THE FIXATION OF ARSENIC WASTES

A thesis submitted for the degree of

Doctor of Philosophy

By

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DECLARATION

The data presented in this thesis is original material. The major findings of this research may, however, be encountered in a number of articles recently submitted for publication.

These publications include:

- The Management of Arsenic Wastes: Problems and Prospects, by M. Leist, R.J. Casey and D. Caridi, Journal of Hazardous Materials, 2000, volume 76, pp. 125-138.
- The Leaching of Cement Immobilized Arsenic, by M. Leist, R.J. Casey and D. Caridi, in press
- An FTIR Investigation into the Solidification/Stabilization of Arsenic Wastes, by M. Leist, R.J. Casey and D. Caridi, in press
- The Fixation and Leaching of Cement Stabilized Arsenic, by M. Leist, R.J. Casey and D. Caridi, in press

Throughout this thesis, where appropriate, work of other authors has been appropriately cited.

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ABSTRACT

Arsenic has found widespread use as a component in a variety of formulations designed to control or eliminate a variety of insect and fungicidal pests. Arsenical wastes are also often produced during the extraction of metals such as copper, gold, nickel and tin. Consequently, there are large numbers of sites contaminated with toxic arsenic residues. The environmental treatment of arsenic is complicated by the fact that it has a variety of valence states. This, coupled with the plurality of regulatory leaching test variants used, has made it impossible to gauge which of a number of Solidification/Stabilization (S/S) processes are the most effective. Cement based Solidification/Stabilization technology currently provides the most promising solution for the disposal of arsenic wastes.

This thesis has shown that Solidification/Stabilization is a technology capable of significantly reducing arsenic leachate concentrations to well below regulatory limits.

This thesis reports studies carried out to evaluate the process of Solidification/Stabilization (S/S) for rendering “safe” a variety of arsenic compounds in both of the common oxidation states, +III and +V. The compounds studied included:

- Arsenic trioxide,
- Arsenic pentoxide,
- Sodium arsenite,
- Sodium arsenate,
- Lead arsenate.

The three S/S formulations, all containing approximately 10% arsenic, investigated were:

- Cement only,
- Cement + ferrous sulfate,
- Cement + lime.

The stability of the S/S formulations was evaluated with both current regulatory leaching tests (i.e., Toxicity Characteristic Leaching Procedure (TCLP) and the Australian Bottle Leaching Procedure), sequential leaching tests, and column leaching tests.

Clear differences in the efficacy of the S/S formulations in immobilizing arsenic were observed. The results did not merely reflect differences in the solubilities of the arsenic compounds formed, but were greatly affected by the interaction (positive or negative) that the arsenic compounds and/or additives had upon the cementation reactions.

Microstructural analysis, using both FTIR and SEM, revealed the greatest changes to the matrices of the [cement + iron] formulations. The lower pHs of these formulations increased the extent of silicate polymerization, which is known to be destructive to cement matrices. Ettringite, which increases porosity, was also identified in these matrices. These detrimental changes to the matrices, coupled with their lower calcium content, explain the generally poorer performance of these matrices. The leaching of calcium has been shown to influence the leaching of arsenic. Those formulations containing large calcium contents were shown to be generally the most successful. The [cement + iron] formulations were shown to leach arsenic levels far in excess of those leached by the formulations containing greater calcium contents ([cement only] and [cement + lime]).

Besides identifying that calcium rich S/S formulations are generally the most effective, regardless of the arsenic oxidation state, this research has identified the following.

1. Even if arsenic is present in the same oxidation state, the success of a given S/S process can vary greatly between one arsenic compound and another.
2. The S/S of arsenical wastes was shown to be the most effective when arsenic was present as the arsenate species (+V).

3. S/S formulations that behave most favorably in one type of leaching test do not always behave as satisfactorily when subjected to a different form of leaching test.

This thesis, while reinforcing the general notion that the current regulatory tests are very severe and consequently not useful as a guide to contaminant levels that may be leached once the treated waste is placed in a landfill, questions the ability of current regulatory tests to positively identify those S/S matrices that will, indeed, behave most favorably. However, the results of this thesis work do not provide sufficient data to recommend a more appropriate alternative regulatory test.

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Chapter 1

1.0 INTRODUCTION

The management of hazardous wastes, such as arsenic, is an issue of current and growing public concern. Arsenic is a waste product from the processing of a variety of ores including copper, gold, nickel, lead and zinc. Arsenic in the past has also been widely used in many agricultural applications as the active ingredient in many herbicides and insecticides. Smelters, tailings dams, areas of former agricultural use and disposal sites constitute sources for potential escape of arsenic into surrounding groundwater and surface water.

Most arsenic compounds are highly toxic, causing dermatitis, acute and chronic poisoning, as well as cancer (Conner 1990). As little as 0.1g of arsenic trioxide, the most important commercial form, can be fatal when ingested (Conner 1990). Thus, because of the toxic nature of arsenic, it is important to develop cost effective, technically feasible methods for the remediation of contaminated sites. There are in excess of a thousand arsenic contaminated soil sites in the Australian State of Queensland (Chappell 1995). In addition to the existing problems of arsenic wastes, there will be an increase in the future production of arsenic wastes as industry begins to process more complicated sulphide ores, such as low grade gold, associated with arsenopyrite, and nickel ores with high arsenic contents (Yamauchi 1997, Zuk 1993). One can also expect that there will be an increase in the global cycling of arsenic due to the progressive industrialization of developing nations.

The safe disposal of arsenic wastes poses a number of problems:

1. Recovery of arsenic is of little economic interest because of the limited number of uses for this element today,
2. Incineration is limited because of the volatilization of arsenic containing compounds.

Arsenic can not be destroyed: it can only be converted into different forms or transformed into insoluble compounds in combination with other elements, such as iron.

In general, there are three options available for dealing with arsenic wastes:

- Concentration and containment
- Dilution and dispersion
- Encapsulation of the material.

There are two major drawbacks associated with the first option: the cost and safety issues. There is little commercial interest in investing in plant and technology to recover arsenic and its compounds when there is a very limited market for the recovered material (where the arsenic is of a relative high purity, it may, however, be economically feasible to recover the arsenic for use in the manufacture of arsenical wood preservatives). Additionally, there are safety concerns associated with the storing of arsenic in a concentrated form and possibly dire consequences associated with any accident at the point of storage.

The second option is superficially attractive to the waste disposal and mining industries, as it offers the possibility for combining numerous waste streams together and in a way which dilutes the hazardous contaminants, thus passing any regulatory limits. However, this does not represent any real technical solution to arsenic contamination, but merely a legislative solution. Long term exposure to low concentrations of arsenic still poses serious health problems including enhanced risks of skin cancers and various internal carcinomas (Naqvi 1997, Yamauchi 1997).

Therefore, at present, the most attractive option for dealing with arsenic wastes lies in encapsulating the contaminated material, usually through solidification/stabilization techniques, and disposing of the treated wastes in secure landfills. Although arsenic is present in moderate to high concentrations in a matrix, the aims of this technology are to ensure that it is so held that it cannot escape to the environment in any significant amounts.

1.1 Background

Arsenic is a relatively common element, present in air (from smelter emissions, coal-fired boilers and herbicide sprays), water (natural mineralization, mine tailings run-off, smelter waste leaching), soil, plants and all living tissue. It ranks twentieth in abundance in the earth's crust, fourteenth in seawater and twelfth in the human body (Woolson 1975). Therapeutic uses of arsenic date back to about 400BC, and, by and large, it was used up until the mid 1940s without any undue effects resulting from its judicious administration. Use of arsenic for poisoning one's enemies similarly dates back to antiquity, and probably reached its zenith in nineteenth century France when it accounted for about one third of all poisoning attempts (Blyth 1885). The subsequent decline in its popularity is attributed to the invention of a sensitive and selective test for arsenic, the Marsh Test, in 1836 (Thorwald 1964).

Large quantities of arsenic are released to the environment as a consequence of industrial and agricultural activities and these can have considerable ecological consequences because of their contamination of air, water and food (particularly seafoods). Chronic low level exposure to arsenicals has been associated with liver, kidney and heart damage, hearing loss, brain abnormalities and impaired resistance to viral infections. Exposure to arsenic has been associated with different types of human cancers, including respiratory cancers and skin cancers (Eisler 1997).

In the past, arsenic was used widely as a component of agricultural herbicides, as the active ingredient in insecticides and as an additive in animal feeds. In the 1940s and 50s, inorganic arsenic compounds, such as lead arsenate and calcium arsenate, were used as herbicides. Arsenic also enters the environment as an impurity accompanying phosphates in fertilizers and detergents.

Industrial contributions to arsenic in the environment include arsenic-rich by-products of the smelting of non ferrous metal ores, principally copper with minor contributions by lead, zinc and gold. There is limited industrial use for arsenic, including as an additive in metallurgical applications, as a decolourant in glass production, as a promotor in catalytic manufacturing processes and as a timber preservative. Chromated copper arsenate (CCA) is the most widely used arsenic based wood preservative.

Other commercially useful forms of arsenic, and, hence, forms likely to be found as industrial and agricultural wastes include:

- Arsenic Trioxide

The major use for As_2O_3 is in the production of agricultural pesticides, including calcium arsenate, arsenic acid, lead arsenate, sodium arsenate, various arsenites, and organic arsenicals. It is also used in the glass industry.

- Cacodylic Acid and Sodium Cacodylate

Dimethylarsinic acid, or cacodylic acid ,$(CH_3)_2AsO_2H$, was widely used as a weed killer and defoliant.

- Metal Arsenites

Sodium arsenite, $NaAsO_2$, is used as a weed killer and corrosion inhibitor. Copper acetoarsenite, $(CH_3CO_2)_2Cu.3Cu(AsO_2)O_3$, or Paris Green, is an insecticide that has been replaced by organic pesticides for crop plants, but is finding use as a mosquito larvicide.

- Arsenic Sulfides

Arsenic trisulfide, As_2S_3, is used in the manufacture of glass, semiconductors and photoconductors, as a pigment, in pyrotechnics, and for depilating hides. It also occurs as a waste product in phosphoric acid manufacture, since it is nearly insoluble in acids. Arsenic sulfide, As_4S_4, has many of the same uses as the trisulfide, while Arsenic pentasulfide, As_2S_5, is used in pigments.

- Metal Arsenates

Calcium, copper, lead, sodium, zinc, and manganese arsenates, $Ca_3(AsO_4)_2$, $Cu(CuOH)AsO_4$, $PbHAsO_4$ [acid-lead-arsenate], $Pb_4(PbOH).(AsO_4)_3.H_2O$ [basic lead arsenate], Na_2HAsO_4, $5ZnO.2AsO_5.4H_2O$, $MnHAsO_4$, have been used as pesticides, herbicides, and fungicides.

1.1.1 Lead Arsenate

Lead arsenate was first introduced in 1892 by the Massachusetts Gypsy Moth Committee to control the gypsy moth (Gianessi 1994). Six years later it was applied to some of the orchards in Connecticut and New York to control the Codling Moth.

During the first twenty years of the twentieth century lead arsenate was applied across the United States from one to three times annually. In the 1904 Yearbook of Agriculture , The U.S. Department of Agriculture (USDA) reported that essentially all commercial apple orchards were treated with arsenic (Marlatt 1904). As the Codling moth began to exhibit resistance to lead arsenate, additional applications of lead arsenate were made . During 1926, Washington growers sprayed their trees four or five times each year with the chemical (Gianessi 1994). Efforts were also made to increase the effectiveness of lead arsenate by applying deposit builders. The deposit builders made it possible to apply a thick coating of lead arsenate on the foliage and fruit. In Northwest America, an average of 60 to 80 gallons of the liquid insecticide was, typically, used in applying a single cover spray to a large tree for Codling Moth control (Gianessi 1994).

Three major problems accompanied the increased use of lead arsenate on apple trees. First, continual absorption of arsenic by the foliage and fruit often resulted in the burning of the foliage and in extreme cases in almost total defoliation as well as blackening of the apples. The second major problem concerned lead arsenate residues that remained on the fruit after harvest. An arsenic ceiling in food was first instituted by the British after an outbreak of poisoning occurred in England in the early 1900s. Eventually the British government established a tolerance of 0.01 grains of arsenic (equal to 1.4 ppm) (Gianessi 1994). A third problem associated with the use of lead arsenate was the build up of the chemical in the soil. The soil residue was toxic to cover crops, such as alfalfa, which had been planted to supply the apples with nitrogen.

1.2 Arsenic Economics

Arsenic is a low-value by-product of the smelting of a variety of gold and base metal ores as well as a common hazardous waste due to its former extensive use as an active ingredient in agricultural herbicides and insecticides. Arsenic wastes may contain many impurities such as lead, iron and selenium. These elements can often be uneconomic to remove and the arsenic is stockpiled as waste. However, where arsenic of a sufficient purity is produced (purity greater than approximately 95%), the arsenic may be economically recovered for use primarily in the manufacture of the arsenical wood preservative, chromated copper arsenate (CCA), and ammonial copper-zinc arsenate (ACZA). The source for the arsenic may be smelter flue dust, slimes, sludges and filter cakes from metal refineries (Ringwood 1994).

In some of the aforementioned arsenic containing wastes, the value of the copper content may be the economic incentive to consider recovery of the Cu and As, together, for CCA and ACZA.

Crude arsenic trioxide can be purified of contaminants and used to make CCA or ACZA. Sodium arsenite or arsenate can be used to make copper arsenate. The arsenite is oxidized to arsenate with oxygen or hydrogen peroxide, and copper sulfate is reacted in the arsenate solution to make copper arsenate [Cu_2AsO_4OH and $Cu_3(AsO_4)_2$]. The latter is solubilized with ammonia for ACZA, or with chromic acid for CCA (Arsenault 1992). Care must be taken that undesirable contaminants are not present in the alkaline arsenic solution that will cause CCA or ACZA sludges or corrosion of treating plant equipment. For example, the presence of chlorine would be a corrosion hazard for treating-plant equipment and for hardware attached to the treated wood (Arsenault 1992). The presence of antimony or iron can cause CCA sludges and/or surface residues on CCA treated wood (Arsenault 1992). The maximum amount of iron that can be tolerated in CCA solution without a rapid increase in precipitation is 75ppm (Arsenault 1992). Therefore, the extraction and separation process used, or crude sources of arsenic used to obtain arsenic for use in making CCA and ACZA must be designed to minimize the amounts of contaminants.

Global production of arsenic trioxide was estimated to be 41,500 metric tonnes in 1999, with China, the world's largest producer, producing some 16,000 tonnes (Reese 2000). Belgium, which produced 9,000 tonnes was the worlds second largest producer (Reese 2000).

The largest end use for arsenic trioxide was in the production of wood preservatives. Production of chromated copper arsentate (CCA) accounted for more than 90% of the domestic consumption of arsenic trioxide in the United States (Reese 1998). Wood preservatives are expected to remain the major use of arsenic. Consequently, the demand for arsenic in the United States should continue to correlate closely with the demand for new housing, and the growth in the renovation or replacement of existing structures. The demand for arsenic trioxide in the manufacture of wood preservatives has increased noticably over the last 20 years, increasing from 970 tonnes in 1971 to 9,100 tonnes in 1981 and 14,300 tonnes in 1991 (Loebenstein 1992). The only other area which has seen an increase in the use of arsenic is the electronics industry. High purity arsenic metal, of 99.9999% or higher purity, is used in the manufacture of crystalline gallium arsenide, a semiconducting material used in optoelectronic circuitry, high speed computers and other electronic devices. All other areas of arsenic usage, such as in the manufacture of agricultural chemicals, have seen a steady decrease in demand.

In general, the demand for arsenic based wood preservatives appears positive, barring greater acceptance of alternative preservatives or new regulatory restrictions on the use of arsenic based wood preservatives. Substitutes for arsenic compounds exist in most of its major uses, although arsenic compounds may be preferred because of lower cost and superior performance. The wood preservatives pentachlorophenol and creosote may be substituted for CCA when odor and paintability are not problems and where permitted by local regulations. A recently developed alternative, ammoniacal copper quaternary, which avoids using chromium and arsenic, has yet to gain widespread usage (Reese 1998).

1.3 Arsenic chemistry

Arsenic, atomic number 33, is one of the elements located in group VA of the periodic table and is classified as a "metalloid". Within this group, metallic characteristics increase as atomic number increases. A characteristic of metals in aqueous solution is the loss of electrons and the resulting formation of cations. Arsenic will lose electrons to enter the +III or +V states, although it exists tightly bound to oxygen, which results in an anionic form (Cullen 1989).

The biogeochemical cycling of arsenic in soils and waters is complex. Arsenic displays a wide range of reactivity in the environment, participating in oxidation-reduction, acid-base, precipitation, adsorption and methylation – demethylation reactions (Ferguson 1972).

Four stable arsenic valence states are known to occur in nature, +V, +III, -III, and 0. The +V or arsenate species include AsO_4^{-3}, $HAsO_4^{-2}$ and $H_2AsO_4^{-1}$. These species are predominant and stable in oxygen rich environments where mild oxidizing conditions are present.

*The other principal form of arsenic is the arsenite or +III state. Arsenite species include $As(OH)_3$, $As(OH)_4^-$, AsO_2OH^{-2} and AsO_3^{-3}. These species are predominant under moderately reducing conditions. The +III species is both more soluble and more mobile than the oxidised state (arsenate, +V).

Arsenic occurs in the environment mainly as the inorganic arsenic oxides, arsenite and arsenate and its simpler methylated forms (e.g. $(CH_3)_3As$ and * $(CH_3)_2AsOOH$).

Elemental arsenic, which is a solid at room temperature, has several allotropes. The common semiconducting forms, often referred to as metallic forms, are all gray, lustrous, crystalline and brittle, while the amphorous allotropes are yellow. Yellow arsenic is very unstable and reverts quickly to the semiconducting form.

Arsenic at waste sites may be present from many natural or man made sources. Arsenic occurs naturally in about 245 mineral species. These include arsenides, sulfides, sulfosalts and oxidation products (oxides, arsenites, and arsentates). In addition, a variety of complex organoarsenic compounds may be present at sites containing waste from coal utilization or oil production (Zuk 1993), or from the disposal of veterinary/human medicines, herbicides, etc.

Arsenic compounds can readily undergo oxidation in aerated soil to form arsenates and be subsequently reduced to arsenites, various alkylarsines and trimethylarsine oxide (TMAO). The arsines are volatile and can become dispersed in air, to return ultimately as oceanic sediments. Organoarsines can be oxidized to methanarsonate or cacodylate. These reactions, a result of oxidation, reduction and microbial activity, are a part of the natural cycling of arsenic in the environment (Woolson 1992).

1.4 Toxicity of Arsenic

The toxicity of arsenic and its compounds has been reviewed by Yamauchi and Fowler (1997) and Naqvi et al (1997). The toxicity of arsenic is complicated because arsenic exists in a variey of oxidation states and in many different inorganic and organic compounds. Inorganic compounds of arsenic are generally considered to be more toxic than organic compounds . Elementary arsenic is not toxic, while inorganic trivalent arsenite is 25 to 60 times as toxic as inorganic, pentavalent arsenate and several hundred times as toxic as methylated arsenic compounds. The toxicities of organo-arsenicals are generally lower than those of inorganic species. The order of decreasing toxicity has been given as R_3As (R = H, Me, Cl, etc.) $>As_2O_3$ (arsenites) $> (RAsO)_n > As_2O_5$ (arsenates) $> R_nAsO(OH)_{3-n}$ (n=1,2) $> R_4As^+$ $>As$ (0) (DeVillers 1995). When arsenic compounds are heated, or come in contact with acids or metals, such as iron, aluminum or zinc, they emit highly toxic fumes.

Arsine gas, AsH_3, is the most dangerous arsenic compound. Its toxicity is due to its ability to break down red blood cells in the human body (Whitacre 1974). However, arsine gas rapidly decomposes in the presence of light and moisture and can be effectively dissipated in the environment (Fowler 1976).

The solubility of arsenicals varies from quite soluble (arsenic acid, sodium arsenite) to virtually insoluble (arsenic trisulfide). Soluble forms are usually more toxic because of their greater potential for absorption by biological species (Naqvi 1997).

All humans are exposed to low levels of arsenic through air, drinking water, food and beverages. For most people, food constitutes the largest source of arsenic intake, with smaller amounts from drinking water and air. The daily total intake is usually less than 200µg, with the daily inorganic arsenic intake not normally exceeding 60µg, whereas a fatal dose of ingested As_2O_3 is about 1 to 2.5mg As/kg of body weight (Pershagen 1984). The current regulatory limit for arsenic in drinking water is 0.05mg/L (WHO 1984). The eight-hour-time-weighted-average exposure standard for arsenic and its compounds is given as 0.05mg/m^3 (NOHSC 1989). Some edible fish, shellfish and seaweed contain elevated levels of arsenic, but this is predominately in an organic form that has low toxicity (Chen 1997).

Arsenic is accumulated in aquatic organisms to a greater extent than terrestrial organisms, with the greatest accumulation occurring in plants at the lowest end of the food chain (Woolson 1975). Invertebrates are generally more sensitive to arsenic than adult fish, while marine organisms can accumulate more arsenic than their freshwater counterparts (Ringwood 1994). Arsenic concentrations between 3 and 49 ppm have been measured in shrimp. At these levels such organisms are not toxic to humans and the arsenic is readily excreted (Woolson 1975). In plants, however, higher concentrations of arsenic have been measured. For example, 11 to 1450 ppm As has been recorded in some lakeweeds and 60 to 142 ppm As found in seaweed (Ringwood 1994).

Above-average levels of arsenic exposure through ingestion have usually been observed among people who live in areas where drinking water has an elevated level of inorganic arsenic, because of natural mineral deposits or contamination from human activities. The concentration of arsenic in unpolluted fresh waters typically ranges from 1 to 10 µg/L rising to 100 to 5000 µg/L in areas of sulfide mineralization and mining. Workers involved in the processing of copper, gold and lead ores; in the use of arsenic as pigments and dyes; in the production and use of agricultural pesticides; and in the manufacturing of glass and various pharmaceutical substances also have high exposure to arsenic.

Through inhalation or ingestion, arsenic compounds can cause dermatitis, acute and chronic poisoning, hair loss, visual disturbances, blindness, a garlic odor on the breath, liver damage, lung fibrosis, neurological damage and lung cancer (LaGrega 1994). Arsenic poisoning is cumulative. The longer exposure continues, the greater the risk that long term diseases, like cancer, will set in. With long term exposure, significant toxic effects can be expected to occur above a daily oral intake of 100 to 200µg (DeVillers 1995). Most ingested and inhaled arsenic is absorbed through the gastro-intestinal tract and lungs into the bloodstream. It is distributed in a large number of organs, including the lungs, liver, kidneys and skin (Hunter 1942). Inorganic arsenic is excreted, unchanged, in the urine during the first hours after the start of exposure. After about eight hours, most arsenic absorbed in the body is converted by the liver to less toxic methylated forms (cacodylic acid and methylarsonic acid), which are efficiently excreted in the urine (Vahter 1983). About three-quarters of a single dose of trivalent inorganic arsenic is eliminated within a few days or, at most, within a week, with the remainder being dispersed in the tissues (NOHSC 1989). In the skin, brain and skeleton the concentrations decrease rather slowly.

Recent work, in China, by Zhang et al (1996) and Shen et al (1997), and in the United States, by Soignet et al (1998), has shown that it is possible to utilise arsenic trioxide in the successful treatment of acute promyelocytic leukemia (APL). In the American work, doses,in the range 0.06 to 0.2 mg/kg body mass per day, were administered over 12 to 39 days (cumulative doses of 150 to 515mg), leading to complete remission in eleven of the twelve patients with APL who had relapsed following earlier chemotherapy. If nothing else, this serves as a reminder that there are no absolutes: the highly toxic poison can also be a lifesaver.

1.5 Treatment and removal of arsenic from waste waters

Techniques for the removal of arsenic from aqueous media fall into several categories: ion exchange; adsorption (activated alumina and activated carbon); ultrafiltration; reverse osmosis; and precipitation or adsorption by metals (predominately ferric chloride), followed by coagulation.

Typically the removal of arsenic from wastewater is only effective when dealing with relatively low concentrations of arsenic. Most studies concentrate on the removal of arsenic at the low μg/L level. Harper and Kingham (1992), Brewster (1992), and Namasivayam (1998), however, have investigated the removal by precipitation and/or adsorption of arsenic at higher levels, 31, 56 and 10 mg/L, respectively. In general, the removal of arsenic by precipitation is most effective for small quantities of highly concentrated arsenic waste. The cost effectiveness of precipitation is diminished when disposing of large quantities of low-concentration arsenic wastes.

Adsorption on alumina or carbon is not well suited to handling high concentrations. The possibility of regeneration provides attractive cost effectiveness, although some studies have raised questions concerning the process reliability of adsorption onto alumina. Incomplete regeneration of the media has been observed in several studies (Hathaway 1987, Clifford 1991). When mass balances were done after regeneration, only 70-80% of the arsenic was recovered. Any subsequent adsorption capacity is decreased as a result of this irreversibly adsorbed arsenic.

In summary, for the removal of arsenic from wastewater:

- **Arsenic removals of up to 99% have been demonstrated using a variety of techniques and initial arsenic concentrations.**

Harper and Kingham (1992), used chemical precipitation to treat contaminated water (containing arsenic) from cleanup activities at a former pesticide facility. Initial laboratory treatment studies included precipitation using either alum, Na_2S or $FeCl_3$ as a coagulant with pH adjustment by hydrated lime. The first sample had an initial arsenic concentration of 9.8 mg/L and coagulant doses were 500 to 1000 mg/L. $FeCl_3$ with hydrated lime resulted in the greatest arsenic removal, in the range of 98-99%. In another sample with an arsenic concentration of 31 mg/L, dosages of $FeCl_3$ ranging from 200 mg/L to 1000 mg/L resulted in arsenic removals of 86-93%. Multiple dosages of coagulants improved the degree of arsenic removal to 98%. The full scale treatment system, including the addition of hydrated lime and ferric chloride, clarification, filtration and carbon adsorption, achieved arsenic removal rates of 97 to 98%. A total of 650,600 litres of wastewater were treated.

Bhattacharyya et al. (1980), investigated precipitation of metals with sodium sulfide. Metal sulfide precipitation is possible over a broad pH range because of the high reactivity of sulfides with heavy metal ions and the low solubilities of heavy metal sulfides. At a pH of 8, heavy metals were 98-99.6% removed with a dosage of 0.6 moles of sulfide to one mole of metal. Arsenic removal was not effective unless sufficient ferric iron was added at a Fe/As mole ratio of 2.

Namasivayam and Senthilkumar (1998) investigated the removal of arsenic (V) from aqueous solution using "waste" Fe(III)/Cr(III) hydroxide, generated electrolytically in the treatment of Cr(VI) containing wastewaters in a fertilizer industry. The authors demonstrated a removal of 97.8% of an initial As(V) concentration of 10 mg/L using an adsorbent dose of 400 mg/50 mL.

Haung and Vane. (1989) investigated arsenic removal (as arsenate) by metal-treated activated carbon in an attempt to improve the adsorption capacity of carbon. The activated carbon was first washed in NaOH or HCl to remove any impurities which might cause interference in the adsorption, and then soaked in various metal ion solutions, namely, $Ba(ClO_4)_2$, $Cu(ClO_4)_2$, $FeSO_4$, $FeCl_2$, $Fe(ClO_4)_2$, $Fe(ClO_4)_3$ and $FeCl_3$, prior to adsorption of arsenic. Of these, activated carbon soaked in ferrous perchlorate achieved the highest arsenic removal. Using metal treated activated carbon an arsenic removal of 99% was achieved on an arsenic solution of concentration 2×10^{-4} M As^{5+}.

- **Better arsenic removal has been found for arsenic in the +5 state (arsenate) than the +3 state (arsenite)**

Cheng et al. (1994), investigated coagulation, one of the most common treatment processes for removing arsenic from water, as a possible treatment for removing arsenic from river water. The authors concluded, as have other authors, including Scott et al. (1995) and Hering et al. (1996), that arsenate is more effectively removed than arsenite and that oxidation of arsenite to arsenate is necessary to achieve effective arsenic removal. Hering (1997) found that As(V) was much more efficiently removed than As(III) during coagulation with ferric chloride (90% versus 30% removal efficiency, respectively).

Tokunaga et al. (1999) investigated the removal of As(V) and As(III) from aqueous solutions, using a variety of salts including lanthanum(III), aluminum(III), calcium(II) and iron(III). For As(III), complete removal was not possible. The greatest success was achieved with iron(III) and lanthanum salts. Iron(III) addition resulted in 40% As (III) removal, while use of lanthanum(III) led to 60% removal. When the same experiments were conducted using As(V), iron(III) successfully removed 76% As(V) while lanthanum(III) removed in excess of 99% of the As(V). Of the other salts investigated, aluminum and polyaluminium chloride (PAC) were capable of removing 40% As(V). Both aluminum and PAC were not effective in removing

As(III) ions. Adjustment of the initial arsenic(V)-to-lanthanum ratio to 1:3 or higher, resulted in arsenic removals which were greater than 99%. The studies were conducted using an initial As(V) concentration of 0.25 mM. The optimum pH was 5 to 10. Earlier work by Tokunaga (1997) reported that the optimum pH was highly dependent upon the form of the lanthanum. The optimum pH range was 3-8, 4-7, and 2-4 for lanthanum hydroxide, lanthanum carbonate and basic lanthanum carbonate, respectively.

- **Arsenic removal by coagulation has found to be more effective using iron (III) than alum.**

Gulledge and O'Connor (1973) simulated coagulation, flocculation, sedimentation and filtration for arsenic removal (from a water sample with an initial arsenic concentration of 0.05 mg/L) by alum and ferric sulfate. Ferric sulfate was more effective, leading to 90 to 100% removal of arsenic, at doses of 10 mg/L to 50 mg/L over the tested pH range of 5-8. Alum was less effective and only comparable with ferric sulfate at a lower pH (5 or 6), and higher concentration (30-50 mg/L).

Hering et al. (1997) investigated arsenic removal by coagulation and found alum was incapable of removing As(III), while ferric chloride was capable of removing approximately 30%. Edwards (1994) also reported that iron(III) is more effective in removing As(III) than alum.

The study by Cheng et al. (1994) used both alum and $FeCl_3$ at three different concentrations, 10, 20 and 30 mg/L , as coagulants. A cationic polymer, added at a concentration of 3 mg/L, was used as a coagulant aid. The study was applied to both bench and pilot scale trials, with the authors concluding that $FeCl_3$ is a much more effective coagulant than alum when compared on an equal weight dosage basis. $FeCl_3$ coagulation is not pH dependent between 5.5 and 7.0, but increasing coagulant dosage will increase As(V) removal. The pH dependence for alum was much more pronounced than that for the iron.

- **Most adsorption onto alumina or carbon takes place within 24 hours.**

Patterson and Passino (1987) investigated arsenic removal by adsorption, using activated alumina. While no measure of effectiveness was indicated, the authors did provide the optimum conditions for the procedure. Adsorption of arsenic on activated alumina was greatly affected by pH. This phenomenon has also been noted by other authors, including Ghosh and Teoh (1985). Maximum adsorption of arsenate occurs at a pH of 5 or less. Kinetic data for adsorption of arsenate on alumina revealed that the removal was rapid in the first 24 hours and then slowed considerably as the reaction approached equilibrium. At pH of 6.5 or less, 95% of the maximum adsorption was attained in less than 24 hours. At a surface loading of 67 μmol/g, the solution concentration of arsenate decreased from 5 to 0.1 mg/l in a few hours. Ionic strength had no effect on the adsorption, and, regardless of temperature, equilibrium adsorption was assumed to be completed in 6 days .

Haung and Fu (1984) investigated the possibility of using activated carbon as a means of adsorbing arsenic and concluded that, generally, powdered activated carbon had better capacity than granular activated carbon for arsenic removal. Further, lignite-based activated carbon, and high-ash-content activated carbon, had much better As(V) removal capacities than bituminous-based activated carbons. Diamadopoulos et al. (1993), found that the removal of arsenic (V) from water was enhanced up to 5 times, for the high-ash activated carbons. Strong interactions between the arsenate ion and the inorganic part (ash) of the activated carbon were proposed to explain these results. Diamadopoulos et al. (1993) investigated the use of fly ash, a high ash carbon, and a by-product of coal-fired power stations, as a means of removing arsenic from solution. The trials were based on arsenic concentrations of 50 mg/L, using fly ash added at 1 g per litre of arsenic solution. Experiments were performed at three pH levels. A pH of four was the most effective. Most adsorption took place in less than 24 hours, and equilibrium was reached within 72 hours. Sen and Arnab (1987) noted that fly ash adsorbed at a slower rate than activated carbon, but in the end was comparable in capacity. Complete removal of arsenic was possible at pH 4. The greatest arsenic removal was achieved at a pH of 4 (80%), which was up to 4 times greater than that at the other two pH levels of 7 and 10.

The cost effectiveness of some arsenic treatment options have been ranked by Chen et al (1999). In general, costs increased in the following order; modified conventional treatment (e.g. coagulation) << activated alumina or anion exchange < reverse osmosis. Despite the ranking of Chen et al (1999), the technology that will best remove arsenic depends on the wastewater quality.

Whether anion exchange or activated alumina is the more cost effective method depends upon the raw water concentrations of sulfate and arsenic. For example, high influent sulfate is expected to shorten anion exchange runs, thus increasing operating costs. In general, the following trends were observed: in low sulfate water (<10 mg/L) anion exchange was a more cost effective control strategy for arsenic. In low arsenic water (<5 μg/L), activated alumina was either cost competitive or favored as a least-cost control option, especially when the sulfate concentration exceeded 10 mg/L in the source water, while in very small systems, anion exchange treatment remained the favored option for arsenic control through a broader range of initial sulfate concentrations (Chen 1999). Possible detriments for anion exchange include using anion exchange beyond the point of sulfate exhaustion. A chromatographic effect allows exhausted exchange resin to release nearly all previously removed arsenic back into treated water at high concentrations (Chen 1999).

The presence of co-occurring inorganic solutes can have a pronounced effect on the removal of arsenic during coagulation. Co-occurring inorganic solutes, such as sulfates and phosphates, may directly compete for surface binding sites and may also influence the surface charge of the ferric oxide, thus indirectly affecting the adsorption of trace contaminants such as arsenic.

While the presence of co-occurring inorganic solutes will, more generally, cause a decrease in the amount of arsenic removed during coagulation, under certain conditions they can actually increase rather than decrease the removal of trace contaminants by adsorption. At pH 9.0, the removal of As(V) (at an initial concentration of 20 µg/L) during coagulation with 4.9 mg/L $FeCl_3$ was enhanced in the presence of 3.0 mM calcium, probably because the calcium counteracted the slight competitive effect of phosphate (Hering 1996). Similar effects were observed for the adsorption of As(V) (at an initial concentration of 35 µg/L) onto preformed hydrous ferric oxide (Hering 1996).

Hering et al. (1997) concluded that removal of As(V) by either ferric chloride or alum was relatively insensitive to variations in source water composition below pH 8. At a pH between 8 and 9 the efficiency of As(V) removal by ferric chloride was decreased in the presence of natural organic matter. Removal of As(III) from source waters by ferric chloride was more strongly influenced by source water composition. The presence of sulfate (at pH 4 and 5) and natural organic matter (at pH 4 through 9) adversely affected the efficiency of As(III) removal by ferric chloride.

The preceding paragraphs have provided numerous examples of how arsenic can be successfully removed from waste waters, but most of the these technologies do not reduce the arsenic concentration to below drinking water standards. There have however been studies that have investigated the absorption of arsenic onto a variety of media including, ferrihydrite, aluminum hydroxide, alumina and carbon to reduce the arsenic content of mine waters to below 20 µg/Litre (Twidwell et al 1999). However, in doing so a new dilemma is created, that is, how to dispose of the more concentrated arsenic product that has been produced. The most likely and feasible solution to this predicament may be to use one of a number of solidification/stabilization techniques.

1.6 Solidification/ Stabilization

Solidification/stabilization (S/S) processes are "non destructive" methods used to immobilize the hazardous constituents in a waste. S/S processes are non destructive, in the sense that they do not remove or reduce the quantities of the hazardous constituents. Typically S/S processes physically sorb, encapsulate, or change the physiochemical form of the pollutant in the waste, resulting in a less leachable product. Concentrations of contaminants in the treated waste are often lower than in the untreated waste, primarily because of incidental dilution by the binder rather than by destruction or removal of the contaminants. S/S processes are effective in treating a variety of difficult to manage waste materials. They are flexible enough to accommodate mixtures of contaminants and economical enough to be used for large volumes of wastes. S/S has been identified as the Best Demonstrated Available Technology (BDAT) for treating a wide range of wastes, however not necessarily arsenic containing wastes.

S/S processes can generally be grouped into two categories:

1. inorganic processes (cement and pozzolanic)
2. organic processes (thermoplastic and thermosetting polymers)

1.6.1 Cement Processes

Of the inorganic binders, Portland Cement has probably had the greatest number of applications. Because cement is a common construction material, the materials and equipment are mass produced and generally inexpensive. Many types of cement have been used for a variety of purposes, but only those classified as Portland Cement have seen substantial use in S/S technology (Conner 1990). Other types of cement, such as alumina or Sorel cement, have not been used extensively for S/S, primarily because of their high cost.

Advantages of cement based processes include (Conner 1990):

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

1.6.1.1 Portland Cement

Portland Cement is made by heating a mixture of limestone and clay, or other materials of similar bulk composition, to a temperature of about 1450°C. Partial fusion occurs and nodules of clinker are produced. The clinker is mixed with a few per cent of gypsum and finely ground to make the cement. The clinker typically has a composition in the region of 67% CaO, 22% SiO_2, 5% Al_2O_3, 3% Fe_2O_3 and 3% of other components (Taylor 1990) and normally contains four major phases called alite, belite, aluminate phase and ferrite phase.

Alite is the most important constituent of all normal Portland cement clinkers, of which it constitutes 50-70% (Taylor 1990). It consists of tricalcium silicate (Ca_3SiO_5) modified by the incorporation of foreign ions, especially Mg^{2+}, Al^{3+} and Fe^{3+}. It reacts relatively quickly with water, and, in normal Portland cements, is the most important of the phases for strength development at ages of up to 28 days (Taylor 1990).

Belite constitutes 15-30% or normal cement clinkers (Taylor 1990). It is dicalcium silicate (Ca_2SiO_4) modified by incorporation of foreign ions. It reacts slowly with water, thus contributing little to the strength during the first 28 days, but substantially to the further increase in strength that occurs at later ages. By one year the strengths obtainable from pure alite and pure belite are about the same under comparable conditions (Taylor 1990).

The aluminate phase constitutes 5-10% of most Portland cement clinkers (Taylor 1990). It comprises tricalcium aluminate ($Ca_3Al_2O_6$), substantially modified in composition and sometimes also structure, by incorporation of foreign ions, especially Si^{4+}, Fe^{3+}, Na^+ and K^+. It reacts rapidly with water and can cause undesirable rapid setting, unless a set controlling agent, usually gypsum, is added.

The ferrite phase makes up to 5-15% of normal Portland cement clinkers (Taylor 1990). It consists of tetracalcium aluminoferrite (Ca_2AlFeO_5), substantially modified in composition by variation in Al:Fe ratio and incorporation of foreign ions. The rate at which it reacts with water appears to be somewhat variable, but in general is high initially and intermediate between those of alite and belite at later ages.

1.6.1.2 Types of Portland Cement

The great majority of Portland cements made throughout the world are designed for general construction use. The specifications with which such cements must comply are similar, but not identical, in all countries and various names are used to define the material, such as OPC (Ordinary Portland Cement) in the UK or Type 1 Portland cement in the USA. As well as "ordinary" Portland cement there are a number of modified cements. Table 1.0 lists the main types of Portland cements and the average values of compound composition for the five main types.

Table 1.0 – Compound composition (%) of common Portland cement types (modified from Neville 1987)

Cement	C_3S	C_2S	C_3A	C_4AF	$CaSO_4$
Type I (ordinary Portland)	59	15	12	8	2.9
Type II (modified cement)	46	29	6	12	2.8
Type III (rapid hardening)	60	12	12	8	3.9
Type IV (low heat)	30	46	5	13	2.9
Type V (sulphate resisting)	43	36	4	12	2.7

Key to table abbreviations:
$C_3S = 3CaO.SiO_2$
$C_2S = 2CaO.\ SiO_2$
$C_3A = 3CaO.Al_2O_3$
$C_4AF = 4CaO.Al_2O_3.Fe_2O_3$

1.6.1.3 Portland Cement hydration

The hydration reactions of cement are complex and are still the subject of some debate. It is, however, generally accepted that, after an initial burst of heat evolution, during which little hydration occurs, an induction period is encountered. This is necessary to retain plasticity. By approximately 28 days at 5 to 30°C, roughly two thirds of the cement will have hydrated. In the period beyond 28 days hydration will still continue, provided moisture is conserved, albeit at a diminishing rate, until, by 1 year, 95 to 98% of the cement will have hydrated (Glasser 1998).

The hydration of Portland cement occurs by a series of consecutive and interacting reactions between clinker material and water. All chemical reactions are written in shorthand notation that is commonly used in the study of concrete chemistry. The notations are outlined in table 1.1

Table 1.1 – Cement Chemistry Notations

Abbreviation	Chemical Formula
C	CaO
S	SiO_2
H	H_2O
A	Al_2O_3
C_2S	$2CaO.SiO_2$
C_3S	$3CaO.SiO_2$
CSH_2	$CaSO_4.2H_2O$
C_3A	$3CaO.Al_2O_3$
C_4AF	$4CaO.Al_2O_3.Fe_2O_3$
C-S-H	$C_3S_2H_3$
CH	$Ca(OH)_2$

Although there may be considerable overlapping of the various reactions, the general rates of hydration proceed in the approximate order (Taylor 1994):

$$C_3A > C_3S > C_4AF > C_2S$$

Within a few minutes of cement hydration, C_3A reacts with gypsum according to the reaction below to form ettringite ($C_6AS_3H_{32}$) (Taylor 1994):

$$C_3A + 3CSH_2 + 26H \rightarrow C_6AS_3H_{32}$$

If gypsum is not available, C_3A reacts with the sulfate in ettringite according to the reaction below to form tetracalcium aluminate ($3C_4ASH_{12}$) (Taylor 1994).

$$2C_3A + C_6AS_3H_{32} + 4H \rightarrow 3C_4ASH_{12}$$

The formation of tetracalcium aluminate ($3C_4ASH_{12}$), above, occurs because of an apparent deficiency of sulfate ions. If a new source of sulfate appears, ettringite can be formed again as shown below (Taylor 1994):

$$C_4ASH_{12} + 2CSH_2 + 16H \rightarrow C_6AS_3H_{32}$$

The reaction of sulfate with calcium hydroxide, and the formation of ettringite after initial stages of cement hydration, are the cause of cement deterioration due to excessive exposure to sulfates. The volume expansion of the paste accompanying these reactions creates internal stresses that ultimately lead to cracking (Taylor 1994).

The two calcium silicates (C_3S and C_2S) are the main cementitious compounds in cement , the former hydrating much more rapidly than the latter. As indicated by the preceding reactions, the reactions of the two calcium silicates are very similar, differing only in the amount of calcium hydroxide formed (as indicated by the masses in the brackets under the reactions) (Neville 1987):

For C_3S:

$$\begin{array}{cccc} 2C_3S + & 6H \rightarrow & C_3S_2H_3 + & 3CH \\ [100] & [24] & [75] & [49] \end{array}$$

For C_2S

$$\begin{array}{cccc} 2C_2S + & 4H \rightarrow & C_3S_2H_3 + & CH \\ [100] & [21] & [99] & [22] \end{array}$$

In a fully hydrated paste, 50 to 60% of the volume is occupied by $C_3S_2H_3$ (C-S-H).

1.6.1.4 Chemical factors affecting solidification

Both the additives and the waste being encapsulated can retard, inhibit, and accelerate the setting of the cement matrix. Studies of the effect which metals and organic additives have on cement hydration have generated considerable interest (Mollah 1995a, Mollah 1995b). General types of interference that can be caused by the chemical constituents added to the cement based S/S system include (Means et al 1995):

- Inhibition of bonding of the waste material to the S/S material;
- Retardation of setting;
- Reduction of stability of the matrix resulting in increased potential for leachability of the waste;
- Reduction of physical strength of the final product.

A vast majority of instrumental techniques including Scanning Electron Microscopy (SEM) and Fourier transform infrared (FTIR) are available to aid in the identification of interferences, a result of the addition of both additives and wastes, such as arsenic, to the setting of the cement matrix. The instrumental technique(s) selected will be dependent upon the type of information being sought.

SEM is useful to characteristic heavy metal uptake in cement stabilized metal wastes and can also be used to identify the formation of compounds detrimental to the cement matrix, such as ettringite. Through the monitoring of vibrational frequencies, FTIR can provide both molecular characterization and insight into molecular structures. During the hydration of cement, the vibrational spectra of groups such as Si-O are known to change with time.

Thus by comparing the vibrational energies of groups, including Si-O, of unadulterated cement with S/S formulations, the effect, if any, that the incorporation of chemical constituents have had can be determined.

1.6.2 Leaching/Extraction tests

The performance of S/S wastes is measured in terms of leaching and extraction tests. There are a vast number of different leaching tests available and one or more may be required for regulatory approval. 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. Table 1.2 outlines a number of the leaching/extraction tests that can be used to gauge the successfulness of the S/S process.

In Australia, the environmental acceptability of a hazardous waste for landfill disposal is determined using the results obtained from either the Toxicity Characteristic Leaching Procedure (TCLP) (U.S. EPA 1992) or the Australian Bottle Leaching Procedure (ABLP) (AS4439.3 1997).

Table 1.2 – Common Leaching/extraction tests (modified from Means et al 1995)

Test Method	Leaching medium	Liquid:Solid ratio	Particle size	Number of extractions	Time of extractions
Aust. Bottle Leach Procedure	Deionized water or acetate buffer[(a)]	20:1	< 2.4 mm	1	18 hours
TCLP	Acetate buffer[(a)]	20:1	< 9.5 mm	1	18 hours
EP Toxicity	0.04 M acetic acid	20:1	< 9.5 mm	1	24 hours
Cal Wet	0.2 M sodium citrate	10:1	< 2.0 mm	1	48 hours
Multiple Extraction Procedure	Same as EP tox, then with sulfuric acid: nitric acid (60:40)	20:1	< 9.5 mm	9 (or more)	24 hours per extraction
Synthetic acid precipitation leach test	(c)	20:1	< 9.5 mm	1	18 hours
Monofilled waste extraction procedure	Deionized water or other for specific site	10:1	< 9.5 mm or monolith	4	18 hours per extraction
Dynamic leach test	Deionized water	(d)	Monolith length to-diameter ratio between 0.2 and 5.0	(d)	Leachant renewed at 0,1,4,7,24,31 ,48,72,79 and 100 hours +
Shake extraction test	Deionized water	20:1	Particulate or monolith as received	1	18 hours

Test Method	Leaching medium	Liquid:Solid ratio	Particle size	Number of extractions	Time of extractions
Equilibrium leach test	Deionized water	4:1	< 150 μm	1	7 days
Sequential chemical extraction	Five leaching solution increasing in acidity	Varies from 16:1 to 40:1	< 45 μm	5	Varies from 2 to 24 hours
Static leach test	(e)	(f)	monolith	1	3, 7, 14, 28, 56, 91, 182 and 364 days
Agitated powder leach test	(e)	10:1	50% < 0.044 mm 50% between 0.074 and 0.149mm	1	28, 56, 91, 182, 273, and 364 days
Soxhlet leach test	Deionized water	Continous flow of redistilled water	monolith	1	3, 7, and 14 days

Key to above table:

(a) = either an acetate buffered solution with pH = 5 or 5.7 mL acetic acid per litre.

(c) = sulfuric acid:nitric acid in 60:40 weight percent mix. pH adjusted with deionized water to 4.2 or 5.0 for site east or west of the Mississippi River, respectively.

(d) = The renewal frequencies are selected based on a known diffusion coefficient. The surface-to-volume ratio must be selected to ensure the contaminant is detected. The renewel frequency must be selected to ensure nonequilibrium condtions prevail.

(e) = Silicate water, deionized water, brine or repository water.

(f) = The volume of leachant is based on the measured geometric surface area of the sample. The volume-to-surface ratio must be between 10 and 200 cm.

1.6.2.1 Landfill Disposal

Presently, an attractive technology available for the disposal of hazardous wastes, such as arsenic, after being rendered "safe" is landfilling.

Landfill has been defined as the engineered deposit of waste onto and into land in such a way that pollution or harm to the environment is prevented (Skitt 1992). Landfills can be classified or grouped into various classes, depending upon the types of wastes that they can accept. For example, the NSW EPA classifies its landfill facilities as shown in table 1.3.

Table 1.3 – Disposal of wastes to the different classes of landfills (NSW EPA 1998)

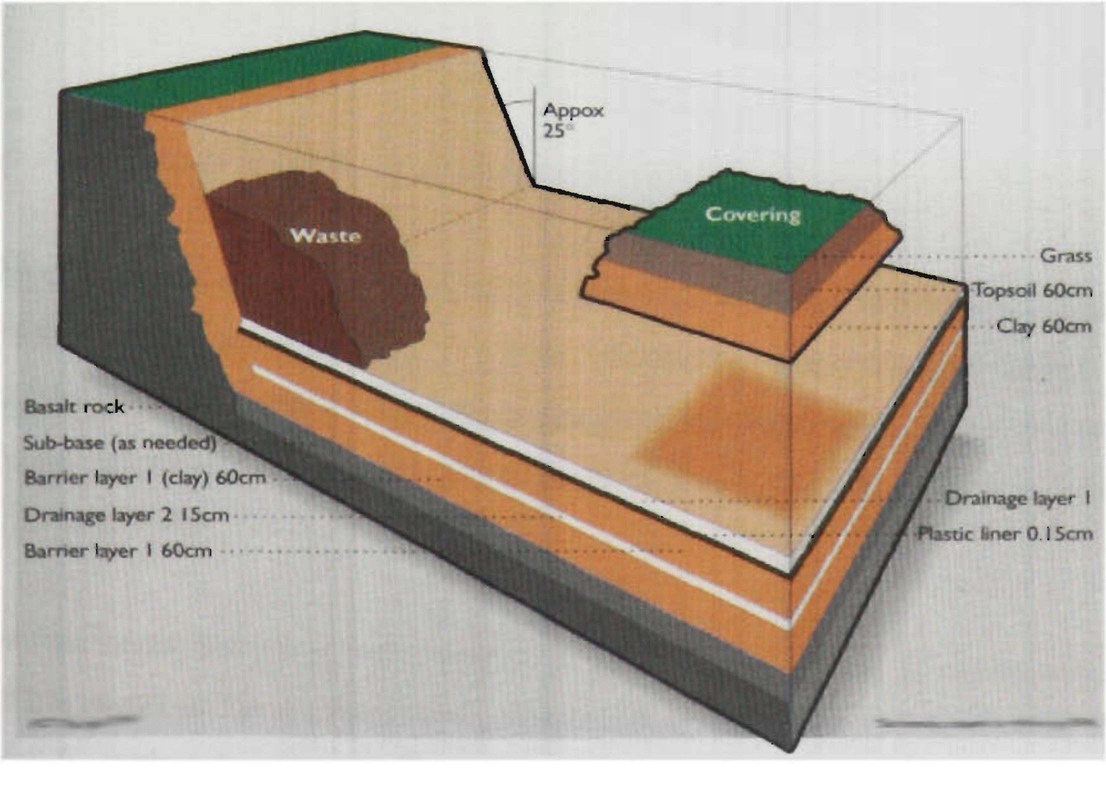
Landfill type	**Wastes able to be received**
Inert Waste Class 2 Landfill	Accepts all wastes that are classified or assessed as inert waste
Inert Waste Class 1 Landfill	Accepts all wastes that are classified or assessed as inert waste except physically, chemically or biologically immoblised, treated or processed waste
Solid Waste Class 2 Landfill	A landfill that accepts wastes that are classified as solid waste including putrescible wastes
Solid Waste Class 1 Landfill	A landfill that accepts wastes that are classified as solid waste excluding putrescible wastes
Industrial Waste Landfill	Also known as monofill or monocell. An isolated landfill unit for disposal of one specific waste type. Able to accept waste classified or accessed as industrial waste

While the way landfills are divided into classes will differ from state to state, and country to country, the type of landfill which accepts hazardous wastes, which have been stabilized, will always be the same. These landfills will be secure landfills, where the prime objectives are to prevent water percolating through the landfill and to collect and treat any leachate (percolating water that gets contaminated by contacting wastes), thereby ensuring that there is no permanent sterilization of the land or waterways.

There are four critical elements in a secure landfill: the natural hydrogeologic setting, a bottom liner, a leachate collection system and a cover. The natural setting can be selected to minimize the possibility of wastes escaping to groundwater beneath a landfill. The other three elements have to be engineered.

Modern, industrial waste landfills are divided into separate cells. where wastes that are similar in nature are emplaced together, but so arranged that mixing with other wastes should not occur. Figure 1.0 illustrates such a waste cell.

Figure 1.0 – A waste cell (CSR 1998)



The bottom of the landfill is sloped, with pipes laid along the bottom to capture the leachate as it accumulates. The pumped leachate is then treated at a wastewater treatment plant.

Two fundamental types of lining material are available for landfills, natural (e.g. clay, shale) and synthetic liners, also known as flexible membrane liners (FML) or geomembranes. Landfills usually employ a mixture of both types of liners. Natural liners such as clay have the advantage of inherent attenuation capacity (a relatively high ion-exchange capacity will inhibit, for example, the migration of heavy metals) and are relatively stable in the presence of a wide range of organic and inorganic compounds, but they are more permeable than FMLs (Westlake 1995). Conversely FMLs have little or no inherit attenuation capacity and are sensitive to organic solvents, but are relatively impermeable. The complementary properties of natural and synthetic materials are optimized in the construction of composite liner systems.

Once each waste cell has been filled a cover or cap is placed over the cell to keep water out, to prevent leachate formation. It will generally consist of several sloped layers of clay or FMLs, overlain by topsoil to support vegetation.

1.6.2.2 General leaching mechanisms

The process of slow extraction of contaminants from the S/S treated waste by water or some other solvent is called "leaching". Leaching can occur when the S/S treated waste is exposed to stagnant leachant or to a flow of leachant through or around the waste. In a disposal scenario, the solvent will usually be groundwater.

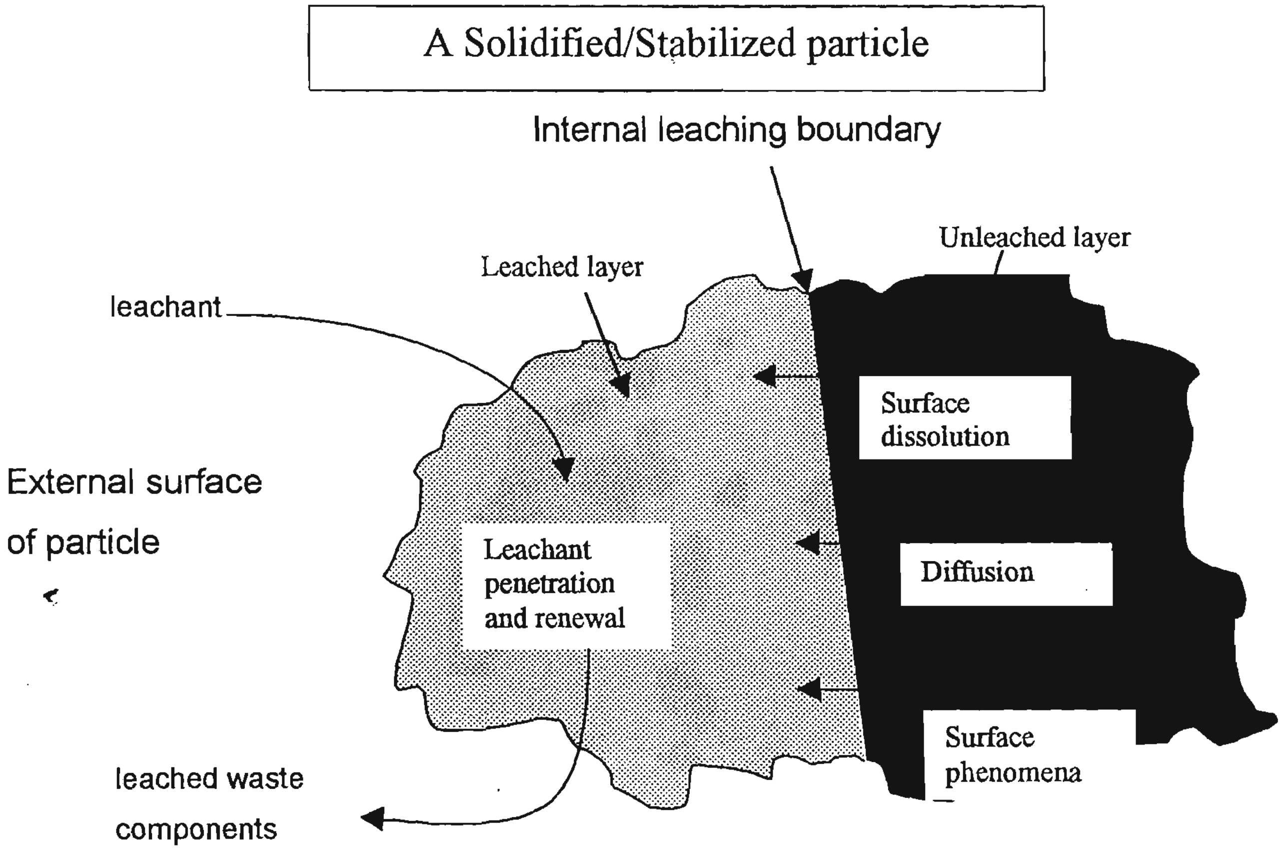
The two basic leaching mechanisms in the leaching process are mobilization and transport of the contaminant. The leachant mobilizes contaminants within the S/S matrix by dissolving the contaminant. Dissolution results from a combination of chemical and physical mechanisms. Examples include bulk dissolution of mineral phases in the S/S treated waste, wash off of surface contaminants, changing chemical parameters such as pH or Eh, dissolving a formerly insoluble phase, desorption of contaminants, or other mechanisms. Under neutral conditions, the leaching rate is controlled by diffusion of the solubilized species. Under acidic conditions, the rate is initially limited by the supply of H^+. After a time, molecular or boundary layer diffusion of the waste constituents, again, becomes rate limiting.

Within the solid waste form, transport of the contaminants can occur by convection or diffusion. As most waste forms have relatively low permeability, diffusion is normally the only process operating. Diffusion occurs by the random motion of individual molecules or ions. Assuming that the solid is in chemical equilibrium when leaching begins, diffusion is driven by the difference in the chemical potential (constituent concentration) between the solid and the fluid leachant. The chemical gradient thus created causes constituents to migrate from the solid to the leachant (Conner 1990).

As the leachant is continually replaced, the concentration of species within the outermost layer becomes progressively depleted. However, leaching does not stop, because, at the same time, the leachant is penetrating the particle and, consequently, maintaining the concentration gradient initially established across the outer surface. This interface of leachant and leaching surface is called the leaching boundary.

As time progresses the concentration of soluble species in consecutive layers becomes depleted and the leaching boundary moves further and further away from the outer surface, i.e., into the particle. As a result, the surface area which constitutes the leaching boundary is continually contracting. Subsequently, the concentration of waste components in the leachant becomes lower and lower, until a point is reached where the rate of dissolution of species at the leaching boundary, their transport out of the particle and the rate at which leachant is renewed, all combine to produce a relatively stable leached concentration. At this point in time, the concentration of leached species does not fluctuate by any significant margin. Summaries of the transport mechanisms and surface phenomena involved in the leaching process are summarized in figure 1.1.

Figure 1.1 Phenomena occurring during the leaching of waste components (modified from Foster 1998)



1.6.3 Solidification/stabilization (S/S) processes

A number of S/S processes, specifically for arsenic, have been investigated. These included fixation with:

- Portland cement (Akhter 1990, Bulcher 1996)
- Portland cement and iron(II) (Artiola 1990, Taylor 1994, Fuessle 2000)
- Portland cement and iron(III) (Taylor 1994, Fuessle 2000)
- Portland cement and lime (Dutre 1998)
- Portland cement, iron and lime (Voight 1996, Palfy 1999)

- Portland cement and fly ash (Chu 1991, Akhter 1997)
- Portland cement and silicates (Chu 1991)

In addition to these studies, which have investigated the aforementioned S/S processes, there has also been limited research into the safe disposal of arsenic wastes by incorporation into slags and encapsulation of arsenic wastes using polymers (Twidwell 1985, DeVillers 1995, Carter 1995).

Twidwell et al (1983, 1985) investigated the stabilization of arsenic by dissolution in slag matrices. The stabilization process involved converting the arsenic oxide contained in the flue dust to calcium arsenate and arsenite, by low temperature air roasting in the presence of lime. The calcium arsenate and arsenite were then dissolved in a molten iron silicate slag matrix. The incorporation of up to 23.5% arsenic into the slags was investigated. All slags passed the U.S. EPA EP Toxicity Test for arsenic extraction. Even the slag with the highest arsenic content (23.5%), which leached 1.8 ppm arsenic, easily passed the EP Toxicity Test limit of 5 ppm arsenic leached.

De Villiers (1995) investigated the fixation of arsenic-containing wastes in lead-zinc blast furnace slags, using a calcium arsenite containing waste. The waste was mixed with the slag and heated at 1300 to 1400°C to dissolve the arsenic into the slag. The arsenic-doped slags contained up to 2.3 wt% arsenic. It was found that arsenic leached out of the slag as the As(III) species and slowly oxidized to As(V) in the leachate solutions. Of four arsenic doped slags, only one passed the Toxicity Characteristic Leaching Procedure regulatory test (having a leachate concentration of less than 5 ppm arsenic).

The disposal of arsenic by incorporation into slags has also been investigated by Riveros and Utigard (2000). Although the leaching tests showed that the slags could meet environmental regulations, the fraction of arsenic leached was no less for the slag samples than for the initial iron arsenate itself.

Carter et al. (1995) investigated the potential for encapsulation of waste by combination with two commodity polymers, recycled high density polyethylene (HDPE) and solprene 1204 (a random styrene butadiene copolymer with a 25% styrene content). They concluded that As_2O_3 could not be suitably bound into HDPE, because the processing temperatures generally employed approach the sublimation temperature. This meant the process was both inefficient and hazardous. When As_2O_3 was stabilized with calcium oxide, volatility was decreased, and arsenic loadings of 17 wt% were possible. The elastomer appeared to have the greater potential, as it proved possible to incorporate As_2O_3 at higher loadings than were possible using HDPE, while calcium arsenite was encapsulated with higher success, with loadings of up to 50% wt. easily attained. Both of these techniques, i.e. incorporation of arsenic into slags and the encapsulation of arsenic using polymers require further evaluation to determine their suitability.

Of the solidification/stabilization formulations investigated, the use of cement and fly ash appears to be the least successful. Fixation of metals using Portland cement and fly ash is believed to occur via the combination of producing an impermeable monolith, which reduces the surface area available for leaching, creating a high pH environment that generally limits the solubility of most metals and limits their leachability, and/or formation of metal complexes with the cement/fly ash matrix (Chu 1991). Akhter et al (1997) has raised serious concerns about the benefit of using fly ash. The work of Akhter et al (1997) yielded results which indicated that the leachability of arsenic is much greater from those solidification/stabilization formulations which contained fly ash. The use of fly ash also has an associated problem of bulking. Since fixed waste is generally buried in a landfill, it is desirable, for cost and space reasons, to bury the smallest quantity possible. Bulking due to treatment by silicates and metal hydroxides is low, approximately 20% or less, while bulking resulting from treatment with cement/fly ash is high, approximately 100%.

Presently, it appears that the solidification/stabilization of arsenic is most successful when cement, cement and iron, cement and lime, or combinations thereof, are used. Akhter et al (1990) investigated various methods for the immobilization of arsenic, cadmium, chromium and lead in contaminated soil. The soil under investigation had an arsenic concentration of 12,200 ppm. The suitability of various combinations of Portland cement, fly ash, blast furnace slag, lime and silica fume was investigated. The only sample in the study showing reasonable leaching performance was that using Portland cement alone, at a dosage of 1 part soil in 0.44 part cement.

Dutre and Vandecasteele (1995) investigated solidification/stabilization of solid waste containing an average of 42% arsenic. Solidification was achieved by adding waste acid (5M hydrochloric acid containing zinc and iron, each approx. 60 g/L, and lead, approx. 150 mg/L), blast furnace slag, slaked lime, cement and water. This process was carried out over two days. The waste, slags and waste acid were all mixed together and then set aside overnight. The mixture was set aside overnight because it is believed that silicon containing acids (H_2SiO_3) are formed, due to a reaction between the acid and the silicate compounds of the binder materials, and which are responsible for further polymerisation on a long term basis (Dutre and Vandecasteele 1995).

The authors also investigated addition of aluminium and barium salts for lowering the leachability of arsenic from the solidified waste by formation of compounds with low solubility products. However, results indicated that lime, thought to allow the formation of a sparingly soluble calcium arsenic compound, was more effective than either of these.

Subsequent optimization of the initial S/S scheme led to omission from the formulation of the waste acid and blast furnace slag. These two ingredients appeared to have little or no effect on the fixation, despite obviation of the route to silicious acids described earlier. Lime addition was the critical element of the process, and consequent simplification allowed for a one day fixation. The revised S/S recipe was (per 10 g of waste), 10 g of lime and 11 g of cement.

More recent work by Dutre and Vandecasteele (1998) examined the solidification/stabilization of a waste fly ash from the metallurgical industry, containing arsenic concentrations ranging from 23% to 47% (wt%). The optimum solidification/stabilization formulation consisted of 8 g of lime, 6 g of cement and 20 mL of water per 10 g of waste material. The solidification process was capable of reducing the leachate concentration from 5 g/L to approximately 5 mg/L. The extraction test used consisted of agitating 100 g of the treated material with 1 L of distilled water for 24 hours. The reduction in the arsenic concentration was due to the formation of $CaHAsO_3$ in the leachate, in the presence of $Ca(OH)_2$.

Palfy et al (1999) investigated the stabilization of a waste material arising from the carbon dioxide scrubbing in the Vetrocoke technology, where As_2O_3 solution is the activator. The aim of the fixation process was to embed calcium and ferric arsenates/arsenites in a cement matrix. The optimum process utilized a Ca:As ratio of 8 (ratios greater than 8 did not lead to a significant reduction in the residual concentration of arsenic in the solution) and a Fe:As mole ratio of 6. After the fixation process, the leachate concentration was 0.823 mg/L compared to 6430 mg/L for the untreated waste. Leaching tests were conducted in distilled water at 25°C with a solid to liquid ratio of 1:10 and a mixing speed of 150 rpm.

Of the successful solidification/stabilization formulations, the use of iron appears to be the most preferred option, partly due to the fact that iron is often a component of process liquors. Hence the use of iron provides the opportunity to dispose of two waste streams at once. The success of using iron is highly dependent upon the oxidation states of both the iron and arsenic (Taylor and Fuessle 1994). The use of iron(II) is preferred for arsenic stabilization because it has proven to be more effective over a wider range of mix designs and over the longer term than iron(III). The use of iron(III) is not recommended for arsenate stabilization, because the fresh cement mix adsorbs ferric ions and doesn't allow adequate solidification/stabilization until long cure times have elapsed (Taylor and Fuessle 1994). Taylor and Fuessle

(1994) suggest that effective conversion of arsenite to arsenate can be accomplished by the addition of hydrogen peroxide, at stoichiometric dosages, with adequate mixing. Emett et al (1998) have outlined a process in which dissolved iron(III), in the presence of UV light, was used to initiate and sustain the oxidation of arsenic(III) in aqueous acid. The photolysis reactions of iron(III) in water involve the transfer of one electron from the complexed ligand, such as organic, hydroxide or chloride species, to the iron(III)-centered orbital, forming Fe(II) and a free radical. The subsequent reaction of the primary free radical results in oxygen being consumed and the arsenic being oxidized. The presence of elements, like Ca, Cd, Zn, Sr, Pb, Cu and Mg, have been reported to promote the stability of iron-arsenate precipitates, as the solubility of arsenic can be lowered significantly over a wide pH interval (Emmett 1998, Khoe et al 1994). Increasing the iron to arsenic mole ratio also results in a greater success in the solidification/stabilization of arsenic using iron. Taylor and Fuessle (1994) recommended that the iron(II)/arsenic mole ratio be at least six, although slightly lower dosages of iron(II) may be effective if cure times of at least 60 days are used.

While the research to date indicates that the use of iron, lime and cement can be beneficial in the solidification/stabilization of arsenic, it is difficult to differentiate between the results obtained by the numerous researchers and draw any firm conclusions on which S/S processes are the most efficient and effective. This is mainly due to two reasons:

1. **The diverse range of arsenic compounds and oxidation states that can be encountered as arsenic waste.**

    The complex chemistry of arsenic, unfortunately, means that a "formulation" which may work with one particular waste may not, and often will not, work with another type of arsenic waste. The works outlined by Buchler et al (1996) and Johnson et al (1980) are good examples of how the success of the fixation varies drastically with the nature of the waste and simply not just the varying arsenic concentrations. TCLP leachate concentrations obtained from Buchler et al (1996) varied from 510 mg/l to 1.7 mg/l. Those S/S processes which contained either sodium arsenate or sodium arsenite were the most successful, with As leachate concentrations of 1.7 and 2.1 mg/l, respectively, while the S/S process which contained arsanilic acid performed least effectively, with arsenic leachate concentrations of 510 mg/l.

The arsenic compounds also have major effects on cement hydration reactions, as shown in solid-state NMR spectra, although there is no direct correlation between degree of hydration in the matrix and arsenic leachability (Buchler 1996). The most leachable compound determined by Buchler et al (1996), arsanilic acid, showed the least effect on cement hydration.

Johnson et al (1980) investigated the stabilization of three different arsenic wastes. Waste No. 1, composed mostly of sulfate and chloride salts, contained approximately 2% organic arsenicals. The second material, Waste No. 2, was a yellow, damp (37% moisture) acidic filter cake, containing approximately 0.9% arsenic in the form of As_2S_3, while Waste No. 3 was a fine white powder, containing 90% As_2O_3.

Each waste was subjected to several identical fixation processes (the exact nature of these processes was not revealed). The three wastes were quite different in their response to fixation attempts, with Waste No. 1 by far performing the worst. Even after fixation, Waste No. 1 still leached an average of 78%. Waste No. 3 performed significantly better than Waste No.1, leaching less than 12% arsenic, while Waste No. 2 performed the best, leaching less than 2% arsenic. Unfortunately, given that the exact nature of the fixation processes was not revealed, the information that can be drawn from this work is limited.

2. The different leaching tests which researchers have utilized to access the leachability of the treated waste.

Due to the differences between the tests, such as the acidity of the leaching fluid, extraction periods, and particle sizes, the results obtained from the various tests can, consequently, be quite different. A detailed description of the leaching tests is provided elsewhere (U.S. EPA 1989), while a brief overview of some of the common leaching tests was provided in table 1.2 (page 28). Of the common leaching tests used, the TCLP and the EPTox are the most similar. Studies have shown that TCLP concentrations can be up to 3.0 times greater than those for the EPTox Test (U.S. EPA 1989). The WET test is generally a more aggressive leaching test than the TCLP, for several reasons. In the WET, solid wastes are crushed to pass a smaller sieve, and the contact time between leaching solution and waste is greater.

