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The Effect of Pozzolans in the Stabilization of Sulfide Tailings

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To my parents, with love and appreciation

Abstract

In recent years the disposal and the treatment of mine waste has been increasingly causing concern to the mining industry. Also due to mining operations such as extraction, processing and waste disposal practices which cause environmental degradation, the industry has been forced to comply with new governmental regulation and public pressure. One of the biggest challenges today is acid mine drainage (AMD), which is associated in particular with sulfide bearing tailings. As a consequence of AMD, heavy metals and sulfates are released into the environment.

This project has studied the effect of lime-based treatments in the stabilization of two sulfide tailings, one waste predominately containing pyrite minerals and the second containing pyrrhotite minerals. Different proportions of pozzolans (fly ash and slag) were also added to the lime-tailings mixtures. The physical properties of the mixtures have been evaluated, using several tests such as strength (unconfined compressive strength), permeability and durability. The mineralogical changes in the treated wastes were also examined. The stabilization process and the treatment validity would not be complete without a chemical analysis of the treated waste; therefore a quantitative analysis was performed, including leaching and extraction tests for some elements (Zn, Mg, Ca, and Fe), and also sulfate measurement. The samples were tested after 1 and 28 days of curing time.

The overall results revealed significant improvements in the physical and the chemical properties of the treated wastes. It is noticeable from the results that the strength largely depends on the binder percentage, water content and size distribution of the treated waste. Also the results indicate treatment effectiveness in relation to permeability. The element analysis showed that iron (Fe) reached undetectable values, while for Mg and Zn, there was a reduction in their concentration of about 0.1 ppm and the Ca concentration increased after 28 days of curing time. Sulfate measurements showed that the reduction in the sulfate concentration reached about 80% with the addition of only about 2%-5% binder. The results also showed that in many instances the high percentages of the binder added to the waste are neither critical nor necessary for the improvement and the stabilization of the waste.

Sommaire

Au cours de ces dernières années, la disposition et le traitement de déchets des mines sont de plus en plus à l'origine des soucis dans l'industrie minière. Aussi, à cause des opérations minières telles que l'extraction, le traitement et les pratiques d'élimination des déchets qui causent la dégradation écologique, l'industrie a été forcée à respecter des nouveaux règlements gouvernementaux et la pression publique. Un des plus grands défis aujourd'hui est le drainage acide des mines (DAM), ce qui est spécifiquement associé avec les alliages résidus des sulfures. En conséquence des DAM, les métaux lourds et sulfates sont libérés dans l'environnement.

Ce projet a étudié l'effet des traitements à la base des chaux dans la stabilisation de deux résidus de sulfure, l'un qui contient majoritairement les minéraux pyrite et l'autre contenant les minéraux pyrrhotine. Les proportions différentes de pourzzolanes (cendres volantes et scories) étaient aussi ajoutées à la chaux-résidue des mélanges. Les propriétés physiques des mélanges ont été évaluées, utilisant plusieurs essais sur les caractéristiques, tels que force (force compressive libre) perméabilité et durabilité. Les changements minéralogiques dans les déchets traités étaient aussi examinés. Le procédé de stabilisation et la validité de traitement ne seraient pas complets sans une analyse chimique des déchets traités; donc une analyse quantitative était exécutée, incluant lixiviation et essais d'extraction pour certains éléments (Zn, Mg, Ca, et Fe), et aussi la mesure des sulfates. Les échantillons étaient essayés après 1 et 28 jours de temps de séchage.

Les résultats généraux révélaient des améliorations significatives dans les propriétés physiques et chimiques des déchets traités. À partir des résultats, il est à remarquer que la force dépend largement du pourcentage de liant, de l'eau contenue et de la distribution de taille des déchets traités. Aussi les résultats indiquent l'efficacité de traitement en ce qui concerne la perméabilité. L'analyse des éléments montrait que le fer (Fe) a atteint des valeurs indétectables, tandis que pour Mg et Zn, il y avait une réduction dans leur concentration de près de 0.1 ppm et la concentration de Ca a accrue après 28 jours de séchage.

La mesure de sulfate a montré que la réduction dans la concentration de sulfate avait atteint près de 80% avec l'addition de près 2%-5% de liant seulement. Les résultats ont montré aussi que dans beaucoup d'exemples les pourcentages élevés du liant ajoutés au déchets ne sont ni critiques ni nécessaires pour l'amélioration et la stabilisation des déchets.

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I would like to express my sincere gratitude to Dr. Ferri P. Hassani for his constant supervision and support throughout this project, and for giving me the chance to participate in several projects during my study. These projects benefited me greatly in gaining valuable knowledge. Thanks are also due to Mr. Mohsen Hossien for his input and guidance, especially in the experimental part of this work when his help was greatly appreciated.

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1.0 Acid Mine Drainage

1.1 Introduction

Progressively over the last few decades, people in the mining industry have realized that the cost of mine waste management makes up a significant portion of the cost of metal production. Today, there is an awareness of this at all levels, from underground to the boardroom, which is leading to improved mining methods so as to minimize waste and better planning of mine waste storage facilities. Acid mine drainage (AMD) control is a key component of these facilities, therefore important efforts have been made to develop new control schemes and to better understand and predict the occurrence of acidic drainage. Oxidation of sulfide minerals is the process which contributes most to acid drainage and to the mobilization of metals from mine waste to the environment (St-Arnaud, 1996). On the other hand considerable knowledge and practical experience has been accumulated, particularly over the past decade, with respect to strategies which effectively predict, control and inhibit acid mine drainage. These positive developments continue to be supplemented on an ongoing basis through the research and practical experience gained from assessments of potential for AMD, the decommissioning of historic mine wastes and the planning of new mines. (Orava, D.A., et al, 1996), It is already established that AMD is the largest environmental problem facing the mining industry today. Technologies to prevent acid drainage from occurring in waste rock piles and tailings sites, and on the walls of open pits and underground mines, need to be developed and demonstrated (Filion et al., 1990).

1.2 The Extend of the AMD Problem

Between 1984 and 1987, CANMET and the mining industry co-sponsored two projects to define the extent of acid generating mine waste at various metal mining sites. Operations in British Columbia, Saskatchewan, Manitoba, Ontario, Quebec, New Brunswick, Newfoundland, Yukon and the Northwest Territories were all identified as having operating and/or abandoned acid generating waste sites, with a total area of over 15,000 hectares (37,000 acres). These wastes were largely the accumulation of forty years of mining since World War II. As for the future over the next twenty years, it seems reasonable to assume that the mining of lower grade ores together with the likelihood of increasing annual mineral production could lead to the accumulation of an equal quantity of acidic tailings and waste rock.

The above surveys do not represent the entire Canadian inventory, since they do not include gold, coal, and uranium or abandoned mine sites for which responsibility has reverted to the crown. Ontario and Quebec, the two provinces with the longest history of mining, have recently completed surveys of their abandoned mine sites. In Ontario, 100 abandoned mine sites were identified of which 20 pose an acidic drainage problem. These 20 sites contain 55 million tons of reactive sulfide tailings over a surface area of 830 hectares (2,030 acres). In Quebec, about 107 abandoned mine sites exist, of which 21 have been classified as hazardous waste sites due to acid drainage. The total area of these twenty sites was estimated at 4,500 hectares (11,110 acres).

The cost of stabilizing reactive wastes is highly site specific, and thus will vary greatly from site to site. Under the most difficult conditions and with the application of existing but unproven technology, the cost of stabilizing some sites has been estimated to be as high as $410,000 per hectare. Applying an average cost of $125,000 per hectare to the existing and future accumulation of acid generating waste, the reclamation cost at non-ferrous metal mines sites is estimated at $3 billion over the next twenty years. Funds required to deal with abandoned sites where liability cannot be established and where the mineral rights have reverted to the crown are estimated to be about $1 billion (Filion M.P., et al.1990).

The same threat is facing the mining industry in the United States, where contaminated mine drainage is one of the most persistent mining-related problems. According to a recent inventory, over 7,000 miles of rivers and streams are adversely affected by coal mine drainage, mostly from mines that have been abandoned for many years. The impact would be even greater except for the fact that mines active since 1978 have been chemically treating their effluent water, at a total cost of over a million dollars a day. Much of the research in this area is therefore directed to the development of less expensive alternatives to chemical treatment, as well as control method appropriate for abandoned mines (Haynes et al., 1991).

1.3 Sources of AMD

Most Canadian base metal, precious metal and uranium mines contain sulfide minerals, either in the ore or in the surrounding waste rock. When these sulfide minerals, particularly *pyrite* and *pyrrhotite*, are exposed to oxygen and water, they begin to oxidize almost immediately. In the absence of calcareous materials, the initial chemical reactions produce acid and liberate heavy metals associated with the waste deposit. As the reactions proceed, temperature and acidity increase, resulting in an increased rate of reaction. Between pH levels of 2 and 4, bacteria and ferric iron catalyze the reactions, and rates can be 20 to 100 times faster than the original chemical reaction (Knapp, 1987). Rainfall and snowmelt flush the toxic solutions from the waste sites into the downstream environment. Other types of earth-moving operations can also generate acid drainage.

Acid drainage may contain very high concentrations of sulfate and ferrous iron, high concentrations of base metals such as lead, copper, nickel, zinc, or silver, and exhibit pH values below 7. If acidic drainage is left uncollected and untreated, the drainage could contaminate groundwater and local water courses, damaging the health of plants, wildlife and fish. (Filion, 1990), other several researchers indicated clearly that the main source for the AMD is the oxidation of the sulfide minerals (Table 1.1), (Good, 1977; Norton, 1992). Table 1.2 shows characteristic of selected AMD waters.

Table 1.1: Metal Sulfides

MINERAL	FORMULA
Pyrite	FeS_2
Pyrrhotite	$Fe_{11}S_{12}$
Chalcopyrite	$CuFeS_2$
Galena	PbS
Sphalerite	ZnS
Arsenopyrite	$FeS_2.FeAs$
Pentlandite	$(Fe.Ni)_9S_8$

Table 1.2: Characteristic of Selected Acid Drainage Waters (Nriagu, 1978)

	Source of Effluent			
	1	2	3	4
	Coal Mine Drainage (Pennsylvania)	**Zinc Mine drainage (Idaho)**	**Uranium tailings Pile (Elliot Lake) (Ontario)**	**Copper smelting (Acid plant Scrubber)**
Constituent	pH 2.7	pH 2.2	pH 2.0	pH 1.8
	(ppm)	(ppm)	(ppm)	(Mg/L)
Acidity as $CaCO_3$	752	-	14,600	-
Aluminum	55	347	588	-
Arsenic	-	-	-	8.2
Cadmium	-	22.5	0.05	0.09
Calcium	194	31.6	416	-
Copper	-	13.4	3.6	0.12
Total Iron	122	16,250	3,200	0.1
Ferrous Iron	96	-	1,750	-
Lead	-	0.8	0.67	0.91
Magnesium	83	1,500	106	-
Manganese	4	2,625	5.6	-
Nickel	-	-	3.2	<0.001
Silicon	41	-	-	-
Sodium	-	0.5	920	-
Uranium	-	-	7.2	-
Zinc	-	14,560	11.4	13.7
Cyanide	-	-	-	<0.005
Nitrate	-	77.5	-	-
Sulfate	1474	63,000	7,440	490

1.3.1 Sulfur and Its Reactions

Sulfur is not as plentiful as oxygen, the first member of group VI, yet it is nevertheless reasonably plentiful, forming about 0.052% by weight of the earth's crust. Many of the world's metals for example, copper, lead, zinc and silver are found principally as sulfides. Elementary sulfur is hardly ever extracted from sulfide ores while in the form of sulfur dioxide, resulting from the roasting of the ores, it is led off and converted to sulfuric acid.

1.3.1.1 Physical Properties of Sulfur

At room temperature, the stable form of sulfur is of a rhombic crystalline variety. The physical properties of sulfur are contained in Table 1.3

Table 1.3: Physical Properties of Sulfur (Hutchinson, 1965)

Atomic Number	**Atomic Weight**	**M. P. °C**	**B. P. °C**	**Density Gm/CC**	**Atomic Radius**	**Ionization Potential, Volts**
16	32.064	118.95	444.6	2.06	1.04	10.36

1.3.1.2 Equilibrium of Sulfur in the Environment

Among the wide variety of inorganic sulfur compounds there are only a few involved in biogenic reactions with the environment (Table 1.4). Although some of the important environmental processes involving sulfur cannot always be expected to attain chemical equilibrium, a model is often useful to determine limiting conditions.

There are three possible dominant species of sulfur, namely the sulfates ($HSO4-$ and $SO42-$), the sulfides ($H2S$, $HS-$, *and* $S2-$) and elemental sulfur. In natural environments the form of sulfur species is closely related to the iron. Stable oxidation states for aqueous sulfur species that are reported in water analyses are mostly forms of $S6+$ (sulfates) or of $S2-$ (sulfides). In hydrothermal or in very polluted waters in anoxic sediment or in flooded soils, intermediate oxidation states such as polysulfides, thiosulfate, thionates and sulfites may occur. These unstable sulfur compounds play an important role in the biological cycle (Zehnder et al., 1980).

Table 1.4: Most Important Inorganic Sulfur Species in the Environment (Zehnder et al. 1980)

Redox State of Sulfur	Name of Compounds
$S^{(+6)}$	Sulfur Trioxide Sulfate
$S^{(+4)}$	Sulfur Dioxide Sulfite
$S^{(+5)}$ to $S^{(+1.67)}$ (1)	Dithionite Polythionites
$S^{(+2)}$	Thiosulfate
S^{0}	Elemental Sulfur
$S^{(-0.33)}$ to $S^{(-1)}$ (1)	Disulfide Polysulfides
$S^{(-2)}$	Sulfide

1.4 Mechanisms of AMD

The mechanism of the acid generation is described by (Nriagu, 1978) as a qualitative mechanism for acid water formation when water and air come into contact with the iron disulfide:

$$\mathbf{2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4} \qquad (1)$$

- In equation 2, ferrous iron is oxidized to ferric iron:

$$\mathbf{4FeSO_4 + 2H_2So_4 + O_2 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O} \qquad (2)$$

- In equation 3, ferric iron is hydrolized to ferric hydroxide:

$$\mathbf{Fe_2(SO_4)_3 + 6H_2O \rightarrow 2Fe(OH)_2 + 3H_2SO_4} \qquad (3)$$

- In equation 4, ferric iron oxidized the pyrite.

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

In equation 1 the sulfur in the iron disulfide is oxidized to sulfate iron by oxygen, in equation 2 ferrous iron is oxidized to ferric iron, in equation 3 ferric iron is hydrolyzed to ferric hydroxide and in equation 4 ferric iron oxidizes the pyrite.

---

[1] In these species more than one oxidation state of sulfur exists, which results in an overall fractional and intermediate valence state.

A similar mechanism described by (Kwong, 1991) occurs in the sulfide tailings containing pyrrhotite where the pyrrhotite is the most susceptible to weathering (oxidation) compared to other sulfide minerals. Also (Kwong, 1991) illustrated oxidation reaction of the pyrrhotite mineral and the mechanism of acid production as the following

$$4FeS + 9\,O_2 + 10\,H_2O = 4Fe(OH)_3 + 4SO_4^{2-} + 8H^+ \qquad (1)$$

$$4FeS_2 + 15\,O_2 + 7\,H_2O = 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+ \qquad (2)$$

$$4FeS + O_2 + 4H^+ = 2FeS_2 + 2Fe^{2+} + 2H_2O \qquad (3)$$

$$2FeS_2 + O_2 + 4H^+ = 4S + 2Fe^{2+} + 2H_2O \qquad (4)$$

$$2S + 3\,O2 + 2\,H2O = 4H+ + 2SO42- \qquad (5)$$

$$4Fe2+ + O2 + 10\,H2O = 4Fe(OH)3 + 8H+ \qquad (6)$$

Equations 1 and 2 describe the complete oxidation of pyrrhotite and marcasite resulting in the precipitation of ferric hydroxide and the release of sulfate and acidity the ambient water. Equations 3 and 4 represent the stepwise oxidation of pyrrhotite to marcasite and in turn to elemental sulfur. Both reactions consume acid and release ferrous iron. Equations 5 and 6 depict the oxidation of the elemental sulfur and ferrous iron, respectively, and both involve the production of acid.

From the above reactions the mechanism of acid generation could be described as sulfides in tailings and waste rock oxidize rapidly in the presence of air and water (pyrite and pyrrhotite are especially reactive), and the acid produced by oxidation liberates heavy metals. These metals and toxic solutions could be washed by rain or snowmelt into the surrounding environment. Ones oxidation begins, the temperature and acidity in the waste pile increase, which in turn speed up the reaction, and when pH drops to between 2 and 4, bacteria and ferric iron create a catalyst for the reaction. Catalyzed reaction rates have been estimated to be 20 to 100 times faster than the original oxidation rate. (Scales, 1991).

1.5 Factors Affecting AMD Generation

There are several factors which can affect the rate and the mechanism of the oxidation of the sulfide tailings and therefore they will affect the process of acid generation (Knapp, 1987):

1) Temperature

The temperature has an influence in biological ferrous ion oxidation by thiobacillus ferrooxidans bacteria, and the optimum temperature is between 33 and 40°C (MacDonald & Clark, 1970).

2) pH

Thiobacillus ferrooxidans, the main bacterial pyrite oxidation, has an optimum growth rate in the acidic pH range 1.5 to 5.0.

3) Oxygen

From the pervious equations it can be noticed that the existence of oxygen is essential in the oxidation of sulfide bearing tailings and the acid production. Also, oxidation of sulfide minerals involves the consumption of oxygen with the production of various species of iron and sulfur that may differ as a result of environmental conditions. Most of the field and laboratory evidence suggests that the most common products of oxidation in tailings are ferrous iron (Fe^{2+}) and sulfate (SO_4^{2-}) (Nicholson et al., 1995).

4) Carbon Dioxide (Biological Effect)

As indicated in the research, if there has been a presence and increase of carbon dioxide in the waste or the system, there will be an increase in growth rate of the Thiobacillus ferrooxidans bacteria (Torma et al., 1972).

5) Nutrients ((Biological Effect)

Nutrient requirements (such as nitrogen and phosphorus) for Thiobacillus ferrooxidans are usually not limiting, as extremely small concentrations are quite sufficient for growth (Nordstrom, 1982).

6) Water Content

The moisture content can be an important variable in determining microbial activity in tailings, as most of the micro-organisms growth require water; however an excess of water in the waste may slow or stop the oxidation process (Scow, 1982).

7) Inhibitors

Several organic and inorganic compounds are known to inhibit Thiobacillus ferrooxidans activity. Included among the most inhibitory compounds are organic and amino acids (Matin, 1978).

8) Surface Area and Mass

It is well documented that the rate of pyrite oxidation is a function of the pyrite surface area (Hoffmann et.al., 1981).

1.6 Treatment Methods of AMD

1.6.1 Introduction

In Canada there are two groups who have taken on the challenge of improving technologies to be applied in the area of the prevention of AMD. These groups are the National Mine Environment Neutral Drainage Program (MEND) and the British Columbia Acid Mine Drainage (BC AMD) Task Force. MEND is a cooperative research organization sponsored, financed and administered by the Canadian mining industry, the Canadian government and the provinces of British Columbia, Manitoba, Ontario, Quebec and New Brunswick. The MEND organizational structure includes a Board of Directors, a Management Committee and six Technical Committees.

The overall objectives of MEND are:

1. To provide a comprehensive scientific, technical and economical basis for the mining industry and governmental agencies to predict, with confidence, the long-term management requirements for reactive tailings and waste rock.

2. To establish techniques that will enable the operation and abandonment of acid-generating tailings and waste rock disposal areas in a predictable, affordable, timely and environmentally acceptable manner.

In Canada, reclamation legislation was first enacted in 1969. The act covered major mines including coal mines and hard rock minerals mines. In 1973, the acts were amended to include coal exploration, mineral exploration, sand and gravel pits and quarries. The Mines Act remained relatively unchanged until 1990. This new act and its accompanying Code provide the framework for reclamation policy in the 1990's. The principle of the act is that all mining and exploration activity will be regulated in a manner that minimizes the environmental and economic risks to the Province. While technology is available to prevent acid mine drainage at most mine sites it is not yet completely available for abandon existing mines with acid mine drainage. These mine sites will require long-term programs to collect and treat acid mine drainage. The provinces will take all reasonable measures to ensure that the quality of drainage from previously abandoned (historic) mine sites with acid mine drainage is improved. Government is committed to continually revising the policy and regulatory framework for acid mine drainage. Modifications to this policy and additional requirements may be considered for individual mines based upon site-specific conditions (Errington, 1991).

The cost of preventing AMD will probably be prohibitive at existing mine sites. The collection and treatment of AMD is often needed, however and is the only practical option at many mine sites, particularly those where acid generation was not anticipated or adequately controlled. The objective of AMD treatment in general is to eliminate acidity, to precipitate heavy metals and to remove suspended solids or other undesirable substances.

Several systems are suitable for collecting both surface runoff and groundwater, but they will require long-term maintenance. Numerous mines are already successfully using chemical plants to treat AMD. Using the following methods:

1) Facilities neutralizing the acidity in the collected liquids with the addition of limestone, hydrate lime or quicklime. Raising the pH to 8-9 precipitates heavy metals, and aeration of the slurry precipitates ferric hydroxide.

2) wetland systems or bogs.
3) marshes and swamps.

1.6.2 Lime Treatment

At the present time, most mining companies rely on the lime treatment neutralization of their acidic waters and for the precipitation of soluble metals as hydroxides. The lime neutralization/precipitation process is the most practical and commonly used treatment method in the mining industry. In general, lime neutralization processes consist of air oxidation, neutralization/precipitation and flocculation followed by solid/liquid separation for dewatering. Due to their high reactivity, availability, and relatively low cost, slaked or unslaked lime are the most common neutralizing reagents used for treating AMD.

The principal chemical reaction in the lime neutralization process is as follows:

$$\mathbf{Ca\,(OH)_2 + Me^{2+} / Me^{3+} + H_2SO_4 \rightarrow Me\,(OH)_2 / Me\,(OH)_3 + H^+ + CaSO_4}$$

(where **Me** represents heavy metals in effluence.)

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 minerals (Dvorak et al., 1991; MacDonald et al., 1989). To improve this technology some modification was suggested by (Riveros, 1995) in order to reduce the lime consumption by 20% than by the extraction of metals (ion exchange) in different stages of the lime treatment process (Figure 1.1).

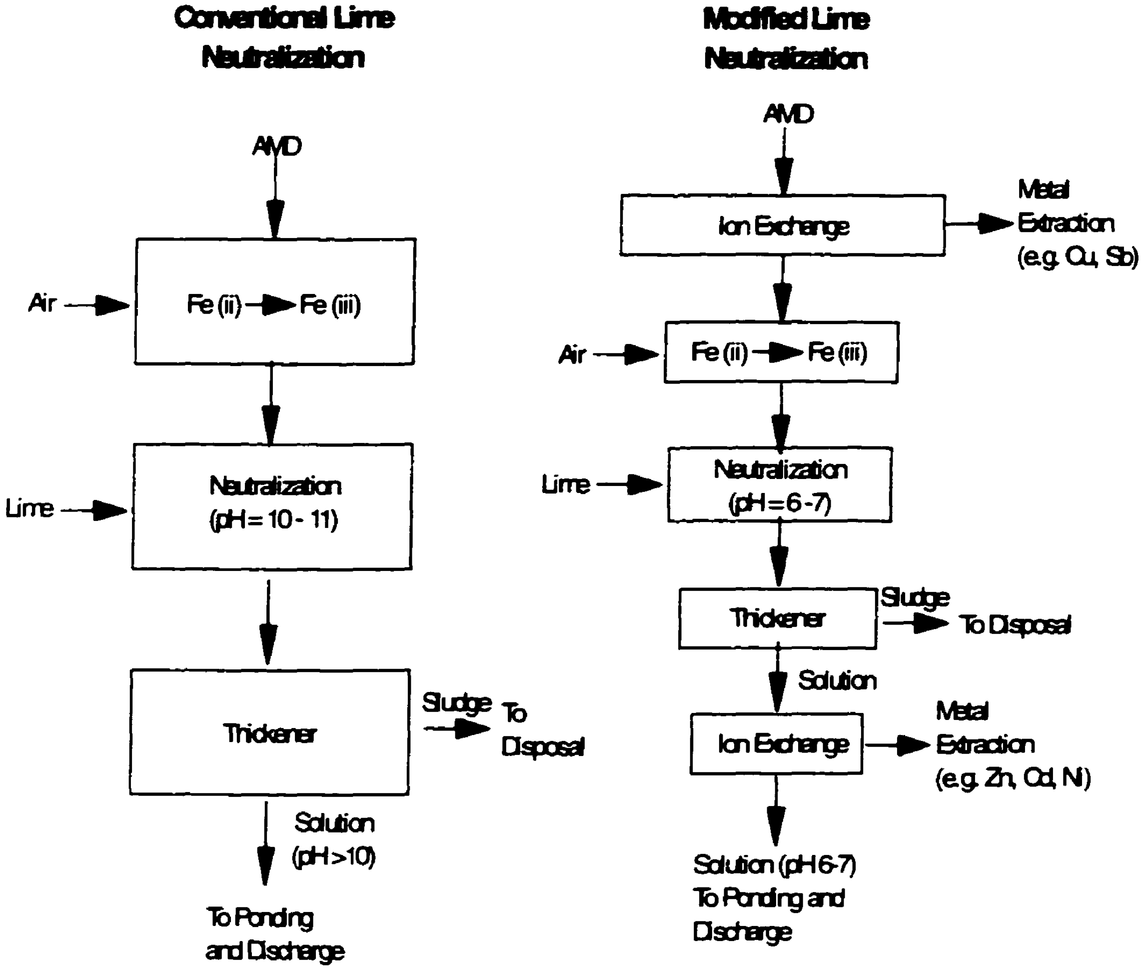

Figure 1-1: Conventional Lime Neutralization Process and Potential Ion Exchange Applications.

1.6.3 Other Chemical Technologies Available in Treatment of AMD

Beside the hydrated lime (calcium hydroxide) treatment, different chemicals are widely used to treat AMD including: limestone (calcium carbonate), soda ash briquettes (sodium carbonate), caustic soda (sodium hydroxide) and ammonia (anhydrous ammonia) is now being used in some locations. Each chemical has its advantages and disadvantages making them more appropriate for a specific condition.

The four primary considerations in selecting the appropriate chemical are the rate and degree of pH increase, its solubility in water (which influence mechanization), handling and cost. Four of the five chemicals can be discussed in relation to cation differences (calcium versus sodium) and anion differences (carbonate versus hydroxide) and each of the four can be compared to ammonia.

1) Calcium vs. Sodium

While calcium products are less expensive than those with sodium, the rate of pH increase achieved by addition of a calcium product is generally slower due to the lower overall solubility of calcium compounds. Limestone, hydrated lime, and soda ash are relatively easy to handle and require few safety precautions. Due to their relatively low solubility, effectiveness and efficiency of AMD treatment are greatly improved by mixing/aeration. Caustic soda, on the other hand, is highly soluble and toxic and must be handled with care.

2) Carbonate vs. Hydroxide

Carbonate materials are easily handled because the products are usually available as relatively large pieces, either in briquette or gravel size. While carbonate materials have been shown to raise pH to 12.0, their effectiveness in neutralizing acidity and precipitating metals is limited because they are prone to develop a surface film or a coat of iron hydroxide. If the water contains high amounts of acidity, carbonate materials will not raise the pH above 9.0.

Hydroxide materials are mostly in the form of powder, flakes or liquid and thus generally more difficult to handle than carbonates. On the other hand, hydroxide materials can easily raise the pH to 12.0 or higher, so over-application of a hydroxide material can produce a very undesirable aquatic situation.

3) Limestone (calcium carbonate)

Limestone has been in use for decades to raise pH and precipitate metals in AMD. It has the cheapest material cost and is the safest and easiest to handle of all chemicals. Unfortunately, its application shows limited success since it has low solubility and the limestone becomes coated very quickly if metals are dissolved in the water. For example, if the iron concentration is above 5 mg/l, the limestone will be rendered ineffective in a short time because the limestone particles become armored. Limestone is not used for AMD with acidity values above 50 mg/l.

4) Caustic Soda (sodium hydroxide)

Caustic soda is a commonly used chemical which is often applied in more remote locations (e.g., if electricity is unavailable), or in low flow and high acidity situations. Caustic raises the pH of the water very quickly, is extremely soluble and is used where manganese is a problem. The system can be gravity fed by tripping the liquid into the AMD. Caustic should be applied at the surface of the pond water because the chemical moves downward into the water. The major drawbacks of the use of liquid caustic for AMD treatment are its high cost and dangers in handling. During winter months, the liquid caustic can freeze.

5) Soda Ash (sodium carbonate)

Soda ash is generally only used in small flow cases with low amounts of acidity. Selection of soda ash for treating AMD is usually based on convenience rather that cost effectiveness. The dispensing system for briquettes can be as simple as employing a box or barrel with water inlets and outflows. As the water contacts the briquettes, a small amount of soda ash dissolves. Gravity keeps the briquettes feeding into the inlet for constant water treatment. If iron is higher than 10 or 20 mg/L, a mixing system will improve efficiency and treatment. Briquettes are easily handled but are expensive. Many different formulations of briquettes are available, so it is important to carefully select the briquettes that are "pure" soda ash or of high quality. The size of the briquette is a clue to its quality; i.e., the smaller the size, the higher the quality. Large briquettes often contain binders, which are mainly pressed hydrated lime.

6) Ammonia (anhydrous ammonia)

Anhydrous ammonia is being used in some areas to neutralize acidity and to precipitate metals in AMD. Ammonia is usually injected into ponds or into inlet water as a vapor and, due to its high solubility, reacts very rapidly and can raise the pH to 9.0 or higher. Ammonia consumes acid (H+) and also generates hydroxyl ions (OH-) which can react with metals and form a precipitate. It should be injected near the bottom of the pond or water inlet because ammonia is lighter than water and rises to the surface. Ammonia is effective for manganese removal, which occurs around a pH of 9.5. The most promising aspect of using ammonia for AMD treatment is its cost when compared with caustic soda. A cost reduction figure of 50 to 70% is usually realized when ammonia is substituted for caustic. The major disadvantages of using ammonia are the hazards associated with handling the chemical and the uncertainty concerning potential biological reactions (Fletcher et al., 1991).

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 preventing AMD appears to be preventing oxygen from coming into contact with sulfides bearing waste materials. Technologies that have shown some promising results so far include water covers, organic covers, wetlands, impermeable soil covers and cementitious covers over the waste containment area. The method of water cover, which involves flooding the area which contains the sulfide waste materials, seems to be the most effective solution available today (Hossein & Hassani, 1993).

1.7 Prevention and Control

Based on the understanding of complex reactions which lead to the AMD generation in the sulfide bearing tailings, measures to inhabit and prevent AMD focus on: (1) preventing sulfide oxidation or (2) slowing down the oxidation process so that the resultant very low rate of acid production is of no significance. As (David et al., 1996), illustrated, the current state of knowledge allows us to:

- determine the acid generating (or consuming) potential of mine waste. This can be done starting at exploration stage;
- model the sulfide mineral oxidation process under different physical, geochemical, and biological environments. This can be done to assess the performance of envisaged mine waste disposal strategies in advance of the development of a mine; and

- inhibit acid generation in tailings, waste rock and other sulfide containing rocks that have the potential to produce acid.

The above authors (David et al., 1996) emphasized the importance of taking measures throughout the mine life cycle (exploration, feasibility, mine production and mine closure) to assess the potential for AMD and to inhabit and control AMD where the potential exists. These measures are consistent with the goal and objectives of environmental protection policies.

A) *Exploration phase*

The key objective, from an AMD inhibition perspective, during this phase is to obtain an early indication of the potential for AMD. Regardless of the extent of the exploration program, investigations could be taken to identify potential acid producing geological formations. As a matter of course during initial exploration, the geology of mineralized zones and surrounding rock formations are mapped and interpreted. Information relevant to AMD potential is also gathered at this time, especially information regarding sulfide mineralogy, carbonates and local AMD occurrence. The type of data that could be gathered as part of a field-mapping program is shown in (Table1.5):

Table 1.5: Summary of Supplemental Field Data for Use in Assessing AMD Potential

Item	Aspects/Characteristics considered
Geological Formation	■ Likelihood of exposing formation
Sulfide Minerals	■ Minerals present ■ Per cent sulfide content ■ Grain size and distribution of sulfides on joints, other discontinuities and within rock mass
Durability	■ Durability, likelihood of slaking
Other	■ Local AMD occurrences

B) *The Mine Production Phase*

This phase involves the development of the mine facilities and the production and processing of ore. Emerging technologies may develop to the point where they may warrant consideration in improving the AMD abatement programs. AMD may be produced but controlled during this phase. When reactive wastes are deposited (e.g. in a waste rock stockpile or tailings area) a portion of the waste material may be subject to sulfide oxidation. Several approaches are being used to counteract this process. Reactive waste rock may be mixed with excess alkaline (buffering) material. Another option could be to collect and treat the AMD until final measures to inhibit AMD can be put into place (e.g. until the waste can be capped). One common approach is, however, to place the reactive materials under permanent water cover at the earliest opportunity and to prevent the oxidation process from occurring to any significant extent.

Planned closure works (i.e. the capping of wastes and revegetation of areas) may be carried out progressively over the operating life of the mine. This approach reduces capital expenditure requirements in the Closure Phase. Other proactive form of Best Management Practices include:

- the monitoring of reactive waste disposal areas;
- where warranted, the continued sampling of mine wastes to confirm acid producing (consuming) potential; and
- ongoing reviews of mine closure plans and waste management requirements.
- site-specific research may also be completed during this phase to provide additional data respecting the performance of AMD inhibition strategies (Orava & Swider, 1996).

C) The Mine Closure Phase

During this phase, the mine site is decommissioned, facilities at the site are removed, works to close out the waste management areas are completed, and the site returned to a state suitable for an envisaged land use. The time required to complete this work vary widely from site to site.

Monitoring programs may continue for a short time to verify the performance of the completed remediation works. In some instances, minimal monitoring and maintenance will be required over the long term (e.g. to maintain structures required as part of the AMD abatement strategy). The funding of the future maintenance requirements being assured through the setting aside of funds (Orava & Swider, 1996).

2.0 The Properties and Use of Pozzolans

2.1 Introduction

Two principal types of inorganic binders are cement and pozzolanic (lime, kiln, dust and fly ash). A pozzolan is a material containing silica or silica and alumina which has little or no cementation value itself but, under some conditions, can react with lime to produce cementitious material. Cement-based and pozzolanic processes or a combination of cement and pozzolans are the methods of choice in different industry today.

This is probably attributable to the low cost of the materials, their applicability to a wide variety of waste types and the ease of operation in the field. The most common inorganic binders are:

- Portland cement
- Lime/fly ash
- Kiln dust (lime and cement)
- Portland cement/fly ash
- Portland cement/lime
- Portland cement/sodium silicate

These binders are routinely used to solidify water-based waste-liquids, sludges, and filter cakes. The lime/fly ash process probably has been used most extensively in the United States, in terms of total volume of waste treated. The treatment of flue gas desulfurization (FGD) sludges from coal-fired power plants accounts for much of the lime/fly ash process application. Specifications are available for a wide variety of cement and pozzolanic materials. Advantages of cement-based processes include (McDaniel et al., 1990; and Conner, 1990):

- Availability of materials locally on a worldwide basis
- Low cost of materials and mixing equipment
- Use of naturally occurring minerals as raw materials for the matrix
- Ability to make a strong physical barrier under adverse conditions
- Flexibility of costume and design the properties for different applications
- Low variability in composition

- Well-known setting and hardening reactions and some existing data on the immobilization of metals

The disadvantages of cement-based processes include:

- Sensitivity of product quality to presence of impurities as high enough concentrations.
- Porosity of the treated waste.
- Waste volume typically increases due to binder addition, although not necessarily more than with other inorganic binders.
- Expertise needed for successful application, although process appears deceptively simple.

