price for hydrated lime, and fly ash as well as laboratory grade of aluminum, which was added to the samples under investigation. However, it is imperative to note that in order to make a more precise economic analysis of this treatment technology, its application to a sub scale model is necessary. It is only then that a more accurate estimate regarding the type and quantity of the treatment agents for this stabilization/solidification technology can be made.

Considering the cost impact of this tailings disposal method on a mining project, we have to look optimistically upon the future to make ettringite formation for stabilization/solidification of reactive tailings economically and environmentally acceptable. Soon, universal standards in mining environmental protection will be inevitable and will create an equilibrium in disposal costs for mining companies all over the world. It will then be affordable to invest in this project.

9.3 Suggestions for Further Studies

Future studies should investigate:

1) The effect of tailings particle size on the formation of ettringite and its stability;

2) Measurement of ettringite expansively in the presence of lower alkaline agent;

3) The potential of using aluminum contained waste materials such as bauxite in formation of ettringite in sulphidic mine tailings;

4) The potential of using natural clay as a source of aluminum in formation of ettringite in lime-remediated sulphidic tailings;

5) To investigate the applicability of the proposed treatment procedure in a sub-scale model for field application.

9.4 Contribution to Knowledge

This study represents the following contributions toward a practical approach in the treatment of acid mine drainage:

1) The concept of ettringite formation as a means of stabilizing and solidifying the potentially acid producing tailings;
2) Evaluation of characteristics and properties of lime, fly ash type "C", and aluminum treated sulphide rich tailings, which include:
    a. Geo-chemical, and geo-environmental performance;
    b. Interactions and bonding mechanisms;
    c. Geotechnical performance;
3) Use of thermodynamic modeling in prediction of lime remediated, aluminum and sulphide mine tailings.

Although this study was conducted on a limited number of tailings samples, the results may bear well significant implications for other sulphide rich tailings samples. In addition, the results presented here formed the basis for the development of an experimental protocol to be used for testing the effectiveness of a given remediation technology or for the preliminary design of a given remediation technology. The approach is developed for the lime-fly ash based considered in the present study, but can be easily extended to a wide array of in-situ remediation schemes.

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Appendix 1

Mass Action Equation

APPENDIX 1

MASS ACTION EQUATIONS (Log k, I=0.0, 25°C)
(Martell and Smith, 1976,1982)

$Ca^{+2} + OH^- \Leftrightarrow CaOH^+$	1.3
$Ca^{+2} + 2OH^- \Leftrightarrow Ca(OH)_2^{0+}(aq)$	−5.19
$Ca^{+2} + SO_4^{-2} \Leftrightarrow CaSO_4^0(aq)$	−2.31
$Ca^{+2} + CO_3^{-2} \Leftrightarrow CaCO_3^0(aq)$	3.15
$Ca^{+2} + HCO_3^{-1} \Leftrightarrow CaHCO_3^+$	1.0
$Al^{+3} + OH^- \Leftrightarrow AlOH^{+2}$	9.01
$Al^{+3} + 2OH^- \Leftrightarrow Al(OH)_2^+$	18.7
$Al^{+3} + 3OH^- \Leftrightarrow Al(OH)_3^0(aq)$	27
$Al^{+3} + 4OH^- \Leftrightarrow Al(OH)_4^{-1}$	33
$2Al^{+3} + 2OH^- \Leftrightarrow Al_2(OH)_2^{+4}$	20.3
$Al^{+3} + SO_4^{-2} \Leftrightarrow AlSO_4^{+1}$	3.89
$H^+ + OH^- \Leftrightarrow H_2O$	14
$H_2O + CO_2 \Leftrightarrow H_2CO_3$	−1.464
$H_2CO_3 \Leftrightarrow HCO_3^- + H^+$	−6.352
$HCO_3^- + \Leftrightarrow CO_3^{-2} + H^+$	−10.33
$HSO_4^- + \Leftrightarrow SO_4^{-2} + H^+$	−1.99
$Fe^{+2} + OH^- \Leftrightarrow FeOH^+$	4.5
$Fe^{+2} + 2OH^- \Leftrightarrow Fe(OH)_2$	7.4
$Fe^{+2} + 3OH^- \Leftrightarrow Fe(OH)_3^-$	10.0
$Fe^{+2} + 4OH^- \Leftrightarrow Fe(OH)_4^{-2}$	9.6