An example, illustrating the difficulty of making any comparisons on the successfulness of S/S processes between studies using different leaching tests, can be found in the work of Chu et al (1991). They conducted studies using both the TCLP and WET tests. When using the TCLP test, treatment using metal hydroxides appeared slightly better than treatment which utilized either silicates or cement/fly ash. The results were 0.02, 0.03 and 0.09 mg/l arsenic, respectively. However, when the same samples were subjected to the WET tests, there were much larger differences between the results obtained for the numerous S/S processes. When using the WET test, treatment using silicates yielded significantly better results than those obtained using metal hydroxides or cement/fly ash. The results obtained were silicates: 3.2 mg/l arsenic; metal hydroxides: 17 mg/l arsenic; and cement/fly ash: 24mg/l arsenic.

1.7. Research Direction

Many processes produce dusts or sludges containing high concentrations of hazardous materials. For example arsenic trioxide is a by product of recovering gold from arsenical gold ores and concentrates. Although the current trend is to minimize wastes and re-use them where possible, there are always some materials, such as arsenic, that are produced which cannot be recycled and must be disposed of in an environmentally safe manner. Since the demand for arsenic and its compounds is far less than the amount being produced annually, there is little economic incentive to invest in equipment and technology to recover arsenic.

The lack of any economic incentive to recover arsenic, and the danger associated with the temporary storage of arsenic wastes, be it in drums or any other unsuitable manner which would result in dire consequences in the case of leaks or fire, has led to interest in technologies for long term or "ultimate" disposal of such hazardous wastes. Stabilization processes were designed to address the needs of ultimate disposal. Stabilization of hazardous waste involves trapping the waste in a stable solid matrix, thus minimizing the escape of hazardous materials by leaching. This process also involves fixing or immobilizing the toxic elements by physical and or chemical means.

A wide range of processes have been used in an attempt to successfully fix arsenic. These include mixing the arsenic with various combinations of cement, lime, iron, silicates, and fly ash. Unfortunately, the additives listed have not all been systematically investigated at the same or similar additive-to- waste ratios, or with similar arsenic compounds. This limits the generality of many of the conclusions that can be drawn from previous research. Due to the complex chemistry of arsenic, the success of any S/S process to attempt to treat arsenic wastes appears highly dependent upon the particular arsenic waste, and not merely the varying arsenic concentrations. This is clearly indicated by the research of Buchler et al. (1996) and Johnson et al (1980).

This thesis presents the results of a study that investigated solidification/stabilization as an option for the safe disposal of highly concentrated arsenic compounds namely:

1. Arsenic pentoxide,
2. Arsenic trioxide,
3. Sodium arsenate,
4. Sodium arsenite,
5. Lead arsenate insecticide.

These arsenic compounds were stabilized using formulations of:

- Cement only
- Cement + lime
- Cement + iron

Each of the above formulations have been chosen as they have achieved a degree of successfulness in section 1.6.3 for the cement based stabilization of arsenic.

Success has been determined by utilizing numerous leaching tests which include:

- Bottle leach tests,
- Sequential leach tests,
- Column leach tests.

The results of this research, which will be progressively discussed in the forthcoming chapters, address the present inadequacies in regards to the fixation and “safe” disposal of arsenic wastes and, hence, lead to more appropriate waste disposal management by:

1. Providing conclusive results on the successfulness of a range of solidification/stabilization procedures, which will be applicable to the hundreds of tonnes of arsenic containing wastes,
2. Comparing and contrasting the results obtained from the numerous leach tests.

Chapter 2

2.0 EXPERIMENTAL

2.1 Materials

The following arsenic compounds were supplied from Chemsal Pty Ltd and used throughout this study:

- Sodium arsenite (brand: Unilab, BDH chemicals)
- Sodium arsenate (brand: Unilab, Univer, Analar)
- Arsenic trioxide (brand: Analar)
- Arsenic pentoxide (brand: BDH chemicals)
- Lead arsenate powder insecticide (brand: ICI chemicals)

All of the arsenic compounds were solids.

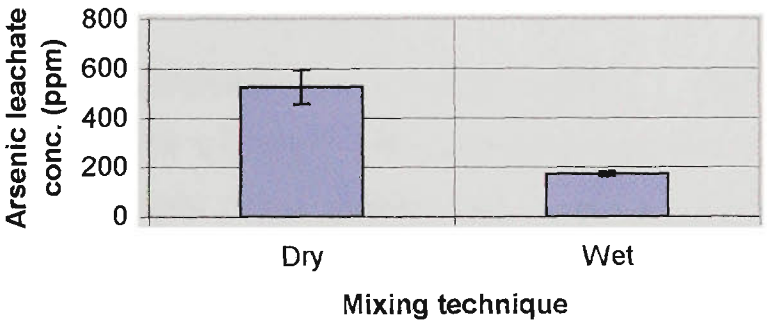
The Solidification/stabilization additives used included:

- Cement (brand: Blue Circle)
- Hydrated Lime (brand: Limil)
- Ferrous sulfate, $FeSO_4.7H_2O$ (brand BDH chemicals)
- Ferric sulfate, $Fe_2(SO_4)_3.9H_2O$ (brand BDH chemicals)
- Ferric chloride, $FeCl_3$ (brand BDH chemicals)

2.2 Solidification/stabilization procedure

The solidified samples were prepared by combining the solidification/stabilization additive(s) and the arsenic sample together and mixing by hand with a plastic spatula. The additives were all added as solids and were mixed thoroughly before water (deionized) was added. In all instances, the arsenic compounds were added as dry solids to the S/S additives. However, if the prime objective is to lower the arsenic leachate concentrations as low as possible, it has been found in this present study (figure 2.0) as well as in previous research (Leist 1997), that the lowest leachate concentrations are obtained when the arsenic compounds are added as a slurry to the S/S formulation, as this facilitates superior contact between the arsenic compound and the various S/S additives. However, as the aims of this present study were primarily to compare and contrast, and to examine the leachability of various S/S formulations, this step was deemed unnecessary and, consequently, omitted.

Figure 2.0 – The effect of combining the arsenic compound as either a dry solid or as a slurry on the leachate concentration when using [cement + iron] stabilization



Note: Leaching test utilized in above example was the Australian Bottle Leaching Procedure (AS 4439.3) using the acetic leaching fluid (5.7mL of acetic acid per litre)

Of the arsenic compounds utilized in this study all but one were fine powders and, therefore, were expected to be uniformly distributed in the stabilized forms. Arsenic pentoxide was the only exception, and was typically in lumps of various sizes. Consequently, the arsenic pentoxide sample was crushed using a mortar and pestle to a sand like consistency before use. All samples were set in acid washed, food grade polyethylene containers, which were sealed and maintained at room temperature (20-23°C) for the duration of the cure time, 28 days. In an attempt to avoid introducing any errors as a result of the mixing technique, each S/S sample, generally in excess of 2000g, was mixed and set in separate 300g sub samples. The total mass of 2000 g was large enough to provide enough samples for all of the tests that were conducted. These sub samples were then combined during the crushing process prior to testing. The technique of coning and quartering was used to select the portion of the S/S material that was required for each test.

The solidification/stabilization formulations used in this study included mixing a single arsenic compound with the S/S additives with consisted of either:

- cement only
- cement + iron
- cement + lime

This is shown in figures 2.1 through to 2.5.

All S/S formulations contained up to 10% arsenic. The cement only formulations, as the name suggests, were comprised only of cement and the arsenic waste. The cement + iron formulations contained approximately 50% cement and 50% ferrous sulfate, while the cement + lime formulations contained 50% cement and 50% hydrated lime. A water to cement and/or lime ratio of 0.5 (w/w) was used. This ratio was used for all the arsenic compounds that were investigated.

The physical properties of the cast products were not determined

Figure 2.1 – Schematic illustration depicting the Sodium arsenite S/S formulations

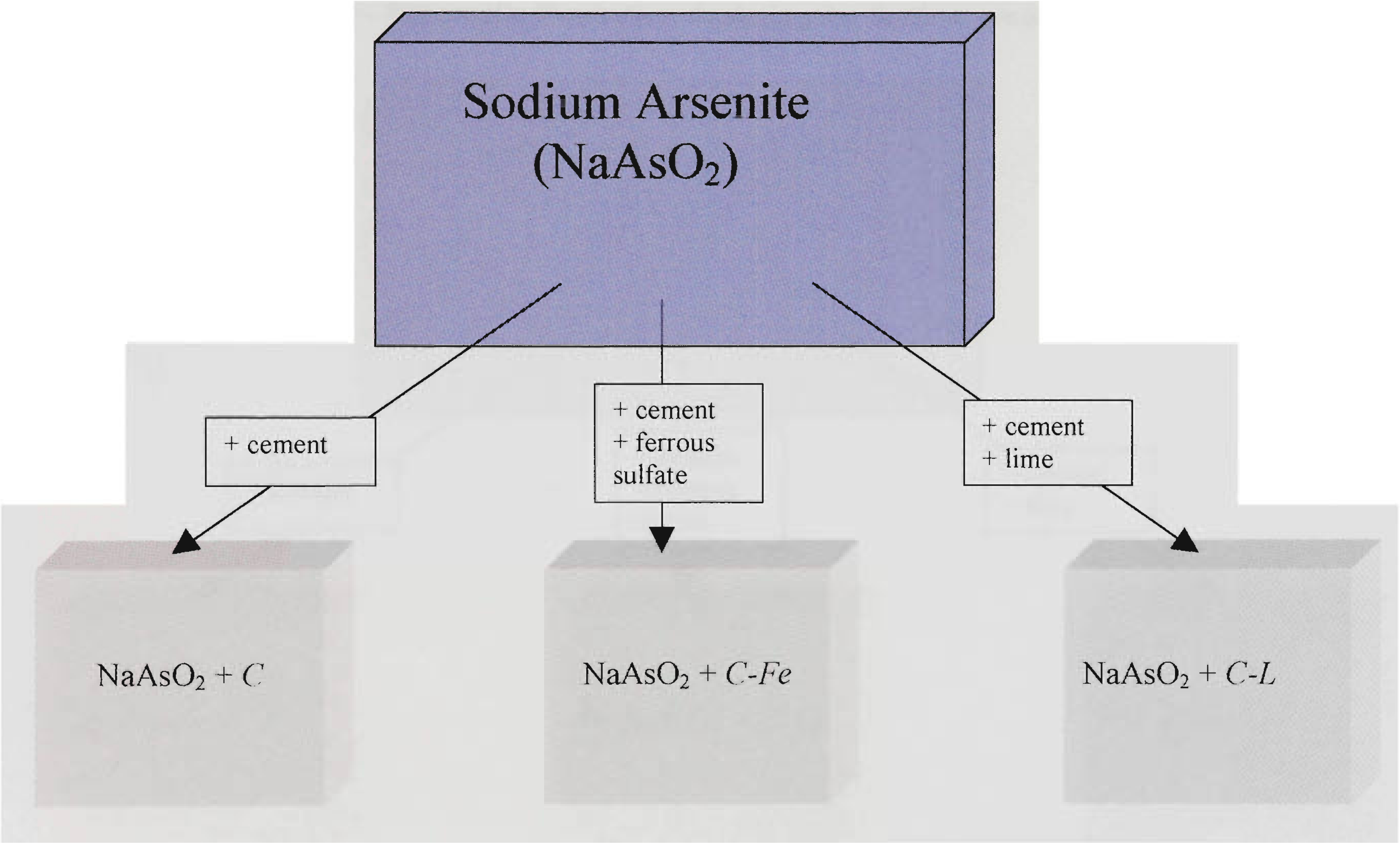


Figure 2.2 – Schematic illustration depicting the Sodium arsenate S/S formulations

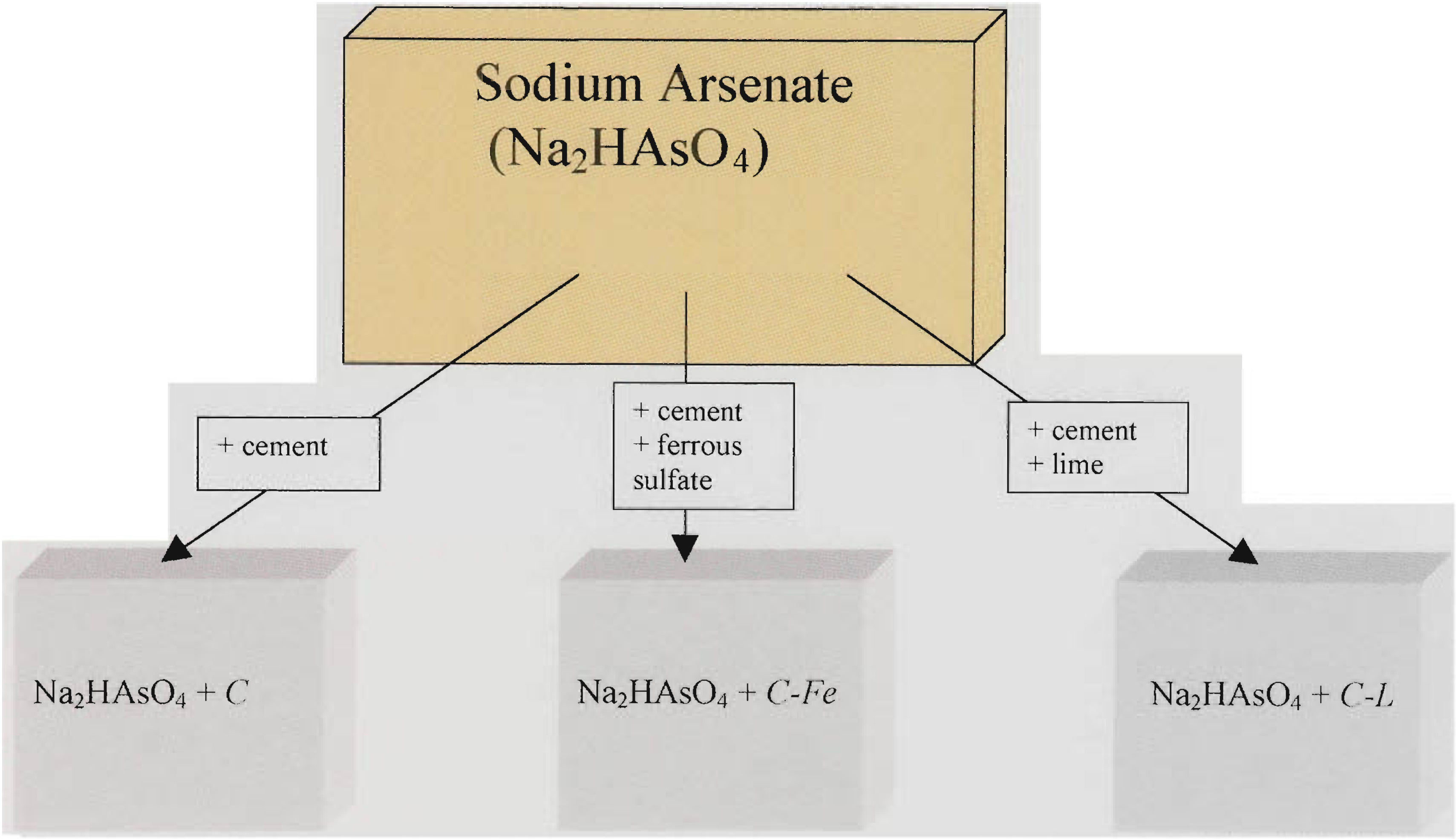


Figure 2.3 – Schematic illustration depicting the Arsenic Trioxide S/S formulations

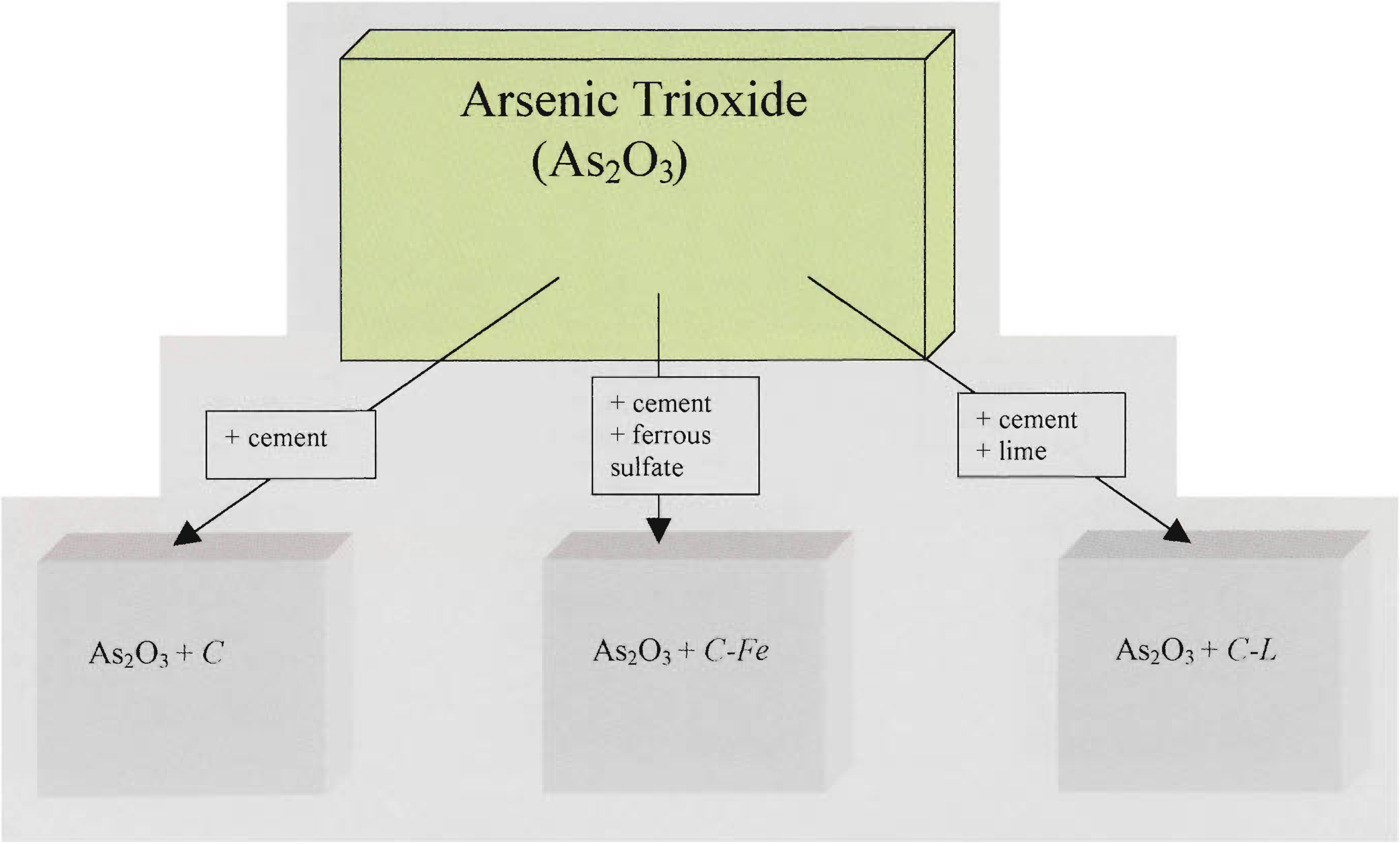


Figure 2.4 – Schematic illustration depicting the Arsenic Pentoxide S/S

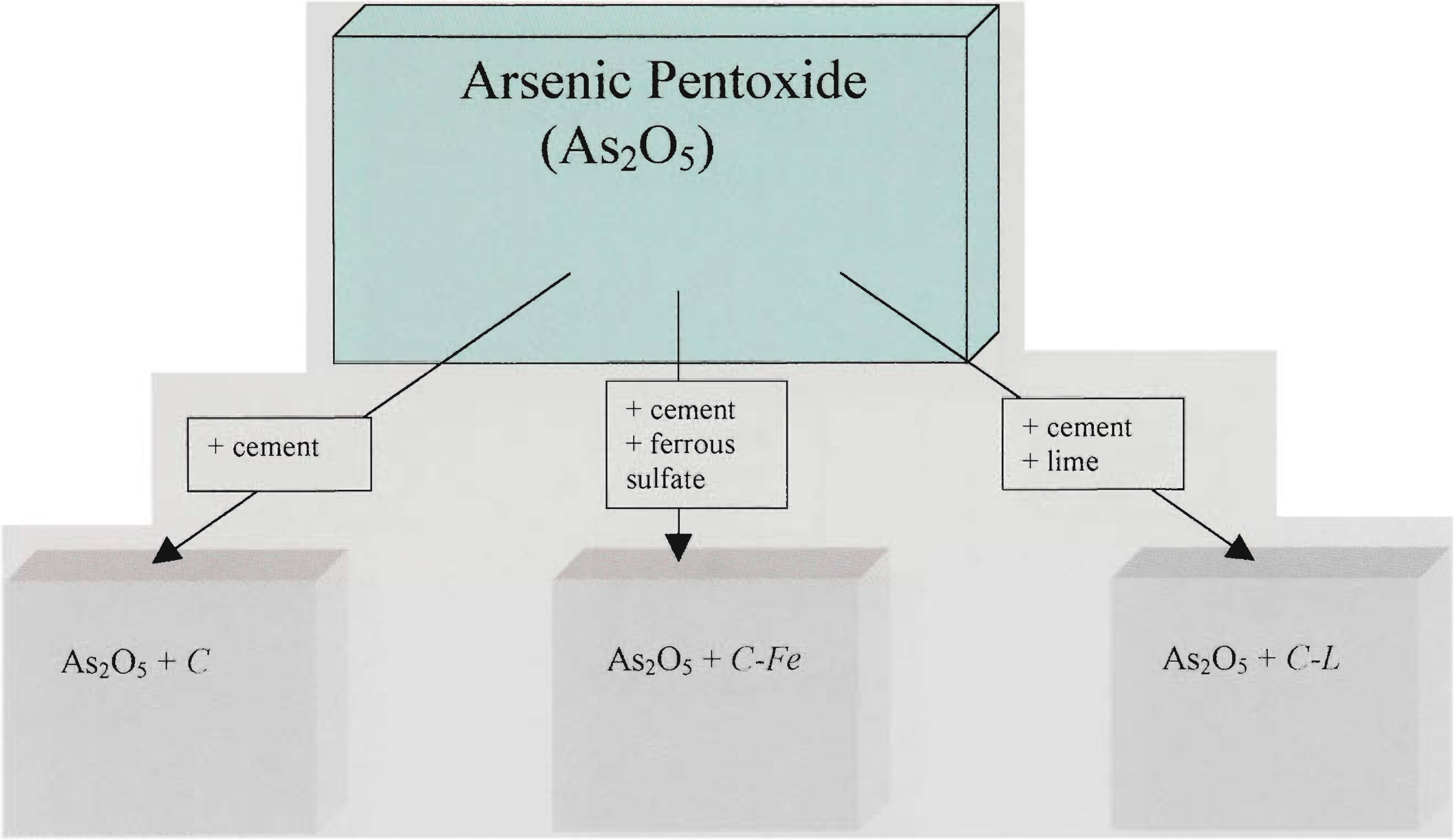
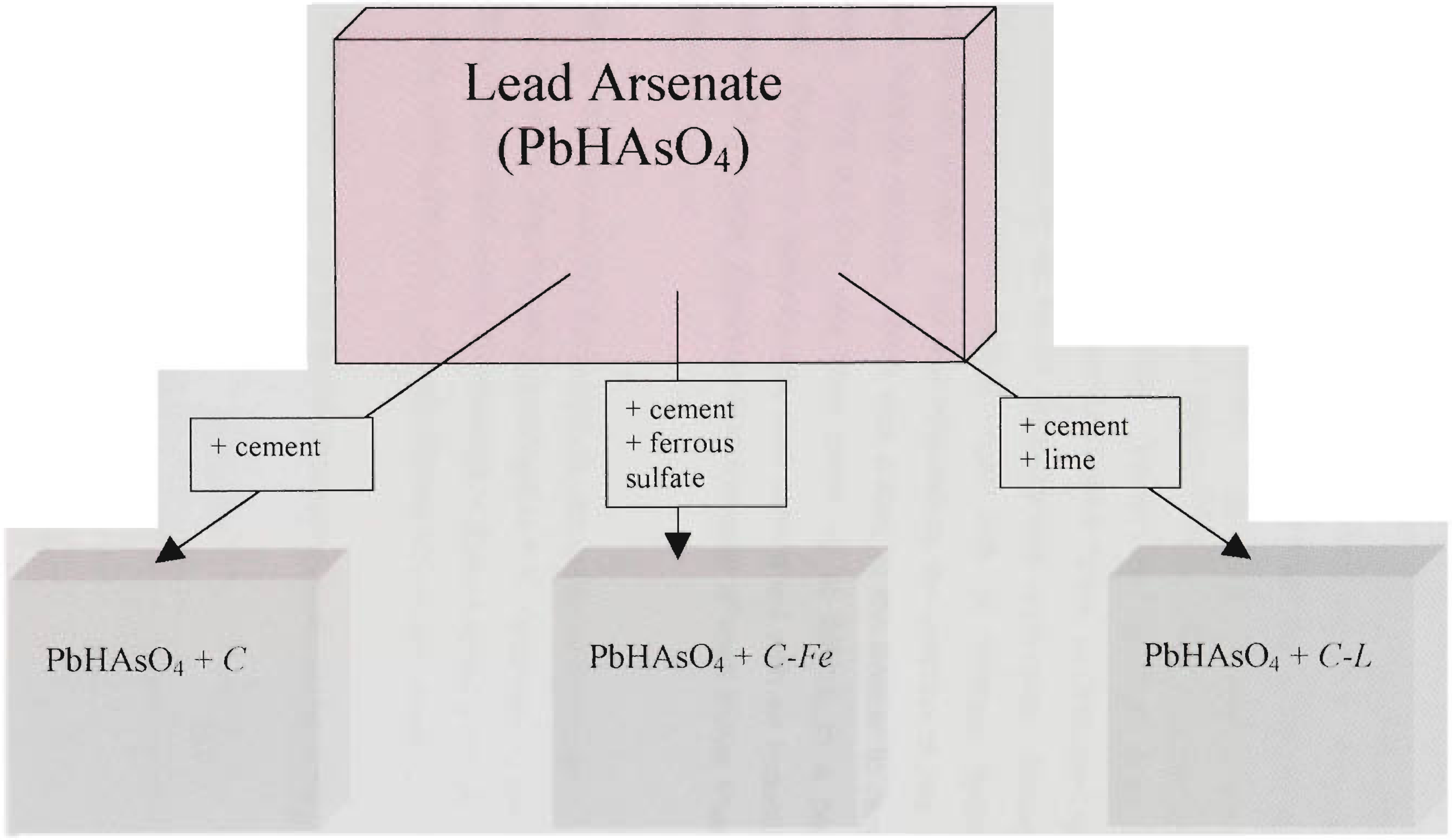


Figure 2.5 – Schematic illustration depicting the Lead arsenate S/S formulations



2.2.1 *Sodium Peroxide Fusion*

The S/S formulations were decomposed for chemical analysis by sodium peroxide fusion. The sodium peroxide fusion was performed in triplicate for each of the S/S formulations after the cure period had elapsed and the formulations had been crushed. The technique of coning and quartering was utilized to select the portion of the sample that was required. The sodium peroxide fusion method involved accurately transferring 0.25g of ground sample (<2.36mm) to a zirconium crucible. Two grams of sodium peroxide and 1 gram of sodium carbonate were added to the crucible and the mixture fused by heating over a Bunsen burner. The crucible was then cooled and placed in a polyethylene plastic beaker along with 100mL of deionized water, followed by the addition of 15 mL of concentrated nitric acid. When the vigorous effervescence ceased, approximately 2mL of 500mL/L hydrogen peroxide solution was added. This was followed by the addition of 2mL of a 5% ammonium fluoride solution, which was added to the beaker to remove any cloudiness. The solution was then made up to 500mL in a plastic volumetric flask. Elemental analysis was then carried out with an Inductively Coupled Plasma (ICP) Atomic Emission Spectrometer (Perkin Elmer Plasma 40 Spectrometer).

The composition of the various S/S formulations, per gram, of dry fixed material, can be observed from tables 2.0 through to 2.4. Appendix A, also contains the data contained in tables 2.0 through to 2.4converted to molar quantities for easier reference to the various formulation stoichiometries.

Table 2.0 – Composition per gram of the arsenic trioxide formulations

	Arsenic	**Calcium**	**Iron**
As_2O_3 + *C*	72.41 ± 2.53 mg	294.81 ± 26.35 mg	14.22 ± 0.78 mg
As_2O_3 + *C-Fe*	97.19 ± 2.91 mg	172.23 ± 7.54 mg	94.77 ± 1.15 mg
As_2O_3 + *C-L*	156.65 ± 0.46mg	347.67 ± 26.00 mg	10.06 ± 0.55 mg

Table 2.1 – Composition per gram of the arsenic pentoxide formulations

	Arsenic	Calcium	Iron
As_2O_5 + *C*	62.60 ± 0.89 mg	339.67 ± 4.93 mg	14.67 ± 0.67 mg
As_2O_5 + *C-Fe*	71.56 ± 1.51 mg	174.76 ± 5.68 mg	76.75 ± 2.96 mg
As_2O_5 + *C-L*	57.70 ± 4.98 mg	335 ± 3.64 mg	8.00 ± 0.80 mg

Table 2.2 – Composition per gram of the sodium arsenite formulations

	Arsenic	Calcium	Iron
$NaAsO_2$ + *C*	74.52 ± 2.53 mg	324.34 ± 16.62 mg	18.93 ± 2.22 mg
$NaAsO_2$ + *C-Fe*	82.53 ± 2.91 mg	200.67 ± 16.50 mg	108.22 ± 1.15 mg
$NaAsO_2$ + *C-L*	84.65 ± 0.46 mg	361 ± 8.72 mg	10.71 ± 0.55 mg

Table 2.3 – Composition per gram of the sodium arsenate formulations

	Arsenic	Calcium	Iron
Na_2HAsO_4 + *C*	58.43 ± 1.22 mg	267.42 ± 9.47 mg	12.29 ± 0.75 mg
Na_2HAsO_4 + *C-Fe*	61.18 ± 2.98 mg	144.54 ± 8.59 mg	69.79 ± 10.02 mg
Na_2HAsO_4 + *C-L*	47.83 ± 1.04 mg	273.33 ± 3.79 mg	6.74 ± 0.25 mg

Table 2.4 – Composition per gram of the lead arsenate formulations

	Lead	Arsenic	Calcium	Iron
$PbHAsO_4$ + *C*	130.00 ± 8.05 mg	49.71 ± 3.40 mg	290.08 ± 7.18 mg	11.95 ± 1.94 mg
$PbHAsO_4$ + *C-Fe*	132.34 ± 11.44 mg	48.33 ± 7.19 mg	139 ± 5.35 mg	73.88 ± 11.53 mg
$PbHAsO_4$ + *C-L*	95.24 ± 1.20 mg	34.07 ± 0.84 mg	224 ± 9.59 mg	8.43 ± 0.94 mg

2.3 Leaching Procedures

The effectiveness of the S/S formulations was evaluated using two types of tests, batch leaching tests and column leaching tests. The portion of the S/S material to be tested was selected using the coning and quartering technique.

2.3.1 Batch Leaching Tests

Two types of batch leaching tests were conducted, i.e., The Australian Bottle Leaching Procedure (AS 4439.3) and the Toxicity Characteristic Leaching Procedure (TCLP) (U.S. EPA 1992).

2.3.1.1 Australian Bottle Leaching Procedure (ABLP)

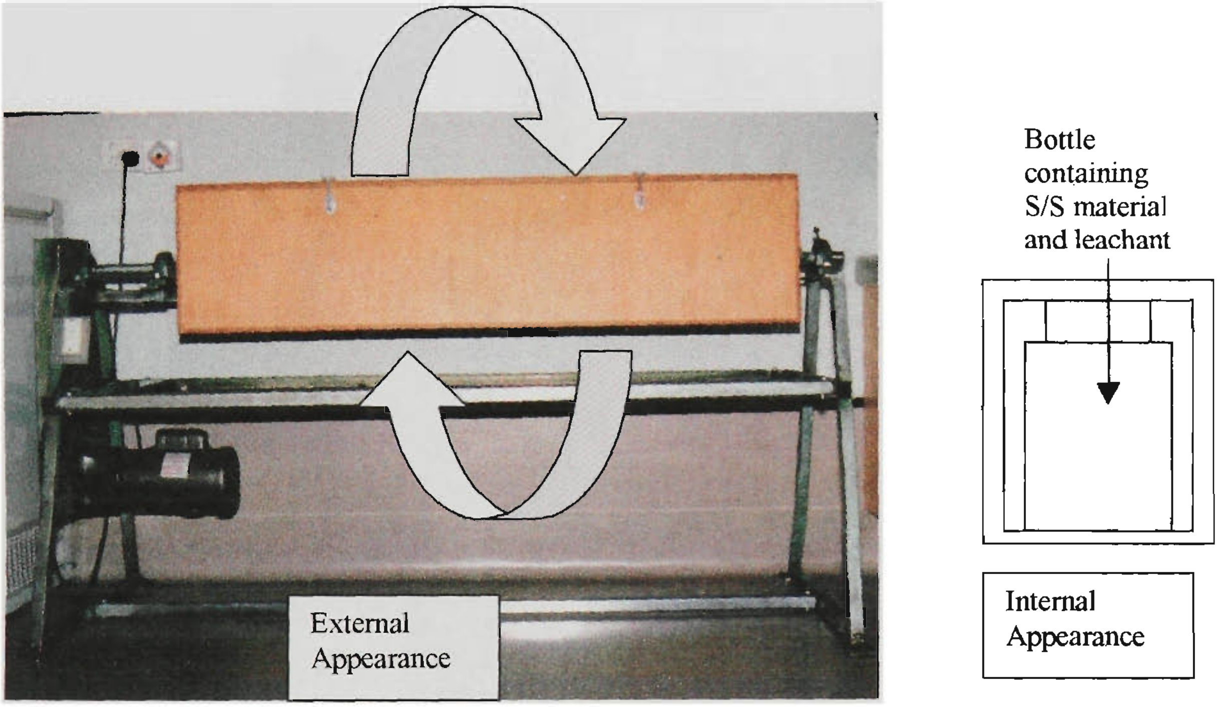
Once the cure times for the S/S formulations had elapsed, the solidified matrix was removed from the plastic container and placed into a mortar where it was crushed to pass through a 2.36mm sieve. As is consistent with the ABLP method, there is no limit on the minimum particle size. The crushed sample was then divided into 100g sub samples. Each of the 100g sub samples was then placed into separate 2000mL polyethylene bottles containing 2000 mL of an extraction fluid. Although the bottle size is designated as 2000mL, sufficient headspace was available for fluid agitation. Two types of extraction fluids were selected on the basis of the Australian Standard 4439.3 test procedures (see Appendix B). They were either:

1. Deionized water
2. Extraction fluid 5.3.2 (5.7mL of glacial acetic acid per litre)

The mixture of the S/S form and extraction fluid was agitated in an end-over-end manner at 30 r.p.m. for 18 ± 2 hours, using an apparatus as depicted in figure 2.6. The fluid was then separated from the solids by means of a positive pressure filtration device (figure 2.7) fitted with a 0.7μm glass fibre filter (brand: Osmonics).

Fluid samples were preserved by acidification to pH<2 with concentrated nitric acid prior to chemical analysis. No differences in atomic emission were noted for samples which were stored for up to 30 days.

Figure 2.6 – Agitation apparatus for The Australian Bottle Leaching Procedure (AS 4439.3)



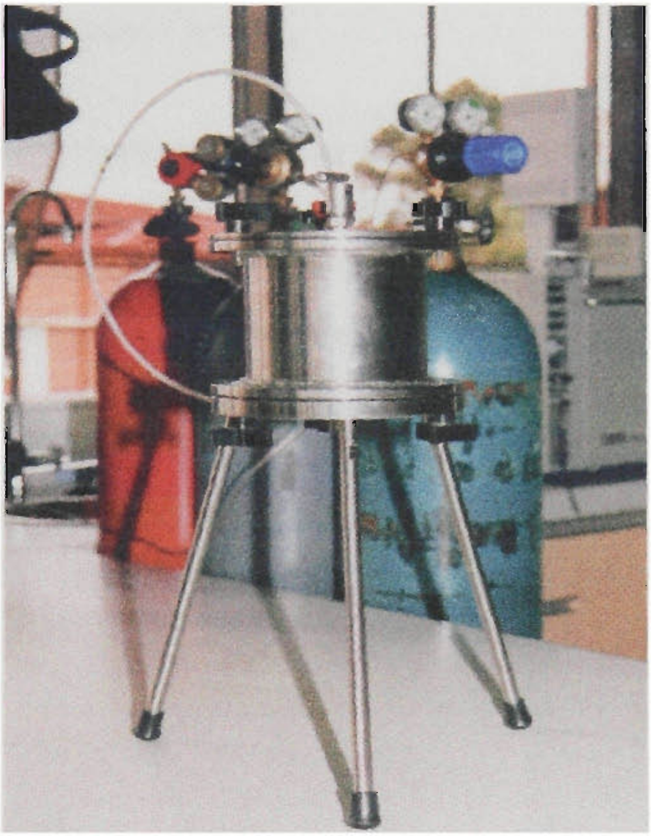
2.3.1.2 *Toxicity Characteristic Leaching Procedure (TCLP)*

The TCLP (U.S. EPA 1992) does not differ substantially from the aforementioned Australian Bottle Leaching Procedure (AS 4439.3). As was the case with the ABLP, the TCLP has no limit as to the minimum size of the test specimen. The only substantial differences between the two tests are in the particle size of the solidified sample which is used for testing and the number of possible leaching fluids to select from.

For the TCLP the solidified/stabilized material was crushed to pass through a sieve of size 9.50mm (as opposed to 2.4mm for the Australian Bottle Leaching Procedure (AS 4439.3)). The only leaching/extraction fluid applicable to the stabilized wastes investigated in this study, as determined by the TCLP (appendix C), was extraction fluid 5.6.2 (5.7mL of glacial acetic acid per litre).

As was the case for the Australian Bottle Leaching Procedure (AS 4439.3) all extraction fluids were made up fresh daily.

Figure 2.7 – Positive pressure filtration device



2.3.1.3 Sequential leach tests

Sequential batch tests were conducted in the same manner as the Australian Bottle Leaching Procedure (AS 4439.3), with the exception that the duration of the overall test was longer. At the end of every 18 hours, the entire leachant was removed for analysis. Fresh leachant was then added and the leaching test recommenced. Sequential leaching (water) tests utilized deionized water as the leaching fluid, while the sequential leaching (acid) tests utilized the Australian Bottle Leaching Procedures (AS 4439.3) acidic leaching fluid (5.7mL of acetic acid per litre).

2.3.1.4 Continual leaching tests

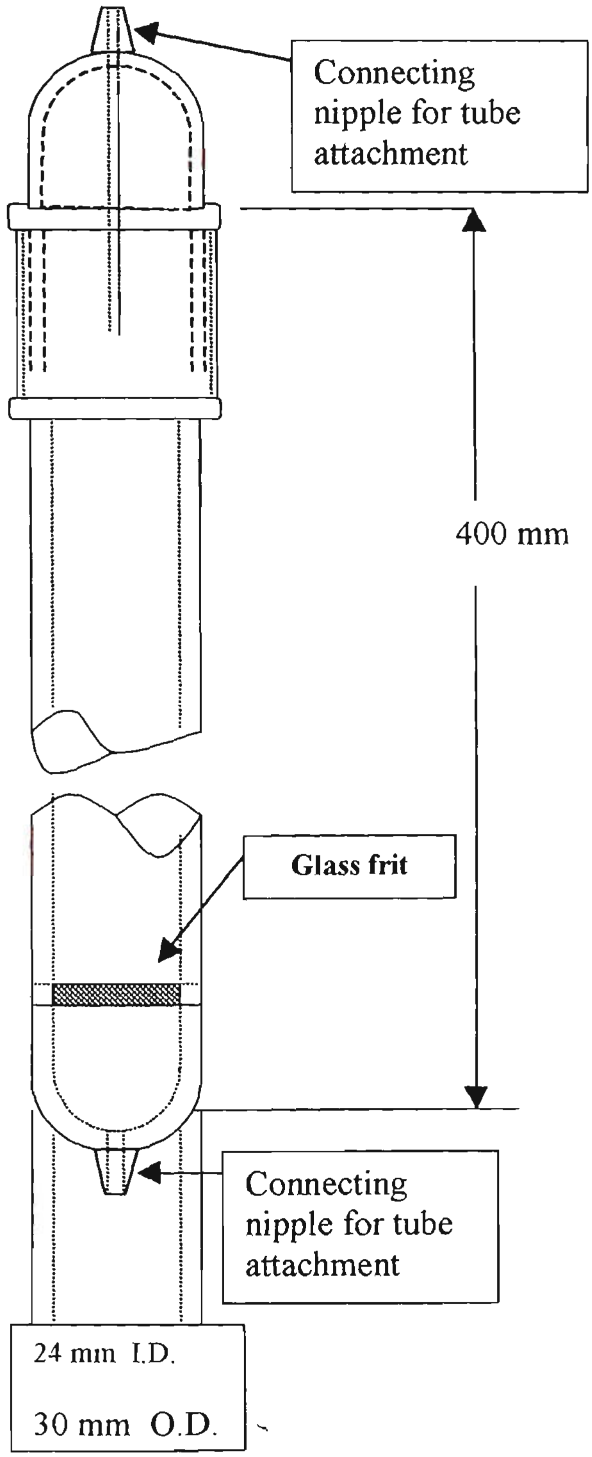
The continual leaching tests were based on either the TCLP (U.S. EPA 1992) or the Bottle Leaching Procedure (AS 4439.3). These tests involved removing portions of the leachate both prior and after the regulatory time frame of 18 hours in order to gain an insight into the leaching behavior of the hazardous constituents.

The removed portion of the leaching fluid (30mL/litre) was replaced with an equal portion of fresh leachate of the appropriate type, i.e. deionized water or the acidic leaching fluid (5.7mL of acetic acid per litre).

2.3.2 Column Leaching

Column leaching methods are designed to be more representative of a landfill situation and provide insight into the long term leaching behavior of solidified/stabilized wastes. The column methods utilized small glass columns (figure 2.8). Each column had a highly porous sintered glass frit inside and near the bottom of the column to support the waste. All column leaching tests were conducted using 100g of solidified product crushed to a sieve size of less than 2.36mm.

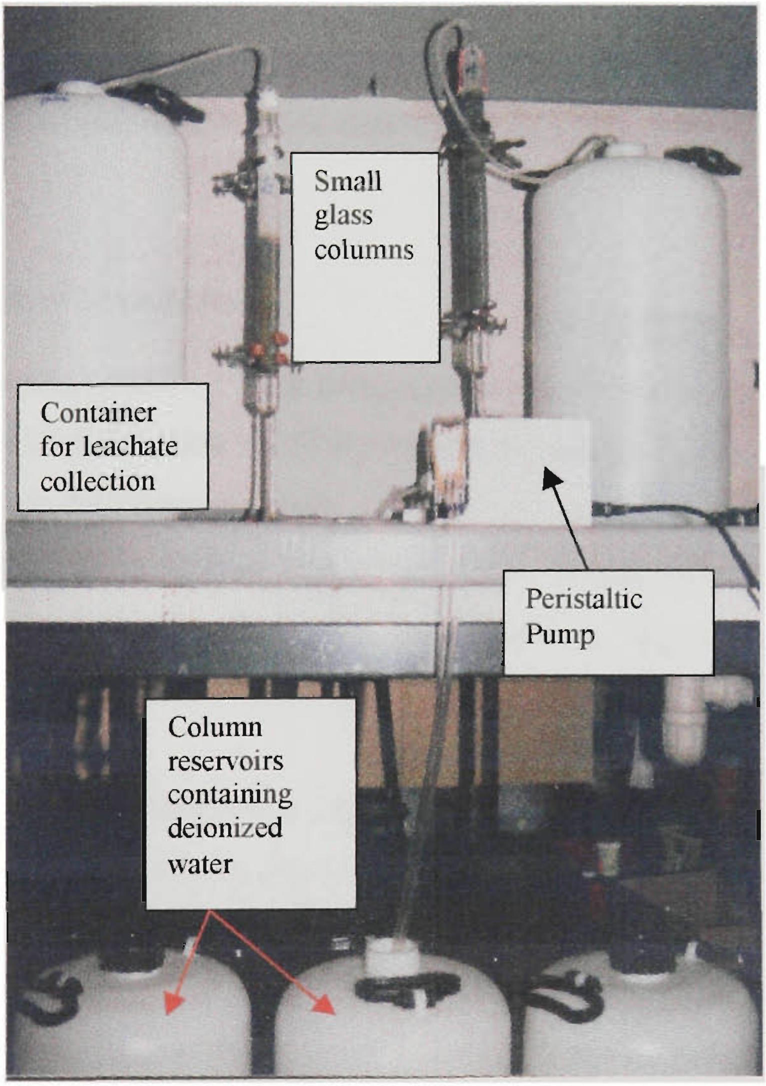
Figure 2.8 – Dimensions of small glass columns used in the column leaching experiments



2.3.2.1 *Column leaching (BLC) tests*

These column leaching tests were set up to allow comparisons with the sequential batch leaching tests and hence utilized a flow rate of 1.85mL/minute. This results in the solidified material coming into contact with the same volume of leaching fluid as in the batch leaching tests, i.e. 2 litres per 18 hours. The leaching fluid for these column leaching tests was deionized water, which was passed through the columns in an up flow manner using a peristaltic pump (brand: Alitea) and Tygon® brand tubing (I.D. 1/8"). Figure 2.9 depicts the setup for the column leaching (BLC) tests.

Figure 2.9 – Column leaching (BLC) setup



2.3.2.2 *Column Leaching (rainfall) Tests*

These column leaching tests utilized a flow rate of 4.65mL/day.

Taking account of column specifications (figure 2.8) this flow rate corresponds to an annual rainfall of 3750mm. This is approximately 5 times the average annual precipitation in Melbourne and 1.75 times the sum of the highest monthly rainfalls in Melbourne over the past 140 years (BOM 2000). In addition, many coastal areas of Australia have rainfalls in the range 2000 to 3200 mm per annum (BOM 2000). Figure 2.10 displays the annual rainfall for Australia during the period from 1st December 1999 to 30th November 2000. Given, also, that older landfills may be subject to water logging conditions and groundwater flow, the figure chosen is a reasonable compromise.

The leaching fluid was applied in a downflow manner to simulate rainfall.

2.4 Analysis of Leachates

All leachates and digestions were analyzed in one of two ways:

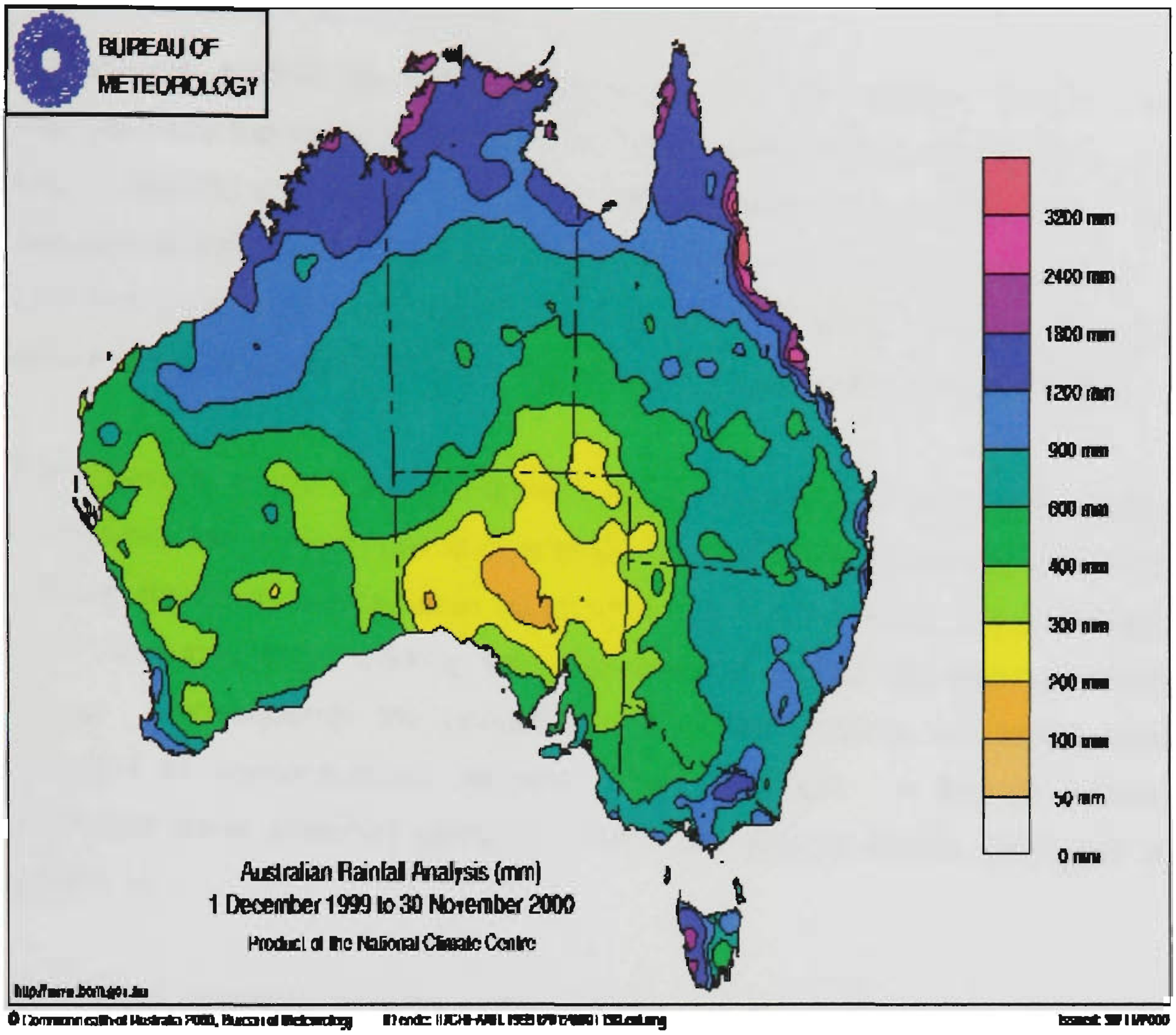
- Inductively Coupled Plasma (ICP) Atomic Emission Spectrometer (Perkin-Elmer Plasma 40 Spectrometer)
- Hydride Generation Atomic Absorption Spectrsocopy (Varian model 1474 Atomic Absorption Spectrometer fitted with a Varian VGA-76 Vapor Generation Accessory)

The ICP was used to determine all iron, calcium and lead concentrations, while arsenic was determined using both of the instrumental methods.

The ICP and AA methods that were followed for the analysis of all leachates will be discussed in the forthcoming sections and can also be found attached as appendices D and E respectively

All plastic and glassware was soaked in 10% HNO_3 for a minimum of 24 hours before use.

Figure 2.10 – Australian annual rainfall



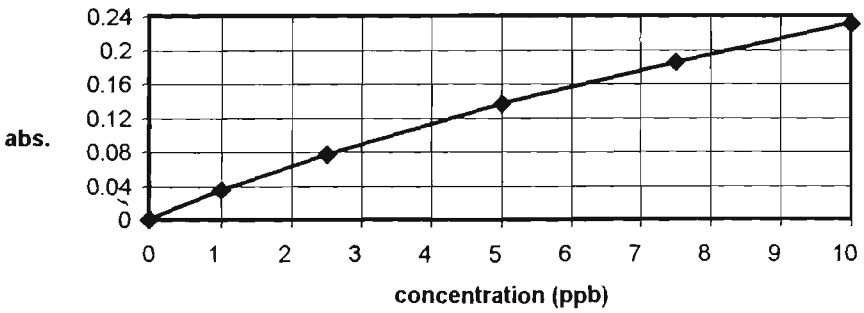
2.4.1 Vapor Generation

To analyze arsenic by hydride generation AA, the sample solution was aspirated into the vapor generation unit, where it was mixed with the reductant (4g L^{-1} $NaBH_4$) and carrier (100 mL L^{-1} HCl) solution in a reaction loop. The gaseous arsenic hydride (AsH_3) thus formed was separated by a gas/liquid unit and swept into the quartz cell, mounted on a single slot burner head, where it was decomposed by the surrounding flame to yield atomic arsenic.

The sensitivity of the vapor generation technique restricts the analytical range to relatively low concentrations of arsenic. Typically, the concentrations of the working standards are between 10 and 100 ppb. In this study, the calibration curve produced when working with standards up to 100 ppb was extremely curved. Consequently the concentrations of the working standards were restricted to concentrations between 1 and 10 ppb. A typical arsenic calibration curve obtained using the 193.7 nm arsenic line is displayed in figure 2.11.

One option available to reduce the curvature of the calibration graph when working with standards of slightly higher concentrations, was to use the other, less sensitive, arsenic analytical line which is at 197.2 nm. This enabled standards up to 25 ppb to be successfully employed, as displayed in figure 2.12.

Figure 2.11 - Arsenic calibration graph using the 193.7 nm line



The optimum conditions for the determination of arsenic using hydride generation atomic absorption are listed in table 2.5.

Figure 2.12 – Arsenic calibration graph obtained using the 197.2 nm arsenic line

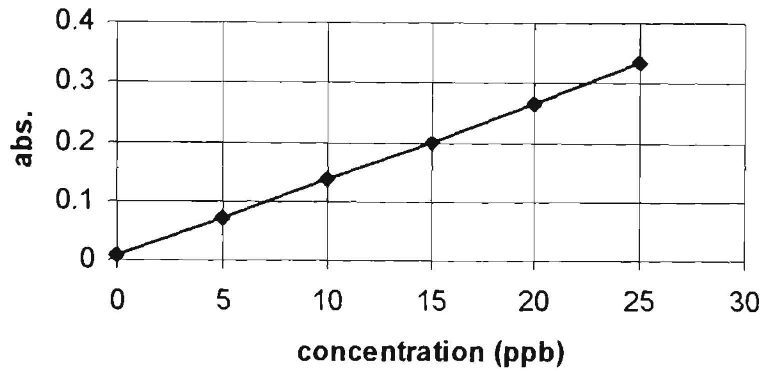


Table 2.5 - Hydride Generation Atomic Absorption working conditions

wavelength (nm) - 193.7

lamp current (mA) - 7

slit width - 1

flame type - air - acetylene

air flow rate (L/min) - 20

acetylene flow rate (L/min) - 8

reductant - 4g L^{-1} $NaBH_4$

carrier - 100 mL L^{-1} HCl

reductant flow rate (mL/min) - 1

carrier flow rate (mL/min) - 1

sample flow rate (mL/min) - 6

2.4.1.1 Potassium Iodide/Ascorbic acid Pretreatment

The determination of total arsenic in the leachate required a sample pretreatment step. An aliquot of the leachate was pipetted into a flask containing equal volumes of concentrated HCl and 5% ascorbic acid/potassium iodide solution and stirred vigorously for 45 minutes. The function of this step was to reduce As(V) to As(III). The borohydride reduction technique used in vapor generation AA is quantitative for the As(III) oxidation state. Consequently, failure to complete this process has been shown to result in large differences in the recorded absorbances (Leist 1997).

2.4.2 Inductively Coupled Plasma (ICP)

The linear working range for the ICP extends over several orders of magnitude. However for the majority of this study a calibration graph spanning the region from 1 ppm to 40 ppm was deemed sufficient. The ICP was standardized with three sets of standard solutions. Samples were analyzed three times, with blanks aspirated in between. Re-calibration was undertaken after every tenth sample to account for any instrumental drift.

The wavelengths used to determine the elements of interest are listed in table 2.6.

Table 2.6 – Wavelengths used for the determination of As, Pb, Fe, Ca

Element	Wavelength (nm)
As	193.696
Pb	220.353
Fe	238.204
Ca	317.933

2.4.3 Interferences

Percent recoveries (spiked samples) were performed routinely to ensure that significant matrix interferences were not present. For all of the column leaching tests, this consisted of spiking every tenth sample with an amount which would result in twice the initial concentration prior to spiking. All spikes were conducted using a 1000 ppm solution containing the elements of interest in this study, namely; arsenic, calcium, iron or lead. The leachate samples obtained from the sequential leaching tests were spiked at more regular intervals than were the column leaching tests, as these were a more aggressive extraction/leaching test and hence likely to result in a more rapidly changing matrix.

Table 2.7 displays the percent recoveries obtained for the sodium peroxide fusion of the S/S lead arsenate insecticide.

No significant problems of interferences were encountered in this study with the majority of the percentage recoveries falling within the range of 90 to 110% as can be observed from appendix F and table 2.7. Those recoveries that did not fall within this range, such as some of the lead arsenate digests (table 2.7) still yielded recoveries of between 80 and 117%.

The lack of any substanial interferences is further illustrated by the good agreement between the arsenic concentrations obtained using both hydride generation AA and ICP as shown in tables 2.8 to 2.10. While the results obtained from both of the techniques can be effected by numerous interferences, the type of interefence problems associated with the two techniques differs.

Table 2.7 – Percentage recoveries of S/S lead arsenate fusion

Element	Fusion Nº	Percentage Recovery
As	1	86%
	2	99.5%
	3	92%
Pb	1	99%
	2	102%
	3	97%
Ca	1	80%
	2	81%
	3	80%
Fe	1	117%
	2	113%
	3	116%

High concentrations of metals have been shown to interfere with the determination of arsenic by HGAAS (Zhu 1995). Metals, especially Co, Cu, Fe, Mo, Ni, and V have been shown to interfere with the determination of arsenic (Zhu 1995).

Interferences in the determination of arsenic by HGAAS can occur during hydride formation, on release from the liquid sample, during transport to the atomizer, as well as interferences at the atomizer.

Because the hydride technique involves oxidation-reduction reactions, it is possible that many interferences involve competitive depletion of sodium borohydride, which prevents quantitative reduction of the element to the hydride. Inter-element interferences can be predicted to some degree from reduction potentials.

If competitive depletion of sodium borohydride, however, is the only interference mechanism, increasing its concentration should reduce interferences. However, work by Voth-Beach *et al.,* (1988) showed that increasing the amount of sodium borohydride increased inter-element interferences. The easily reducible interferent elements produced a more rapid deposition of the reduced metal onto surfaces in the hydride generator and this process was always associated with interference effects.

Although interference mechanisms include oxidation-reduction reactions, there are other reactions involving precipitation and adsorption mechanisms. Physical adsorption of the volatile hydride onto reduced metal surfaces and subsequent decomposition appears to be a major interference mechanism (Voth-Beach *et al.,*1988).

Interferences associated with the ICP can be classified as spectral or non-spectral interferences. Spectral interferences include direct spectral line overlaps, broadened wings of intense spectral lines, ion-atom recombination, continuum emission, molecular band emission and stray (scattered) light from the emission of elements at high concentrations. Non-spectral interferences include both physical and chemical interferences. Chemical interferences are caused by molecular compound formation, ionization effects and thermochemical effects associated with sample vaporization and atomization in the plasma. In ICP the sample aerosol is injected directly into the ICP torch, consequently subjecting the constituent atoms to temperatures of about 6000 to 8000°K. Because this results in almost complete dissociation of molecules, significant reduction in chemical interferences is achieved.

Table 2.8 – Agreement between ICP and HGAAS concentrations calculated for $NaAsO_2$ + *C* leachates

ICP (ppm As)	HGAAS (ppm As)
1.51	1.53
2.18	2.02
4.95	4.77
7.48	6.96
10.35	10.11
11.36	11.03
12.29	11.76
12.19	11.65
12.92	13.03
13.75	13.46
13.47	13.46
13.53	13.32
12.53	12.15
12.39	12.03
10.95	10.88
10.29	10.76
9.08	9.17

Table 2.9– Agreement between ICP and HGAAS concentrations calculated for $NaAsO_2$ + *C-L* leachates

ICP (ppm As)	HGAAS (ppm As)
1.87	1.82
1.90	1.79
1.93	1.80
1.76	1.33
1.90	1.46
1.82	1.41

Table 2.10 – Agreement between ICP and HGAAS concentrations calculated for $NaAsO_2$ + *C-Fe* leachates

ICP (ppm As)	HGAAS (ppm As)
8.16	8.36
6.80	6.66
7.45	6.91
8.39	8.51
8.71	9.12
7.94	8.11
6.64	6.91
8.36	8.41
8.70	9.23
10.05	10.37

2.5 Electrode measurements

As well as monitoring the levels of arsenic, calcium, iron and lead where applicable, the pH, redox potential and conductivity were also routinely monitored.

2.5.1 pH

The pH was determined with a glass electrode in combination with a Ag/AgCl reference electrode connected to a Activon Cyberscan 500 meter. The pH meter was calibrated daily with BDH pH 4, 7, 10 colour coded buffers.

2.5.2 Redox potential

Redox potential was determined with a platinum electrode together with a Ag/AgCl (3 M) reference probe connected to a Activon Cyberscan 500 meter. In order to be able to compare voltages determined using the Standard Hydrogen Electrode, it was, therefore, necessary to add 200 mV to the recorded potentials. All Eh values displayed in this thesis have been so converted.

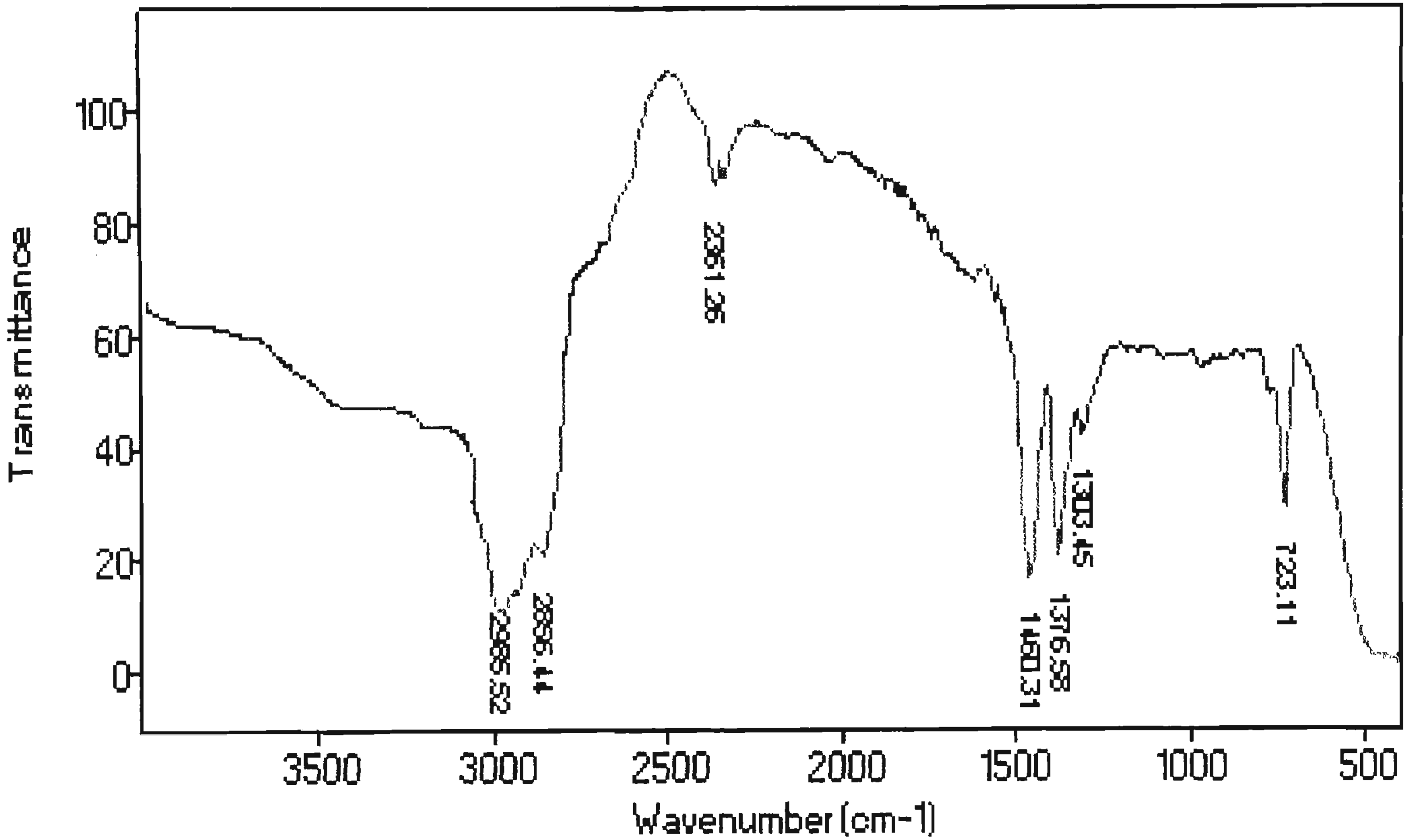
2.5.3 Conductivity

The electrical conductivity of all leachates was monitored with a Eutech Cybernetics TD Scan 10, hand held conductivity meter. The meter was calibrated daily with a 1412 μs/cm (0.02M KCl) and a 2.76 μs/cm (0.01M KCl) standards.

2.6 FTIR spectral data

Infrared spectra were recorded in the 500 – 4000 cm^{-1} region with a Bio-Rad 25 FTIR instrument. Each FTIR spectrum was the result of a total of 16 scans. The IR spectra of the solid samples were obtained using nujol mulls. This consisted of dispersing the solid sample throughout the oil, thus making the solid transparent enough for the IR radiation to pass through. Since the mineral oil is a saturated hydrocarbon, it, too, generates peaks. The peaks associated with the mineral oil are those located at approximately 1376 cm^{-1} and 1460 cm^{-1} as well as a broad absorption at approximately 2900 cm^{-1}. Although not normally associated with nujol, peaks were observed at ~2300 and ~ 723 cm^{-1}, as can be viewed from the blank nujol spectrum (figure 2.13).

Figure 2.13 Nujol FTIR Spectrum



2.7 Scanning Electron Microscopy (SEM) Examination

Scanning electron microscopy with x-ray emission analysis was carried out on a series of samples to enable understanding of the relationship between the cement lattice structure, arsenic waste, and treatment additives. A representative sample from each of the arsenic pentoxide S/S formulations investigated, was coated with carbon from a carbon string source in a Denton vacuum evaporator, prior to analysis using a Phillips XL Series SEM.

Chapter 3

3.0 BATCH LEACHING

Batch leaching tests are rapid and inexpensive methods for assessing the potential hazards posed by S/S wastes. Batch tests consist of agitating a waste sample, with a predefined quantity of liquid, for a specified time and subsequently analyzing for prescribed contaminants in the liquid. In Australia, all regulatory leaching tests are batch leaching tests. The two tests used in Australia are the TCLP (U.S. EPA, 1992) and the Australian Bottle Leaching Procedure (ABLP) (AS 4439.3). These were described in Chapter 2. This chapter presents results of these tests and comments on their significance. All tests were completed in triplicate with the results shown the average of these replicates.

3.1 Regulatory leach tests[1]

The success of any solidification/stabilization process to treat hazardous wastes, such as arsenic, is judged by comparing the leachate concentration of the particular element(s) with a list of regulatory limits. In Australia, the TCLP (U.S. EPA 1992) and the Australian Bottle Leaching Procedure (ABLP) (AS 4439.3) regulatory limits for arsenic are 5.0 mg/L. Table 3.0 and 3.1 contain the Bottle Leaching Procedure results for the arsenite and arsenate-containing S/S formulations respectively. From table 3.0, it can be clearly observed that those formulations containing the additional iron(II) were the worst performers with both the sodium arsenite and arsenic trioxide. Both of

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[1] All batch tests were performed in triplicate

these formulations clearly exceed the regulatory limit of 5 ppm and, hence, would not be suitable for landfill disposal. The iron formulations were also the least successful for the arsenate-containing formulations, as shown in table 3.1.

Table 3.0 – The Bottle Leaching Procedure: leachate concentrations of arsenic (arsenite-containing formulations)

S/S formulation[2]	Deionized water leachant [As]/mg L^{-1}	Acid leachant [As]/mg L^{-1}
$NaAsO_2$ + *C*	1.73 ±0.40	1.80 ± 0.01
$NaAsO_2$ + *C-Fe*	8.15 ± 0.21	144 ± 8.78
$NaAsO_2$ + *C-L*	2.48 ± 0.06	1.40 ± 0.07
As_2O_3 + *C*	1.04 ± 0.13	1.97 ± 0.09
As_2O_3 + *C-Fe*	36.61 ± 0.73	407 ± 27
As_2O_3 + *C-L*	0.79 ± 0.01	1.17 ± 0.02

Table 3.1 – The Bottle Leaching Procedure: leachate concentrations of arsenic (arsenate-containing formulations)

S/S formulation[2]	Deionized water leachant [As]/mg L^{-1}	Acid leachant [As]/mg L^{-1}
Na_2HAsO_4 + *C*	0.73 ± 0.03	2.54 ± 0.17
Na_2HAsO_4 + *C-Fe*	3.63 ± 0.18	525 ± 68.30
Na_2HAsO_4 + *C-L*	0.10 ± 0.02	0.40 ± 0.03
As_2O_5+ *C*	0.29 ± 0.02	2.09 ± 0.04
As_2O_5+ *C-Fe*	2.05 ± 0.10	1036 ± 69.78
As_2O_5+ *C-L*	0.20 ± 0.01	0.58 ± 0.04

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[2] An explanation of the composition of these S/S formulations was provided in Chapter 2, pp. 47 to 51

3.1.1 The effect of the arsenic oxidation state

Besides indicating that the solidification/stabilization processes have significantly reduced the leachate concentrations, table 3.2 also shows that the lowest leachate concentrations were consistently recorded for those S/S formulations containing pentavalent arsenic. This is despite the fact that, prior to treatment, pentavalent arsenic was not always associated with lower arsenic leaching (table 3.2).

The lower percentages of arsenic leached, in conjunction with the fact that both As(V) containing formulations performed the best, is evidence that the attempts to fix the arsenic have been partly successful. Calcium arsenates are known to be less soluble than calcium arsenites, while iron stabilization also performs best when the arsenic is present in the pentavalent state (Leist et al 2000).

Table 3.2 – Percentage of arsenic leached using the untreated arsenic salts and the Australian Bottle Leaching Procedure

Arsenic compound	**% Leached Untreated**	**Leachate conc. (treated) [As]/mg L^{-1}**
Sodium arsenite	100%	1.7 – 8.2
Sodium arsenate	64%	0.1 – 3.6
Arsenic trioxide	~29%	0.8 – 3.6
Arsenic pentoxide	~60%	0.2 – 2.0

The results obtained in Table 3.2 are the average of those obtained when using both leachant types, deionized water and the acetic acid (5.7 mL/lire) leachant

3.2 Toxicity Characteristic Leaching Procedure (TCLP)

For all substances, the regulatory limits for both the Bottle Leaching Procedure and the TCLP are identical. The two tests, while having significant similarities, also have notable differences. While the extraction process, which entails end-over-end agitation, is the same in both tests, the two tests differ in respect to the particle size which is used. The Australian Bottle Leaching Procedure utilizes a sample that has been crushed to less than 2.40mm, while the TCLP uses stabilized waste crushed to pass through a sieve of size 9.50mm. The leaching or extraction fluids used in the two tests can also differ. The stabilized wastes investigated in this study qualify for the use of deionized water or extraction fluid 5.3.2 (5.7mL of acetic acid per litre) when using the Bottle Leaching Procedure. The TCLP, however, allows for the use of only one type of extraction fluid, leaching fluid 5.6.2 (5.7 mL of acetic acid per litre).

The effect, which the differences between the two leaching methodologies can have on results, can be observed from tables 3.3 and 3.4.