In general, a pozzolan is defined as a siliceous or aluminous/siliceous material which reacts in the presence of lime and water to produce stable, insoluble, cementitious materials similar in nature to the hydration products of Portland cements. The pozzolan normally needs to be in a fine-grained, reactive form to yield satisfactory reaction kinetics. Pozzolans, include natural volcanic ash, puminite, opaline shales and cherts, calcined diatomaceous earth, burnt clay and fly ash. Ferrous blast furnace slags and steel slags also exhibit pronounced pozzolanic properties and are widely used in the preparation of special Portland cements.

Pozzolanic activity greater than a specified minimum can be expected if the material used meets the specification for fly ash normally produced from burning either anthracite or bituminous coal (Type F) or lignite or sub-bituminous coal (Type C). Some Type C fly ashes have enough lime to be not only pozzolanic but also self-cementing (Table 2.1) (Smith, 1993). Lime/fly ash treatment is relatively inexpensive and with careful selection of materials, can reliably convert waste to a solid material. In general, lime/fly ash-solidified wastes are not considered as durable as Portland cement-treated wastes.

Common problems with lime/pozzolan reactions involve interference with the cementitious reaction that prevents bonding of materials. The bonds in pozzolan reactions depend on the formation of calcium silicate and aluminate hydrates. Therefore, the interferences are largely the same as for cement-based processes (Means et al., 1995).

Pozzolans may consist of small amounts of crystalline material but tend to be amorphous in nature; upon hydration they form cementitious compounds similar to those of Portland cement. Portland cement is considered to be cementitious since it contains large quantities of silica and lime – the primary building blocks of binders. Most pozzolans are deficient in lime and require its addition to become chemically active. Figure 2.1 is a ternary diagram representation of the three most typically abundant compounds, silica (SiO2), lime (CaO), and aluminate (Al2O3), which make up a binder system and shows the relative placement of major binder groups with respect to each other (Hassani & Archibald, 1998).

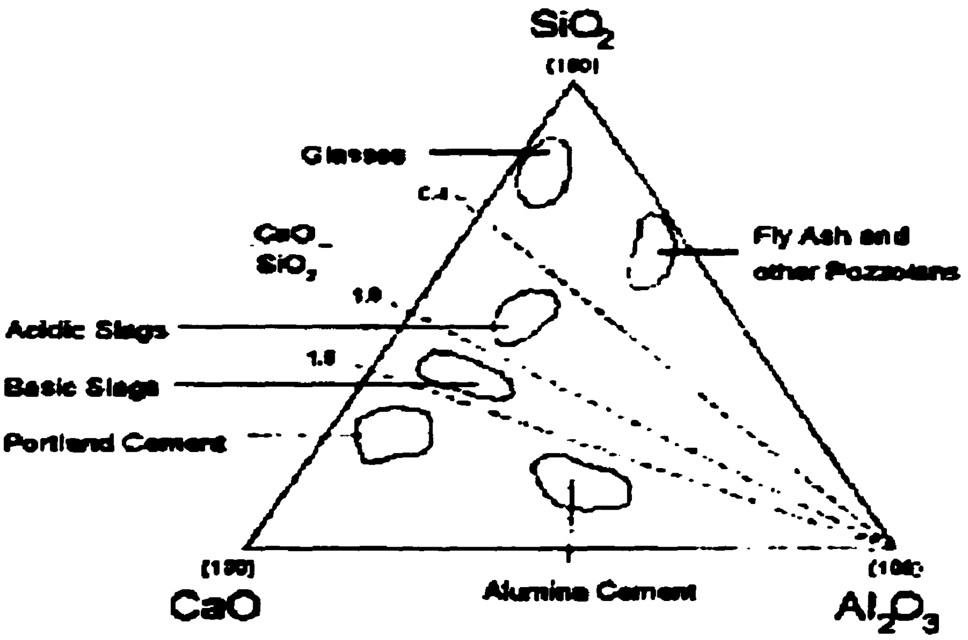

Figure 2.1: Ternary Diagram of Binders. (Douglas & Malhotra, 1987)

Table 2.1: Characterization of Fly ashes (Smith, 1993)

Chemical Analysis	**Class F (Fly Ash)**	**Class C (Fly Ash)**
Silicon Dioxide,SiO2	51.86	30.97
Aluminum Oxide,Al2O3	24.16	17.08
Titanium Dioxide, TiO2	1.16	1.0
Iron Oxide,Fe2O3	13.85	5.27
Calcium Oxide, CaO	3.04	30.07
Magnesium Oxide, MgO	1.53	7.14
Potassium Oxide, K2O	3.13	0.18
Sodium Oxide, Na2O	0.62	2.68
Sulfur trioxide,SO3	0.06	3.37
Phosphorus pentoxide P2O5	0.24	1.06
Strontium Oxide, SrO	0.12	0.52
Barium Oxide, BaO	0.15	0.62
Manganese Dioxide, MnO2	0.06	0.05
Physical Analysis		
Density	2.28	2.77
Retained on #325 Sieve	14.5	15.4

2.2 Portland Cement

The addition of water transforms the cement to hard mass, the reason being that chemical reactions create a system of interlocking crystals that weave the material together. It is not the cement itself but the mixture of cement and water that form the binding agent in concrete. The cement compounds may react with water in many different ways and for convenience, this reaction usually known as "hydration".

In cement chemistry it is commonly accepted to use a simplified notation where the oxides of calcium, silicon, aluminum and iron are represented respectively by C, S, A and F. Tricalciumsilicate would normally be written as $3CaO.SiO_2$, but, in this system it is simply C_3S. Water (H_2O) is written as H. Portland cement is basically a mixture of calcium silicates and consists predominantly of tricalciumsilicates and dicalciumsilicates, which are written in abbreviation as C_3S and C_2S respectively. Tricalcium aluminate (C_3A) and alumino ferrites (C_4AF) are also present.

Typical weight proportions for a normal Portland cement are as follows:

C_3S............60%

C_2S............15%

C_3A............ 8%

C_4AF...........10%

The ASTM types of Portland cement are defined as follows:

Table 2.2: Portland Cement Types

Type	Description
I	For use when the special properties specified for any other type are not required
II	For general use, more especially when moderate sulfate resistance or moderate heat of hydration is desired
III	For use when high early strength is desired
IV	For use when a low heat of hydration is desired
V	For use when high sulfate resistance is desired

2.2.1 Silicate Hydration

The setting of Portland cement is predominantly related to the hydration of the silicate components:

Calcium Silicates + Water = Calcium-silicate-hydrate (Gel) +Ca $(OH)_2$

The most spectacular change is the transformation of low surface area anhydrous compounds to the gel-like hydrates. The surface area, which is the area open to chemical reaction, has increased a thousand fold after completion of hydration. The reaction rates of C_3S and C_2S differ appreciably but the final hydration products are chemically identical: a gel-like, micro crystalline calcium silicate hydrate of rather indefinite composition. Of the two silicates, C_3S is primarily responsible for the hardening reaction in the early stages of hydration, within the first few days and weeks. C_2S, the more slowly reacting compound, is thought to be responsible for the longer term and continuing development of strength which can extend for months or even years.

2.2.2 Aluminate Hydration

The hydration of aluminates is greatly influenced by the presence of gypsum. In the absence of gypsum ($CaSO_4.2H_2O$), the reaction of C_3A with water is very violent and leads to immediate stiffening of the paste, known as flash set. (Not to be confused with a false set, which is due to dehydration of gypsum.). In the presence of gypsum, the gypsum and C_3A react first to form a calcium trisulphate aluminate hydrate called ettringite:

$$\mathbf{C_3A + 3(CaSO_4.2H_2O) + 32H == C_3A.3(CaSO_4.2H_2O).H_{32}}$$

This reaction continues until all available gypsum is consumed. When no more gypsum is available, ettringite reacts with more C_3A and water to form monosulphate hydrate:

$$\mathbf{C_3A.3(CaSO_4.2H_2O).H_{32} + 2C_3A + 4H == C_3A.(CaSO_4.2H_2O).H_{12}}$$

The C_4AF reacts with gypsum in a similar fashion but is much slower. The hydration of the aluminates is of great practical importance because they affect the setting properties of cement.

2.2.3 Hydration Mechanism and Kinetics

Various theories have been put forward to explain setting and hardening of cement. The first and oldest is the Le Chatelier principle which says that all cement compounds first go into solution after which recrystallisation takes place into an interlocking maze. The Colloidal theory, first proposed by W. Michaelis, considers that cohesion results from formation of a colloidal gelatinous mass, which occurs without cement compounds actually dissolving, by a direct solid state reaction. In all probability, both mechanisms actually occur. However, the solid state reaction is believed to be more dominant, since it accounts best for strength, swelling, shrinkage, creep and autogenous healing of cracks.

In a cement paste, under normal conditions, the hydration process does not usually go to completion. Even after several years a typical microstructure will show residual grains of unhydrated cement embedded in a matrix mainly composed of CSH gel. The reason is that during hydration the reaction products form coatings around the cement grains and these coatings progressively inhibit the access of water to the anhydrous material.

The presence of unhydrated clinker material can have some interesting effects. For example, if the cement is ground up and mixed again with water it will set a second time and develop a degree of strength, that, although inferior to the strength achieved in the first setting, can nonetheless be substantial. It is even possible that if microcracks develop in a concrete structure, they can heal themselves by renewed hydration (autogeneous healing). The process of hydration can be accelerated or retarded by various measures:

A) Addition of Chemical Accelerators or Retarders

The accelerating effect of calcium chloride ($CaCl_2$) results from an increase in the calcium ion (Ca^{2+}) concentration and increasing the solubility of the aluminate ions. Retardation is effected by precipitation of the Ca^{2+} ions into insoluble or sparingly soluble compounds (phosphates, saccharides, etc). Generally, the higher the Ca^{2+} concentration in the aqueous phase, the higher the rate of hydration of C_3S, and the higher the rate of hardening.

B) Temperature

This is very important in practical applications. The rate of hydration roughly doubles for each 10°C increase in temperature.

C) Changing the Fineness of Cement

The higher the fineness, the more reactive (surface) area exposed and the higher the rate of hydration.

D) Changing the Composition of Cement

A distinction is made between active and non-active clinker. Increasing the rate of hydration and thus the early strength development is usually done at the expense of ultimate strength. One reason for this phenomenon is that the microstructure of a cement subjected to accelerated hydration is usually coarser and less favorable for strength development. Another reason is that at high rates of hydration large quantities of hydration products are formed around unhydrated particles which impede the late hydration. On the other hand, retardation (slower hydration) allows the formation of a microcrystalline or rather gel-like structure of large surface area with resulting higher strength.

2.2.4 Heat of Hydration

During the hydration process, heat is liberated; that is, the reaction is exothermic. Under typical conditions, the temperature of a paste may rise by tens of degrees (Table 2.3). This phenomenon can present quite a problem in laying concrete structures of large section. Under normal conditions, around 30% of the total heat available is generated within the first day after mixing and around 50% within the first 3 days. Since the thermal conductivity of concrete is low, it acts as an insulator thus containing the heat within itself. Temperature increases of up to 50°C may result, which through thermal expansion and contraction may cause cracking. Appropriate safeguards must be taken. The heat evolved is directly related to the degree of hydration of the various components of cement.

Table 2.3: Heat of hydration of Cement Components

Cement	**Heat of Hydration (J/g at 21C)**	
Component	***3 days***	***28 days***
C_3S	245	380
C_2S	50	105
C_3A	890	1380
C_4AF	290	495

The heat of hydration can therefore be varied to some extent by adjusting fineness and composition of cement. Decreasing C_3A and C_3S contents, as is done in Type LH (low heat) cement, will lower the heat evolution during hydration.

2.2.5 Physical Structure of Hydrated Cement

Because of the fine scale of the hydrates involved, the microstructure has been most usefully studied by electron microscope. Electron micrographs have shown that within two hours after the addition of water, the originally angular and crystalline grains of cement become coated with a gelatinous envelope of hydrate material. The grains are bridged at their points of contact by these coatings. The network of relatively weak bonds thus formed accounts for the loss of plasticity of the paste at this time; that is, for the setting effect. The structure can be broken up easily but will quite quickly set again as the cement grains recoagulate. The irreversible development of strength during the hardening period, which begins after some three to five hours, is associated with a distinct change in the microstructure of the cement. The initial gel coatings develop fine surface protuberances. Over a period of time they grow into thin, densely packed fibrils radiating like porcupine quills from the individual grains of cement. This fibrillar development is the calcium-silicate-hydrate gel product of the reaction between the cement silicates and water. At the same time calcium hydroxide precipitates as a by-product and forms the large angular crystals that are so prominent in the microstructure. As hydration proceeds the gel fibrils gradually interpenetrate in the region between the adjacent cement grains. The interwoven mesh work thereby created eventually consolidates to form a rigid matrix that effectively binds the mass composed of residual grains of unreacted cement, the crystalline products of hydration and, in a concrete, the sand and aggregate material.

2.2.6 Volume of Hydrated Cement

During the process of hydration, the bulk volume of the solid material approximately doubles. Nevertheless the total volume of the cement paste actually decreases slightly. This is because water, when combined with the hydration products, takes up less space than the "free water." Approximately 18% of the volume is taken up by pores which are partially filled with water.

2.2.7 Calcium Hydroxide

As is evident from the hydration reaction equation (see above), the other major component of hydrated cement, apart from the CSH gel, is calcium hydroxide Ca $(OH)_2$, which is closely interwoven into the micro crystalline CSH structure. Calcium hydroxide does not contribute to the strength; it has however some interesting features. In concrete it may react with finely dispersed siliceous and aluminous materials to form insoluble compounds, which do contribute to strength formation. This reaction is commonly referred to as a pozzolanic reaction. Because of calcium hydroxide, the pH of cement paste is high, approximately 12.5, and this passivates and protects reinforcing steel in concrete against corrosion. This protective effect may be reduced by the reaction of calcium hydroxide with the carbon dioxide (CO_2) present in air. This reaction, known as carbonation, causes the formation of insoluble calcium carbonate, with the result that the pH is lowered and its protective effect lost. The rate of carbonation varies with cement content, water/cement ratio, permeability (compaction) of concrete and climatic conditions.

2.3 Fly Ash

Fly ash is the by-product from the burning of very finely ground coal in modern power stations. It is collected from the exhaust gases in electro-static precipitators. The resultant material is extremely fine, with about 90% passing through a 45-micron sieve. As stated earlier fly ash and pozzolan in general have little or no cementation value itself, unless mixed with cement or lime and water. In any case the ash treatments are used effectively in a wide range of stabilization application and concrete mixtures (Ferguson, 1993). Fly ash is the modern equivalent of the volcanic ashes (pozzolans) used in the very early hydraulic cements of Greece and Rome.

2.3.1 The Use of Fly Ash in Concrete

Research into the use of fly ash has been carried out for over fifty years, following the re-introduction of natural pozzolans into concrete many years before. Researchers and design engineers quickly learned that not only was fly ash a suitable cementing material in concrete once activated, but that it offered some characteristics to enhance the quality of concrete. As with the other ingredients of concrete, fly ash has to be of high quality. In brief, the requirements for a fly ash for use in high quality concrete are:

A) Chemical Requirements

1. A high proportion of reactive oxides of silica and alumina.
2. A low percentage of carbon (preferably less than 3%).
3. A low percentage of magnesium oxide.
4. A low percentage of alkalis, primarily oxides of sodium and potassium.
5. A low percentage of phosphorus.
6. A low percentage of sulfur.

B) Physical Requirements

1. Fineness greater than 75% passing a 45 micron sieve (AS 3582.1).
2. High percentage of spherical particle shape.
3. Acceptable color (although not always of importance).

The better the quality of the fly ash as defined above, the greater will be the effect on the performance of concrete. Fly ash imparts certain changes to the concrete mix, as a result of:

1. The physical benefits of the filling of the voids at the lower end of the aggregate grading scale
2. The lubricating effect of the spherical ash particles improves workability, thus reducing water demand, for a given slump
3. At early stages of hydration, bonds develop between the fly ash particles and both the cement and aggregate particles
4. As hydration proceeds, a pozzolanic reaction occurs between the calcium hydroxide liberated by the cement hydration and the silicon and aluminium compounds of the fly ash, producing further hydraulic compounds.

This last reaction is an important aspect of fly ash concrete, as it is responsible for:

1. Long term strength growth
2. Improvement in impermeability.

2.3.2 The Effect of Fly Ash on Portland Cement and Concrete Properties

Following are the effects:

A) Water Demand

Fine, spherical ash can reduce water demand by 10% or more.

B) Workability

Even at equal slump, fly ash mixes are usually more workable, due to the lubricating effect of the spherical particles and greater volumes of fines.

C) Setting Time

Setting time is usually slightly extended over straight cement concrete mixes.

D) Early Strength

For mixes producing equal strength at 28 days, fly ash mixes tend to have slightly lower strength at early ages than straight cement mixes. After 28 days, such fly ash mixes develop higher ultimate strength.

E) Shrinkage

Shrinkage is affected by water demand; thus fly ashes of good quality which reduce water also tend to reduce shrinkage.

F) Creep

Generally, fly ash has a beneficial effect on creep in concrete.

G) Heat of Hydration

Heat generation in concrete is primarily due to the hydration reaction of Portland cement. The replacement of Portland cement with fly ash reduces the amount of cement present and therefore the amount of heat generated. The pozzolanic reaction contributes much less heat than the equivalent cement hydration reaction.

H) Sulfate Attack and Chloride Resistance

Most fly ash concretes, at least those with low lime fly ash, show improved resistance to sulfate attack. The higher impermeability of fly ash concrete provides increased protection against the diffusion of chloride ions in concrete.

I) Alkali-Aggregate (Silicate) Reaction

The partial replacement of cement with fly ash tends to reduce the potential for alkali-silicate reaction. Research shows that an alkali reaction takes place with the fly ash rather than with the aggregate, and that this reaction is not as expansive. The combined result is that, provided the fly ash is suitable (i.e. low alkali content), the expansion can be very substantially reduced. However it should be recognized that in assessing the potential for alkali-silicate reaction, one needs to consider the mineralogy of the aggregate and the total amount of alkali available from all sources.

J) Tensile Strength

For a given compressive strength, the tensile strength of a fly ash mix will normally be enhanced, due to reduced water demand, improved mix design and greater bond development. This is particularly so at later ages (28 days and beyond).

K) Modulus of Elasticity

At early ages, the modulus of elasticity tends to be slightly reduced, while at later ages the figure is marginally higher.

L) Curing Requirements

At early ages, all concrete needs to be protected from the environment to ensure adequate moisture is retained to achieve proper curing. Curing has a considerable influence on the long-term durability of concrete, with more stringent curing being required at higher water/cement ratios. Poor curing is detrimental to any concrete, irrespective of the type of cementitious binder. However with fly ash concrete, a greater benefit is obtained from extended curing.

2.3.3 The Effect of Fly Ash on the Sulfate Attack

Normal Portland cement concretes are known to expand and, at times, crack on long exposure to sulfate waters containing more than 1,000 ppm sulfate. This phenomenon, called "sulfate attack", and generally attributed to ettringite formation. Although other researchers pointed that the formation gypsum could be the reason behind the sulfate attack (Mehta, 1983).

Sulfate attack is a two-phased process:

1. Sulfates combine with soluble calcium hydroxide, generated from the hydration of Portland cement, to form calcium Sulfate or gypsum. The volume of the resulting gypsum is greater than the sum of its components, causing internal pressures which fracture the concrete.
2. Aluminate compounds from Portland cement are attacked by sulfates, forming a compound called ettringite. Ettringite formation ruptures the concrete in the same way gypsum formation does.

Fly ash has been found to be most effective in reducing this deterioration in two important ways:

1. The pozzolanic activity of the fly ash binds it to free lime (calcium hydroxide) released in the hydration of Portland cement. The fly ash and calcium hydroxide combine in cementitious compounds trapping the calcium hydroxide so that it is no longer available for reaction with Sulfates. This prevents the formation of gypsum.
2. The cementitious compounds formed when fly ash and calcium hydroxide bond block bleed channels and capillary pores in the concrete making it impervious to aggressive dissolved Sulfates. Since the sulfates cannot combine with cement aluminates, ettringite cannot occur.

Studies by the Bureau of Reclamation show that properly proportioned concrete utilizing up to 35% fly ash will withstand sulfate attack far better than conventional Portland cement. The Bureau compared plain mixes and fly ash mixes using regular Type I cement, moderate sulfate resisting Type II cement and sulfate resisting Type V cement. Exposure conditions ranged from the normal test of continuous soaking in sodium sulfate to the severe test of alternating wet and dry exposure to sodium sulfate. In all instances, fly ash concrete dramatically outperformed conventional Portland cement concrete. These tests clearly demonstrated that Type II cement with fly ash outperformed Type V cement alone and that Type V cement with fly ash was the most resistant to sulfate attack.

Further work has correlated the chemistry of a given fly ash with its ability to resist Sulfate attack through a mathematical equation called the R factor. The formula for determining R factor is as follows:

$$\mathbf{R = (CaO - 5)/(Fe_2O_3)\ (\%)}$$

By this formula, as CaO (calcium oxide) increases and/or Fe_2O_3 (iron oxide) decreases, sulfate resistance decreases due to fly ash chemistry. Limits have been established by the Bureau of Reclamation, requiring progressively lower R values as sulfate attack severity increases. These values are outlined in Table 2.4.

Table 2.4: (R) Values Vs. Sulfate Resistance

R Limits[1]	**Sulfate Resistance**[2]
< 0.75	Greatly improved
0.75 - 1.5	Moderately improved
1.5 - 3.0	No significant change[3]
> 3.0	Reduced

Although the R factor is an important criteria for selecting a fly ash for use in sulfate resistance, another fly ash property may enable a higher than desirable R factor to

---

[1] For very severe cyclic conditions of wetting and drying or for MgSO4 reduce the R value by 0.50.

[2] Slightly improved to slightly reduced.

[3] Compared to a Type II cement control at 0.45 W/C.

be used successfully. A high quality fly ash acts as a strong water reducer and aids in reducing the water/cementitious ratio. Lowering the water/cementitious ratio significantly can lead to a more sulfate resisting concrete. To ensure the most durable concrete possible, fly ash is an essential ingredient when the project will be vulnerable to attack by sulfates or other aggressive compounds.

2.4 Slag

Slag is a by-product of iron manufacture. When quenched rapidly with water it changes to a glassy state and when finely ground, it develops the property of latent hydraulicity. Some of the slags so produced are, in themselves, cementitious materials to a certain degree, whereas others become so in the presence of activators such as Portland cement and calcium sulfate. Their performance in concrete is, however, independent of whether they are inherently cementitious or not (Malhotra, 1993)

There are different types of slags but the most common types are blast-furnace slag (granulated), and non-ferrous slag (Table 2.5). Blast-furnace slag (BFS) results from the fusion of the calcium from the limestone with the siliceous aluminous residues from the iron ore in the blast furnace. Major oxides in BFS are not free but are combined. It is the physical state of BFS that is fundamental to its cementitious properties. Non-ferrous slags generally refer to copper, nickel, zinc or lead slags extracted from sulfide concentrates by pyrometallurgical treatment. This process includes three different operations: roasting, smelting and converting. During the smelting and converting stages, different slags are produced. The smelter slag is either discarded without treatment or granulated with excess water and the chemical composition of the non-ferrous slag consists of high iron oxide and lower calcium oxide, opposite of the BFS slag composition (Farsangi, 1996).

Slag has been used in concrete manufacturing since the 1960s, and enhances the overall properties of concrete. In the meantime slags are widely used as a pozzolan to enhance the performance of cemented hydraulic mine fill and rock fill. The effect of slags in the hydraulic fill (mill tailings as aggregates) was examined by E.G. Thomas (1978), who concluded that slags increase the compressive strength of cemented fill. This is accomplished by pozzolanic action as well as by the improvement of the physical characteristics of the fill as aggregates (Figure 2.2).

Table 2.5: Typical Chemical and Physical Composition of Slag

Oxides	BFS	CSF
SiO_2	38	94
AL_2O_3	9	1
Fe_2O_3	0.8	1
CaO	40	0.5
MgO	12	1.1
SO_3	-	0.5
S (Sulfide)	1.8	-
Total Alk.as Na_2O	0.5	0.1
LOI	-	2.5
Physical properties		
Blaine (Cm^2/g)	4,500	2,000
45μm (% retain)	2	-
S. gravity	2.9	2.2

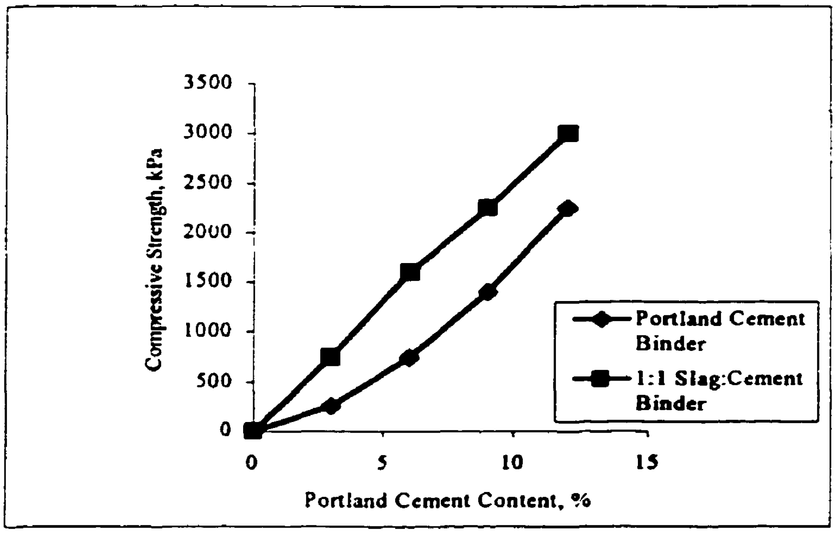

Figure 2-2: Compressive Strength Produced by 1:1 Slag: Cement Binder and by Portland Cement Binder at 224 Days in Cemented Fill vs. Portland Cement Content (Thomas 1978)

Properties of Concrete Containing Slag:

A) *Workability*

The lower relative density of ground slag causes an increase in paste volume. Compared to Portland cement, ground slag occupies about 9% more solid volume for the same mass. Thus, for equal weight of cement and equal water contents, this increase in paste volume generally benefits workability in mixes with low cement contents or where the aggregates lack the fine fraction.

B) Setting Time

The setting times for blended cements are generally longer than for Portland cements. As the percentage of slag increases in the blended cement or the concrete the setting or stiffening time extends. An increase in slag content from 35% to 65% increases the initial setting by approximately 60 minutes. The delayed setting of blended cements allows concrete to be worked for longer periods. This is of benefit in avoiding the formation of cold joints in large pours and in hot weather concrete pouring.

C) *Bleeding*

The bleeding capacity and bleeding rate of concrete is affected by the ratio of the surface area of the solids to the unit volume of water. When slag is used as a cement replacement, these effects depend on the fineness of the slag compared to the Portland cement and the combined effect of the total cementitious material. If the slag is finer than Portland cement and substituted on an equal basis, bleeding is reduced. Conversely, if the slag is coarser, the rate of bleed increases. Blended cements containing slag and manufactured by the intergrinding process generally cause a reduction in bleeding tendency.

2.4.1 Effect of Slag in Properties of Hardened Concrete

A) Compressive Strength

Strength development in concrete containing ground granulated blast-furnace slag as a cement replacement, at normal temperatures, develops more slowly than that made from Portland cement. The degree of decline in early-age strength is a function of a number of variables. These include slag activity, method of proportioning and the slag content of the blend.

Slag cements in current use produce concrete having equivalents of 28-day compressive strengths for equal mass replacements of Portland cement. Slag contents are normally at 25% by mass. At normal curing temperatures, the slag component reacts at a slower rate than does Portland cement resulting in a lower compressive strength at 7 days. A higher replacement rate of slag for equal binder contents reduces strength at all ages. This appears to be due to non-optimum gypsum contents particularly at replacement rates in excess of 50%.

B) *Flexural Strength and Drying Shrinkage*

Blended cements containing slag generally yield higher moduli of rupture at ages beyond 7 days than do concretes without slag, particularly when slag is used at optimum proportions. This is thought to be a result of the increased denseness of the paste in the concrete. It is well documented in literature that creep and shrinkage are related to the sulfate (gypsum) content of cement, and to cement chemistry and fineness.

C) *Thermal Cracking*

Granulated slags and fly ashes (as mention early) have been commonly used as ingredients of blended cements as separate cementitious constituents to reduce the temperature rise in mass concrete. It is important to note that, although the heat of solution method for determining the heat of hydration of cements indicates the total heat release potential of cement, it unfortunately does not indicate the rate of temperature rise, which is important in mass concrete applications.

D) Slag Resistance to Sulfate Attack

Generally, slag cement concretes have been shown to have a higher level of sulfate resistance than Portland cement concrete. It was found that even mortars containing 30% slag replacement were more resistant to sulfate attack than mortars made from Portland cement alone. The reason for the better performance of slag blends compared to Portland cement is unclear. It is thought that the performance is associated with the lowering of the C_3A level in the concrete, reduction in the concentration of soluble calcium hydroxide in the paste matrix due to the reaction with the slag and changes to the internal pore structure of the paste.

2.5 Lime (Quicklime)

Calcium Oxide (CaO) is Known by various names, such as lime, quicklime, and unslaked lime. Calcium Oxide is classed as having a strong base and, because of its activity and low cost, it is used more extensively in commercial processes than any other base. Calcium oxide reacts with water to form calcium hydroxide:

$$\mathbf{CaO + H_2O = Ca\ (OH)_2}$$

Calcium hydroxide is sparingly soluble in water, only 1.7 grams dissolving in a liter of water at room temperature. Even though calcium hydroxide has limited solubility it is a ready supply of hydroxide ions, because the solid continues to dissolve as hydroxide ions are removed from the solution during chemical reaction: i.e., the equilibrium shift to the right (Nebergall, 1980).

$$\mathbf{Ca\ (OH)_2\ (solid) \Rightarrow Ca^{+2} + 2OH^{-}\ (Dissolved)}$$

Amongst the numerous admixture treatment agents, some are eligible for both improvement/solidification and stabilization, depending on the amount that will be admixed to the material. One such double action agent is lime. In general, when mixed with lime all fined-grained soils exhibit improved plasticity, workability and volume change characteristics. Furthermore, most clayey soils also exhibit improved strength, stress-strain, and fatigue characteristics, and develop lower values of hydraulic conductivity, therefore the general objectives of mixing lime with soil are to improve or control volume stability, strength and stress-strain properties, permeability and durability. Volume stability (control of swelling and shrinkage processes) can be improved by replacement of high hydration cations, such as sodium (Na^{+}), by the low hydration cations such as calcium (Ca^{+2}) and/or magnesium (Mg^{+2}) and by cementation due to the formation calcium aluminate and/or calcium silicate hydrates (CAH and CSH respectively). 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 arrangement and by prevention of the swelling. Permeability is altered by modification of pore size and size distribution. It can be increased or decreased depending upon the percentage of lime added and final compactive effort applied (Dermatas, 1994).

2.6 Lime Fly ash Processes

Compositions including lime fly ash have comprised the largest volumes of wastes treated in the United States. This is largely due to the use of this technology in the electric power industry to solidify fluegas sludges from fossil fuel-burning power plants; however, lime fly ash processes have also been widely used in other industrial application such as remedial action projects. Cementitious products typically are mixtures of gel, semi-crystalline, and crystalline structures. Many of the reactions are analogous to those of Portland cement, and in general, these reactions are slower than those of cement and do not produce exactly the same products in term of chemical and physical properties. However there is some improvement in the physical properties (strength and permeability) of the treated material (Conner, 1990).

Also a study indicates the effectiveness of lime/fly ash in the stabilization of fine grain soil by increasing the strength of the mixture (Linn et al, 1988). And the maximum strength gain was achieved with lime content between 4 and 7 percent by weight of the soil, together with fly ash added at between 30 and 50 percent by weight of the lime.

2.7 Chemical Fixation and Solidification of Waste

2.7.1 Introduction

Cement and pozzolan are used extensively in chemical fixation or "solidification/stabilization" (S/S) of waste. These treatment processes are being used increasingly to treat a wide variety of wastes, both solid and liquid. Generally, S/S processes are designed and used to accomplish one or more of the following objectives:

- Reduce contaminant/pollutant mobility or solubility.
- Improve the handling and physical characteristics of the waste by producing a solid with no free liquid.
- Decrease the exposed surface area across which transfer or loss of contaminated may occur.

Numerous other terms such as "immobilization" and "fixation" have been used to refer to S/S technology. "Solidification" refers to a process in which materials are added to the waste to produce a solid. This may or may not involve a chemical bonding between the toxic contaminated and the additive. "Stabilization" refers to converting a waste to a more chemically stable form. This conversion may include solidification, but it almost always includes use of a physicochemical reaction to transform the contaminated to a less mobile or less toxic form. Note that biological processes such as bioremediation are not included in this definition of S/S.

The of S/S processes applied to manage numerous types of wastes, such as those covered by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) remediation projects. Some of these wastes include nuclear, municipal ash, and wastewaters and slurries (Means et al., 1995). In the meantime, for decades, mines in Canada and the United States have been using Portland cement alone, with fly ash, or in combination with solid mine wastes to produce cemented hydraulic backfill, which has helped eliminate the need for structural pillars or walls within an ore body. Portland cement has also been used by various waste generators and operators of waste disposal sites. In the 1950s relatively little industrial liquid waste residue was produced; however, some concentrated wastes were produced directly from processes such as steel pickling, and it is with these wastes that lime/fly ash processes first came to be used. Lime neutralized the acid content and fly ash, soil, or Portland cement was then added to produce a solid that could be easily landfilled (Conner, 1990). This process is being developed currently and is increasingly being used in the treatment of tailings with the potential of AMD as discussed in the previous section of this work.

2.7.2 Process Optimization

The bench-scale treatment and stabilization offer an excellent opportunity to fine tune the S/S process for site-specific waste. Process optimization includes the following types of activities:

- Determining the trade-offs between reducing the binder: waste ratio and associated cost savings versus process performance
- Determining the optimal sequence of binder or additives in terms of processing rate and process performance
- Evaluating the sensitivity of the S/S process to slight variations in binder amounts, curing conditions, and/ or mixing efficiency
- Evaluating the sensitivity of the S/S process to expected variations in waste properties (average vs. worst-case contaminant concentrations, variable matrix properties, etc.)

Process optimization is an important step in maximizing cost-effectiveness and determining process sensitivities. As Means et al., 1995 and others illustrated that many tests can be applied to measure the performance of the S/S processes. Some of these tests are mandated by federal, state, or local regulations, whereas others can be employed to provide additional assurance that a given S/S process is appropriate for its intended use.

2.7.3 Performance Tests

2.7.3.1 Physical Tests

Tests were made to provide information relating the physical characteristics of the treated and untreated waste. Example of these tests includes moisture content, particle size analysis, Atterberg limits, permeability and strength (a detail description of some of these tests will follow in the next sections).

2.7.3.2 Leaching/Extraction tests

The performance of stabilized wastes is generally measured in terms of leaching and extraction tests. A number of different leaching tests are available, and one or more may be required for regulatory approval. These regulation set a certain criteria on maximum permissible concentration in the leachate, or water quality guidelines (Tables 2.6, 2.7) (Wilson, 1995). However, no single test program would be used more than the two or three of the leaching/extraction tests described below. In general, leaching tests measure the potential of a stabilized waste to release contaminants to the environment. In all tests, the waste is exposed to a leachant and the amount of contaminant in the leachate (or extract) is measured and compared to a previously established standard, which may be a regulatory standard of baseline leaching data for the untreated waste. When using leaching tests to evaluate immolization performance of S/S-treatment, potential effects of the reduction in contaminant concentration per unit mass of waste due to binder addition should be considered. The treated waste may give reduced contaminant concentration in the leachate due to waste dilution independent of any immobilization mechanism.