$Cu^{+2} + OH^- \Leftrightarrow CuOH^+$	6.3
$Cu^{+2} + 2OH^- \Leftrightarrow Cu(OH)_2$	13.6
$Cu^{+2} + 3OH^- \Leftrightarrow Cu(OH)_3^{-1}$	13.7
$Cu^{+2} + 4OH^- \Leftrightarrow Cu(OH)_4^{-2}$	16.4
$2Cu^{+2} + 2OH^- \Leftrightarrow Cu_2(OH)_2^{+2}$	17.7
$Cu^{+2} + SO_4^{-2} \Leftrightarrow CuSO_4$	2.36
$Cu^{+2} + CO_3^- \Leftrightarrow CuCO_3$	6.57
$Cu^{+2} + 2CO_3^- \Leftrightarrow Cu(CO_3)_2^{-2}$	9.92
$K^+ + OH^- \Leftrightarrow KOH$	−0.5
$K^+ + SO_4^{-2} \Leftrightarrow KSO_4^-$	0.85
$Mg^{+2} + OH^- \Leftrightarrow MgOH^+$	2.58
$4Mg^{+2} + 4OH^- \Leftrightarrow Mg_4(OH)_4^{+4}$	16.3
$Mg^{+2} + SO_4^{-2} \Leftrightarrow MgSO_4$	2.23
$Mg^{+2} + CO_3^{-2} \Leftrightarrow MgCO_3$	2.83
$Mg^{+2} + HCO_3^{-2} \Leftrightarrow MgHCO_3^+$	0.95
$Zn^{+2} + OH^- \Leftrightarrow ZnOH^+$	5.0
$Zn^{+2} + 2OH^- \Leftrightarrow Zn(OH)_2$	10.2
$Zn^{+2} + 3OH^- \Leftrightarrow Zn(OH)_3^-$	13.9
$Zn^{+2} + 4OH^- \Leftrightarrow Zn(OH)_4^{-4}$	15.6
$Zn^{+2} + ZnOH^+ \Leftrightarrow Zn_2OH^{+3}$	0.0
$Zn^{+2} + SO_4^{-2} \Leftrightarrow ZnSO_4$	2.38
$Zn^{+2} + 2SO_4^{-2} \Leftrightarrow Zn(SO_4)_2^{-2}$	1.73
$Zn^{+2} + 3SO_4^{-2} \Leftrightarrow Zn(SO_4)_3^{-4}$	1.7
$Zn^{+2} + 4SO_4^{-2} \Leftrightarrow Zn(SO_4)_4^{-6}$	1.7
$Zn^{+2} + HCO_3^- \Leftrightarrow ZnHCO_3^{+2}$	1.5

$Cr^{+3} + OH^{-} \Leftrightarrow CrOH^{+}$	10.1
$Cr^{+3} + 2OH^{-} \Leftrightarrow Cr(OH)_2$	17.3
$Cr^{+3} + 3OH^{-} \Leftrightarrow Cr(OH)_3^{-}$	32.6
$4Cr^{+3} + 4OH^{-} \Leftrightarrow Cr_4(OH)_4^{+8}$	47.51
$4Cr^{+3} + 6OH^{-} \Leftrightarrow Cr_4(OH)_6^{+6}$	73.59
$Cr^{+3} + SO_4^{-2} \Leftrightarrow CrSO_4^{-2}$	2.6
$CrOHSO_4 + H^{+} \Leftrightarrow CrSO_4^{+} + H_2O$	4.56

$Mn^{+2} + OH^{-} \Leftrightarrow MnOH^{+}$	3.4
$Mn^{+2} + 4OH^{-} \Leftrightarrow Mn(OH)_4^{-2}$	7.7
$2Mn^{+2} + OH^{-} \Leftrightarrow Mn_2OH^{+3}$	3.4
$Mn^{+2} + 3OH^{-} \Leftrightarrow Mn_2(OH)_3^{+}$	18.1
$Mn^{+2} + SO_4^{-2} \Leftrightarrow MnSO_4$	2.26
$Cr^{+2} + HSO_4^{-} \Leftrightarrow MnHSO_4^{+}$	1.8