Table 3.3 - Arsenic leachate concentrations

Leach Test	**$PbHAsO_4$ + *C*** [As]/mg L^{-1}	**$PbHAsO_4$ + *C-Fe*** [As]/mg L^{-1}	**$PbHAsO_4$ + *C-L*** [As]/mg L^{-1}
ABLP (deionized water)	3.51 ± 0.06	2.75 ± 0.16	0.62 ± 0.01
ABLP(acidic leachate)	3.57 ± 0.43	32.46 ± 4.07	1.27 ± 0.02
TCLP (acidic leachate)	3.58 ± 0.67	30.07 ± 2.50	1.97 ± 0.14

Table 3.4 – Lead leachate concentrations

Leach Test	**$PbHAsO_4$ + *C*** **[Pb]/mg L^{-1}**	**$PbHAsO_4$ + *C-Fe*** **[Pb]/mg L^{-1}**	**$PbHAsO_4$ + *C-L*** **[Pb]/mg L^{-1}**
ABLP (deionized water)	9.45 ± 1.16	0.15 ± 0.02	240.36 ± 7.17
ABLP (acidic leachate)	6.40 ± 0.79	1.01 ± 0.09	145.07 ± 3.37
TCLP (acidic leachate)	2.27 ± 0.37	0.42 ± 0.05	87.39 ± 16.18

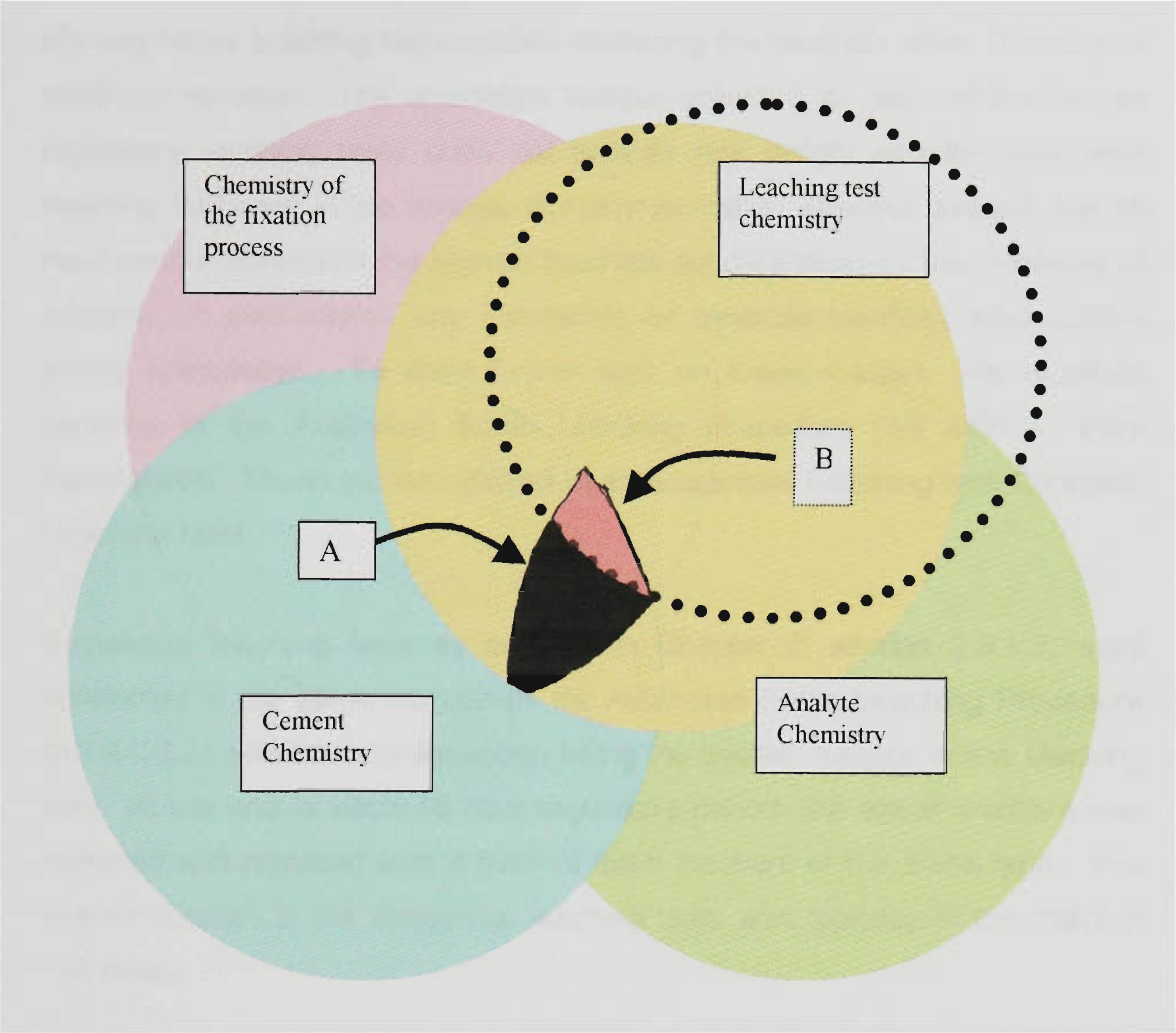
Tables 3.3 and 3.4 show the arsenic and lead concentrations obtained for the solidification/stabilization of a lead arsenate insecticide, which has been tested using both of the regulatory leaching tests. From table 3.3 (the arsenic leachate concentrations), it can be seen that those formulations which were lower than the regulatory limit using the Bottle Leaching Procedure with the acidic leachant, were also lower than the regulatory limit when the TCLP was utilized. The leachate concentrations obtained from the two tests were broadly similar. The greatest differences were obtained between those tests using the acidic leachant and those using deionized water. When deionized water was used, all three S/S formulations were clearly under the regulatory limit, as opposed to two of the three when the acidic leaching fluid was used.

Given that the lead regulatory limit, like arsenic, is set at 5 mg/L, table 3.4 indicates that, with respect to the lead concentration, only the $PbHAsO_4$ + *C-Fe* formulation would be under the regulatory limit. This same formulation exceeded the arsenic regulatory limit on test regimes. Unlike previously, notable differences can be observed between the lead leachate concentrations obtained from the TCLP and the Bottle Leaching Procedure when using the same acidic leachant. For all of the three S/S formulations, the lead leachate concentrations were significantly higher when the Bottle

Leaching Procedure was used. Indeed, formulation $PbHAsO_4$ + *C*, with a leachate concentration of 2.27 ppm is under the regulatory limit of 5 mg/L when the TCLP is used. However, when the Bottle Leaching Procedure was used, this same formulation would now exceed the regulatory limit with a leachate concentration of 6.40 mg/L. The fact that higher leachate concentrations resulted using the ABLP is not totally unexpected. It will be recalled from Chapter 2, the ABLP uses stabilized waste that has been crushed to a size of less than 2.40 mm, smaller than that used in the TCLP (<9.50 mm). The lead leachate concentrations and leachate pH rose even higher 2 out of 3 times when deionized water was utilized. For example, the leachate concentration for the $PbHAsO_4$ + *C* formulation rose from 2.27 to 6.40 to 9.45 mg/L as testing changed from the TCLP, to the Bottle Leaching Procedure (acidic leachant) and finally to the Bottle Leaching Procedure (deionized water). The relationship between the lead concentration and pH will be discussed in depth later in this chapter.

The waste which is to be fixed, the fixation process, the cement setting reactions and eventually the leaching tests, all interact in a complex manner, with the "final" result dependent on the overall chemistry of the situation. This scenario is shown schematically in figure 3.0. In figure 3.0, the circles represent each of the major factors that impact upon the success of the immobilization process. The area in which all four circles intersect, "A" can be regarded as the leachate result obtained. Alteration of any one of the four aspects, such as the leaching test, shown in figure 3.0 as the dotted circle, alters the overlap region "B" and, in reality, alters the leachate concentration. "Success" in one test, with one analyte, does not imply either "success" with another analyte, or "success" in what appears a similar test. Thus, it is not possible to make a clear, concise statement on the agreement or disagreement between the results obtained from the regulatory leaching tests and combinations of leaching fluids. It very much appears that the agreement or disagreement between the results obtained from the various leaching options will vary according to the particular hazardous constituent that is being investigated and, secondly, the nature of the fixation process which is being employed, as well as the test used.

Figure 3.0 – Schematic representation illustrating factors that influence the final leachate concentration obtained



Each circle represents an aspect that can affect the final leachate concentration. The area representing the leaching of the analyte can be considered the area that all circles share "A". Altering one aspect , such as the leaching test (dotted circle) will alter the area of overlap ("B"), which in reality changes the final result, the leachate concentration.

3.3 Modifications to regulatory leaching procedures

As alluded to in this chapter, and as outlined more specifically in Chapter 2, the regulatory leaching tests involve analyzing the leachate after 18 hours of continual agitation. The one single sample collected for each of the current regulatory leaching tests does not provide any insight into the long term leaching behavior of the wastes, nor any indication whether, indeed, the 18 hour period represents the highest leachate concentration for the elements of interest. It also makes any comments on possible leaching mechanisms purely speculative. To shed further light on these matters, two modified versions of the Australian Bottle Leaching Procedure (AS 4439.3) were investigated. These will be referred to as Sequential Leaching and Continual Leaching tests.

Sequential leaching tests as outlined in Chapter 2, section 2.3.1.3, were conducted in the same manner as the Australian Bottle Leaching Procedure (AS 4439.3) with the only exception being the overall duration of the leaching test. At the end of each 18 hour regulatory period, the entire leachant was removed and replaced with 2 litres of fresh leachant of the same type. The overall duration of the sequential leaching tests was typically of the order of 160 hours.

The Continual Leaching tests, described in detail in Chapter 2, section 2.3.1.4, consisted of removing small portions (30mL/litre) of the leaching fluid, analyzing the removed portion and replacing with an equal portion of fresh leachate of the appropriate type (either deionized water or the acidic leaching fluid (5.7 mL of acetic acid per litre)) and continuing the test. Sampling was conducted at intervals both prior to and after the regulatory time frame of 18 hours.

3.3.1 Sequential Leaching[3]

As indicated in chapter 2, Two types of sequential leaching tests were employed in this study, one utilizing deionized water, while the other used the acidic leaching fluid (5.7mL acetic acid per litre). Both of the sequential leaching tests utilized the crushed stabilized wastes which had been crushed to the specifications required by the Australian Bottle Leaching Procedure (AS 4439.3).

3.3.1.1 Sequential leaching (water)

The sequential leaching (water) results for each of the four arsenic salts are shown in figures 3.1 through to 3.3. These figures contain a plot of the arsenic concentration determined in the leachate at the end of each 18 hour period. Figure 3.1, which displays the sequential leaching results for the cement only formulations, shows that, during each of the successive 18 hour leach periods, the arsenic concentrations tend to increase, especially for those formulations incorporating the arsenite species, i.e $NaAsO_2$ + *C* and As_2O_3 + *C*. While the cement only formulations tended to exhibit increases in arsenic concentration over time, the majority of the solidification/stabilization formulations tended to leach arsenic at levels which were broadly similar during each 18 hour period, for the duration investigated (figures 3.1, 3.2 and 3.3). The major exceptions to this were the formulations As_2O_3 + *C-Fe* (figure 3.2) and $NaAsO_2$ + *C-L* (figure 3.3). These two formulations, especially As_2O_3 + *C-Fe,* demonstrated significant reductions in arsenic leachate concentrations followed by slight increases towards the end of the investigation period.

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[3] Sequential leaching tests involve the removal of the entire leachate every 18 hours

Figure 3.1 – Sequential leaching (water) [Cement only] stabilization

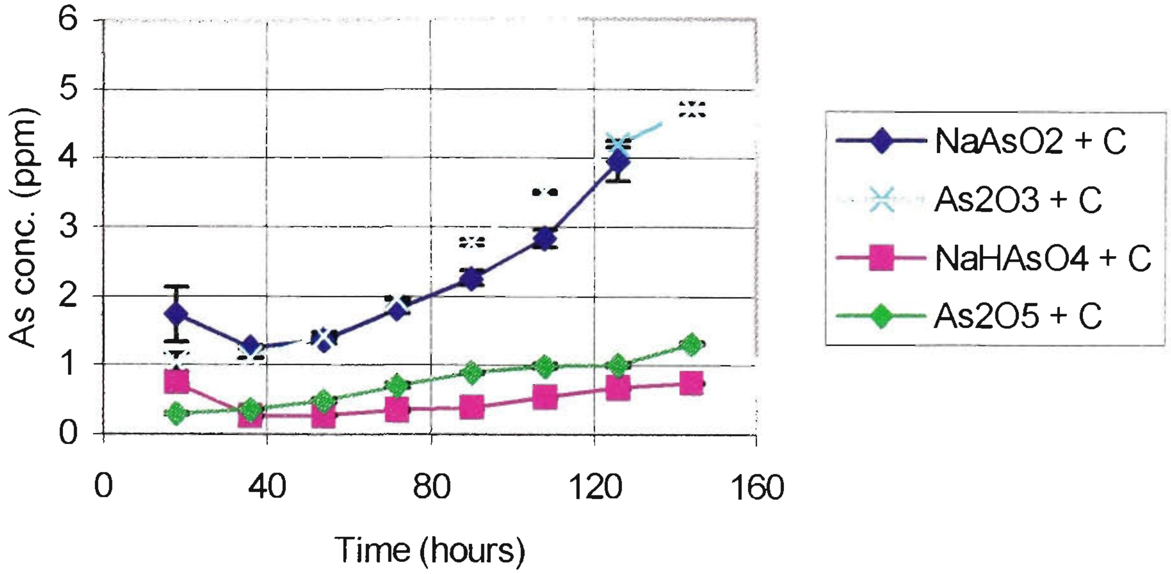


Figure 3.2 – Sequential leaching (water) [Cement + iron] stabilization

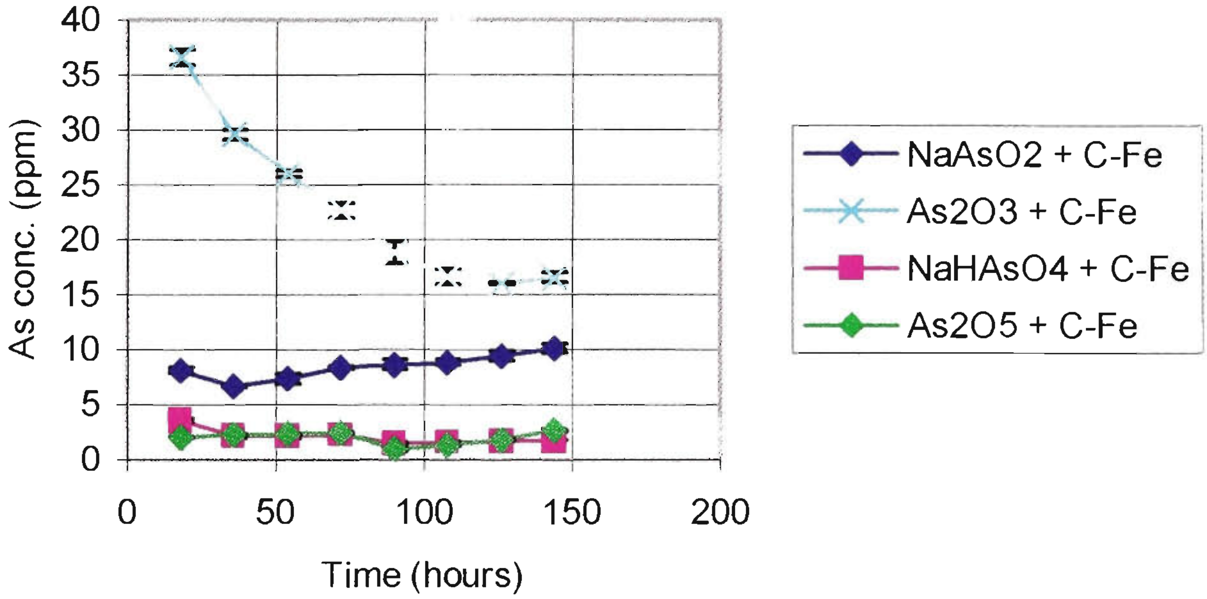
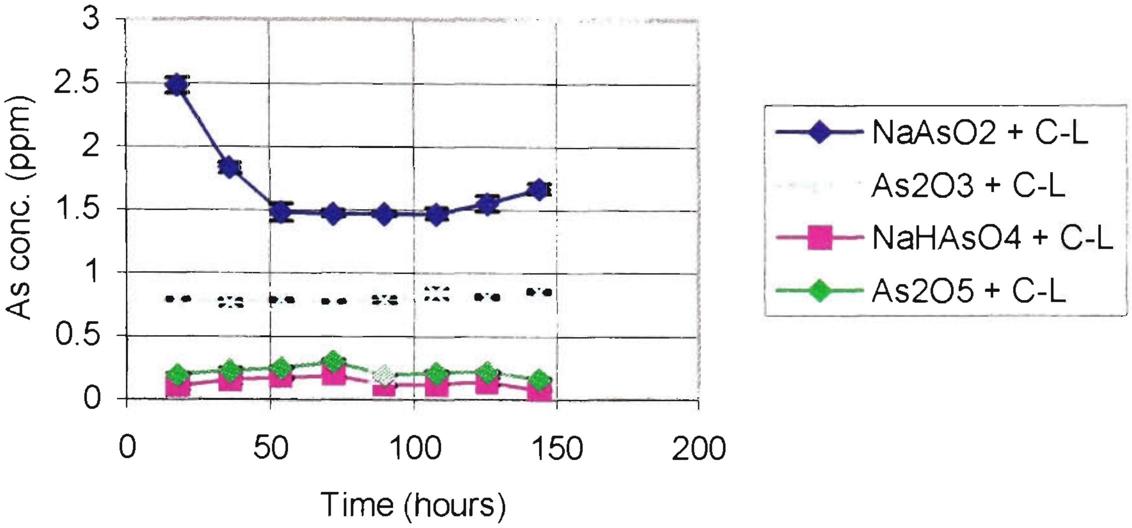


Figure 3.3 – Sequential leaching (water) [Cement + lime] stabilization



The decrease in the arsenic leachate concentrations towards the latter portions of the investigation period for the [cement + iron] formulations is not due to a substantial decrease in the total arsenic available for leaching. Figures 3.4 and 3.5 clearly show that less than 4% of the total arsenic is leached during these tests. The reduction in the arsenic leachate concentrations is a result of the ABLP (AS 4439.3) having achieved most of its destructive ability on these weaker matrices. Instead of the arsenic's release to the leachate as a result of both diffusion and the creation of new surfaces (and hence "new" arsenic being exposed to the leachant) diffusion only forces are now the sole means of transporting arsenic into the leachate. The [cement only] formulations, not surprisingly, exhibited behavior opposite to that of the weaker matrices. The stronger[4] [cement only] matrices were able to withstand most of the destructive forces of the ABLP (AS 4439.3). Consequently, diffusion forces initially were the controlling factor for the release of arsenic into the leachate. The increase in the arsenic leachate concentrations towards the latter portions of the investigation are as a result of two forces, continuing diffusion of arsenic into the leachate, as well the ABLP (AS 4439.3) now beginning to weaken and break down the matrices and exposing new surfaces and arsenic to the leachant.

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[4] Strength refers to the mechanical strength (physical property)

3.3.1.1.1 Leaching mechanism

Leaching of contaminants out of cement based waste forms is believed to be primarily a diffusion controlled process (Dutre and Vandecasteele 1996). The solution of the diffusion equation depends on the initial and boundary conditions. The cement-based waste form is assumed to be a semi-infinite medium, which implies that the mass of constituents removed from the waste form is negligible in comparison to the total mass in the waste form. The contaminants are initially assumed to be uniformily distributed in the waste form and to have a zero surface concentration once leaching begins. With the assumption of a consistant diffusion coefficient, the diffusion flux J across the solid/solution interface of a semi-infinite medium can be expressed as

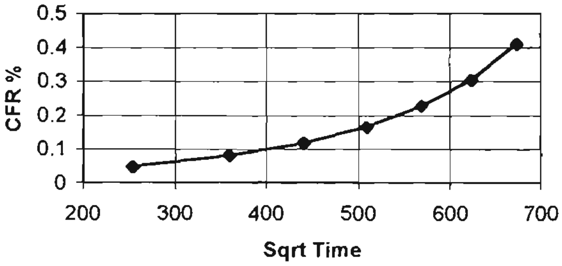
$$J = \sqrt{}De/\pi t\ .\ Co$$

Where Co = initial concentration of the leaching substance in the S/S waste specimen (mg/cm^3), De = effective diffusion coefficient (cm^2/s) and t = leach time (s)

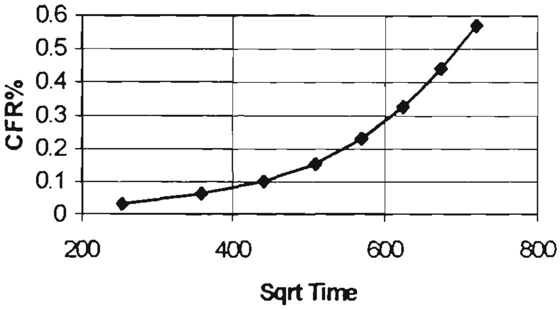
Diffusion control can be demonstrated by constructing a plot of the cumulative fraction of the hazardous constituent released (CFR) versus the square root of the leaching time (SQRT). If this graph yields a straight line, then the leaching mechanism is, indeed, consistent with diffusion control (Dutre and Vandecasteele 1996). As can be observed from figures 3.4 and 3.5, the majority of the S/S formulations yielded a near perfect straight line when the arsenic CFR was plotted against the SQRT, with the majority of R^2 values in the range of 0.98 to 0.99, thus indicating that the release mechanism was a diffusion controlled process as expected. While, as expected, the release of arsenic into the leachate was shown to be largely diffusion based, deviations could however be observed and are no doubt, a result of the reasons discussed previously in Chapter 1. Diffusion may be only one of a number of factors that contributed to the leaching of arsenic. Other contributing factors such as pH will be discussed progressively throughout this chapter.

Figure 3.4 – Sequential leaching (water) CFR arsenic versus SQRT, *Arsenite formulations*

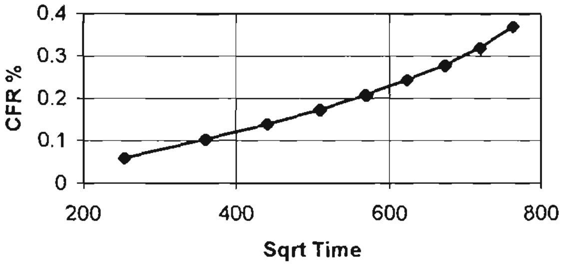
$NaAsO_2$ + *C* $R^2 = 0.8938$



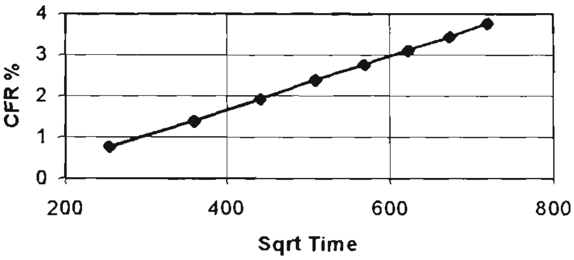
As_2O_3 + *C* $R^2 = 0.8726$



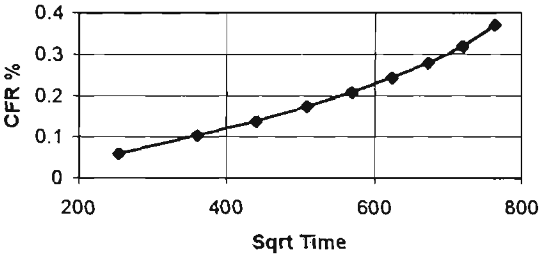
$NaAsO_2$ + *C-Fe* $R^2 = 0.9618$



As_2O_3 + *C-Fe* $R^2 = 0.9994$



$NaAsO_2$ + *C-L* $R^2 = 0.9724$



As_2O_3 + *C-L* $R^2 = 0.9764$

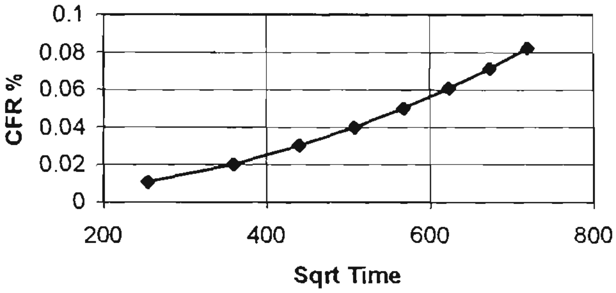
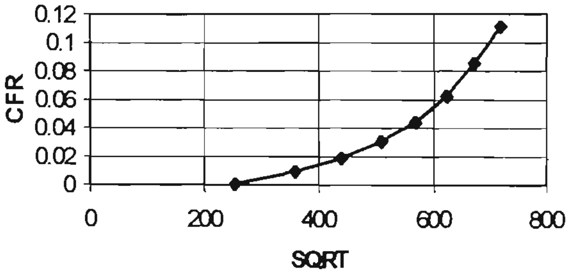
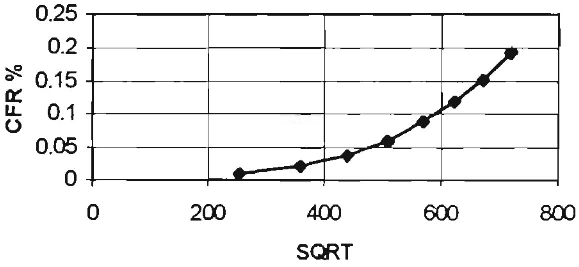


Figure 3.5 – Sequential leaching (water) CFR arsenic versus SQRT, *Arsenate formulations*

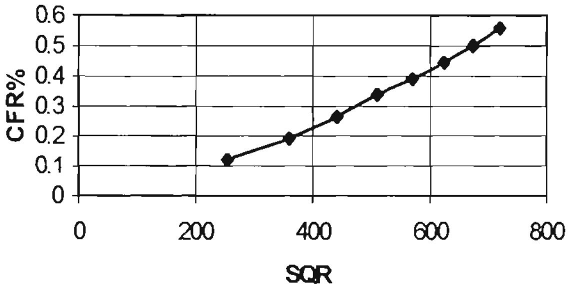
Na_2HAsO_4 + *C* R^2 = 0.895



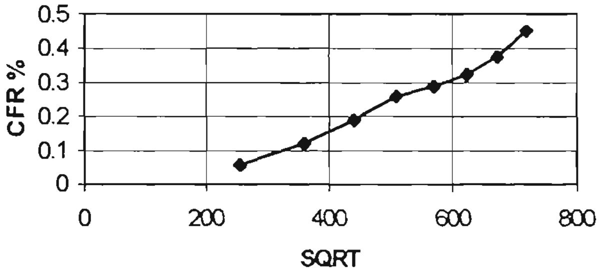
As_2O_5 + *C* R^2 = 0.9059



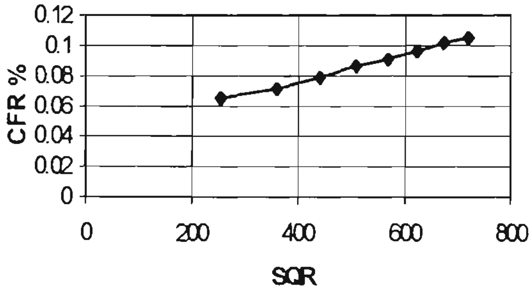
Na_2HAsO_4 + *C-Fe* R^2 = 0.9929



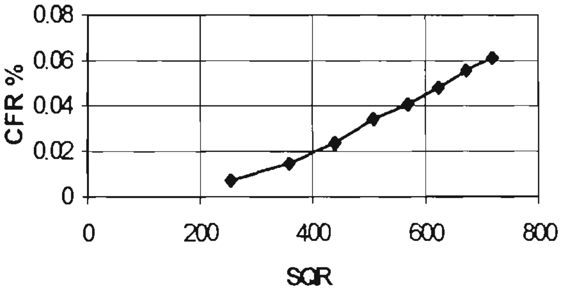
As_2O_5 + *C-Fe* R^2 = 0.9852



Na_2HAsO_4 + *C-L* R^2 = 0.994



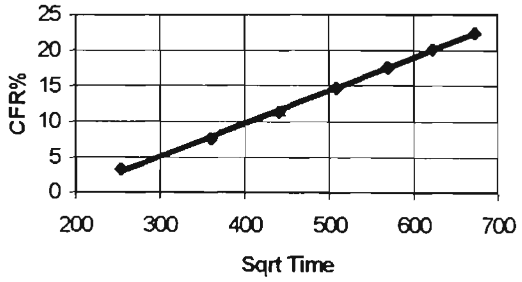
As_2O_5 + *C-L* R^2 = 0.9904



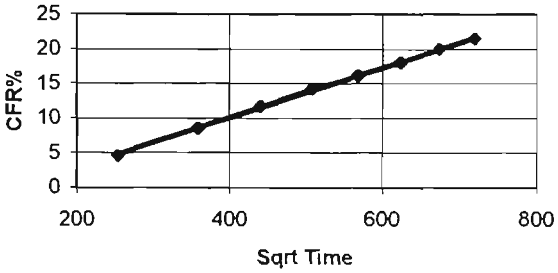
Figures 3.6 and 3.7 contain the graphs of CFR versus the SQRT for the calcium levels leached from the arsenite and arsenate containing formulations respectively. For the calcium CFR, all formulations, including the cement only formulations, yielded extremely high correlation coefficients, above 0.977. The slight curvature that was exhibited for calcium from some of the formulations may be an artifact of the depletion of calcium from the more readily leachable outer leaching boundary. Unlike arsenic, substantial calcium quantities were leached. For example the As_2O_3 + *C-Fe* formulations leached close to 60% of its total calcium content.

Figure 3.6 – Sequential leaching (water) CFR calcium versus SQRT, *Arsenite formulations*

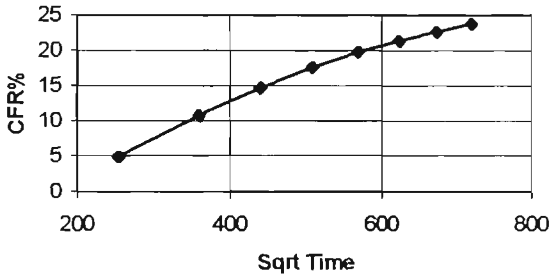
$NaAsO_2$ + *C* $R^2 = 0.9991$



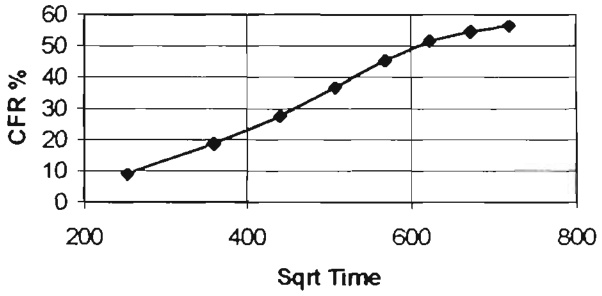
As_2O_3 + *C* $R^2 = 0.9994$



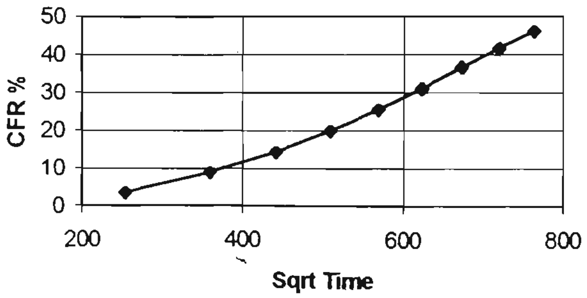
$NaAsO_2$ + *C-Fe* $R^2 = 0.9796$



As_2O_3 + *C-Fe* $R^2 = 0.9874$



$NaAsO_2$ + *C-L* $R^2 = 0.9826$



As_2O_3 + *C-L* $R^2 = 0.9842$

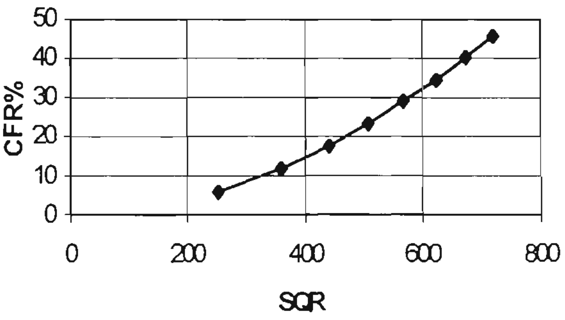
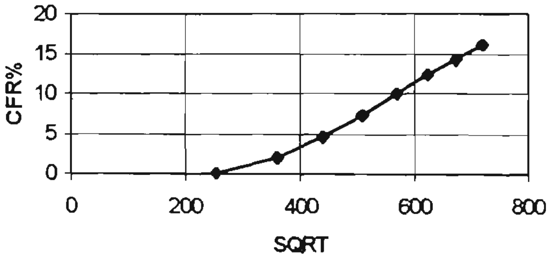
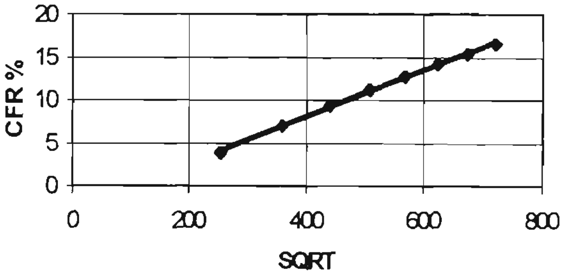


Figure 3.7 – Sequential leaching (water) CFR calcium versus SQRT, *Arsenate formulations*

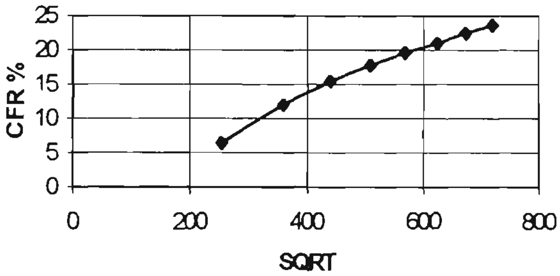
Na_2HAsO_4 + *C* $R^2 = 0.9842$



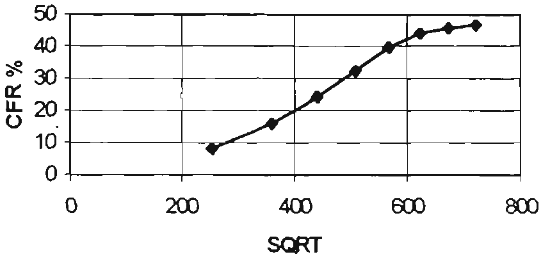
As_2O_5 + *C* $R^2 = 0.9986$



Na_2HAsO_4 + *C-Fe* $R^2 = 0.9806$

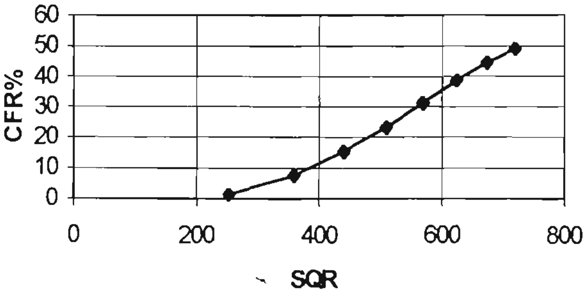


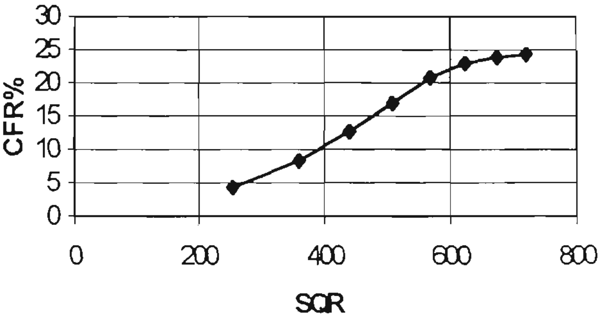
As_2O_5 + *C-Fe* $R^2 = 0.977$



As_2O_5 + *C-L* $R^2 = 0.977$

Na_2HAsO_4 + *C-L* $R^2 = 0.9864$





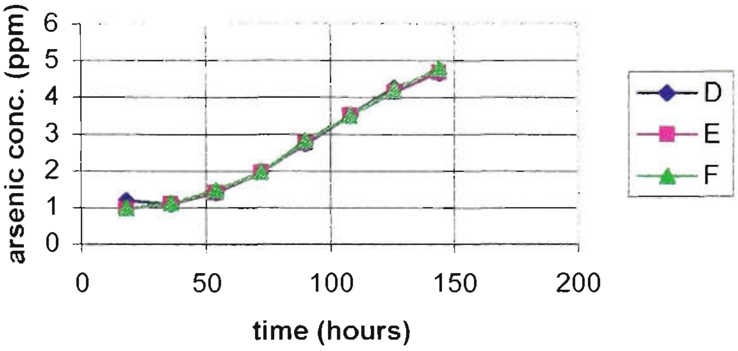
3.3.1.1.2 Precision of the Sequential leaching (water) tests

Each of the sequential leaching (water) tests was performed in triplicate (labeled “D”, “E”, & “F”). As can be observed from figures 3.8 through to 3.11, regardless of the arsenic compound or the S/S formulation, the precision exhibited in the results collected from these tests was more than acceptable. The majority of the formulations as can be observed from these figures yielded arsenic levels which are essentially co-linear, although not with a gradient of zero for the reasons stipulated earlier.

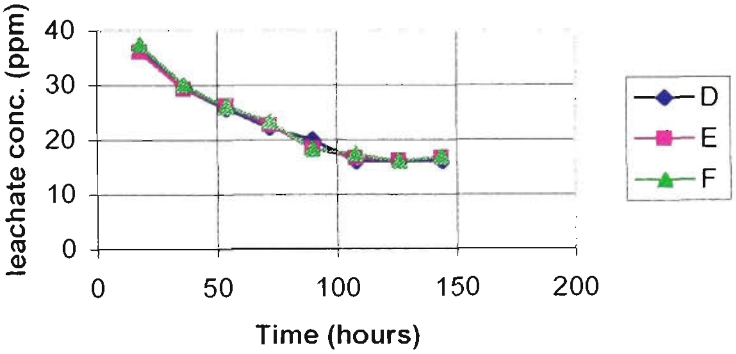
Some formulations, however, did exhibit small peaks and troughs. These can be largely attributed to the design of the sequential leaching tests. It will be recalled from the brief outline provided earlier in this chapter, or the more detailed description provided in Chapter 2, that these tests involve the removal of the entire leachant and replacement with fresh leachant of the same type. To avoid losing any of the test sample, as would be the case if the entire contents were filtered, the last hundred or so millilitres of the leachant was decanted from the test bottle after the S/S material was given time to settle. Consequently, for some of the weaker matrices especially, the removal of the leachant became an increasingly difficult task during the middle stages of the investigation. During the middle period of the investigation large quantities of fine material were produced, increasing the difficulty in removing the leachate. After this time, the amount of this fine material reduced, making the decanting process an easier task. Hence, any of the small peaks or troughs (± ~1ppm), such as those which can be observed from figures 3.9 are a consequence of the inability to efficiently and effectively remove the entire leachate.

Figure 3.8 – Precision of the arsenic trioxide S/S formulations

As_2O_3 + *C*



As_2O_3 + *C-Fe*



As_2O_3 + *C-L*

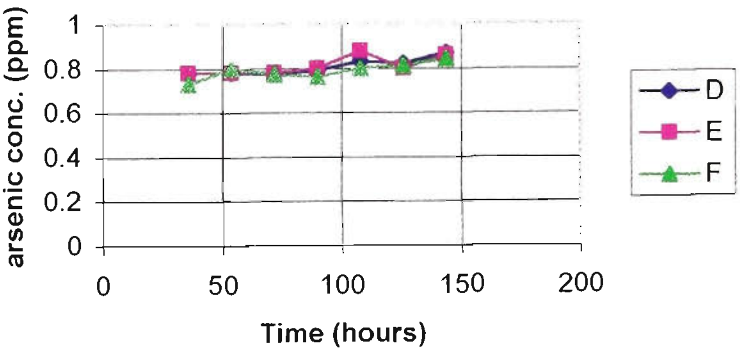
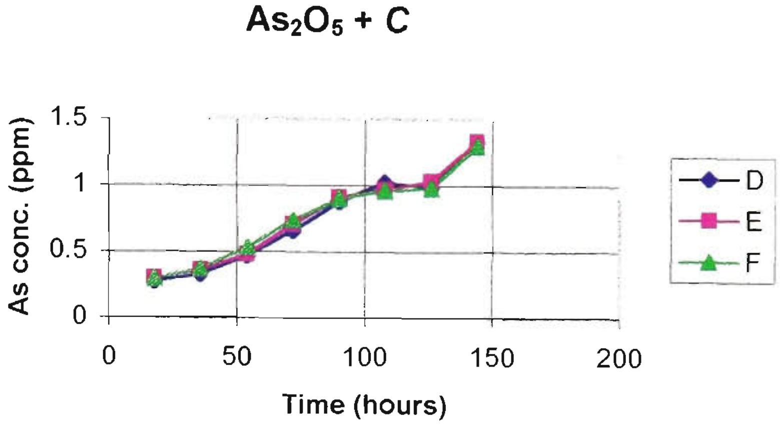
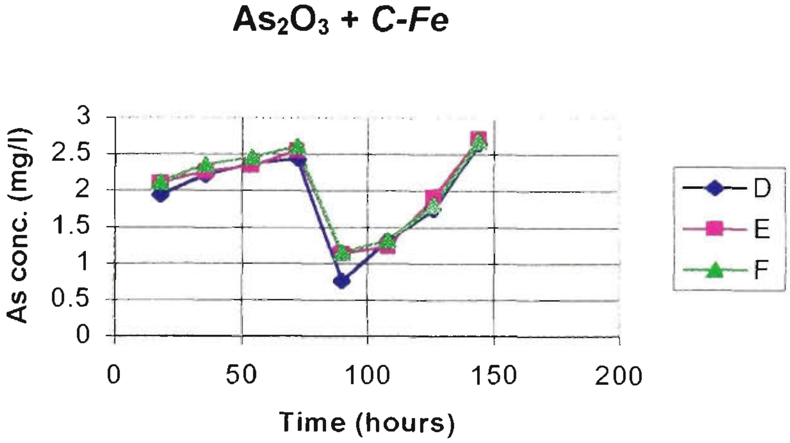


Figure 3.9 – Precision of the arsenic pentoxide S/S formulations





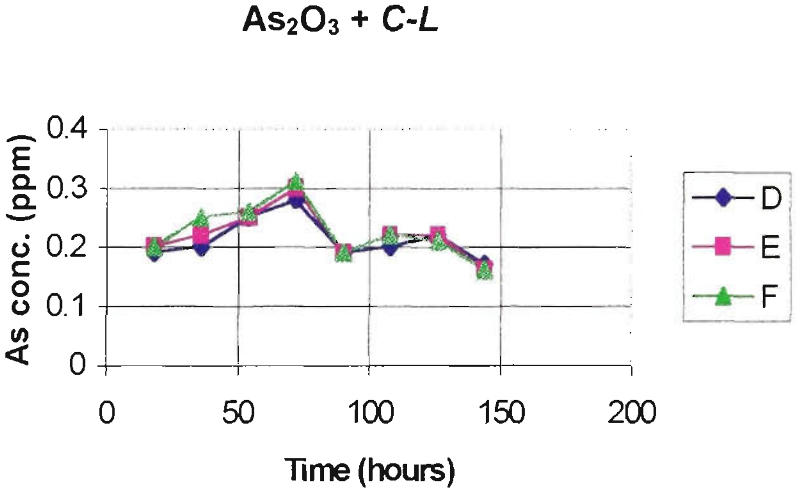
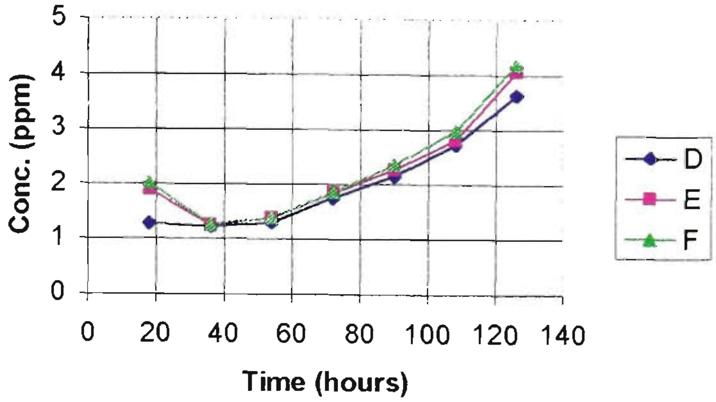
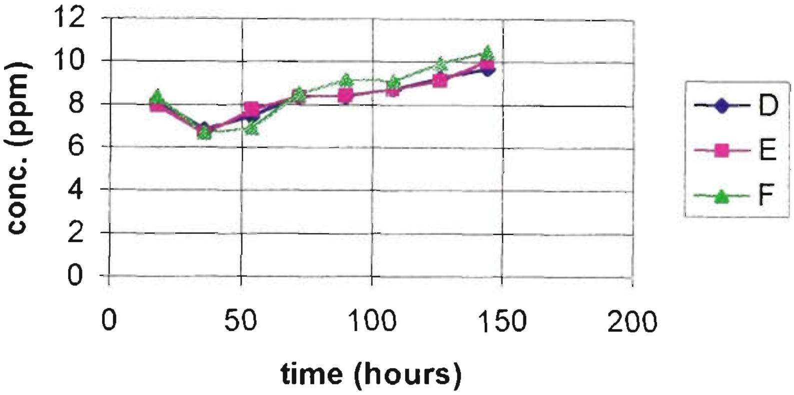


Figure 3.10 – Precision of the sodium arsenite S/S formulations

$NaAsO_2$ + *C*



$NaAsO_2$ + *C-Fe*



$NaAsO_2$ + *C-L*

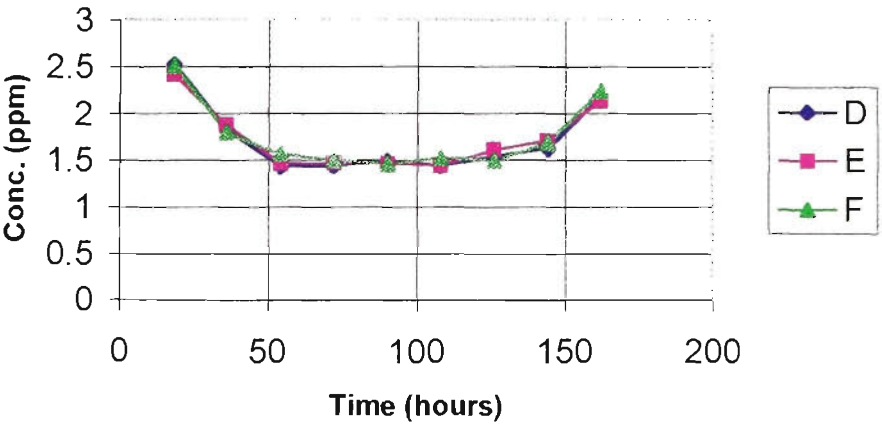
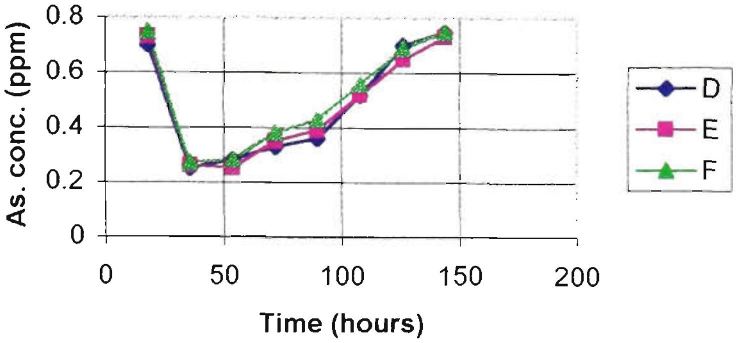
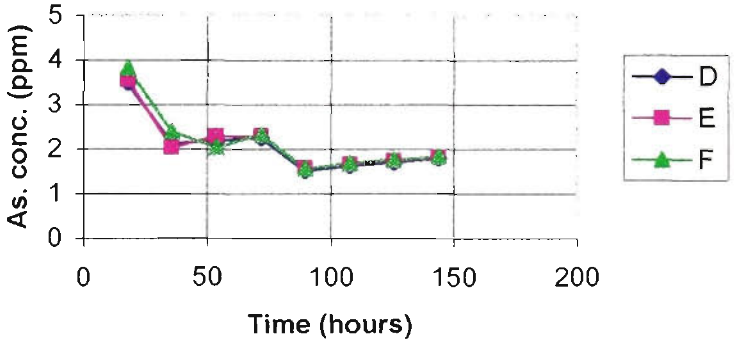


Figure 3.11 – Precision of the sodium arsenate S/S formulations

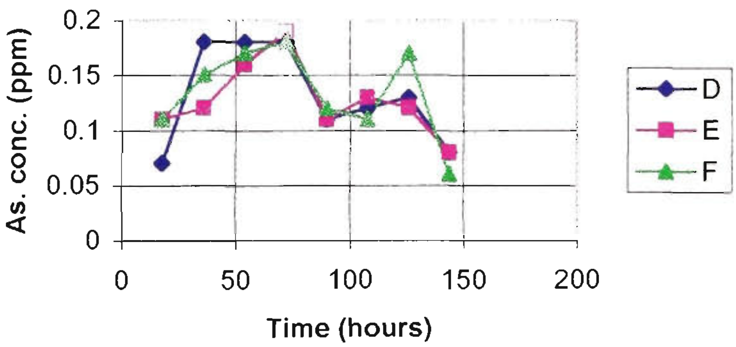
Na_2HAsO_4 + *C*



Na_2HAsO_4 + *C-Fe*



Na_2HAsO_4 + *C-L*



3.3.1.2 Sequential leaching (acid)

Further leaching, using the acetic leaching fluid, results in a significant increase or decrease in arsenic leachate concentrations, when compared to the levels obtained after the regulatory time of 18 hours (tables 3.0 and 3.1). The significant changes in the arsenic leachate concentrations for the various S/S formulations can be observed from figures 3.12 to 3.14.

Figure 3.12 – Sequential leaching (acid) [cement only] stabilization

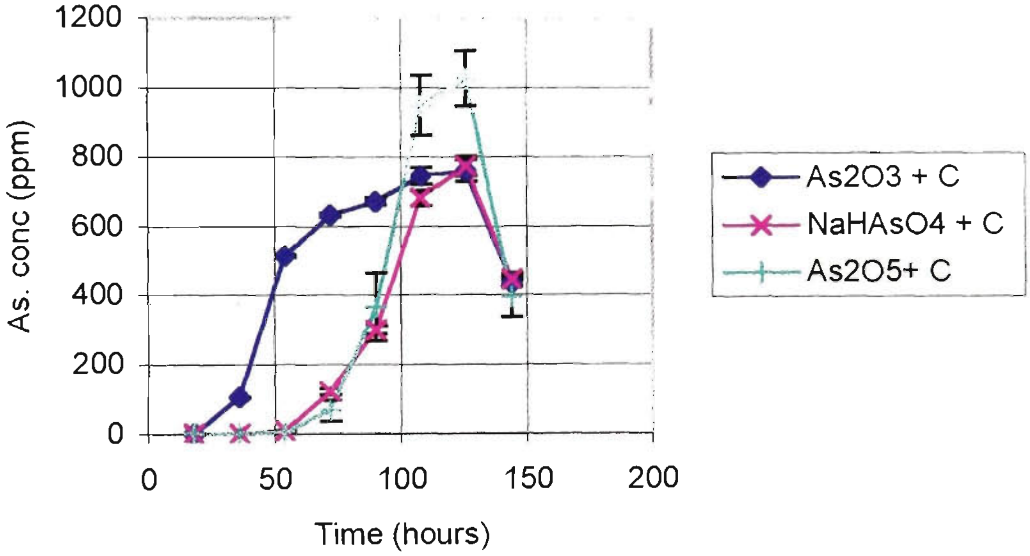


Figure 3.13 – Sequential leaching (acid) [cement + iron] stabilization

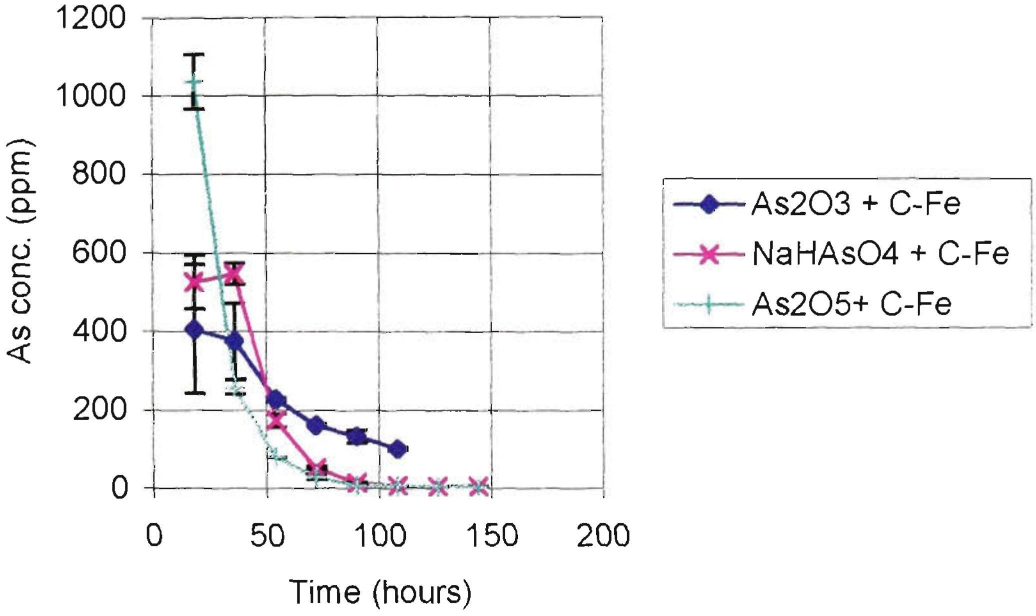
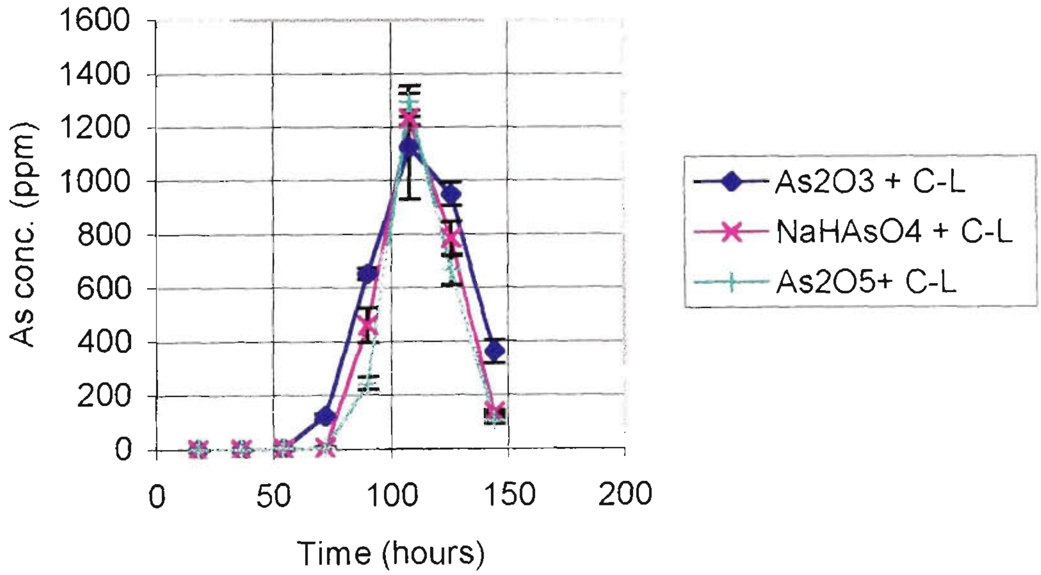


Figure 3.14 – Sequential leaching (acid) [cement + lime] stabilization



The iron formulations, after yielding substantially higher leachate concentrations initially, when compared with the other formulations, yielded lower arsenic concentrations for each of the successive leaching periods. The exact opposite occurred for the other two formulations, [cement only] and [cement + lime] (figures 3.15 and 3.17). Both of these formulations showed substantial increases in the arsenic leachate concentrations, despite their initial resistance in doing so.

The greater success of the [cement + iron] formulations may be attributable to the greater porosity of these matrices (an investigation into the microstructure of the matrices will be provided in Chapter 5). All S/S matrices that came into contact with the acidic leachant, leached 100% of their calcium content, as opposed to those tests which utilized dionized water as the leachant, in which the most successful of the formulations ([cement only] and [cement + lime]) leached no greater than 50% of their total calcium content. If the [cement + iron] formulations had a greater porosity, as tests of their microstructure suggest, this aids larger arsenic and calcium levels in the leachate and hence provides an increased opportunity for the formation of calcium-arsenic precipitates. The greater success of the [cement + iron] formulations may also be a result of oxidation of ferrous ion to ferric ion and formation of ferric arsenate (scorodite phases). Scorodite phases are known to be highly insoluble, especially at the lower pHs associated with the [cement + iron] leachates (i.e. ~8 vs > 11 for the other two formulations. The possibility of arsenic removal using iron will be discussed in some detail latter in the chapter.

The [cement only] and the [cement + lime] formulations with a reduced porosity would presumably leach more calcium and less arsenic as the leaching boundary moves more slowly inward. By the time the leaching boundary moves sufficiently inward to where there is a greater percentage of arsenic, substantial quantities of calcium would have already been leached, diminishing the chances for the formation of further calcium-arsenic precipitates. Hence, the plots for the [cement only] and [cement + lime] formulations exhibited a peak at the latter stages of the tests, when the Ca:As ratios present in the leachates were no longer large enough to aid in substantial re-precipitation of the arsenic. After the arsenic peaks that were exhibited in figures 3.12 and 3.14, the arsenic leachate concentrations begin to fall, a result of the majority of the easily leachable arsenic having already been leached. By the time the arsenic peak is observed upward of 80% of the total arsenic present had been leached.

This trend was found to be the case for both the Australian Bottle Leaching Procedure (AS 4439.3) and the TCLP (U.S. EPA 1992). For all three of the lead arsenate formulations, as shown in figures 3.15 through to 3.17, the arsenic concentrations leached using both of the regulatory leaching tests over each of the successive leaching intervals were identical.

Figure 3.15 – Similarities between the sequential leaching results obtained using both the TCLP and the ABLP for the $PbHAsO_4$ +*C* formulation

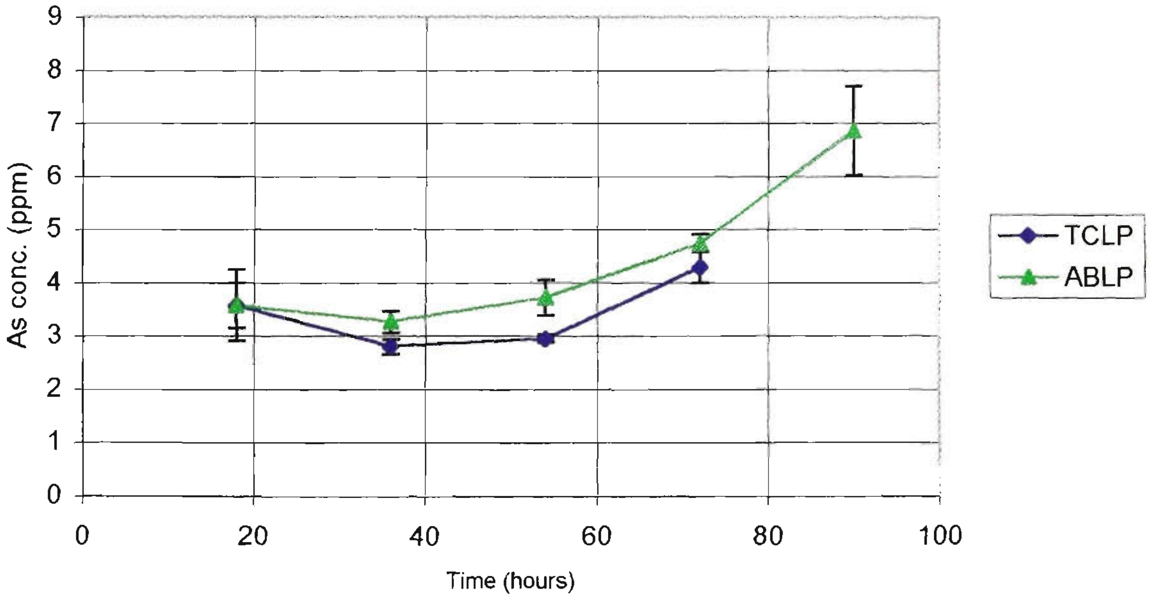


Figure 3.16 – Similarities between the sequential leaching results obtained using both the TCLP and the ABLP for the $PbHAsO_4$ +*C-Fe* formulation

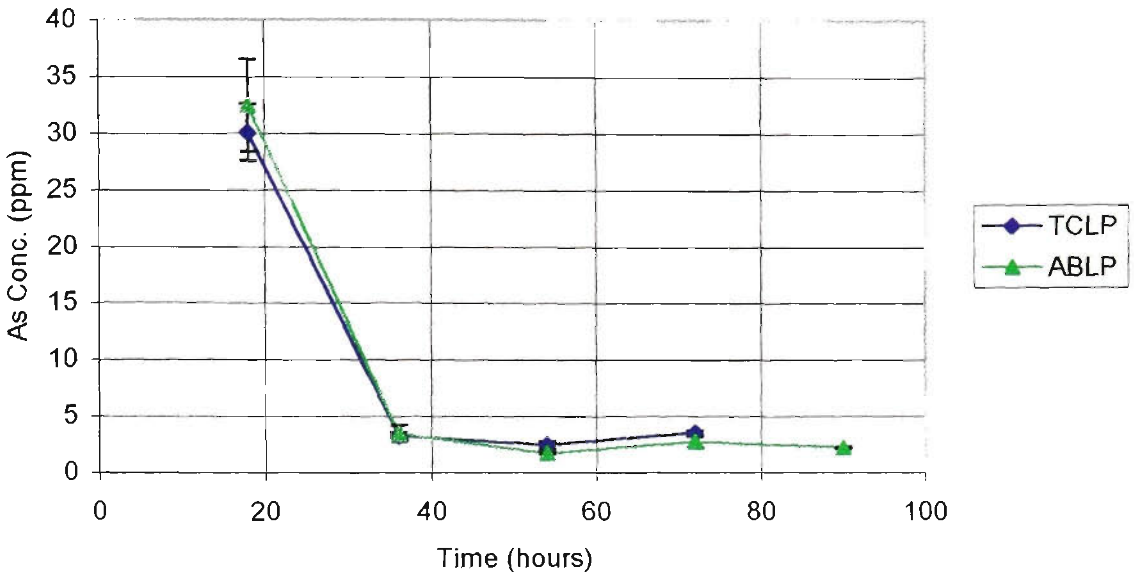
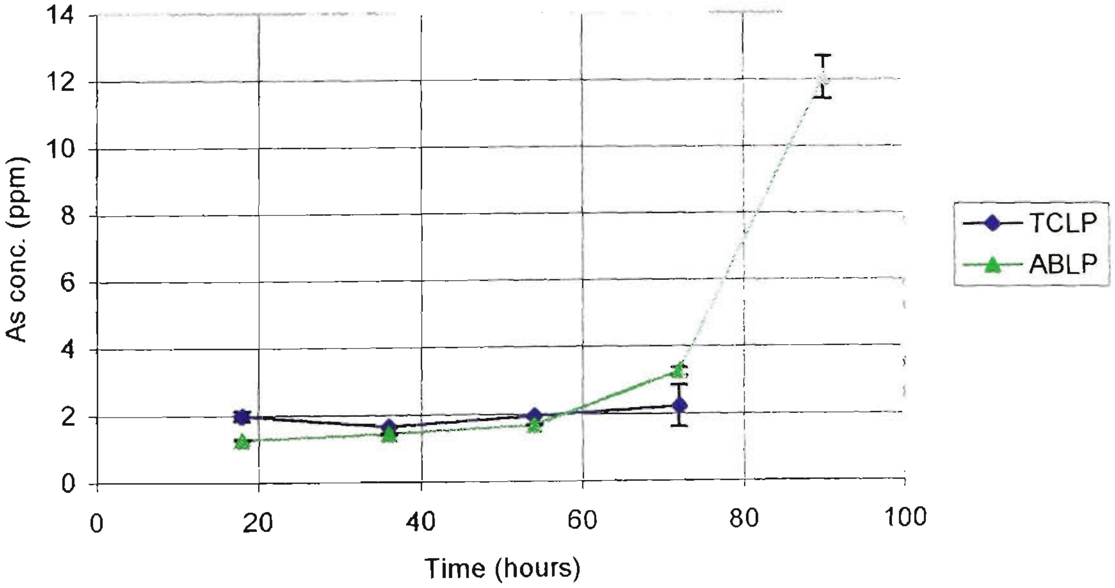


Figure 3.17 – Similarities between the sequential leaching results obtained using both the TCLP and the ABLP for the $PbHAsO_4$ + *C-L* formulation



Just as the lead concentrations leached using both of the regulatory leaching tests differed at the end of the 18 hour regulatory period (table 3.4), the differences continued for each of the successive leaching intervals in the sequential leaching tests. However, as can be observed from figures 3.18 to 3.20, the overall trend, i.e an increase or decrease in the lead concentration, was the same for both of the sequential leaching tests, ABLP or TCLP.

Figure 3.18 – Similarities between the lead sequential leaching results obtained using both the TCLP and the ABLP for the $PbHAsO_4$ +C formulation

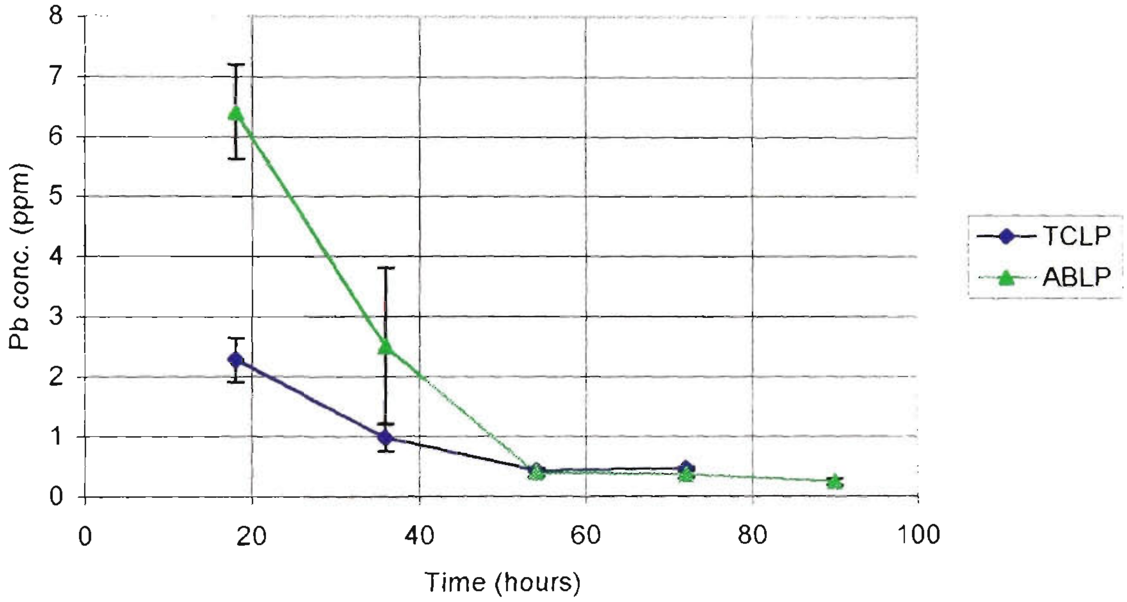


Figure 3.19 – Similarities between the lead sequential leaching results obtained using both the TCLP and the ABLP for the $PbHAsO_4$ +*C-Fe* formulation

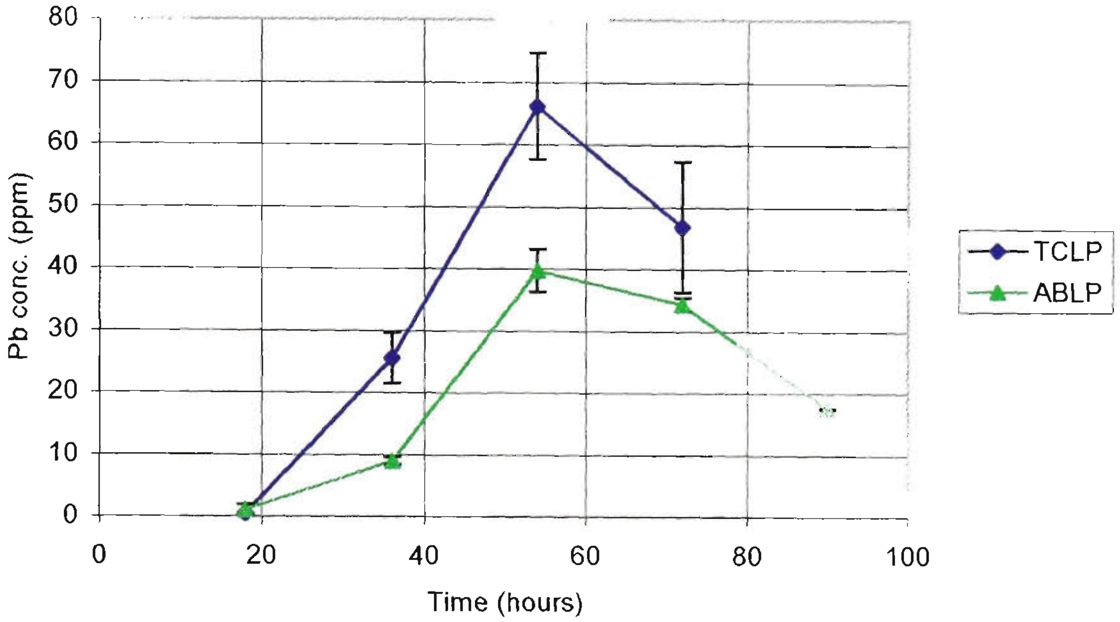
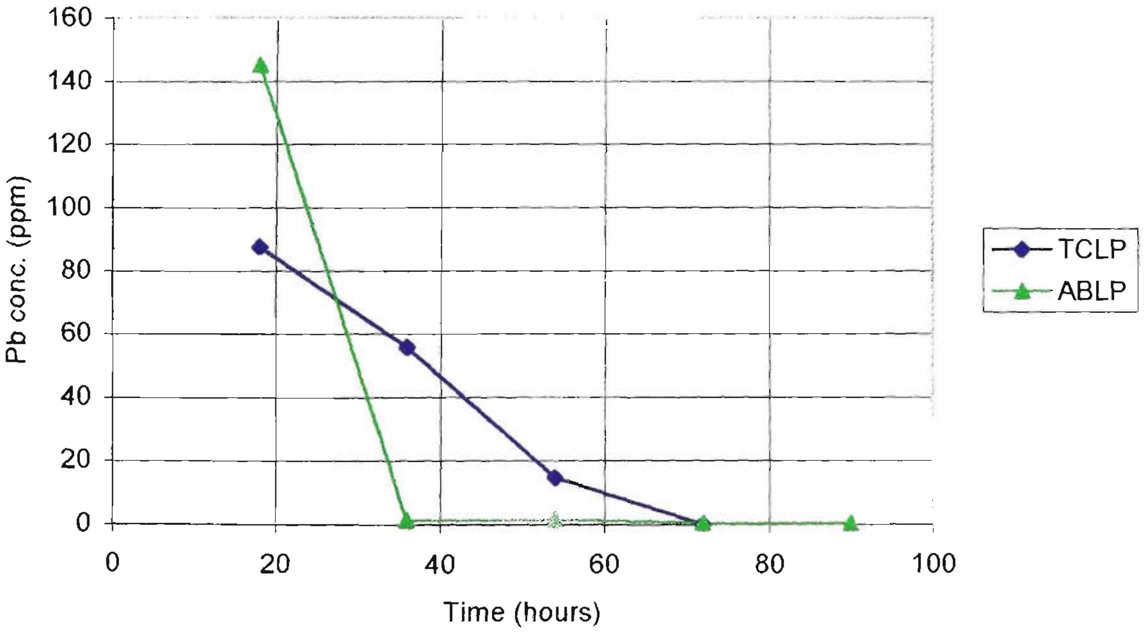


Figure 3.20 – Similarities between the lead sequential leaching results obtained using both the TCLP and the ABLP for the $PbHAsO_4$ +*C-L* formulation



3.3.1.2.1 Leaching mechanism

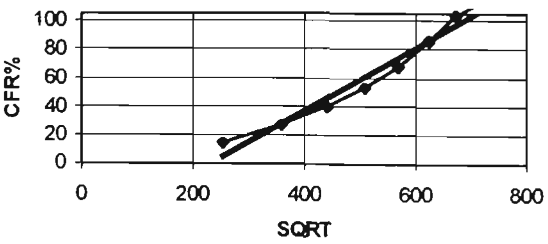
The leaching of the contaminants from the S/S formulations when using the sequential leaching (acid) tests can not be considered diffusion based. The majority of the formulations did not yield linear relationships between the CFR and the SQRT as can be observed from figures 3.21 to 3.23. Even those formulations that did exhibit a linear relationship can still not be considered diffusion based processes. As one of the assumptions of diffusion based leaching has not been met, as for the leaching of the contaminants to be considered diffusion based no more than 20% of a leachable species is allowed to leach (Dutre and Vandecasteele 1995). Figures 3.21 to 3.23 show that for both arsenic and calcium anywhere from 40 to 100% of these elements was leached.