Many leaching tests require sample size reduction. The major issues in selecting a size reduction approach are: 1) avoid contamination of the sample, 2) avoid partitioning of contaminants into a specific size fraction, and 3) avoid loss of contaminants, particularly volatile organics. The typical steps in size reduction are sample fragmentation, grinding and sizing. Fragmentation is best done with a hammer and anvil and should be minimized to avoid metal contamination of the waste. Grinding can be done with agate, dense alumina or tungsten-carbide equipment. Mortar and pestle or mechanical grinders can be selected based on the sample throughput of the laboratory. Sizing should be done with nylon or other nonmetal screens. As mentioned above there are several leaching tests such as the Toxicity Characteristic Leaching Procedure (TCLP), Extraction Procedure Toxicity (EP Tox) Test, Dynamic Leach Test (DLT) and others, and each test is suitable for a certain type of waste. The TCLP test will be discussed in more detail because its procedure has been used in this project.

2.7.3.3 Toxicity Characteristic Leaching Procedure (TCLP)

In the TCLP test, waste samples are crushed to a particle size less than 9.5 mm and extracted with an acetate buffer solution with a pH of 5 or an acetic acid solution with a pH of 3, depending on the alkalinity of the waste. Note, however, that the TCLP leachate is poorly buffered and that the pH of the leachate upon contact with the waste may be much greater, having a pH of 10-11 or more, depending on the initial alkalinity of the waste. The acetate buffer is added only once at the start of the extraction. A liquid-to-solid ratio of 20:1 is used for an extraction period of 18 hours. The leachate is filtered prior to conducting the contaminant analyses. This test is used to evaluate the leaching of metals, volatile and semivolatile organic compounds, and pesticides from wastes that are categorized under RCRA as characteristically toxic and can be used on other wastes as well.

The TCLP has been most commonly used by U.S.EPA and state agencies to evaluate the leaching potential of stabilized wastes, and TCLP is the test required by RCRA implementing regulations (40 CFR Part 261) for determining toxicity. Measurement of pH in the extract can help elucidate the pH-dependence of contaminated leaching.

The TCLP does not provide data on long-term stability. In fact, recent studies show a significant effect of curing time on both TCLP results and the chemical structure of the stabilized waste, as evidenced by spectroscopic analysis. These observations underline the limitations of the TCLP tests as an indicator of the long-term leaching of stabilized waste and emphasize the need for other types of leaching data.

2.7.3.4 Chemical Tests

Teatability testing usually involves collecting chemical data to define the waste composition and to assess the binder performance, these tests include pH, Oxidation/Reduction Potential (Eh), Electrical Conductivity, Metal Analysis, and others.

A) pH

The pH is a measure of the hydrogen ion activity and indicates the acid-to-base balance of material. The pH of untreated and S/S-treated wastes, waste leachates or soils from the intended disposal site can be analyzed by U.S. EPA SW-846 Method 9045.

Equal weights of soils/solids and deionized water are mixed and allowed to settle for 1 hour. The pH of the supernatant liquid is then measured electrometrically. The leachibility of many metals is a function of the pH. The pH may also affect the leachability of some base, neutral and acid fraction compounds.

B) Oxidation/Reduction Potential (Eh)

The oxidation/reduction potential (Eh) characterizes the electrochemical state of the media being measured. Data on the Eh of untreated or treated waste, waste leachates or soils from the intended disposal site can be very useful. The Eh can be determined from ASTM D 1498. Numerous metals can exist in multiple oxidation states. For example, chromium can exist as Cr(III) or Cr(VI) and arsenic as As(V). The leachability of these metals depends on their oxidation state; therefore, Eh can indicate the stability of various chemical species in the waste's chemical environment.

2.7.3.5 Microcharacterization

These tests can be applied for detail analysis of the structure of S/S- treated waste or to better understand the physicochemical form of the target contaminants. The one test of this category of tests used in this project is X-ray diffraction (XRD), which examines the crystal structure of a material. X-rays are scattered and diffracted by the lattice structure of crystals, yielding patterns characteristic to various crystals based on the lattice spacing. The crystalline components of a mixture, including the crystalline phases of the contaminant or contaminants, in amounts of 1% or more, can be identified individually from the X-ray diffraction patterns produced. Noncrystalline components are not detected however. There are several Microcharacterization tests which are typically applied to the treated waste such as Fourier Transform Infrared (FTIR) Spectroscopy, Scanning Electron Microscopy (SEM), Nuclear Magnetic Resonance (NMR) and Optical Microscopy (Means et. al., 1995).

Table 2.6: Leachate Quality Criteria (Concentrations in mg/L)

	Leachate Extraction Procedure					
Inorganic Parameters	**USEPA EP Tox**	**USEPA TCLP**	**Ontario LEP**	**Quebec**	**B.C. SWEP**	**TDGR CGSB**
Arsenic	5.0	5.0	5.0	5.0	5.0	5.0
Barium	100.0	100.0	100.0	-	100.0	100.0
Boron	-	-	500.0	-	500.0	500.0
Cadmium	1.0	1.0	0.5	2.0	0.5	0.5
Chromium	5.0	5.0	5.0	5.0	5.0	5.0
Copper	-	-	-	10.0	100.0	-
Lead	5.0	5.0	5.0	5.0	5.0	5.0
Mercury	0.2	0.2	0.1	0.2	0.1	0.1
Nickel	-	-	-	10.0	-	-
Selenium	1.0	1.0	1.0	1.0	1.0	1.0
Silver	5.0	5.0	5.0	-	5.0	5.0
Uranium	-	-	2.0	-	10.0	2.0
Zinc	-	-	-	10.0	500.0	-
Total Metals	-	-	-	10.0	-	-

Table 2.7: Water Quality Guidelines (Concentration in mg/L)

	MMLER[1]				
Inorganic Parameters	**I[2]**	**II[3]**	**III[4]**	**Canadian Drinking Water**	**MISA[5]**
Arsenic	0.5	0.75	1.0	0.05	0.5
Barium	-	-	-	1.0	-
Cadmium	-	-	-	0.005	-
Chromium	-	-	-	0.05	-
Copper	0.3	0.45	0.6	≤ 1.0 [6]	0.3
Lead	0.2	0.3	0.4	0.01	0.2
Mercury	-	-	-	0.001	-
Nickel	0.5	0.75	1.0	-	0.5
Selenium	-	-	-	0.01	-
Uranium	-	-	-	0.1	-
Zinc	0.5	0.75	1.0	≤ 5.0 [4]	0.5
PH	6.0	5.5	5.0	6.5-8.5 [4]	6.0-9.5

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[1] Metal Mining Liquid Effluent Regulation.

[2] Maximum authorized monthly arithmetic mean concentration.

[3] Maximum authorized concentration in a composite sample.

[4] Maximum authorized concentration in a grab sample.

[5] Ontario Municipal and Industrial Strategy For Abatement.

[6] Aesthetic objective.

3.0 Tailings Disposal Methods and Management

3.1 Introduction

This project is more relevant to surface disposal method and tailings treatment; however, there were several methods known for the disposal of the sulfide tailings. This section will discuss in brief these methods and the general aspect of reclamation.

The Canadian mining industry is the third largest in the world and although it is very successful industrially, the extraction of ore minerals poses some environmental problems. There are over 500 million tons of acid tailings in Canada, covering an area of 9000 ha (Brown, 1991). Long-term mine waste management involves difficult decision-making, especially for old sites where sulfide minerals have oxidized over long periods and acid conditions are fully established. When acidic conditions are left to prevail for long periods, metal are stored in solid forms that can easily be dissolved; this dissolution process can continue for long periods even after oxidation has ceased (St-Arnaud, 1996). Among the methods for disposing of the mine tailings, the principle methods are surface disposal (tailings pond), backfill (underground disposal) and underwater disposal.

In the meantime, due to the large quantities of wastes and their potential for degrading the environment, any attempt to utilize even small portion of these mineral wastes would contribute to an overall reduction of environmental problems associated with disposal and would aid in the conservation of mineral resources by reducing future demand placed on presently unextracted mineral reserves (Marshal, 1982).

3.2 Surface Disposal

The design of surface tailings impoundment depends largely on the potential impact of the impoundment on surface and groundwater resources, the type of retaining structure and its stability and the availability of construction materials at the site. There are many methods of deposition of slurry as well as the final configuration required for reclamation. The tailings dams often begin as small starter dams and grow to great heights during the operational life of the mine. Abandoned tailings dams continue to impound the fine tailings and the surface water that may collect in the pond, and if the dams are not correctly designed, protected and maintained, they are subject to failure in the long term, particularly under flood conditions, earthquake loadings or as the of result long-term erosion (Mitchell, 1993).

Surface disposal facilities for tailings, if designed properly, can perform a variety of treatment functions, which include the removal of suspended solids, and the stabilization of oxidizable constituents.

The main disadvantages of surface disposal can be summarized as follows:

1) The difficulties associated with maintaining consistent control over the various treatment functions,
2) Provision of a good flow distribution system,
3) Segregation of drainage from non-contaminated areas
4) The relatively large surface area required. This last disadvantage in particular imposes increased difficulties on reclamation procedures. Dusting and erosion can also present potential problems (Hossein et al., 1991).

3.3 Underwater Disposal

As discussed earlier, oxidation of sulfide minerals is the process, which contributes most to acid drainage and to the mobilization of metals from mine waste to the environment. This process can only be inhibited by limiting oxygen contact with the mine waste. Comparative laboratory studies have clearly demonstrated that the best way to inhibit oxygen entry is by covering mine waste with water (Payant et al., 1995).

Water covers and underwater disposal are now considered universally as feasible options for the management of waste rock and tailings. An applied example exists at the Louvicourt mine near Val D'Or, Quebec. At this site, tailings from polymetallic concentrate are being placed directly under a permanent water cover in a 96 hectare area confined by engineered earth dams. After almost two years of operation, underwater tailings disposal seems to be safe and easy to maintain. Monitoring of the water cover is being done to access its efficiency and to provide additional information useful for future water cover designs. Louvicourt is a good example of state-of-the-art mine planning which minimizes costs to future generations. In another study, Ritcey (1991) concluded that there were evidence that the oxidation process has stopped, therefore; the acid generation occurs when different types of sulfide tailings are deposited in deep water (lake). This method however requires a deep body of water and the tailings must be chemically harmless.

The long-term benefits of water covers may be complemented by aquatic plants, which create a self-sustaining organic barrier over the mine waste, enhancing physical and chemical stability. At Brenda Mines in British Columbia, it was shown that successful aquatic plant growth could be established in tailings pond. Brenda's experience on plant selection, nutrient dosage and planting techniques can be transferred to other sites. A new field trial is now under way at the Heath Steele tailings pond in New Brunswick, where highly alkaline water conditions present new biological challenges (St-Arnaud, 1996).

3.4 Reclamation

Reclamation is defined as recreating the original topography and re-establishing the previous land use. Reclamation may include a number of procedures including landscaping, soil amelioration, revegetation and chemical/physical stabilization. Generally there are three options for the actual management or reclamation of mined lands:

1) To leave the land as it was when the mining was completed. This option has become socially and economically unacceptable, and some form of reclamation is now required by all provinces.
2) To restore the land to its original condition, this option is impossible to achieve for both technical and economical reasons.
3) To reclaim the land to an ecologically improved and more socially acceptable condition. This option is the most widely accepted in Canada and it embraces both reclamation and rehabilitation.

3.4.1 Site Preparation (Landscaping)

Landscaping includes all activities related to the removing of soils and overburden, disposal of wastes and the modification of disturbed lands and disposal sites in order to facilitate reclamation of the mine areas.

The site preparation includes:

1) Contouring stopes in backfilled pits and reshaping waste rock dumps
2) Reconstructing or diverting drainage channels
3) Burying toxic wastes or elimination of other physical inhibitors to plant growth
4) Covering barren waste rock, tailings or disturbed areas with previously stored topsoil
5) Grading and leveling of the topdressed areas in order to prevent excessive runoff and erosion.

3.4.2 Revegetation

Principally, revegetation is the process of establishing a vegetative cover on the mineral wastes or mined areas so as to:

1) Stabilize erodible stopes in order to minimize stream pollution.
2) Control dust.
3) Minimize aesthetic value.
4) Facilitate crop production.
5) Reduce oxidation/potential acid mine drainage.

There are two approaches to revegetation of mine waste and disturbances. The first is to accept adverse soil and the site conditions they exist and choose plants, which have tolerance to the main environmental factors inhabiting plant growth (native species). The second is to improve the soil and the site conditions to make them suitable for growth of particular species (Marshal, 1982).

3.5 Underground Disposal (Backfill)

Over the past thirty years, the use of backfill has been growing throughout the mining world. Reasons for this acceptance are many and vary, and include benefits in improved ground control, decreased mining costs, improved ventilation and almost complete elimination of fire danger (Wayment, 1978). In the meantime, in response to reducing AMD problems, reactive tailings could be restored underground. This placement could be as a part of cemented or uncemented backfill in order to provide some structural support to the mine (Wheeland et. al., 1991).

Different materials can be used in the backfill, such as crushed rock, natural occurring sand or other materials. Today, the most common materials used to backfill, by a wide margin, include mill tailings, which are transported to the stope as a slurry. Generally, the tailings are classified, with the amount of classification varying in different mining areas. Classification always results in some portion of the minus-200-mesh material being removed, thereby increasing the settling rate and permeability.

In suitable types of metal ore deposits, mill tailings properly processed and placed in a stopping area constitute an excellent support system. Tailings from some mining areas will provide better support than tailings from other mining areas. For example, tailings, which are predominantly quartz, will provide better support than tailings composed of some other weaker minerals. Tailings with better grading will also generally be less compressible than one that is poorly graded. Compared to a timber support system it is usually less costly, more flexible and, as a rule, will provide more support in terms of preventing ground movement. During the past twenty-five years or so, three factors have had a direct impact on the development of backfill technology:

1) cement addition to fill
2) environmental pressures
3) resource conservation pressures

The reasons for backfilling include ground stability control, economics, environmental considerations and the need for preparation of a working floor, as in cut and fill operations for example. The environmental concern has grown in recent years and this trend is unlikely to end. Backfill operational concerns include backfill transportation, bulkheads, quality control, fill material preparation, placement, maintenance, labor and stope preparation

3.5.1 Backfill Design

With regards to the design rationale, the basic mechanical properties of fill that have been identified as being important to backfill design are:

- compressive strength
- permeability (for slurry backfill)

The unconfined compressive strength of fill required in mining operations varies over a wide range depending on its application. In cut and fill mining, the 28-day compressive strength that is required is generally lower than 1 MPa, but in delayed backfill with pillar recovery, it be much higher at up to 5 MPa and even 7 MPa. Permeability is an extremely important fill property, which affects the stope dewatering capability, and it should be taken into account in slurry fill design. There is no designated provision for a percolation rate, but the universally accepted rate in the mining industry is 100 mm/h. Placed slurry fill should preferably have a percolation rate slightly above this value. The tailings backfilling system has other significant advantages over most other support systems (Hassani & Archibald, 1998).

3.5.2 Advantages of Tailings Backfilling

A) The logistics of a tailings backfilling system are certainly an important advantage; comparing the logistics of a tailings backfilling system to other systems such as timber, steel sets or even rock bolts. With tailings fill, material is carried in a relatively small-diameter pipeline from surface to the stope. All other systems, with exception of formed concrete, require loading discrete pieces or structural shapes, using cages and horizontal transport systems underground to get from surface to the stope. This multiple handling becomes more critical the deeper mining goes. Multiple handling can prohibit the mining depth simply because of the complexity and cost of getting structural support shapes underground at great depths. It is much easier to hang a 3-inch pipeline from the mill to the stope.

B) Another advantage is that tailings backfill provides an extremely flexible system in term of changes in ore body geometry, such as stope width, dip and length. It is quite simple to leave low-grade ore or pile of waste in a stope with this system. It provides an excellent inexpensive working platform, which can accommodate both men and large mining equipment, such as 5- and 8-yard LHD units. As mentioned previously, underground ventilation generally improves when tailings backfill is used. In its place, fill is essentially impervious to air flow and thus available air can be entirely used at working faces, where it is more required, instead of experiencing large losses in unfilled gob areas.

3.5.3 Problems and Limitations

There are some problems and limitations associated with the conventional use of mill tailings as a support system:

A) One limitation is that backfilling with tailings is inherently cyclic; i.e., when filling is complete, the stope is out of production. In addition, it will be out of production until dewatering of the fill reaches a given point. This obviously varies with the size distribution of the tailings and rate of filling.

B) Another limitation is that conventional tailings backfill can be used only with difficulty in some types of deposits; for example, filling stopes in tabular deposits is very difficult, particularly if it is required that the fill be tight to the back.

C) Probably the biggest single problem associated with conventional tailings backfill is water. Especially in the case of hydraulic fill, the most economic way to transport solids to the mining area is a tailings-water slurry. However, the introduction of water creates a significant problem underground.

For example, stopes require extensive preparation prior to filling. Buckheads must be built and, depending on how tight the rock, the footwall and hanging wall may have to be covered partially or completely with a filtering material. This preparation is expensive both in terms of material and labor. Even with all the careful preparation, once filling begins other problems, which are water related, may develop. For example, some solids will escape from the stope during the drainage and decanting of water. Obviously, the amount of solids escaping in this way will vary with the fill material and the rate of filling. Leaks in and around bulkheads result in considerable spillage of tailings, further contributing to clean-up problems on sills and ditches (Wayment, 1978).

During the last decade efforts have been concentrated on developing the backfilling method by paying attention to:

1) proper grain size distribution.
2) feasible filling process, i.e. the most economical way to mix and transport the filling materials to the stopes.
3) optimize the ratio of water/cement.
4) consider the possibility of replacing cement by (other) cheaper binding agents.

3.5.4 Backfill Classification

The backfill material is usually classified according to the fill material used and the water to solid ration and other factors. A summery of backfill methods is given in Table 3.1.

Table 3.1: Property Comparison of the Principal Backfilling Methods (Modified from Landriault et al., 1996 & Henderson et al., 1997)

Properties	**Slurry Fill**	**Paste Fill**	**Rockfill**
Placement State	60% to 75% solids (by weight)	75% to 65%solids (by weight	Dry
Underground Transport System	Borehole/pipeline via gravity	Borehole/pipeline via gravity, can be pumped	Raise, mobile equipment separate cement system
Binder Application	Cemented or uncemented	Cemented only	Cemented or uncemented
Water to Cement Ratio (w/c)	High w/c ratio, low binder strength	Low to high w/c ratio. Low to high binder strength	Low w/c ratio, high binder strength
Placement Rate	100 to 200 Tonne/hr	50 to 200 Tonne/hr	100 to 400 Tonne/hr
Segregation	Slurry settlement and segregation low strength development	No segregation	Stockpile and placement segregation reduced strength end stiffness
Stiffness	Low stiffness	Low or high stiffness	High stiffness if placed correctly
Tight Filling	Cannot tight fill	Easy tight fill	Difficult to tight fill
Binder Quality	Requires large quantity of binder	Usually lower quantity of binder required	Moderate binder quantities
Barricades	Expensive	Inexpensive	Not necessary
Water Runoff	Excessive water runoff	Negligible water runoff	No water runoff
Capital Costs	Low capital costs	Higher than slurry fill	Moderate capital costs
Operating Costs	Low distribution costs; lowest cost for an uncemented fill	Lowest cost for a cemented fill	High operating costs fill

4.0 Methodology and Testing Procedures

4.1 Objective

The main objective of this project is to study the effect of lime/fly ash and lime/slag treatment in the stabilization of two types of sulfide-rich tailings (pyrite and pyrrhotite). Considering that sulfide tailings are the main sources of AMD and also that the goal of this project is to examine the development and mechanisms of the changes in the physical properties such as strength, durability, and permeability associated with tailings solidification. To provide more information on the effects of this treatment, the chemical aspect of the treated tailings will be evaluated, in terms of quantitative analysis to the sulfate and metal concentration in treated wastes.

The tailings are treated with binders of various types and proportions, and the binders consisting of lime and pozzolans (fly ash and slag). As a control, the tailings are also treated with low percentages of regular Portland cement. The scope of this study does not include the chemistry of tailings oxidation or the rate of oxidation, and the heat generation associated high sulfide content tailings was also excluded.

4.2 Materials

1) Tailings

To achieve the above objective, two types of sulfide-rich tailings were used, first tailings (Sample #1) predominately contain a high percentage of pyrite minerals, and in the second tailings (Sample #2), the major mineral containing sulfide is pyrrhotite. The samples were received from the mine in plastic buckets. After the appropriate labeling, the samples were air-dried for 4-5 days and then crushed with mortar and pestle and kept in sealed plastic buckets to be used in further experiments.

Several preliminary tests were carried out to assess the basic physical and chemical characteristics of the tailings, and furthermore, several chemical analyses and physical tests were done to study the changing behavior of the tailings when mixed with lime/fly ash -slag.

2) *Lime, Fly ash and Slag*

In addition to the lime (CaO) two types of pozzolans were used: fly ash (type C) which could be characterized as calcium rich, contrary to the copper slag. Tables 4.1 and 4.2 show their composition, as provided by the supplier. Lime used in this project is of the commercial type.

Table 4.1: Composition of Fly ash Type C

Chemical Analysis	**Class C (Fly ash)**
Silicon Dioxide,SiO2	53.30
Aluminum Oxide,Al2O3	23.63
Titanium Dioxide, TiO2	0.71
Iron Oxide,Fe2O3	4.40
Calcium Oxide, CaO	12.45
Magnesium Oxide, MgO	1.15
Potassium Oxide, K2O	0.42
Sodium Oxide, Na2O	3.03
Sulfur trioxide,SO3	0.20
Phosphorus pentoxide P2O5	0.12

Table 4.2: Composition of Copper Slag

Component	**Wt.%**
Iron (Fe)	40
Zinc (Zn)	3
Copper(Cu)	1
Lead (Pb)	0.5
Aluminum Oxide,Al2O3	4
Silicon Dioxide,SiO2	27
Calcium Oxide, CaO	1

4.3 Sample Preparation

Each type of tailings (pyrite and pyrrhotite) was mixed with lime-fly ash, lime-slag and lime-cement, so that three groups were made for each type of tailings. For sample #1 (pyrite) the groups were numbered 1, 2 and 3 and for sample #2 (pyrrhotite) the groups were numbered 4, 5 and 6. In groups 1 and 4 samples were mixed with different percentages of fly ash type C, in groups 2 and 5 samples were mixed with slag, and in groups 3 and 6, 2% and 5% of Portland cement was added to each type of tailings. Each individual sample was labeled (BxSy), where x is the group number and y sample number in the group. Tables 4.3 and 4.4 show the proportion of binders in samples #1 and #2. Samples were cured for 28 days and several chemical and physical tests were conducted. All tests were prepared according to the ASTM standard, unless stated otherwise.

Table 4.3: Binder Composition for Pyrite Tailings

Sample	Group No.	Sample #	Lime%	Fly ash%	Slag%	P.C%
Sample #1 (pyrite)	1	B1S1	0	0	0	0
		B1S2	5	0	0	0
		B1S3	5	2	0	0
		B1S4	5	5	0	0
		B1S5	5	10	0	0
		B1S6	5	20	0	0
	2	B2S3	5	0	2	0
		B2S4	5	0	5	0
		B2S5	5	0	10	0
		B2S6	5	0	20	0
	3	B3S3	5	0	0	2
		B3S4	5	0	0	5

Table 4.4: Binder Composition for Pyrrhotite Tailings

Sample	Group No.	Sample #	Lime%	Fly ash%	Slag%	P.C%
Sample #2 (pyrrhotite)	4	B4S1	0	0	0	0
		B4S2	3	0	0	0
		B4S3	3	2	0	0
		B4S4	3	5	0	0
		B4S5	3	10	0	0
		B4S6	3	20	0	0
	5	B5S3	3	0	2	0
		B5S4	3	0	5	0
		B5S5	3	0	10	0
		B5S6	3	0	20	0
	6	B6S3	3	0	0	2
		B6S4	3	0	0	5

4.3.1 Mixing

The air dried tailings were mixed with water, using a water-to-solid ratio of 0.3 by weight, taking into consideration the weight of the binder. The water/tailings mixture was left for 15-30 minutes to insure the full saturation of the tailings with water and the pH stabilization to some degree. Then required percentage of lime was added and after the mixing the slurry was left, for approximately one hour, then the alternative binder (slag, or fly ash) was added and firmly mixed. In the case of cement addition no lime was added and then several tests were preformed in each mixture.

4.4 Preliminary Experiments

4.4.1 Moisture content of the tailings

The measurement of the moisture content, both in the natural state and under controlled test conditions, can provide useful information or data of classifying cohesive soils and of assessing their engineering properties. Naturally occurring soils nearly always contain water as part of their structure, the moisture content of a soil is assumed to be the amount of water within the pores between the soil grains, which is removable by oven drying at 105-110°C. It is expressed as a percentage of the mass of dry soil, dry meaning the result of oven drying at temperature to constant mass, usually for period of about 12-24 h. (Liu & Evett 1990). Although the tailings were air dried, it is necessary to consider the water content in the tailings after the air drying. The water content for the two tailings (1 & 2) is presented in Table 4.5.

The moisture content, w, is given by the equation:

$$w\ (\%) = (Mw/Md)*100$$

Where: Mw, is the mass of water removed by drying at 105-110°C

Md, is the mass of dried soil.

Table 4.5: Moisture Content for Pyrite and Pyrrhotite Tailings
(Weight in grams)

Sample No.	Try No.	Weight of dry container	Weight of cont.+wet soil	Weight of cont.+ dry soil	Moisture loss	Moisture content (%)	Average
(pyrite) Tailings #1	1	1.60	30.50	29.4	1.1	3.95	3.64
	2	1.71	45.00	43.6	1.4	3.34	
(pyrrhotite) Tailings #2	1	1.01	34.02	33.00	1.02	3.19	2.67
	2	1.50	39.50	38.70	0.80	2.15	

4.4.2 Liquid limit Determination

There are four states of consistency (degree of firmness) for fine-grained soils: liquid, plastic, semisolid and solid. The dividing line between liquid and plastic states is the liquid limit; the dividing line between plastic and semisolid states is the plastic limit; and the dividing line between semisolid and solid states is the shrinkage limit. As explained above, the liquid limit is quantified for a given soil as specific water content, and from physical standpoint, it is the water content at which the shear strength of the soil becomes so small that the soil "flows" to close a standard groove cut in a sample of soil when it is jarred in a standard manner (Liu & Evett, 1990).

The two tailings types used in the experiments are silty-like material, which makes it difficult to use the liquid limit device, which requires making grooves in the sample. Therefore, the cone-penetrometer method is applied (BS 1377: part 2:1990:4: 3). This method is based on the measurement of the penetration into the soil of a standardized cone of specific mass. At the liquid limits, the cone penetration into the soil is 20 mm.

About 300g of soil (tailings) were put in a glass plate of distilled water, added and mixed with a spatula for at least 10 minutes and then the paste pressed against the side of the cup to avoid trapping air, and the middle of the cup was filled. Finally, the cup was filled and level so that the top surface was aligned with the rim, using the straight-edge. The cup was replaced under the tip of the cone and then the cone was released, the cone penetration was measured (between 15-25 mm) and the moisture content of the soil were measured, with the addition of more water to the soil the same procedure was repeated (Head, 1992). The results are presented in Tables 4.6 and 4.7 and Figures 4.1 and 4.2.

Table 4.6: Determination of the Liquid Limit for Pyrite Tailings

Tailings No:	**Test No.**	**1**	**2**	**3**	**4**
Tailings # 1 (Pyrite)	Cone penetration mm	14.5	18.0	19.5	23.1
	Container no.	R1	R2	R3	R4
	Wet soil & Container (g)	12.4	12.4	12.6	13.0
	Dry soil & Container (g)	10.8	10.7	10.8	10.9
	Weight of Container (g)	1.7	1.6	1.6	1.2
	Dry soil (g)	9.1	9.1	9.2	9.7
	Moisture Content%	17.3	18.7	19.6	21.6
	Liquid Limit	**19.5**			

Table 4.7: Determination of the Liquid Limit for Pyrrhotite Tailings

Tailings No:	**Test No.**	**2**	**3**	**4**	**5**	**6**
Tailings # 2 (Pyrrhotite)	Cone penetration mm	14.5	15.8	16.2	22.9	25.4
	Container No.	F1	F2	F3	F4	F5
	Wet soil & Container (g)	12.8	18.4	13.2	14.2	17.5
	Dry soil & Container (g)	11.7	16.8	12.1	12.0	14.6
	Weight of Container (g)	1.1	1.6	1.1	1.6	1.2
	Dry soil (g)	10.6	15.2	11.0	10.4	13.4
	Moisture Content %	10.1	10.9	10.2	21.6	21.5
	Liquid Limit	**16.0**				

Figure 4.1:Liquid Limit-Tailings #1(Pyrite)

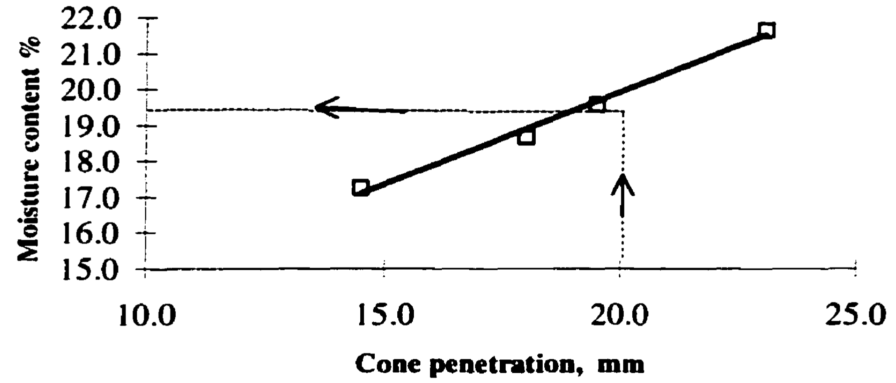
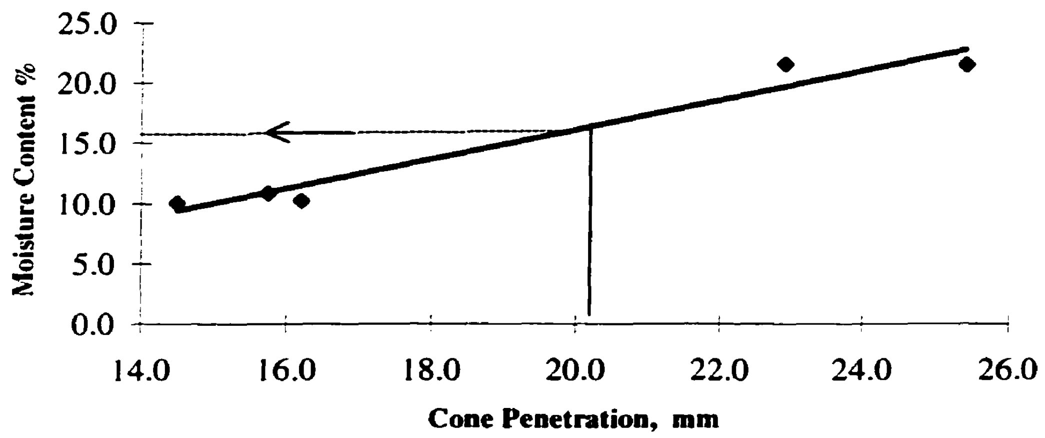


Figure 4.2:Liquid Limit -Tailings #2 (Pyrrhotite)



4.4.3 Grain-Size Analysis

Grain-size analysis is widely used in civil engineering for the classification of soils. Grain-size analysis is also utilized as a part of the specifications of the soil for airfields, roads, earth dams and other soil embankment construction. The standard grain-size analysis test determines the relative proportions of different grain sizes as they are distributed among certain size ranges.

The grain-size analysis of soils containing relatively large particles is accomplished using sieves. Soils with small grain sizes cannot generally be analyzed using sieves, because of the very small size of sieve opening that would be required and the difficulty of getting such small particles to pass through, therefore grain-size analysis for these tailings is done, by other methods hydrometer analysis. The hydrometer method is based on Stokes' law, which suggests that the larger the grain size, the greater it's settling velocity in a fluid.

If a soil sample contains both large and small particles, its grain size analysis can be performed using a combination of two methods described. (Cheng & Evett, 1990). In this project the combination of these methods was used. About 300 g of tailings were washed using a # 270 sieve. Then, the portion of tailings retained on the sieve # 270 was subjected to a dry sieving on sieves #20, 40, 100 and 200, and finally the portion which passed # 270 sieve was subjected to a sub-sieve analysis.

4.4.3.1 Sub-Sieve Sizing

For particle analysis, the elutriation and sedimentation techniques are well known procedures designed to provide a sizing distribution on the basis of hydrodynamic similarity. This means that all particles which have the same specific gravity and the same free-falling velocity in a given fluid are considered as being the same size, irrespective of variations in their physical dimensions. In sedimentation techniques, the material to be sized is dispersed in a fluid and allowed to settle under controlled conditions. The weight of the sediment or the specific gravity of the suspension is measured by various means as a function of time, and the two variables are then calculated to give a particle size

1) Description and Method

The Cyclosizer is an elutriator, as it separates a sample into specific size fractions by a technique, which depends on the force produced by the relative velocities of the particle and the elutriating fluid. It differs from conventional elutriation, however, in that the elutriating action takes place in a hydraulic cyclone where the fluid is spinning and centrifugal forces many times those due to gravity are acting on the particles. In addition, the flow patterns within the cyclone are very stable and changes in ambient conditions are not nearly so critical as in a conventional procedure for elutriation. Also, the high shearing forces, which are developed in a cyclone, overcome any natural tendency for the fine material to flocculate and an excellent dispersion of the particles is ensured.

The Cyclosizer consists of a console cabinet on which five cyclones are mounted together with sample container assembly, rotameter, pressure gauge, thermometer and electrical control panel. In the lower portion of the cabinet is a pump and water tank, which is connected to the main supply.

2) Procedure

To determine the size distribution of the two types of the tailings about 200-250 g was taken from the buckets where the tailings had been kept when they were received. This portion of the samples was washed using tap water over a # 270 sieve, the mixture collected in a bucket then carefully filtered. The cake was retained on the filter and the portion retained on the sieve oven-dried at 110°C for 24 hours. Then the soil was retained on a # 270 sieve subjected to dry sieving, some of the of the soil passed a # 270 sieve (in a dry sieving) mixed with the soil which passed a # 270 sieve in the wet sieving to insure a better sampling procedure for the Cyclosizer.

About 50 g of each tailings was passed through a # 270 sieve in wet sieving (well mixed with the portion passed a # 270 sieve in dry sieving). Then, they were put in a Cyclosizer sample holder and tested under controlled conditions at a temperature of 8°C and a flow rate of 170 L/min., with a test duration of 15 min. Finally, the test samples were retained in each of the five cyclones collected and air-dried.

3) Calculations

The weight percentages retained in the five cyclones have been determined, it is necessary to calculate the effective particle separation sizes under the condition of the test, to do this, correction factor must be determined for each of the four variable and multiplied with the limiting particle separation size for each cone, Table 4.8.

Thus for each cyclone:

$de = di \cdot f1 \cdot f2 \cdot f3 \cdot f4$

where de = effective particle separation size of a cyclone,

di = limiting particle separation size of the same cyclone

and f1, f2, f3, f4 are the separate correction factors for temperature, particle density, flowrate and time, respectively.

The standard values of the variables are:

(a)	Water flowrate	11.6 litres per minute,
(b)	Water temperature	20 °C,
(c)	Particle density	2.65 g / cc,
(d)	Time of elutriation	infinite.