$H^{+} + H_3SiO_4^{-} \Leftrightarrow H_4SiO_4$	9.86
$H^{+} + H_2SiO_4^{-} \Leftrightarrow H_3SiO_4^{-}$	13.1
$2H^{+} + 2H_2SiO_4^{-2} \Leftrightarrow H_2(H_2SiO_4)_2^{-2}$	26.5
$4H^{+} + 4H_2SiO_4^{-2} \Leftrightarrow H_4(H_2SiO_4)_4^{-4}$	55.9
$6H^{+} + 4H_2SiO_4^{-2} \Leftrightarrow H_6(H_2SiO_4)_4^{-2}$	78.2

$As(OH)_3 + H_2O \Leftrightarrow H^{+} + As(OH)_4^{-}$	-9.29

$Pb^{+2} + OH^{-} \Leftrightarrow PbOH^{+}$	6.3
$Pb^{+2} + 2OH^{-} \Leftrightarrow Pb(OH)_2$	10.9
$Pb^{+2} + 3OH^{-} \Leftrightarrow Pb(OH)_3^{-}$	13.9
$2Pb^{+2} + OH^{-} \Leftrightarrow Pb_2OH^{+3}$	7.6
$3Pb^{+2} + 3OH^{-} \Leftrightarrow Pb_3(OH)_4^{+3}$	32.1
$4Pb^{+2} + 4OH^{-} \Leftrightarrow Pb_4(OH)_4^{+4}$	35.1
$6Pb^{+2} + 8OH^{-} \Leftrightarrow Pb_6(OH)_8^{+6}$	68.4
$Pb^{+2} + 2CO_3^{-2} \Leftrightarrow Pb(CO_3)_2^{+2}$	9.5
$Pb^{+2} + SO_4^{-2} \Leftrightarrow PbSO_4$	2.75
$Pb^{+2} + 2SO_4^{-2} \Leftrightarrow Pb(SO_4)_2^{-2}$	2.38

SOLUBILITY PRODUCTS (pCO_2=3.5atm)
(1. Reardon, 1993: 2. Baes and Mesmer, 1976; 3. Stumm and Morgan, 1981)

$CaCO_3(s) \Leftrightarrow Ca^{+2} + CO_3^{-2}$	-8.35^1
$CaSO_4.2H_2O(s) \Leftrightarrow Ca^{+2} + SO_4^{-2} + 2H_2O$	-4.64^1
$Ca(OH)_2(s) \Leftrightarrow Ca^{+2} + 2OH^-$	5.19^1
$Al(OH)_3(s) \Leftrightarrow Al^{+3} + 3OH^-$	33.5^1
$Ca_6Al_2O_3(SO_4)_3.32H_2O \Leftrightarrow 6Ca^{+2} + 2Al(OH)_4^- + 3SO_4^{-2} + 4OH^- + 26H_2O$	-43.13^1
$4CaO.Al_2O_3.13H_2O \Leftrightarrow 4Ca^{+2} + 2Al(OH)_4^- + 6OH^- + 6H_2O$	-27.49^1
$2CaO.Al_2O_3.8H_2O \Leftrightarrow 2Ca^{+2} + 2Al(OH)_4^- + 2OH^+ + 3H_2O$	-13.04^1
$3CaO.Al_2O_3.6H_2O \Leftrightarrow 3Ca^{+2} + 2Al(OH)_4^- + 4OH^+$	-19.95^1
$Ca_4Al_2O_6SO_4.12H_2O \Leftrightarrow 4Ca^{+2} + 2Al(OH)_4^- + SO_4^{-2} + 4OH^- + 6H_2O$	-27.62^1
$Fe(OH)_2(s) \Leftrightarrow Fe^{+2} + 2OH^-$	-15.1^3
$FeCO_3(s) \Leftrightarrow Fe^{+2} + CO_3^{-2}$	-10.63^3
$Cu(OH)_2(s) \Leftrightarrow Cu^{+2} + 2OH^-$	-19.32^2
$Mg(OH)_2(s) \Leftrightarrow Mg^{+2} + 2OH^-$	-11.15^2
$Zn(OH)_2(s) \Leftrightarrow Zn^{+2} + 2OH^-$	-12.45^2
$Cr(OH)_3(s) \Leftrightarrow Cr^{+3} + 3OH^-$	28.6^2
$Mn(OH)_2(s) \Leftrightarrow Mn^{+2} + 2OH^-$	12.8^2
$MnCO_3(s) \Leftrightarrow Mn^{+2} + CO_3^{-2}$	-10.4^2
$0.25As_4O_6(cubic) + 1.5H_2O \Leftrightarrow As(OH)_3(aq)$	-0.68^3
$PbO(s) \Leftrightarrow Pb^{+2} + 2H_2O$	12.72^2
$SiO_2(s, quartz) + 2H_2O \Leftrightarrow Si(OH)_4$	-3.4^3
$SiO_2(s, amorphous) + 2H_2O \Leftrightarrow Si(OH)_4$	-2.73^3