For the [cement only] and the [cement + lime] formulations, the plots of the CFR versus the SQRT could be divided into two and even perhaps three sections. The first section, which displayed an initial resistance, had a gradient close to zero. The second section where the leaching boundary had made significant inroads consequently leached the greatest arsenic levels and had the largest gradient. For the third section, where the majority of the easily leachable arsenic had already been leached, the gradient once again approached zero.

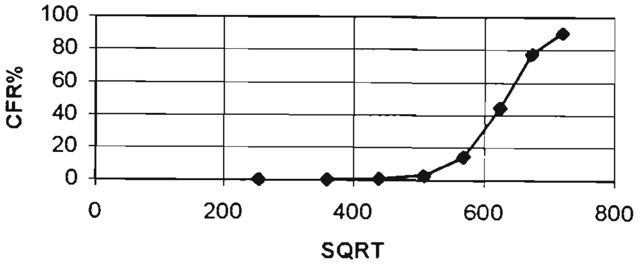
As discussed in Chapter 1, section 1.6.2.2 (page 32) leaching can be affected by a number of mechanisms, including changes in pH which can in turn effect the solubility of the various phases and hence dictate their concentrations in the leachate. As opposed to the sequential leaching tests which utilized deionized water as the leachant, the sequential leaching tests that used the acidic leachant produced leachates that demonstrated notable changes in the leachate pH throughout the investigation period (see figures 3.56 and 3.57, page 156). The effect or influence which parameters such as pH and redox potential appear to have on the leachate concentrations will be progressively discussed throughout this and the following chapter.

Figure 3.21 – CFR versus SQRT for the Arsenic Pentoxide Formulations

As_2O_5 + *C* (Calcium) $R^2 = 0.967$

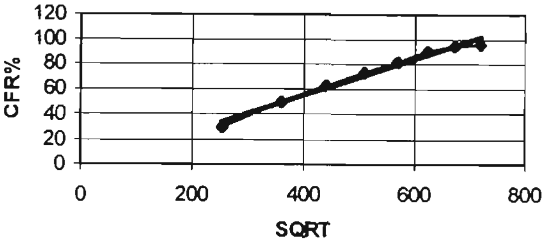


As_2O_5 + *C* (Arsenic)

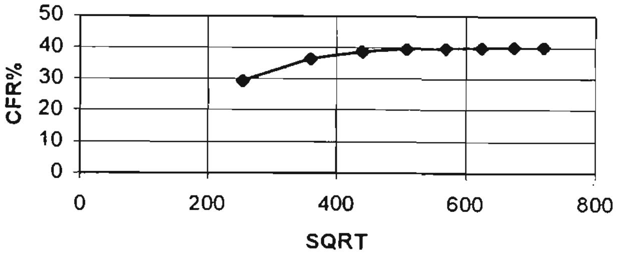


As_2O_5 + *C-Fe* (Calcium)

$R^2 = 0.9903$

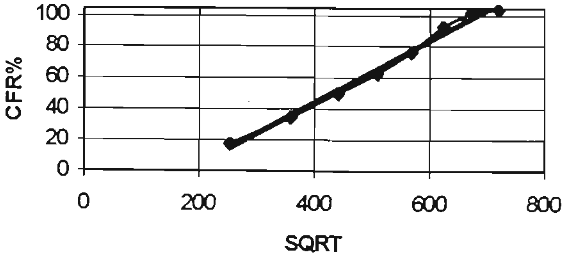


As_2O_5 + *C-Fe* (Arsenic)



As_2O_5 + *C-L* (Calcium)

$R^2 = 0.9898$



As_2O_5 + *C-L* (Arsenic)

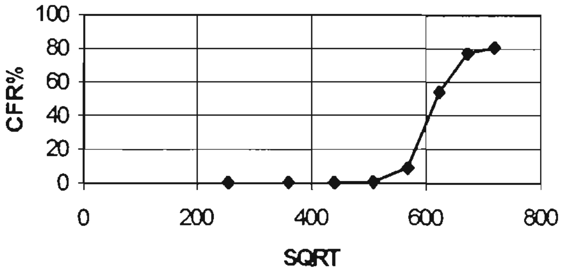
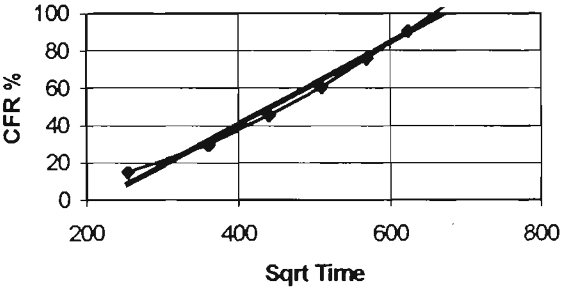
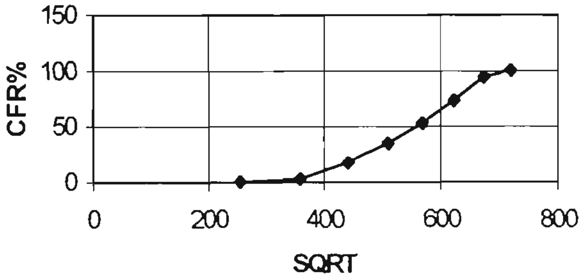


Figure 3.22 – CFR versus SQRT for the Arsenic Trioxide Formulations

As_2O_3+ *C* (Calcium) R^2 = 0.988

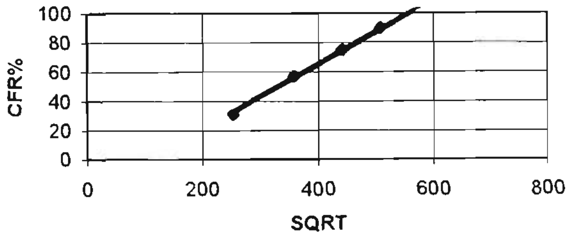


As_2O_3+ *C* (Arsenic)



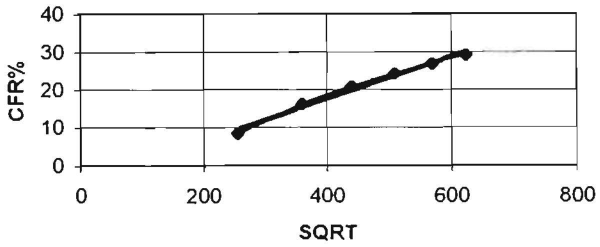
As_2O_3+ *C-Fe* (Calcium)

R^2 = 0.9984



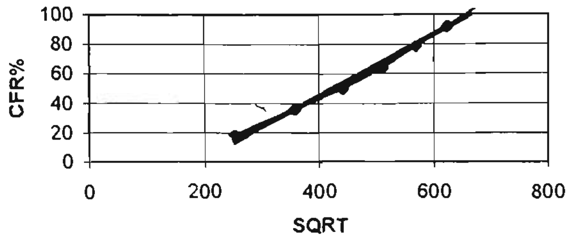
As_2O_3+ *C-Fe* (Arsenic)

R^2 = 0.9862



As_2O_3+ *C-L* (Calcium)

R^2 = 0.993



As_2O_3+ *C-L* (Arsenic)

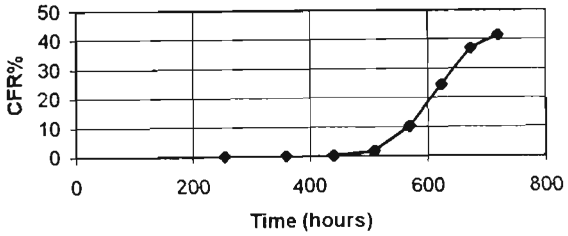
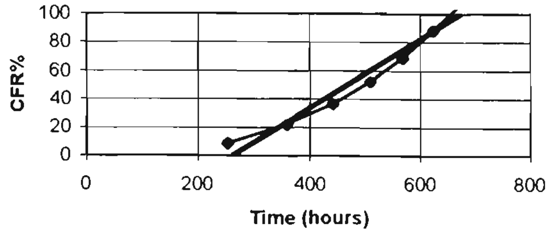


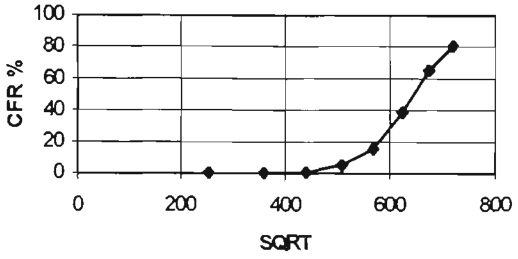
Figure 3.23 – CFR versus SQRT for the Sodium Arsenate Formulations

$NaAsO_2$ + *C* (Calcium)

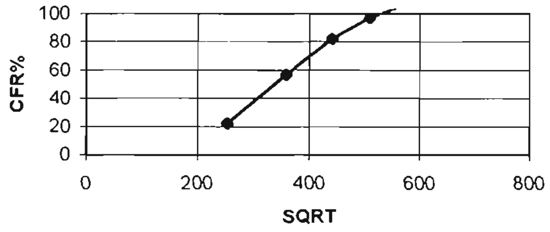
$R^2 = 0.9708$



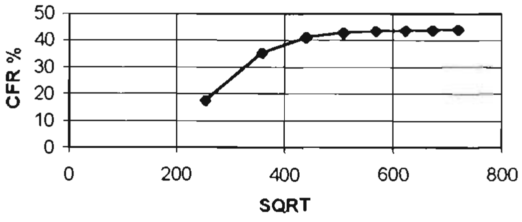
$NaAsO_2$ + *C* (Arsenic)



$NaAsO_2$ + *C-Fe* (Calcium)

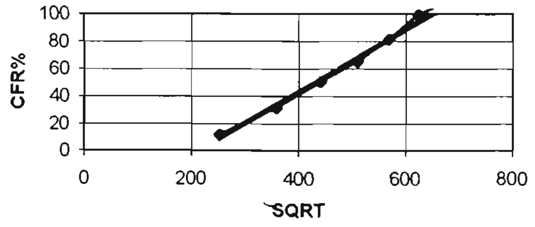


$NaAsO_2$ + *C-Fe* (Arsenic)

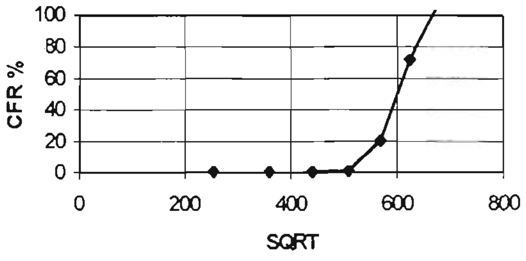


$NaAsO_2$ + *C-L* (Calcium)

$R^2 = 0.9913$



$NaAsO_2$ + *C-L* (Arsenic)

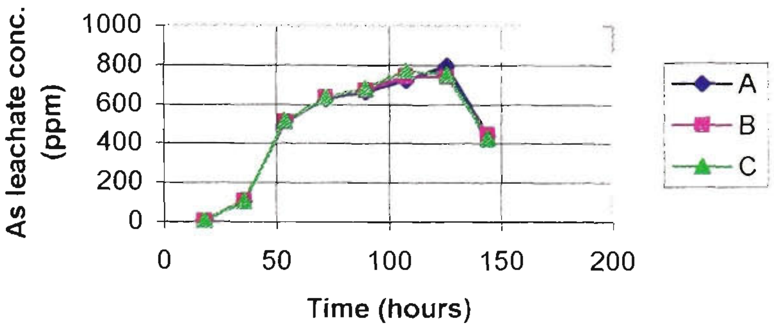


3.3.1.2.2 Precision of the Sequential Leaching (acid) tests

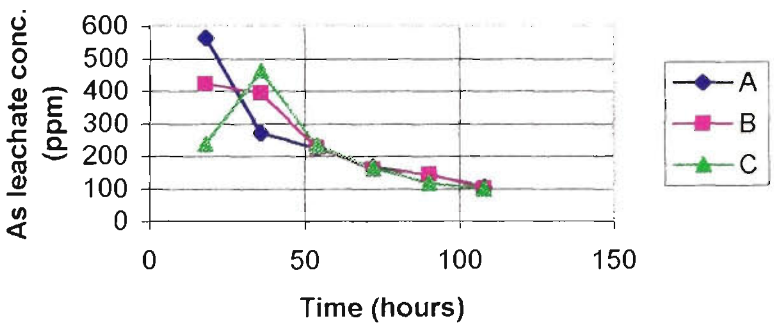
As was the case with the Sequential leaching (water) tests, the Sequential leaching tests employing the acidic leachant (5.7 mL acetic acid per litre) were performed in triplicate. Despite the fact that the leachate concentrations could increase dramatically over a single 18 hour interval, for the vast majority of the S/S formulations the precision was equal to that obtained when the less aggressive deionized water leachant was used. The precision exhibited by the Sequential leaching (acid) tests can be observed from figures 3.24 through to 3.28. The large peaks and troughs exhibited for these tests are purely as a result of the leachant, not the leachant renewal procedure.

Figure 3.24 – Precision of the Sequential leaching (acid) tests and the Arsenic Trioxide formulations

As_2O_3 + *C*



As_2O_3 + *C-Fe*



As_2O_3 + *C-L*

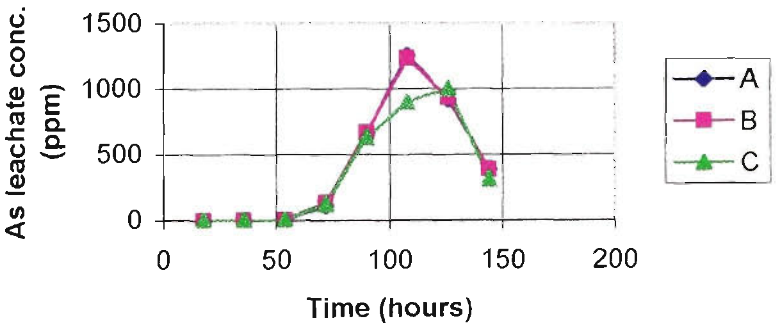
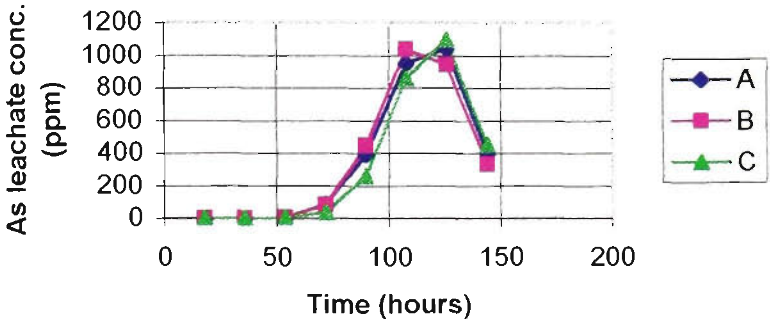
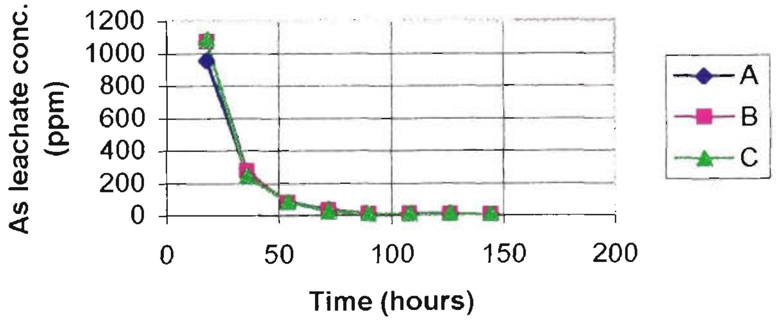


Figure 3.25 – Precision of the Sequential leaching (acid) tests and the Arsenic Pentoxide formulations

As_2O_5 + *C*



As_2O_5 + *C-Fe*



As_2O_5 + *C-L*

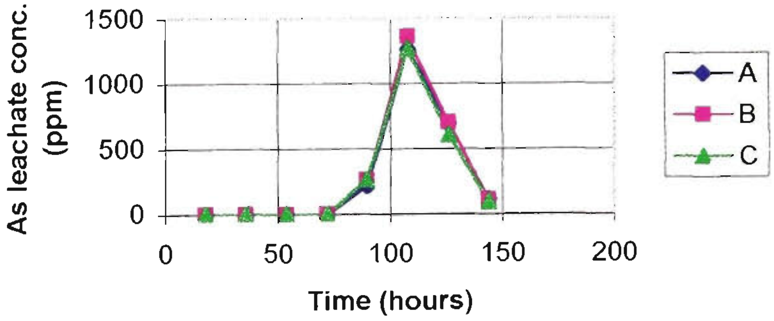
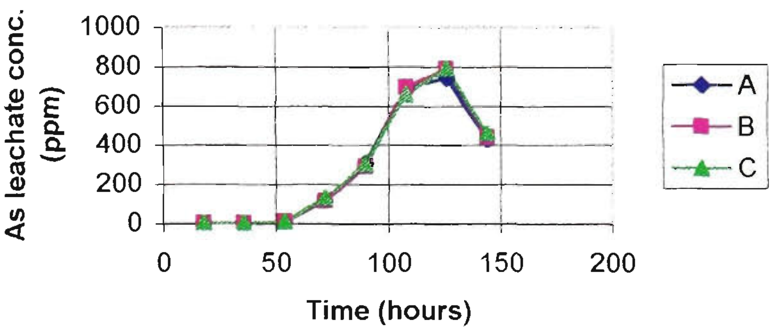
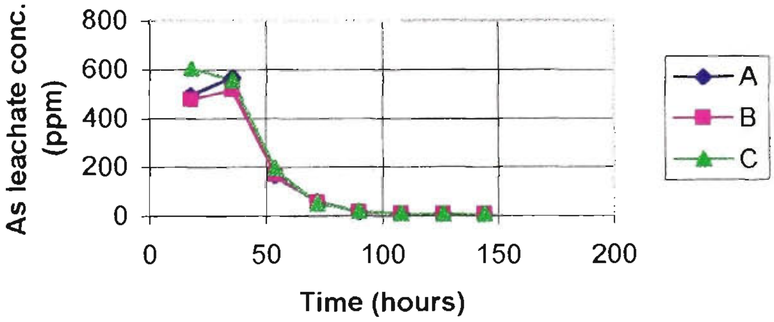


Figure 3.26 – Precision of the Sequential leaching (acid) tests and the Sodium Arsenate formulations

Na_2HAsO_4 + *C*



Na_2HAsO_4 + *C-Fe*



Na_2HAsO_4 + *C-L*

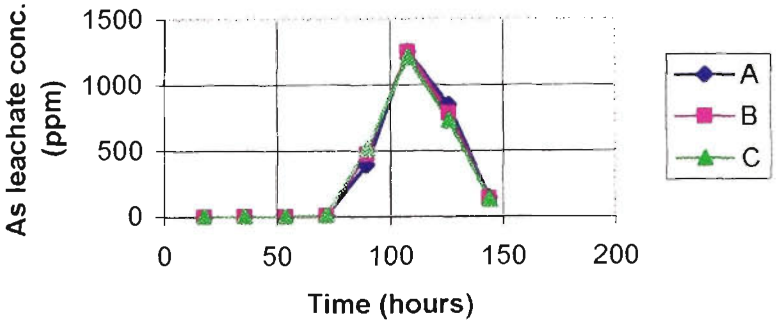
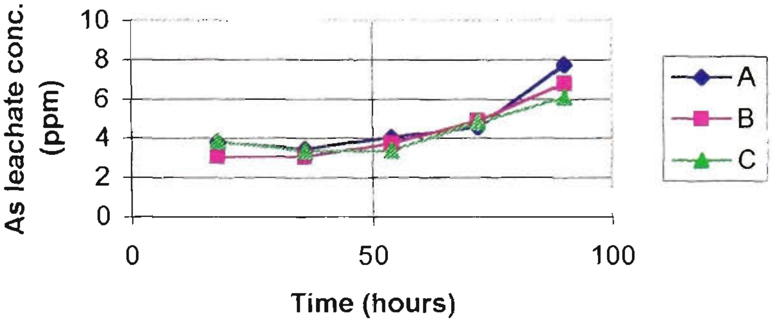
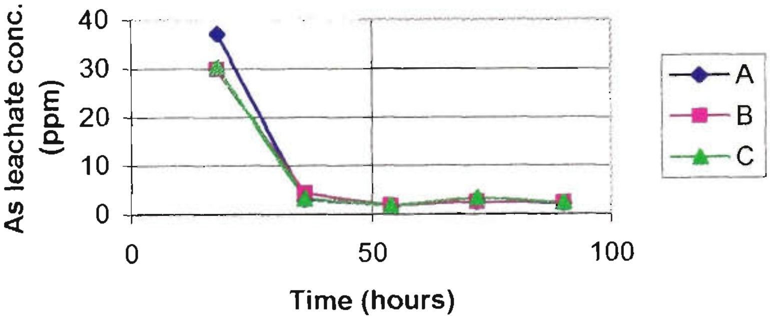


Figure 3.27 – Precision of the Sequential leaching (acid) tests and the Lead Arsenate formulations (Arsenic concentrations)

$PbHAsO_4$ + *C*



$PbHAsO_4$ + *C-Fe*



$PbHAsO_4$ + *C-L*

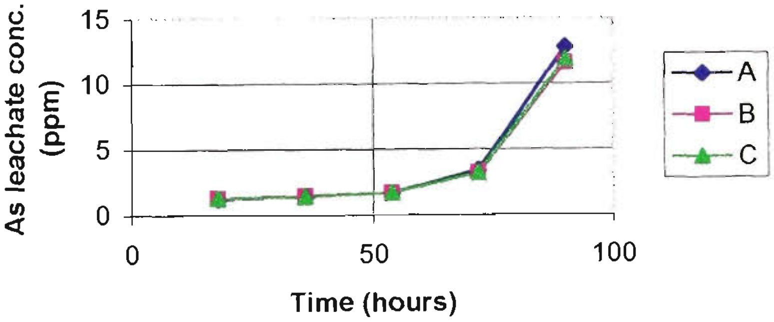
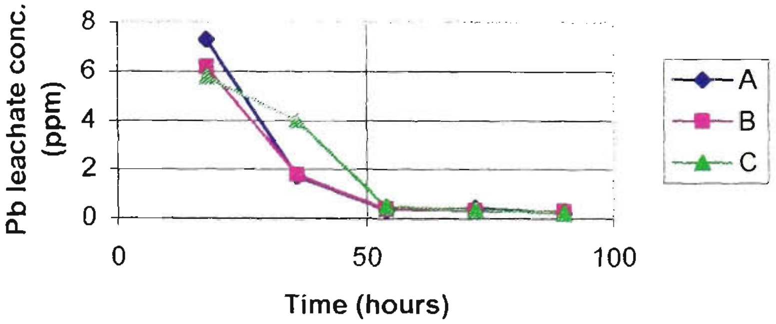
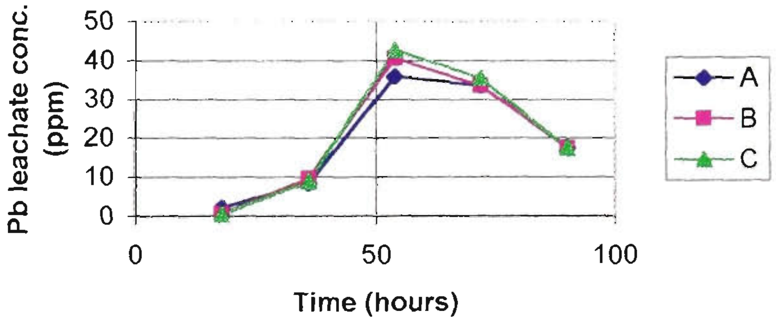


Figure 3.28 – Precision of the Sequential leaching (acid) tests and the Lead Arsenate formulations (Lead concentrations)

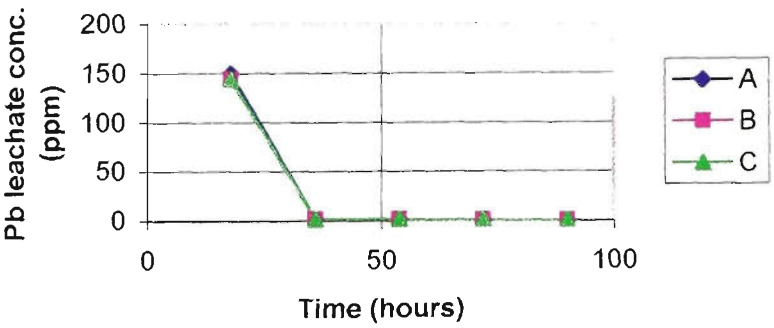
$PbHAsO_4$ + *C*



$PbHAsO_4$ + *C-Fe*



$PbHAsO_4$ + *C-L*

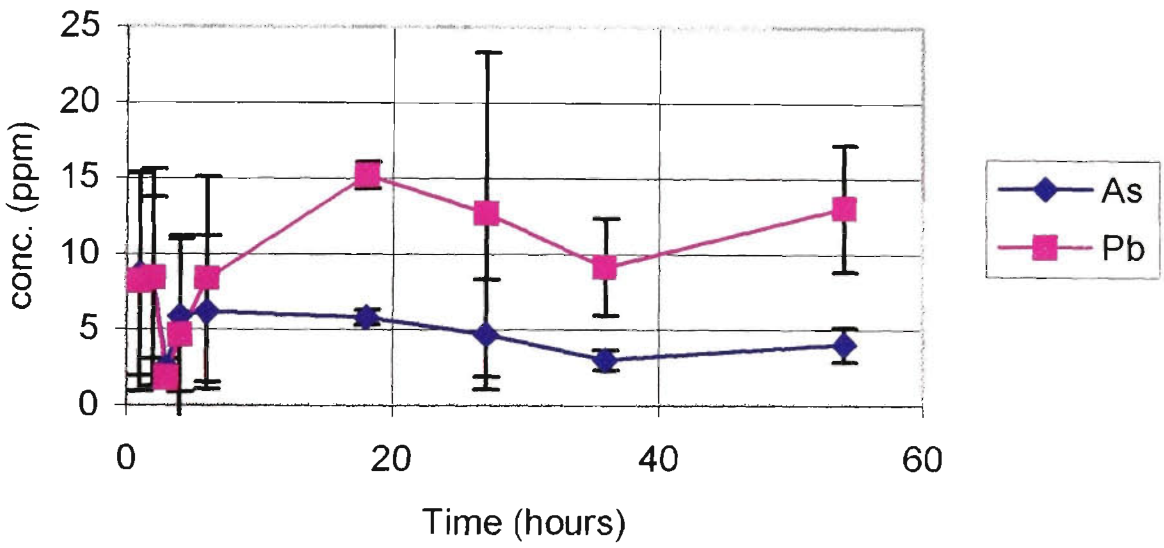


3.3.2 Continual leaching[3]

The principle aim of the Continual Leaching Tests was to investigate whether the 18 hour time duration of both current regulatory tests, is indeed indicative of the highest leachate concentrations for the elements of interest.
Continual Leaching Tests were conducted on the lead arsenate formulations, since its formulations provide the opportunity to monitor two hazardous components, lead and arsenic, concurrently.

Figure 3.29 displays the results obtained for the continual leaching tests using the Bottle Leaching Procedure with deionized water and the [cement only] stabilized lead arsenate insecticide.

Figure 3.29 – Continual Bottle Leaching (Deionized water leaching fluid) Cement Stabilized Lead Arsenate



From this figure (3.29) it is clear that the highest leachate concentrations were obtained at or beyond the regulatory time of 18 hours. These results are clearly the opposite to those obtained for the same formulation when subjected to the acidic leachant (5.7 mL acetic acid per litre). Figure 3.30

---

[3] Continual leaching tests involved removing and replacing 30mL/L portions of the leachate

shows that when the [cement only] formulation was leached with the more aggressive acetic leachant the highest leachate concentrations for both lead and arsenic were recorded at 6 hours. By 18 hours the levels for both lead and arsenic were reduced, falling even further by the end of the investigation period. Continual leaching using the TCLP with the same leaching fluid and sample also yielded the highest leachate concentrations prior to the 18 hour period used for regulatory purposes (figure 3.31). However, unlike the Bottle Leaching Procedure, the highest leachate concentrations were obtained at the initial stages of the leaching test. This could be a result of the larger particles being broken down, exposing new surfaces to the extraction fluid.

Figure 3.30 – Continual Bottle Leaching (Acetic leaching fluid) Cement Stabilized Lead Arsenate

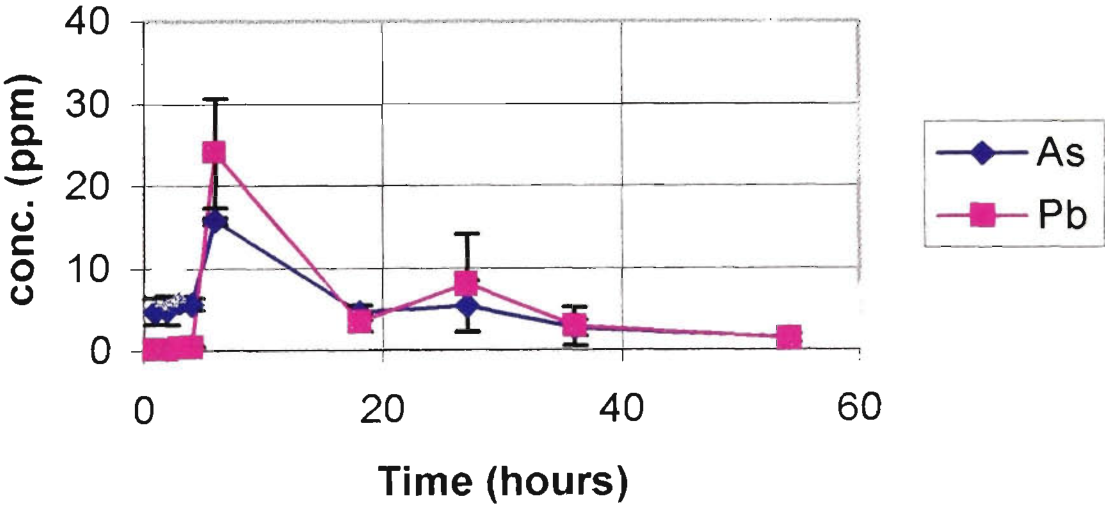
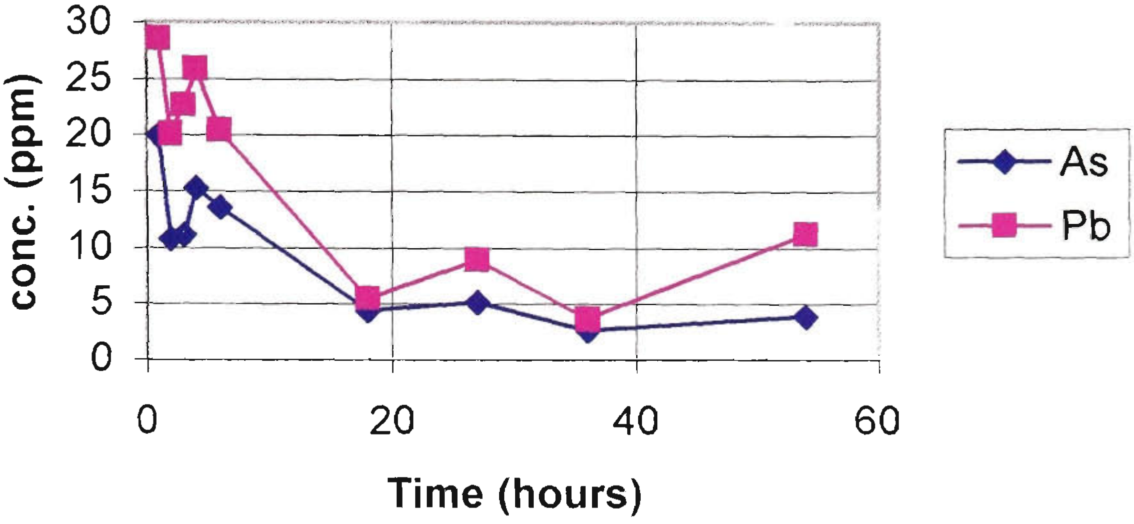


Figure 3.31 – Continual TCLP Leaching (Acetic leaching fluid)
Cement Stabilized Lead Arsenate



As was found to be the case when using the Sequential Leaching Tests, the leaching trends exhibited by the various formulations, (i.e., [cement only], [cement + iron] and [cement + lime]) were shown to differ significantly, obviously a direct consequence of their unique matrices. Figure 3.30, showing the leachate concentrations obtained for the [cement only] formulation using the acidic leachant, indicates the highest concentrations were obtained prior to the regulatory time (18 hours). However, figures 3.32 and 3.33, which display the recorded concentrations for the $PbHAsO_4$ + *C-Fe* and the $PbHAsO_4$ + *C-L* formulations respectively, using the same leachant type, show that this is not always the case. Figure 3.32 and 3.33 indicate that the highest arsenic leachate concentrations were obtained well in excess of the regulatory time period. The Lead concentrations leached by the $PbHAsO_4$ + *C-L* were also at their greatest well beyond the 18 hour period.

Figure 3.32 – Continual Bottle Leaching (Acetic leaching fluid) [cement + iron] Stabilized Lead Arsenate

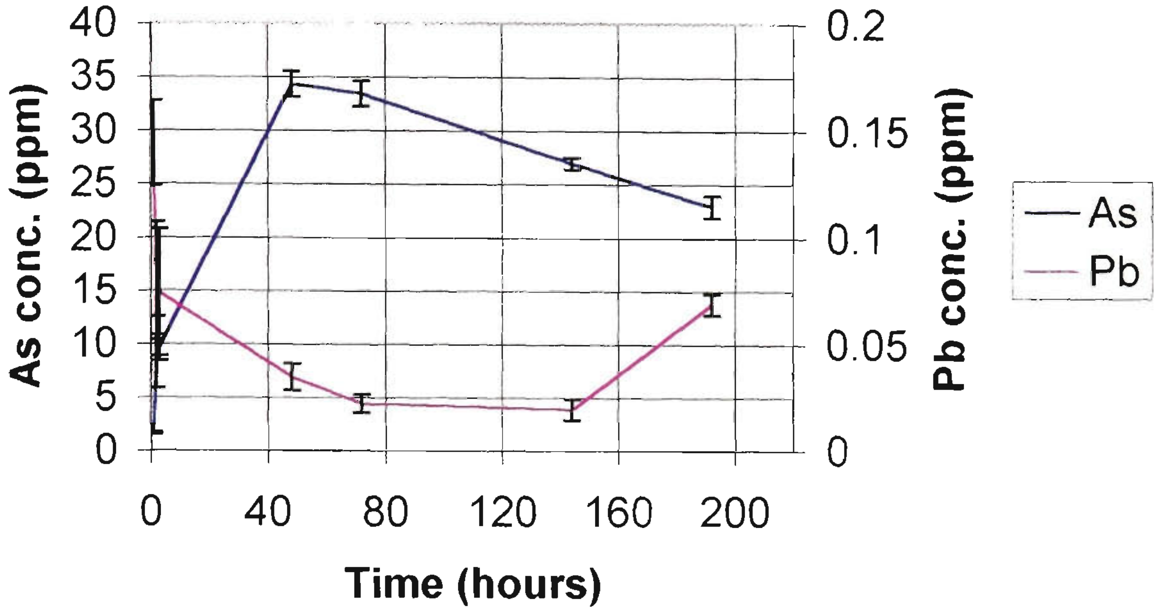
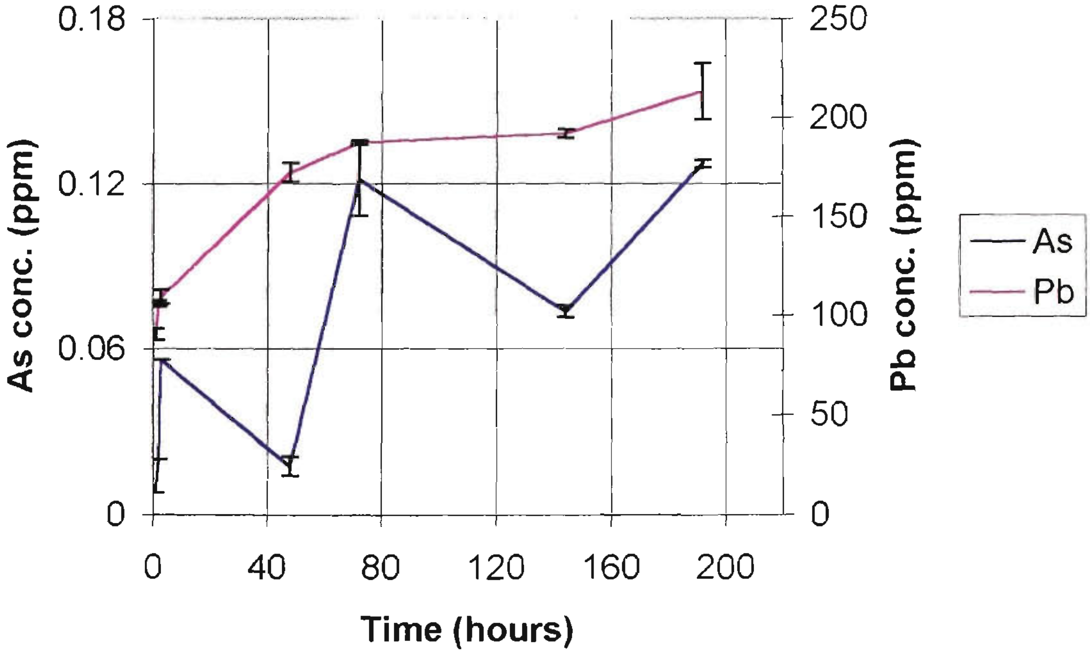


Figure 3.33 – Continual Bottle Leaching (Acetic leaching fluid) [cement + lime] Stabilized Lead Arsenate



The results contained in figures 3.29 through to 3.33 are counter intuitive, since it would, at face value, be reasonable to expect leached concentrations to either increase with time or remain constant. The fact that concentrations of some elements in some of the formulations decreased with leaching time suggests the presence of mechanisms which are re-precipitating dissolved elements such as arsenic. Given that the agitation process used for these tests does not allow the tested material to settle, the tests provide near ideal conditions for the adsorption and precipitation of insoluble compounds. It is proposed, as will be discussed in more detail in the subsequent section, that co-leaching of calcium from the matrix leads to the formation of insoluble arsenites and arsenates, thus refixing the leached arsenic. This contributes to explaining why the [cement + lime] formulations achieved the greatest success in stabilizing arsenic.

DeVillers (1995) also ran continual type batch leaching tests, using different leachant types to those used in this study, to access the stabilization of arsenic which had been incorporated into slags. DeVillers (1995) also found that leachate concentrations can decrease over time due to sorption processes, proposing that the reduction, unlike in this present study, was due to sorption on hydrous ferric oxide. As will be shown to a greater extent in the following sections, such a process is unlikely to have contributed to the reduction in the arsenic leachate concentrations in this study. Besides the lower iron contents of the formulations used in this study, a further explanation why such a process did not apparently control the removal of arsenic from the leachate in this study, may be the pHs of the leachates. In this study the leachate pHs of the [cement only] and [cement + lime] formulations were in the range of 11 to13, as can be observed from table 3.5 which contains the recorded pHs for the [cement + lime] formulations. As can be observed from figures 3.34 and 3.35, maximum sorption of arsenic has been shown in previous studies to occur at more neutral pH levels.

Table 3.5 – pH recorded for the leachates collected from the continual leaching of $PbHAsO_4$ + *C-L*

Time at which leachate was collected (hours)	Leachate pH
1	12.84
2	12.86
3	12.86
48	12.97
72	13.00
144	12.99
192	12.98

Figure 3.34 – Arsenite sorption on hydrous ferric oxide (Dzombak and Morel, 1990)

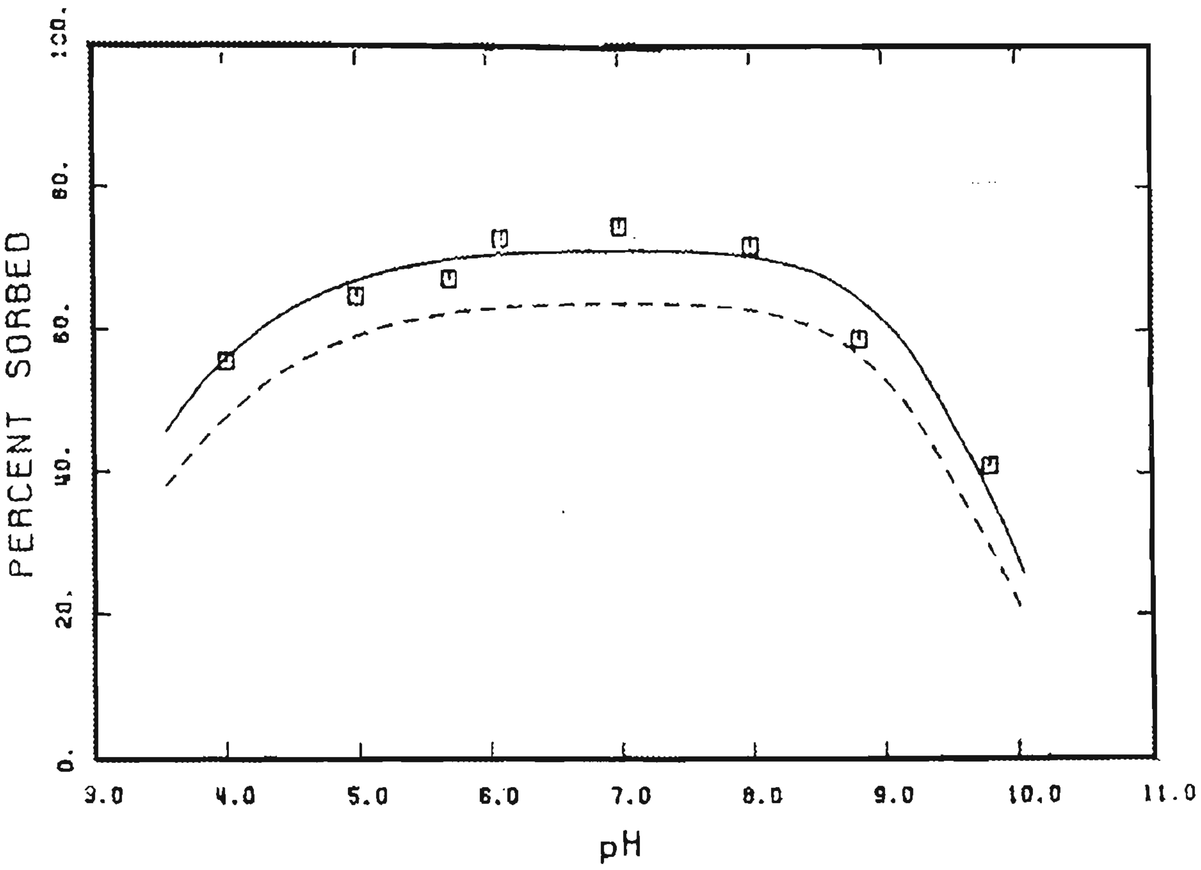
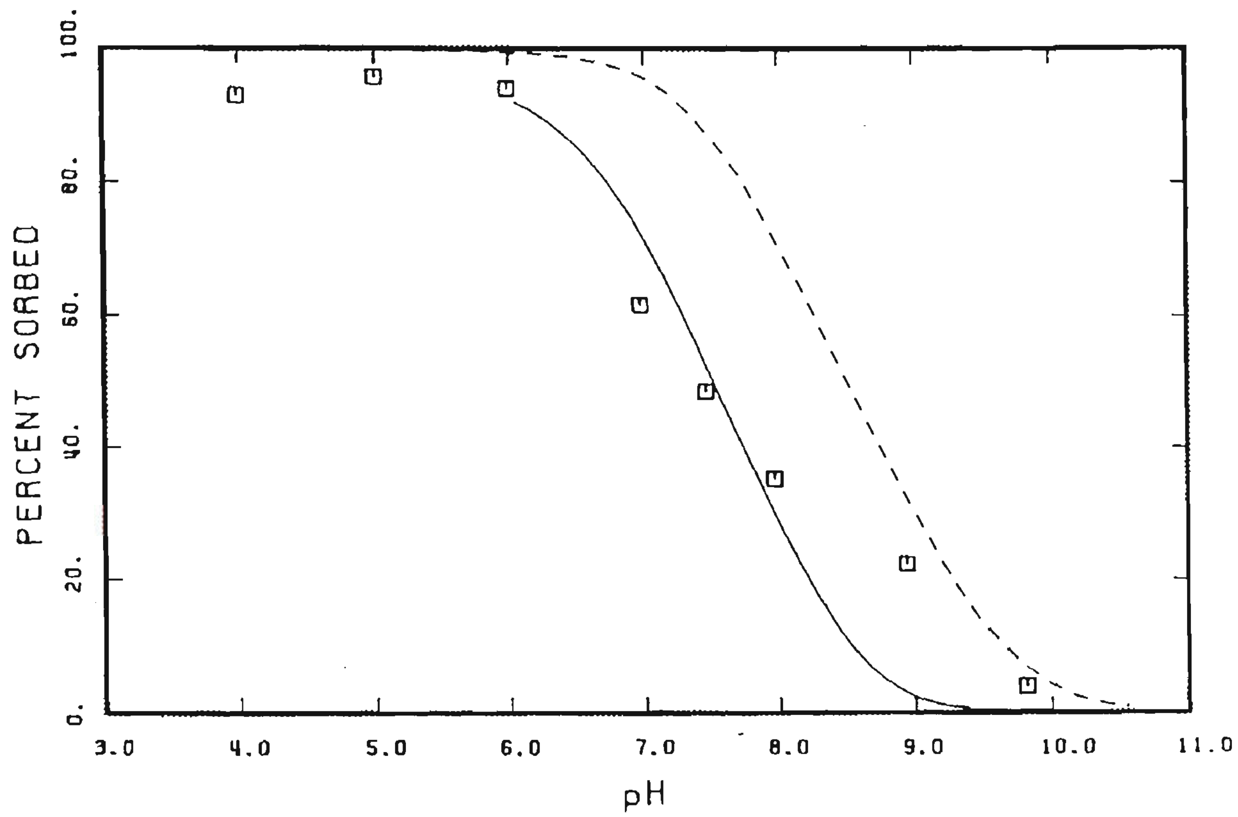


Figure 3.35 –Arsenate sorption on hydrous ferric oxide

(Dzombak and Morel, 1990)



Sorption of arsenic onto surfaces of the leaching and filtration apparatus is not considered sufficient to cause any distortion of the leaching results. No information has been found in the literature to suggest that arsenic is adsorbed on clean glass or plastic surfaces in any pH region (DeVillers 1995). Massee et al (1981) investigated sorption losses for a number of elements including arsenic from a 10^{-7}M (7.5 ppb) arsenate solution in distilled water and artificial sea-water during storage in containers made of borosilicate glass, high-pressure polyethylene or PTFE. Radioactive solutions were used to detect trace level losses due to sorption. Prior to testing, the container surfaces were cleaned by shaking with 8M nitric acid followed by washing with distilled water. Measurements were made for pHs of 1, 2, 4 and 8.5 for storage times of 1 minute to 28 days. Loses for arsenic were found to be insignificant on all container materials considered, irrespective of solution, matrix composition or pH.

Given that figures 3.29 through to 3.33 clearly showed that the time required to obtain the maximum leachate concentrations varies from matrix to matrix, and, consequently, that the regulatory time of testing for both of the ABLP (AS 4439.3) and the TCLP (US EPA 1992) does not necessarily reflect the time at which the largest leachate concentrations are obtained, it was deemed unnecessary to continue Continual Leaching with the other arsenic compounds and formulations. It was decided instead to concentrate the research on alternative types of leaching, principally column leaching tests, the results of which will be discussed in Chapter 4.

3.4 Lime Stabilization

The use of lime to precipitate arsenic as calcium arsenite or arsenate from solution has been widely practised. Investigations by Nishimura (1983, 1985), as well as Robins (1985), have identified a number of calcium arsenic precipitates. Two arsenites, $Ca(AsO_2)_2$ and $Ca(AsO_2)_2.Ca(OH)_2$ and five arsenates, $CaH_4(AsO_4)_2$, $Ca_2H_2(AsO_4)_2$, $Ca_5H_2(AsO_4)_4$, $Ca_3(AsO_4)_2$ and $Ca_3(AsO_4)_2.Ca(OH)_2$ were identified.

From the data presented thus far, it has been clear that those formulations which included the addition of lime, and hence calcium, were generally the most successful. The subsequent sections, 3.4.1 through to 3.4.3 will further investigate the relationship that exists between the calcium and arsenic levels and will examine the effectiveness of calcium to reduce the arsenic leachate concentrations, be it from aqueous arsenic solutions or the solidification/stabilization of arsenic.

3.4.1 Aqueous arsenic removal using calcium

The ability of calcium to precipitate arsenic from solution was investigated in this present study. The experiments involved combining an aqueous arsenic solution (either arsenic pentoxide or trioxide), initial concentration 200 ppm, with calcium (in the form of solid calcium chloride) at various mole ratios, and mixing with the aid of a magnetic stirrer for a period of 24 hours. After this, the samples were filtered using the same apparatus as required for both regulatory leaching tests and the elemental composition determined by ICP as outlined in chapter 2.

Figure 3.36 clearly indicates that for the removal of arsenic from aqueous solutions, the greater success was achieved when arsenic was present in the pentavalent state. Calcium arsenates are less soluble than arsenites (DeVillers 1995).

Figure 3.36 - The effect of the arsenic oxidation state on the removal of arsenic using calcium (pH = 12.43)

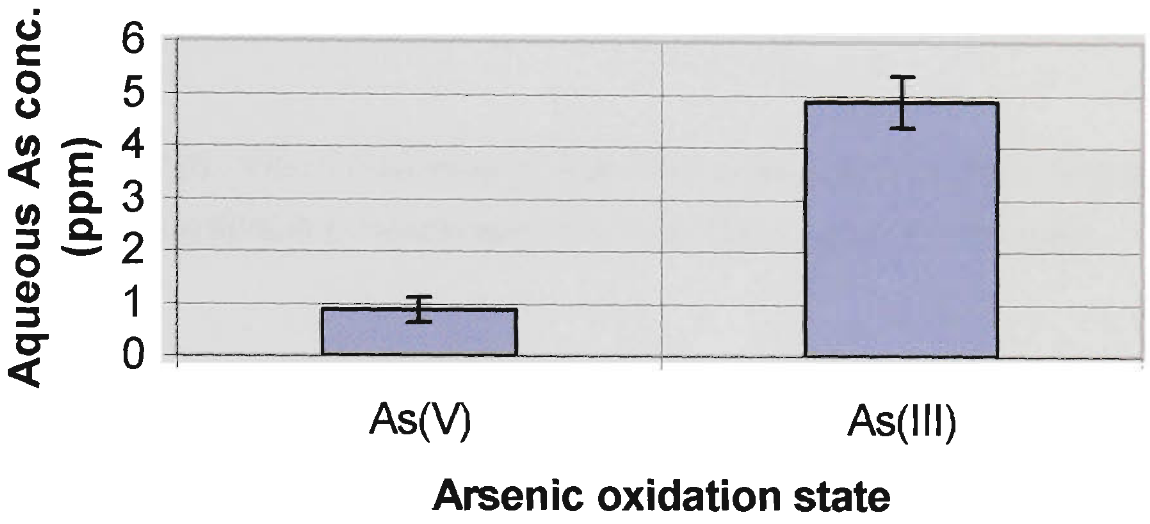
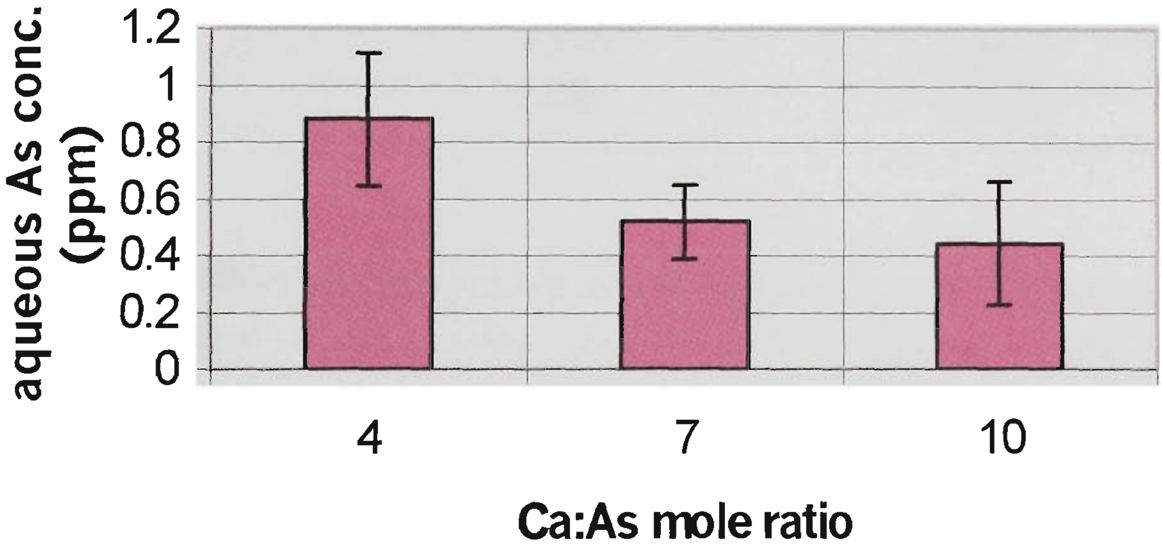


Table 3.6 – Comparison of the effectiveness of arsenic removal from a solution of an initial arsenate concentration of 200ppm (pH = 12.73)

	Calcium – arsenate precipitation	**Ferrous sulfate precipitation**
Fe:As or Ca:As Mole ratio	Aqueous arsenic concentration (ppm) remaining in solution	Aqueous arsenic concentration (ppm) remaining in solution
4	0.88	144.7
10	0.44	0.26

The results of a comparison of arsenic removal efficiency using either calcium or iron (ferrous sulfate) can be observed from table 3.6. Only at the relatively high mole ratio of 10:1 did the effectiveness of the iron-arsenic removal compare with the effectiveness of the calcium-arsenic removal. A large portion of the arsenic was removed when using a Ca:As mole ratio of 4:1. Hence, little further improvement could be identified as the Ca:As mole ratio was increased. The effect of increasing the Ca:As mole ratio from 4 to 7 to 10 is shown more clearly in figure 3.37.

Figure 3.37 – The effect of increasing the Ca:As mole ratio on reducing the aqueous arsenate concentration from an initial value of 200 ppm



3.4.2 Solidification/stabilization using calcium

Just as increasing the Ca:As mole ratio yielded little further improvement above a mole ratio of 7, increasing the Ca:As mole ratio from 10 to 11 has yielded little, if any, additional improvement in the solidification/stabilization of sodium arsenate (table 3.7).

Table 3.7 – The effect of increasing the Ca:As mole ratio in the solidification/stabilization of sodium arsenate

Ca:As mole ratio	Percentage of Arsenic leached using the ABLP (deionized water)	Percentage of Arsenic leached using the ABLP (acidic leachant)
10	0.03%	0.03%
11	0.02%	0.05%

Vircikova et al (1999) showed that a Ca:As ratio higher than 8 did not lead to a significant reduction in the residual concentration of arsenic in solution. Vircikova's work helps to explain why the data contained in tables 3.0 and 3.1 showed that those formulations that had the greatest calcium content generally were the best performing S/S formulations. The iron formulations, as can be observed form table 3.8, had Ca:As mole ratios approximately half as large as those contained in the other formulations investigated.

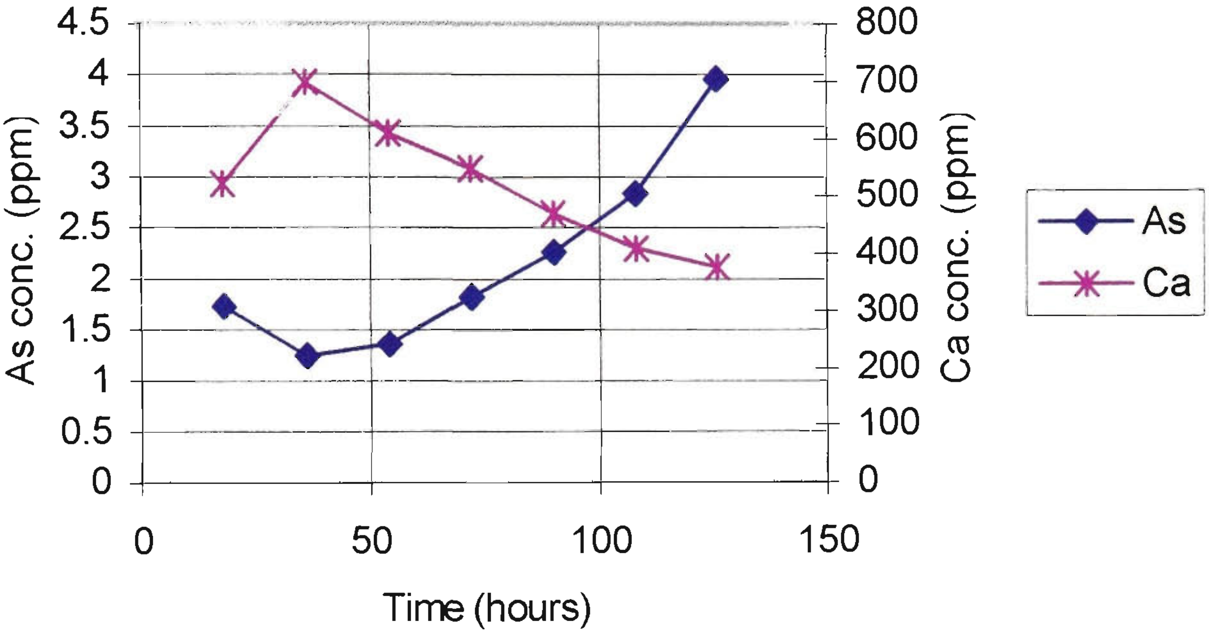
Table 3.8 - The Ca:As mole ratios of the S/S formulations

S/S formulation	Ca:As mole ratio
$NaAsO_2$ + *C*	8.13
$NaAsO_2$ + *C-Fe*	4.57
$NaAsO_2$ + *C-L*	10.9
As_2O_3 + *C*	7.60
As_2O_3 + *C-Fe*	3.30
As_2O_3 + *C-L*	10.3
Na_2HAsO_4 + *C*	8.56
Na_2HAsO_4 + *C-Fe*	4.44
Na_2HAsO_4 + *C-L*	10.7
As_2O_5 + *C*	10.1
As_2O_5 + *C-Fe*	4.57
As_2O_5 + *C-L*	10.9

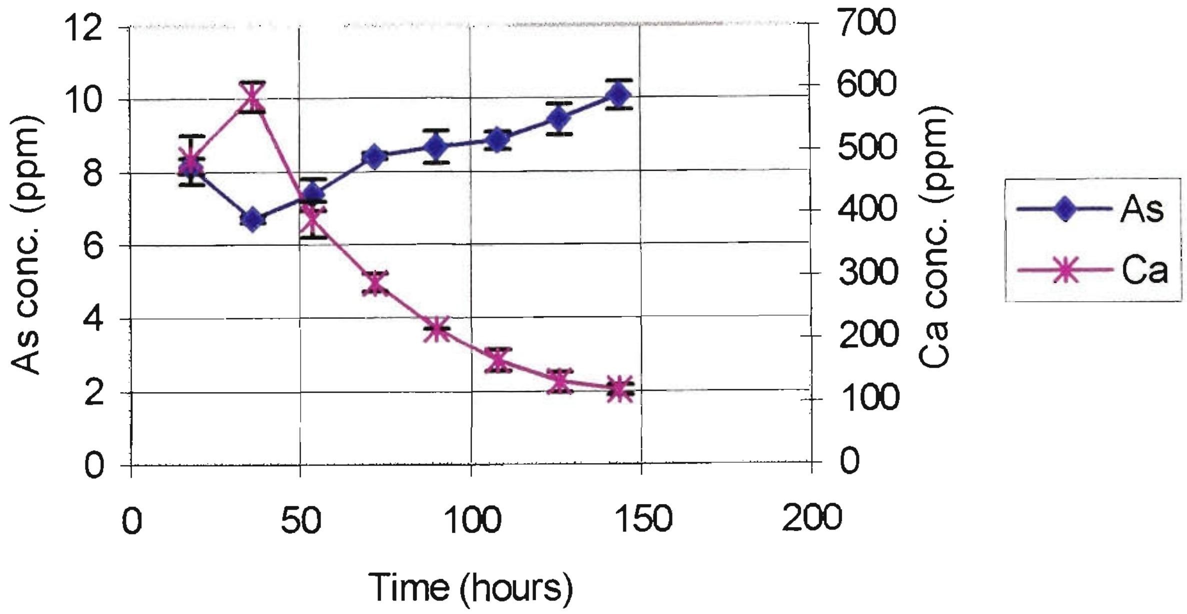
The strong influence which the calcium levels have upon the arsenic levels can be observed from figures 3.38 through to 3.41.