Table 4.8: Limiting Particle Separation Size at the Standard Condition

Cyclone No.	L.P.S.S
1	44 microns ±2
2	33 microns ±1
3	23 microns ±1
4	15 microns ±1
5	11 microns ±1

From the corresponding graphs in the machine manual correction factors for tailings #1 and #2 are shown in the Table 4.9. The effective separation size to the nearest micron is listed in Table 4.10. The grain size distribution curves are shown in Figures 4.3 and 4.4.

Table 4.9: Correction Factors

Factor	Tailings # 1	Tailings # 2
Temperature, f1	1.18	1.18
Particle specific gravity, f2	.79	0.69
Flowrate, f3	1.01	1.01
Time, f4	.94	.94
Overall correction factor	.89	0.77

Table 4.10: The Effective Separation Size to the Nearest Micron

Cyclone No.	Tailings # 1	Tailings # 2
1 (44 micron)	39	34
2 (33 micron)	29	25
3 (23 micron)	20	18
4 (15 micron)	13	12
5 (11 micron)	10	9

Figure 4.3:Grain -Size distribution curve (Pyrite)
Sample #1

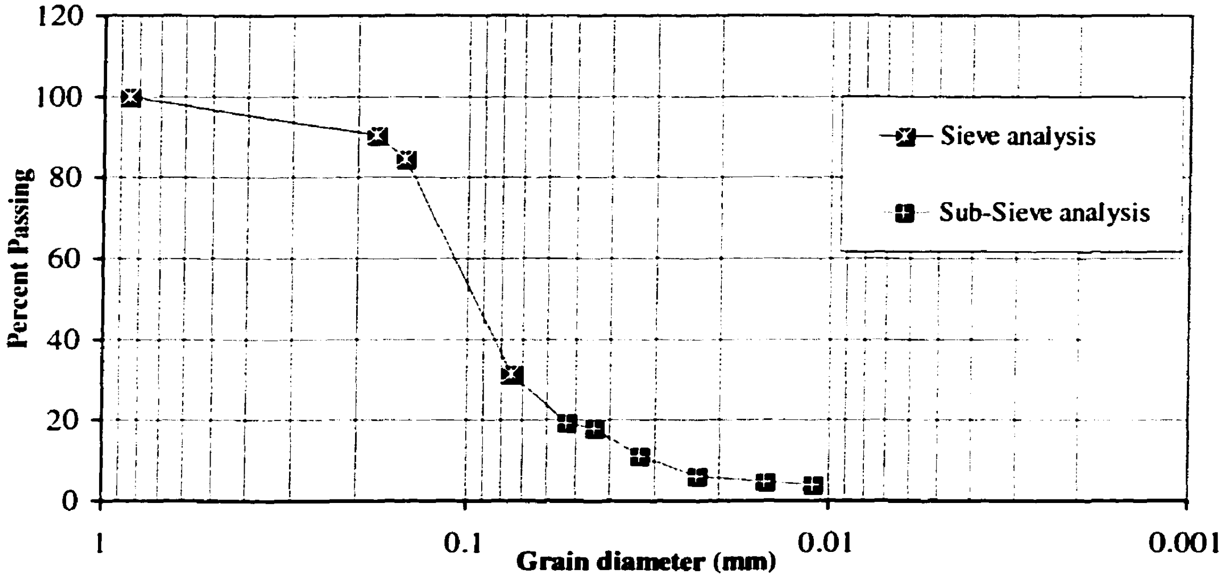
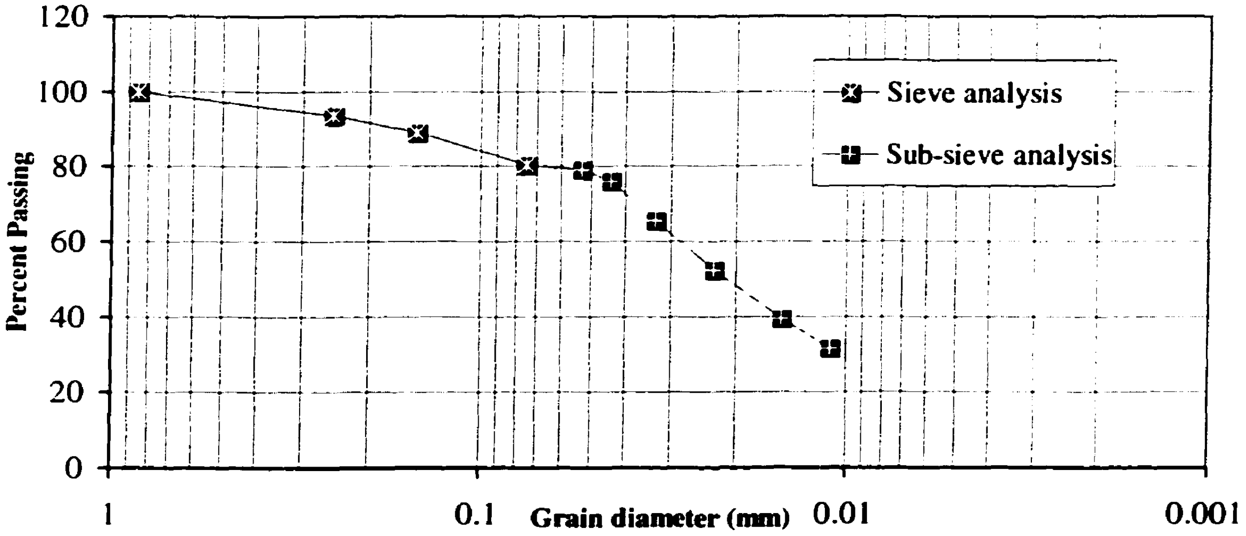


Figure 4.4 Grain -Size distribution curve (Pyrrhotite)
Sample # 2



4.4.4 Determination the Specific Gravity of the Tailings

In general, the term specific gravity is defined as the ratio of the weight of a given volume of material to the weight of an equal volume of water. Alternatively, specific gravity of soil may be defined as the ratio of the unit weight of solids (weight of solids divided by volume of solids) in the soil to the unit weight of water. In the equation:

$$Gs = (Ws/Vs)/\gamma_\omega = Ws/(Vs^*\gamma_\omega) \qquad (1)$$

where Gs = specific gravity of soil (dimensionless)

Ws = weight of solids, (g)

Vs = volume of solids, cm^3

γ_ω = unit weight of water (1 g/cm^3)

To determine the specific gravity of the two tailings # 1 & 2 about 50 g (Ws) put in a pycnometer, which is then filled with distilled water, for elimination the air bubbles the contents boil gently for at least 10 min. while occasionally rolling the pycnometer to assist the removal of the air. The next step is to determine the weight of the pycnometer when filled with water and soil, Wpws, and then measure the temperature of the soil and water mixture, from the calibration of the pycnometer the weight pycnometer when filled with water (Wpw) can be determined at the observed temperature Ti°C and at temperature Tx°C. With these data known the specific gravity can be computed from equation (1) (Liu & Evett, 1990). The result presented in Table 4.11.

Table 4.11: Specific Gravity of the Tailings

Sample No.	Tailings #1	Tailings #2
Weight of dry, clean pycnometer, Wp (g)	181.55	181.15
Weight of pycnometer + water, Wpw (g)	678.80	679.00
Water temperature, Ti (C)	21.00	21.00
Weight of pycnometer + soil + water, Wpws (g)	713.50	717.90
Temperature, Tx (C)	30.00	20.00
Weight of pycnometer + water at Tx, Wpw (at Tx) (g)	677.63	679.11
Weight of solids, Ws (g)	50.00	50.00
Conversion factor, K	1.00	1.00
Specific gravity, G=(K*Ws)/(Ws+Wpw(at Tx)-Wpws)	**3.54**	**4.46**

4.5 Testing Procedure

4.5.1 Chemical Analysis

4.5.1.1 Lime Addition and pH

The pH is a measure of hydrogen ion activity and indicates the acid-to-base balance of material. It is widely accepted that cement and pozzolan-base waste forms rely heavily on pH control for metal containment. In fact, some investigators believe that this is the only important factor in metal fixation. The high pH is desirable because metal hydroxides have minimum solubility in the range of pH 7.5-11. Several researchers indicate the important of a high pH in formation of several minerals such as ettringite which contribute to formation of cementitious substance (Conner, 1990), (see Chapter 2).

To establish optimum pH condition in the waste (increase the pH to 11-12) different percentages of lime (CaO) were added to 5 grams of both pyrite and pyrrhotite tailings after the mixing, water was added to the mixture with solid/water ratio of 1:1 and placed in the shaker for 1 hour. The material was left for 24 hours to stabilize the pH and then the pH value was measured. The results given in Table 4.12.

Table 4.12: Optimization of the Lime Content

Sample	Lime%	pH	Sample	lime%	pH
Pyrite	0	2.5	**Pyrrhotite**	0	5.6
	1	7		1	10.2
	2	10.6		2	11.58
	3	11		3	12.23
	5	12.36		4	12.48
	8	13		5	12.55
	10	N/A		7	12.51

4.5.1.2 Leaching and Extraction Test

When the ground or surface water contacts or pass through material, each constituent dissolve at some finite rate. Even in the most impermeable solidified waste-or clay, concrete, brick or glass for that matter, water will eventually permeate if there is a driving force. Wherever water penetrates, some of the waste dissolves, therefore, when a waste, treated or not, is exposed to water a rate of dissolution can be measured (leaching). The water is called the leachant and the contaminated water that has passes through the waste is the leachate (Conner, 1990 and Means et. Al., 1995).

Leaching tests measure the potential of a stabilized waste to release contaminants to the environment. In all tests, the waste was exposed to leachant and the amount of contaminants is measured and compared to previously established standard (See Chapter 2).

In this project modified version of TCLP test is applied, however most of the standard procedures were followed, the modification made in the leachant used, instead of the acetate buffered solution with pH = 5 or acetic acid with pH=3, the leaching medium is distilled water buffered with sulfuric acid with pH =2.5. The reason is that in these types of wastes the acidic acid is more likely to form due to the high sulfide content in the tailings, and the use of sulfuric acid is logical to simulate what could happen in the actual environment.

The treated tailings (tables4.3 and 4.4) are cured for 28 days and the TCLP tests are preformed after 1day and 28 days. About 1 gram from each sample is mixed with the TCLP solution with a liquid - to-solid ratio of 10:1, the material is placed in plastic tube and subjected to extraction using mechanical shaker for 18 hours. The leachate filtered through 0.45μm filter paper and after filtration the solution is acidified using few drops of nitric acid. Then, using the original solution three dilutions of 1/10, 1/100 and 1/1000 are made with distill water.

4.5.1.3 Element Analysis

Element analysis was conducted using flame atomic absorption (FLAA) and the machine used was a Parkin-Elmer 3500. The analysis is done for four elements: calcium (Ca), iron (Fe), magnesium (Mg) and zinc (Zn). The Fe was measured because of the waste and the slag contain considerable amounts of iron, and the Ca because the lime and the fly ash contain Ca, thus it is important to monitor these two elements. Mg and Zn are chosen as control elements to observe the effectiveness of the treatment. Results after 1 and 28 days of curing time are shown in Tables 4.13 to 4.16.

4.5.1.4 Sulfate Measurement

The necessity of the sulfate measurement is that the sulfate is a major product of AMD in sulfide-rich tailings. The sulfate ($SO4^{-2}$) was measured using a DIONEX DX-100 Ion Chromatographer. Before the injection of samples in the machine, standard solutions were prepared and their sulfate content was measured (for the calibration of the test machine). Then the results from each sample were compared with these standards. The results are presented in Tables 4.13 to 4.16.

Table 4.13: Pyrite Tailings- Results of TCLP after 1 day Curing
(Concentrations in ppm)

Group #	Wt.%	Sample	Fe	Ca	Mg	Zn	SO^{-4}. Con.
Group 1 (Fly ash)	0	B1S1	386.00	0.00	17.00	4.80	1773.40
	0	B1S2	8.60	651.00	1.00	2.70	1375.83
	2	B1S3	4.60	433.00	0.21	3.90	1014.35
	5	B1S4	14.30	481.00	0.80	4.00	1085.57
	10	B1S5	3.20	446.00	0.40	3.10	930.39
	20	B1S6	1.30	326.00	0.20	3.30	753.01
Group 2 (Slag)	2	B2S3	0.34	496.00	0.10	3.60	1164.12
	5	B2S4	4.68	372.00	0.21	4.10	1592.71
	10	B2S5	7.40	504.00	0.39	3.70	1300.57
	20	B2S6	2.30	415.00	0.21	3.30	882.37
Group 3 (Cement)	2	B2S3	4.20	452.00	0.09	3.50	904.16
	5	B2S4	2.34	418.00	0.12	3.40	702.85

Table 4.14: Pyrite Tailings-Results of TCLP after 28 Days Curing
(Concentrations in ppm)

Group #	Wt.%	Sample	Fe	Ca	Mg	Zn	SO^{-4}. con.
Group 1 (fly ash)	0	B1S1	327.0	0.0	26.00	2.90	1071.10
	0	B1S2	0.0	358.0	0.20	0.10	515.30
	2	B1S3	0.0	3862.0	0.19	0.02	749.50
	5	B1S4	0.0	3701.0	0.12	0.03	563.40
	10	B1S5	0.0	3029.0	0.13	0.03	460.60
	20	B1S6	0.0	2734.0	0.10	0.03	412.40
Group 2 (Slag)	2	B2S3	0.0	2016.0	0.07	0.02	486.20
	5	B2S4	0.0	1433.0	0.11	0.03	824.50
	10	B2S5	0.0	2887.0	0.09	0.04	573.30
	20	B2S6	0.0	2508.0	0.10	0.03	563.20
Group 3 (Cement)	2	B2S3	0.0	2895.0	0.03	0.02	352.90
	5	B2S4	0.0	3178.0	0.01	0.40	196.80

Table 4.15: Pyrrhotite Tailings- Results of TCLP after 1 day Curing

(Concentrations in ppm)

Group #	Wt.%	Sample	Fe	Ca	Mg	Zn	SO^{-4}. Con.
Group 4 (Fly ash)	0	B4S1	501.00	54.00	3.60	3.40	1062.39
	0	B4S2	5.90	637.00	1.10	3.30	1068.60
	2	B4S3	8.10	714.00	0.90	3.30	1068.89
	5	B4S4	6.10	659.00	1.00	3.50	887.04
	10	B4S5	23.30	624.00	0.80	3.40	828.20
	20	B4S6	11.60	523.00	0.70	3.30	656.61
Group5 (Slag)	2	B5S3	18.70	751.00	1.30	3.30	754.98
	5	B5S4	7.90	645.00	2.10	3.40	798.36
	10	B5S5	22.40	537.00	2.60	3.80	740.27
	20	B5S6	18.50	618.00	2.00	3.60	632.38
Group 6 (Cement)	2	B6S3	23.50	742.00	0.60	3.60	496.40
	5	B6S4	1.20	678.00	0.20	3.30	405.14

Table 4.16: Pyrrhotite Tailings- Results of TCLP after 28 Days Curing

(Concentrations in ppm)

Group #	Wt.%	Sample	Fe	Ca	Mg	Zn	SO^{-4}. Con.
Group 4 (Fly ash)	0	B4S1	414.0	222.0	138.00	0.25	841.2
	0	B4S2	0.0	1370.0	0.30	0.04	851.3
	2	B4S3	0.0	1926.0	0.03	0.02	689.3
	5	B4S4	0.0	3898.0	0.06	0.02	488.2
	10	B4S5	0.0	2775.0	0.17	0.02	502.0
	20	B4S6	0.0	5128.0	0.35	0.02	592.9
Group5 (Slag)	2	B5S3	0.0	2546.0	0.04	0.03	660.2
	5	B5S4	0.0	3859.0	0.08	0.04	518.6
	10	B5S5	0.0	3015.0	0.06	0.04	457.4
	20	B5S6	0.0	4132.0	0.03	0.02	312.8
Group 6 (Cement)	2	B6S3	0.0	3441.0	0.18	0.02	338.6
	5	B6S4	0.0	2777.0	0.18	0.03	460.9

4.5.2 Physical Tests

4.5.2.1 Unconfined Compressive Strength

The Unconfined Compressive Strength (UCS) test measures the strength of a material without lateral confinement. It is applicable to cohesive soil-like materials that do not release water during loading (ASTM D 2166) or to molded cylinders (ASTM D1633 or C109). For ASTM D 2166, 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.

The mixtures listed in Tables 4.3 and 4.4 were poured into plastic molds. Three samples of each mixture were made, the molds were compacted to remove the air trapped in the mold, the surface of the sample was leveled, samples were rapped with plastic and restored in a humid room with a temperature of about 20 to 25 °C and humidity at 80-90% to avoid moisture loss. The molds were of 30mm average diameter and a height of 64 mm. The height to diameter ratio was 2.1-2.5. Samples were tested after 1 and 28 curing days.

After appropriate measurement, the sample was placed under the compression and subjected to uniaxial loading. The loading rate was 0.5-1.5 mm/min., so that the maximum loading time did not exceed 15 minutes. Then the resulting stress and strain were measured. For each applied load, an axial unit strain ($\in$) was computed by dividing the specimen's change in length ΔL by its initial length L0, according to the equation:

$$\in = \Delta L / L0$$

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

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

The 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 result of the UCS tests are presented in Tables 4.17 to 4.22. In addition the modulus of elasticity was examined. Typical stress-strain curves were plotted for selected batches, as shown in Appendix B.

Table 4.17: UCS, Pyrite Tailings, 5% Lime and Fly ash Mixtures
*(Control: Tailings without lime or fly ash)

		1 Day		28 Days	
Sample #	**Fly ash%**	**Stress (kPa)**	**σ_{n-1}**	**Stress (kPa)**	**σ_{n-1}**
B1 S1*	0	N/A	N/A	N/A	N/A
B1 S2	0	40.67	1.18	52.25	5.40
B1 S3	2	102.81	28.72	145.56	56.02
B1 S4	5	127.81	3.56	143.36	2.08
B1 S5	10	94.84	8.78	118.87	21.07
B1 S6	20	150.89	29.45	175.48	32.74

Table 4.18: UCS, Pyrite Tailings, 5% Lime and Slag Mixtures

		1 Day		28 Days	
Sample #	**Slag%**	**Stress(kPa)**	**σ_{n-1}**	**Stress(kPa)**	**σ_{n-1}**
B2 S3	2	75.64	5.54	137.99	84.07
B2 S4	5	70.38	1.47	161.15	51.22
B2 S5	10	75.80	7.61	235.27	55.04
B2 S6	20	88.80	1.06	598.89	15.46

Table 4.19: UCS, Pyrite Tailings and Cement Mixtures

		1 Day		28 Days	
Sample #	**Cement%**	**Stress(kPa)**	**σ_{n-1}**	**Stress(kPa)**	**σ_{n-1}**
B3 S3	**2**	59.88	5.71	394.48	67.39
B3 S4	**5**	127.04	9.83	744.79	42.38

Table 4.20: UCS, Pyrrhotite Tailings, 3% Lime and Fly ash Mixtures
*(Control: Tailings without lime or fly ash)

		1 Day		28 Days	
Sample #	**Flyash(%)**	**Stress (kPa)**	σ_{n-1}	**Stress (kPa)**	σ_{n-1}
B4 S1*	0	5.40	3.15	0.00	N/A
B4 S2	0	181.03	20.14	9.06	N/A
B4 S3	2	184.34	5.37	22.66	11.92
B4 S4	5	190.39	21.99	57.79	23.97
B4 S5	10	162.31	16.27	85.04	11.84
B4 S6	20	160.41	7.03	132.90	20.81

Table 4.21: UCS, Pyrrhotite Tailings, 3% Lime and Slag Mixtures

		1 Day		28 Days	
Sample #	**Slag (%)**	**Stress (kPa)**	σ_{n-1}	**Stress (kPa)**	σ_{n-1}
B5 S3	2	35.01	4.23	74.57	15.02
B5 S4	5	33.87	1.44	110.35	4.17
B5 S5	10	48.18	4.67	196.85	78.60
B54.6	20	58.96	6.36	21.31	26.81

Table 4.22: UCS, Pyrrhotite Tailings and Cement Mixtures

		1 Day		28 Days	
Sample #	**Cement(%)**	**Stress (kPa)**	σ_{n-1}	**Stress (kPa)**	σ_{n-1}
B6 S3	2	59.03	6.02	209.87	4.24
B6 S4	5	40.08	8.56	297.65	1.48

4.5.2.2 Freeze and Thaw (F&T)

Two samples from each mixtures (Tables 4.3 and 4.4) were subjected to a cycle of freezing up to -10 °C for a period of 24 hours and then removed to a humidity controlled room with a temperature was about 25°C for the same period of time. The samples had the same dimensions as the samples tested for UCS. After 28 - days of curing, the samples were tested for UCS. The results are shown in Tables 4.23 and 4.24.

Table 4.23: F&T Results, Pyrite Tailings (28-Days Curing)
(*Control: Tailings without lime or fly ash)

Additive	Sample #	Wt.(%)	Stress (kPa)	σ_{n-1}
Fly Ash	B1 S1*	0	0.00	0.00
	B1 S2	0	137.07	3.06
	B1 S3	2	198.81	4.60
	B1 S4	5	283.31	4.60
	B1 S5	10	301.73	6.13
	B1 S6	20	306.06	3.06
Slag	B2 S3	2	212.90	-
	B2 S4	5	172.82	7.66
	B2 S5	10	250.81	1.53
	B2 S6	20	268.15	4.60
Cement	B3 S3	2	309.31	1.53
	B3 S4	5	425.22	3.06

Table 4.24: F&T Results, Pyrrhotite Tailings (28-Days Curing)
(*Control: Tailings without lime or fly ash)

Additive	Sample #	Wt.(%)	Stress (kPa)	σ_{n-1}
Fly Ash	B4 S1*	0	0.00	0.00
	B4 S2	0	0.00	0.00
	B4 S3	2	64.49	1.53
	B4 S4	5	99.15	1.53
	B4 S5	10	270.31	1.53
	B4 S6	20	39.57	N/A
Slag	B5 S3	2	54.74	3.06
	B5 S4	5	105.65	1.53
	B5 S5	10	194.48	13.79
	B5 S6	20	127.32	111.83
Cement	B6 S3	2	50.41	3.06
	B6 S4	5	244.31	90.39

4.5.2.3 Permeability (Hydraulic Conductivity) Tests

There are two types of laboratory tests for direct measurement of soil permeability. The "constant head" method is used for soils of high permeability (such as sands), while the other method is the "falling head" 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 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 required (Head, 1992).

The mixtures listed in Tables 4.3 and 4.4 (except cement mixtures) were poured into a modified permeameter cell with a diameter of 30 mm and a length of 64 mm. Samples were restored in the humidity controlled room for 28-days. Before 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 to eliminate entrapped air. When the water in the plastic inlet tube on the top of the mold reached an equilibrium with the water in the sink (allowing for capillary rise in the tube), the sample was assumed to be saturated

The standpipe was filled with water to height (h1), then to start the test he exit tube was opened and simultaneously the time recorded. The water was allowed to flow through the sample until the standpipe was almost empty and the end time recorded as well as (h2) the drop in the water level, and the water temperature. The test was repeated twice.

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 to h2, s

The permeability was corrected by multiplying the computed value by the ratio of viscosity of water at the test temperature of the water at 20 °C. The results obtained are shown in Tables 4.25 and 4.26.

Table 4.25: Permeability Results for Pyrite Tailings

a=0.315 cm^2, A=7.07 cm^2, L=6.4 cm, Temperature 22°C,
Temperature Correction factor = 0.9531

	Wt.%	**Sample No.**	**Head h_1 (cm)**	**Head H_2 (cm)**	**Time t (sec)**	**Permeability at T °C, k_T (cm/s)**	**Permeability at 20 °C, k_T (cm/s)**	**Average (cm/s)**
Fly Ash	0	B1S1	150	30	1.2E+03	3.8E-04	3.6E-04	3.5E-04
			150	30	1.3E+03	3.5E-04	3.3E-04	
	0	B1S2	152	30	1.8E+03	2.6E-04	2.4E-04	2.9E-04
			152	25	1.5E+03	3.4E-04	3.3E-04	
	2	B1S3	157	148	4.6E+03	3.7E-06	3.5E-06	2.3E-06
			150	147	5.5E+03	1.0E-06	9.9E-07	
	5	B1S4	157	131	1.4E+04	3.6E-06	3.4E-06	3.4E-06
			157	148	4.6E+03	3.6E-06	3.5E-06	
	10	B1S5	157	144	5.4E+03	4.6E-06	4.3E-06	4.5E-06
			157	143	5.5E+03	4.8E-06	4.6E-06	
	20	B1S6	157	150	6.2E+03	2.1E-06	2.0E-06	2.8E-06
			157	153	2.0E+03	3.7E-06	3.5E-06	
Slag	2	B2S3	157	145	2.8E+03	8.0E-06	7.7E-06	6.3E-06
			157	143	5.2E+03	5.1E-06	4.9E-06	
	10	B2S5	157	135	9.0E+03	4.8E-06	4.6E-06	5.6E-06
			157	129	8.1E+03	6.9E-06	6.6E-06	
	20	B2S6	157	140	8.4E+03	3.9E-06	3.7E-06	4.1E-06
			157	135	9.0E+03	4.8E-06	4.6E-06	

Table 4.26: Permeability Results for Pyrrhotite Tailings
a=0.315 cm^2, A=7.07 cm^2, L=6.4 cm, temperature 22°C,
Temperature correction factor = 0.9531

	Wt.%	Sample No.	Head h_1 (cm)	Head h_2 (cm)	Time t (sec)	Permeability at T °C, k_T (cm/s)	Permeability at 20 °C, k_T (cm/s)	Average (cm/s)
Fly Ash	0	B4S1	157	50	6.0E+02	5.4E-04	5.2E-04	4.7E-04
			157	50	7.5E+02	4.3E-04	4.1E-04	
	0	B4S2	157	60	6.6E+02	4.2E-04	4.0E-04	3.5E-04
			157	60	8.4E+02	3.3E-04	3.1E-04	
	2	B4S3	157	95	2.7E+03	5.3E-05	5.1E-05	4.4E-05
			157	95	3.6E+03	4.0E-05	3.8E-05	
	5	B4S4	157	90	2.3E+03	7.0E-05	6.6E-05	5.2E-05
			157	95	3.7E+03	3.9E-05	3.7E-05	
	10	B4S5	157	75	3.2E+03	6.6E-05	6.3E-05	5.4E-05
			157	92	3.2E+03	4.8E-05	4.6E-05	
	20	B4S6	157	45	1.3E+03	2.7E-04	2.6E-04	2.7E-04
			157	60	9.0E+02	3.0E-04	2.9E-04	
Slag	2	B5S3	157	100	5.7E+03	2.3E-05	2.1E-05	2.1E-05
			157	100	6.0E+03	2.1E-05	2.0E-05	
	10	B5S4	157	100	3.6E+03	3.6E-05	3.4E-05	3.5E-05
			157	90	4.2E+03	3.8E-05	3.6E-05	
	15	B5S5	157	110	6.0E+03	1.7E-05	1.6E-05	1.7E-05
			157	110	5.7E+03	1.8E-05	1.7E-05	
	20	B5S6	157	95	6.9E+03	2.1E-05	2.0E-05	2.0E-05

4.5.2.4 X-Ray Diffraction

X-ray diffraction (XRD) examines the crystal structure of a material (see Chapter 2). Selected samples were taken from Groups 1, 2 and 3 to present pyrite tailings and from Groups 4,5 and 6 for pyrrhotite. These samples are listed in Tables 4.27 and 4.28. Each sample contains different percentages of fly ash or slag or cement. The mixture was kept in plastic containers under humid conditions and then oven dried for 30 min. in temperatures of around 30-40°C. Then, the chunks were lightly ground to pass through a # 200 sieve, the powder subjected to the XRD test in an X-ray machine (Rigaku D/Max 2400). For the mineral analysis and search JADE software was used. The test was conducted after 1 and 28 days of curing time. The x-ray analysis is shown in appendix A.

Table 4.27: Composition of Selected Sample for the X-Ray, Pyrite Tailings

Sample	Group No.	Sample #	Lime %	Fly ash %	Slag %	P.C %
Sample #1 (pyrite)	1	B1S1	0	0	0	0
		B1S2	5	0	0	0
		B1S4	5	5	0	0
		B1S5	5	10	0	0
		B1S6	5	20	0	0
	2	B2S4	5	0	5	0
		B2S6	5	0	20	0
	3	B3S4	5	0	0	5

Table 4.28: Composition of Selected Sample for the X-Ray, Pyrrhotite Tailings

Sample	Group No.	Sample #	Lime %	Fly ash %	Slag %	P.C %
Sample #2 (pyrrhotite)	4	B4S1	0	0	0	0
		B4S2	3	0	0	0
		B4S4	3	5	0	0
		B4S5	3	10	0	0
		B4S6	3	20	0	0
	5	B5S4	3	0	5	0
		B5S6	3	0	20	0
	6	B6S4	3	0	0	5

5.0 Discussion and Data Analysis

5.1 Preliminary Experiments

5.1.1 Moisture Content and Liquid Limit

The tailings received from the mine were saturated with water, after air drying for 4 to 5 days, their moisture content was measured. Although the results of the moisture content is not considered to be the natural moisture content of the soil, it is however important to evaluate such property at the beginning. Because many experiments depend on the initial water in the tailings. The results in Table 4.5 show that both tailings after oven drying contain some water. The moisture content for pyrite tailings is 3.64% and 2.67% for the pyrrhotite tailings.

The moisture content by itself is not sufficient to define the state of consistency of a clay or soil; however, if the moisture content related to the liquid limit and the plastic limit will give better indication about the soil consistency. The results of liquid limits for both tailings are show in Figures 4.1 and 4.2, and Tables 4.6 & 4.7. The liquid limit for the pyrite tailings is 19.5% and for the pyrrhotite is 16%, which indicates that both tailings have relatively close liquid limit.

5.1.2 Specific Gravity

In general specific gravity (density) is an important property for many applications in soil engineering. The results in Table 4.11 show that the specific gravity for pyrite and pyrrhotite tailings were 3.54 and 4.46, respectively; indicating that both samples have a high specific gravity and the samples contain metals such as iron and iron oxide.

5.1.3 Grain-Size Analysis

The analysis of soils by particle size provides a useful engineering classification system for soils, and there are many application of particle size analysis in geotechnology, construction of backfill and concreting materials. This is especially true in backfill technology and paste fill design, where the tailings are usually deslimed to meet the percolation requirement. Also the surface area of the soil has a significant effect in solidification mechanisms. The results in Figures 4.3 and 4.4 show that from tailings #1 (pyrite), about 80% of the tailings retain on sieve # 270 (53 micron), having a diameter range from 0.85 to0.053 mm, as compared with the most soil classification about 80% of tailings #1, consider to fit the designation of coarse sand to coarse silt.

As for the tailings #2 (pyrrhotite) the result show a gradual distribution within the sample, and only about 20% retained on # 270 sieve (53 micron); indicating that the pyrrhotite tailings is much finer than tailings #1 (pyrite), about 80% are considered to be as medium silt.

5.2 Chemical Analysis

5.2.1 Lime Addition and pH

The main reasons for the addition of lime to the tailings is to raise the pH to a certain level such that the solubility of many oxides that form during the hydration process is a minimum. This optimum level of pH was previously discussed and is different from one mineral or oxide to another. However, the majority of researchers believe that the optimum pH level for such a condition is between 10-11.5. Both tailings are very acidic, the initial pH being around 2, and requiring a considerable amount of lime to bring the pH up to around 12, taking into account that eventually the pH will drop with the addition of fly ash and slag. Another reason for the lime addition is that the performance of the Pozzolan (fly ash and slag) is to be improved when mixed with lime and water (see Chapter 2). To optimize the pH lime, gradually added to the tailings from 1% up to 10% by weight to both tailings and pH was measured (Table 4.12). From the results, 5% of lime was enough to raise the pH level of pyrite tailings to 12, as for the pyrrhotite tailings only 3% was enough to bring the pH to that level. That is more evident from the elements analysis which indicated that the pyrrhotite tailings contain more calcium. Lime was used in this experiment because it is more reactive than most of other sources of calcium such as limestone or calcium.

5.2.2 Elements Analysis and Sulfate Measurements

The results of the elements analysis for calcium (Ca), iron (Fe), magnesium (Mg), zinc (Zn) and sulfate (SO^{-4}) after 1 and 28 days of curing time are shown in Tables 5.13 to 5.16 for both types of tailings.

5.2.2.1 Pyrite Tailings

In group 1, pyrite tailings were mixed with fly ash type C (see Table 4.3). The results of sulfate measurements and elements analysis are shown in Figures 5.1 to 5.12. The pyrite control sample (without lime or fly ash) released 1,773 ppm of sulfate, 386 ppm of Fe, 17 ppm of Mg and no Ca was released, which confirms the initial test for the pH measurement. With the addition of only lime, the sulfate concentration declined to 1,400 ppm after one day of curing. With the introduction of the fly ash to the mixture the sulfate continued to decline with the increase of the fly ash amount. With the addition of 2% fly ash, the reduction in sulfate concentration was about 45% after 1 day curing (compared with the control sample) and the trend continued with the increase of the fly ash added. And with the addition of 20% fly ash the sulfate concentration decreased by 60% after 1 day of curing. After 28 days of curing the sulfate concentration decreased by 72% with 2% fly ash and 78% with the addition of 20% fly ash. The overall reduction in the sulfate released after 28 days (without lime or fly ash) of curing is about 20 to 50% compared with the same percent of fly ash after 1 day of curing. In the interval between 2% and 20% fly ash, the decrease in the amount of sulfate released is about 50%.

The elements analysis shows that the control sample contain 386 ppm of Fe (iron), 17 ppm Mg, 4.8 ppm Zn and no Ca. With the addition of the only 2% of fly ash the Fe is totally immobilized in 28 days. The concentration of Mg and Zn declined to less than 0.1 ppm after 28 days. The Ca concentration after 1 day of curing showed a decrease with the addition of the fly ash (it reached 50% with addition of 20% fly ash). After 28 days however the amount of Ca released increased significantly, which, could be attributed to unreacted lime in the mix or the lime bound was easily extracted by the used TCLP solution.