Appendix 2

Thermodynamic Modeling Program

Thermodynamic Modeling Program Used To Model The Formation Of Ettringite In Lime Remediated Sulphidic Mine Tailings

```
      PROGRAM CDEXP (c1)
      EXTERNAL FCN
      REAL*8 ATOF
      REAL XPH
      CHARACTER*7 Y(25)
      CHARACTER*20 c1
      COMMON XPH
      COMMON G1,G2,G3,G4,G5,G6
      DIMENSION X(80),F(80),PAR(1),WK(20000)
      c1 (20:20)=char (0)
      print*,c1
      WRITE(7,40)
40    FORMAT (10X,'PROGRAM junk - CALCULATES SPECIES DISTRIBUTION
     1',/,18X,'Cd-OH-Cl-Na system')
99    CONTINUE
      xph=at of (c1)
      NSIG=5
      ITMAX=100
      PAR(1)=0.0
      FNORM=0.0
      N=74
      ITER=0
      XLAST=0.0
      A=0.5092
      B=0.3283
      X(1)=-4.0
      X(2)=-3.22
      X(3)=-11.5
      X(4)=-3.5
      X(5)=-4.36
      X(6)=-4.8
      X(7)=-17.0
      X(8)=-28.6
      X(9)=-21.1
      X(10)=-26.5
      X(11)=-27.86
      X(12)=-27.4
      X(13)=-12.0
      X(14)=-5.95
      X(15)=-5.01
      X(16)=-7.52
      X(17)=-3.5
      X(18)=-4.2
      X(19)=-9.05
      X(20)=-6.4
      X(21)=-21.46
```

```
X(22)=-9.0
X(23)=-13.17
X(24)=-11.5
X(25)=-10.5
X(26)=-9.84
X(27)=-6.0
X(28)=-7.0
X(29)=-17.0
X(30)=-5.5
X(31)=-5.0
X(32)=-17.27
X(33)=-17.29
X(34)=-7.0
X(35)=-8.0
X(36)=-3.8
X(37)=-10.36
X(38)=-6.52
X(39)=-3.5
X(40)=-3.2
X(41)=-5.08
X(42)=-5.66
X(43)=-8.8
X(44)=-5.5
X(45)=-4.3
X(46)=-3.5
X(47)=-2.5
X(48)=-2.7
X(49)=-7.7
X(50)=-6.0
X(51)=-9.1
X(52)=-12.0
X(53)=-6.0
X(54)=-20.0
X(55)=-16.22
X(56)=-15.17
X(57)=-5.02
X(58)=-21.6
X(59)=-18.3
X(60)=-4.92
X(61)=-8.5
X(62)=-6.25
X(63)=-4.4
X(64)=-8.1
X(65)=-7.14
X(66)=-8.6
X(67)=-8.5
X(68)=-10.9
X(69)=-5.97
X(70)=-9.33
X(71)=-7.7
X(72)=-4.0
```

```
X(73)=-3.5
X(74)=-30.3
Y(1)='oh'
Y(2)='SO4'
Y(3)='HSO4'
Y(4)='Ca2+'
Y(5)='CA(OH)'
Y(6)='CASO4'
Y(7)='AL'
Y(8)='AL(OH)'
Y(9)='AL(OH)2'
Y(10)='AL(OH)3'
Y(11)='AL(OH)4'
Y(12)='AL2(OH)2'
Y(13)='ALSO4'
Y(14)='H2CO3'
Y(15)='HCO3'
Y(16)='CO3'
Y(17)='CaCO3(aq)'
Y(18)='CaHCO3-'
Y(19)='MN+2'
Y(20)='MNOH'
Y(21)='MN(OH)4'
Y(22)='MNSO4'
Y(23)='MNHSO4'
Y(24)='FE+2'
Y(25)='FEOH'
Y(26)='FE(OH)2'
Y(27)='FE(OH)3'
Y(28)='FE(OH)4'
Y(29)='CU+2'
Y(30)='CUOH'
Y(31)='CU(OH)2'
Y(32)='CU(OH)3'
Y(33)='CU(OH)4'
Y(34)='CUSO4'
Y(35)='CUCO3'
Y(36)='K+'
Y(37)='KOH'
Y(38)='KSO4'
Y(39)='MG+2'
Y(40)='MGOH'
Y(41)='MGSO4'
Y(42)='MGCO3'
Y(43)='MGHCO3'
Y(44)='ZN+2'
Y(45)='ZNOH'
Y(46)='ZN(OH)2'
Y(47)='ZN(OH)3'
Y(48)='ZN(OH)4'