Figure 3.38 – Relationship between Calcium and Arsenic levels in the sequential leaching (water) leachates for the Sodium Arsenite formulations

(A) $NaAsO_2$ + C



(B) $NaAsO_2$ + C-Fe



(C) $NaAsO_2$ + C-L

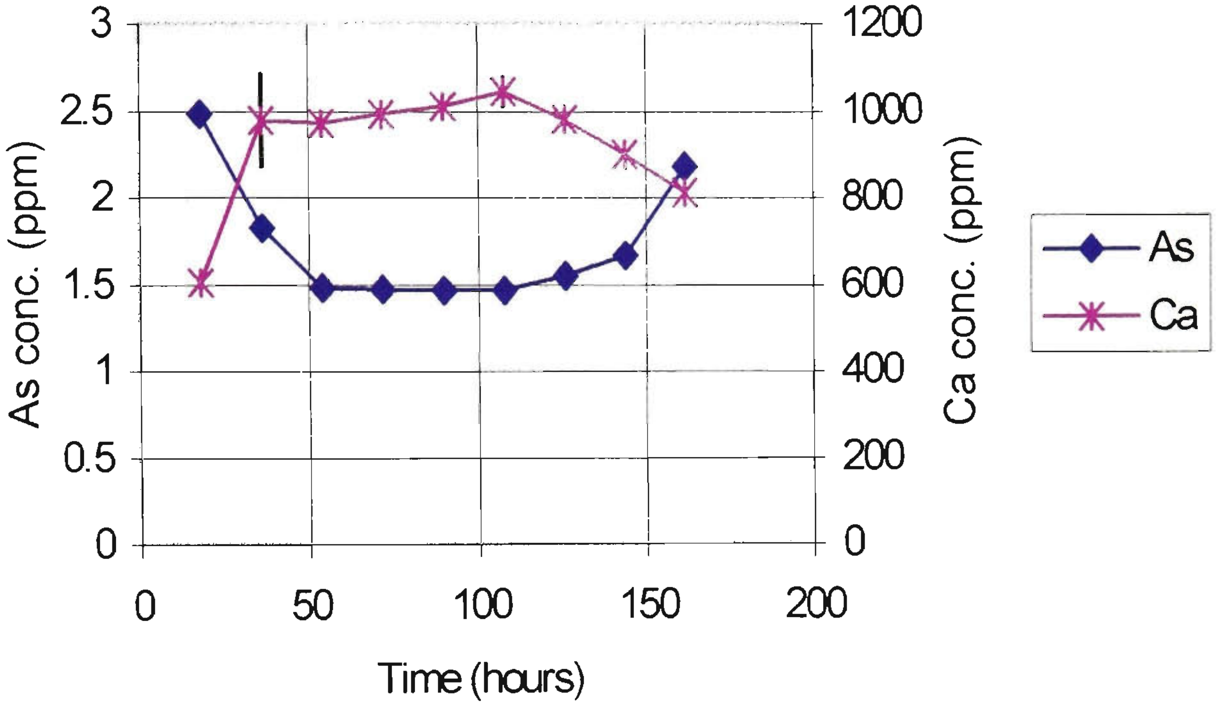
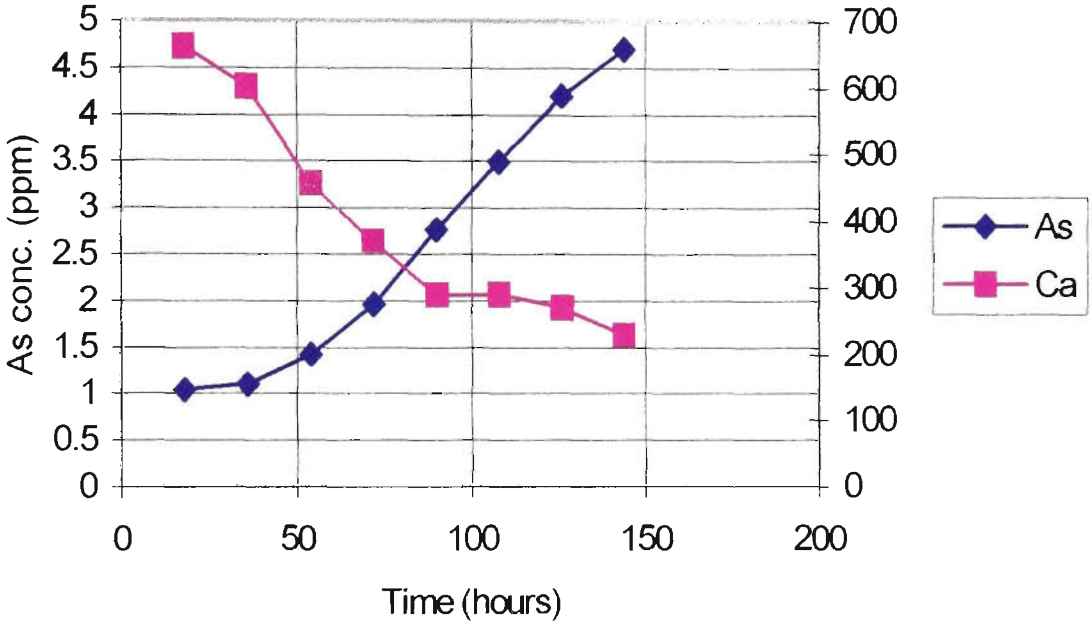
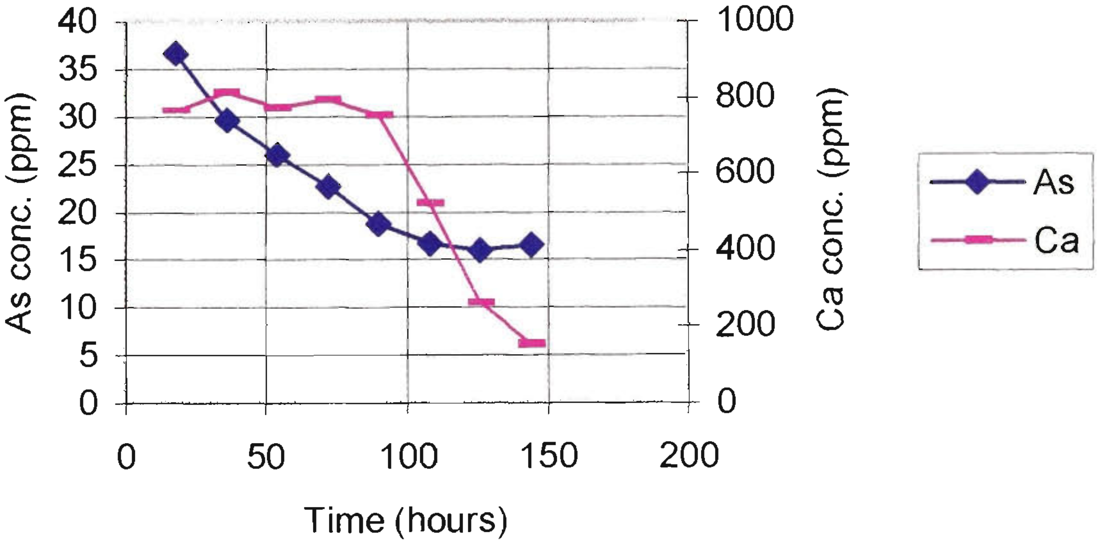

3
2.5
2
1.5
1
0.5
0
As conc. (ppm)
1200
1000
800
600
400
200
0
Ca conc. (ppm)
0
50
100
150
200
Time (hours)
As
Ca

Figure 3.39 – Relationship between Calcium and Arsenic levels in the sequential leaching (water) leachates for the Arsenic Trioxide formulations

(A) As_2O_3 + *C*



(B) As_2O_3 + *C-Fe*



(C) As_2O_3 + *C-L*

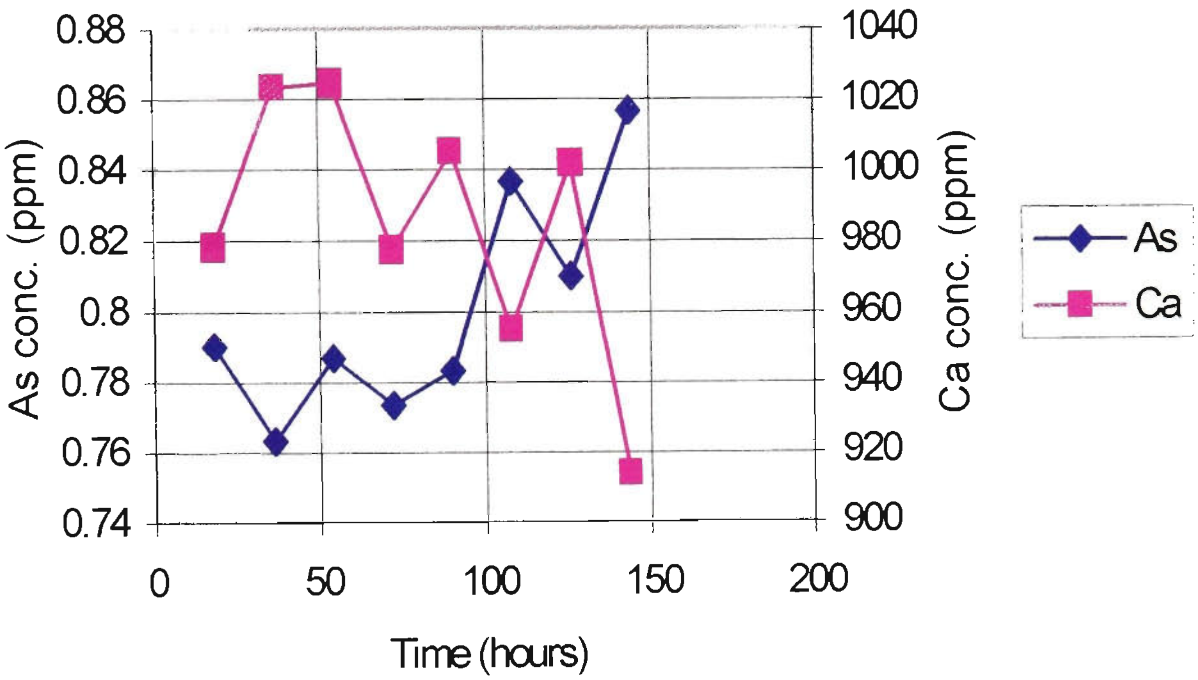
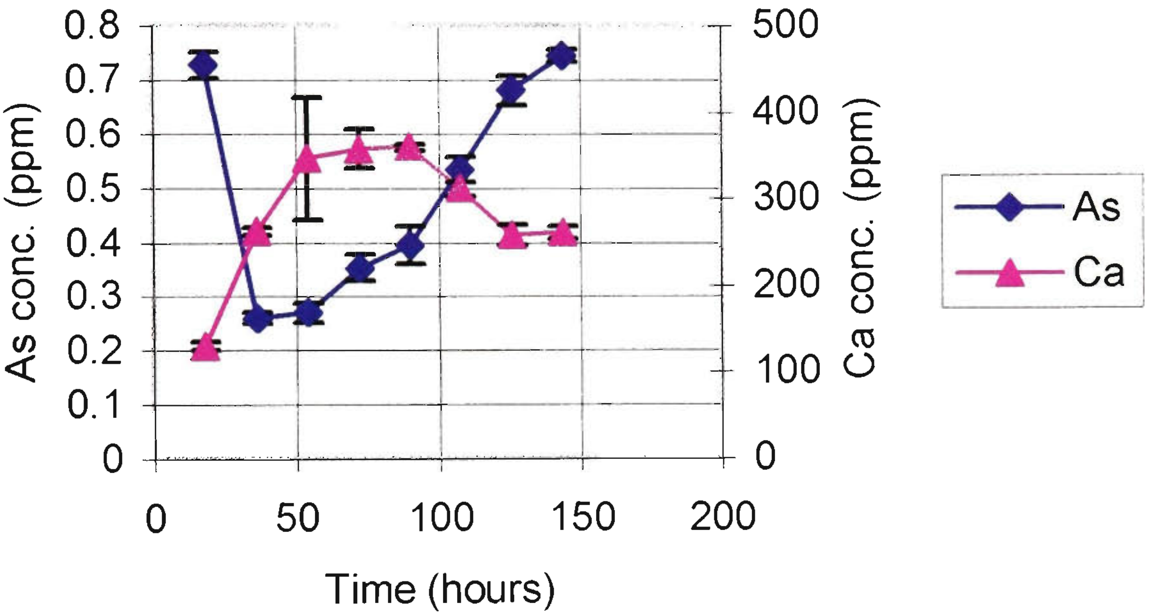
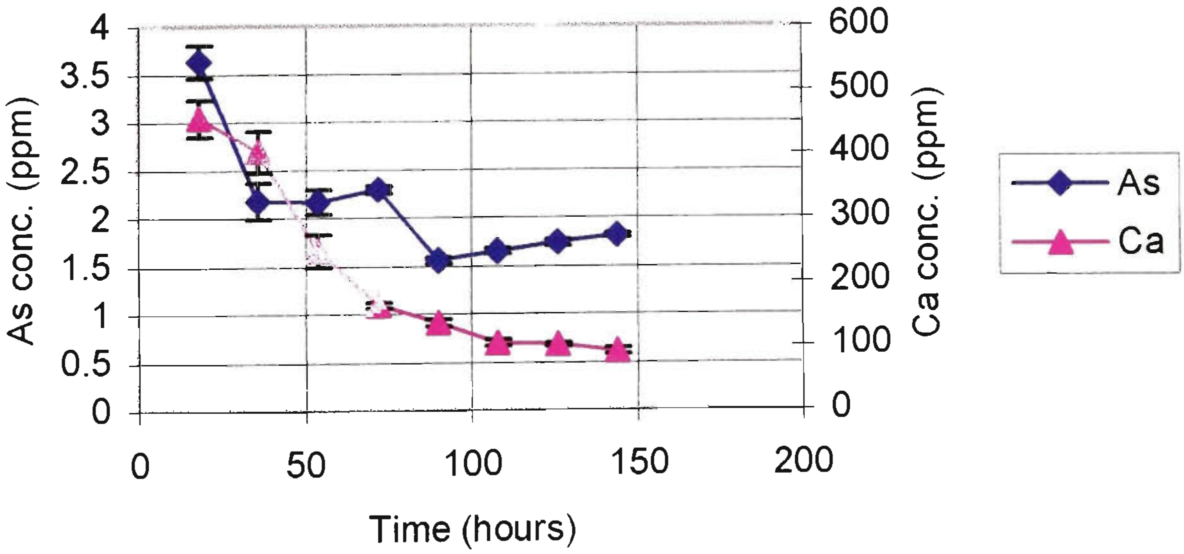

0.88
0.86
0.84
0.82
0.8
0.78
0.76
0.74
As conc. (ppm)
1040
1020
1000
980
960
940
920
900
Ca conc. (ppm)
0
50
100
150
200
Time (hours)
As
Ca

Figure 3.40 – Relationship between Calcium and Arsenic levels in the sequential leaching (water) leachates for the Sodium Arsenate formulations

(A) Na_2HAsO_4 + *C*



(B) Na_2HAsO_4 + *C-Fe*



(C) Na_2HAsO_4 + *C-L*

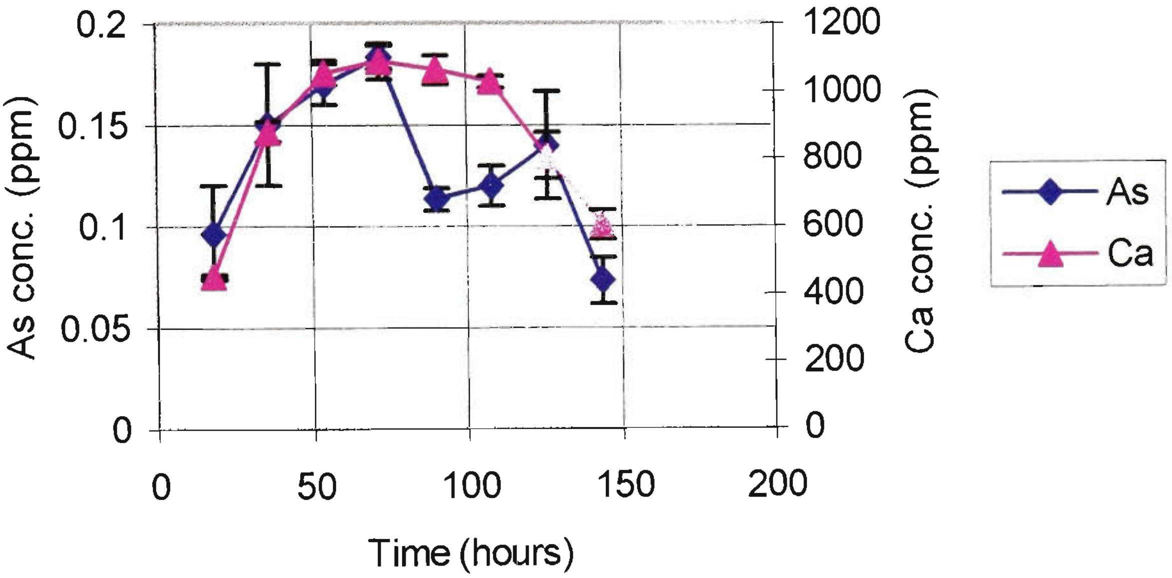
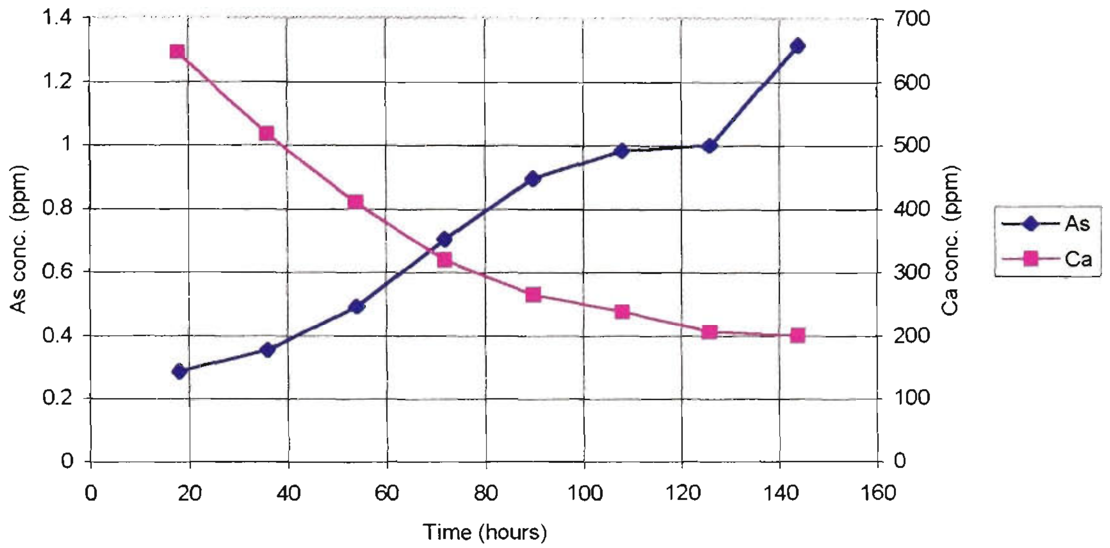
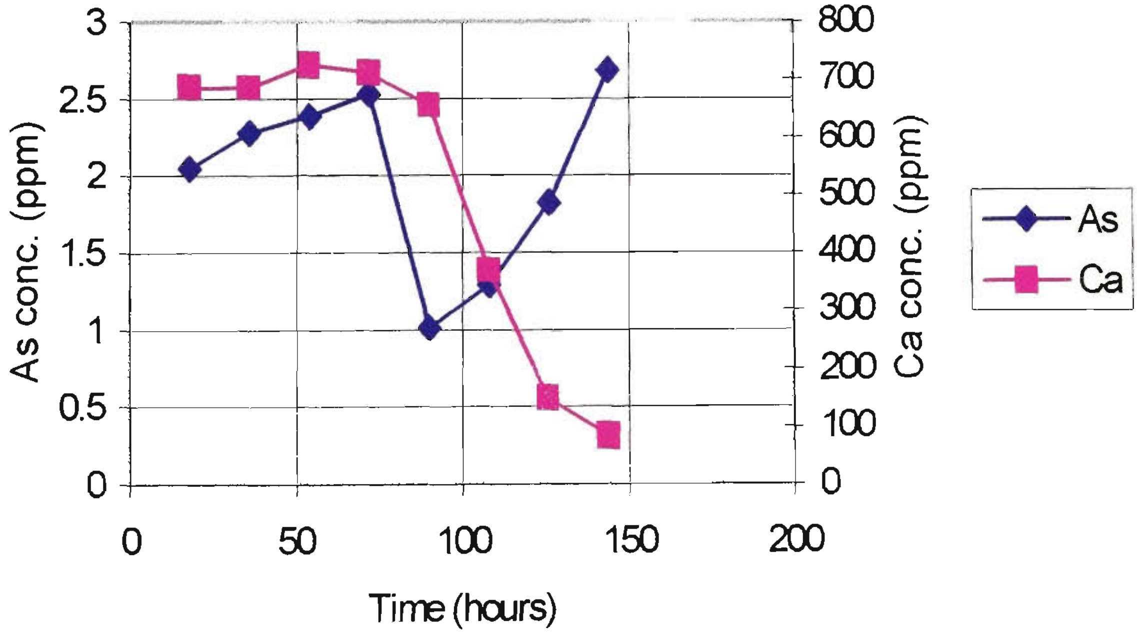


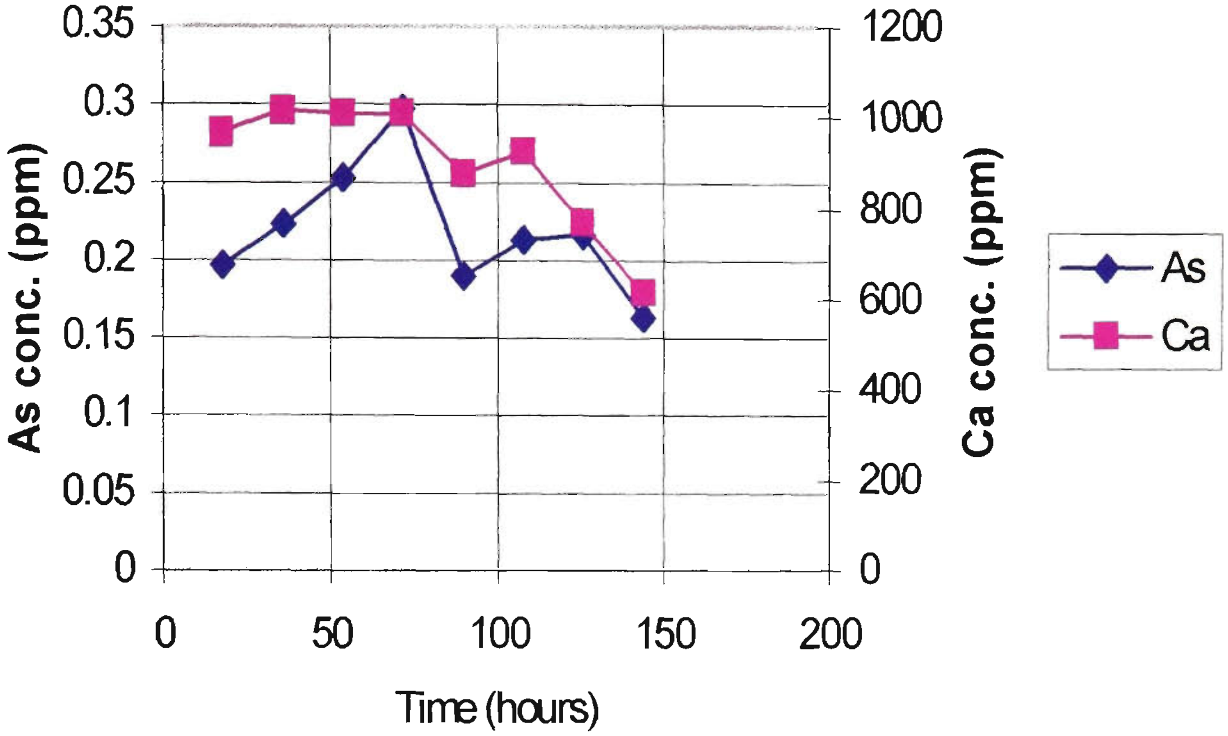
Figure 3.41 – Relationship between Calcium and Arsenic levels in the sequential leaching (water) lechates for the Arsenic pentoxide formulations

(A) As_2O_5 + *C*



(B) As_2O_5 + *C-Fe*





(C) As_2O_5 + *C-L*

Especially for the arsenite containing formulations, whenever an increase in the calcium concentration is observed there is an associated decrease in the arsenic concentration and vice versa.

The majority of the arsenate-containing formulations, which leached noticeably less arsenic, showed a slight decrease in the dependence upon the calcium concentrations. Instead of the fluctuations in the arsenic concentrations being directly related to fluctuations in the calcium concentrations, some of the arsenic leachate concentrations now merely followed the same trends as the calcium concentrations, i.e., falls in the calcium concentration resulted in falls in the arsenic concentration of the leachate. This suggests that the calcium arsenate product had already been formed, as opposed to forming in the leachate.

3.4.3 Scanning Electron Microscopy

Inspection of As_2O_5 + *C* formulations with a scanning electron microscope has resulted in identification of crystals whose composition consisted of calcium and arsenic, as can be observed in figure 3.42 and its associated EDXA, figure 3.43. This proof of the formation of a calcium-arsenic product explains the strong relationship, which has been shown to exist between arsenic and calcium concentrations.

Figure 3.42 - Scanning Electron Microscope Identification of a Calcium-Arsenic product

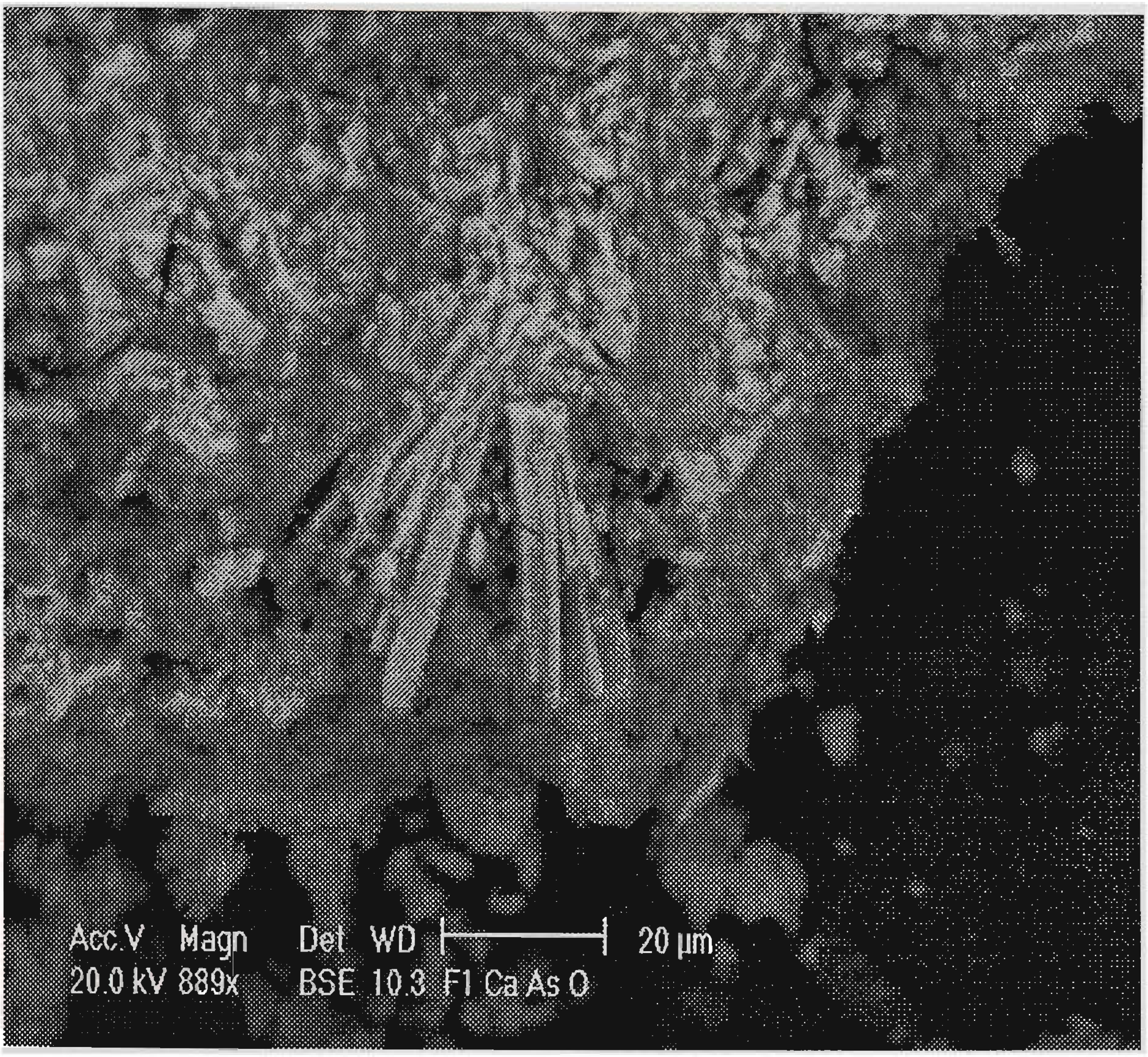
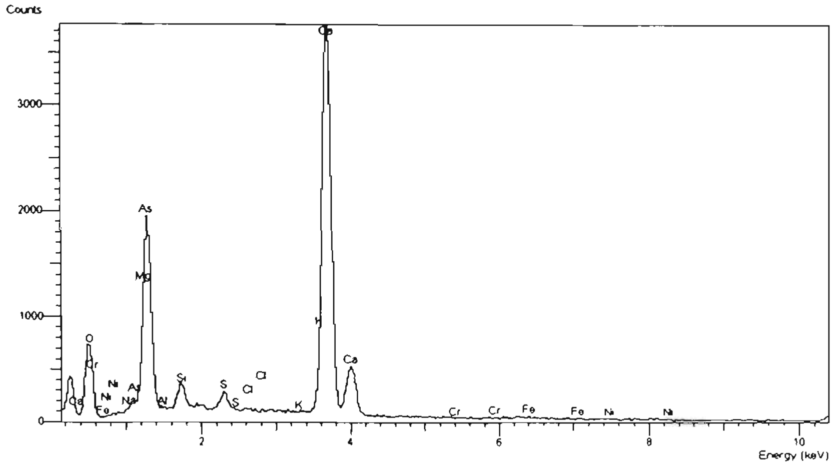


Figure 3.43 EDXA spectra of product identified in figure 3.42



3.5 Iron stabilization

The use of iron to remove or stabilize arsenic has been widely practised as discussed in Chapter 1. In this study, investigations were undertaken using ferrous sulfate as the iron source. As Artiola et al (1990), Fuessle and Taylor (2000) and Taylor and Fuessle (1994) showed, this iron salt can be quite successful in the S/S of arsenic wastes. In addition, the use of ferrous sulfate can be quite economical, as it is available as a K001 waste (Fuessle and Taylor 2000), thus allowing two wastes to be disposed of simultaneously.

From tables 3.0, 3.1 and 3.3 in this chapter it was clearly apparent that the iron formulations were the least effective for the stabilization of arsenic, regardless of the arsenic compound. It is well established that iron-arsenic stabilization is only effective when arsenic is present in the pentavalent +V state (Emett et al 1998, Krause et al 1989, Fuessle and Taylor 2000, Taylor and Fuessle 1994, Tozawa and Nishimura 1984, Tozawa et al 1977, Tozawa et al 1978). This may help explain why the arsenite containing formulations were the worst performing. However, tables 3.1 and 3.3 showed that, even when the arsenic compound was present in the +V state, the solidification/stabilization processes involving the use of additional iron were still by far the least effective of the formulations investigated. However, although these tables contain arsenic compounds which were present in the pentavalent state, the Fe/As mole ratios used were relatively low, with all ratios 2 or lower, as shown in table 3.9. Arsenic solubility has been shown to decrease with increasing Fe/As(V) ratios (Krause and Ettel 1989), as predicted by the common ion effect.

Table 3.9 – Fe:As mole ratios utilized

S/S formulation	Fe:As mole ratio
As_2O_3 + *C-Fe*	1.31
As_2O_5 + *C-Fe*	1.44
$NaAsO_2$ + *C-Fe*	1.78
Na_2HAsO_4 + *C-Fe*	1.53
$PbHAsO_4$ + *C-Fe*	2.05

Given that Artiola (1990) had success in the stabilization of arsenic using Fe:As mole ratios less than 2, the dire performances exhibited by the iron containing formulations in this study can not be solely as a result of the Fe:As mole ratios that were investigated. Additional factors that may help explain the general poor performance of the [cement + iron] formulations will be dealt with in Chapter 5. Chapter 5 presents the findings of a microstructural analysis of the various S/S formulations.

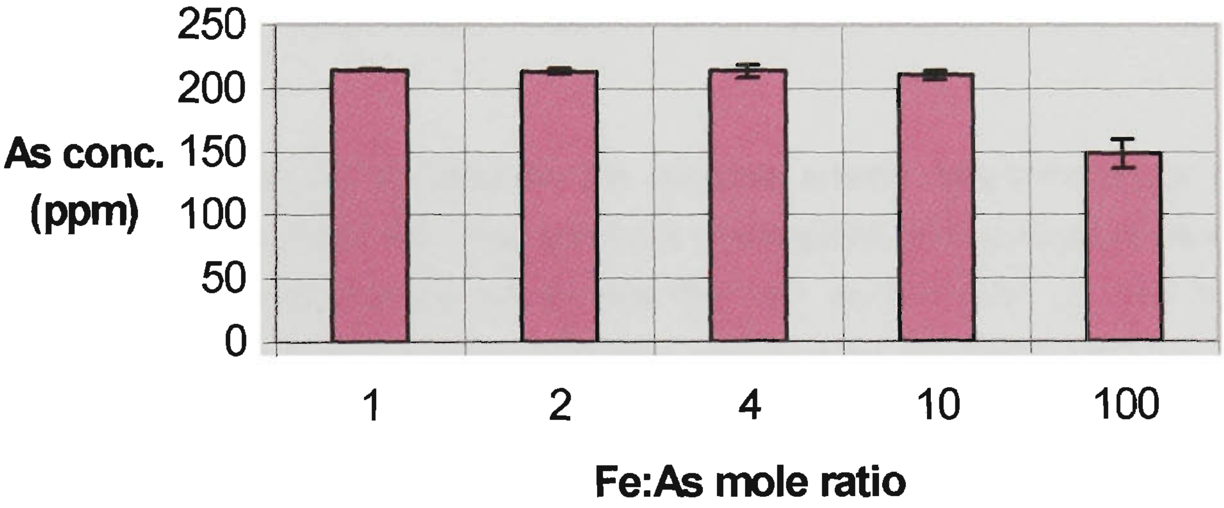
While no proof of the formation of an iron arsenate product could be found during the SEM analysis, even if such a product was formed, its solubility can vary remarkably as a wide range of "iron arsenate" species are possible. This is possible not only because of variable Fe:As ratios, but also due to variability in the crystallinity, sulfate levels and inclusion of other base metals. This variability can, not surprisingly, have tremendous effects on the success of the treatment processes. Papassiopi et al (1994) and Broadbent et al (1996) demonstrated notable differences in the solubility of ferric arsenates formed at either different precipitation temperatures, or using starting materials of varying qualities. Research conducted at the Imperial College (MIRO 1995) has also highlighted that the stability, measured by the solubility of As, can vary tremendously for the different products, with crystalline scorodite ($FeAsO_4.2H_2O$) displaying a solubility of arsenic two orders of magnitude lower than amphorus ferric arsenate.

3.5.1 Aqueous arsenic removal using iron

Research was conducted to examine the effect which both pH and the Fe:As mole ratio had upon the aqueous arsenic concentration. These studies involved combining an aqueous solution of arsenic pentoxide with the iron source (solid) and mixing the solution with the aid of a magnetic stirrer for a period of 24 hours. After the agitation period, the solution was filtered using the positive pressure filter and filters required for both the Australian Bottle Leaching Procedure (AS 4439.3) and the TCLP (US EPA 1992), and the filtrate analyzed for arsenic.

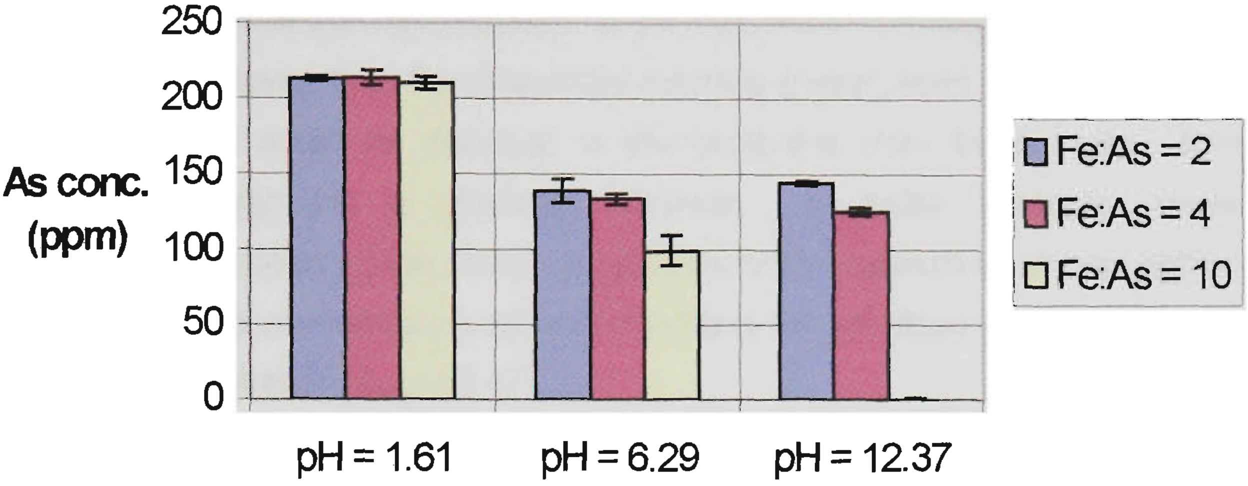
Studies utilizing ferrous sulfate, the same iron source used in all of the S/S formulations utilizing iron, showed that increasing the Fe:As mole ratio had little effect on lowering the arsenic concentration at Fe:As mole ratios between 1 and 10. Only at extremely large Fe:As mole ratios of 100, could a decrease in the initial arsenic concentration of 215 ppm be observed (figure 3.44). These studies were conducted at a pH of 1.61, which was the pH of the solution without any adjustment. The lack of any significant reduction in the arsenic concentration as the Fe:As mole ratio was increased from 1 is no surprise, given the fact that, like the arsenic concentrations, the iron content in the solutions after filtering, had not differed from that initially present.

Figure 3.44 The effect of increasing the Fe:As mole at a pH of 1.61 on the aqueous arsenic concentration



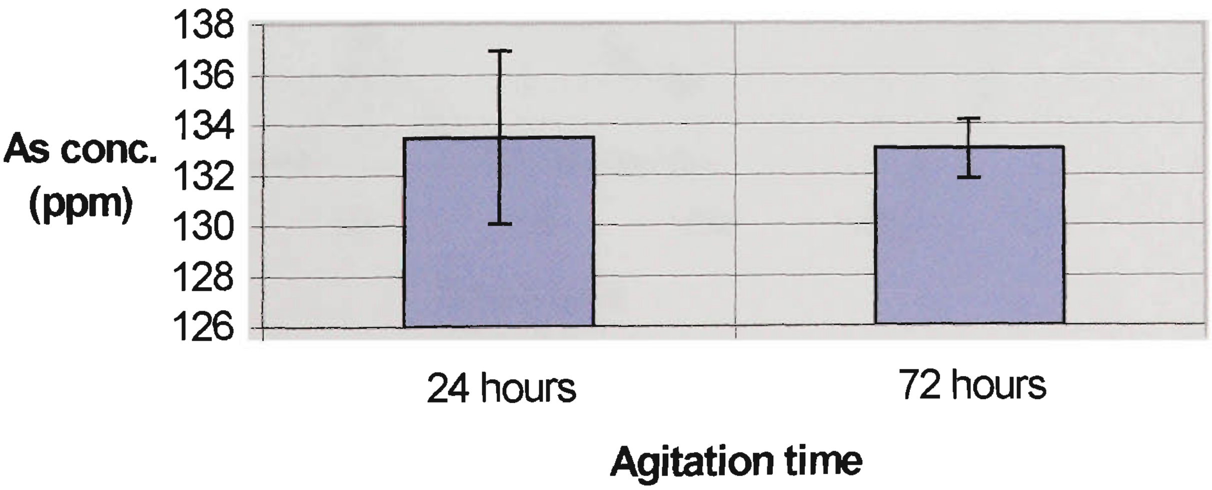
Increasing the pH of the arsenic solution to which the iron was added, to mirror levels more likely to be encountered in a highly alkaline cement matrix, was seen to have some impact on the success of arsenic removal. However, above a pH of 6.3 (pH adjustment was made using a 5M NaOH solution), little change in success was noted, most likely due to the fact the iron is present as Fe^{2+}. Only at a pH of 12.4 and an Fe:As mole ratio of 10 could the aqueous arsenic concentration be significantly decreased to 0.26 ± 0.06 mg/L (figure 3.45).

Figure 3.45– The effect of pH and the Fe:As mole ratio on the aqueous arsenic concentration



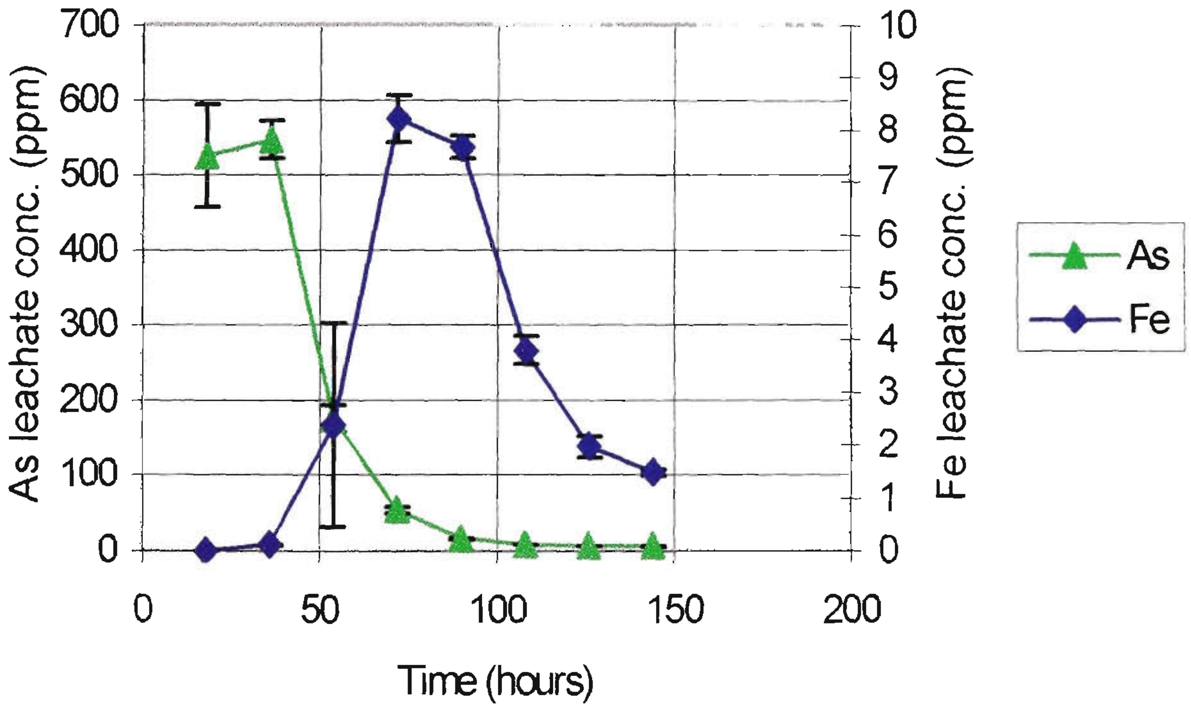
The failure of the iron to decrease the aqueous arsenic concentration, at the majority of Fe:As mole ratios and pH levels investigated, is unlikely to be due to the contact time between the arsenic and the iron. An increase in contact time between the arsenic and iron, from 24 hours to 72 hours, was shown not to yield any significant reduction in the arsenic concentration, as is shown in figure 3.46. At low pH values, arsenic is found mainly as H_3AsO_4, so little if any complexation can occur with either iron or calcium.

Figure 3.46 The effect of the contact time between iron and arsenic on the aqueous arsenic concentration



Throughout the course of conducting the Sequential Leaching experiments, little if any iron could be detected in any of the leachates (ICP detection limit for iron <100 ppb). Only in the leachates of the sequential-leaching-acid tests could notable quantities of iron be detected. In the sequential leaching (acid) tests, the pH was notable lower than the sequential leaching (water) tests (see section 3.7) hence why iron could be detected in the leachates from these tests. Iron hydroxide at high pH is relatively insoluble. In those instances where measurable quantities of iron could be detected, unlike calcium as shown earlier, the iron leachate concentration appeared to have no influence upon the arsenic leachate concentration (figure 3.47).

Figure 3.47- Iron and arsenic leachate concentrations from the Sequential leaching (acid) of Na_2HAsO_4 + *C-Fe*



3.5.2 The effect of the iron oxidation state on arsenic stabilization

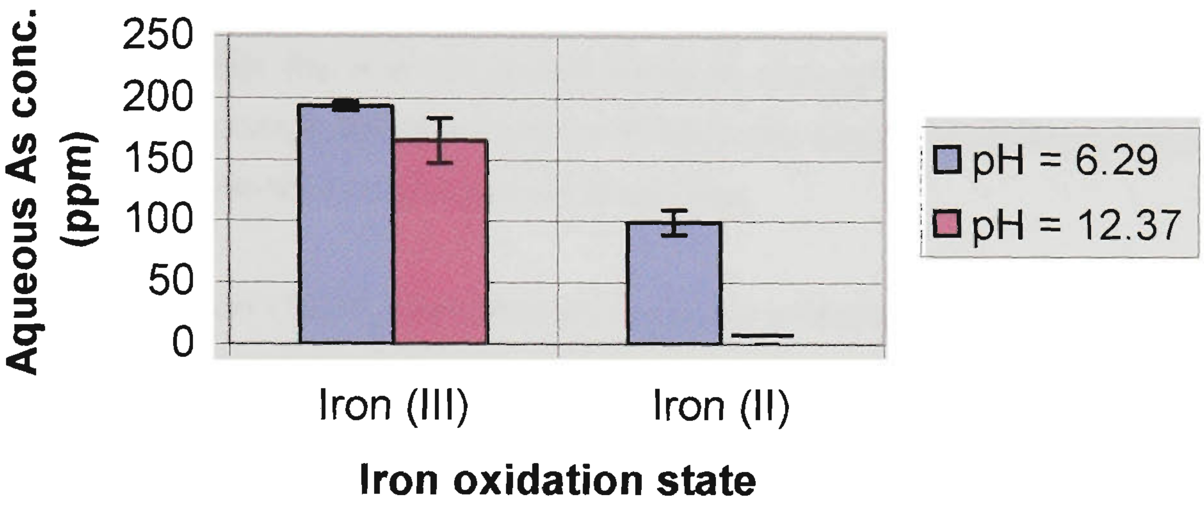
Trials investigating the use of iron primarily focused on the use of ferrous sulfate (iron II). Fuessle and Taylor (2000) state that ferrous sulfate is preferable for arsenic S/S because it is effective over a wider range of mix designs and over the long term. Fuessle and Taylor (2000) and Taylor and Fuessle (1994) recommended against the use of iron (III), since the fresh cement matrix absorbs ferric ion and does not permit adequate S/S until long cure times have elapsed. Also, the ferrous arsenate solubility product is less than the ferric arsenate solubility product. Despite these recommendations experimentation was undertaken to examine the effectiveness of ferric sulfate, given the poor performance of ferrous sulfate.

3.5.2.1 Aqueous arsenic removal using iron(II) or iron(III)

For the removal of arsenic from an aqueous solution whose initial arsenate concentration was 200 mg/L, ferrous sulfate was clearly more effective than ferric sulfate as can be observed from figure 3.48 (Fe:As ratio =10). It is also evident that the alteration of the pH has had an effect on the successfulness of arsenic removal in figure 3.48.

Arsenic removal was found to be reduced at both pH extremes by a number of authors including Taylor and Fuessle (1994).

Figure 3.48 - Comparison of arsenic removal using ferrous sulfate and ferric sultate from an aqueous solution whose initial arsenic concentration was 200 ppm



The solubility of arsenic is expected to increase markedly at pH extremes.

At high pH

$$FeAsO_4(s) + 3OH^-(aq) \rightarrow Fe(OH)_3(s) + AsO_4^{3-}(aq)$$

At low pH

$$FeAsO_4(s) + H^+(aq) \rightarrow Fe^{3+}(aq) + HAsO_4^{2-}$$

When the system has appreciable hydroxide ion concentrations another complication can arise from the competition of the hydroxide ion for the iron(III) species. The extreme insolubility of $Fe(OH)_3(s)$ ($K_{sp} = 4 \times 10^{-38}$ Dutre et al 1999) as opposed to $FeAsO_4.2H_2O$ (s) ($K_{sp} = 5.7 \times 10^{-21}$ Dutre et al) provides a large driving force for this competition

$$FeAsO_4(s) + 3OH^-(aq) \Leftrightarrow Fe(OH)_3(s) + AsO_4^{3-}(aq)$$

The equilibrium constant for this reaction is

$$Ksp\ (FeAsO_4)/Ksp\ (Fe(OH)_3) \quad = 1.4 \times 10^{17}$$

which indicates that the reaction should lie far to the right. The only hope of maintaining low arsenic concentrations is to keep the solution sufficiency acidic so that the concentration of hydroxyl ion is very low.

Taylor and Fuessle (1994) calculated the solubility of $FeAsO_4$ for weakly basic solutions at pH from 6.0 to 8.0. An enormous increase in the solubility of $FeAsO_4$ could be observed as the pH increased. For example, the solubility at a pH of 6 was calculated to be 0.01 ppm, while at a pH of 8 the solubility has increased, substantially, to 1100 ppm. The Fe(II)-arsenic compounds would be expected to exhibit similar behavior, however to a lesser extent given that the Ksp for $Fe(OH)_2$ is larger than for the tri-hydroxides. Therefore, when dealing with simple precipitates of $FeAsO_4(s)$, it can be concluded that the pH must be kept in the range of 3.0 to 7.0 in order for the arsenic to be effectively immobilized.

As in this study the greatest reduction in the arsenic concentration was observed at high pH levels, it would be fair to assume that sorption onto iron hydroxides was the reason for the reduction in the aqueous arsenic concentration. Lockemann (1911) found that arsenic is strongly adsorbed onto the surface of freshly precipitated $Fe(OH)_3$. This was used as an antidote for arsenic poisoning during the early part of the twentieth century.

Figure 3.48 also displayed that iron(II) was clearly more effective than iron(III). Given that $Fe(OH)_3$ is known to less soluble than $Fe(OH)_2$, this is the opposite to what was expected. This may be an artifact of the increased sulfate content of ferric sulfate ($Fe_2(SO_4)_3.9H_2O$) as opposed to ferrous sulfate ($FeSO_4.7H_2O$). Co-occuring inorganic solutes, such as sulfate, may directly compete for surface binding sites and may also influence the surface charge of the oxide, thus indirectly affecting the adsorption of arsenic (Hering et al 1996).

3.5.2.2 Solidification/stabilization using either iron(II) or iron(III)

Differences could be observed in the effectiveness of the S/S of sodium arsenate when the two different iron salts were utilized as can be observed from figures 3.49 and 3.50. When the leaching fluid used was deionized water, the ferrous sulfate containing formulations performed the best. However, when the acidic leaching fluid (5.7mL acetic acid per litre) was utilized, the ferric sulfate containing formulation performed the best. The acidic leachant also had a notable effect on the pH of the leachate. For example, for the ferric sulfate formulations, when deionized water was the leachant, the leachate pH was 11.62, whereas when the acetic acid leachant was utilized the pH of the leachate had dropped to 8.68. If you recall from figures 3.34 and 3.35 (pages 117 and 118 respectively) arsenite and arsenate sorption onto hydrous ferric oxides occurs to more favorable extents at pH levels between 4 and 8. Arsenic which was taken into solution during these leach tests could have sorbed onto the surfaces of the breakdown products of the S/S formulations. It is thought that hydrous ferric oxides are formed from the slow dissolution and subsequent precipitation of the iron either added to the S/S formulation, or what was originally present in the cement. The hydrous ferric oxides (HFO) are formed in the leach bottles when Fe(II) species in solution are oxidized to Fe(III) species and precipitate as an amphorous or crytocrystalline product. This last sentence is the key to explaining the differences in the results contained in figure 3.50. Clearly the formulation that used the Fe(III) (ferric sulfate) was the most effective as the iron was already in the correct oxidation state. Ferrous sulfate was however the most successful formulation when leaching with deionized water (figure 3.49), clearly absorption onto HFO was not responsible for the reduction in the arsenic leachate concentration. As with these tests the pH was not favorable and also little if any iron could be detected in the leachates obtained from these tests. For the tests using the deionized water no iron could be detected in the leachates (Fe detection limit 0.01 mg/L). It was also noted, as can be observed from table 3.10, that the most successful formulations, such as the [cement + ferric sulfate] formulation, when subjected to the acidic leachant, were the formulations that contained the largest Ca:As ratio in the leachate.

Figure 3.49 - ABLP arsenic leachate concentrations from the [cement + iron] stabilization of sodium arsenate using deionized water as the leachant

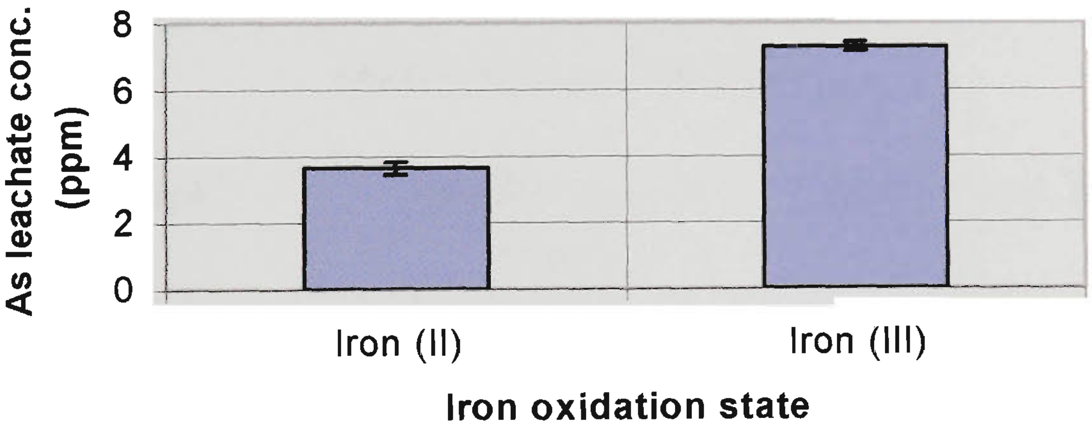


Figure 3.50 - ABLP arsenic leachate concentrations from the [cement + iron] stabilization of sodium arsenate using using the acidic leachant

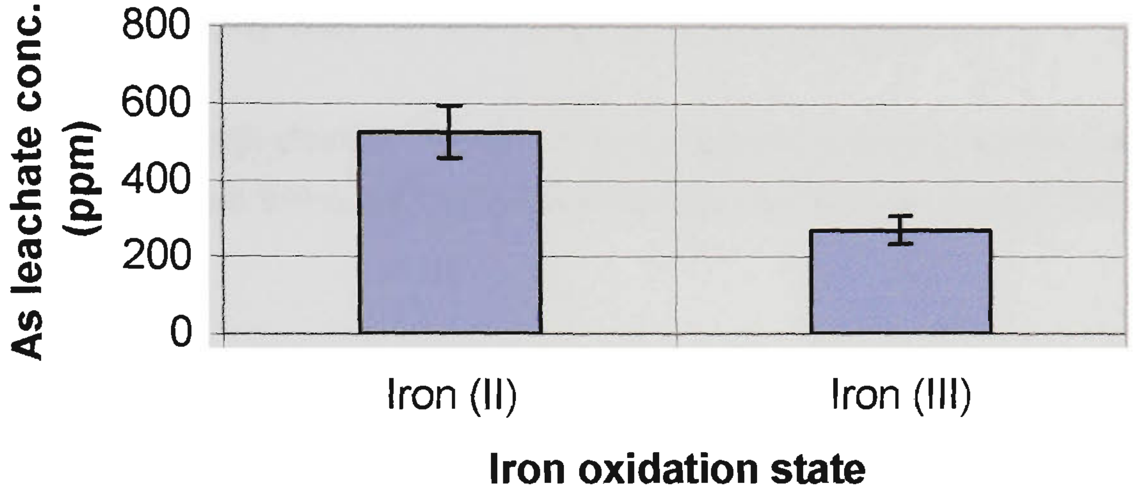


Table 3.10 - Ca:As mole ratios present in cement + iron sodium arsenate leachates

Leachant	Cement + ferrous sulfate	Cement + ferric sulfate
Deionized water	235	139
Acidic leachant	2.93	5.20

3.5.2.2.1 Arsenic stabilization using ferric chloride

The use of ferric chloride to reduce aqueous arsenic concentrations has been widely practiced (Harper and Kingham 1992, Cheng et al 1994, Hering et al 1997, Edwards 1994). Studies were conducted to compare the effectiveness of ferric chloride with the other iron salts that have been investigated.

The solidification/stabilization of arsenic pentoxide using ferric chloride yielded results similar to the S/S of sodium arsenate using ferric sulfate (figures 3.51 and 3.52).

Figure 3.51 - ABLP (deionized water) leachate concentrations obtained for the cement + ferrous sulfate and cement + ferric chloride stabilization of arsenic pentoxide

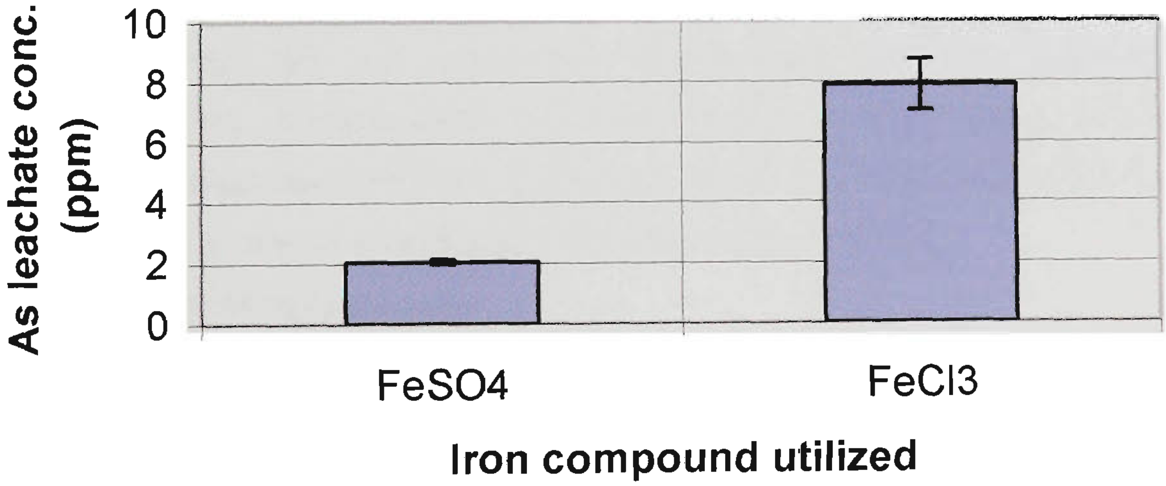
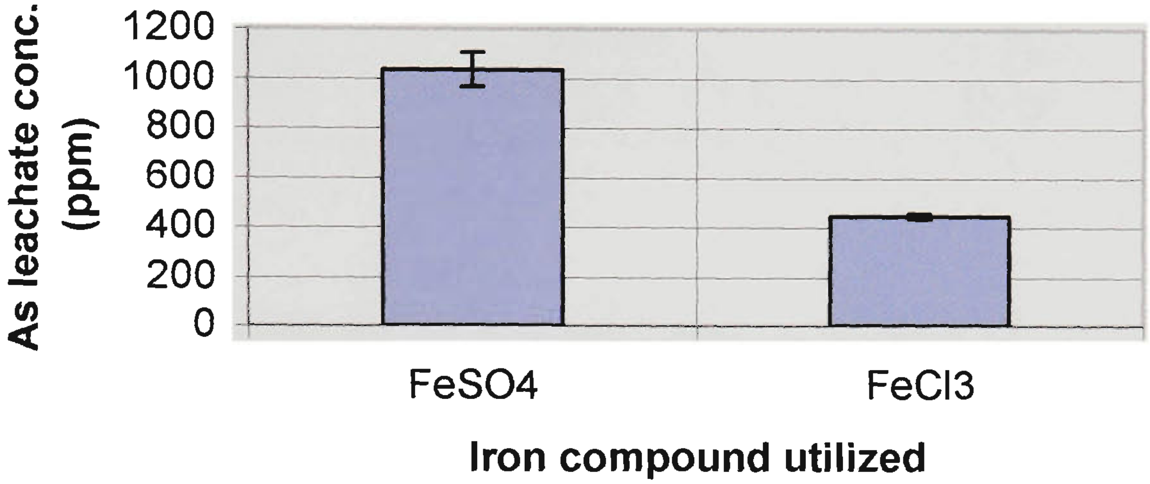


Figure 3.52 - ABLP (acidic leachant) leachate concentrations obtained for the cement + ferrous sulfate and cement + ferric chloride stabilization of arsenic pentoxide



The S/S formulation using the iron (III) salt performed worse than the iron (II) salt when using the deionized water leachant. However, when subjected to the acidic leachant, the iron (III) salt performed clearly better than the formulation comprising iron (II). Consequently, the same explanation provided for the ferric sulfate-sodium arsenate formulations (page 145) also can apply here. That is, it may be a result of one, or a combination of both, of the following:

- Dissolution of ferric hydroxides
- Fluctuations in the Ca:As mole ratios present in the leachate

The Ca:As mole ratios present in the leachates of the cement + iron formulations can be observed from table 3.11.

Table 3.11 - Ca:As mole ratios present in [cement + iron] Arsenic pentoxide leachates

Leachant	Cement + ferrous sulfate	Cement + ferric chloride
Deionized water	588.30	513.30
Acidic leachant	4.27	13.25

Given that chlorides are considered cement setting accelerators, one may have been forgiven for thinking that the addition of ferric chloride may have aided the S/S process. However, mild accelerators, such as chloride ions, can slow setting at higher concentrations. Treated-waste properties, such as porosity or flexural and compressive strength, may be reduced. Chlorides have also been identified as inhibitors and capable of altering cement properties (Means et al 1995). There is, typically, a threshold below which the contaminant has no measurable effect. Because S/S treatment performance is influenced by complex interactions of waste material and binder, it is usually not possible to quantify the threshold. Given the high arsenic content of the wastes being investigated, large quantities of additives would be required. It is apparent that, at the large additive-to-waste ratios that are required, the additives are having a more destructive effect upon the matrix than the arsenic compounds themselves. The large amount of calcium leached from the [cement + ferric chloride] formulations, when subjected to the aggressive acidic leachant, suggests that the addition of ferric chloride has increased the porosity of the cement matrix, thereby allowing the leaching boundary to move more rapidly through the matrix.

3.6 Lead stabilization

The actual mechanism, through which the fixation of lead species in cement-immobilized waste is achieved, is still a contentious issue, with some investigators believing lead hydroxide is encapsulated in the silica matrix of the cement, thereby preventing its removal until destruction of the matrix itself, while others believe that lead is retained as a relatively insoluble silicate rather than a hydroxide. Thevenin et al (1999) suggested that the immobilization of lead using Portland Cement probably occurs by one or a combination of the following mechanisms:

- Addition: C-S-H + Pb → Pb-C-S-H
- Substitution: C-S-H + Pb → Pb-S-H + calcium
- Precipitation of new compound: Pb + OH + Ca + SO_4 → mixed salts

Lead immobilization in cement was also investigated by Bhatty et al (1987). His conclusion was that lead is included, by an addition reaction, in calcium silicate hydrates. Alford and Rahman (1981) and Balzamo et al (1992) suggest that mixed salts are precipitated in a colloidal, gelatinous form. The salts were shown to be sensitive to the pH of the pore solutions and to undergo fluctuations and reprecipitation. Other researchers have stated that lead fixation is due to a double phenomenon: first the precipitation of a metallic hydroxide and then encapsulation of this compound in the C-S-H phase. Bishop (1988) found that lead is bound together with Ca, Si, and to a lesser extent Al.

Whatever the exact nature of the fixation process, it is evident that pH plays a crucial role. At lower and higher pH, the amphoteric nature of lead is demonstrated, with the leaching of lead increasing rapidly (Conner 1990, Bruell et al 1999, Sanchez et al 2000). Minimum lead leaching in nearly all S/S systems occurs when the pH is maintained between about 8 and 10 in the leachate (Conner 1990).

From table 3.4 (page 77) it was clear that, regardless of the regulatory leach test employed, the [cement + lime] formulations clearly leached the most lead. For example, when subjected to the Australian Bottle Leaching Procedure (AS 4439.3) using deionized water as the leachant, the [cement + lime] formulation leached 240.36 ± 7.17 mg/L, while the [cement only] formulation leached 9.45 ± 1.16 mg/L. One reason for this difference may be the leachate pH. As mentioned previously, pH is well known to effect the solubility of lead. The pH of the [cement + lime] leachate was 12.43 ± 0.04, while the pH of the [cement only] leachate was noticeably lower (11.80 ± 0.01). An effect of leachate pH on the solubility of lead may also account for the better performance of those regulatory leach tests employing the acetic leachant (5.7mL acetic acid per litre) than those using the less aggressive deionized water leachant. Just as the leachate lead concentration decreased for the cement only S/S formulation, using the Australian Bottle Leaching Procedure (AS 4439.3) with the acetic leachant (6.40 ± 0.79 mg/L), so did the leachate pH (11.49 ± 0.06). The TCLP (US EPA 1992) leached an even lower lead concentration of 2.27 ± 0.37 mg/L. Not suprisingly the leachate pH had also decreased further to 11.36 ± 0.02.

Of all the S/S formulations, it was clear from table 3.4 (page 77) that the [cement + iron] S/S formulation leached the lowest lead concentrations. The success of this formulation may be partly due to two reasons:

- The lower leachate pH,
- The addition of iron to these formulations.

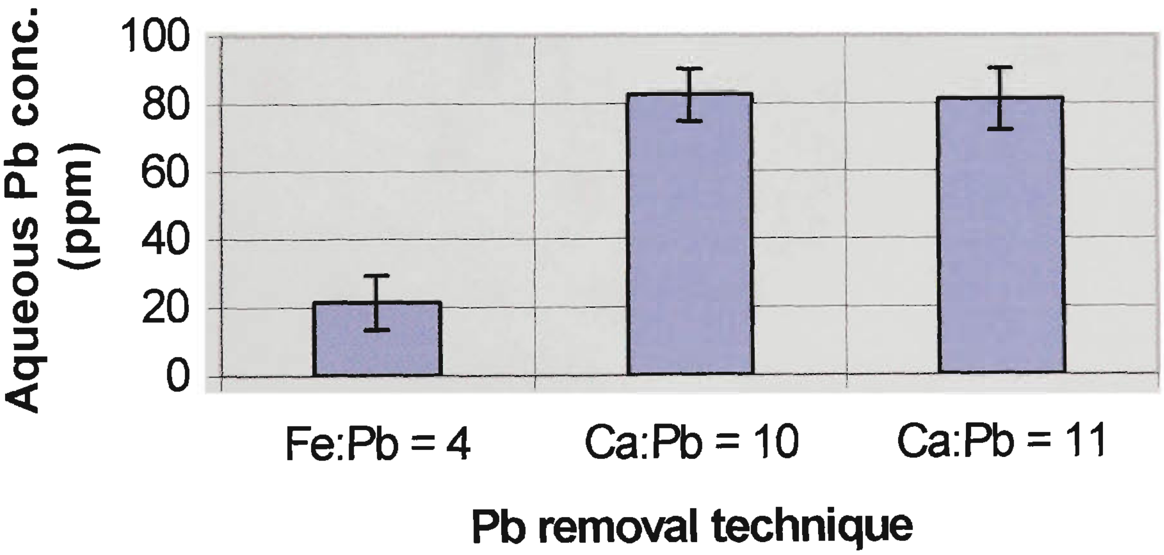
It has been shown that those formulations that have leachate pH values closer to 9 or 10, leach lower lead concentrations. The pH for the [cement + iron] formulations was always lower than the other two formulations, as can be observed from Table 3.12. Secondly, iron has been shown to be beneficial for removing lead from aqueous solutions. Smith et al (2000) had success in the removal of lead, in the low to medium mg/L range, at pH 5 or higher, using recycled iron material. Indeed, the present investigation has also shown that iron is effective in reducing the aqueous lead concentration. Even at lower mole ratios, removal of lead using iron was clearly more effective than calcium (figure 3.53) Increasing the Ca:As mole ratio to 11, as was the Ca:As mole ratio in the [cement + lime] formulations, yielded no significant further improvements.

Table 3.14 - Leachate pHs recorded for the lead arsenate formulations

S/S Formulation	ABLP (deionized water)	ABLP (acidic leachant)
$PbHAsO_4$ + *C*	11.80 ± 0.02	11.49 ± 0.06
$PbHAsO_4$ + *C-Fe*	11.12 ± 0.07	7.91 ± 0.12
$PbHAsO_4$ + *C-L*	12.43 ± 0.04	12.31 ± 0.01

Figure 3.53 – Comparison of Lead removal techniques

(pH = 12.37)



3.7 pH

In this study, the pH of the leachates has been dictated by the amount of calcium present, either present from the cement, or from the addition of lime. Upon adding water to lime, $Ca(OH)_2$ is formed, which easily dissolves and gives OH^- and Ca^{2+} ions, thus having an effect on the pH of the leachate.

From the sequential leaching experiments, utilizing both the acidic and deionized water leachants, it is clear that the pH and the calcium concentration follow the same trend (figures 3.54 and 3.55). This held true for all of the solidification/stabilization formulations, not just those that had lime added.

Figure 3.54 –Sequential leaching (water) As_2O_3 + *C-L*

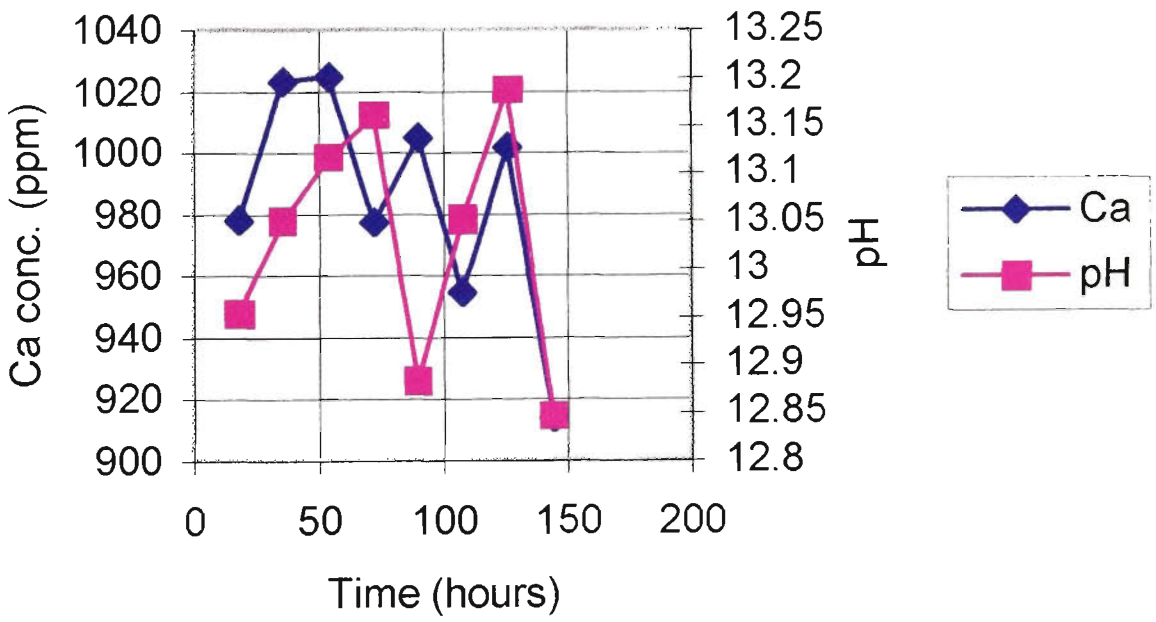
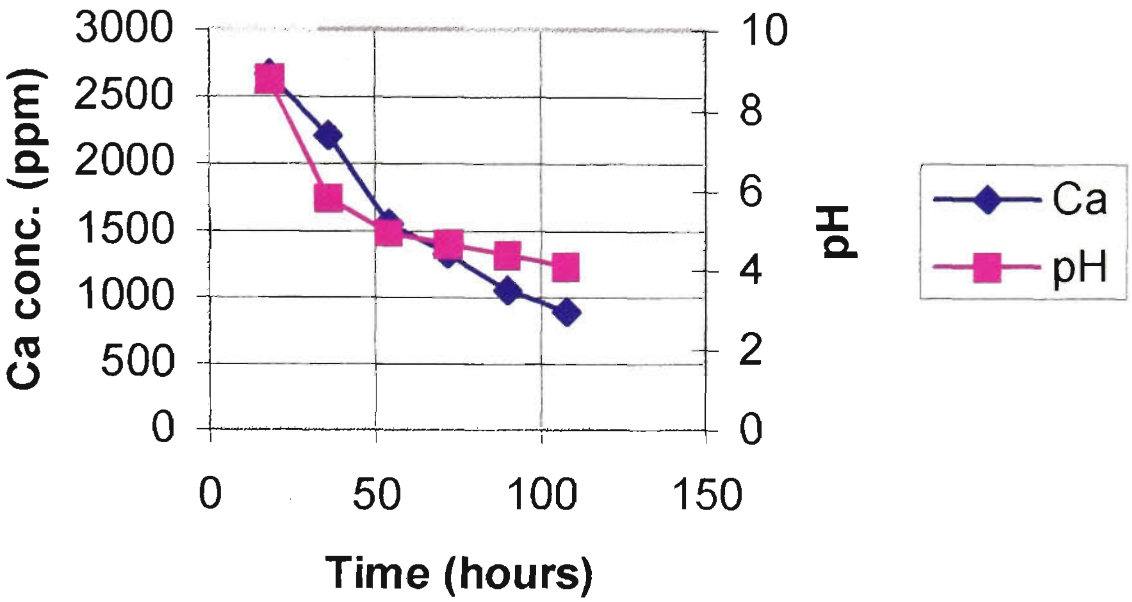


Figure 3.55- Sequential leaching (acid) As_2O_3 + *C-Fe*



It is, therefore, not surprising that those formulations containing the lowest percentage of calcium, i.e. the [cement + iron] formulations, had the lowest pH. As can be seen from figures 3.56 and 3.57, for both of the sequential leaching tests, those involving the use of water and acid, the iron formulations with the lowest calcium content had the lowest leachate pH values.

Figure 3.56 – Sequential leaching (water) pH values

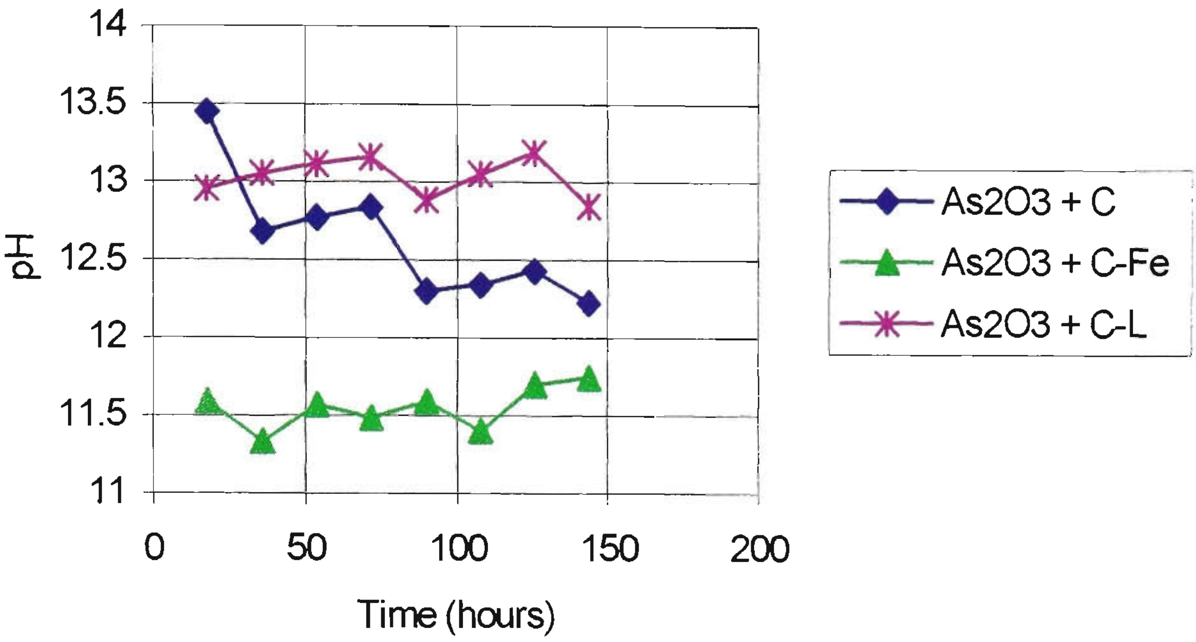
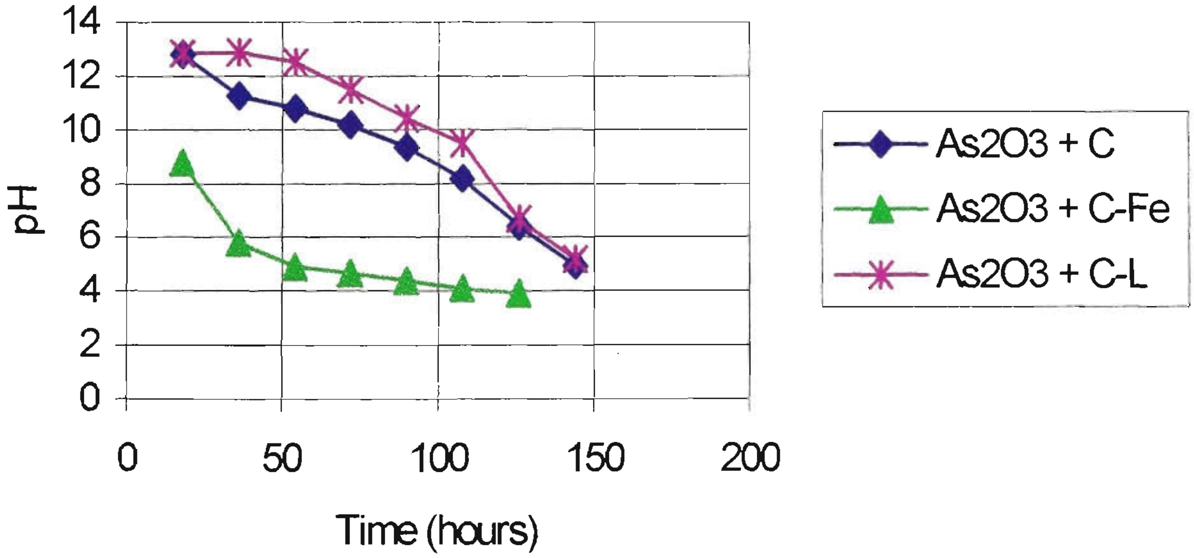


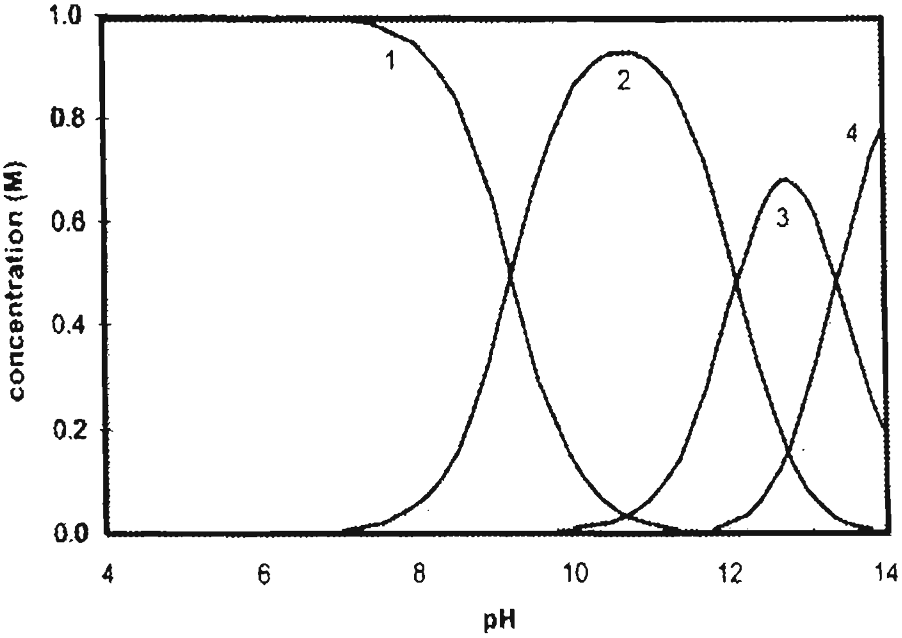
Figure 3.57 – Sequential leaching (acid) pH values



The lowest arsenic leachate concentrations were found at high pHs, where arsenic has been reported to be most soluble (Cherry 1986). However, in the present work when the pH was high, the calcium concentrations were also high, which consequently aided in the precipitation and, hence, removal of arsenic.