Figure 5.1: Sulfate Concentration In Pyrite Tailings and FA. Mixtures

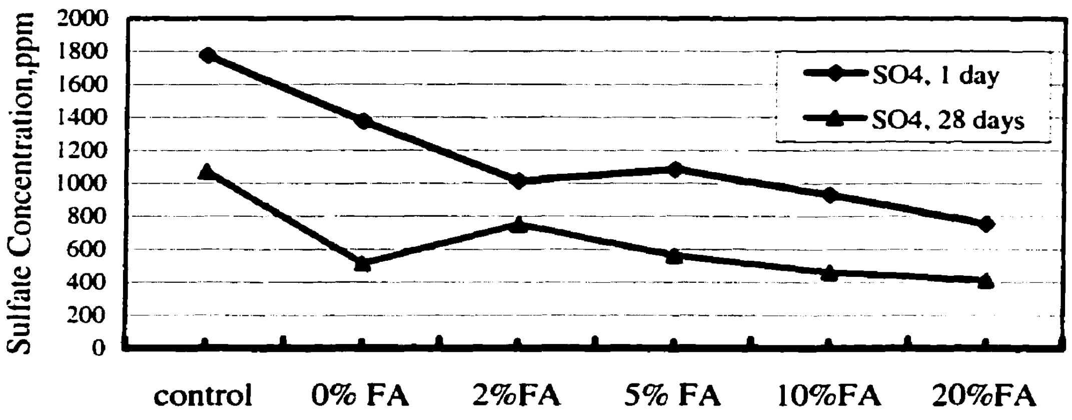


Figure 5.2: Sulfate Concentration In Pyrite Tailings& Slag Mixtures

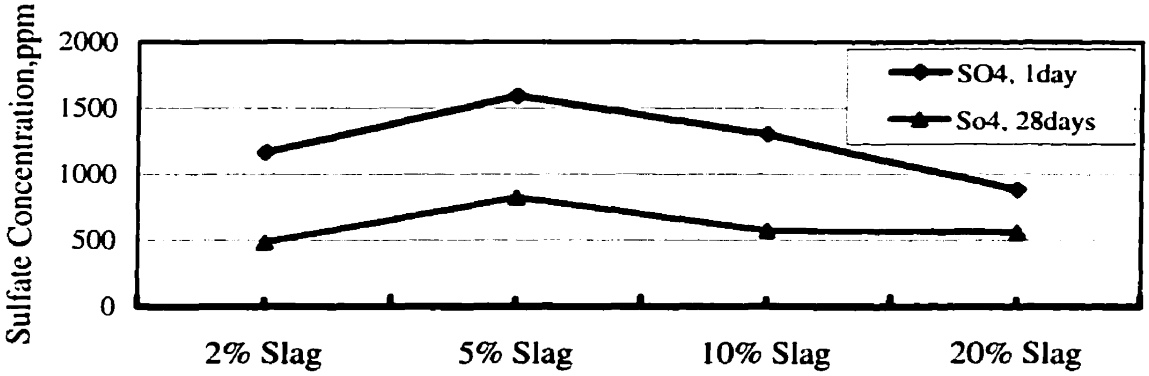
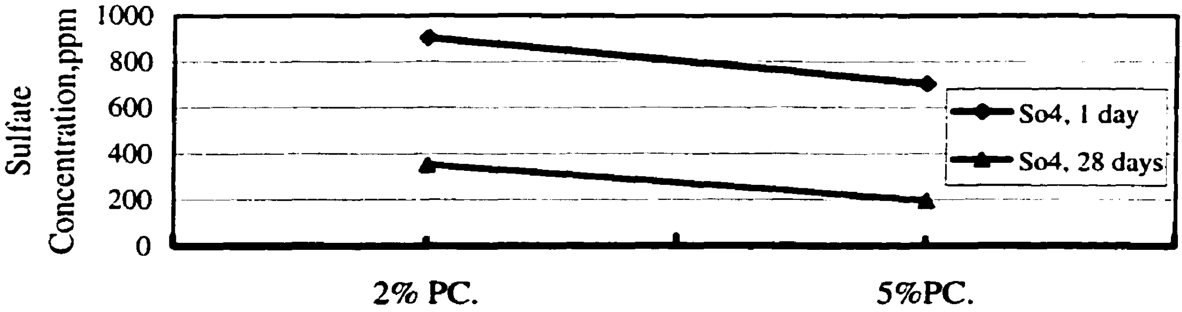


Figure 5.3: Sulfate Concentration In Pyrite Tailings& PC. Mixtures



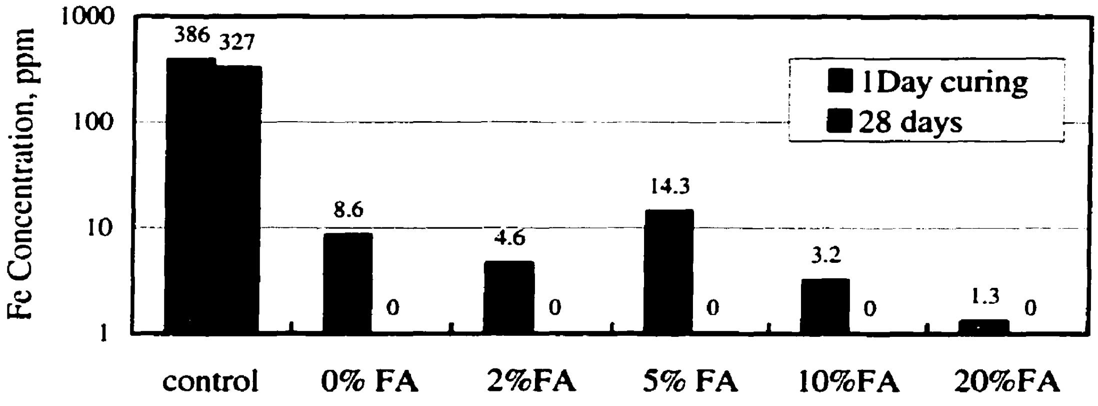


Figure 5.4:Fe Concentration In Pyrite Tailings& FA.

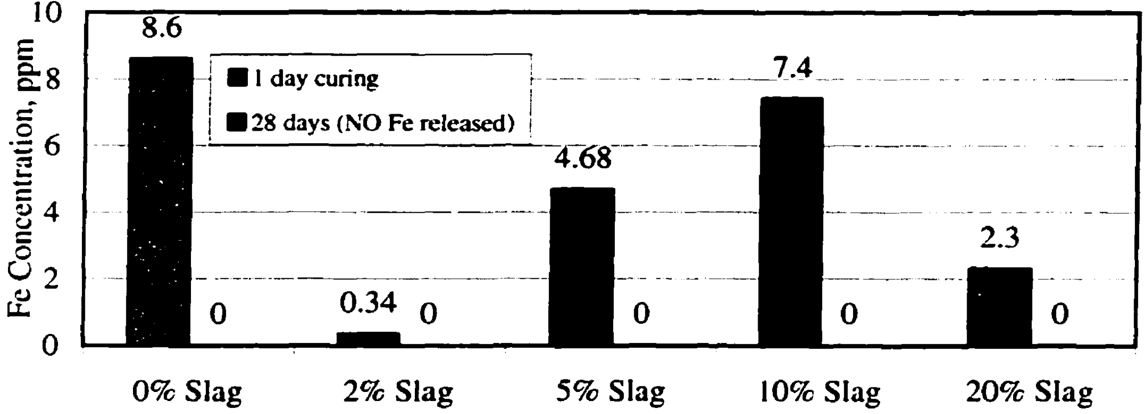


Figure 5.5:Fe Concentration In Pyrite Tailings & Slag

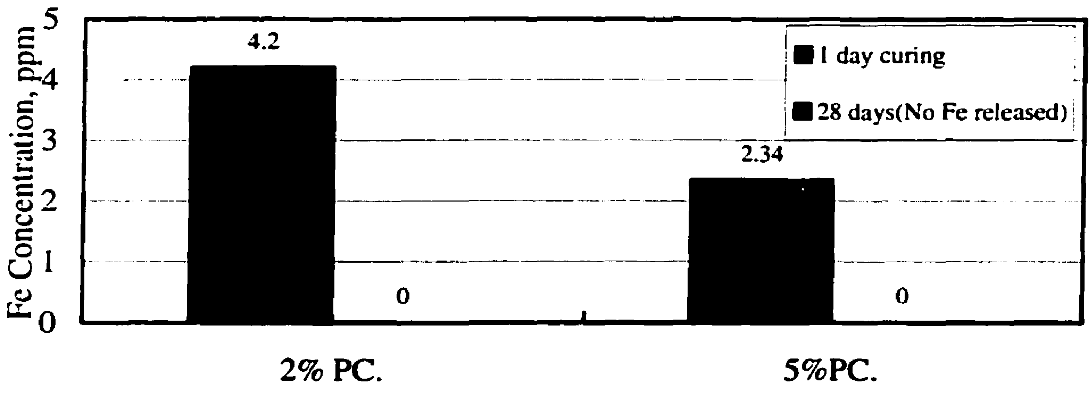


Figure 5.6:Fe Concentration In Pyrite Tailings& P.C.

Figure 5.7:Mg & Zn Concentration In Pyrite Tailings& FA.

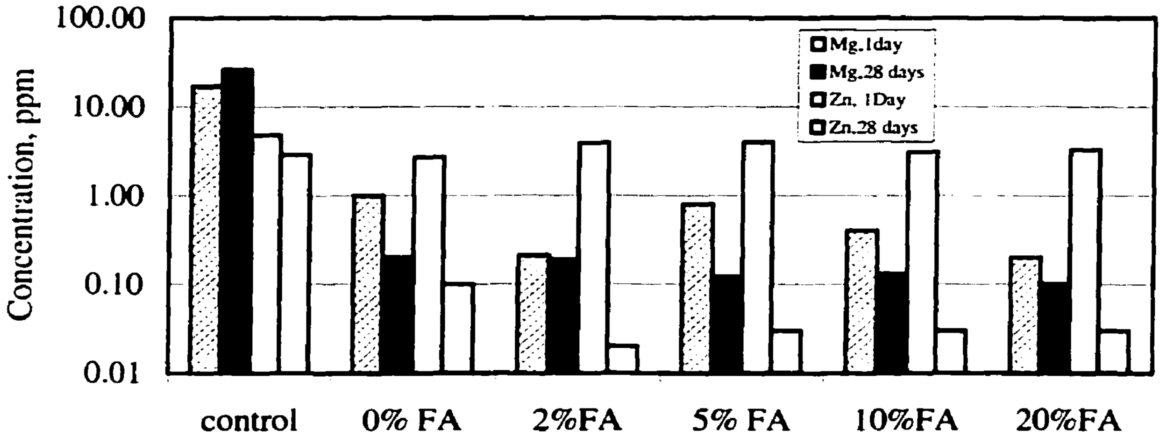


Figure 5.8:Mg & Zn Concentration In Pyrite Tailings& Slag

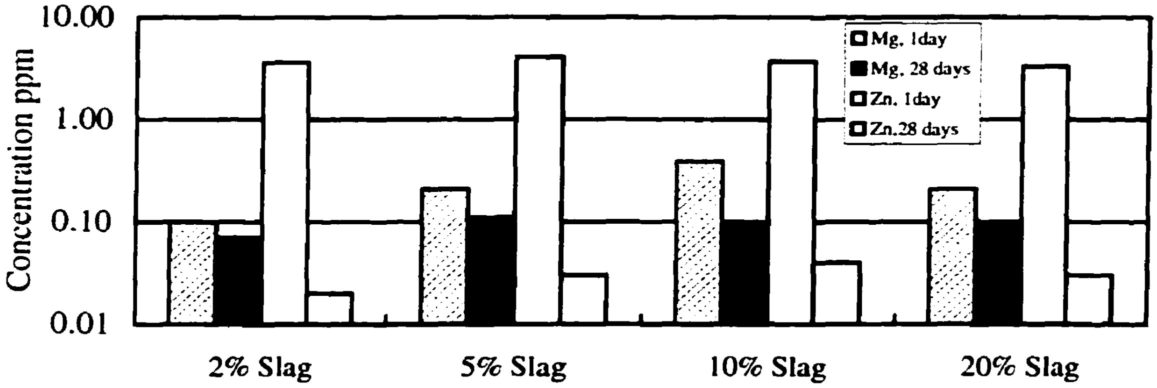


Figure 5.9:Mg & Zn Concentration In Pyrite Tailings& PC.

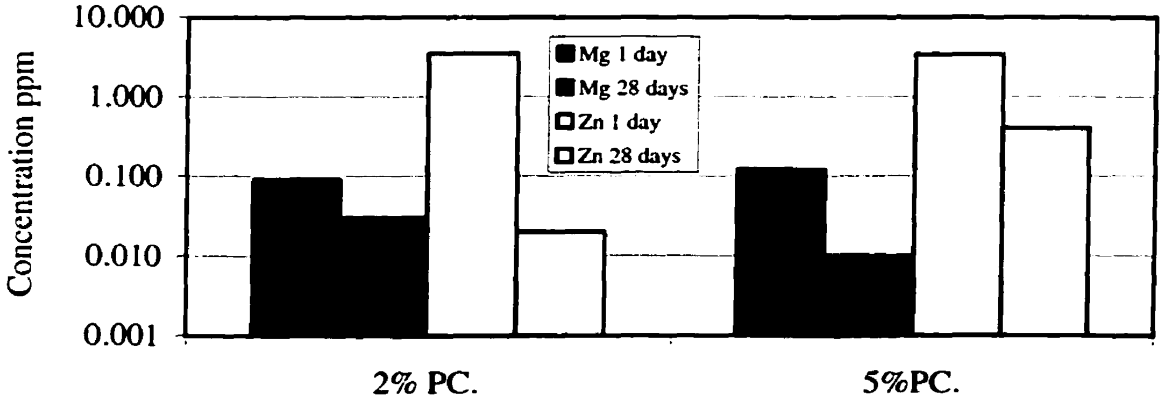


Figure 5.10:Ca Concentration In PyriteTailings& FA.

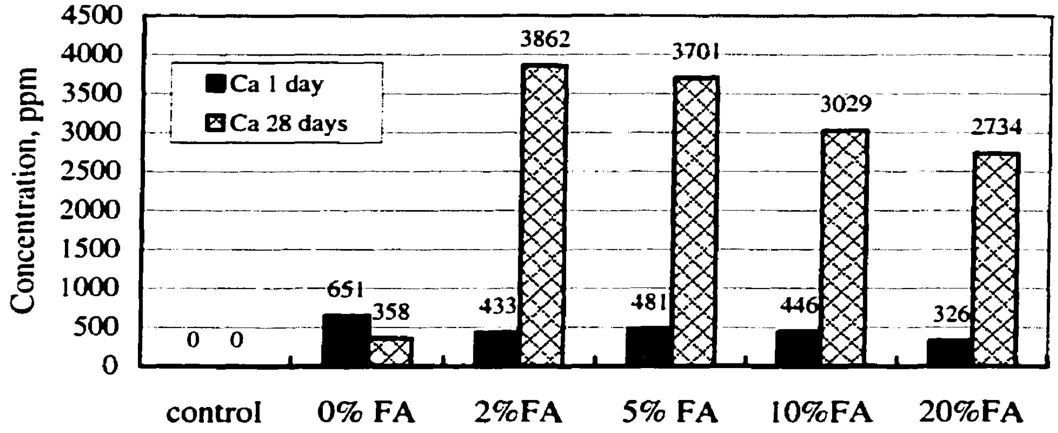


Figure 5.11:Ca Concentration In Pyrite Tailings& Slag

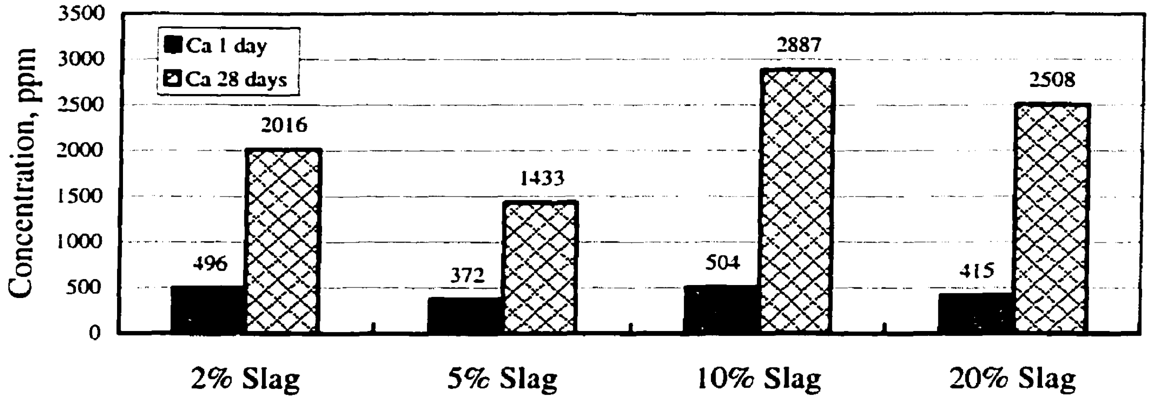
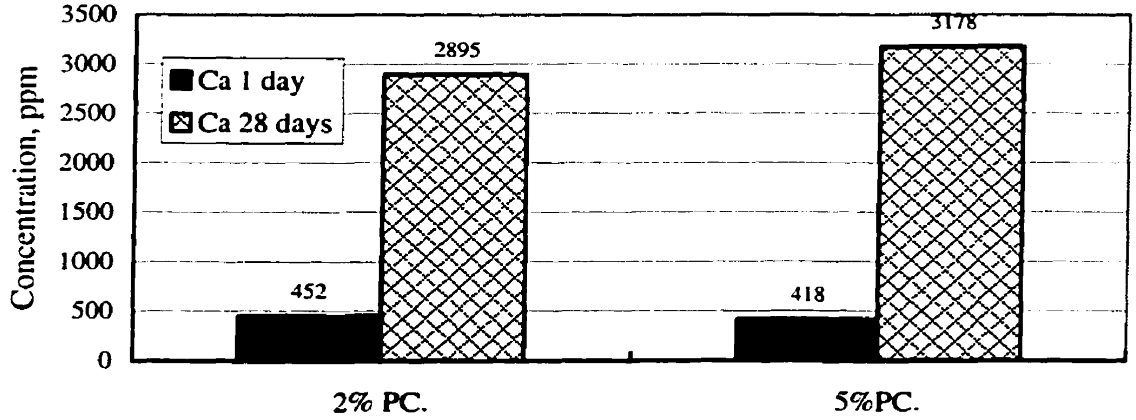


Figure 5.12:Ca Concentration In Pyrite Tailings& PC.



At the same time the Ca concentration declined with the addition of more fly ash. In the second group (pyrite tailings and the slag mixtures) and the third group (pyrite and cement mixture, no lime added), a trend almost similar to the t pyrite fly ash mixtures was noticed, and in all element concentrations and sulfates as well; although the copper slag contained considerable amounts of iron (40%) and less calcium (1%) compared with the fly ash.

5.2.2.2 Pyrrhotite Tailings

The result of the pyrrhotite tailings and fly ash, slag, and cement mixtures are shown in Figures 5.13 to 5.22. In pyrrhotite the control sample, about 1,062.4 ppm of sulfate, 500 ppm of Fe, 222 ppm of Ca, 138 ppm of Mg, and 0.25 ppm of Zn were released. This means that in the pyrrhotite sample less sulfate and Zn leached compared with the pyrite sample and more Ca and Mg. That is why a lesser amount of lime was required (3%) to optimize the pH level in pyrrhotite tailings. In pyrrhotite (fly ash, slag and cement) mixtures sulfated release decreased with the addition of the fly ash, slag and cement. However, with 2% of fly ash there was no significant decrease in the sulfate concentration but with the addition of 5% of fly ash the reduction was about 52% and remained steady with higher percentages of fly ash. In the case of the pyrrhotite-slag mixtures, the reduction of the sulfate was about 70% after 28 days. And the lower percentage of the slag did not show any significant effect in the sulfate immobilization. Pyrrhotite and cement mixed with sulfate released about 50% less than the original sample and that with 5% cement after 28 days of curing.

For other elements the same trend was repeated as in the pyrite tailings. This indicates that there was total immobilization for the Fe after 28 day, and an increase in the calcium concentration after 28 days of curing. Mg and Zn concentrations decreased to below 0.1 ppm after 28 days.

Figure 5.13: Sulfate Concentration In Pyrrhotite Tailings & FA Mixtures

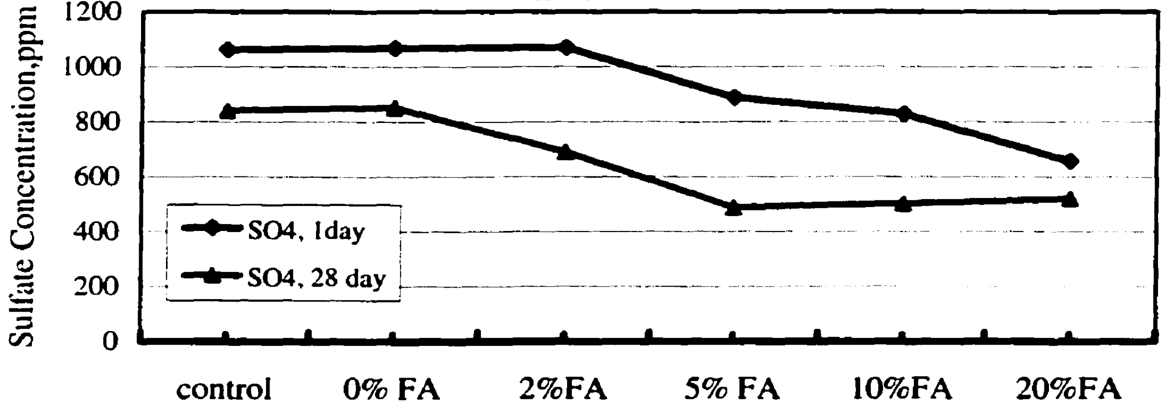


Figure 5.14: Sulfate Concentration In Pyrrhotite Tailings& Slag Mixtures

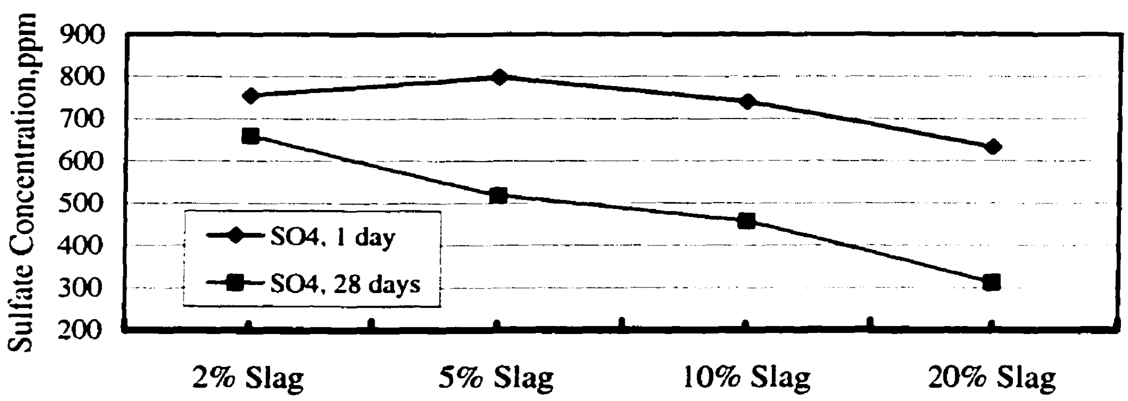


Figure 5.15: Sulfate Concentration In Pyrrhotite Tailings& PC. Mixtures

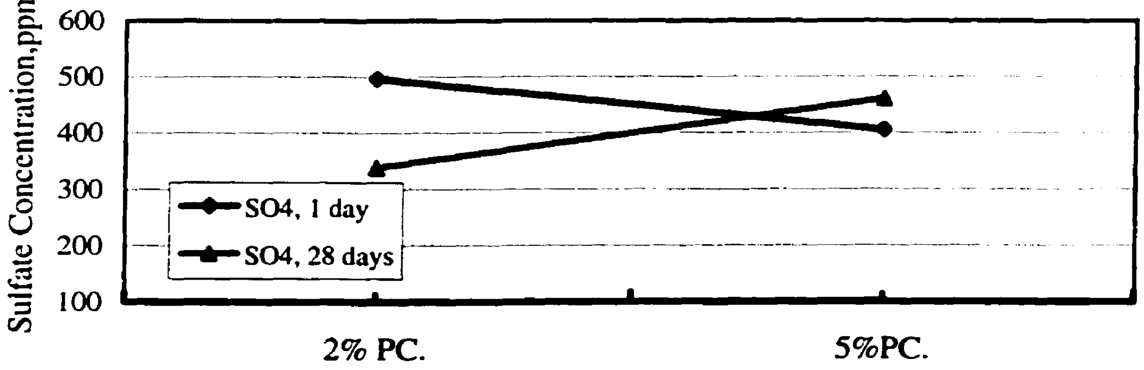


Figure 5.16:Fe Concentration In PyrrhotiteTailings& FA.

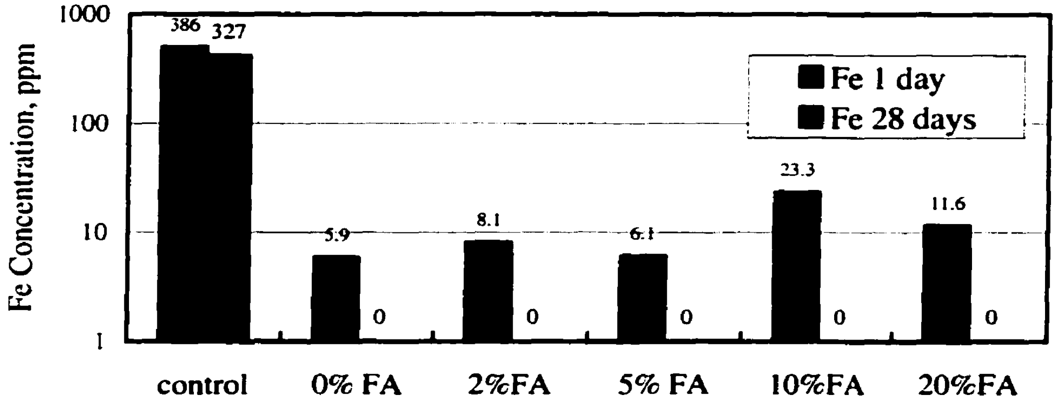


Figure 5.17:Ca Concentration In PyrrhotiteTailings& FA.

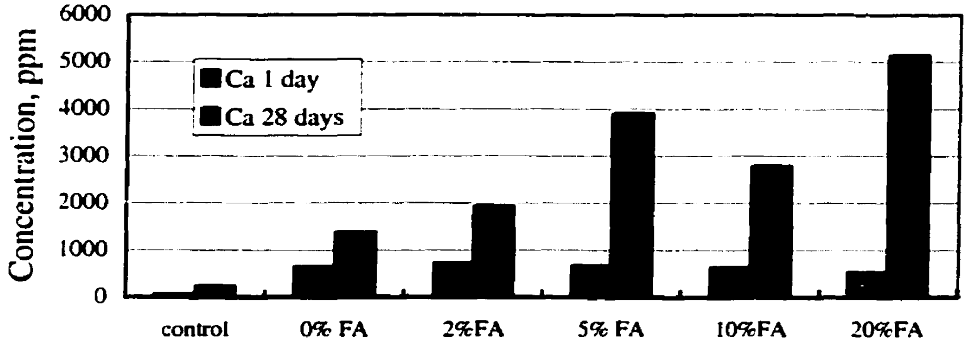


Figure 5.18:Ca Concentration In Pyrrhotite Tailings& Slag

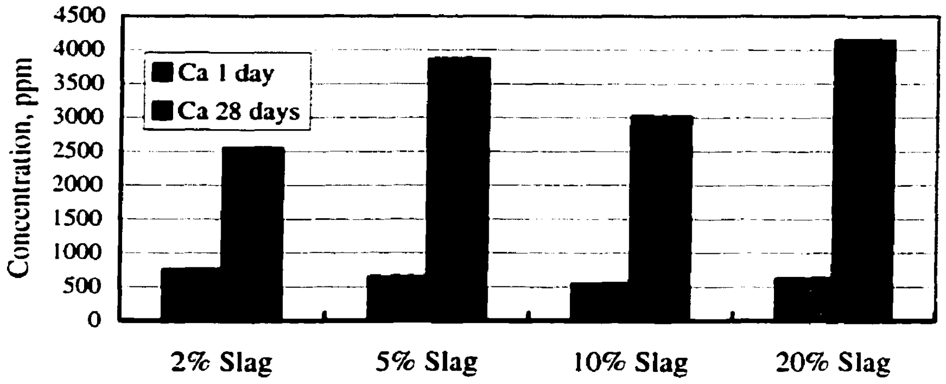


Figure 5.19:Ca Concentration In Pyrrhotite Tailings& PC.

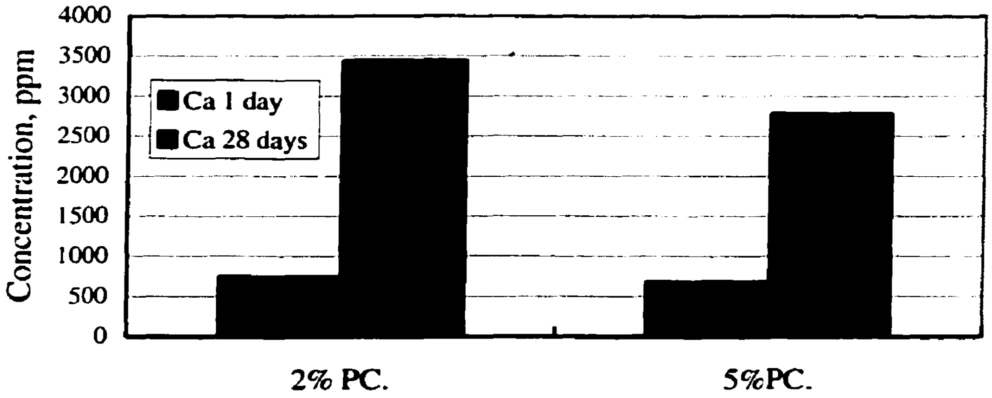


Figure 5.20:Mg & Zn Concentration In PyrrhotiteTailings& FA.

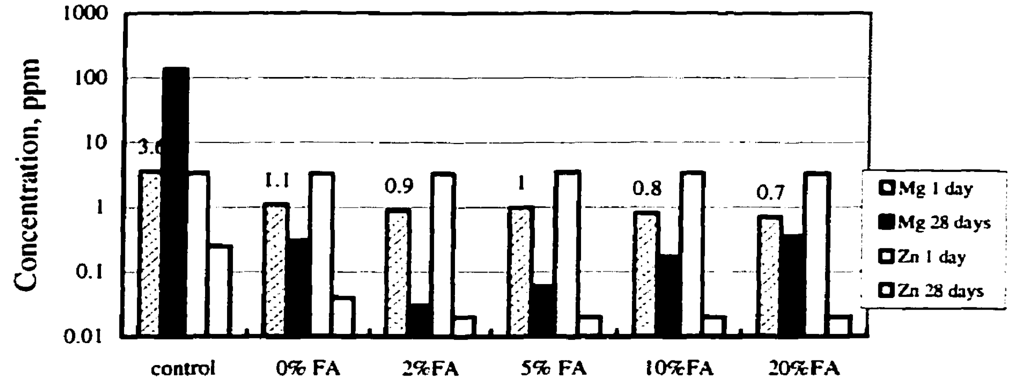


Figure 5.21:Mg & Zn Concentration In Pyrrhotite Tailings& Slag

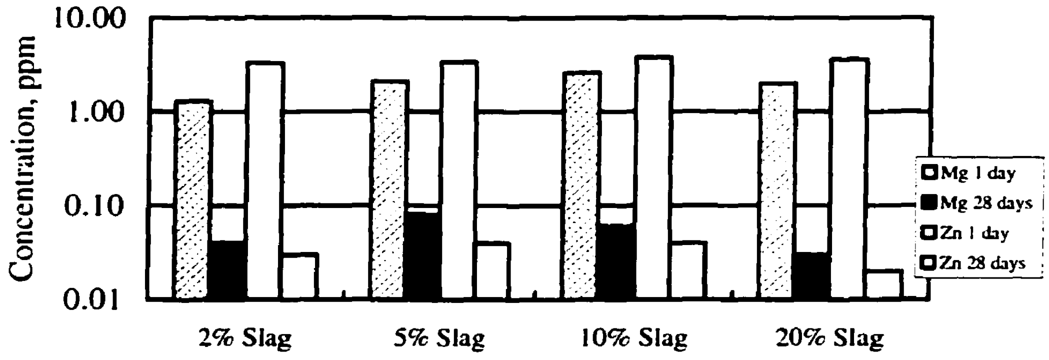
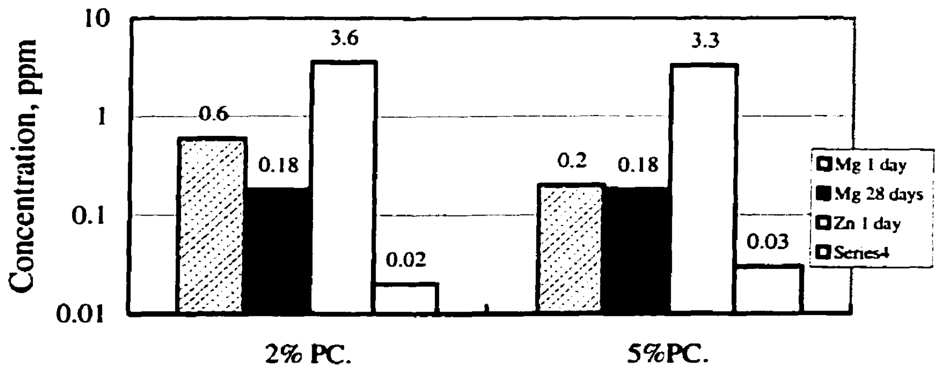


Figure 5.22:Mg & Zn Concentration In Pyrrhotite Tailings& PC.



5.3 Physical Tests

5.3.1 Unconfined Compressive Strength (UCS)

The need to dispose large amounts of mill tailings often poses serious environmental problems. The use of mill tailings as aggregates for cemented backfill or the disposal of the tailings as in the tailings ponds, usually require serious investigation as to the mechanical and physical properties to determine the suitability of the treated waste to a given application or another. In the meantime fly ash and slag both are industrial solid wastes and can be utilized as soil stabilizers (Chu et al., 1993). In this project the UCS test combined with different methods was used to evaluate the mechanical and physical property of the treated tailings, and the solidification process which took place with the addition of different binders. The result of the UCS test for the pyrite and pyrrhotite tailings with different percentages of fly ash, slag and cement for 1 and 28 days of curing time are presented in Figures 5.23 to 5.30.

5.3.1.1 Tailings/Fly ash Mixtures

The result in Figures 5.23 and 5.29 show the effect of fly ash type C in the strength development of pyrite tailings after 1 and 28 days of curing. The mixtures gained some strength with addition of 2% fly ash after 28 days up to 52 kPa and the strength continued to increase with addition of 5, 10, and 20% of fly ash and up to 197 kPa. This indicates that the strength increased by about 73% with the increase of fly ash content from 2% to 20%. It was also noticed that the control sample with no lime or fly ash did not develop any strength. Since in general the compressive strengths of ash treated materials are dependent upon moisture content at the time of compaction, strict moisture control is required (Ferguson, 1993).

The results of UCS for the pyrrhotite tailings and the fly ash are presented in Figures 5.26 and 5.30. Based on the results, comparing the pyrite/fly ash mixture, pyrrhotite/fly ash mixture, in general, showed lower strength after 28 days of curing. The maximum

Figure 5.23:UCS, Pyrite Tailings& FA

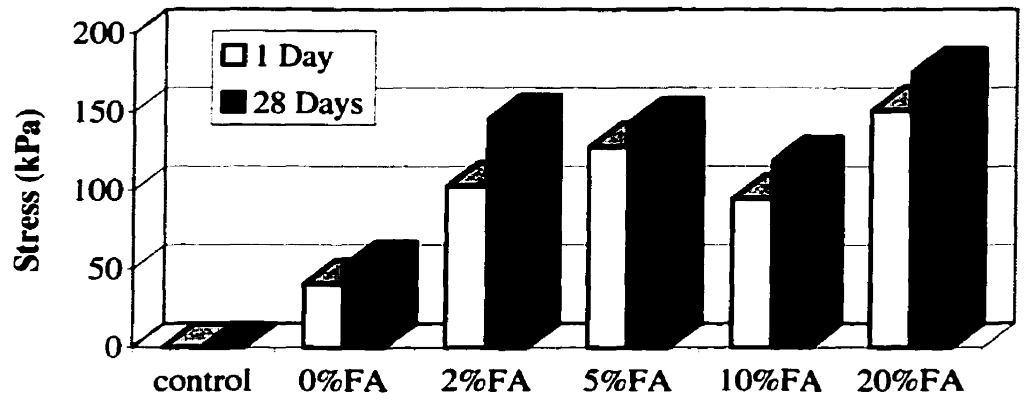


Figure 5.24:UCS, Pyrite Tailings& Slag

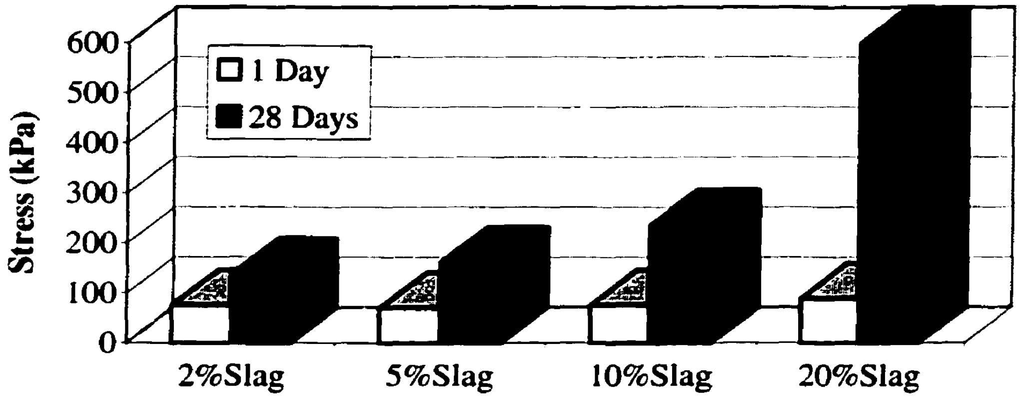


Figure 5.25:UCS, Pyrite Tailings& PC.