Y(49)='ZNSO4'
```

```
      Y(50)='ZN(SO4)2'
      Y(51)='ZN(SO4)3'
      Y(52)='ZN(SO4)4'
      Y(53)='ZNHCO3'
      Y(54)='CR+3'
      Y(55)='CROH'
      Y(56)='CR(OH)2'
      Y(57)='CR(OH)3'
      Y(58)='CRSO4'
      Y(59)='CROHSO4'
      Y(60)='PB+2'
      Y(61)='PBOH'
      Y(62)='PB(OH)2'
      Y(63)='PB(OH)3'
      Y(64)='PB2OH'
      Y(65)='PB3(OH)4'
      Y(66)='PB4(OH)4'
      Y(67)='PB6(OH)8'
      Y(68)='PB(CO3)2'
      Y(69)='PBSO4'
      Y(70)='PB(SO4)2'
      Y(71)='H4SIO4'
      Y(72)='H3SIO4'
      Y(73)='H2SIO4'
      Y(74)='H6SI4O12'
      G1=0.0
      G2=0.0
      G3=0.0
      G4=0.0
      G5=0.0
      G6=0.0
7     ITER=ITER+1
      XISTR=0.5*(10**X(1)+4.0*10**X(2)+10**X(3)+4.0*10**X(4)
     1+10**X(5)+9.0*10**X(7)+4.0*10**X(8)+10**X(9)+10**X(11)
     1+16.0*10**X(12)+10**X(13)+10**X(15)+4.0*10**X(16)
     1+10**X(18)+4.0*10**X(19)+10**X(20)+4.0*10**X(21)
     1+10**X(23)+4.0*10**X(24)+10**X(25)+10**X(27)
     1+4.0*10**X(28)
     1+4.0*10**X(29)+10**X(30)+10**X(32)+4.0*10**X(33)
     1+10**X(36)
     1+10**X(37)+10**X(38)+4.0*10**X(39)+10**X(40)+10**X(43)
     1+4.0*10**X(44)+10**X(45)+10**X(47)+4.0*10**X(48)
     1+4.0*10**X(50)
     1+16.0*10**X(51)+36.0*10**X(52)+10**X(53)+9.0*10**X(54)
     1+10**X(55)+10**X(56)+10**X(59)+4.0*10**X(60)
     1+10**X(61)+10**X(63)+9.0*10**X(64)+4.0*10**X(65)
     1+64.0*10**X(66)+16.0*10**X(67)+4.0*10**X(68)
     1+4.0*10**X(70)
     1+10**X(72)+4.0*10**X(73)+10**X(74))
      WRITE(*,58) ITER,XISTR
58    FORMAT('ITERATION No.:',I2,3X,'IONSTR:',F8.4)
```

```
               XISTR=XISTR**0.5
               G1=-A*XISTR/(1.0+(5.0*B*XISTR))+0.06*XISTR**2
               G2=4.0*G1
               G3=9.0*G1
               G4=16.0*G1
               G5=25.0*G1
               G6=36.0*G1
               XTEST=ABS(G1-XLAST)
               IF(XTEST.LT.0.001)GO TO 151
     150       CALL ZSPOW(FCN,NSIG,N,ITMAX,PAR,X,FNORM,WK,IER)
               XLAST=G1
               GO TO 7
     151       WRITE(*,200)XPH,G1,G2,G3,G4,G5,G6
     200       FORMAT(5X,4F11.4)
               WRITE(*,100)  (X(I), I=1,74)
     100       FORMAT(F8.4)
     999       END
               SUBROUTINE FCN(X,F,N,PAR)
               COMMON XPH
               COMMON G1,G2,G3,G4,G5,G6
               DIMENSION X(80),F(80),PAR(1),WK(20000)
               F(1)=-14.0-XPH-X(1)-G1
               F(2)=-1.99+X(3)-X(2)-XPH-G2