Dutre and Vandecasteele (1998) suggest that the calcium-arsenic compound which is responsible for the reduction of the arsenic concentration could be $CaHAsO_3$, as $HAsO_3^{2-}$ was the dominant arsenic species present at the pH at which their experiments were conducted. The form of the arsenate or arsenite species which is dominant is dictated by pH, as shown in figures 3.58 and 3.59. Consequently, the poor performance of the [cement + iron] formulations may be partly attributable to both the lower Ca:As mole ratios which these formulations contained (table 3.7 page 123) as well as the lower pHs of these formulations, which may have resulted in different species of arsenic being present and hence different calcium-arsenic precipitates being formed.

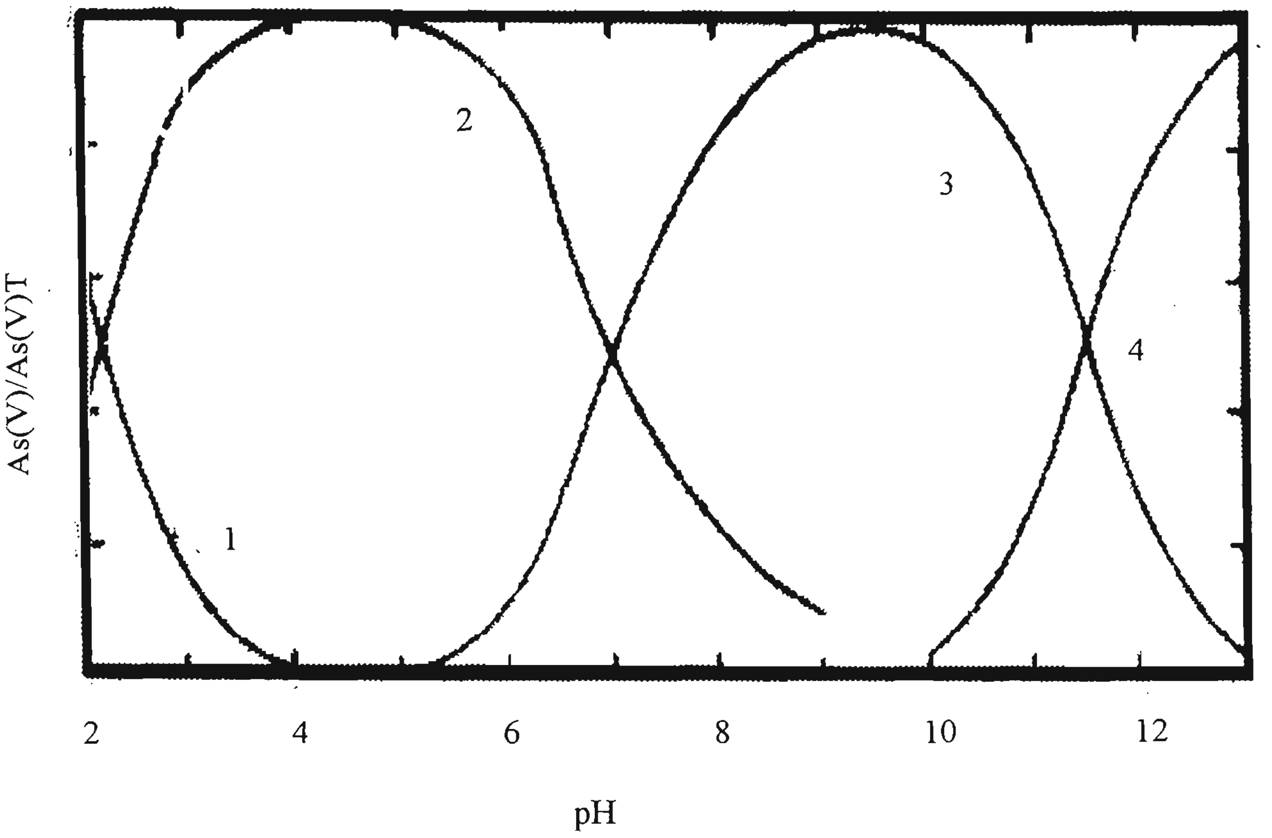
Figure 3.58 - Different forms of As(III) in aqueous solutions as a function of pH (Dutre and Vandecasteele 1998)



Key to above figure:

1 = H_3AsO_3
2 = $H_2AsO_3^-$
3 = $HAsO_3^{2-}$
4 = AsO_3^{3-}

Figure 3.59 - Different forms of As(V) in aqueous solutions as a function of pH (Gupta and Chen 1978)



Key to above figure:

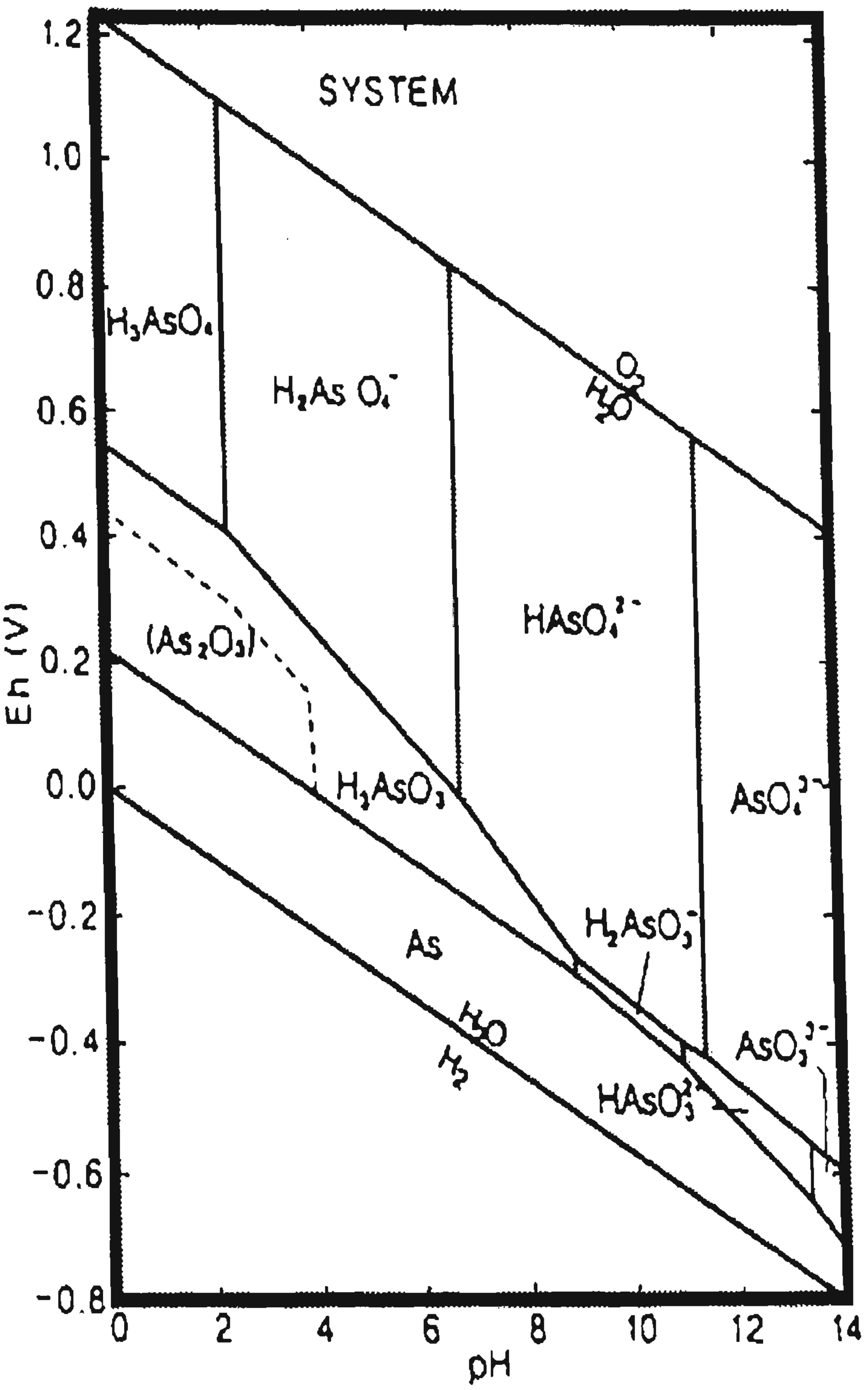
1 = H_3AsO_4

2 = $H_2AsO_4^-$

3 = $HAsO_4^{2-}$

4 = AsO_4^{3-}

Figure 3.60 - Eh-pH diagram for arsenic (Bowell 1994)



3.8 Redox potential

Arsenic is significantly affected by changes in redox potential, which cause changes in oxidation state and speciation. Under mildly reducing conditions, As(III) is present as the arsenious acids H_3AsO_3, $H_2AsO_3^-$, and $HAsO_3^{2-}$. At higher Eh conditions, As(V) is present as the arsenate species H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}. As can be observed from figure 3.60, the Eh-pH diagram for the system As-O-H at 25°C and 1 atmosphere, under reducing (low Eh) conditions, As(III) is the dominant form and is generally more mobile and soluble (as discussed previously) (Bowell 1994).

As can be observed from figures 3.61 to 3.63, which show the ordinary redox potentials (mV)[5] for the sequential leaching (water) leachates, the arsenate containing formulations always exhibited higher leachate redox potentials, as expected. This suggests that the arsenic salts remained primarily in the same oxidation state they were in, prior to containment in the cement matrix.

Figure 3.61 – Redox potentials of the Sequential Leaching (water) leachates of the [cement only] formulations

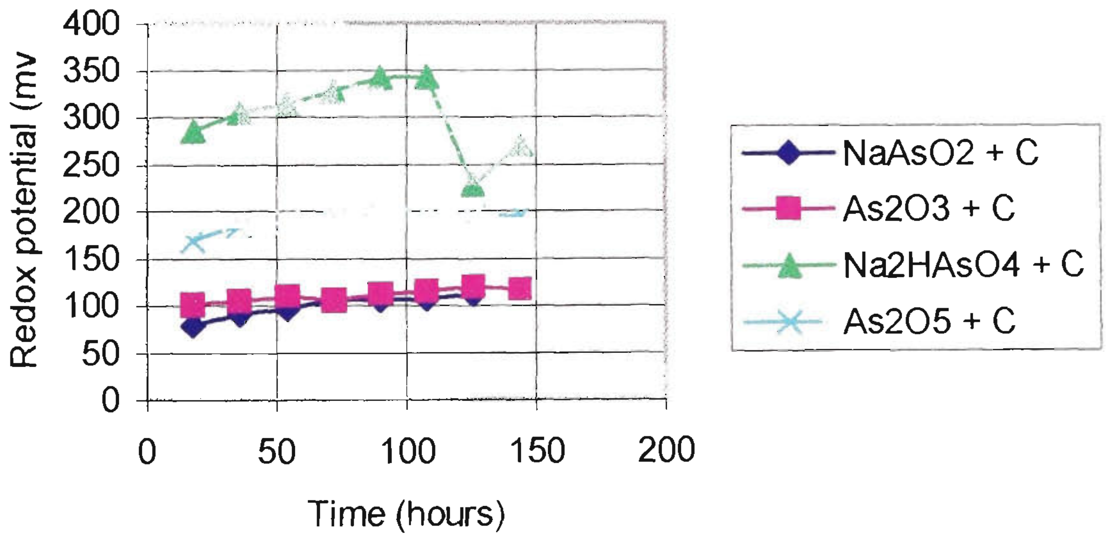


Figure 3.62 – Redox potentials of the Sequential Leaching (water) leachates of the [cement + iron] formulations

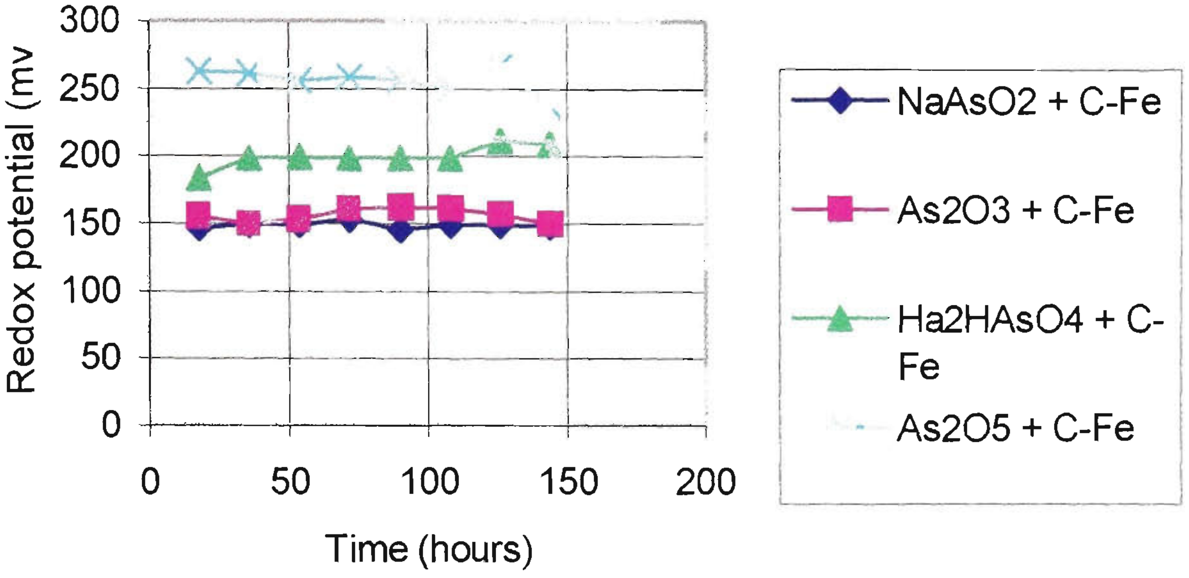
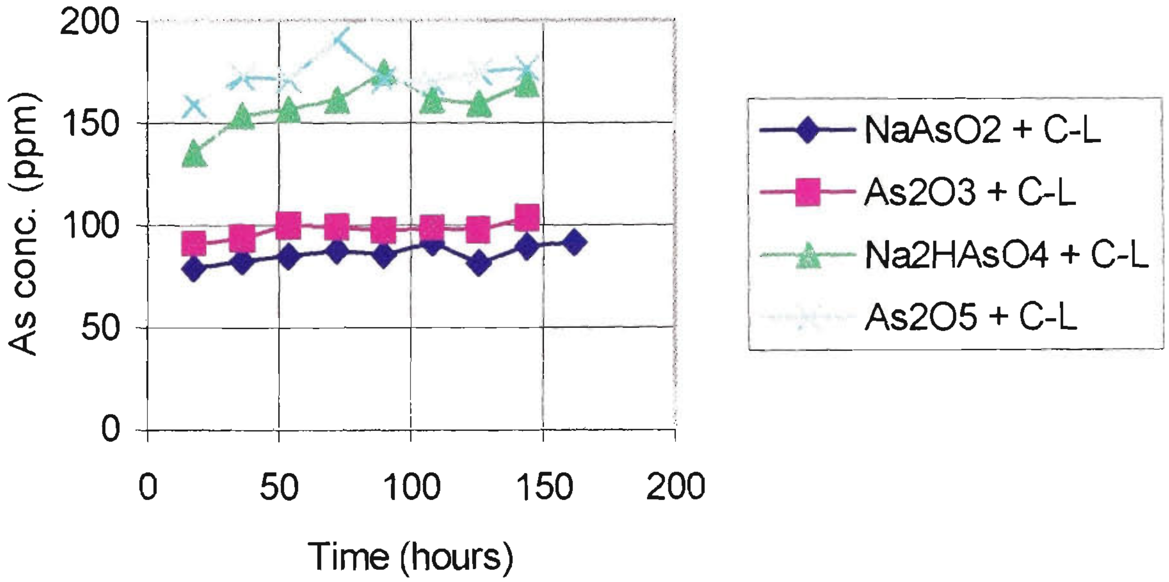


Figure 3.63 – Redox potentials of the Sequential Leaching (water) leachates of the [cement + lime] formulations



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[5] Note: Figures 3.61 to 3.63 refer to "mixed potentials" as opposed to single ones as shown in figure 3.60

As well as being able to see differences in the redox potentials of those formulations containing arsenite or arsnate salts, it was also possible to see differences in the redox potentials of the leachates from the various S/S formulations of the same arsenic salt. These can be observed in figures 3.64 and 3.65. The differences were consistent, whether the leachant used was deionized water or the acidic leaching fluid (5.7mL acetic acid per litre), as can be observed from figure 3.66.

Figure 3.64 - Redox potentials recorded from the leachates of the arsenic trioxide formulations (deionized water leachant)

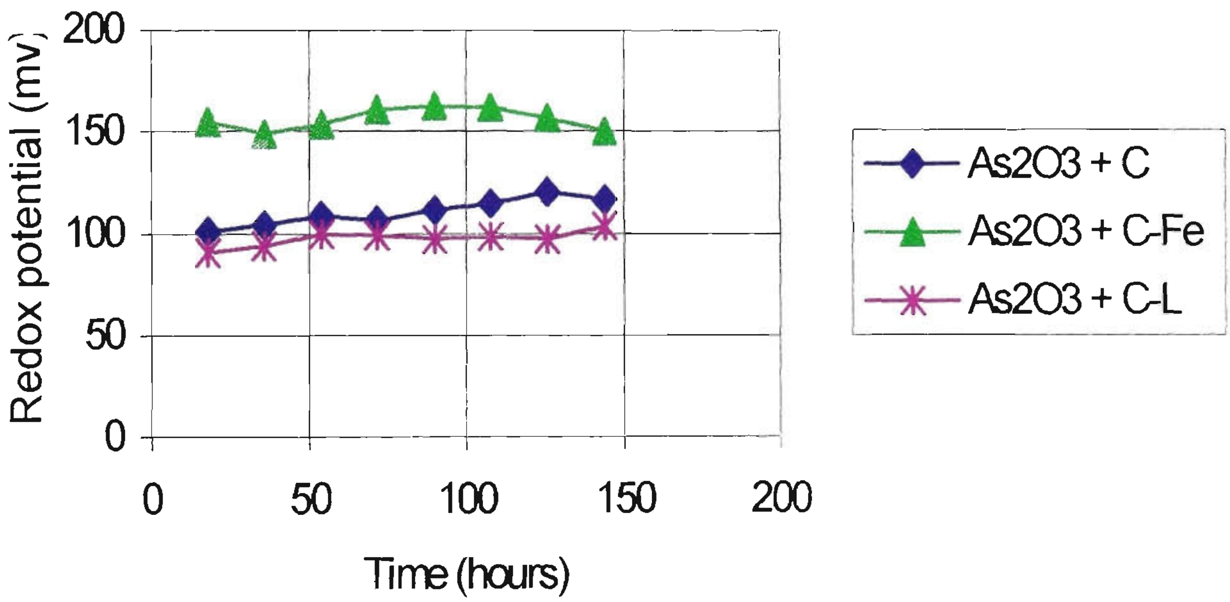


Figure 3.65 – Redox potentials recorded from the leachates of the arsenic pentoxide formulations (deionized water leachant)

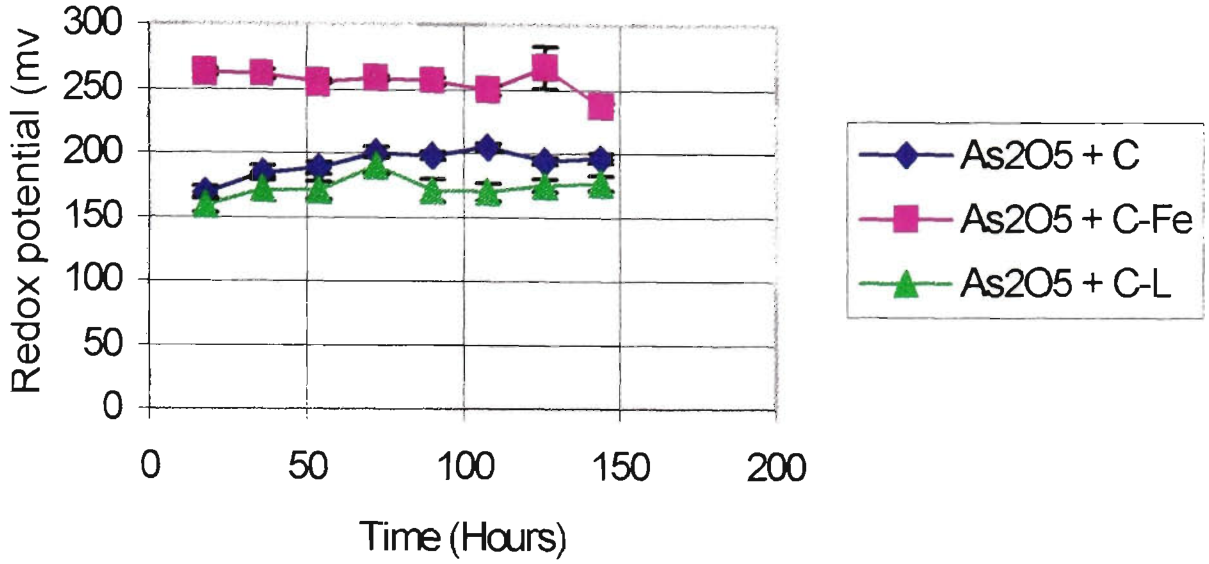
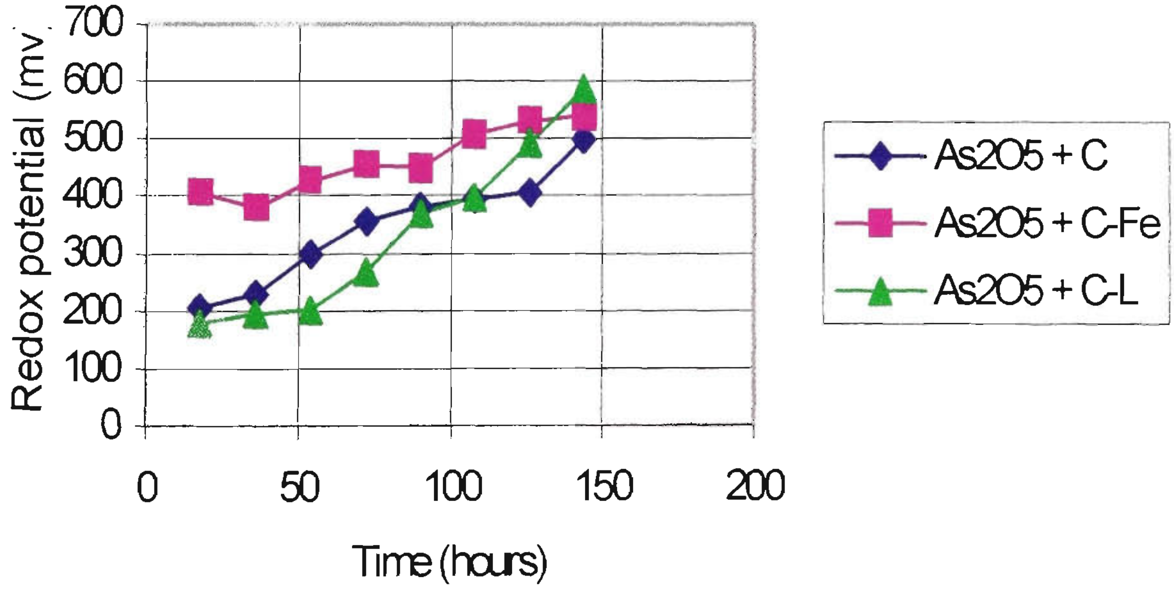


Figure 3.66 – Redox potentials recorded from the leachates of the arsenic pentoxide formulations (acidic leachant)



Given that, generally, As(III) is more soluble than the As(V) species, it is not unreasonable to expect that greatest arsenic leaching would occur at low Eh conditions, where the more soluble As(III) is the dominant form. However, figures 3.65 and 3.66 show that, in fact, the contrary is true. Of the arsenic trioxide formulations, those which were the most successful were (As_2O_3 + *C*) and (As_2O_3 + *C-L*). The cement-only and the [cement + lime] formulations (As_2O_5 + *C* and As_2O_5 + *C-L*) were also the most successful with arsenic pentoxide. However, from figures 3.65 and 3.66 it is evident that, for both of the arsenic salts, the most successful formulations also had the lowest redox potentials. Figures 3.67 through to 3.69 show that, for the same S/S formulation, once again, the scenario which led to the least arsenic being leached, i.e. the sequential leaching tests utilizing the water leachant, had the lowest leachate redox potentials. This, however, does, indeed, make sense if prior results are considered in conjunction with figures 3.70 and 3.71 From these figures, it is apparent that high pH values are related to low redox potentials, and low pH values are linked to higher redox potentials. Further, it has been shown that pH is closely rated to the calcium levels, and the calcium levels are linked to the arsenic leachate concentrations. Hence, it would be expected, as was the case, that the more successful solidification/stabilization formulations would have leachates with lower Eh values, since this would mean that the leachates would have higher pH and higher calcium levels and consequently lower dissolved arsenic concentrations.

Figure 3.67 – Redox potentials of the Na_2HAsO_4 + *C* formulations when leached with deionized water or the acidic leachant

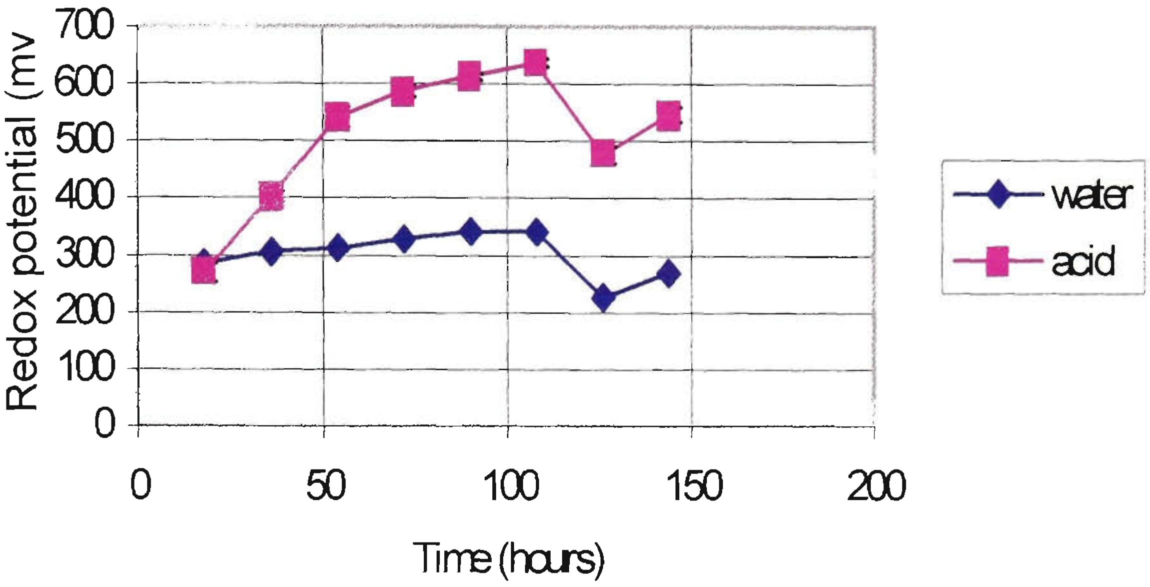


Figure 3.68 – Redox potentials of the Na_2HAsO_4 + *C-Fe* formulations when leached with deionized water or the acidic leachant

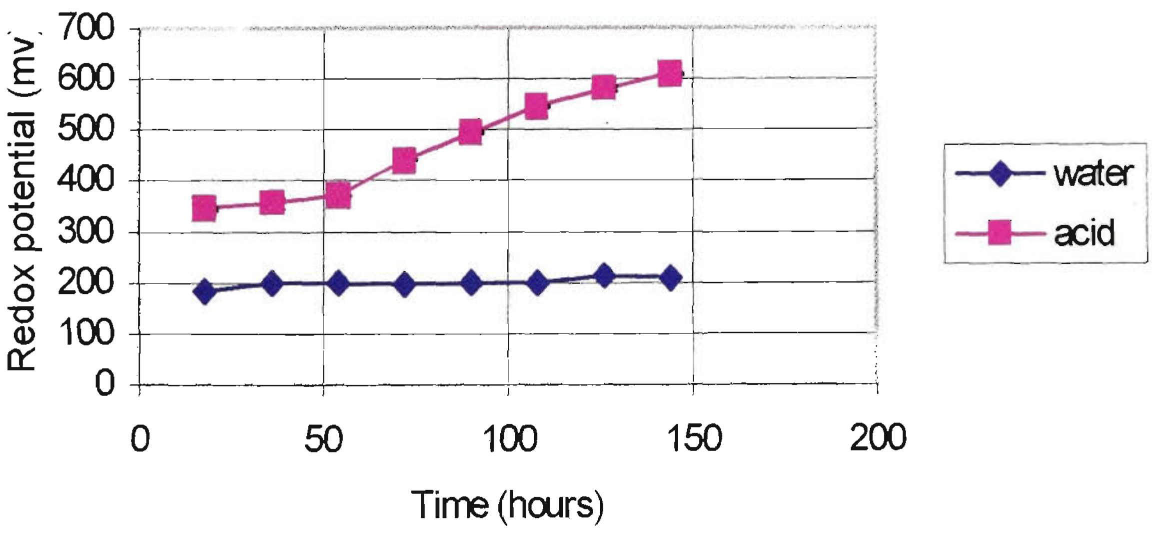


Figure 3.69 – Redox potentials of the Na_2HAsO_4 + *C* formulations when leached with deionized water or the acidic leachant

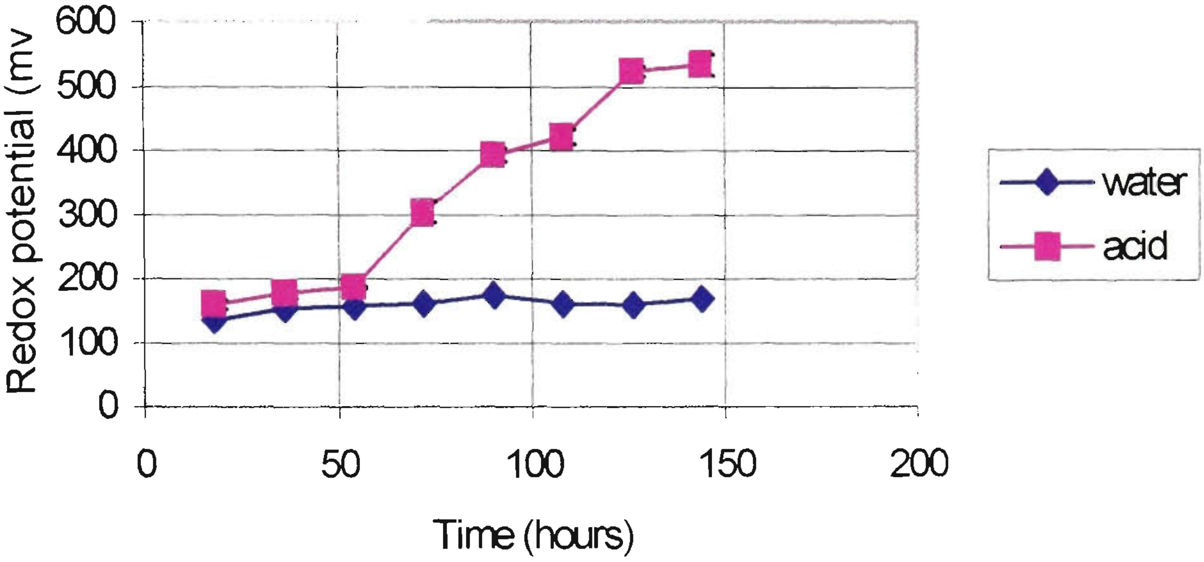


Figure 3.70 – Sequential leaching (acid) As_2O_3 + *C-Fe* , redox potential versus pH

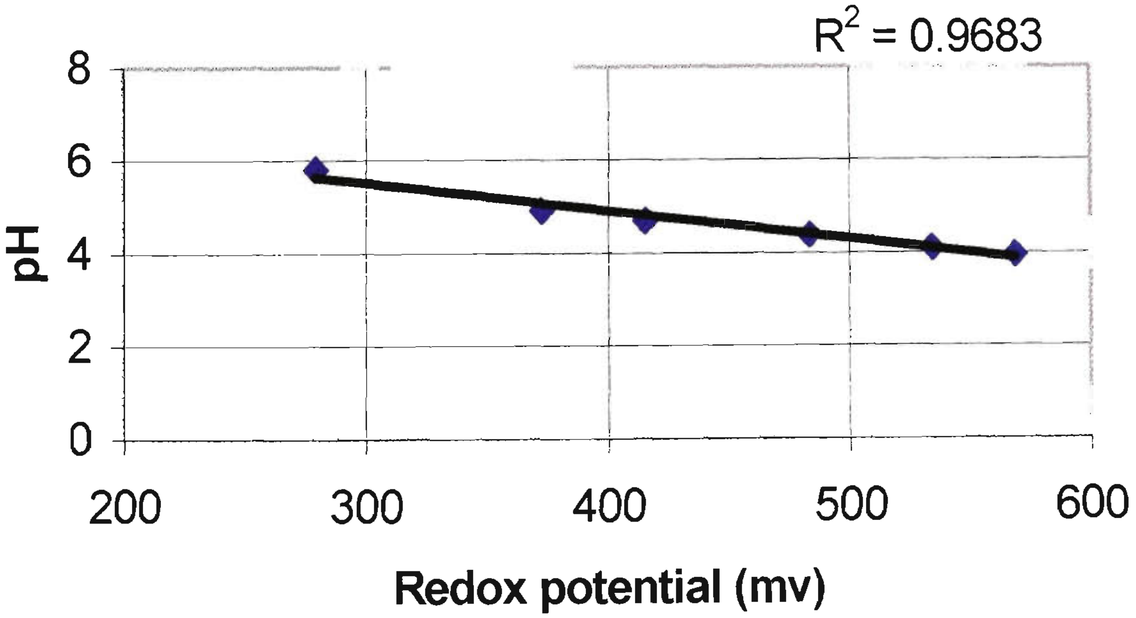
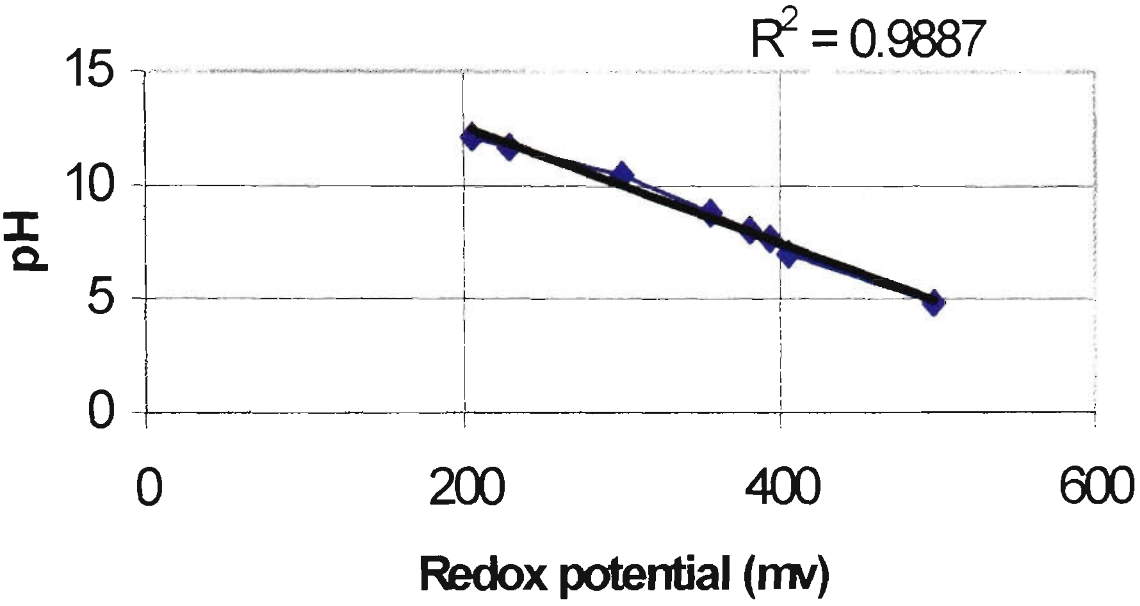


Figure 3.71 – Sequential leaching (acid) As_2O_5 + *C*, redox potential versus pH



3.9 Conductivity

The electrical conductivity of a solution is a measure of its ability to carry current. Conductivity varies with the concentration and type of ions present. Figures 3.72 through to 3.79 display the recorded conductivities for both the Sequential Leaching (water) and Sequential Leaching (acid) tests. Not surprisingly, the leachates from the Sequential Leaching (acid) tests had higher initial conductivities, corresponding to the larger number of ions that the more aggressive leaching fluid had dissolved from the cement matrix. For the majority of the leaching period, especially so for the Sequential Leaching (water) tests, the most successful of the S/S formulations, i.e., the [cement + lime] formulations recorded the highest conductivities. This was found, also, to be the case for the lead arsenate S/S formulations.

Figure 3.72 – Conductivities for arsenic pentoxide formulations: Sequential leaching (water) leachates

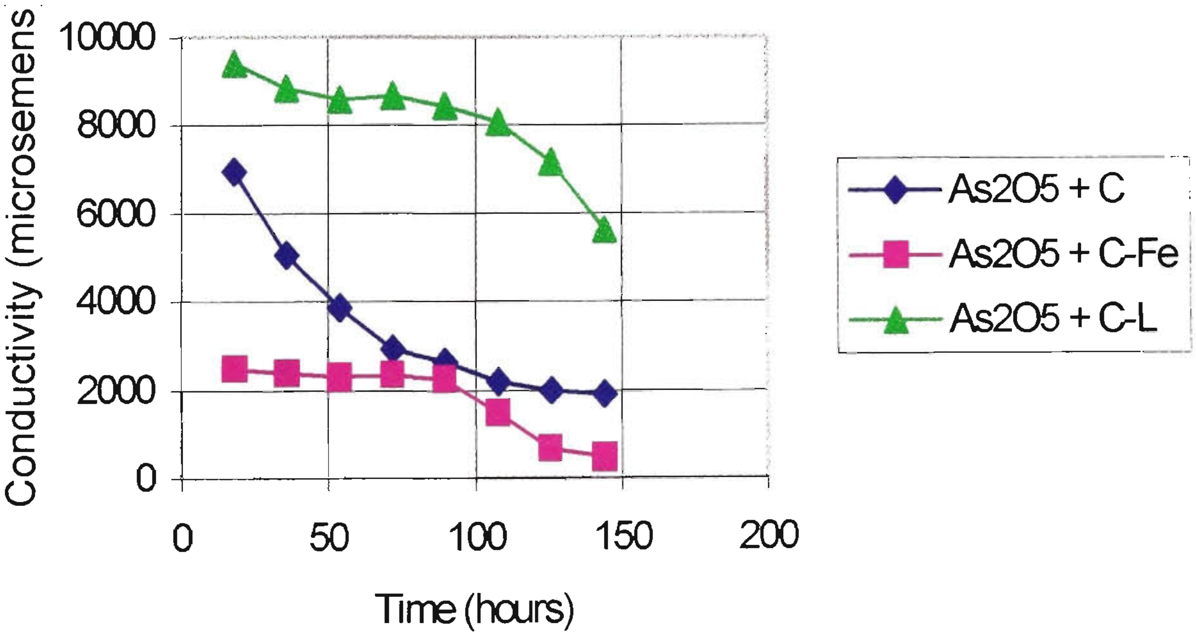


Figure 3.73 – Conductivities for arsenic pentoxide formulations: Sequential leaching (acid) leachates

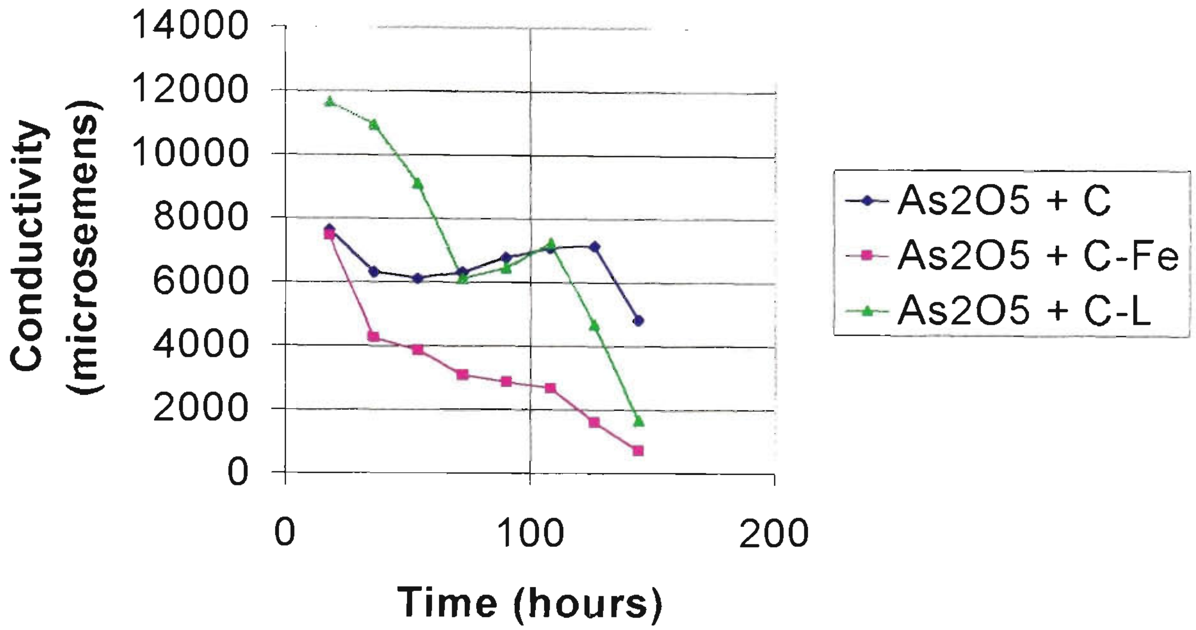


Figure 3.74 – Conductivities for arsenic trioxide formulations: Sequential leaching (water) leachates

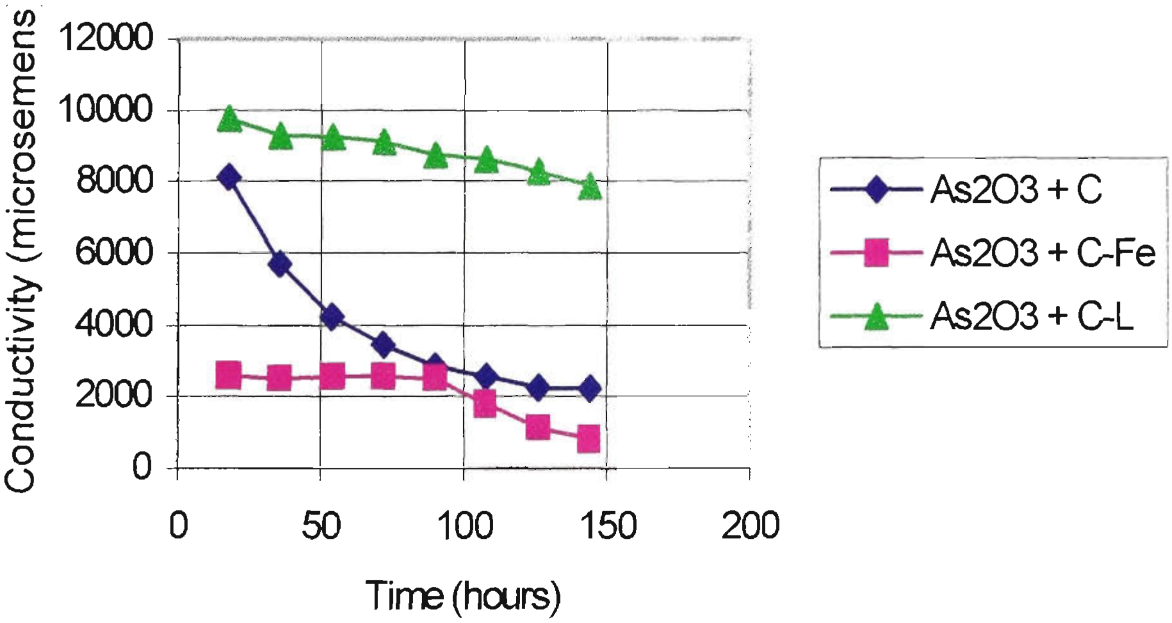


Figure 3.75 – Conductivities for arsenic trioxide formulations: Sequential leaching (acid) leachates

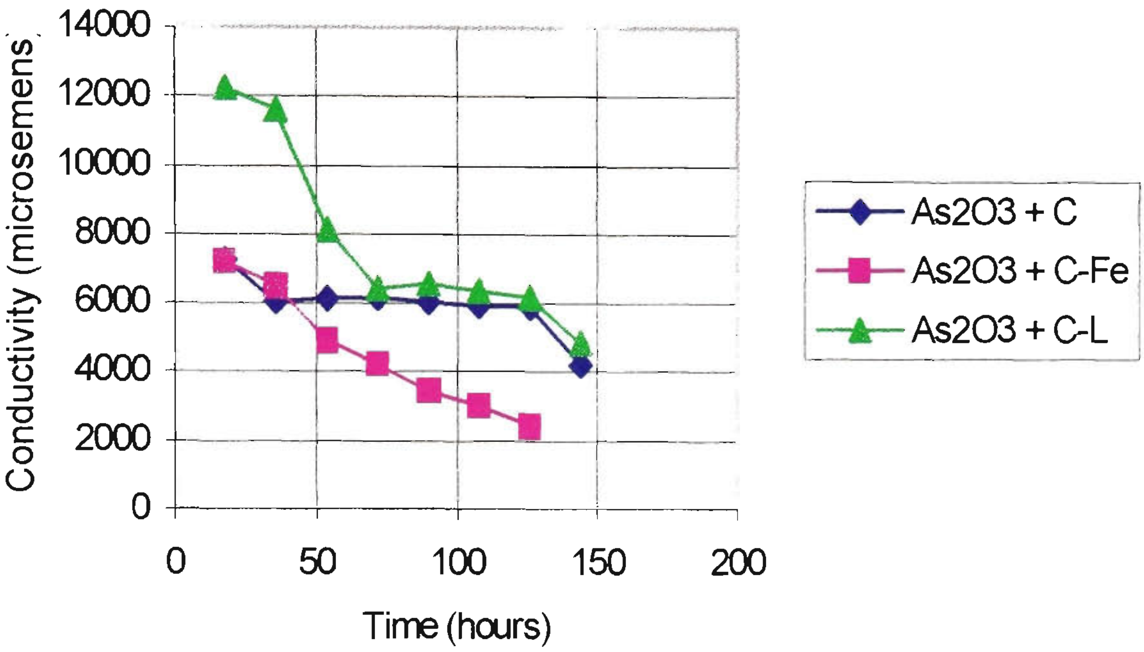


Figure 3.76 – Conductivities for sodium arsenate formulations: Sequential leaching (water) leachates

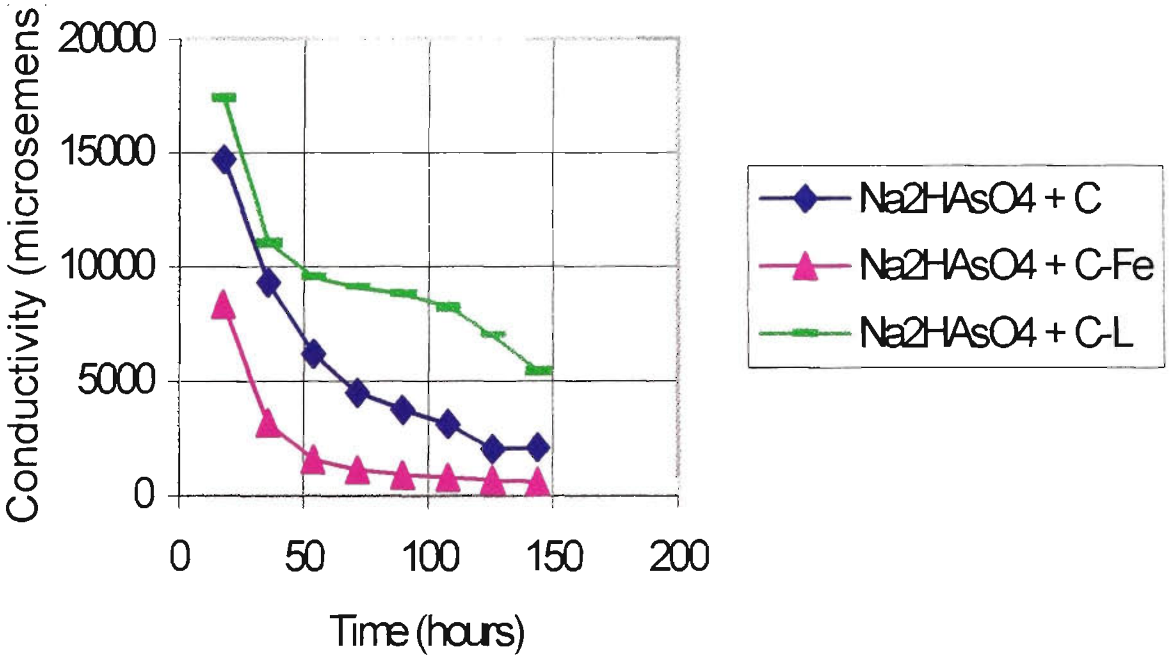


Figure 3.77 – Conductivities for sodium arsenate formulations: Sequential leaching (acid) leachates

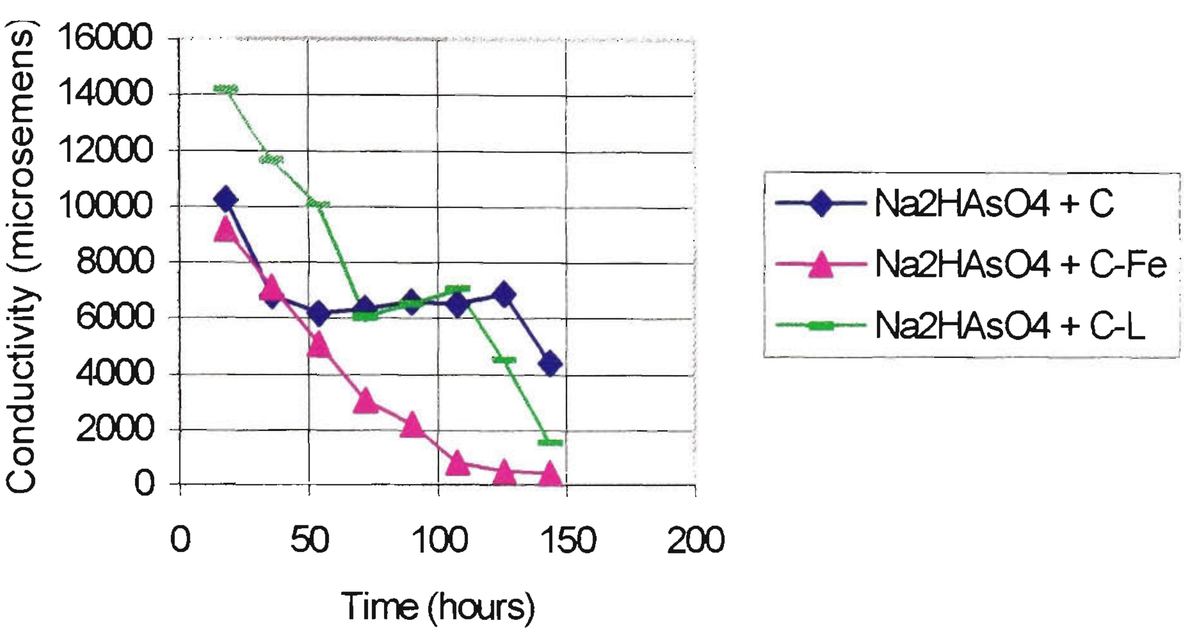


Figure 3.78 – Conductivities recorded for the lead arsenate formulations Sequential leaching (water) leachates

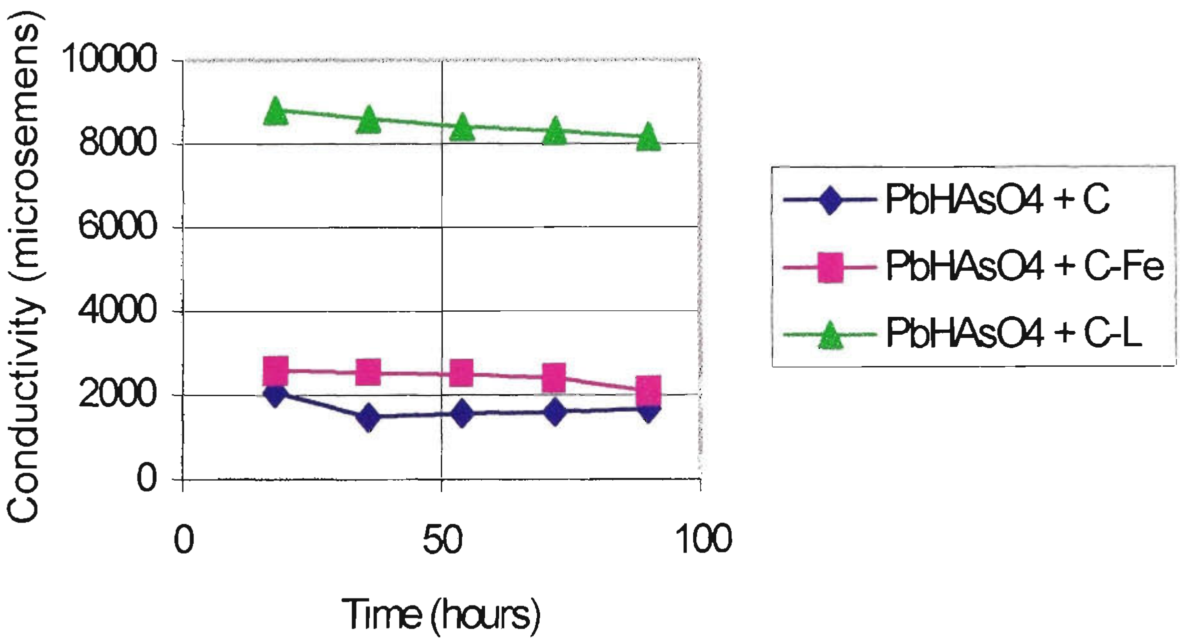
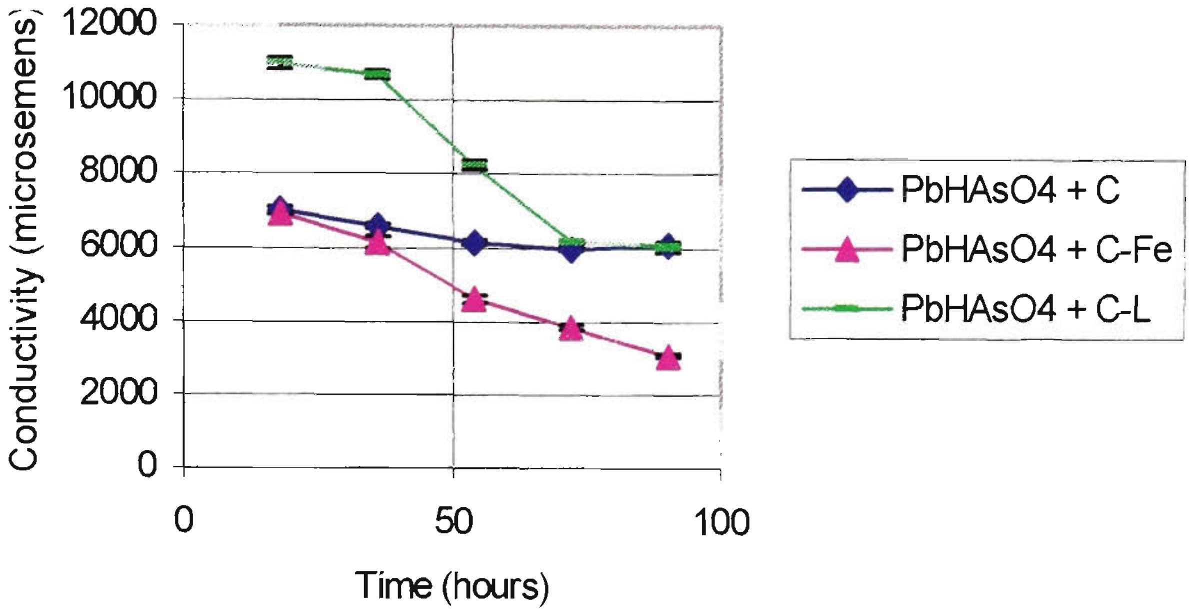


Figure 3.79 – Conductivities for lead arsenate formulations: Sequential leaching (acid) leachates



The conductivities recorded do not appear to correlate with either changes in the calcium or arsenic concentrations in the leachate. For example, the conductivities of the Sequential Leaching (water) tests and the sodium arsenate S/S formulations (figure 3.76) exhibited an initial decrease followed by period of "leveling off". However, as can be observed from figure 3.80, this does not correspond to the behavior exhibited by the calcium concentrations of the leachate, as the calcium leachate concentration from the [cement-only] and the [cement + lime] formulations rose initially, and then fell towards the end of the investigation period. The conductivities recorded certainly do not correspond to changes in the arsenic leachate concentrations. If they did, a significant change in the recorded conductivities of the Sequential Leaching (acid) tests, would occur since, in these tests, the arsenic concentrations increased from a couple of mg/L to a few hundred mg/L over a 18 hour period. No corresponding changes could be observed in the conductivities. Foster (1998) also found no correlation between changes in the conductivity and the concentration of arsenic. Additionally, no correlation could be observed between the conductivity of the lead arsenate S/S formulations and fluctuations in the lead leachate concentration, as can be seen from figures 3.81 to 3.83. Obviously, those ions resulting in fluctuations in the recorded conductivity in this research and that of Foster's (1998), are those which have no effect upon the leaching of calcium, arsenic and lead.

Figure 3.80 – Calcium leachate concentrations from sodium arsenate formulations, sequential leaching (water)

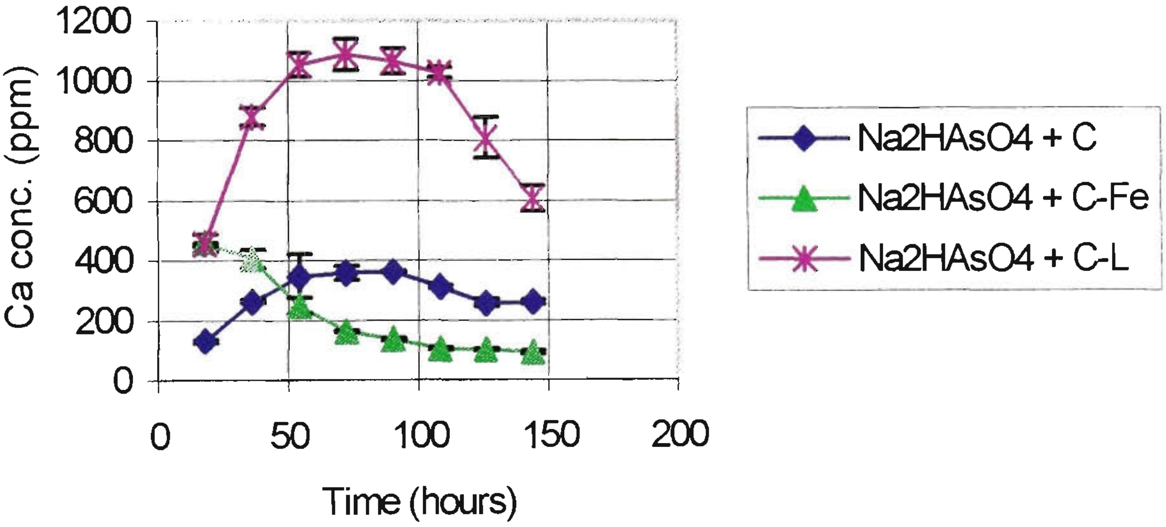


Figure 3.81 – Lead and conductivity, $PbHAsO_4$ + *C* leachates

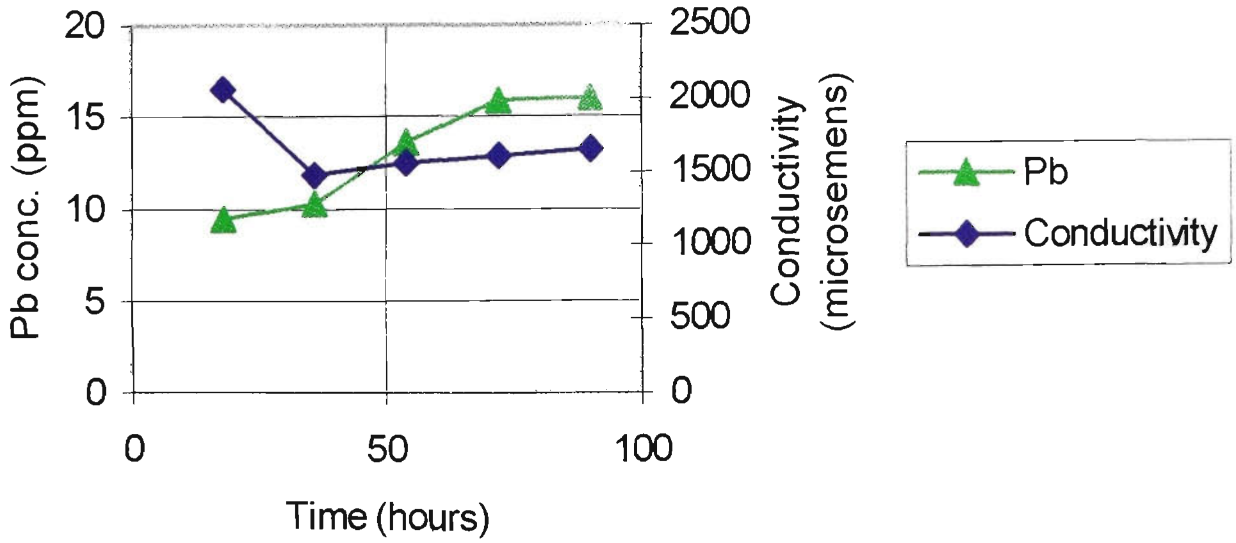


Figure 3.82 – Lead and conductivity, $PbHAsO_4$ + *C-Fe* leachates

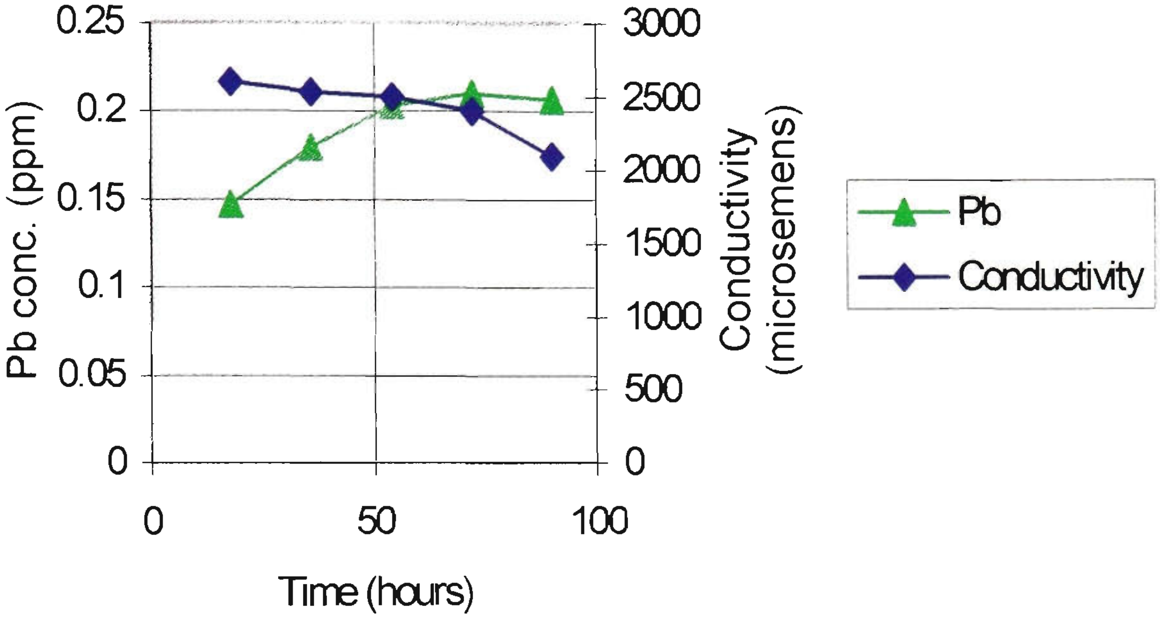
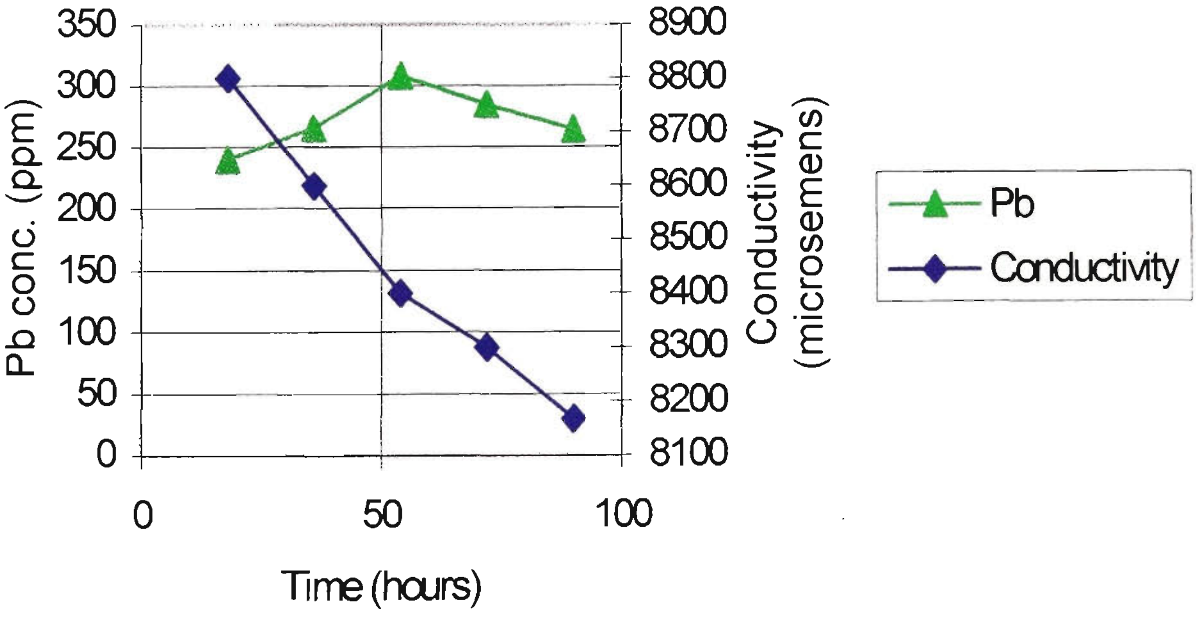


Figure 3.83 – Lead and conductivity, $PbHAsO_4$ + *C-L* leachates



3.10 Batch leaching overview

This chapter has examined the leaching of arsenic compounds, in both the +III and +V oxidation states, that have been stabilized individually using the following formulations:

- Cement only
- Cement + iron
- Cement + lime

The efficacy of the stabilization processes has been evaluated using current regulatory leaching procedures, the Toxicity Characteristic Leaching Procedure (TCLP) (U.S. EPA 1992) and the Australian Bottle Leaching Procedure (ABLP) (AS 4439.3) as well as modified versions of these tests.

The TCLP (U.S. EPA 1992) and the ABLP (AS 4439.3) were shown to yield similar arsenic leachate results for cement stabilized lead arsenate insecticide when using identical leachants. Lead, known to be stabilized by means different to that of arsenic, yielded results that were different when subjected to either of the regulatory tests, even when the same leachant type was used.

Both of the current regulatory tests are batch tests. Batch tests consist of agitating a waste sample, with a predefined quantity of liquid, for a specified time (18 hours). Despite their rapid nature, the current regulatory tests made it possible to identify those S/S formulations that showed the most promise. Both the TCLP (U.S. EPA 1992) and the ABLP (AS 4439.3) identified those S/S formulations that contained the largest Ca:As mole ratios as the most successful. This was found to be the case regardless of the arsenic oxidation state or compound investigated. While the Fe:As mole ratios of the S/S formulations investigated in this study were all less than 2, the fact that Artiola et al (1990) had success with Fe:As mole ratios <2, proves that low additive to waste ratios alone were not responsible for the dire performances of the [cement + iron] formulations. Trials comparing the removal of arsenic from aqueous solutions using both calcium and iron were able to further show the superiority of calcium over iron for reducing arsenic concentrations.

Due to their rapid nature, and the fact that the design of the tests is such that only one sample is required (i.e. at the end of the 18-hour period) makes any conclusions about the leaching mechanism purely speculative. The sequential leaching tests conducted in this investigation addressed these shortcomings. The sequential leaching tests, through the calculation of leachability indexes and the plotting of the calcium and arsenic concentrations leached over time, were able to further emphasize the dependence arsenic has upon calcium. The tests also made it possible to identify the main arsenic leaching mechanism. The leaching of arsenic for all of the S/S formulations investigated was shown to be diffusion based.

In this chapter, the effect which the conductivity, pH and redox potential has had upon the leachate concentrations was also investigated. Fluctuations in the conductivity of the leachates were shown to neither influence or be influenced by changes in the arsenic, calcium or lead concentrations. The pH however, was shown to be influenced by the calcium leachate concentration and the redox potential was shown to correlate with fluctuations in the pH. It was also confirmed that high pH values are related to low redox potentials and consequently low pH values linked to higher redox potentials. The behavior between redox potentials and pH has been well documented and can be observed from figure 3.60 or any pH and Eh diagram.

Chapter 4

4.0 COLUMN LEACHING

Column leach tests involve placing the stabilized waste in a column, through which an appropriate leaching medium is passed. As discussed in Chapter 2, two column leaching protocols have been utilized in this study, with both using deionized water as the leachant. The column (BLC) leaching setups utilized a flow rate of 1.85 mL/minute, while the column (Rainfall) leaching tests had a significantly lower flow rate of 4.65 mL/24 hours. All tests were conducted in triplicate, with the results shown the average of these replicates. The technique of coning and quartering was used to select the portion of the S/S formulations that used in each of the tests.

4.1 Column (BLC) tests

From the work, described in Chapter 3, on batch and sequential batch leaching tests which utilized deionized water as the leachant, it was apparent that those formulations with the highest Ca:As mole ratio were the most successful, i.e., generated leachates with the lowest arsenic concentrations. For those formulations containing the arsenic (V) salts (figures 4.0 and 4.1), the data generated from the column (BLC) leaching tests, yield somewhat different conclusions. While still indicating that those formulations containing iron(II) were the worst performing of the S/S formulations, the cement only formulations performed the best, even though they contained lower Ca:As mole ratios than the [cement + lime] formulations. The [cement + lime] formulations performed even worse for the +III arsenic salts as shown in figures 4.2 and 4.3. When those formulations containing the +III arsenic salts were subjected to the column (BLC) leaching tests, the [cement + lime] formulations were either clearly the worst, or equally as bad as the iron formulations.