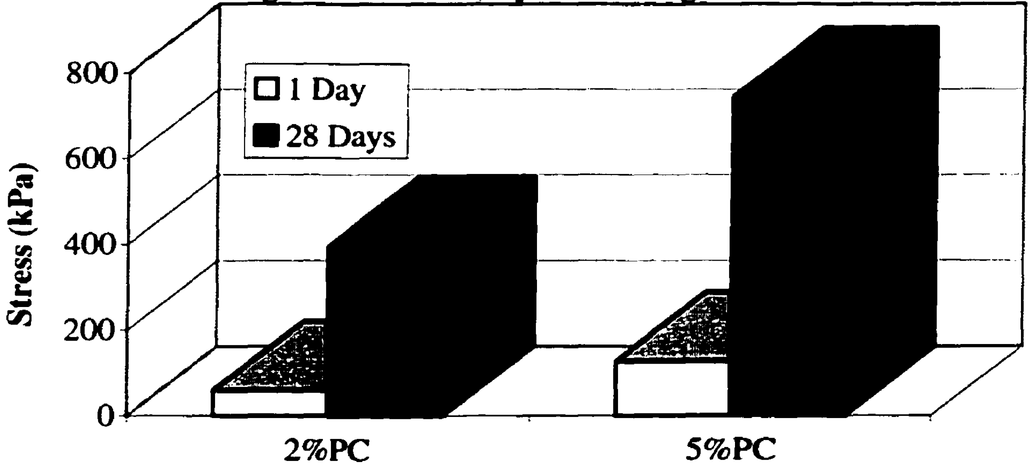


Figure 5.26:UCS, Pyrrhotite Tailings & FA

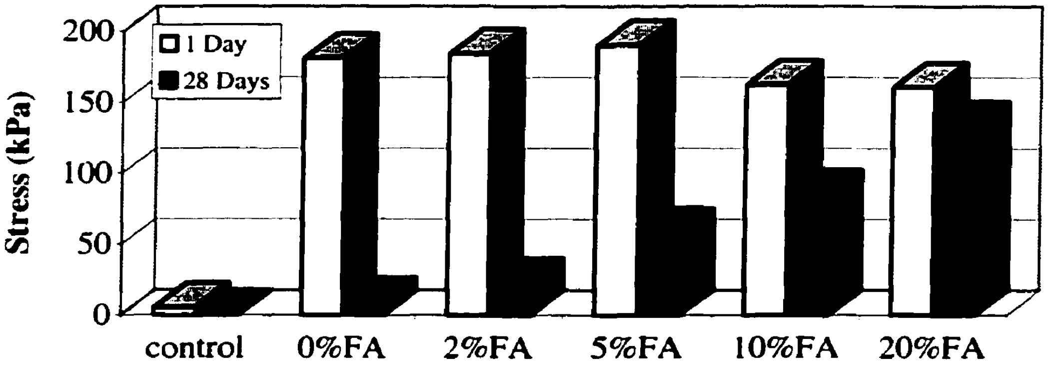


Figure 5.27:UCS, Pyrrhotite Tailings & Salg

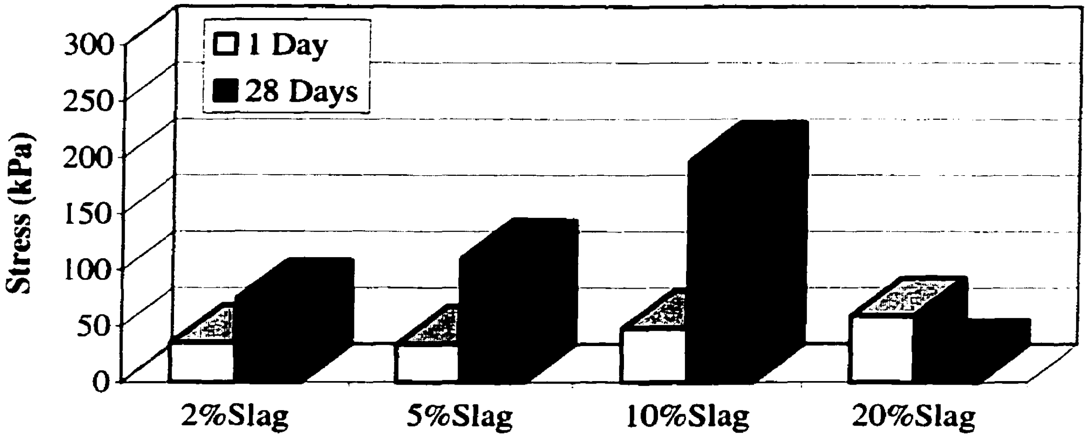


Figure 5.28:UCS, Pyrrhotite Tailings & PC.

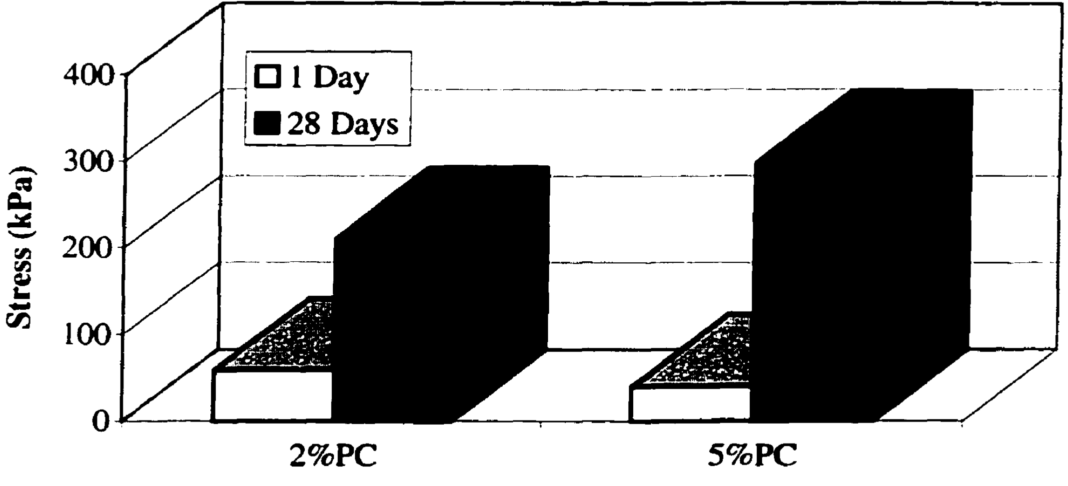


Figure 5.29:Compressive Strength Values for Pyrite Tailings (28 Days)

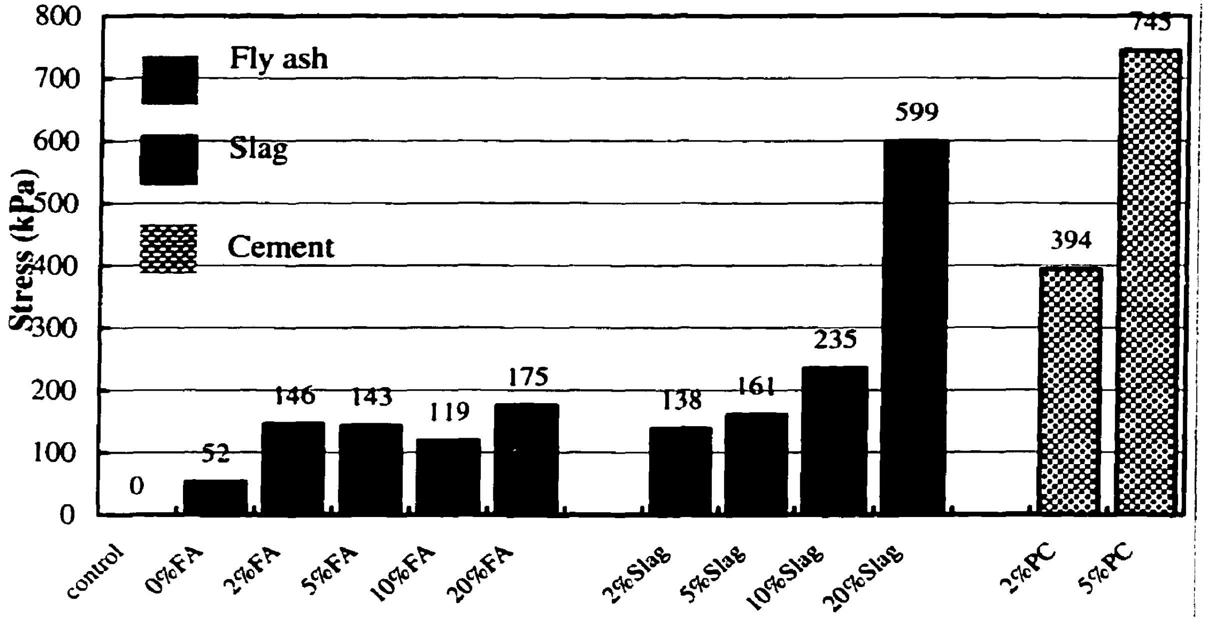
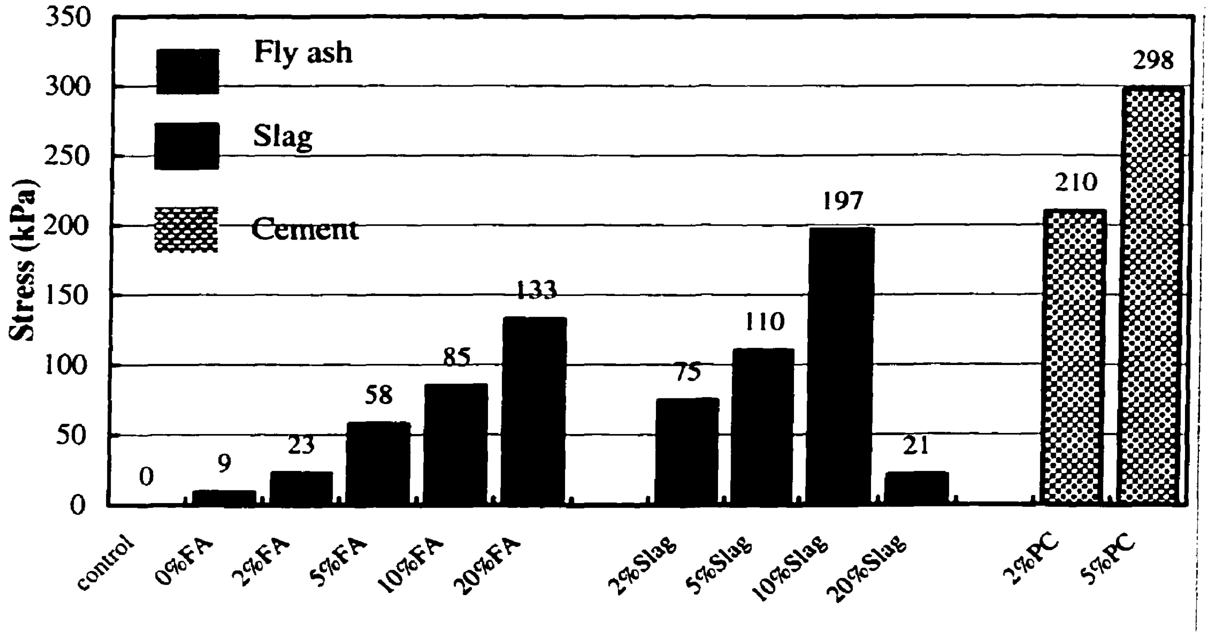


Figure 5.30:Compressive Strength Values for Pyrrhotite Tailings (28 Days)



strengths for 2%, 5%, 10% and 20% fly ash with the pyrrhotite tailings were 9, 23, 58, 85 and 133 kPa, respectively. The higher strength values gained after 1 day of curing time is a clear indication of the effect of the water content in the strength development. As the type of the failure after 1 day is more elastic compared with the failure type after 28 days (which is a brittle failure) and also this phenomenon could be attributed to the formation of gypsum. Also, it was noticed that, some samples lost some strength with the addition of fly ash. However, there is a trend after the 28 days indicating that the strength increased with the increase of fly ash content in the tailings. Studies have shown that fly ash stabilized soils continue to gain significant strength at a steady rate for at least 90 days.

Beside the above explanation the effect of the grain size distribution of pyrrhotite tailings (about 80% pass # 270 sieve) needs to be considered in the strength development compared to pyrite tailings (20% pass # 270 sieve).

5.3.1.2 Tailings/Slag Mixtures

Figures 5.24, 5.27, 5.29 and 5.30 show the result of UCS for the pyrite and pyrrhotite mixture with the slag. In pyrite/slag mixtures the strength increased gradually with the increase of the slag proportions up to 599 kPa having 20% slag. In the pyrrhotite/slag mixtures the UCS increased gradually with 2%, 5%, and 10% of the slag; however, the strength decreased to the lowest value by adding 20% of slag. This could be related to the moisture content of the mixture, considering that copper slag has low water absorption compared with the fly ash. Also sample remains contain more water when mixed with higher amounts of slag, and this may indicate that the optimum slag content for the pyrrhotite tailings in this condition is lower than 20%. Such values could be attributed to several factors such as the grain size of the pyrrhotite tailings, the optimization of the water content and the chemical composition of the slag (low calcium high iron content) comparing with the fly ash type C.

5.3.1.3 Tailings/Cement Mixtures

Because of economic reasons, most studies are based in finding ways to replace or reduce the cement content, especially in the backfilling design.

The high price of the Portland cement compared to the alternative binders such as fly ash and slag, in some cases the alternative binders (fly ash and slag) are used as percentage of the total binder to replace part of the total content of the cement. In this project the cement is added to the tailings mainly to examine the mechanism of the solidification of the cement in the tailings and to see the mineralogical changes associated with cement/tailings mixtures. Although it is known that cement is considered to be a strong pozzolan in comparison with the fly ash and slag. Only 2% and 5% percent were added to the tailings.

The UCS results for the tailings/cement mixtures are shown in Figures 2.25 and 5.28 to 5.30. The pyrite tailings with the Portland cement showed high values in compressive strength of up to 700 kPa with 5% of cement and about 400 kPa with 2%. The same percentages of cement with the pyrrhotite tailings showed lower UCS of 214 kPa with 2% Portland cement and 307 kPa with 5% cement. It should be noted that pyrrhotite tailings showed lower compressive strength values with the fly ash and slag mixtures. However, previous studies indicate that the strength of Portland cement/tailings mixtures increases with time and cement content (Ford, 1978).

5.3.2 X-Ray Diffraction

5.3.2.1 Mineralogical Changes in Pyrite Tailings

Most of the commercial inorganic (cement, Fly ash, and Kiln dusts) material used in solidification process. These materials solidified by very similar reactions and which have been thoroughly studied in connection with the Portland technology used in making concrete. While the pozzolanic reactions of the processes using fly ash and kiln dusts are not identical to those of Portland cement, but the general reactions are similar. The combination of three oxides SiO_2, CaO +MgO and Al_2O_3+Fe_2O_3, (all these reagents have the same active ingredients as far as solidification reactions are concerned), expresses the essential composition of any of these materials, even though the actual compounds are not all simple oxides, but more complex silicates and aluminates in many cases (Conner, 1990).

In these experiments the objective was to examine the mineralogical changes associated with the pyrite and pyrrhotite tailings when treated with fly ash, slag and cement and to observe what type of minerals were formed with each combination. Some minerals and oxides are believed to be major in the solidification process such as silicates, aluminates and calcium silicates.

In the control sample for pyrite tailings, the dominated minerals are quartz (SiO_2) in 2θ (2-theta) value 27° with intensity of 100% and pyrite at 2θ value of 31,33,56° with an intensity about 50%, a trace of Gismondine ($Ca\ AL_2Si2O_8 \cdot 4H_2O$) at 2θ value of 20.9° and also a trace of Moganite (SiO_2).

By the addition of 5% lime and 5% fly ash to the pyrite tailings some changes were observed. The pyrite mineral intensity increased to about 100%, the same as the intensity of the silicates, which increased to 100%. After 1day of curing, the intensity of pyrite decreased to about 50%, and in the meantime several new minerals appeared, such as Kehoeite in 2θ values 40.5°, 56.2°, and 26.5°, with intensity of 100% and the mineral Ettringite ($Ca6\ Al_2\ (SO_4.SiO_4.CO_3)3\ (OH)\ 12\ .26H_2O$) in 2θ values of 9.09°, 15.773°, 22.898° and 34.975°, and from the same group of Ettringites and silicates other minerals were noticed in the X-ray results, such as Sturmanite, Muscovite and Nemite. In 28 days there were no noticeable new minerals that appeared, but the intensity of some silicates and ettringites in particular increased to 67%. By increasing the amount of the fly ash to 20% the same minerals as in 5% fly ash were observed as in the X-ray result, however the only change in the result after 28 which was a decline in the pyrite and ettringite intensity.

The pyrite/slag mixture also having the addition of 5% slag showed several changes compared with the original composition of the tailings which was similar to a certain extend to the tailings/fly ash mixtures. Some of the new minerals found after one day of curing in the slag/pyrite mixtures were: gypsum $CaSO_4$, calcite $CaCO_3$ with intensity less than 50%. The pyrite and the quartz still have the highest peaks, but, after 28 days of curing there is a reduction in these new minerals intensities were less than 25%. With 20% of the slag added to the pyrite the result after one day is similar to the one obtained after one day for 5% slag but in 28 days the intensity of the minerals such as

Nimite, Moscovite, Ettringite, and Sturmanite was increased, and at the same time the intensity of the pyrite peaks declined to about 50%.

The pyrite/cement mixture examined in the mixture contains 5% of Portland cement after one day. The X-ray results indicated the formation of new minerals beside the quartz and the pyrite. These minerals are: Gosmondine (Ca AL_2Si2O_8. $4H_2O$), Sturmanite $Ca_6Fe_2(SO4)_2$ $(OH)_{12}$ 26 H_2O, ettringite (Ca6 Al_2 $(SO_4.SiO_4.CO_3)3$ (OH) 12 $.26H_2O$) in 2θ values of 9.09°, 15.773°, 22.898° and 34.975°, CaCO3, Bontonite and Paraspurrite Ca_5 $(SiO_4)2CO_3$, although the intensity of most of these minerals after one day of curing is less than 50%. After 28 days there is increase of up to 50%, and the quartz and pyrite have a higher intensity at about 100%.

5.3.2.2 Mineralogical Changes in Pyrrhotite Tailings

In the control sample for the pyrrhotite tailings, the mineralogy is mainly dominated by the presence of the pyrrhotite (Fe_7 S_8) mineral in several forms. These peaks appear in 2θ values of 30°, 32°, 44°, 54° and also the samples contain traces of iron oxides such as magnetite (Fe_3O_4) and Magesioferrite ($MgFe_2O_4$) and Trevorite-ferroan (Ni, Fe) Fe_2O_4.

By addition of only 5% of lime to the pyrrhotite tailings there are no noticeable changes in the X-ray result beside the shifting of some pyrrhotite peaks, with a decrease in some of them and an increase in others. With the fly ash present in the system (10%) there are insignificant changes in addition to the formation of Gismondine (Ca AL_2Si2O_8. $4H_2O$). However, in 28 days of curing, calcium aluminum oxide (Ca Al_2O_4) was formed. The same types of minerals were formed in the pyrrhotite tailings when mixed with 5% and 20% of slag. The only change that occurred was the formation of gypsum (Ca SO_4 $2H_2O$), and an almost identical trend followed when 5% of Portland cement was added to the pyrrhotite tailings. Because of two tailings contained up to 60% pyrite and pyrrhotite minerals (according to the supplier's chemical analysis), it is difficult to make a conclusive judgment of the overall trends. It is clear that the formation and the appearance of new mineral and oxides, which did not exist in the original tailings, is the main reason for the redaction and immobilization of the sulfate and other elements (Fe, Mg, and Zn) tested by the TCLP test earlier. There is a possibility that other Microcharacterization such as Scanning Electron Microscopy and quantitative analysis that can provide more detailed information.

5.3.3 Freeze and Thaw

Durability testing evaluates the ability of materials to withstand environmental conditions such as freezing and thawing (ASTM D4842), wetting or drying for a number of such cycles, so that the material might withstand without failure. This is an indication of its physical stability. Other performance tests such as UCS, flexural strength and permeability can be conducted on the material after each cycle to determine the change in the performance due to climatic effects. These tests could help to obtain more detailed information about the effect of the climatic stress in the performance of the treated samples.

The data of the UCS test after a cycle of freeze and thaw for 28 days of curing are resented in Figures 5.31 and 5.32. The results of the pyrite/fly ash mixture showed an increase in strength from 137.7 kPa with 2% of fly ash to 306.06 kPa with 20% of fly ash (about 55%). Also there was an increase with the slag addition to the pyrite tailings from 212.9 kPa to 268.15 kPa, its was noticeable that the increase was not significant, but, at about 25% when the slag amount increased from 2% to 20%. The pyrite/cement mixtures under these conditions showed improvement in the strength from 309.31 kPa to 425.23 kPa with an addition of 2% and 5% of cement, respectively.

Pyrrhotite/fly ash gained some strength with 2% and 5% of fly ash (64.49 kPa, 99.15 kPa, respectively) at about 35%. Then, with the addition of fly ash the strength increased to 270 kPa with 10% fly ash (increased about 62% in the interval of 5% to 10%). When the fly ash amount was increased to 20% the strength dropped to 40 kPa. The pyrrhotite/slag mixture showed improvement in strength with the addition of slag up to 10% (strength gain is 194.48 kPa). Then again the strength decrease with the 20% slag added to 127 kPa. The pyrrhotite/cement mixtures gained strength under these conditions, the strength with 2% is about 50kPa and with 5% of cement the strength of the pyrrhotite improved to about 244.31 kPa. It is clear that the strength was changed as a result of climatic effects or due to the freezing conditions. The freezing could influence the hydration process of the pozzolans.

Figure 5.31:Compressive Strength Values for Pyrite Tailings (F&T Condition)

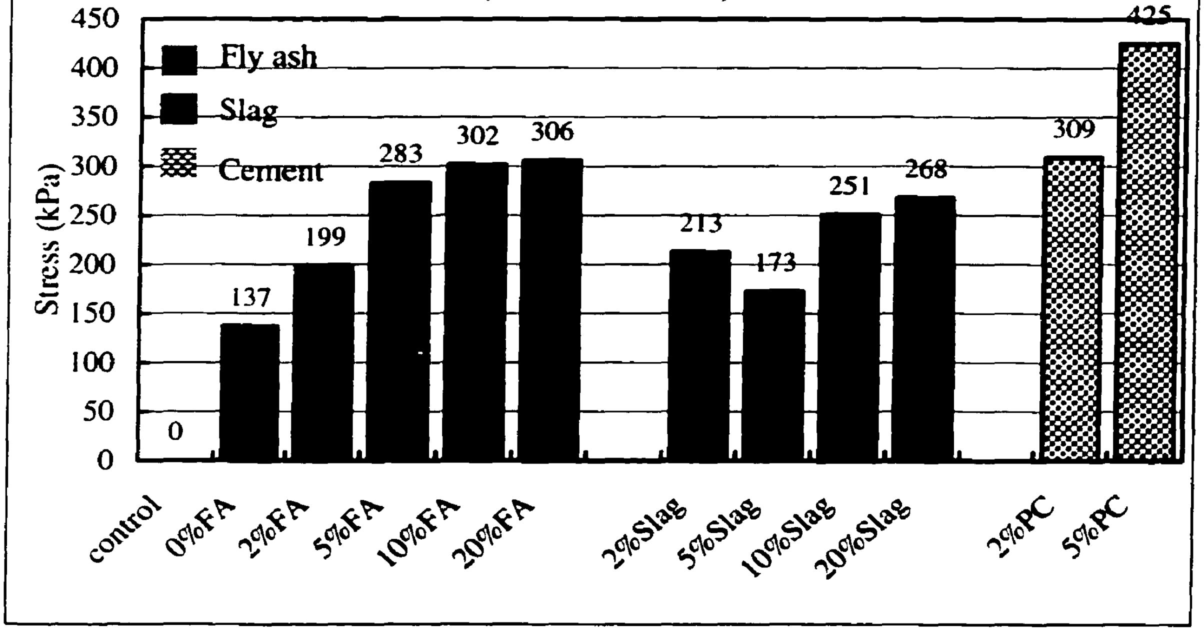
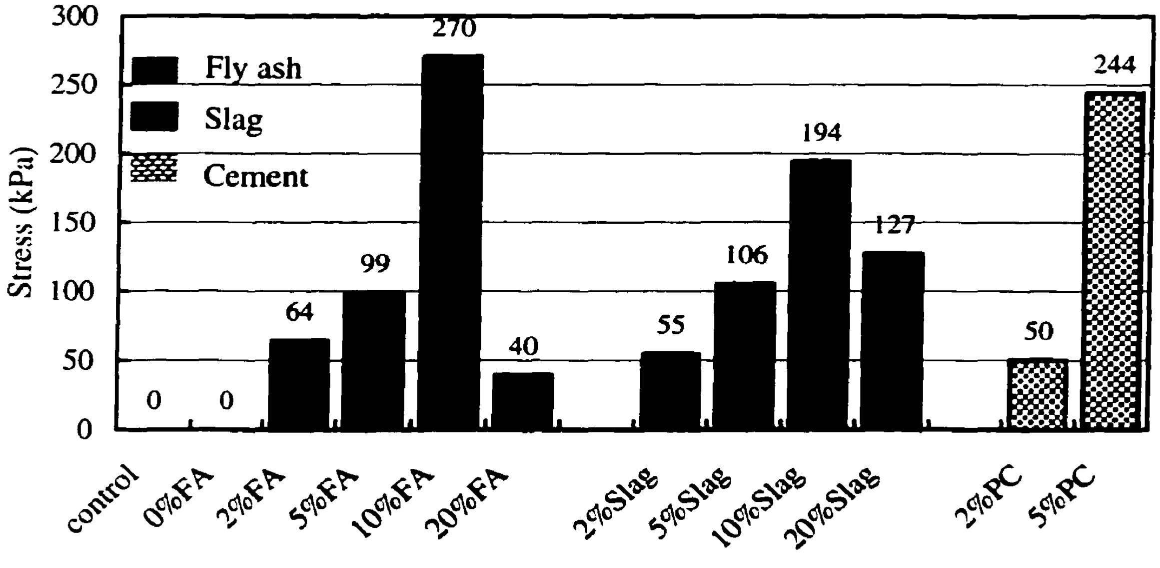


Figure 5.32:Compressive Strength Values for Pyrrhotite Tailings (F&T Condition)



In general, the pyrite tailings showed more stability under the freeze and thaw conditions than the pyrrhotite. As in the USC, this was due to the grain size distribution of the tailings. To achieve more accurate evaluation of the mixture's performance further investigation will be required, such as with x-ray and chemical analysis.

5.3.4 Permeability (Hydraulic Conductivity) Tests

Permeability is a measure of fluids passing through the tortuous pore structure of the waste or the treated waste. Typical values of stabilized wastes range from 10^{-4} to 10^{-8} cm/s (U.S.EPA, 1989). This can be compared to clay, which is typically less than 10^{-6} cm/s, where a value of $<10^{-5}$ cm/s is recommended for stabilized waste planned for land burial. A high permeability is not a great problem as the contaminates in the waste do not easily leach to the water (Means et al., 1995). However, in engineering application, the stabilized soil permeability is essential as in backfill technology, specifically in the hydraulic fills, where usually the fill has a moisture content of 30-40 wt. percent and must be dewater to around 20 wt. percent before being able to perform its ground support and operating role. When as much water is taken off, a significant quantity of water is removed by exudation and percolation, where both mechanisms are related to fill permeability. Also the permeability of the stabilized waste is relevant to some degree if it is used as a cover material.

According to Thomas (1978), permeability is a property unique to the porous medium and independent of the fluid flowing and hydraulic gradient, and permeability combined with the property of the porous medium and the fluid flowing. Although both permeability and percolation rates apply to the flow of a unique fluid at certain temperatures with the added restriction that the hydraulic gradient in the percolation case is taken as unity. For soils, which need to be compacted for use as a fill, laboratory permeability tests can provide valuable data, provided that the samples are prepared in an appropriate manner. For example, the permeability will depend upon the degree of compaction applied to the sample and whether the soil is compacted dry or wet. From the results it could be seen that there was a general reduction in the strength compared to the same mixtures when they were not subjected to the freeze and thaw conditions. It was observed that the overall performance of the fly ash/tailings is better than the performance of the slag/tailings mixture. This could be attributed to the ability of the fly ash to react and at the same time, to some degree, as a drying agent. Thus the fly ash absorbed and consumed the access of water in the mixture better than the type of the slag used in this case. Also it should be considered, the effect of the moisture content of the mixtures, especially when they are cured in different optimum moisture content. The field conditions should be reproduced as closely as practicable (Head, 1992).

The results in of the permeability tests as depicted in Figures 5.33 and 5.34 point to several changes concerning the permeability of the treated tailings. In general, for the pyrite tailings there is a reduction in permeability with the addition of both slag and fly ash. The control sample has a permeability coefficient (k) of $3*10^{-4}$ and with the addition of 2, 5, 10, and 20% of fly ash the reduction is $2.8 *10^{-6}$. The same tailings samples showed lower results with slag addition at permeability range of between $4*10^{-6}$ and $6.3*10^{-6}$ cm/s.

The pyrrhotite/fly ash combinations also showed a decrease in permeability, the original sample showed a permeability of $4.7*10^{-4}$ cm/s, and with the fly ash addition the permeability values decreased by an average of 85% to 90%. In the pyrrhotite/slag mixture there was a significant change in the permeability; it decreased by 90% from the untreated sample and the change varied from $2.1*10^{-5}$ to $2.0 *10^{-5}$.

The permeability for the cement/tailings was not measured in the project however the addition of Portland cement to these type of tailings is more likely to reduce permeability (Thomas, 1978). The general reduction in permeability could be attributed to the tailings, fly ash and slag grain size distribution as well as to an improvement in the overall physical properties of the mixtures.

Figure 5.33: Permeability Results for Pyrite Tailings

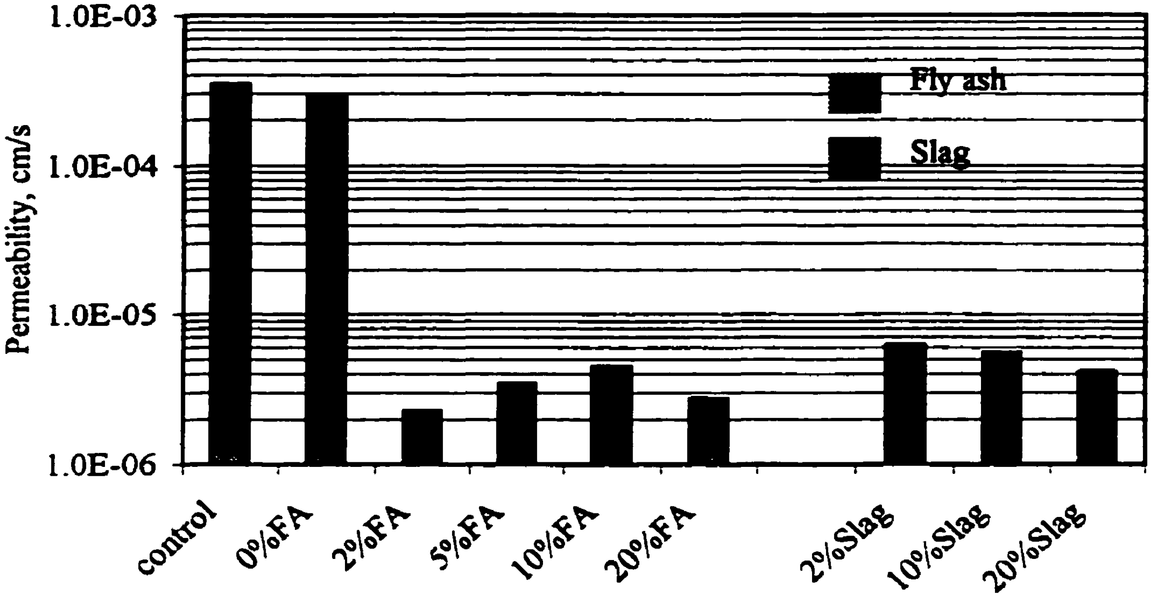
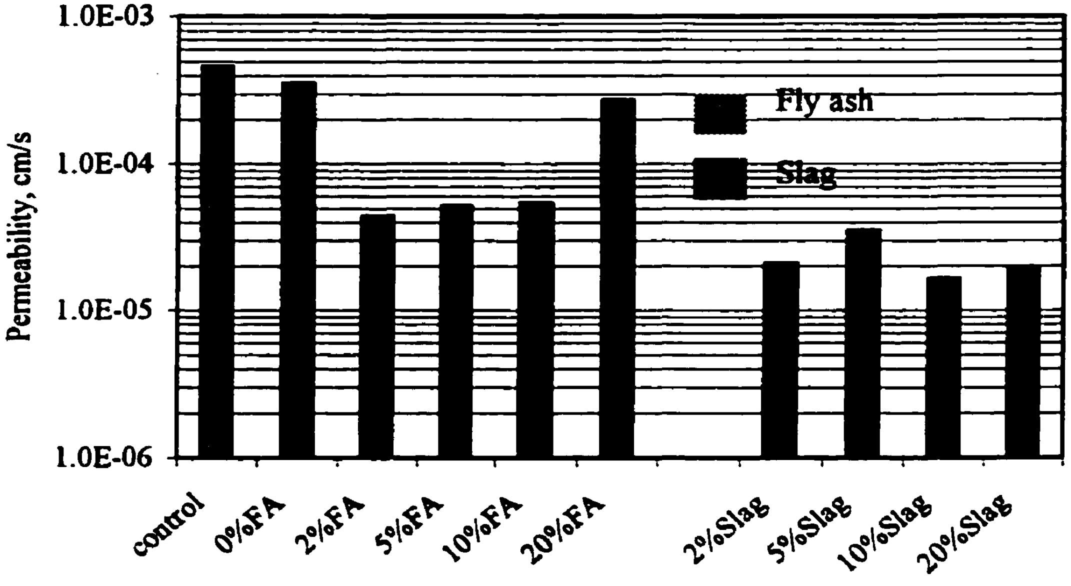


Figure 5.34: Permeability Results for Pyrrhotite Tailings



6.0 Conclusions and Recommendations

1) Conclusions

- Based on the results obtained from the several chemical analyses and physical testing for two types of sulfide rich- tailings (pyrite and pyrrhotite) which were treated with different variables of lime, fly ash and slag, the following conclusion can be drawn:

- Based on the elements analysis, lime-based treatment is effective in the significant reduction in the leachability for iron, magnum and zinc, in both type of tailings. In most instances, this reduction required only the addition of lime.

- The increase of fly ash and slag added to the tailings as a general trend decreased the sulfate concentration leached from mixtures, however the decrease was not substantial when high percentages of fly ash and slag were added compared to small percentages.