               F(3)=-1.3+X(5)-X(1)-X(4)-G1-G2
               F(4)=-2.31+X(6)-X(4)-X(2)-2*G2
               F(5)=-9.01+X(8)-X(7)-X(1)+G2-G3-G1
               F(6)=-18.7+X(9)-X(7)-2.0*X(1)+G1-G3-2.0*G1
               F(7)=-27.0+X(10)-X(7)-3.0*X(1)-G3-3.0*G1
               F(8)=-33.0+X(11)-X(7)-4.0*X(1)+G1-G3-4.0*G1
               F(9)=-20.3+X(12)-2.0*X(7)-2.0*X(1)+G4-2.0*G3-2.0*G1
               F(10)=-3.89+X(13)-X(7)-X(2)+G1-G3-G2
               F(11)=-10**(-3.11)+10**X(2)+10**X(3)+10**X(6)+10**X(13)
               F(12)=-10**(-3.06)+10**X(4)+10**X(5)+10**X(6)+10**X(17)
               1+10**X(18)
               F(13)=-10**(-6.65)
              1+10**X(7)+10**X(8)+10**X(9)+10**X(10)
              1+10**X(11)
              1+2*10**X(12)+10**X(13)
               F(14)=6.34+XPH+X(15)-X(14)+G1
               F(15)=10.34+XPH+X(16)-X(15)+G1-G2
               F(16)=-10**(-4.97)+10**X(14)+10**X(15)+10**X(16)
              1+10**X(17)+10**X(18)
               F(17)=-3.15+X(17)-X(4)-X(16)-G2-G2
               F(18)=-1.0+X(18)-X(4)-X(15)+G1-G2-G1
C         MANGANESE SPECIATION (REDUCED)
               F(19)=-3.4+X(20)-X(19)-X(1)+G1-G2-G1
               F(20)=-7.7+X(21)-X(19)-4*X(1)+G2-G2-4*G1
               F(21)=-2.26+X(22)-X(19)-X(2)-G2-G2
               F(22)=-1.8+X(23)-X(19)-X(3)+G1-G2-G1
               F(23)=-10**-4.14+10**X(19)+10**X(20)+10**X(21)+2*10**X(22)
              1+2.0*10**X(23)
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C       IRON SPECIATION (REDUCED)
             F(24)=-4.5+X(25)-X(24)-X(1)+G1-G2-G1
             F(25)=-7.4+X(26)-X(24)-2*X(1)-G2-2*G1
             F(26)=-10.0+X(27)-X(24)-3*X(1)+G1-G2-3*G1
             F(27)=-9.6+X(28)-X(24)-4*X(1)+G2-G2-4*G1
             F(28)=-10**-5.8+10**X(24)+10**X(25)+10**X(26)+10**X(27)
           1+10**X(28)
C       COPPER SPECIATION (2+)
             F(29)=-6.3+X(30)-X(29)-X(1)+G1-G2-G1
             F(30)=-13.6+X(31)-X(29)-2*X(1)-G2-2*G1
             F(31)=-13.7+X(32)-X(29)-3*X(1)+G1-G2-3*G1
             F(32)=-16.4+X(33)-X(29)-4*X(1)+G2-G2-4*G1
             F(33)=-2.36+X(34)-X(29)-X(2)-G2-G2
             F(34)=-6.57+X(35)-X(29)-X(16)-G2-G2
             F(35)=-10**-9.5+10**X(29)+10**X(30)+10**X(31)+10**X(32)
           1+10**X(33)+10**X(35)
C       POTASSIUM SPECIATION
             F(36)=0.5+X(37)-X(36)-X(1)-G1-G1
             F(37)=-0.85+X(38)-X(36)-X(2)+G1-G1-G2