Figure 4.0 – Column (BLC) leaching of arsenic pentoxide formulations

Cumulative mass (mg) leached

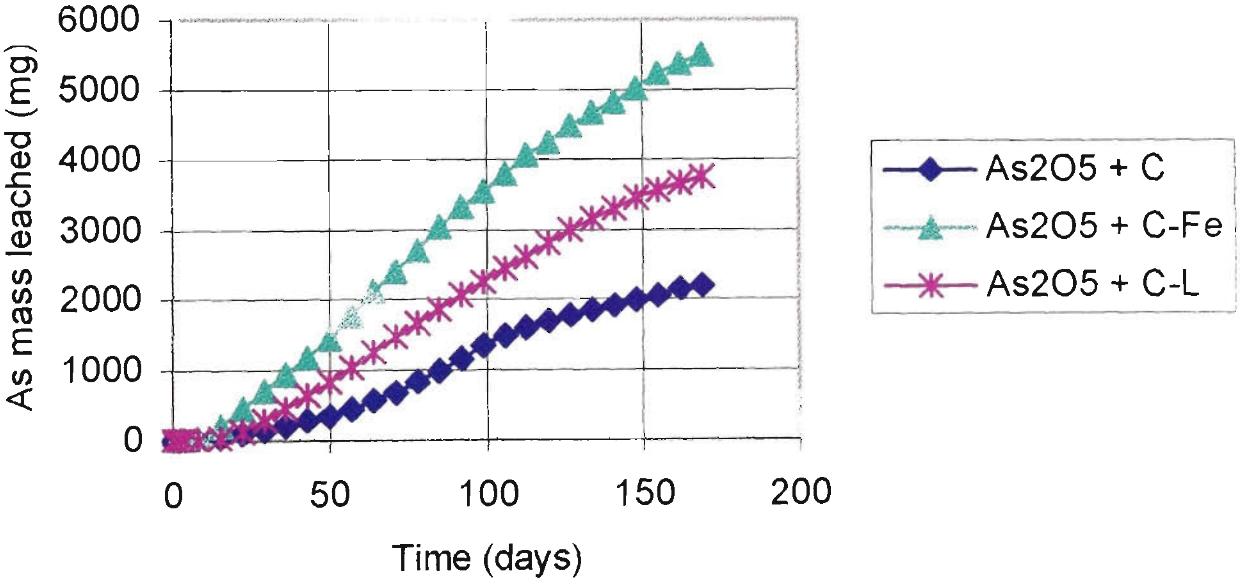


Figure 4.1 – Column (BLC) leaching of sodium arsenate formulations

Cumulative mass (mg) leached

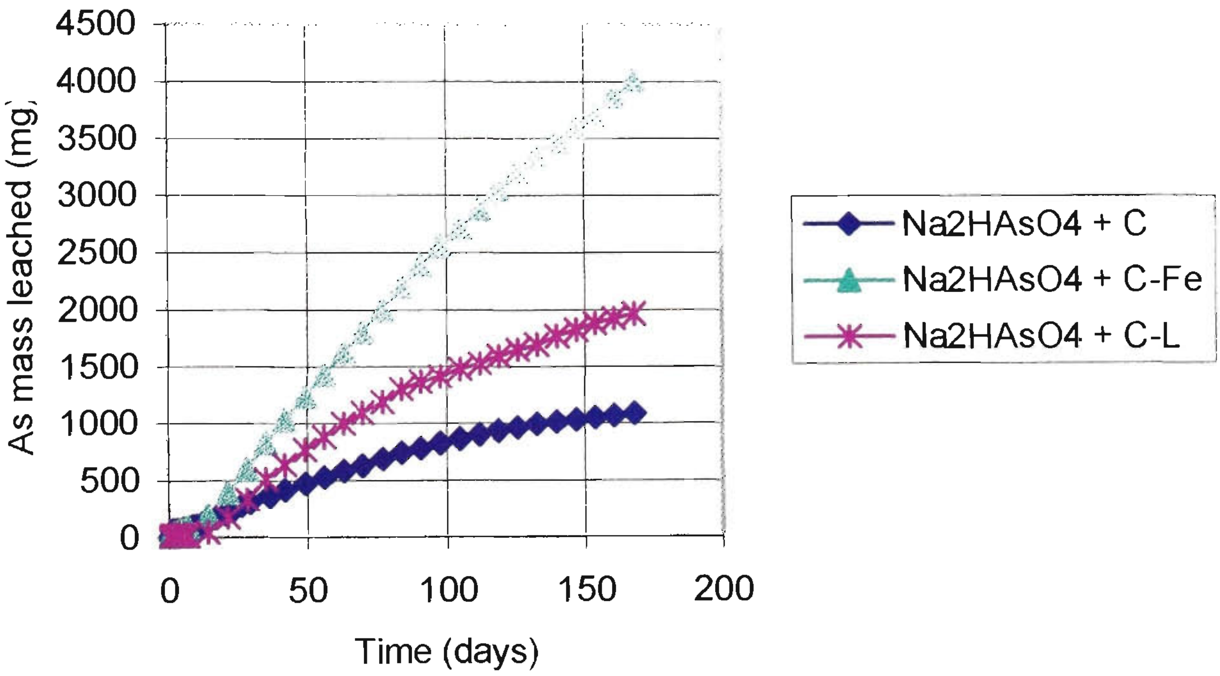


Figure 4.2 – Column (BLC) leaching of arsenic trioxide formulations

Cumulative mass (mg) leached

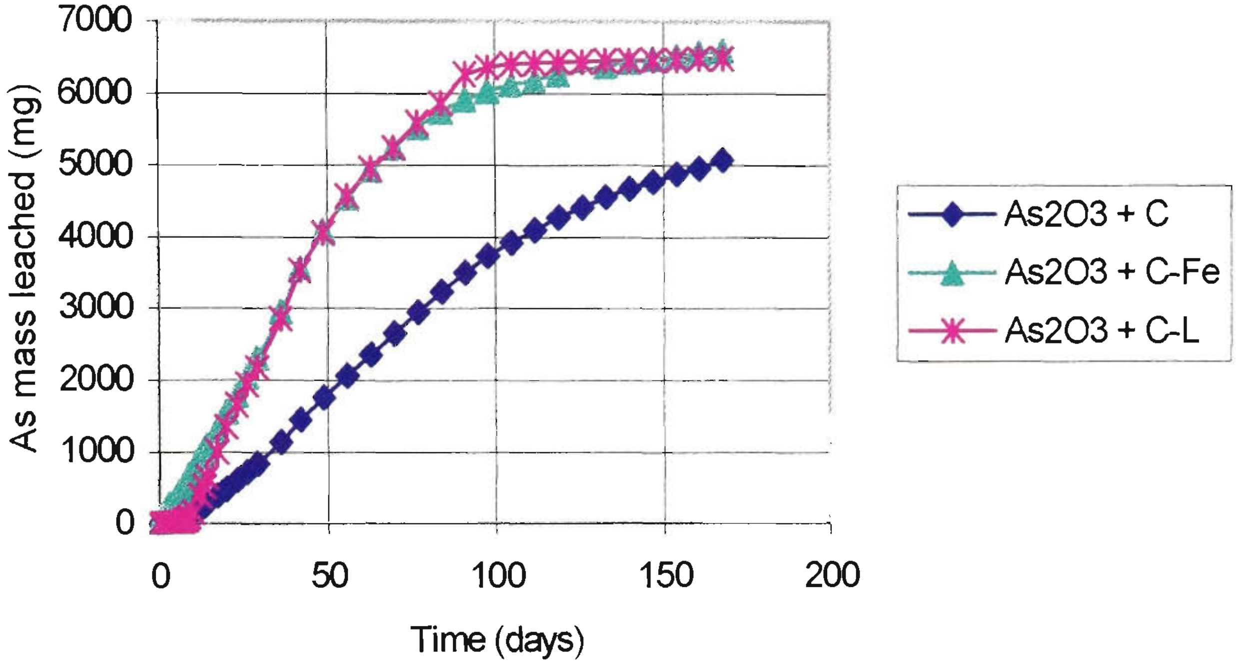
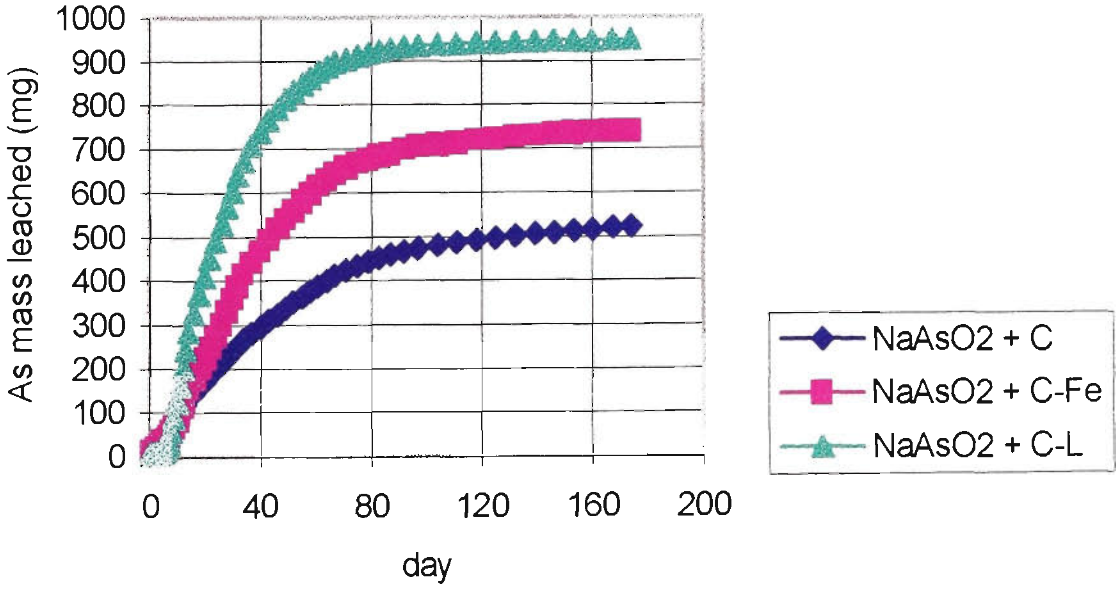


Figure 4.3 – Column (BLC) leaching of sodium arsenite formulations

Cumulative mass (mg) leached



While those formulations containing the highest levels of calcium were no longer the best performing, the leaching of calcium still appears to influence the leaching of arsenic as can be observed from figures 4.4 through to 4.7. As the calcium leachate concentration decreases, the arsenic leachate concentration increases.

Figure 4.4 – Relationship between the calcium and arsenic concentrations for the As_2O_3 + *C* formulation

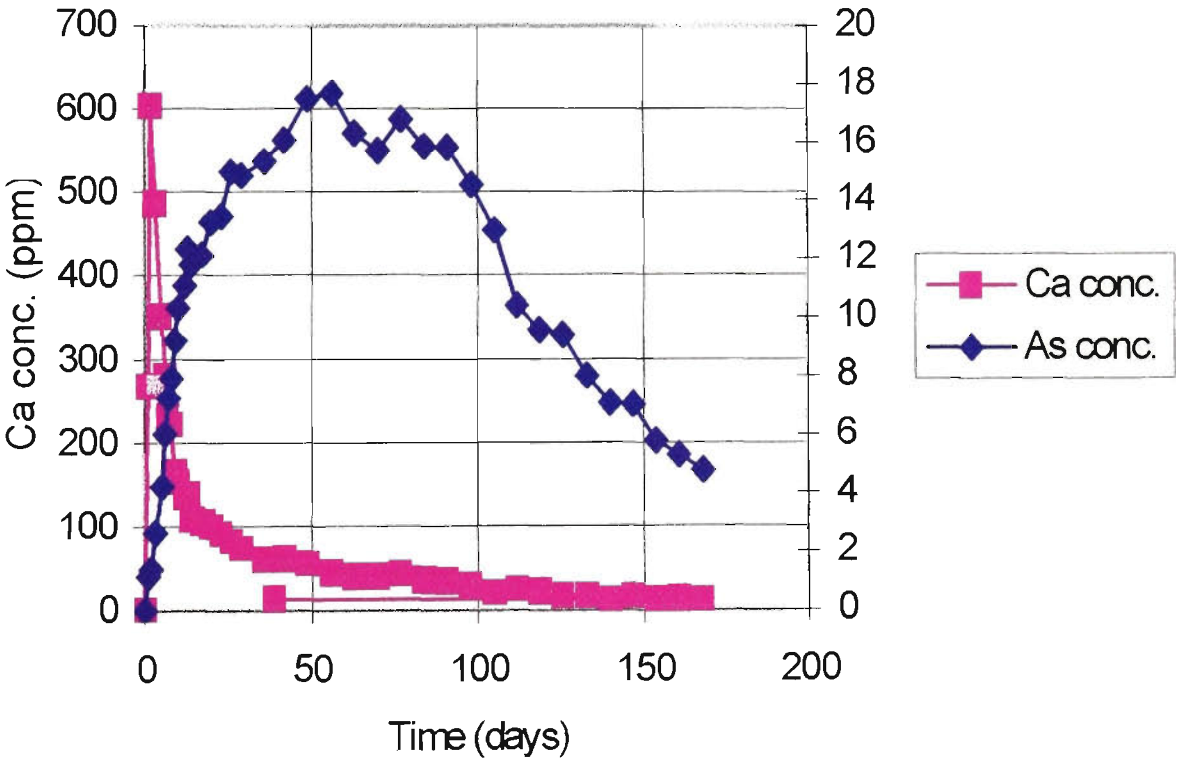


Figure 4.5 – Relationship between the calcium and arsenic concentrations for the As_2O_3 + *C-L* formulation

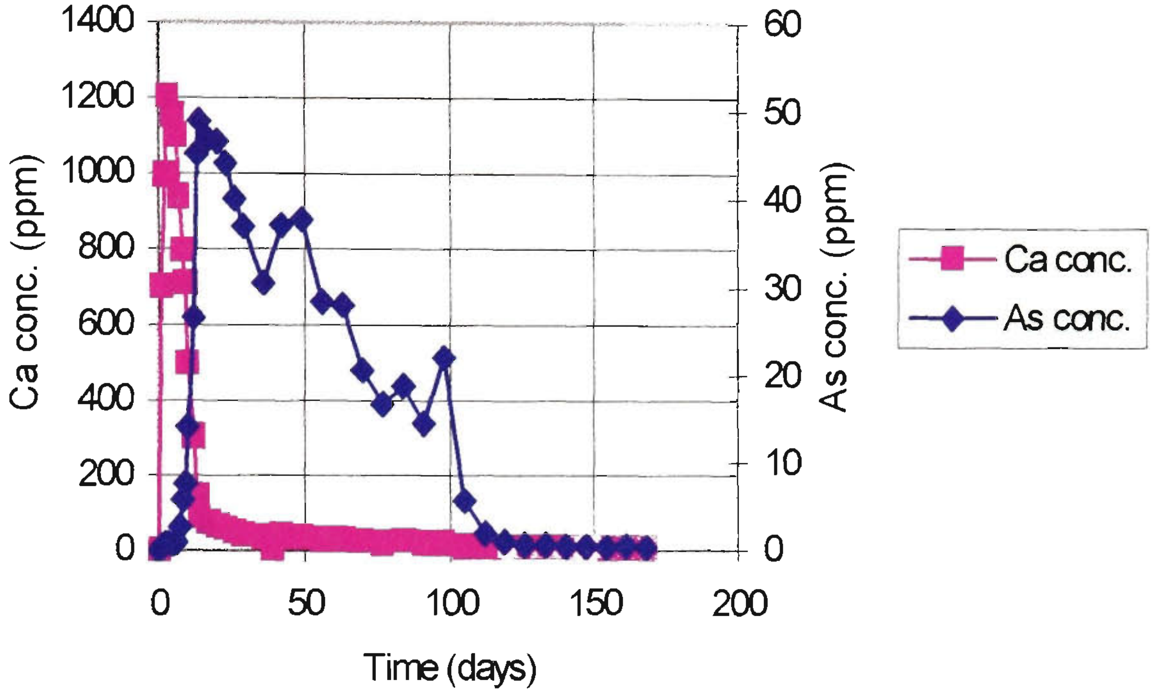


Figure 4.6 – Relationship between the calcium and arsenic concentrations for the As_2O_5 + *C* formulation

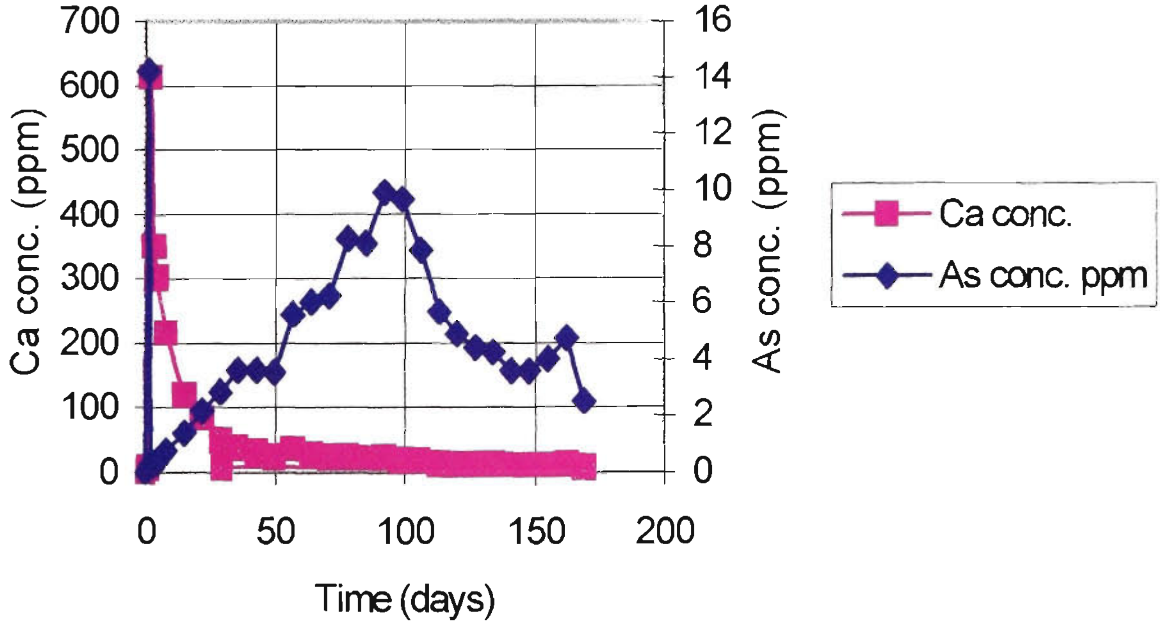
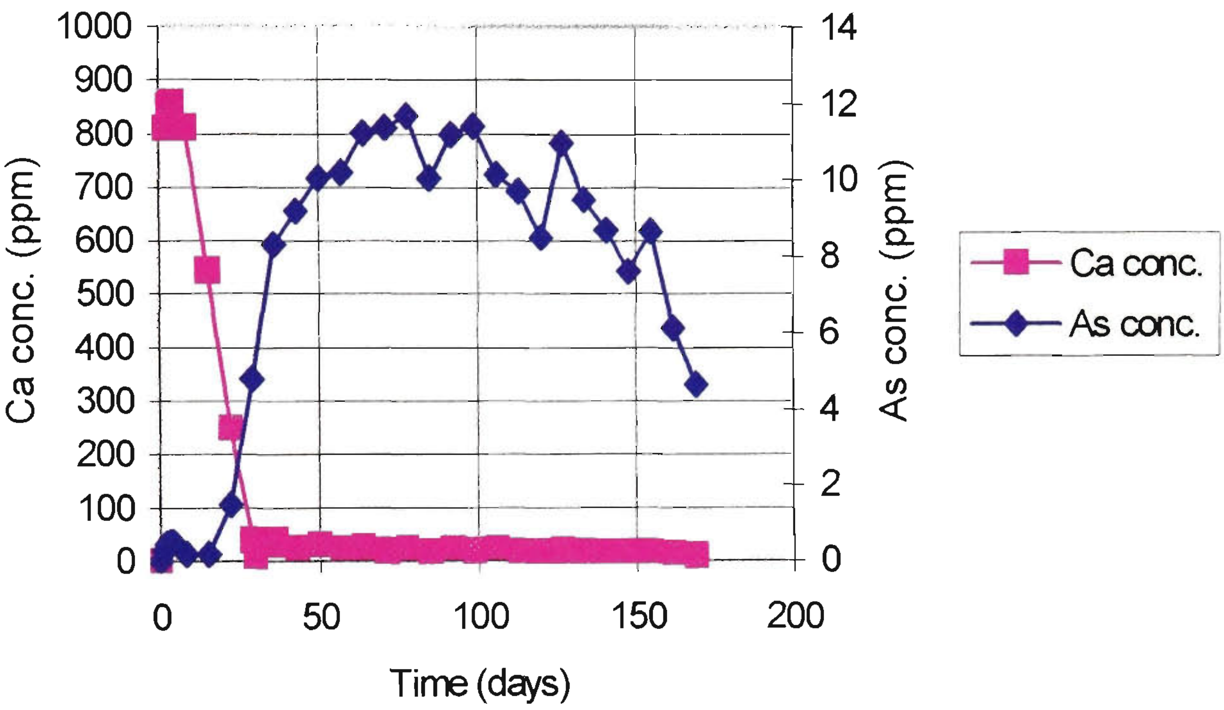


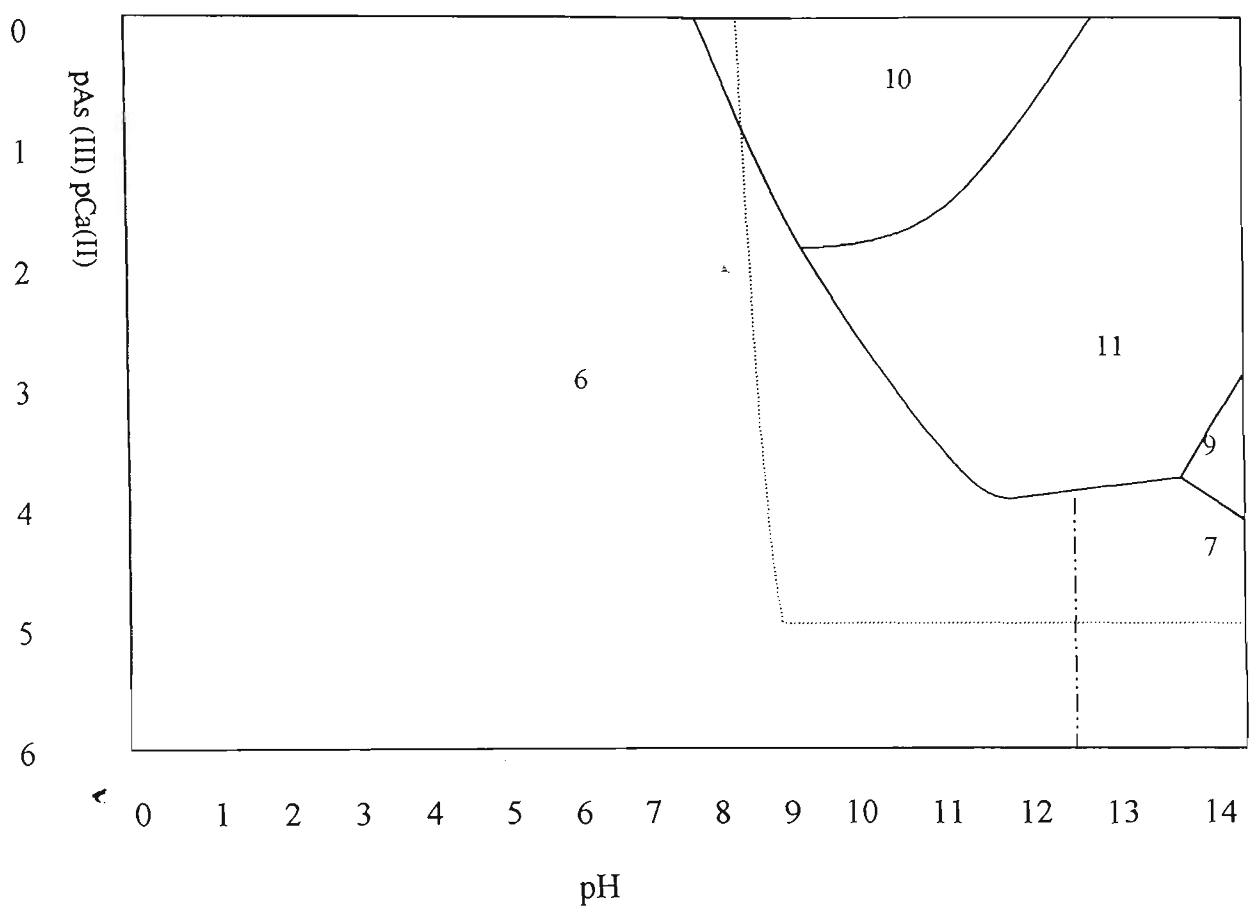
Figure 4.7 – Relationship between the calcium and arsenic concentrations for the As_2O_5 + *C-L* formulation



4.1.1 Calcium – arsenic decomposition

It has been realized in recent years that arsenic precipitated as either calcium arsenite or arsenate can decompose (Robins, 1985). Robins showed that atmospheric carbon dioxide caused calcium arsenate to decompose to $CaCO_3$ (at pHs over 7.5) releasing arsenic into solution. De Villers (1995), using stability diagrams ("solubility"/pH diagrams) for the Ca(II)-As(III)-water system and the Ca(II)-As(V)-water system at 25°C and taking into account atmospheric CO_2 (partial pressure $CO_2=10^{-3.47}$ atmosphere), identified calcium arsenites and arsenates likely to decompose (figures 4.8 and 4.9).

Figure 4.8 - Log activity-pH diagram for the calcium (II) – arsenic (III) water system (Glastras 1988)



Key to above diagram:

The effect of atmospheric carbon dioxide is to cause calcium carbonate to be stable in the region to the upper right of the dashed line.

6 = Ca^{2+}

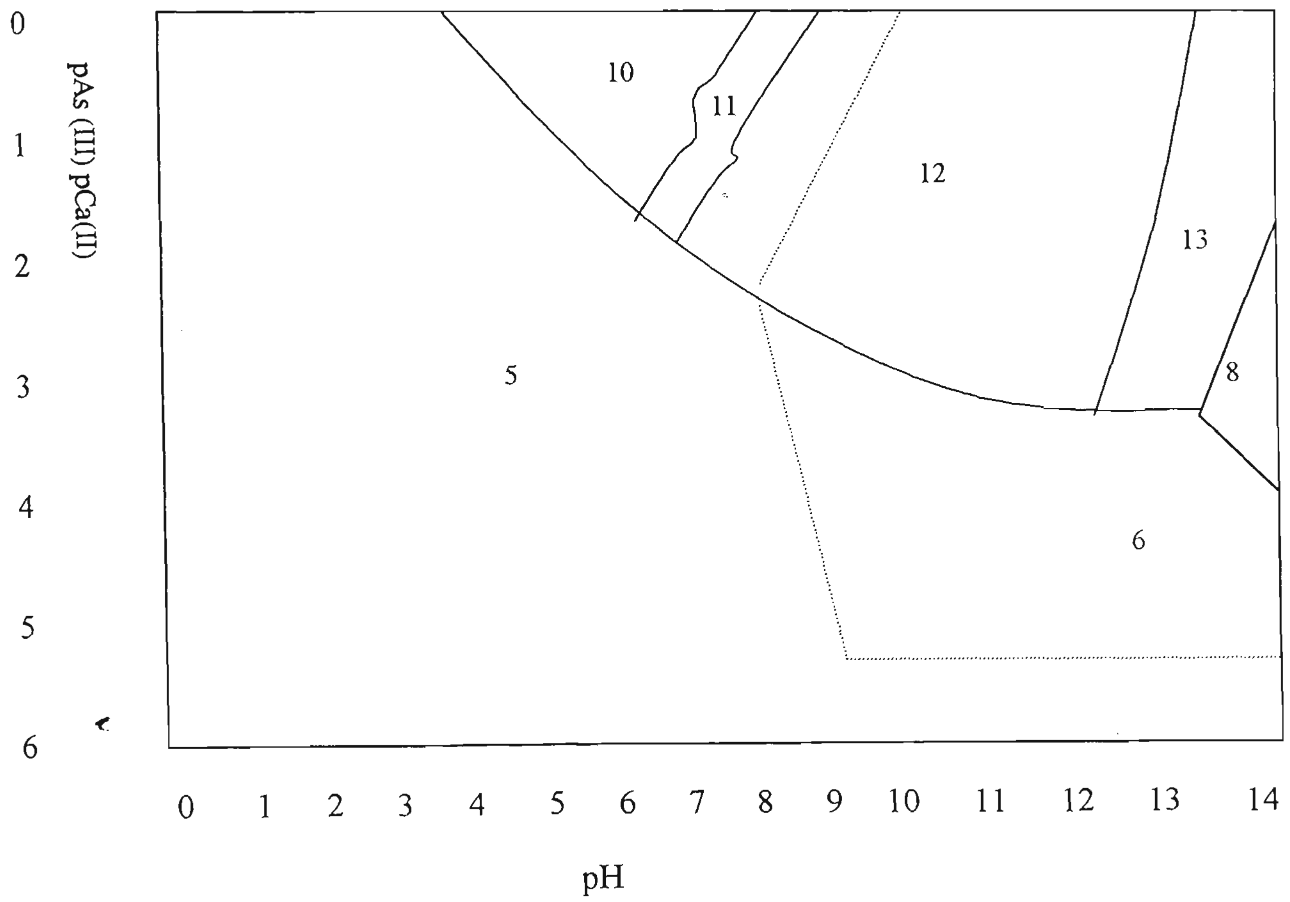
7 = $CaOH^+$

9 = $Ca(OH)_2$ (s)

10 = $Ca(AsO_2)_2$ (s)

11 = $Ca(AsO_2)_2.Ca(OH)_2$

Figure 4.9 - Log activity-pH diagram for the calcium (II) – arsenic (V) water system (Glastras 1988)



Key to above diagram:

The effect of atmospheric carbon dioxide is to cause calcium carbonate to be stable in the region to the upper right of the dashed line.

6 = Ca^{2+}
7 = $CaOH^{+}$
8 = $Ca(OH)_2$ (s)
10 = $CaHAsO_4$ (s)
11 = $Ca_5H_2(AsO_4)_4$ (s)
12 = $Ca_3(AsO_4)_2$ (s)
13 = $Ca_3(AsO_4)_2$. $Ca(OH)_2$

The calcium arsenites and calcium arsenates formed at high pH (to the right of the dashed line), decompose to calcium carbonate due to the influence of atmospheric carbon dioxide. According to De Villers (1995) and figures 4.8 and 4.9, the arsenite $Ca(AsO_2)_2$ and the arsenates, $CaHAsO_4$, $Ca_5H_2(AsO_4)_4$, and $Ca_3(AsO_4)_2$, can be stable in the presence of atmospheric CO_2 (at pHs to the left of the dashed line).

An example of how arsenic precipitated as basic calcium arsenite [$Ca(AsO_2)_2.Ca(OH)_2$] can be converted to the more soluble calcium arsenite [$Ca(AsO_2)_2$] and to arsenite ion by reaction with carbon dioxide is given by the following reactions (Cote and Constable 1987):

1. Conversion of excess lime to calcium carbonate:

$$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O$$

2. Conversion of basic calcium arsenite to calcium arsenite:

$$Ca(AsO_2)_2.Ca(OH)_2 + H_2CO_3 \rightarrow Ca(AsO_2)_2 + CaCO_3 + 2H_2O$$

3. Mobilization of the arsenite ion:

$$Ca(AsO_2)_2 + H_2CO_3 \rightarrow 2HAsO_2 + CaCO_3$$

Even though these reactions are probably rapid, the rate of conversion is limited by the availability of the carbonates that are introduced with the fresh leachant. If the conversion to the more soluble calcium arsenite was the governing factor for the release of arsenic, the rate of arsenic leaching would be controlled by the rate of leachant renewal (Cote and Constable 1987). This can be either confirmed or ruled out by comparing the amount of arsenic leached to the amount of carbonates added with the leachant. Tables 4.0 and 4.1 outline the number of moles of arsenic leached and the number of moles of carbonates added with the leachant for both sodium arsenite and arsenic trioxide respectively. These were the two salts for which the [cement + lime] formulations performed the worst when using the column (BLC) leaching tests.

Table 4.0 – Results for the sodium arsenite formulations

Formulation	**Moles of arsenic present in S/S formulation**	**Moles of arsenic released in the leachate**	**Moles of H_2CO_3 added**
$NaAsO_2$ + *C*	0.099	0.050	$1.01 * 10^{-3}$
$NaAsO_2$ + *C-Fe*	0.110	0.066	$1.01 * 10^{-3}$
$NaAsO_2$ + *C-L*	0.113	0.071	$1.01 * 10^{-3}$

Table 4.1 – Results for the arsenic trioxide formulations

Formulation	**Moles of arsenic present in S/S formulation**	**Moles of arsenic released in the leachate**	**Moles of H_2CO_3 added**
As_2O_3 + *C*	0.097	0.068	$9.78 * 10^{-4}$
As_2O_3 + *C-Fe*	0.129	0.088	$9.78 * 10^{-4}$
As_2O_3 + *C-L*	0.209	0.087	$9.78 * 10^{-4}$

The number of moles of H_2CO_3 is based on a partial pressure of $10^{-3.5}$ atm which results in a H_2CO_3 concentration in distilled water of approximately $10^{-5.65}$M.

Given that, as shown previously, the stoichiometry of the reactions relating to the decomposition of calcium arsenites are 1:1, it can be safely assumed that, since the estimated number of moles of carbonates added are not of the same order of magnitude as the amount of arsenic mobilized, the decomposition of the calcium arsenites was not the controlling factor for the release of arsenic into the leachate.

The [cement + lime] formulations released a significantly larger percentage of arsenic into the leachate than did the cement only formulations as mentioned previously. This discrepancy is most likely due to differences in the strengths of the cement matrix. During the crushing process it was noted that the [cement - only] matrix was the strongest of the S/S formulations, while the [cement + lime] formulations were considerably weaker.

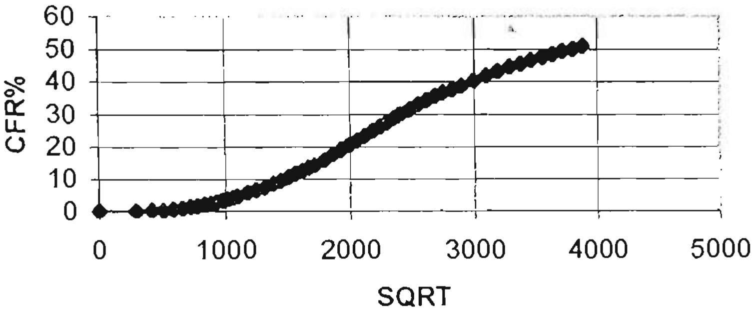
4.1.2 Leaching mechanism

Figures 4.10 to 4.13 show plots of the cumulative fraction released (CFR) versus the square root of time (SQRT). Given the linear relationships exhibited by these figures, diffusion may re one factor responsible for the leaching of arsenic and calcium. However for all the S/S formulations, regardless of the arsenic salt, the plots could be divided into at least two and perhaps three linear portions. All formulations showed an initial period of resistance to the leaching of arsenic. This was then followed by a period of increased leaching as the leaching boundary moved inward, followed by a period of reduced leachability for the majority of the S/S formulations, suggesting an equilibrium had been reached.

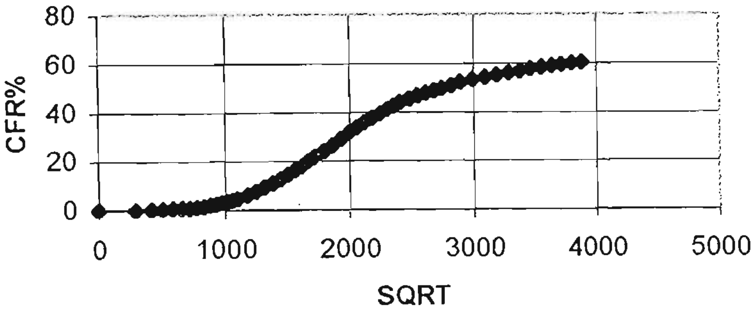
While the leaching of both arsenic and calcium may have be partly responsible due to diffusion processes, the lack of any of the plots exhibiting a single linear relationship would suggest that diffusion processes were not the only processes operating. Factors such as the concentrations of other constituents in the leachant and the leachate pH would have influenced the arsenic leachate concentration as was shown to be the case in Chapter 3. Indeed, it has already been shown in section 4.1, that the levels of calcium in the leachate appear to impact upon the arsenic leachate concentration. Factors such as pH and redox potential will be discussed in detail later in this chapter.

Figure 4.10 – CFR versus SQRT for the sodium arsenite S/S formulations

(A) $NaAsO_2$ + *C*



(B) $NaAsO_2$ + *C-Fe*



(C) $NaAsO_2$ + *C-L*

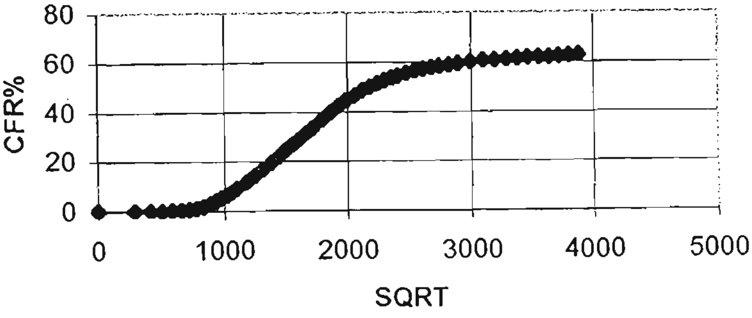
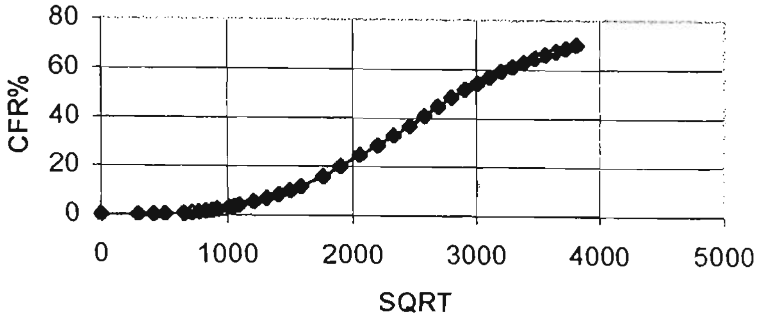
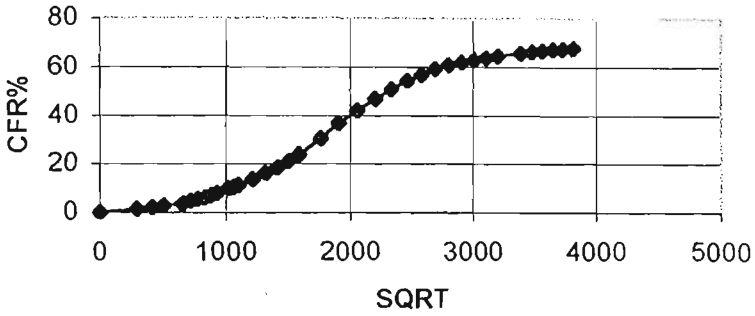


Figure 4.11 – CFR versus SQRT for the arsenic trioxide S/S formulations

(A) As_2O_3 + *C*



(B) As_2O_3 + *C-Fe*



(C) As_2O_3 + *C-L*

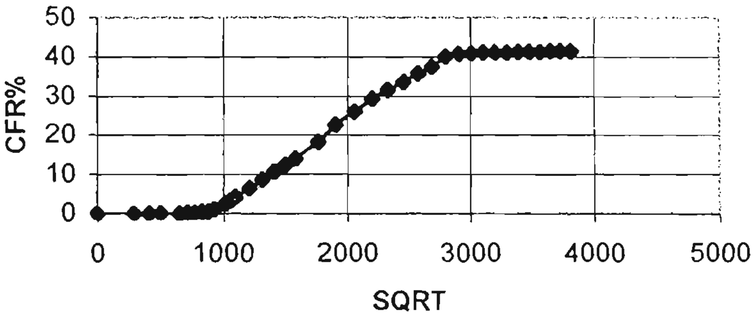
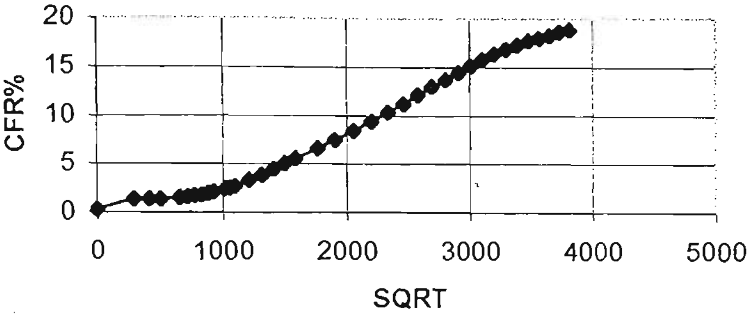
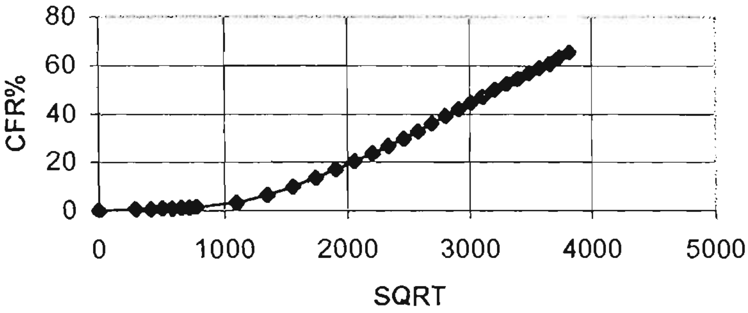


Figure 4.12 – CFR versus SQRT for the sodium arsenate S/S formulations

(A) Na_2HAsO_4 + *C*



(B) Na_2HAsO_4 + *C-Fe*



(C) Na_2HAsO_4 + *C-L*

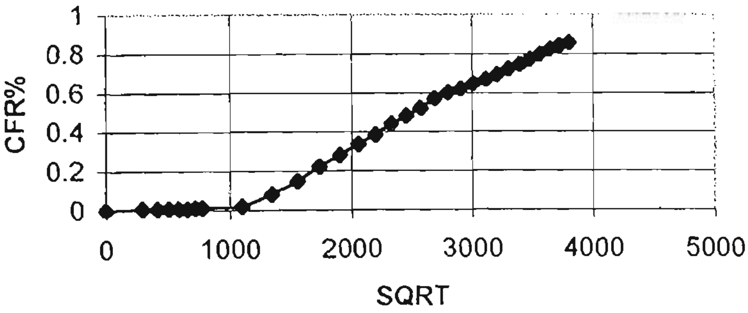
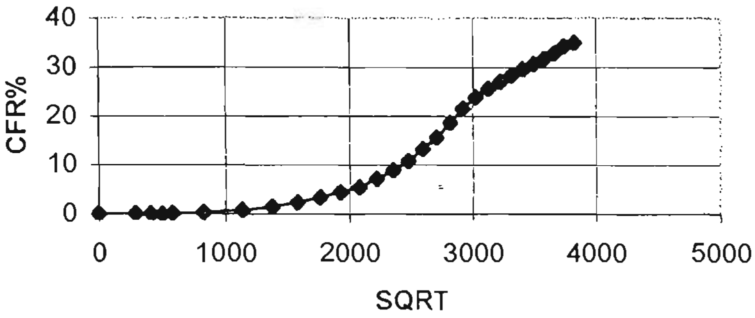
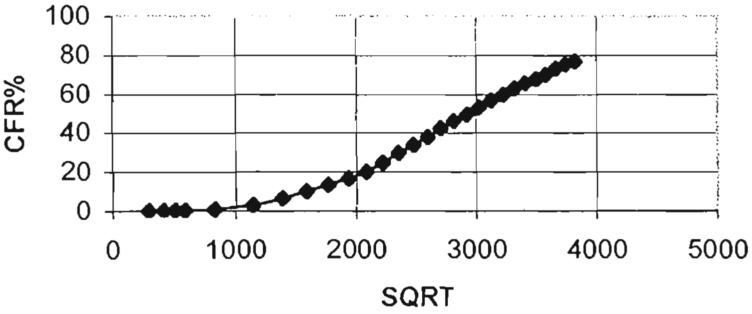


Figure 4.13 – CFR versus SQRT for the arsenic pentoxide S/S formulations

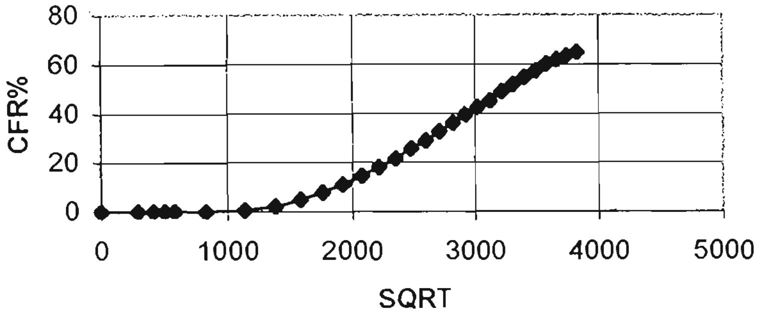
(A) As_2O_5 + *C*



(B) As_2O_5 + *C-Fe*



(C) As_2O_5 + *C-L*



4.1.3 Column (BLC) leaching versus Sequential Batch Leaching

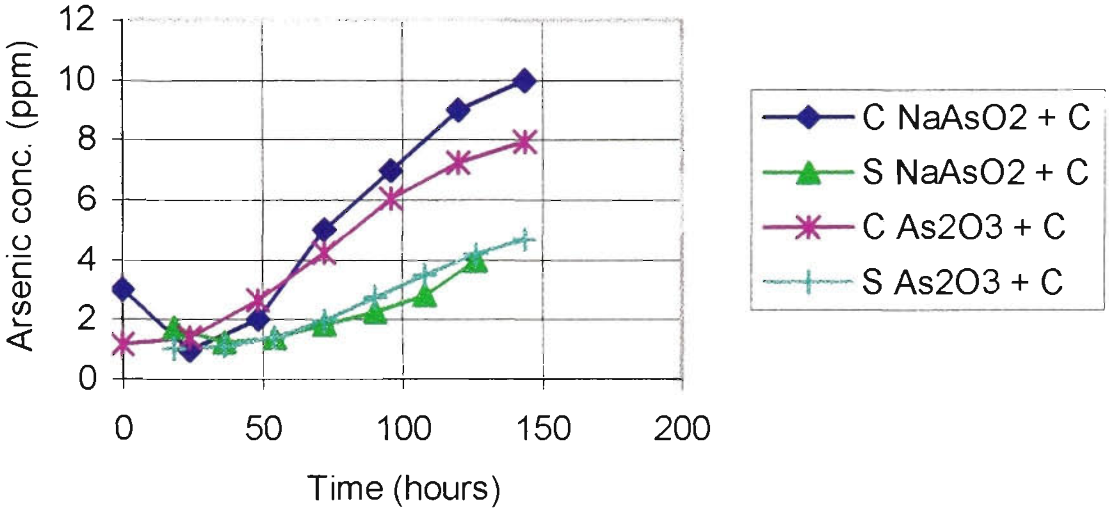
The column (BLC) leaching tests, with a flow rate of 1.85 mL/minute, were primarily set up to make comparisons with the sequential batch leaching tests. The flow rate of 1.85 mL/minute equates to 2 litres per 18 hours, the same liquid to solid ratio used in the regulatory batch tests.

In field and laboratory column leaching scenarios, the solid granular particles are stationary and the leachant flows through or around the solid particles and carries away dissolved constituents. In the sequential batch leaching scenarios, agitation is used to cause fluid to flow past particles and accelerate the dissolution of constituents in the material. For most continuously agitated systems, kinetic eddy-viscosity and shear is high, resulting in the fluid and chemical boundary layers being compressed and not likely to constitute a resistance to diffusion (Van der Sloot et al 1997).

Despite the significant differences which exist in the leaching methodology between the sequential batch leaching and column leaching tests, the leachate concentrations were not all that dissimilar, as can be observed from figures 4.14 and 4.15. The similarities between the concentrations obtained from the two types of leaching tests also extended to the calcium concentrations as can be observed from figures 4.16 and 4.17.

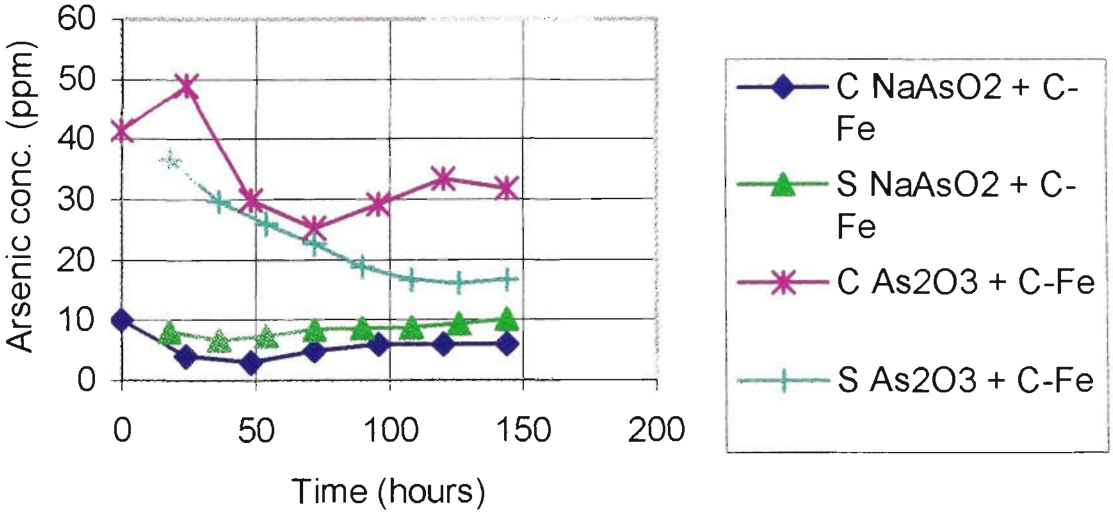
Figure 4.14 – Comparison between Column (BLC) leaching and Sequential Batch leaching - Arsenite S/S formulations

(A) cement only



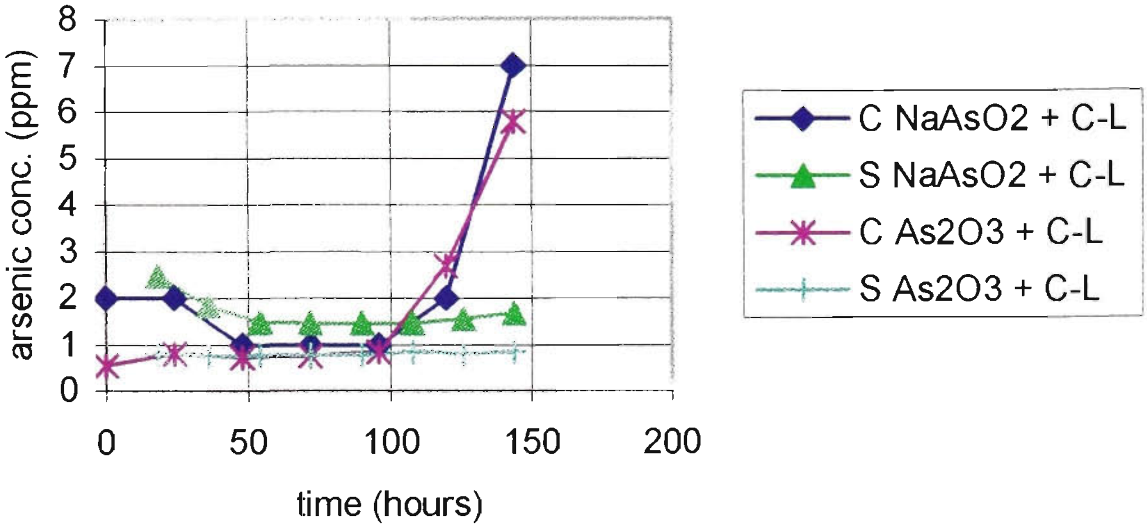
key to figures 4.14(a) – "C" indicates those formulations subjected to column (BLC) leaching
"S" indicates those formulations subjected to sequential batch leaching

(B) cement + iron formulations



key to figures 4.14(b) – "C" indicates those formulations subjected to column (BLC) leaching
"S" indicates those formulations subjected to sequential batch leaching

(C) cement + lime formulations

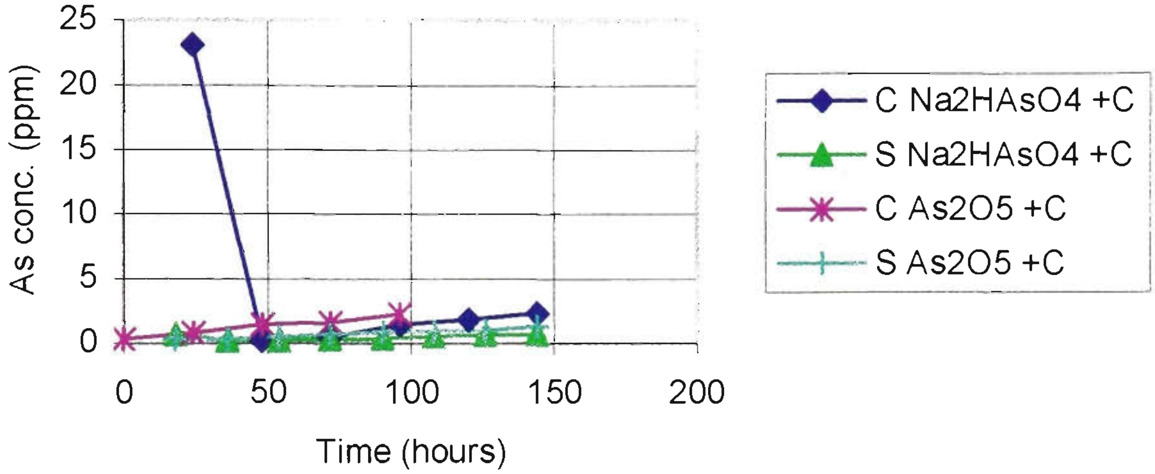


key to figures 4.14(c) – "C" indicates those formulations subjected to column (BLC) leaching

"S" indicates those formulations subjected to sequential batch leaching

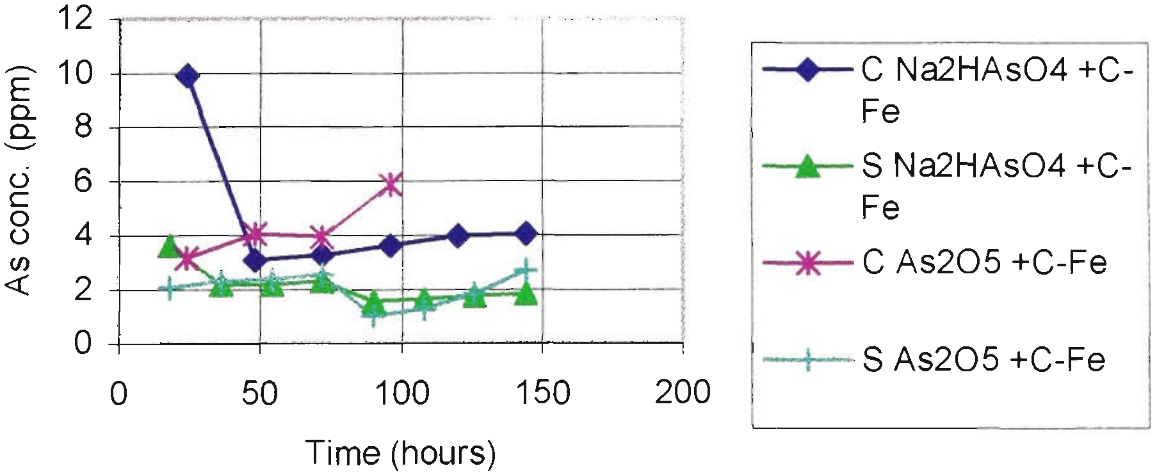
Figure 4.15 – Comparison between Column (BLC) leaching and Sequential Batch leaching - Arsenate S/S formulations

(A) cement only formulations



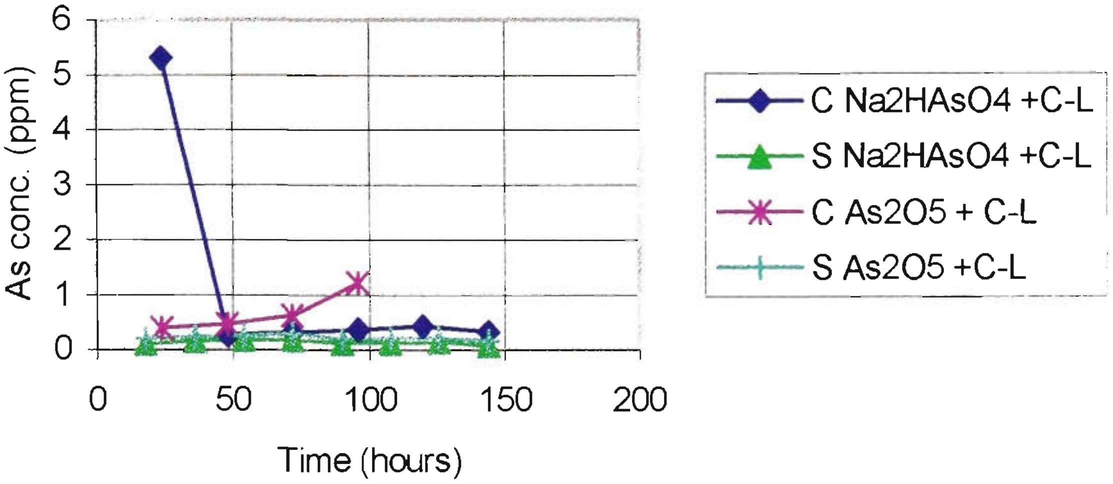
key to figures 4.15(a) – "C" indicates those formulations subjected to column (BLC) leaching
"S" indicates those formulations subjected to sequential batch leaching

(B) cement + iron formulations



key to figures 4.15(b) – "C" indicates those formulations subjected to column (BLC) leaching
"S" indicates those formulations subjected to sequential batch leaching

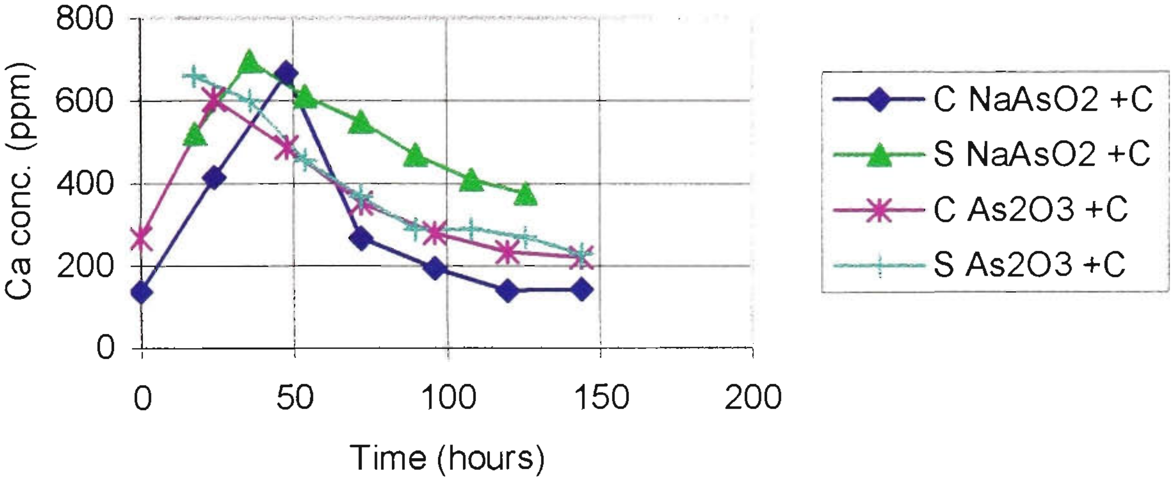
(C) cement + lime formulations



key to figures 4.15(c) – "C" indicates those formulations subjected to column (BLC) leaching
"S" indicates those formulations subjected to sequential batch leaching

Figure 4.16 – Comparison between Column (BLC) leaching and Sequential Batch leaching - Arsenite S/S formulations Calcium levels

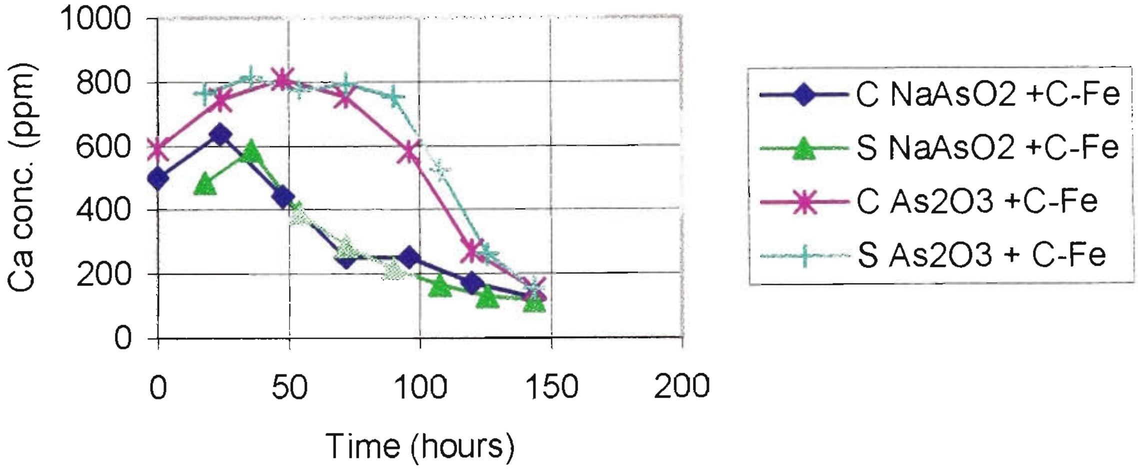
(A) cement only formulations



key to figures 4.16(a) – "C" indicates those formulations subjected to column (BLC) leaching

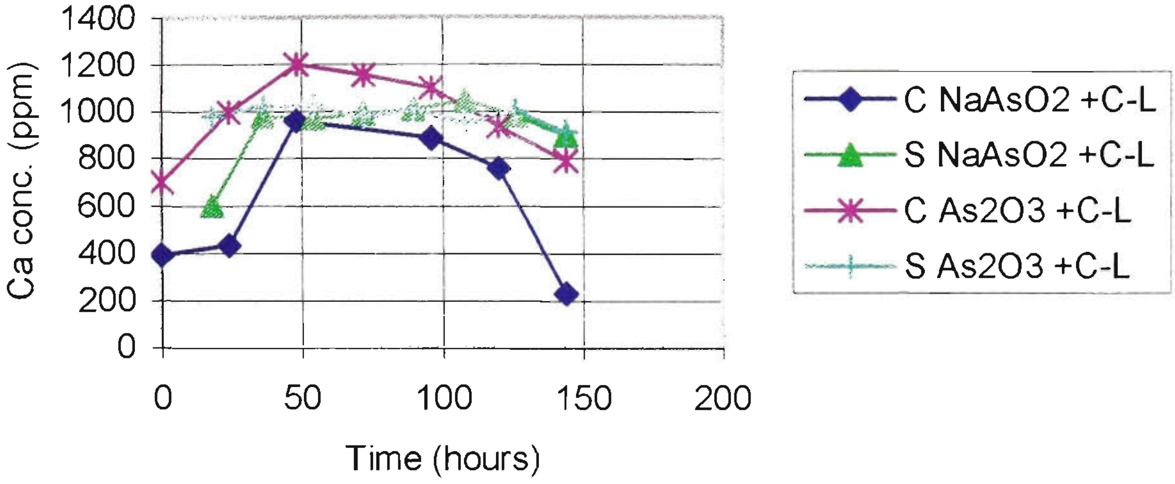
"S" indicates those formulations subjected to sequential batch leaching

(B) cement + iron formulations



key to figures 4.16(b) – "C" indicates those formulations subjected to column (BLC) leaching

"S" indicates those formulations subjected to sequential batch leaching



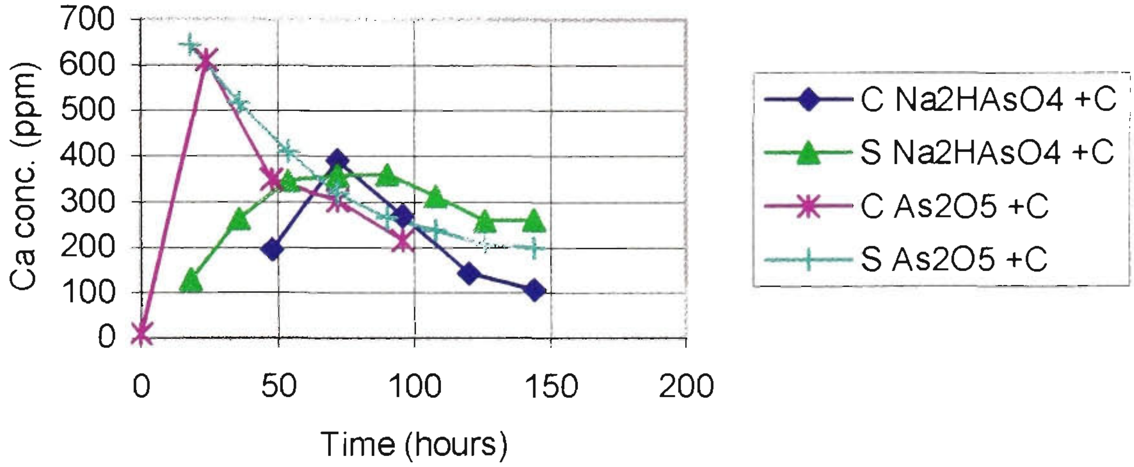
(C) cement + lime formulations

key to figures 4.16(c) – "C" indicates those formulations subjected to column (BLC) leaching

"S" indicates those formulations subjected to sequential batch leaching

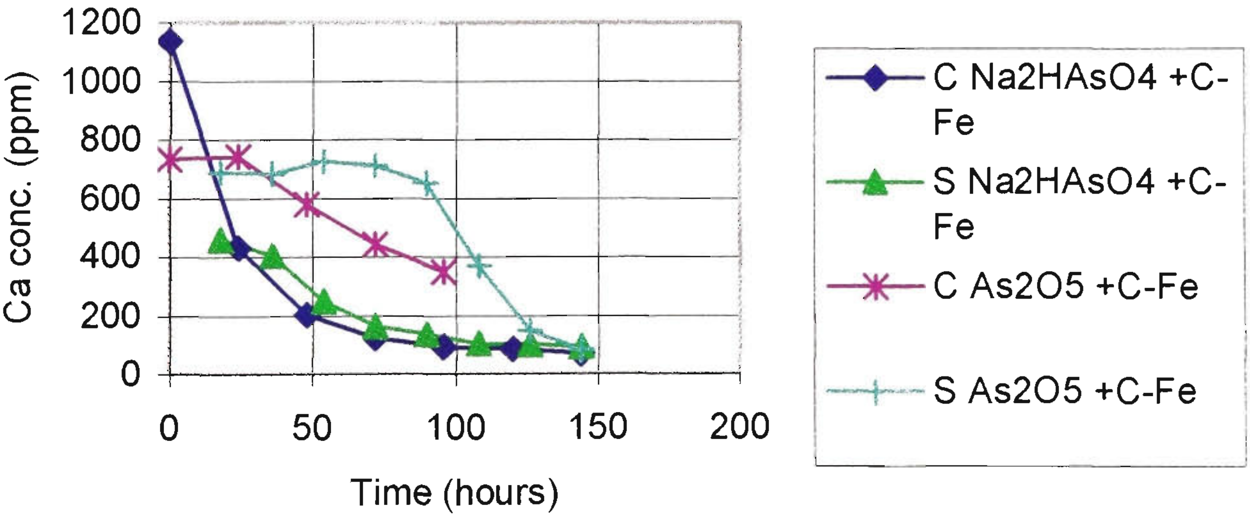
Figure 4.17 – Comparison between Column (BLC) leaching and Sequential Batch leaching - Arsenate S/S formulations Calcium levels

(A) cement only formulations

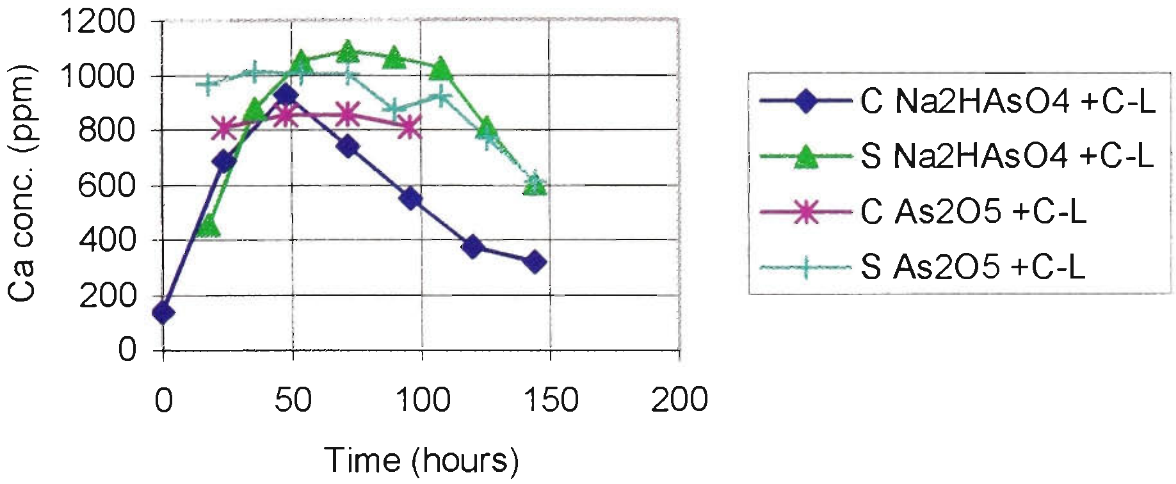


key to figures 4.17(a) – "C" indicates those formulations subjected to column (BLC) leaching
"S" indicates those formulations subjected to sequential batch leaching

(B) cement + iron formulations



key to figures 4.17(b) – "C" indicates those formulations subjected to column (BLC) leaching
"S" indicates those formulations subjected to sequential batch leaching



(C) cement + lime formulations

key to figures 4.17(c) – “C” indicates those formulations subjected to column (BLC) leaching
“S” indicates those formulations subjected to sequential batch leaching

For the majority of the S/S formulations, neither test constantly produced the highest arsenic concentrations. For example, inspection of the data obtained from the sodium arsenite formulations, shows that column leaching produced higher arsenic concentrations than the sequential batch leaching tests for the [cement - only] formulation (figure 4.18). However, this scenario was completely reversed for the S/S formulation involving the use of iron (II) ($NaAsO_2$ + *C-Fe)* as can be observed from figure 4.19. For the formulation using cement and lime ($NaAsO_2$ + *C-L*), the two leaching processes produced arsenic concentrations that were similar over the majority of the leaching period (figure 4.20).