- Iron was fully immobilized with the addition of lime only after 28 days of curing, and the magnesium and the zinc concentration decreased to about 0.1 ppm after the same period of curing. That is an indication of the solidification process with time has effected the leachability of these elements.

- The lime concentration after 1 day of curing remained relatively low, however after 28 days of curing, a significant increase was observed and that could be attributed to unreacted lime or the formation of the gypsum ($Ca\ SO_4$), which is later disintegrated, releasing more calcium into the leachate or the extract.

- The treatment was effective in the improvement of all examined physical properties of the mixtures compared with untreated tailings (control samples). The unconfined compressive strength of the mixture increased with the addition of the binder percentage, with improvement in the permeability of the treated tailings.

- The treated material showed little deterioration in the durability tests (freeze and thaw) that could be related to the effect of the freeze in slowing the hydration of the fly ash and the slag. Therefor, more analysis was required to determine whether the deterioration can be attributed to only the water content (hydration) or to any other reaction.

- The type of the sulfide mineral (pyrite or pyrrhotite) in the tailings did not appear to make a tangible difference in the overall results; however, the difference may be related to the characterization of each type of tailings and its composition.

2) Recommendations

- A detailed quantitative analysis of the mineralogical composition of the treated and untreated tailings in combination with the x-ray analysis, and further analysis for other elements such as arsenic, copper, sodium, etc.

- Applying the treatment under different water content, and different lime percentages. Because solubility of the lime, pH, and the water content are related in a way that when more water added the pH tend to increase comparing to the same amount of lime with lesser water.

- A long-term investigation in the effectiveness of the treatment. Although the short-term investigation showed improvement in the chemical and physical properties of the tailings, the long-term stability should be studied, especially with regards to the sulfate attack, considering that these types of tailings contain over 60% of pyrite or pyrrhotite mineral.

- Optimization and formation of minerals and oxides such as silicates and ettringite which, according to many studies, are responsible for the improvement and stabilization of the treated wastes.

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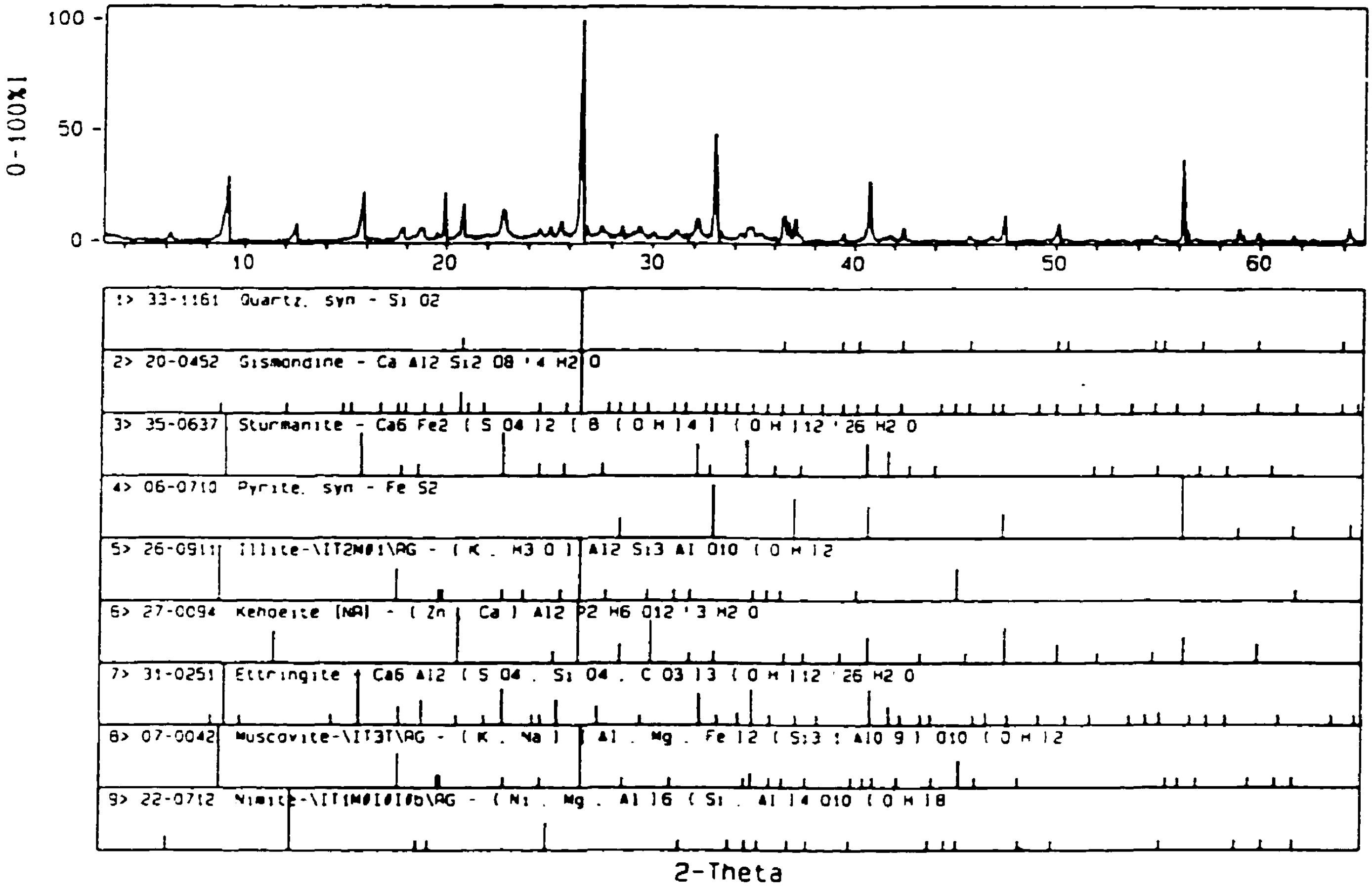
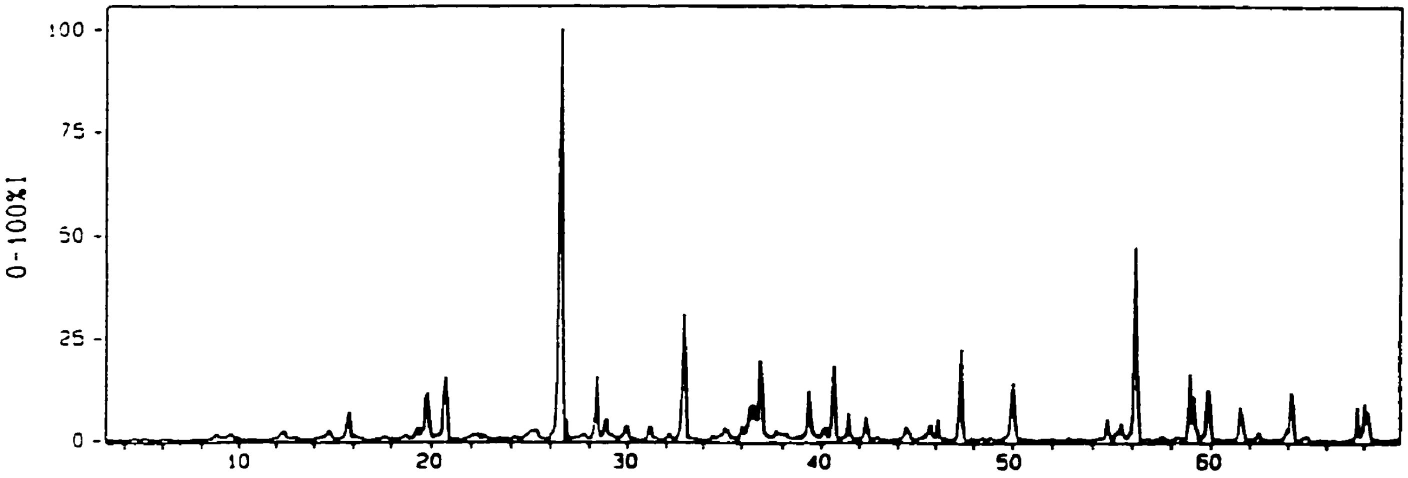
Appendix A

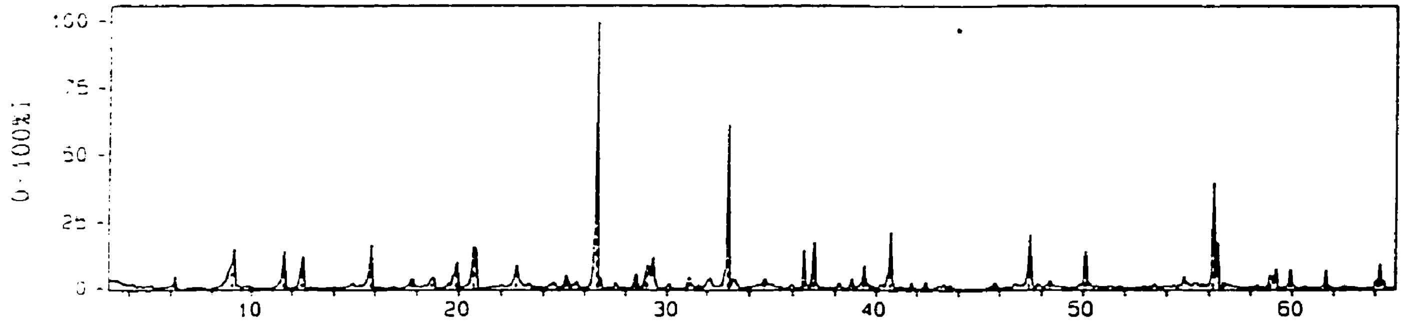
Appendix A

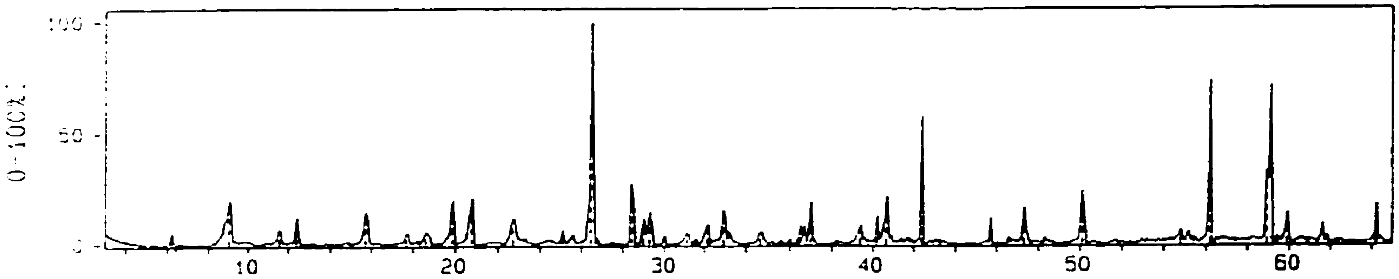
Detail mineral analysis for sample B1S4 (5% Lime and 5% Fly Ash) after 28 days of curing time.), using mineral analysis and search software JADE.

Pyrite Tailings, Sample B1S4, 5% Lime and 5% Fly Ash, 28 days




Pyrite Tailings, Sample B1S1(Control), 1 day


Pyrite Tailings, Sample B1S2, 5%Lime, 0%FA, 1 day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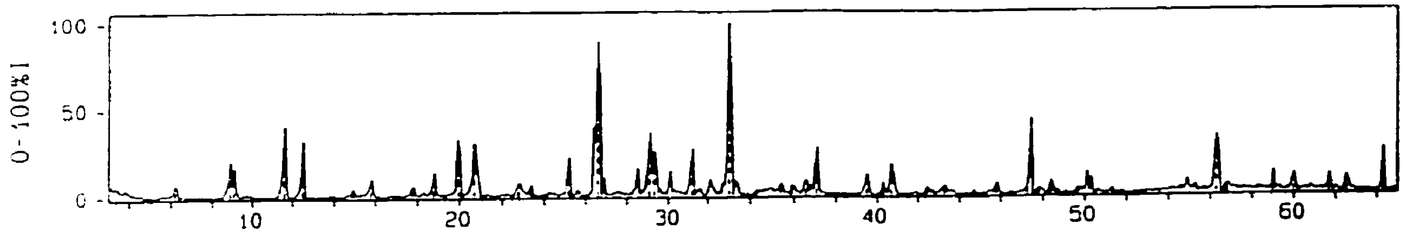
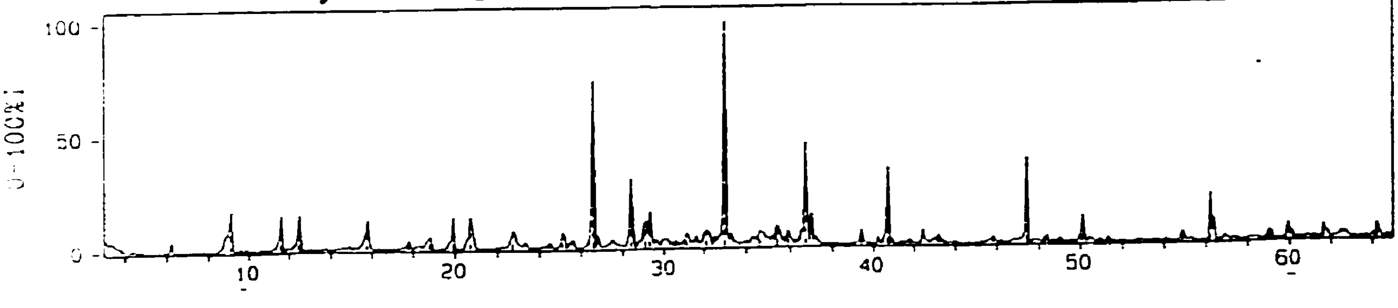
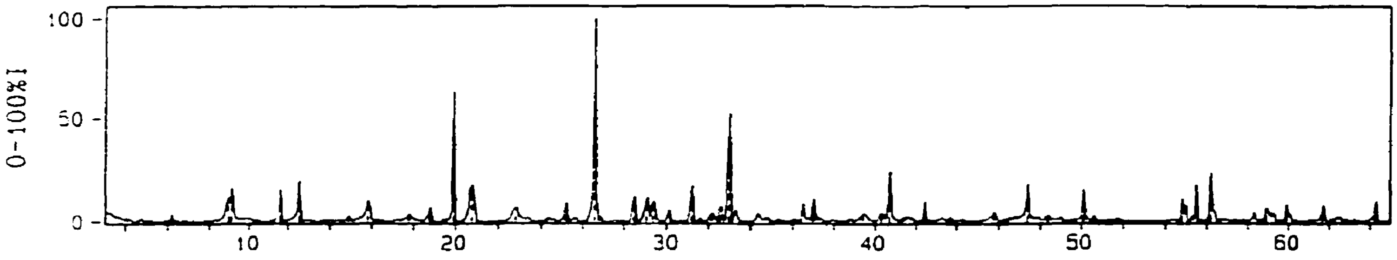
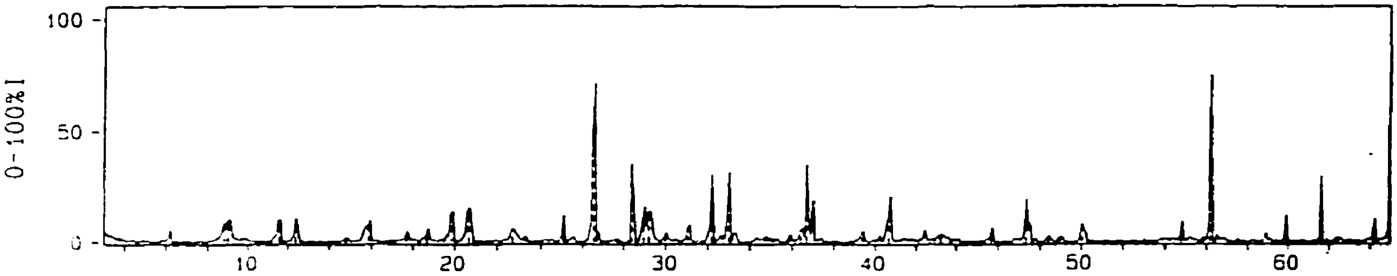

Pyrite Tailings, Sample B1S5, 5% Lime , 10%FA, 1 day


Pyrite Tailings, Sample B1S6,5% Lime, 20% FA, 1day

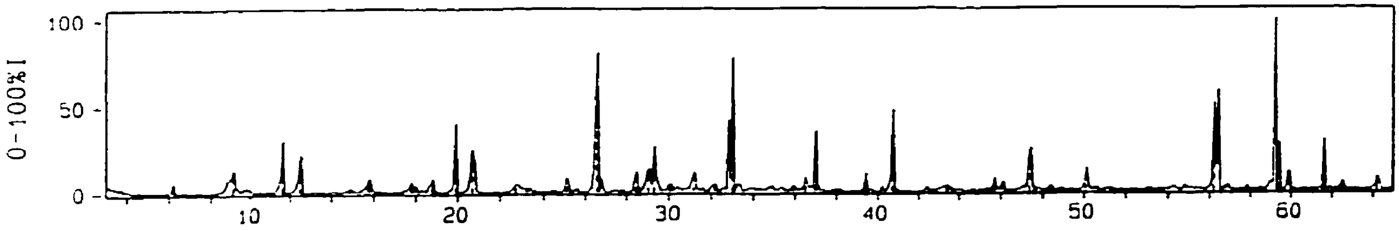
Pyrite Tailings, Sample B2S4, 5%Lime, 5% Slag, 1day



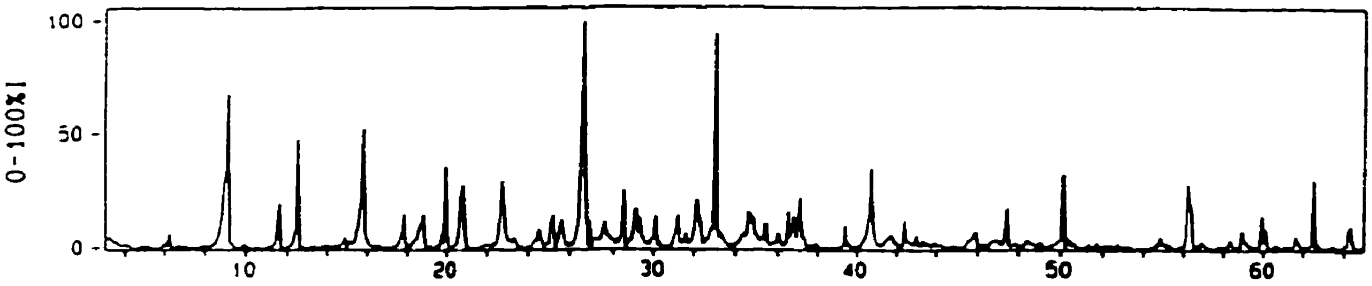
Pyrite Tailings, Sample B2S6, 5% Lime, 20% Slag, 1 day



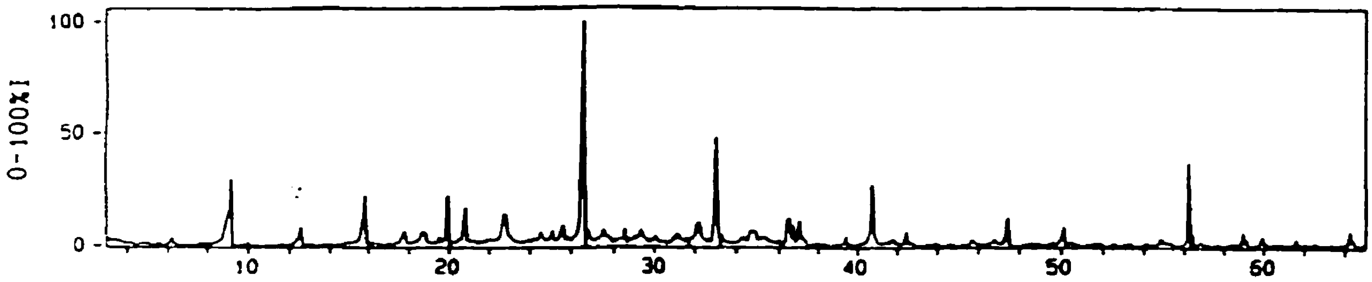
Pyrite Tailings, Sample B3S4, 5% Lime, 5% P.C., 1 day



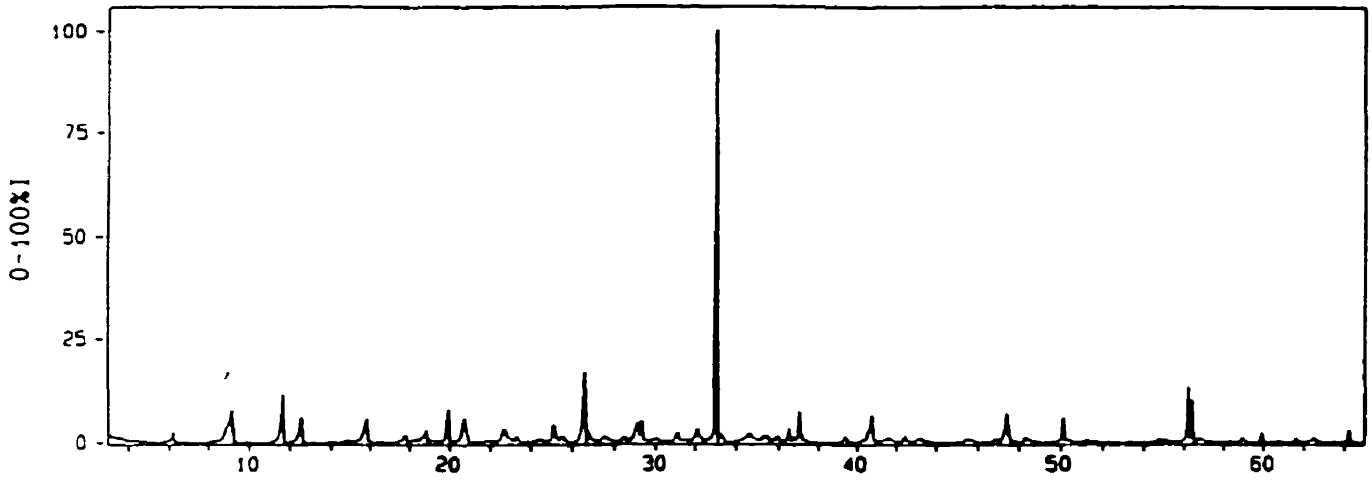
Pyrite Tailings, Sample B1S2, 5%Lime, 0%FA, 28 days



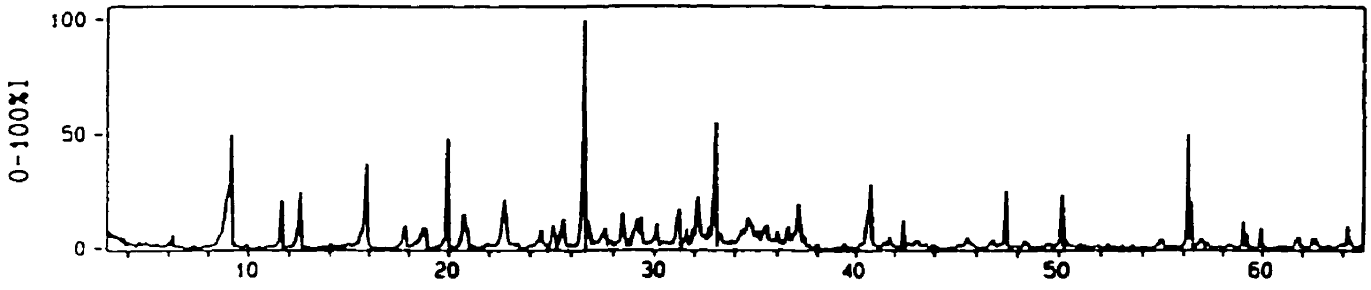
Pyrite Tailings, Sample B1S4, 5%Lime, 5% FA, 28 day



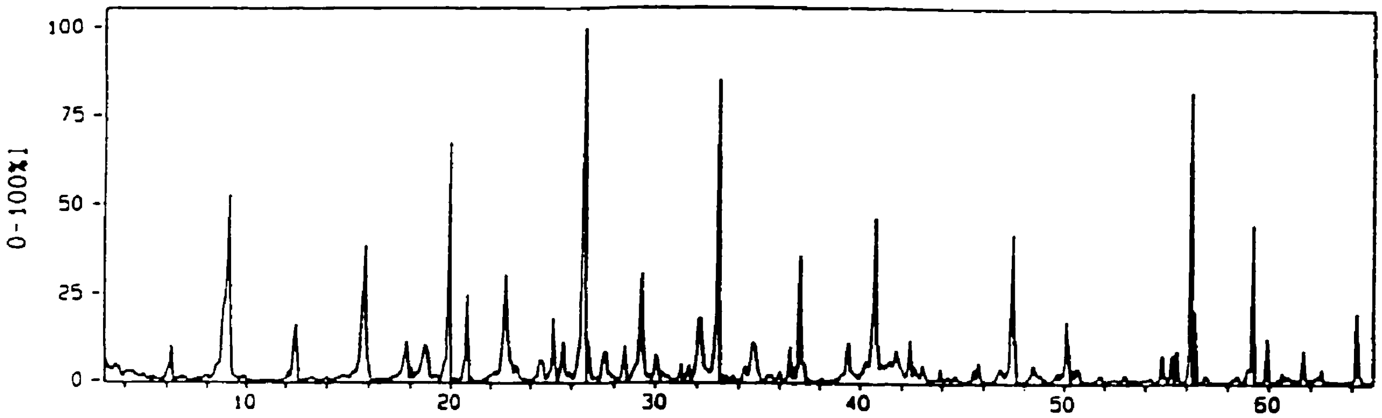
Pyrite Tailings, Sample B1S5, 5% Lime, 10%FA, 28 days



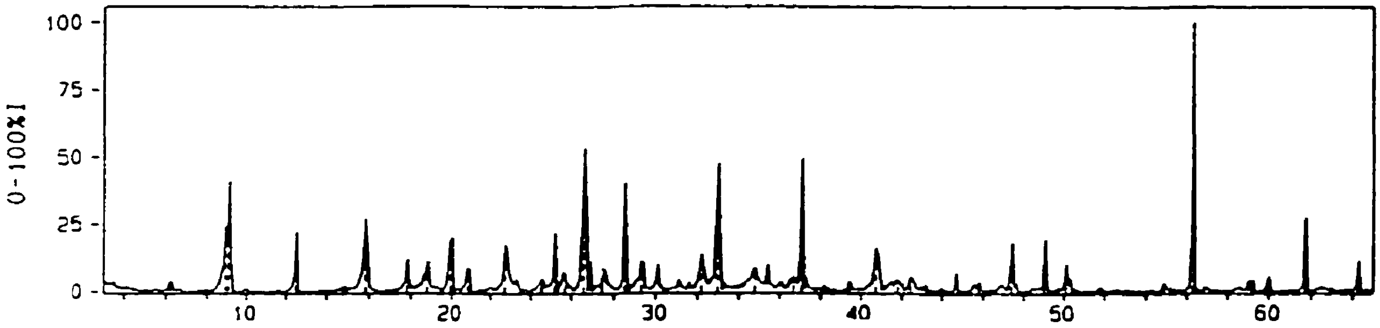
Pyrite Tailings, Sample B1S6, 5% Lime, 20% FA, 28 days



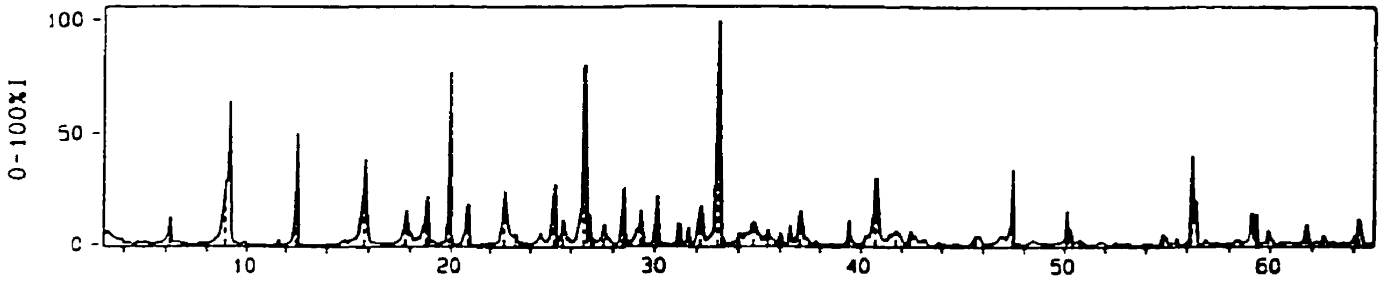
Pyrite Tailings, Sample B2S4, 5%Lime, 5% Slag, 28 days



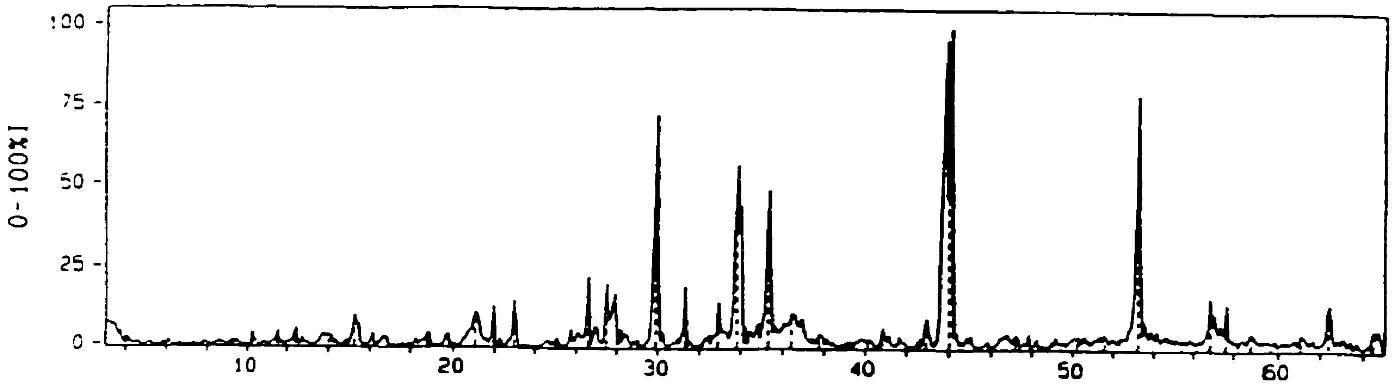
Pyrite Tailings, Sample B2S6, 5% Lime, 20% Slag, 28 days



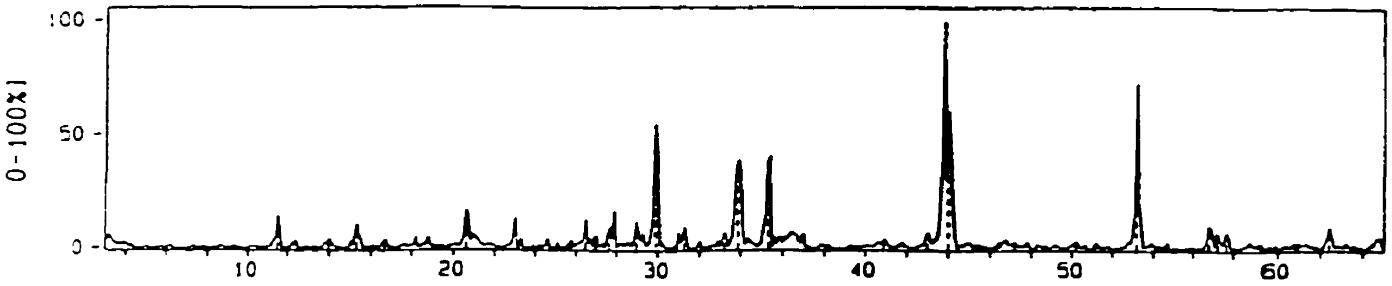
Pyrite Tailings, Sample B3S4, 5% P.C., 28 days



Pyrrhotite Tailings, Sample B4S1 (Control), 1 day

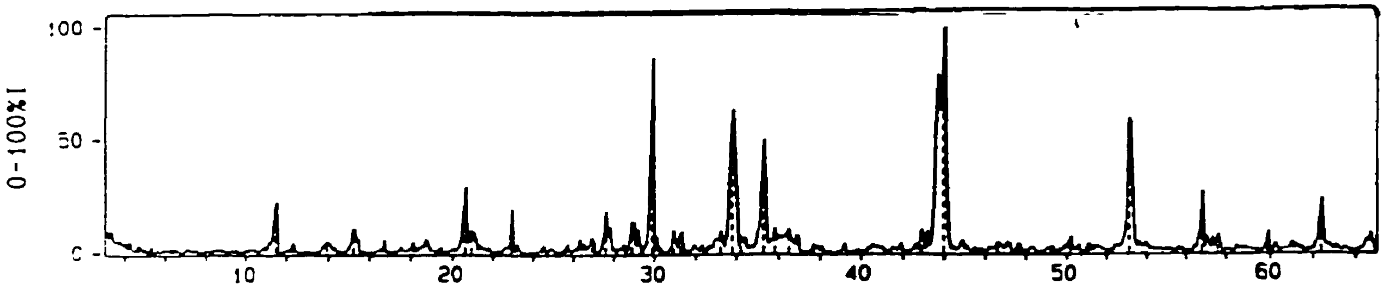


Pyrrhotite Tailings, Sample B4S2, 3%Lime, 0%FA, 1 day

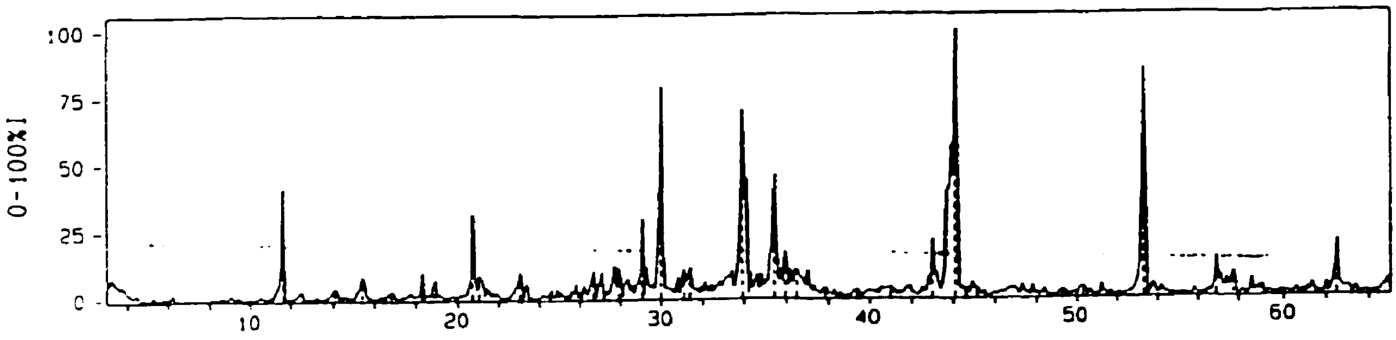


Pyrrhotite Tailings, Sample B4S4, 3%Lime, 5% FA, 1day

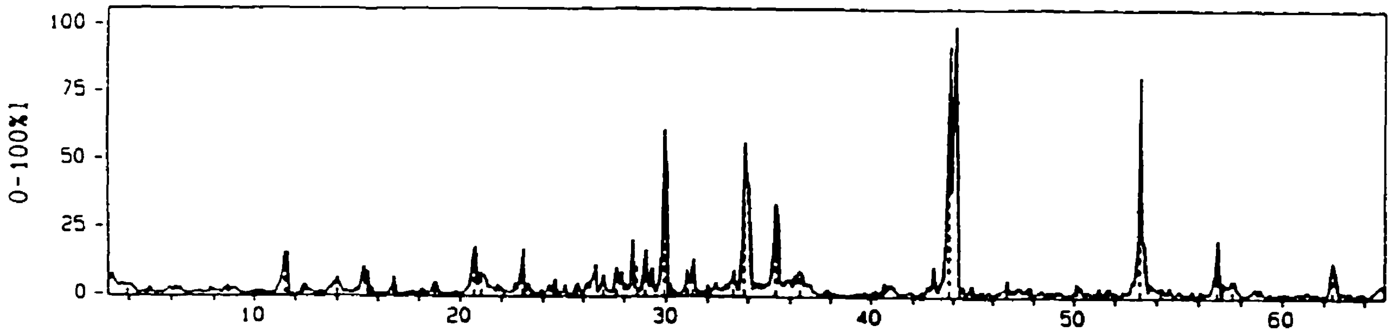
Pyrrhotite Tailings, Sample B4S5, 3% Lime, 10%FA, 1 day