             F(38)=-10**(-3.81)+10**X(36)+10**X(37)+10**X(38)
C       MAGNESIUM SPECIATION
             F(39)=-2.58+X(40)-X(39)-X(1)+G1-G2-G1
             F(40)=-2.23+X(41)-X(39)-X(2)-G2-G2
             F(41)=-2.83+X(42)-X(39)-X(16)-G2-G2
             F(42)=-0.95+X(43)-X(39)-X(15)+G1-G2-G1
             F(43)=-(-10**(-6.2))+10**X(39)+10**X(40)+10**X(41)
           1+10**X(42)+10**X(43)
C       ZINC SPECIATION
             F(44)=-5.0+X(45)-X(44)-X(1)+G1-G2-G1
             F(45)=-10.2+X(46)-X(44)-2*X(1)-G2-2*G1
             F(46)=-13.9+X(47)-X(44)-3*X(1)+G1-G2-3*G1
             F(47)=-15.6+X(48)-X(44)-4*X(1)+G2-G2-4*G1
             F(48)=-2.38+X(49)-X(44)-X(2)-G2-G2
             F(49)=-1.73+X(50)-X(44)-2*X(2)+G2-G2-2*G2
             F(50)=-1.7+X(51)-X(44)-3*X(2)+G4-G2-3*G2
             F(51)=-1.7+X(52)-X(44)-4*X(2)+G5-G2-4*G2
             F(52)=-1.5+X(53)-X(44)-X(15)+G1-G2-G1
             F(53)=-10**(-5.8)+10**X(44)+10**X(45)+10**X(46)+10**X(47)
           1+10**X(48)+10**X(49)+10**X(50)+10**X(51)
           1+10**X(52)+10**X(53)
C       CHROMIUM SPECIATION (3+)
             F(54)=-10.07+X(55)-X(54)-X(1)+G2-G3-G1
             F(55)=-17.3+X(56)-X(54)-2*X(1)+G1-G3-2*G1
             F(56)=-32.63+X(57)-X(54)-3*X(1)-G3-3*G1
             F(57)=-2.6+X(58)-X(54)-X(2)+G1-G3-G2
             F(58)=-4.65+X(58)-XPH-X(59)+G1
             F(59)=-10**(-5.02)+10**X(54)+10**X(55)+10**X(56)+10**X(57)
           1+10**X(58)+10**X(59)
C       LEAD SPECIATION
             F(60)=-6.3+X(61)-X(60)-X(1)+G1-G2-G1
             F(61)=-10.9+X(62)-X(60)-2*X(1)-G2-2*G1
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      F(62)=-13.9+X(63)-X(60)-3*X(1)+G1-G2-3*G1
      F(63)=-7.6+X(64)-2*X(60)-X(1)+G3-2*G2-G1
      F(64)=-32.1+X(65)-3*X(60)-4*X(1)+G2-3*G2-4*G1
      F(65)=-35.1+X(66)-4*X(60)-4*X(1)+G4-4*G2-4*G1
      F(66)=-68.4+X(67)-6*X(60)-8*X(1)+G6-6*G2-8*G1
      F(67)=-9.5+X(68)-X(60)-2*X(16)+G2-G2-2*G2
      F(68)=-2.75+X(69)-X(60)-X(2)-G2-G2
      F(69)=-2.38+X(70)-X(60)-2*X(2)+G2-G2-2*G1
      F(70)=-10**(-4.53)+10**X(60)+10**X(61)+10**X(62)
     1+10**X(63)+2*10**X(64)+3*10**X(65)+4*10**X(66)
     1+6*10**X(67)+10**X(68)+10**X(69)+2*10**X(70)
C    SILICIC ACID
      F(71)=-9.46+X(71)-X(72)-XPH-G1
      F(72)=-12.56+X(72)-X(73)-XPH+G1-G2
      F(73)=12.57+X(74)+XPH-4*X(71)+G2
      F(74)=-10**(-3.3)+10**X(71)+10**X(72)+10**X(73)
     1+10**X(74)
      RETURN
      END
```