Pyrrhotite Tailings, Sample B4S6, 3% Lime, 20% FA, 1day




Pyrrhotite Tailings, Sample B5S4, 3%Lime, 5% Slag, 1day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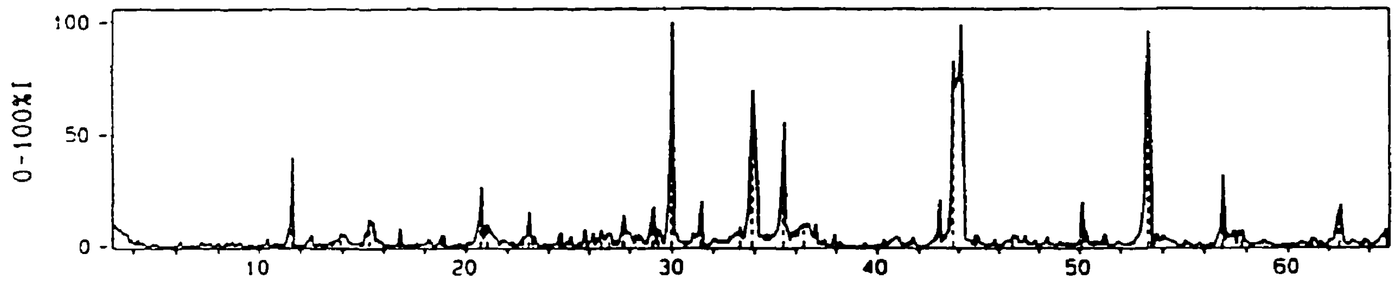
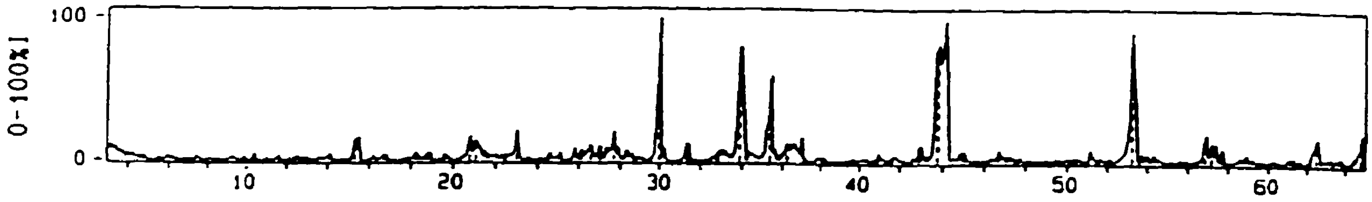
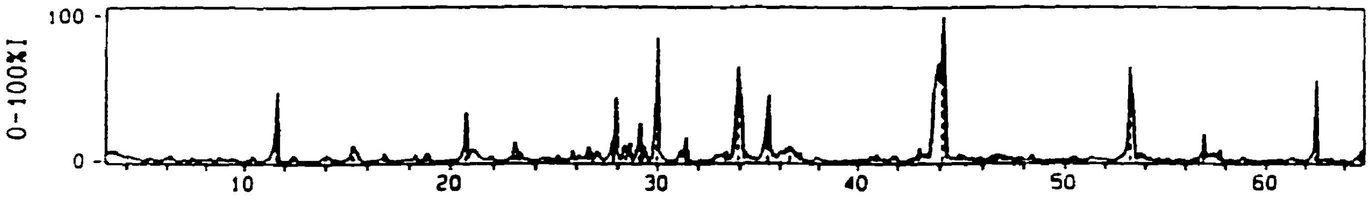
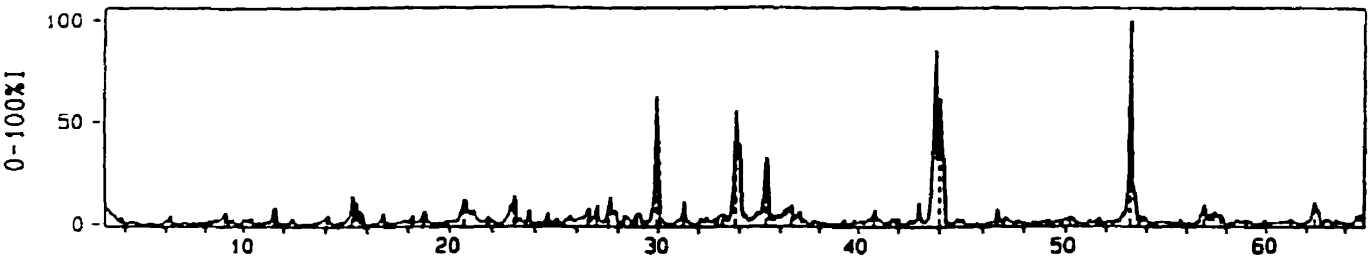

Pyrrhotite Tailings, Sample B6S4, 5% P.C., 1day



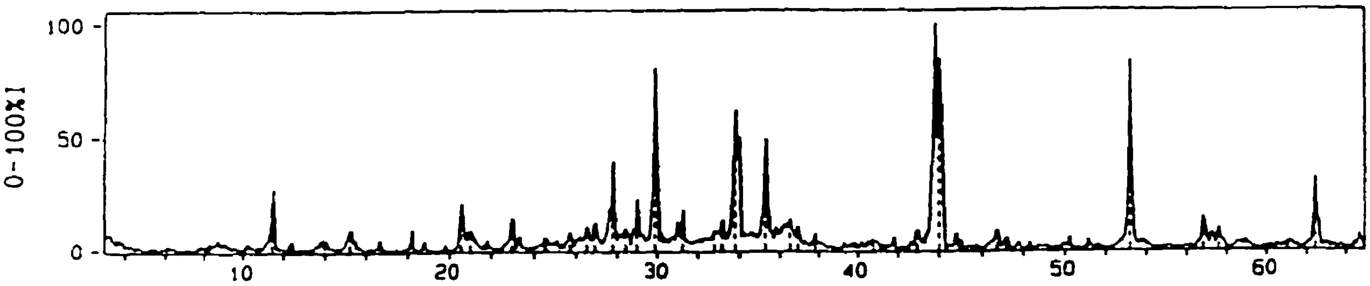
Pyrrhotite Tailings, Sample B4S1 (Control), 28 days



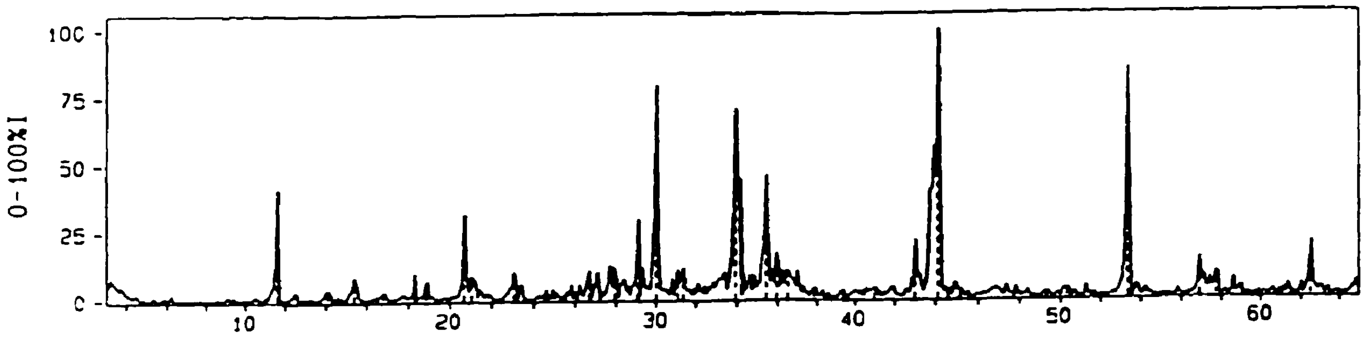
Pyrrhotite Tailings, Sample B4S2, 3%Lime, 0%FA, 28 days



Pyrrhotite Tailings, Sample B4S4, 3%Lime, 5% FA, 28 days

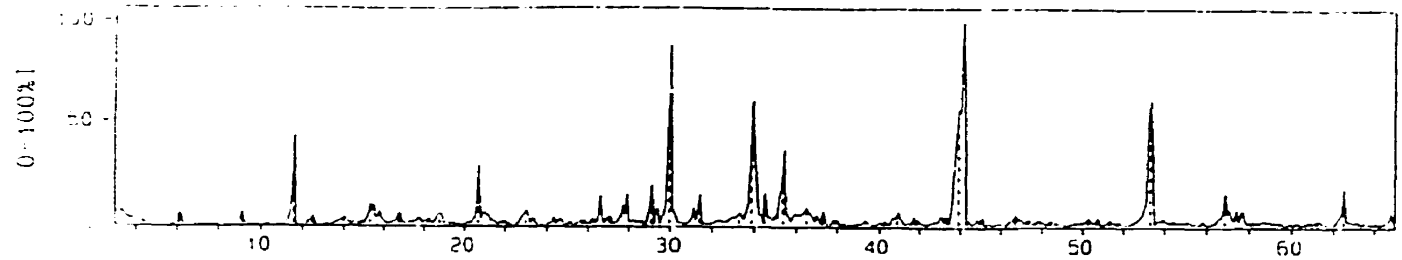


Pyrrhotite Tailings, Sample B4S5, 3% Lime, 10%FA, 28 days

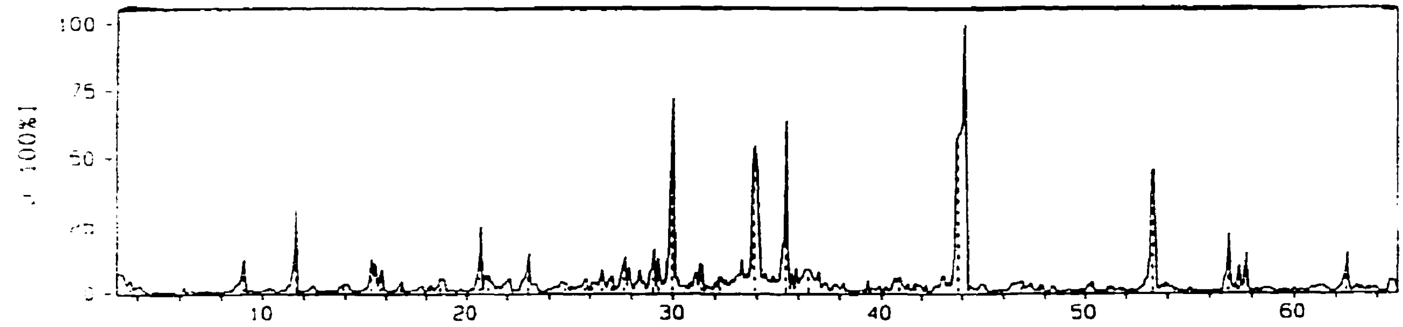


Pyrrhotite Tailings, Sample B4S6, 3% Lime, 20% FA, 28 days

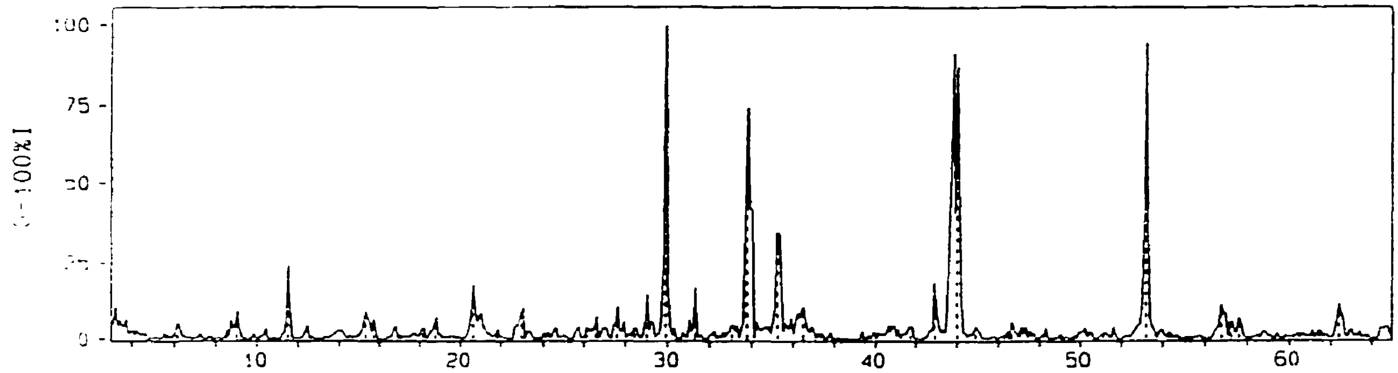
Pyrrhotite Tailings, Sample B5S4, 3%Lime, 5% Slag, 28 days



Pyrrhotite Tailings, Sample B5S6, 3% Lime, 20% Slag, 28 days

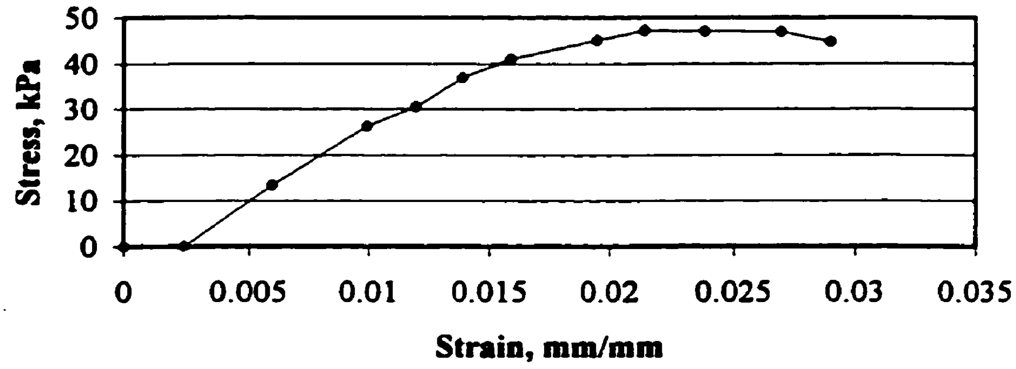


Pyrrhotite Tailings, Sample B6S4, 5% P.C., 28 days

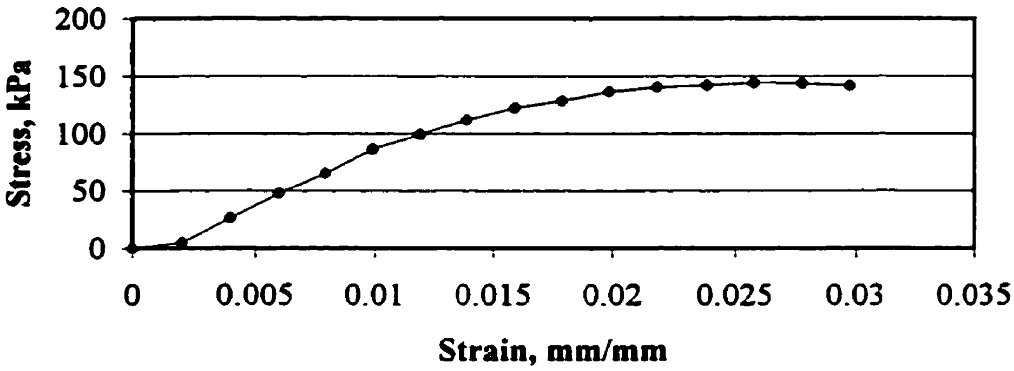


Appendix B

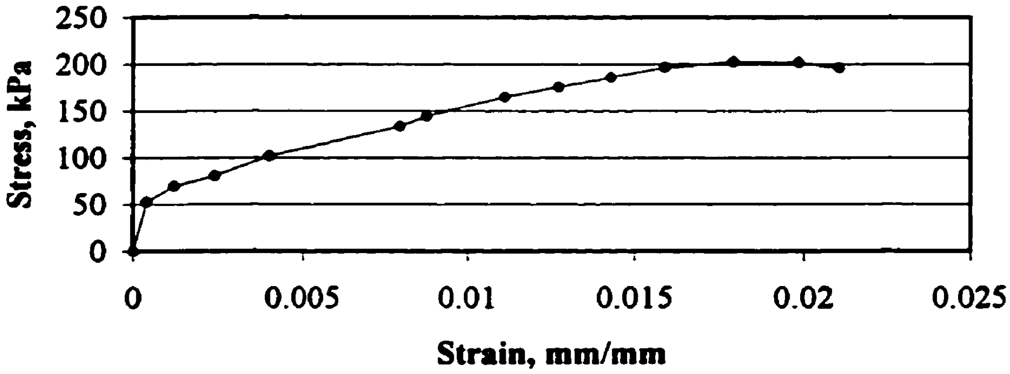
Stress - Strain Curve: Sample B1S2, 28 days

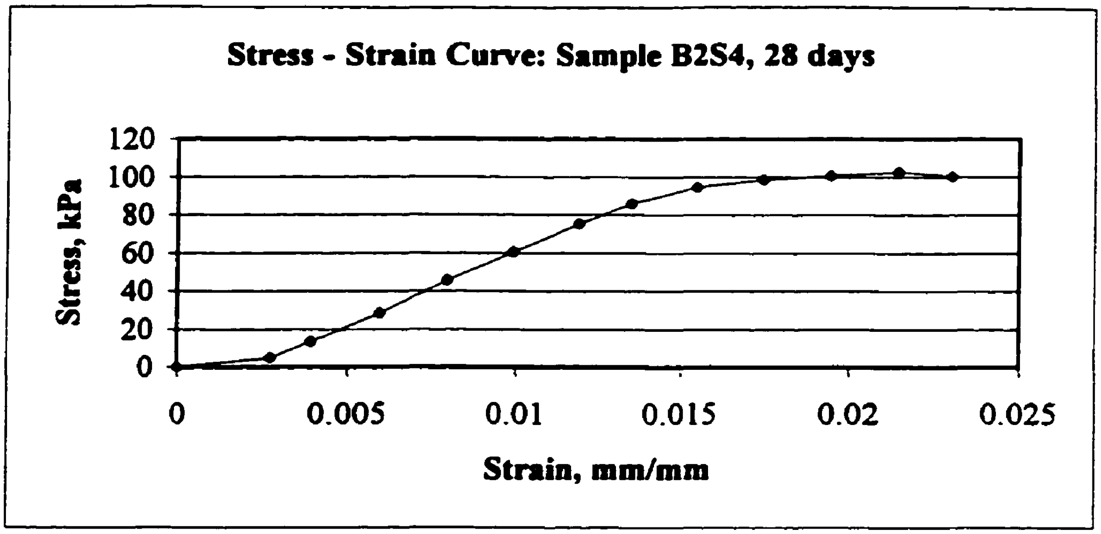


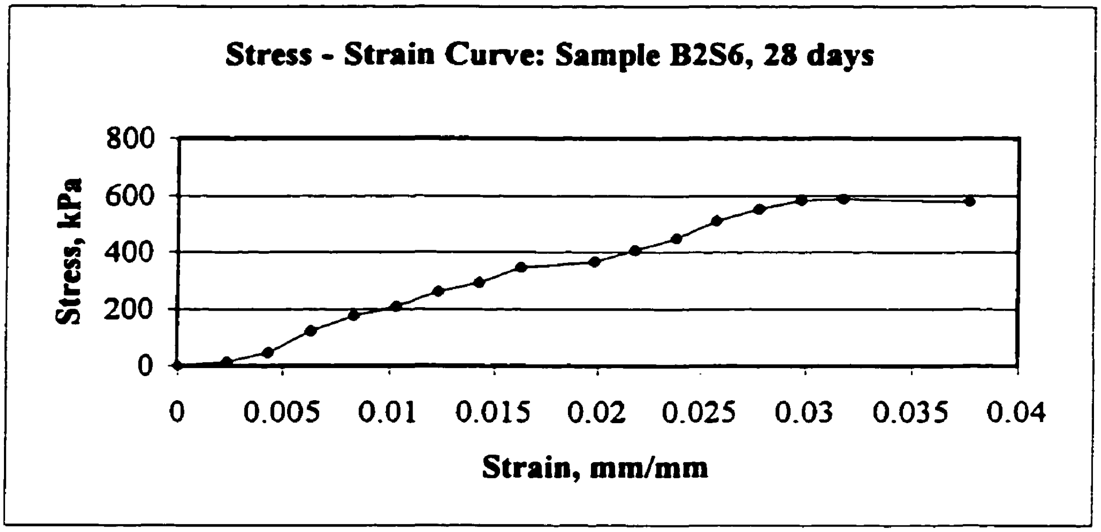
Stress - Strain Curve: Sample B1S4, 28 days

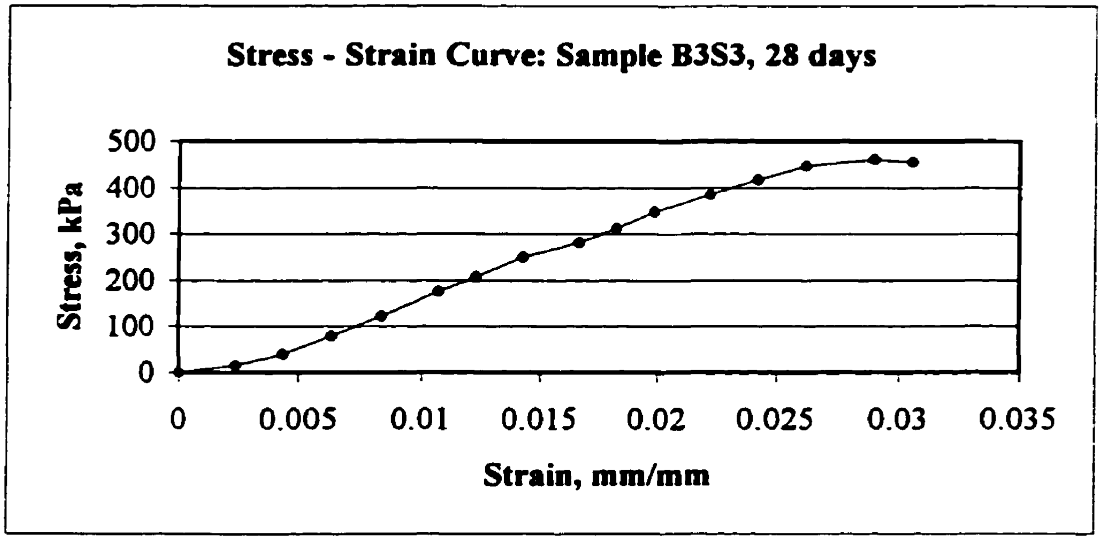


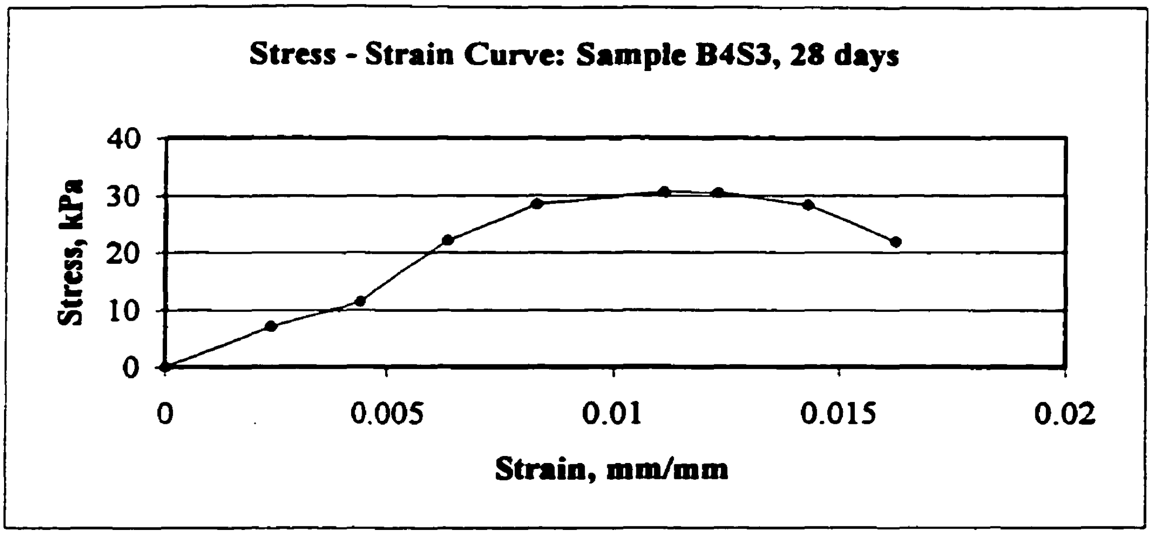
Stress - Strain Curve: Sample B1S6, 28 days

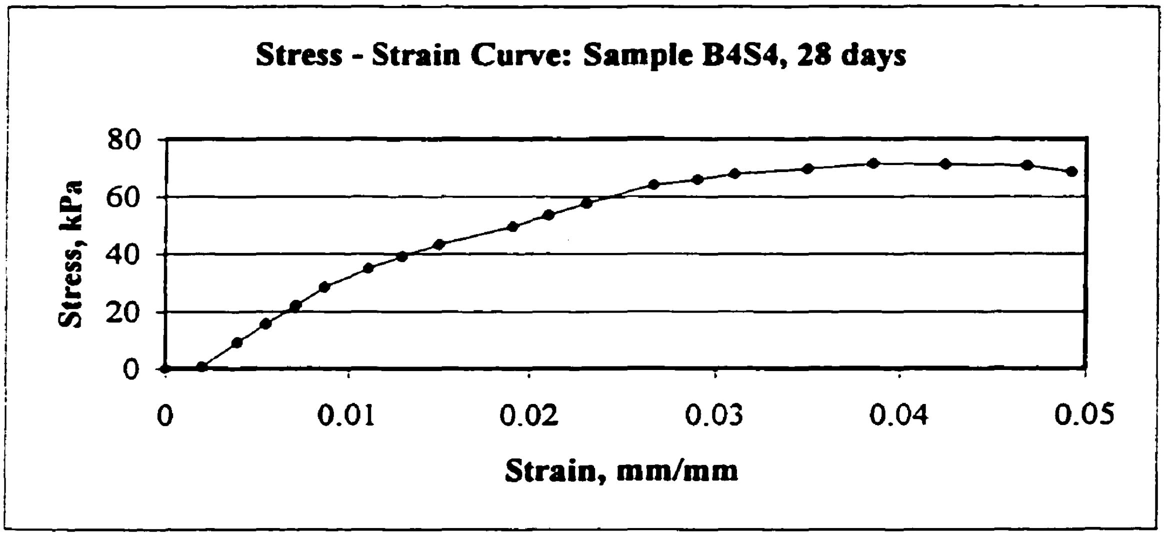


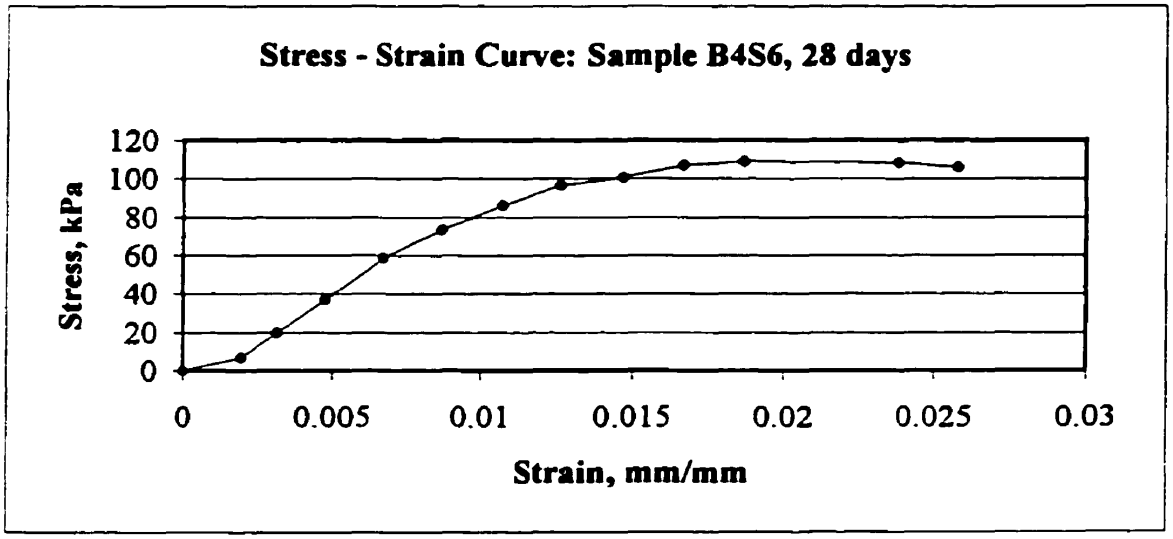

Stress - Strain Curve: Sample B2S4, 28 days

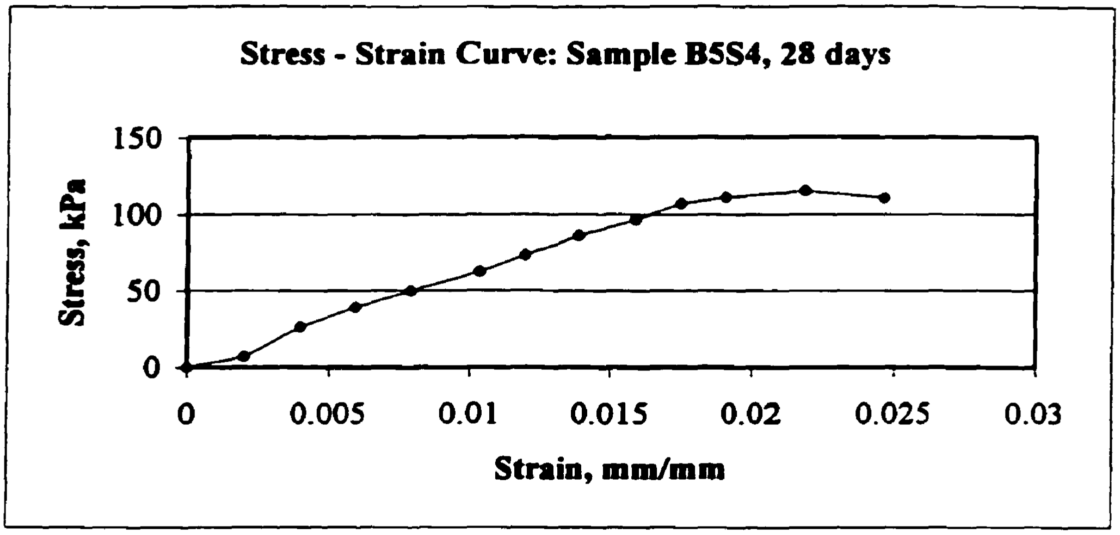

Stress - Strain Curve: Sample B2S6, 28 days


Stress - Strain Curve: Sample B3S3, 28 days

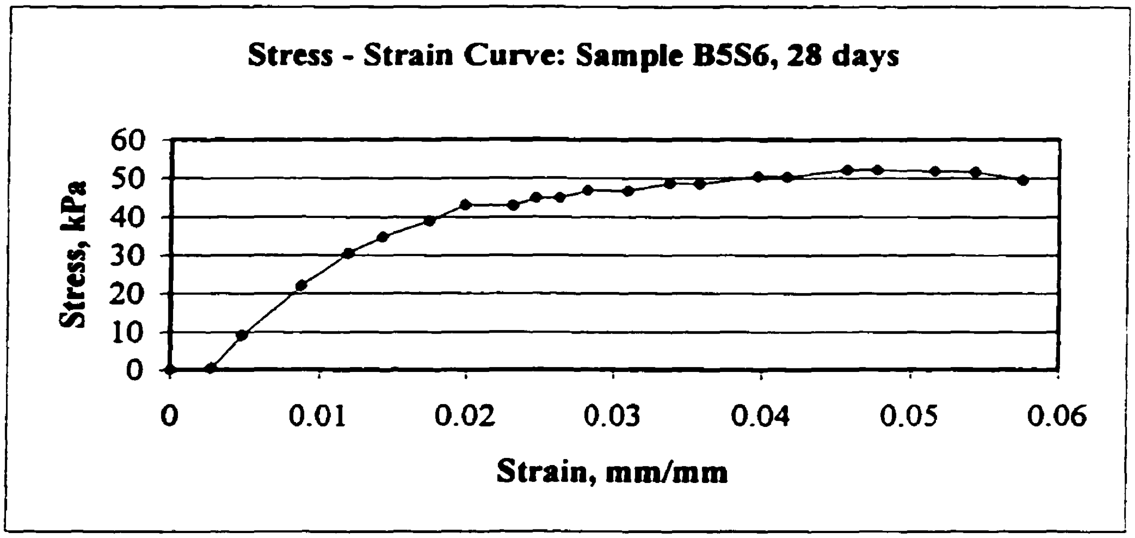

Stress - Strain Curve: Sample B4S3, 28 days
Stress, kPa
40
30
20
10
0
0
0.005
0.01
0.015
0.02
Strain, mm/mm


Stress - Strain Curve: Sample B4S4, 28 days
Stress, kPa
80
60
40
20
0
0
0.01
0.02
0.03
0.04
0.05
Strain, mm/mm

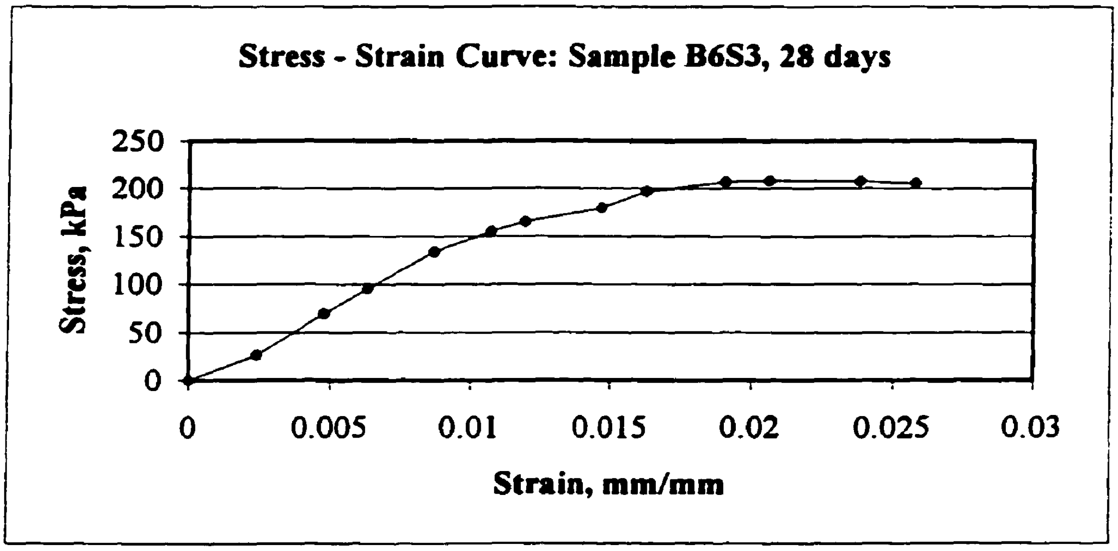

Stress - Strain Curve: Sample B4S6, 28 days
Stress, kPa
120
100
80
60
40
20
0
0
0.005
0.01
0.015
0.02
0.025
0.03
Strain, mm/mm



Stress - Strain Curve: Sample B5S4, 28 days



Stress - Strain Curve: Sample B5S6, 28 days



Stress - Strain Curve: Sample B6S3, 28 days