Figure 4.18 – Sequential leaching versus column (BLC) leaching

$NaAsO_2$ + *C*

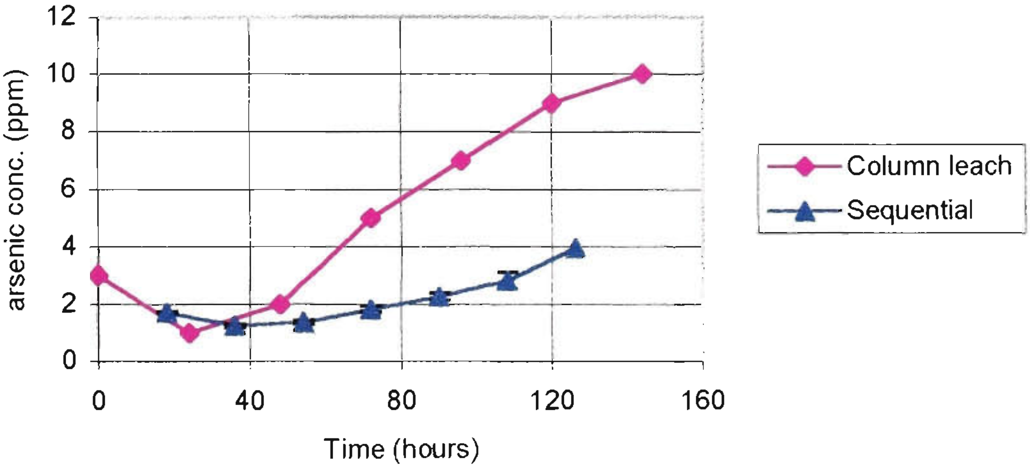


Figure 4.19 – Sequential leaching versus column (BLC) leaching

$NaAsO_2$ + *C-Fe*

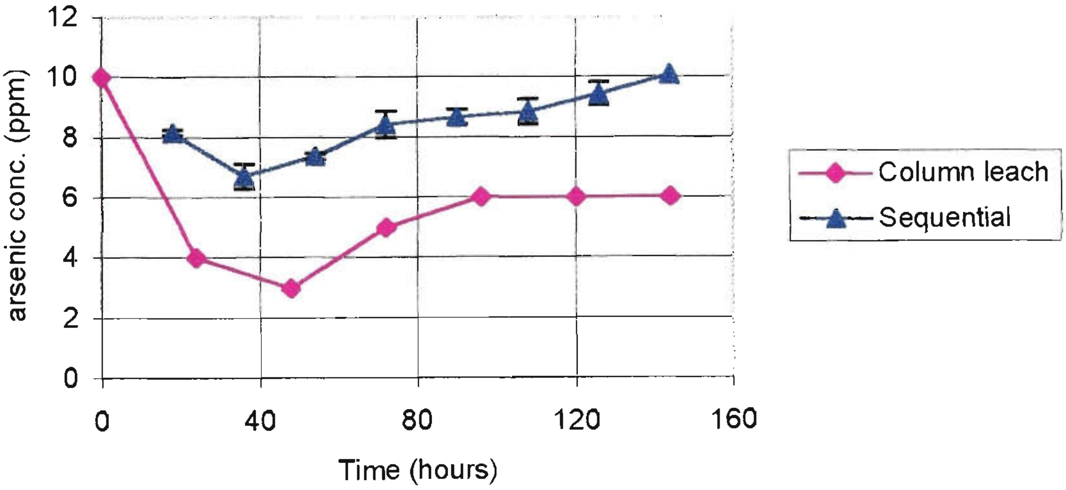
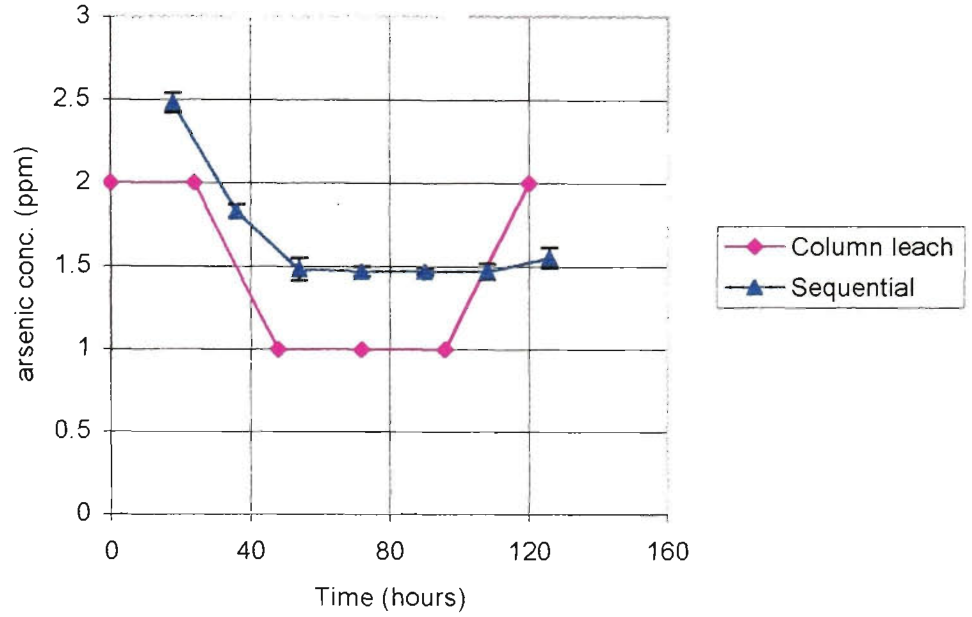


Figure 4.20 – Sequential leaching versus column (BLC) leaching

$NaAsO_2$ + *C-L*



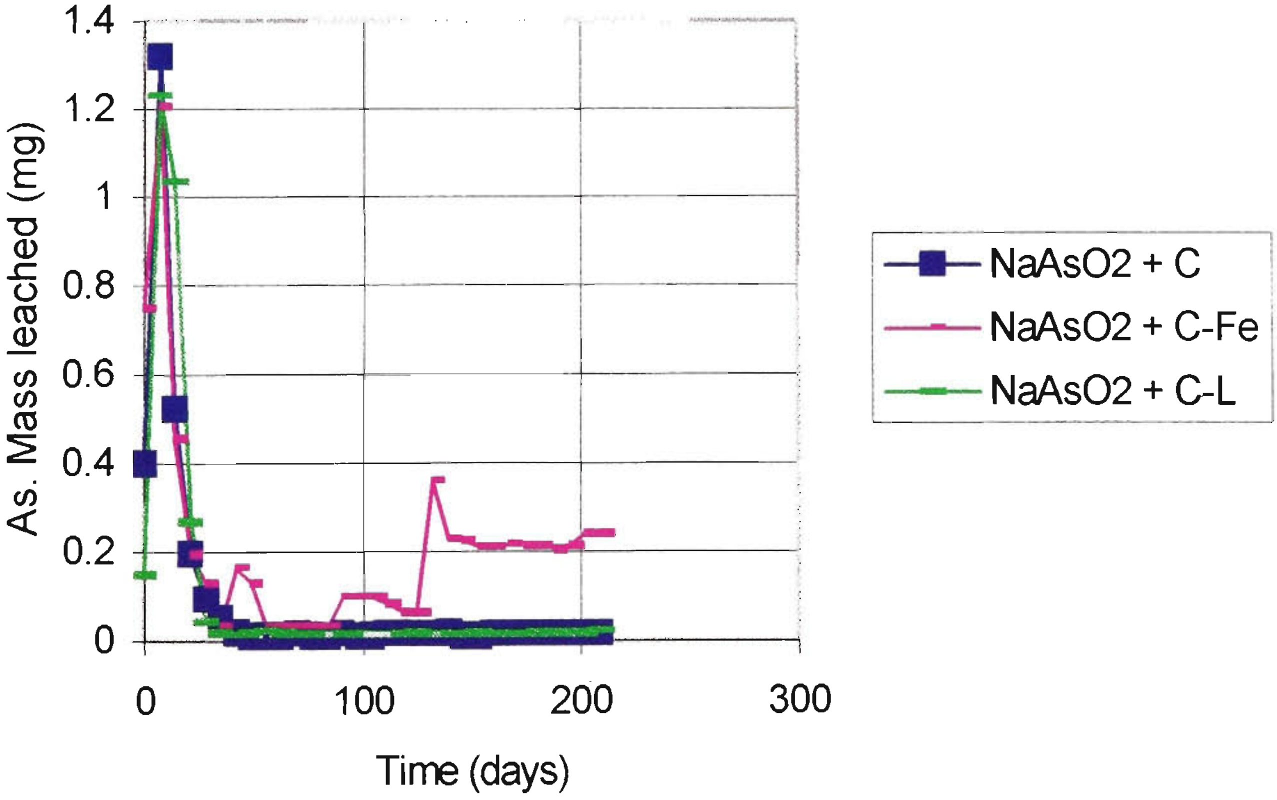
The only arsenic salt for which one leaching test constantly produced a higher arsenic leachate concentration was sodium arsenate. For all three of the sodium arsenate-containing formulations, the column leaching tests produced high initial leachate concentrations, suggestive of a column wash-off effect. The leachates collected during this initial period had arsenic concentrations anywhere up to 20 times those which were collected at subsequent leaching intervals.

4.2 Column (Rainfall) leaching tests

The column (Rainfall) leaching tests utilized a flow rate of 4.65 mL/day. When taking into account the column specifications (chapter 2), this is approximately 5 times the average annual precipitation in Melbourne and 1.75 times the sum of the highest monthly rainfalls in Melbourne over the past 140 years (BOM 2000).

The leachate concentrations obtained from the column (Rainfall) leaching tests typically mirror the pattern exhibited in figure 4.21, which displays the masses of arsenic leached for the sodium arsenite formulations. The largest masses of arsenic leached were obtained at the commencement of the tests, suggestive of a column wash off effect.

Figure 4.21 - Mass of arsenic leached for the Sodium Arsenite formulations



The decreases in the mass of arsenic leached after the initial period are a result of the depletion of soluble arsenic species in the outer layers of the waste particles. When the leached concentration stabilizes, it indicates that the dissolution of arsenic species at the internal leaching boundary and their subsequent transport through the particle has reached a constant rate. The sudden increase in the mass of arsenic leached for the [$NaAsO_2$ + *C-Fe*] as shown in figure 4.21, is most likely due to channeling effects, whereby a new, previously unexposed, region of the packed waste has now been exposed to the leachate, thus destroying the equilibrium which had been previously established.

By comparing the cumulative mass of arsenic leached from the arsenic pentoxide and the arsenic trioxide formulations, figures 4.22 and 4.23 respectively, it is apparent that, as was the case with the sequential leaching tests, the arsenate containing formulations have had considerable less arsenic leached than their arsenite containing counterparts. Figures 4.22, 4.23 and 4.24 also indicate that the iron-containing formulations were, by far, the worst performing of the S/S formulations. These were also the worst performing formulations when tested with the batch or sequential batch leaching tests. Hence, it appears that, for the majority of the arsenic compounds, the current regulatory tests are useful as predictors of the performance each of the formulations will have when subjected to conceptually more realistic leaching tests. For all four of the arsenic salts investigated, the [cement + iron] formulations have leached the largest arsenic masses for the majority of the leaching investigation period. However, for the sodium arsenate S/S formulations, the cement and [cement + lime] formulations leached considerable more arsenic during the first weeks of the leaching tests. The large masses of arsenic which were leached by these formulations during the commencement of the column (rainfall) leaching tests can be observed from figure 4.26. Consequently, the cumulative masses of arsenic leached by the [cement – only] and the [cement + lime] formulations were greater than the cumulative mass of arsenic leached by the [cement + iron] formulations (figure 4.25).

Figure 4.22 - Cumulative mass of arsenic leached from the Column (rainfall) leaching tests - Arsenic pentoxide formulations

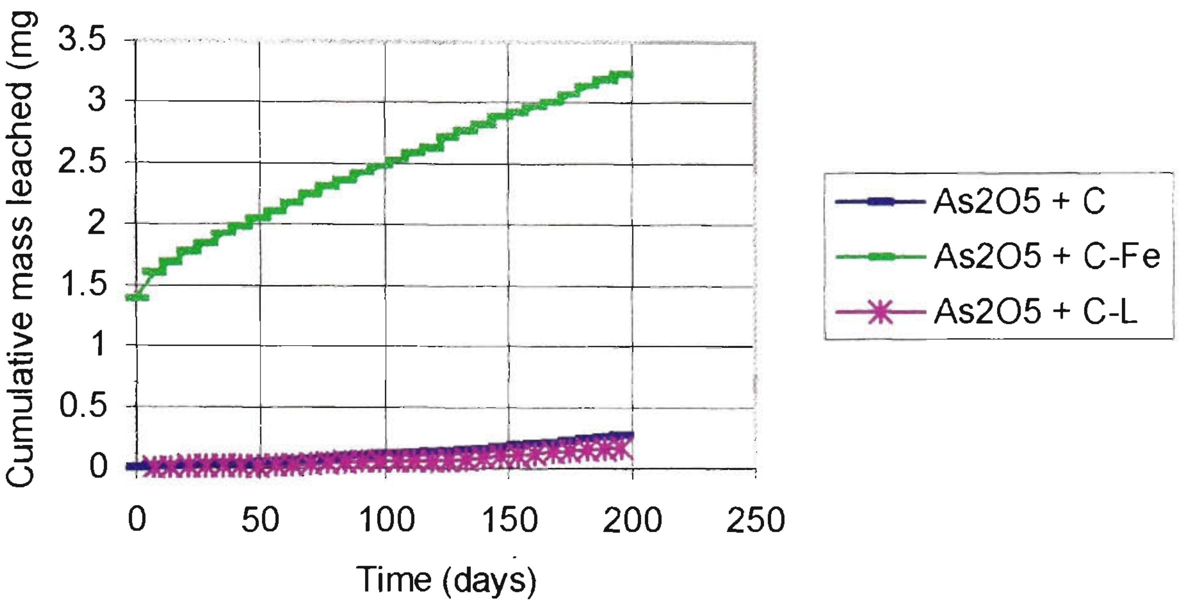


Figure 4.23 - Cumulative mass of arsenic leached from the Column (rainfall) leaching tests - Arsenic trioxide formulations

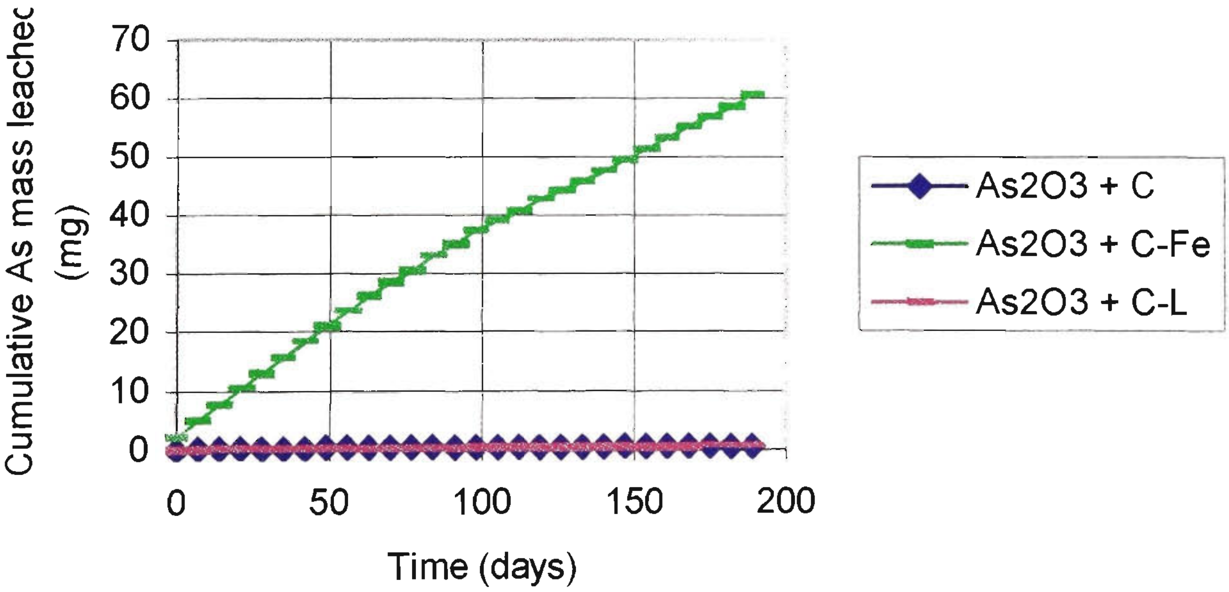


Figure 4.24 - Cumulative mass of arsenic leached from the Column (rainfall) leaching tests – Sodium Arsenite formulations

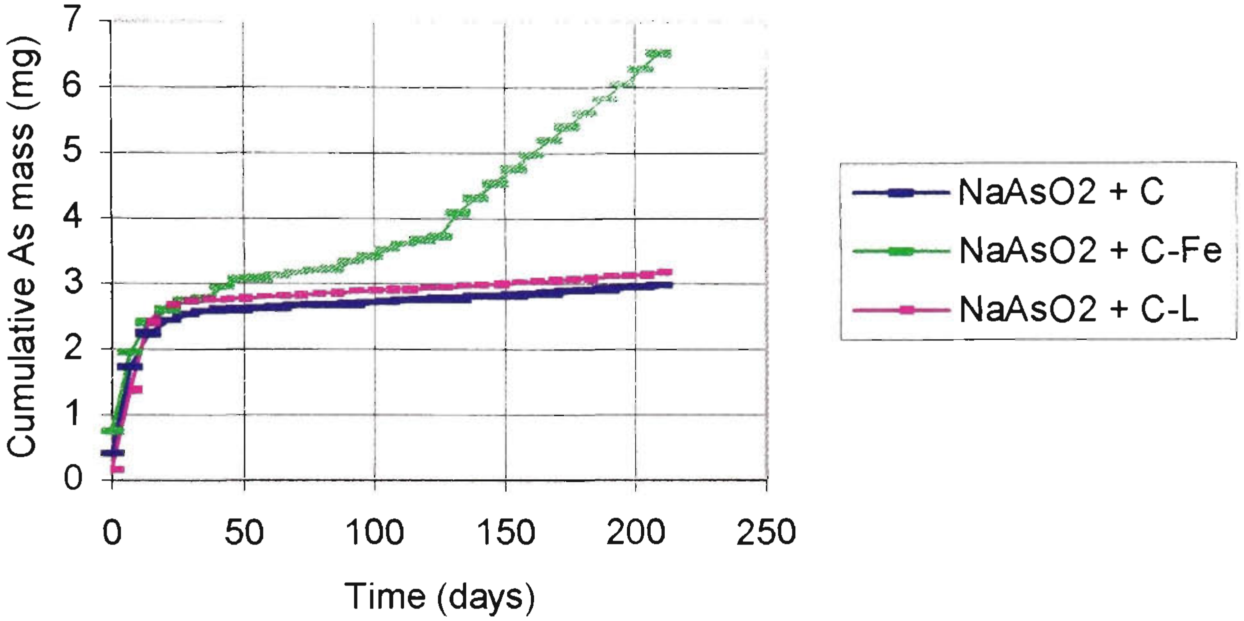


Figure 4.25 - Cumulative mass of arsenic leached from the Column (rainfall) leaching tests – Sodium Arsenate formulations

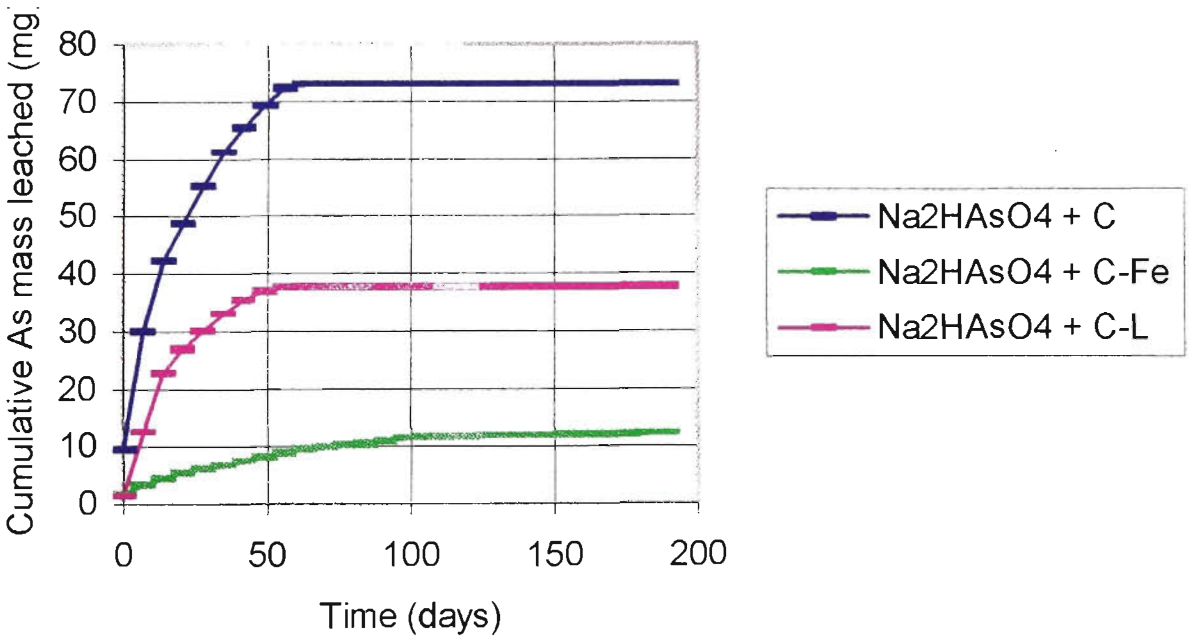


Figure 4.26 – Weekly masses of arsenic leached from the Column (rainfall) Leaching tests – Sodium Arsenate formulations

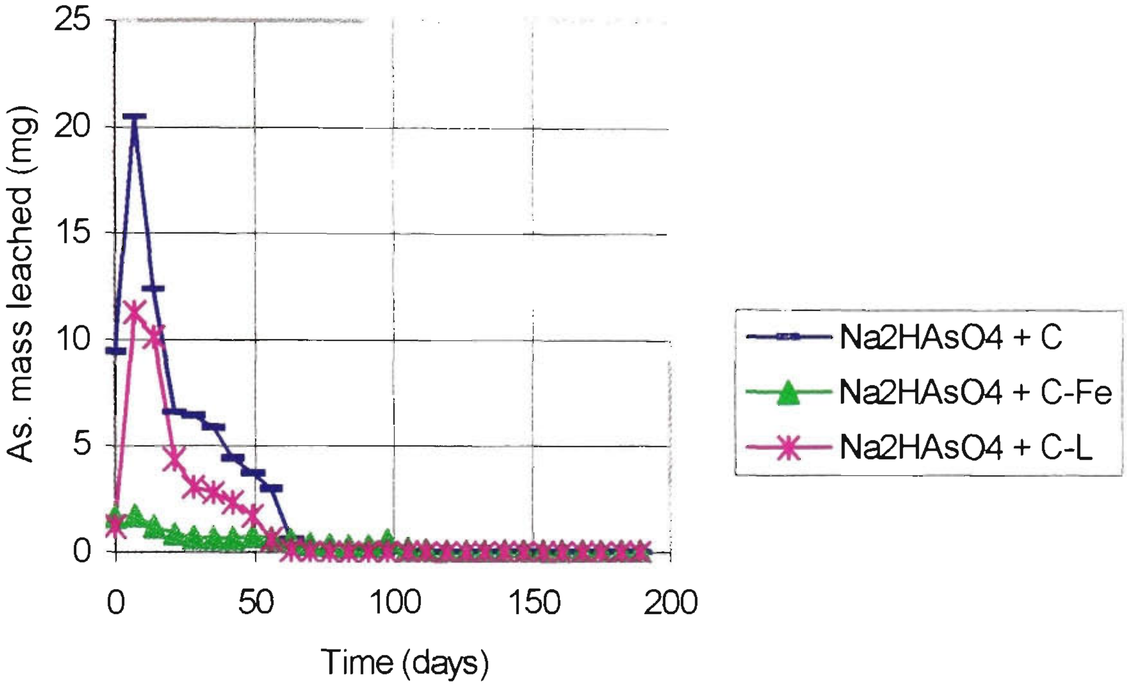
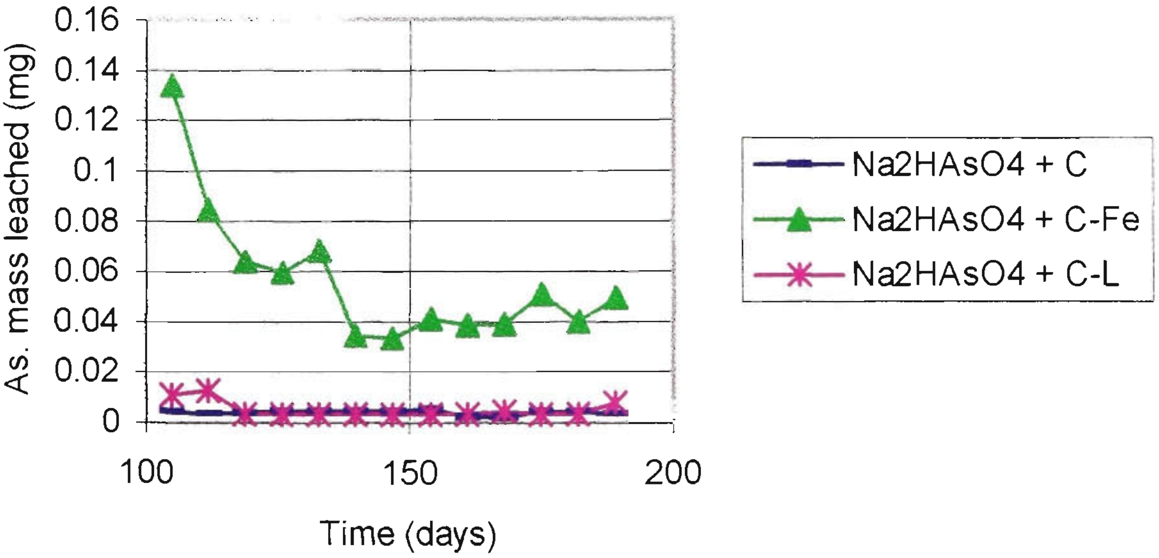


Figure 4.27 – Mass of arsenic leached during days 100 to 200 Sodium Arsenate formulations



After the high initial masses leached, figure 4.27 demonstrates that the masses of arsenic leached approach those that would be expected, given the results exhibited by the other arsenic salts, i.e., the [cement + iron] formulations leach the highest levels. When subjected to the column (BLC) leaching tests, the sodium arsenate formulations also yielded very high initial leachate concentrations.

Figures 4.28 and 4.29 indicate that, as was the case with the sequential leaching tests (Chapter 3), the leaching of arsenic appears linked with the leaching of calcium. During the initial periods, where very high arsenic leachate concentrations were exhibited, extremely low calcium concentrations were recorded. Only as the calcium leachate concentrations dramatically increased, did the arsenic leachate concentrations reduce (figures 4.28 and 4.29). The [cement + iron] formulation (Na_2HAsO_4 + *C-Fe)* did not leach the extremely high initial arsenic concentrations and, not surprisingly, the pattern of calcium release was also significantly different. High calcium concentrations were leached for the entirety of the leach test, as can be observed from figure 4.30. The increased calcium leachate concentration for the [cement + iron] formulations may be attributable to greater porosity of the matrix for these formulations, thereby allowing the leaching boundary to move inward significantly more quickly, thus mobilizing more arsenic and, most importantly, allowing calcium to be leached much more readily.

The large quantities of arsenic leached at the commencement of the column (rainfall) leaching tests were unique to the arsenic-containing sodium salts, especially sodium arsenate. These problems are probably related to the effect which these arsenic salts have upon the cement matrix. However, as the problem was unique to the sodium containing salts, it would be reasonable to say that it is, indeed, the sodium and not the arsenic component of these salts which is causing the majority of the problems. Conner (1990) has identified both sodium arsenate and sodium containing compounds generally, as substances which are capable of inhibiting cement reactions.

Figure 4.28 - Arsenic and calcium levels leached using column (rainfall) leaching, Na_2HAsO_4 + *C* formulation

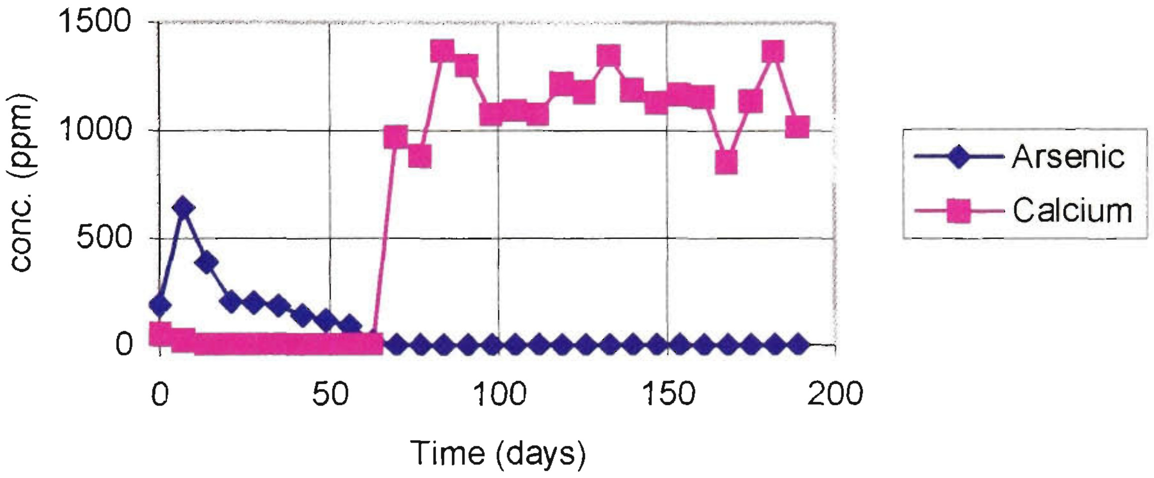


Figure 4.29 - Arsenic and calcium levels leached using column (rainfall) leaching, Na_2HAsO_4 + *C-L* formulation

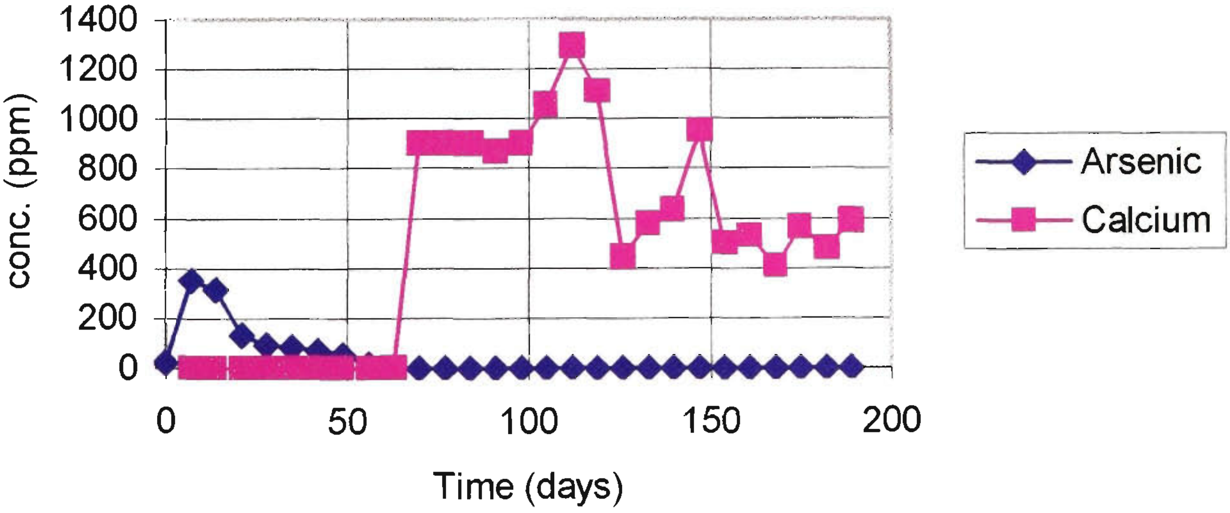
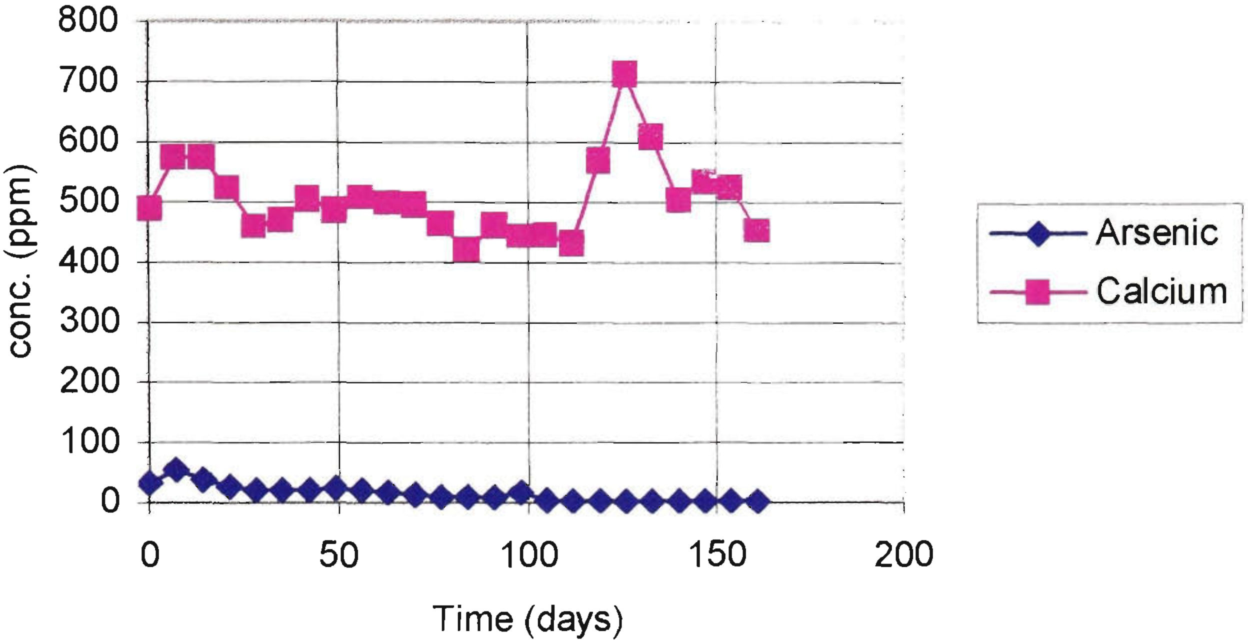


Figure 4.30 - Arsenic and calcium levels leached using column (rainfall) leaching, Na_2HAsO_4 + *C-Fe* formulation

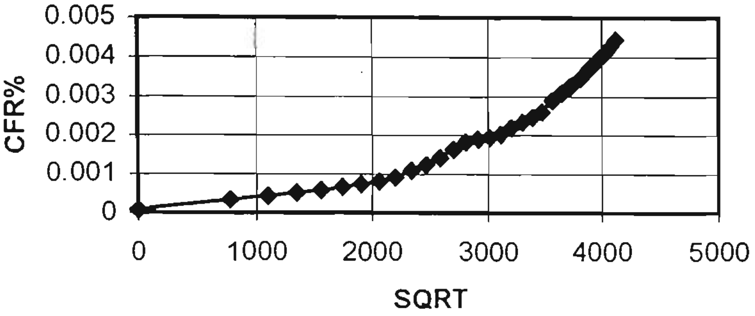


4.2.1 Leaching mechanism

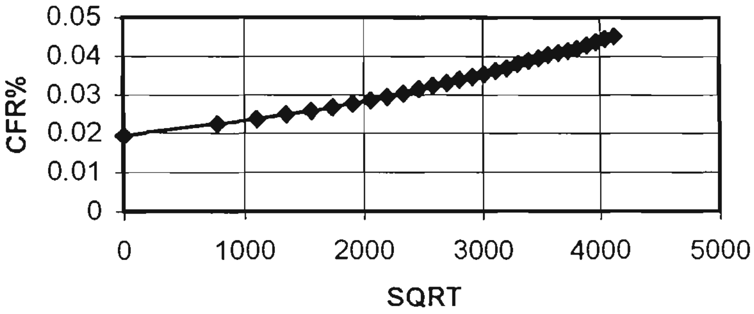
Leaching of contaminants into the leaching water results from the mass transport of the contaminants contained in the solidified waste form. Different transport processes may occur in these waste forms: diffusion, dissolution, ion exchange, corrosion, surface effects. It is believed that leaching of contaminants out of the cement-based waste form is mostly a diffusion controlled process (McIsaac and Croney 1991). The semi - linear relationship which exists between the CFR and the SQRT for the column (rainfall) leaching tests (figures 4.31 through to 4.36), suggests, as expected, that the leaching of arsenic is by a diffusion based mechanism. The majority of the S/S formulations, however, as shown by the plots, tended to exhibit two linear portions throughout the six month investigation period. For example, the arsenic pentoxide formulations tended to exhibit a period of initial resistance, while the sodium arsenite and especially the sodium arsenate formulations exhibited initial periods of enhanced arsenic leaching, followed by reduced arsenic leaching. As the column (rainfall) leaching tests utilized a smaller and hence less destructive flow rate, some degree of cement lattice curing could have taken place during the tests which would be capable of effecting the porosity and other parameters that would influence the leaching of arsenic. Not suprisingly, given the relationship which was discussed earlier between the arsenic and calcium levels, the plots of CFR versus the SQRT for calcium for the sodium arsenate formulations were the exact opposite to those depicting the arsenic levels, i.e the greatest percentage of calcium was leached towards the latter part of the investigation period.

Figure 4.31 – CFR versus SQRT, Arsenic Pentoxide formulations Arsenic levels

As_2O_5 + *C*



As_2O_5 + *C-Fe*



As_2O_5 + *C-L*

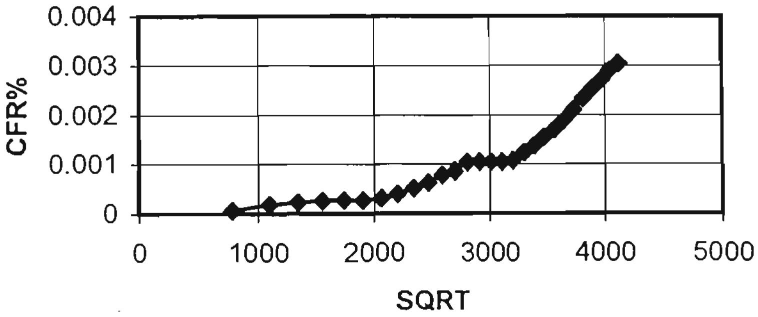
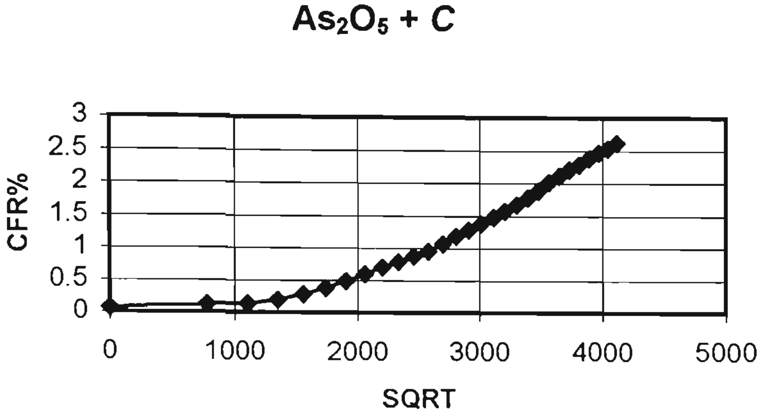
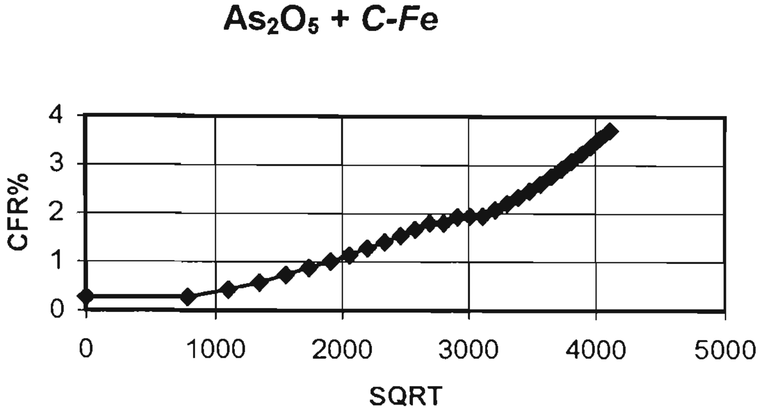


Figure 4.32 – CFR versus SQRT, Arsenic Pentoxide formulations Calcium levels





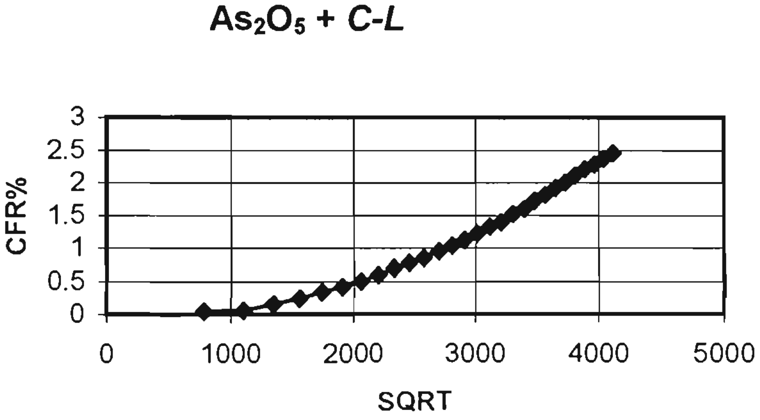
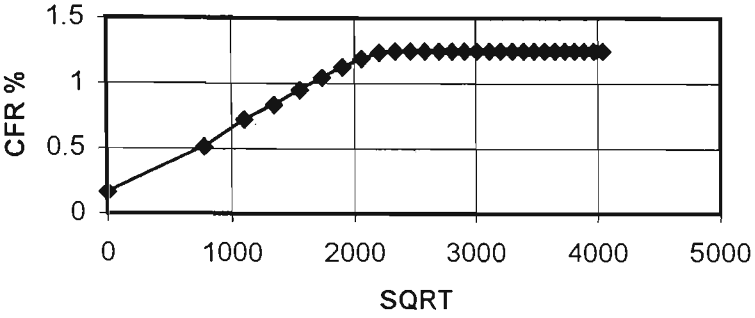
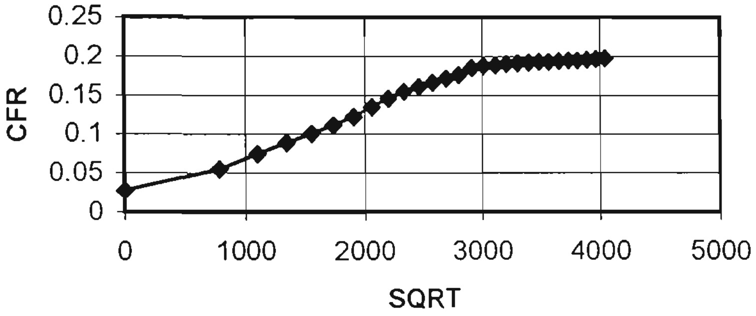


Figure 4.33 – CFR versus SQRT, Sodium Arsenate formulations Arsenic levels

Na_2HAsO_4 + *C*



Na_2HAsO_4 + *C-Fe*



Na_2HAsO_4 + *C-L*

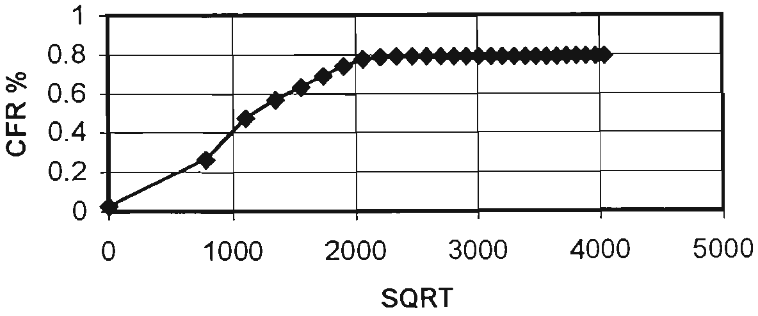
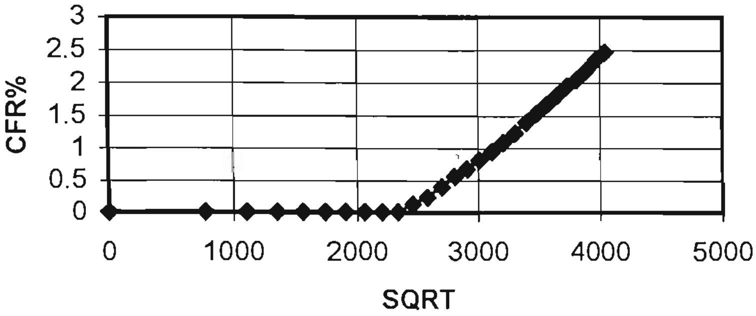
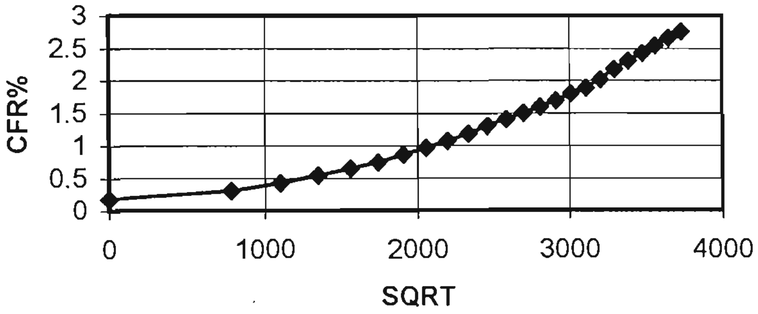


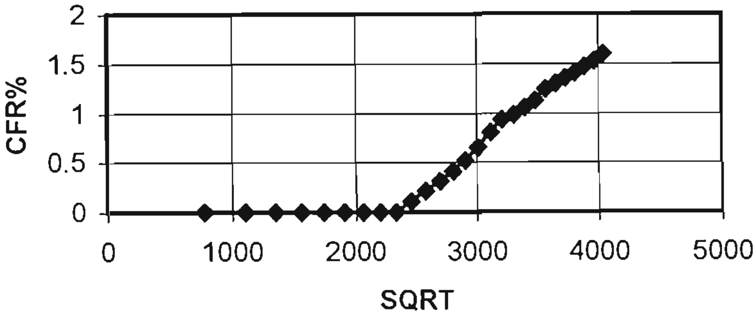
Figure 4.34 – CFR versus SQRT, Sodium Arsenate formulations Calcium levels



Na_2HAsO_4 + *C*



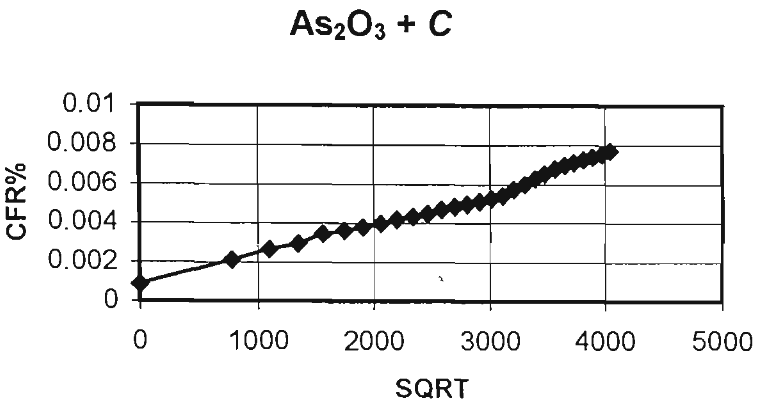
Na_2HAsO_4 + *C-Fe*

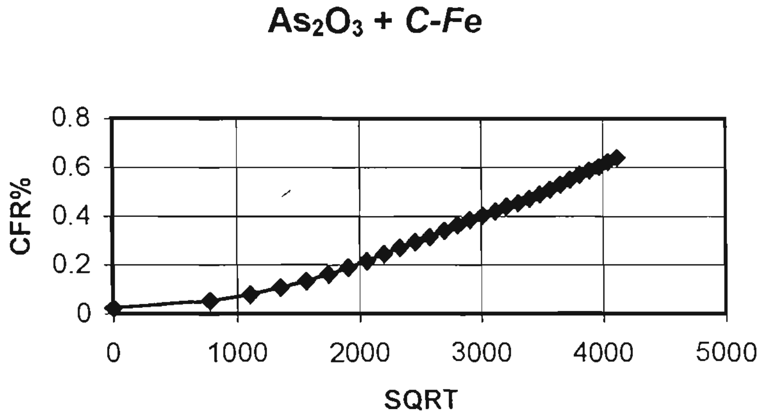


Na_2HAsO_4 + *C-L*

Figure 4.35 – CFR versus SQRT, Arsenic Trioxide formulations

Arsenic levels


As_2O_3 + *C*


As_2O_3 + *C-Fe*

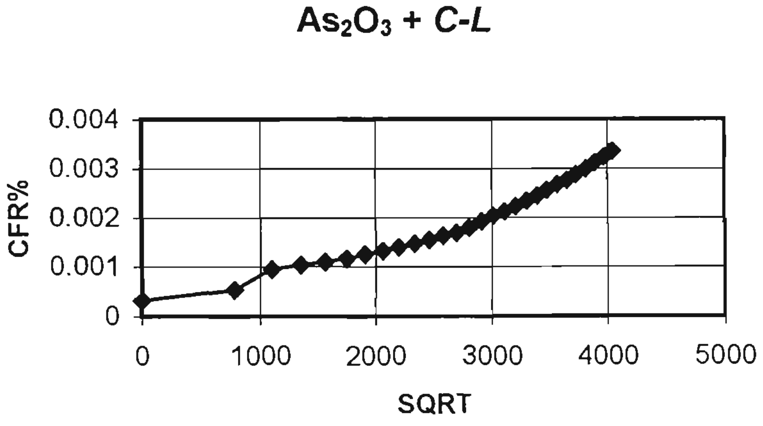
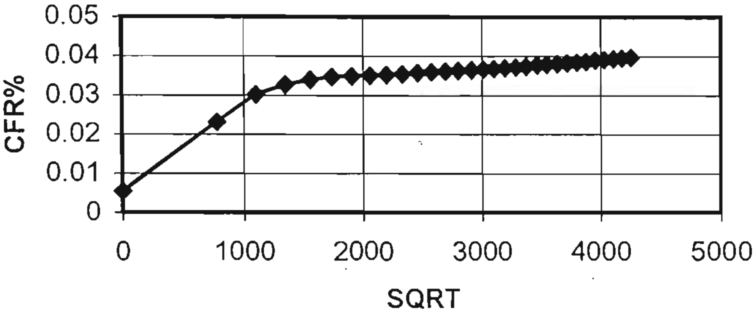
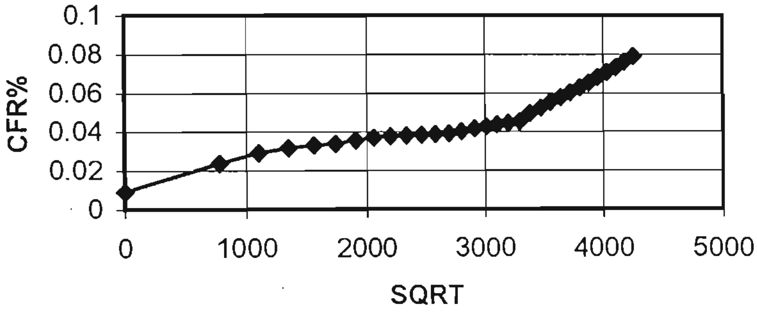

As_2O_3 + *C-L*

Figure 4.36 – CFR versus SQRT, Sodium Arsenite formulations Arsenic levels

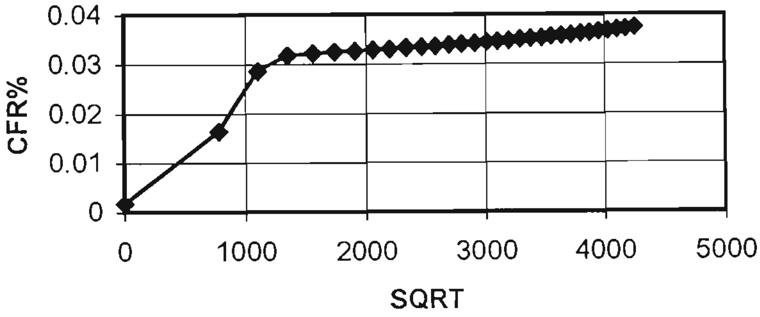
$NaAsO_2$ + *C*



$NaAsO_2$ + *C-Fe*



$NaAsO_2$ + *C-L*



4.2.2 Column (rainfall) leaching versus Column (BLC) leaching

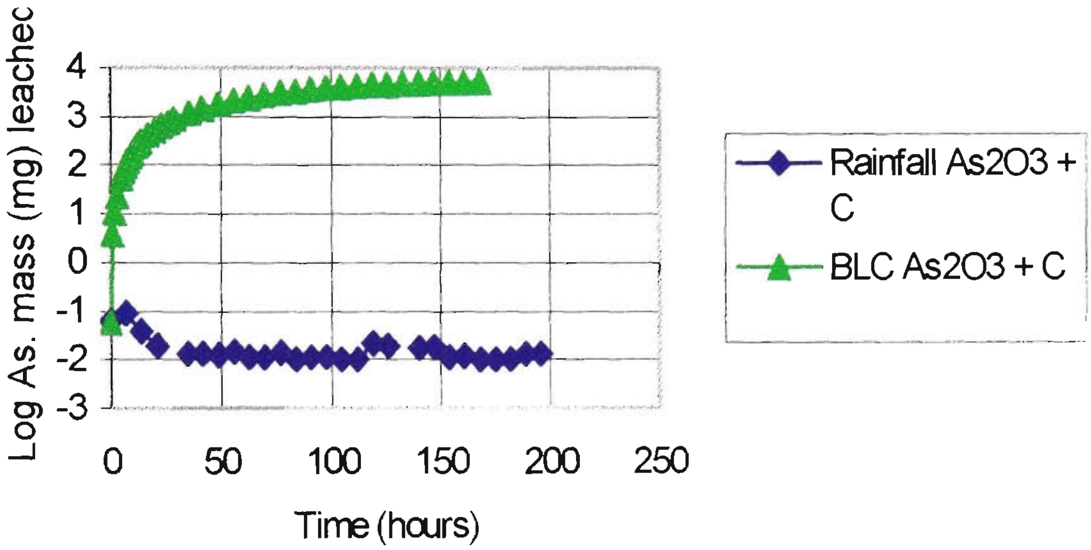
Despite the only differences between the two column leaching setups being the flow rate, the results obtained from the two column leaching tests were quite different. As described earlier in this chapter, when the Column (BLC) tests were utilized, the cement-only formulations were the most successful, despite these formulations having a lower Ca:As mole ratio, compared to the [cement + lime] formulations. However, when the Column (rainfall) leaching tests were performed, the majority of the results obtained mirrored those from the batch leaching tests, i.e., [the cement + iron] formulations were clearly the worst, while the [cement + lime] formulations, generally, were the best performing.

If the aim of the column leaching tests is to identify which formulations will behave the best when subjected to field conditions, it appears that this can only be achieved after careful selection of the flow rate. Those S/S formulations that leach the lowest levels of a hazardous constituent at one flow rate, do not necessarily behave the best when the flow rate is either increased or decreased as has been clearly shown in this chapter. Figures 4.37 through to 4.40 display the differences in the arsenic mass leached from the two column leaching tests. These figures contain a plot of the mass of arsenic leached (mg As/mL leachant) over the duration of the tests. From these figures, it is apparent that it is not possible to predict the levels or masses leached based on the results obtained from one particular column test employing a specific flow rate, for another column leaching test, using a different flow rate. The difference between the levels leached from the column leaching tests towards the latter periods of the investigation bears little resemblance to the difference in the solid to liquid ratio (573), which exists between the two tests. For example, the difference in the levels leached between the two column leaching tests for the As_2O_3 + *C-Fe* is merely a factor of 20, while the difference in the masses leached for the Na_2HAsO_4 + *C-L* is, approximately, a factor of 17,000.

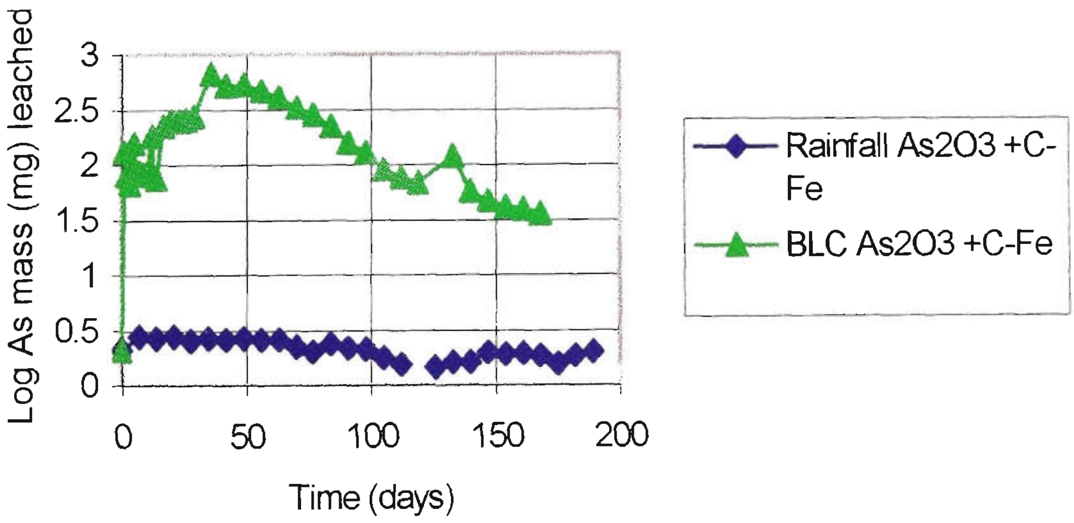
Figure 4.37 – Comparison between the masses of arsenic leached from the column(rainfall) and column (BLC) leaching tests

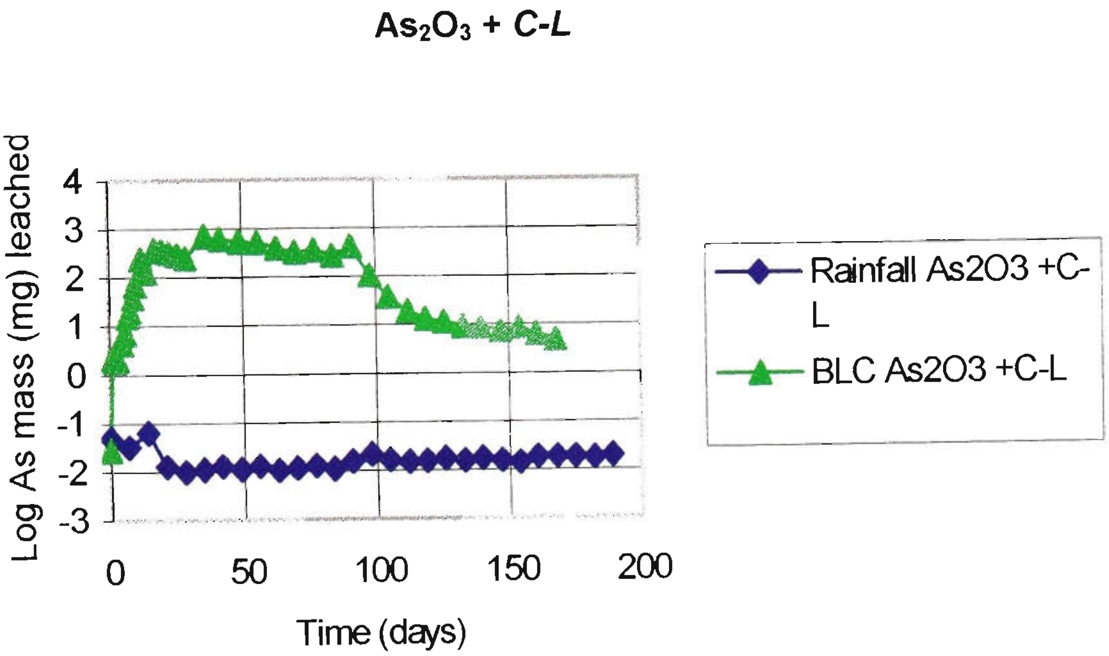
Arsenic Trioxide formulations

As_2O_3 + *C*



As_2O_3 + *C-Fe*

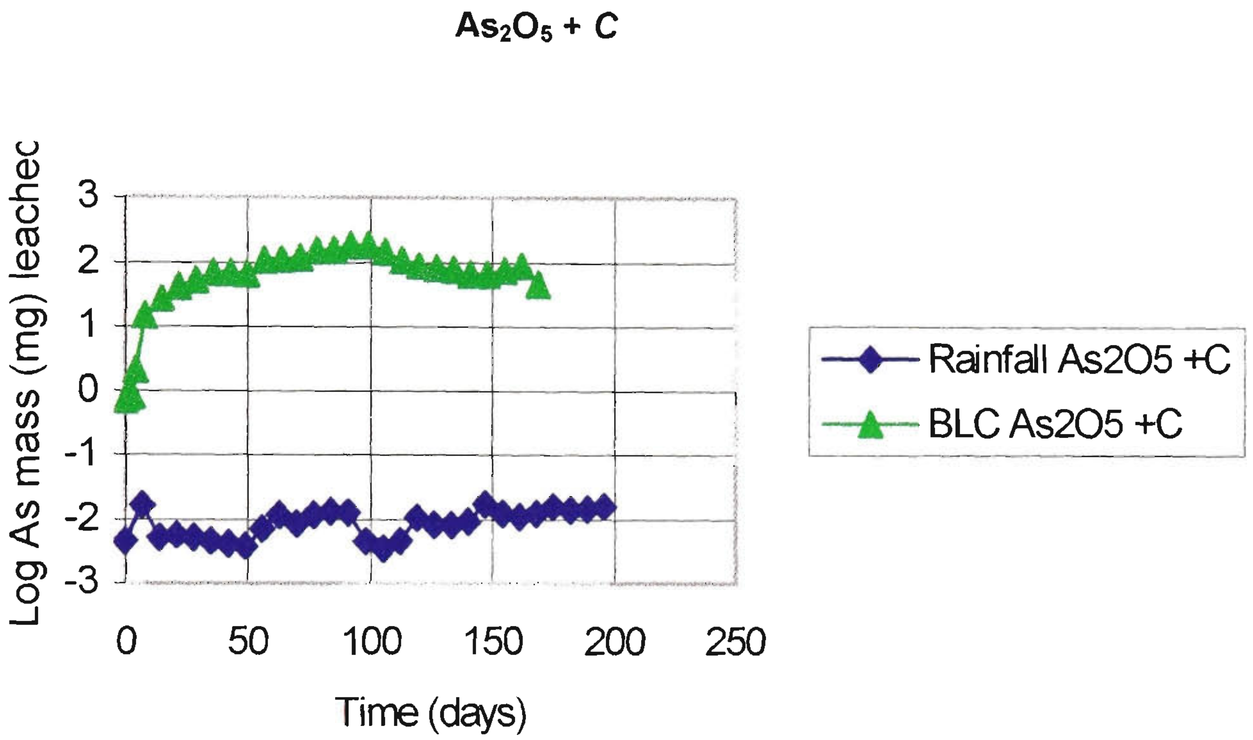


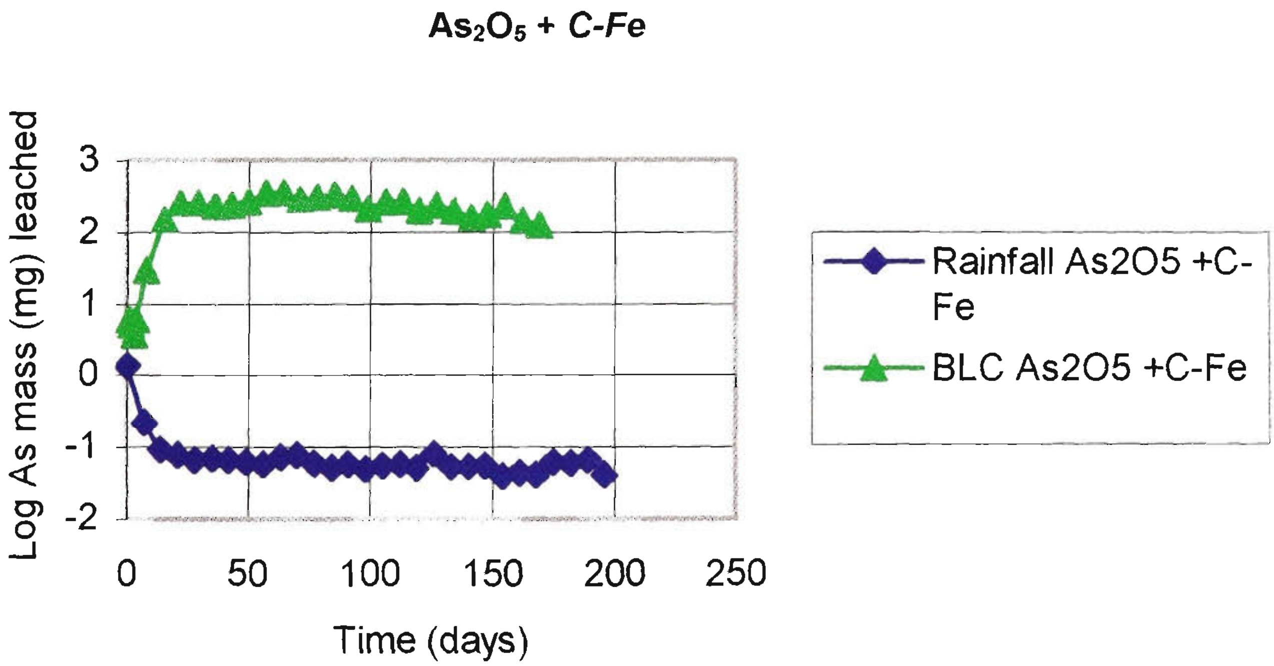


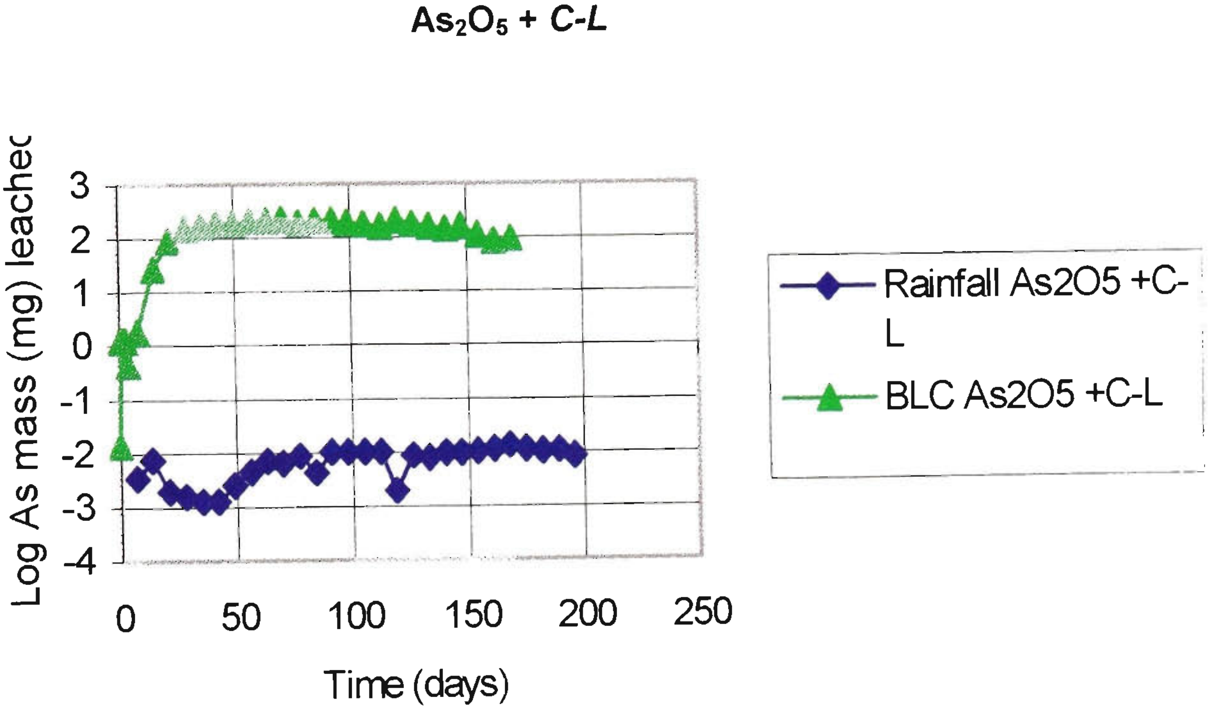
As_2O_3 + *C-L*

Log As mass (mg) leached
4
3
2
1
0
-1
-2
-3
0
50
100
150
200
Time (days)
Rainfall As2O3 +C-L
BLC As2O3 +C-L

Figure 4.38 – Comparison between the masses of arsenic leached from the column(rainfall) and column (BLC) leaching tests Arsenic Pentoxide formulations





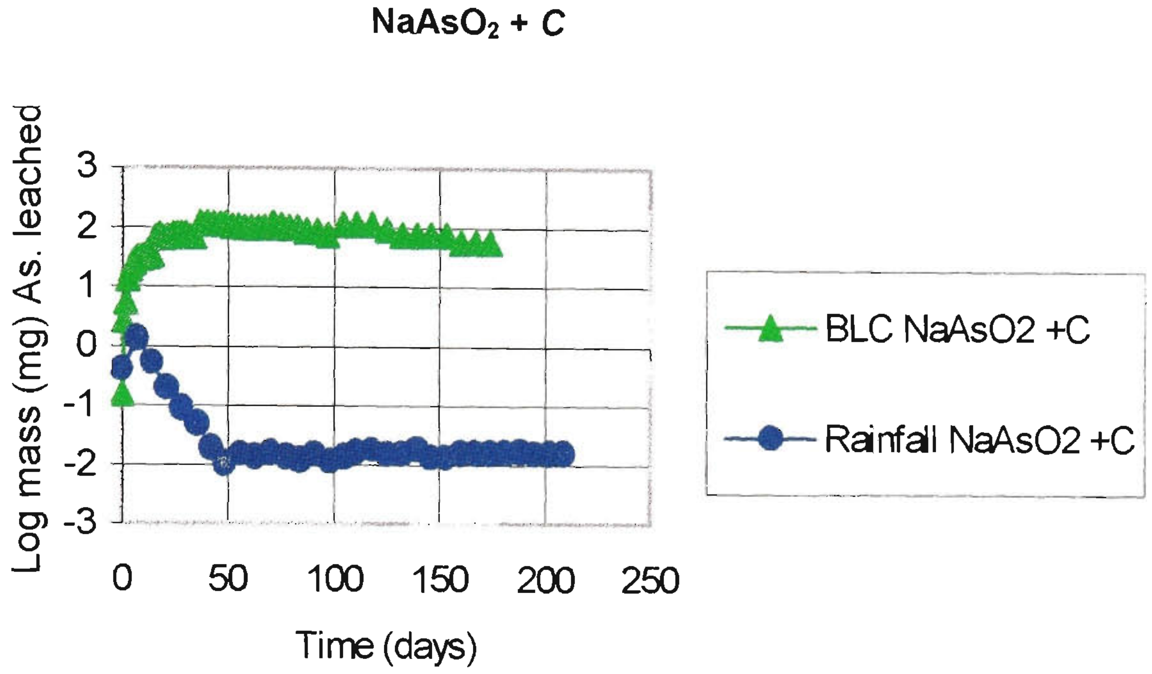


As_2O_5 + *C-L*

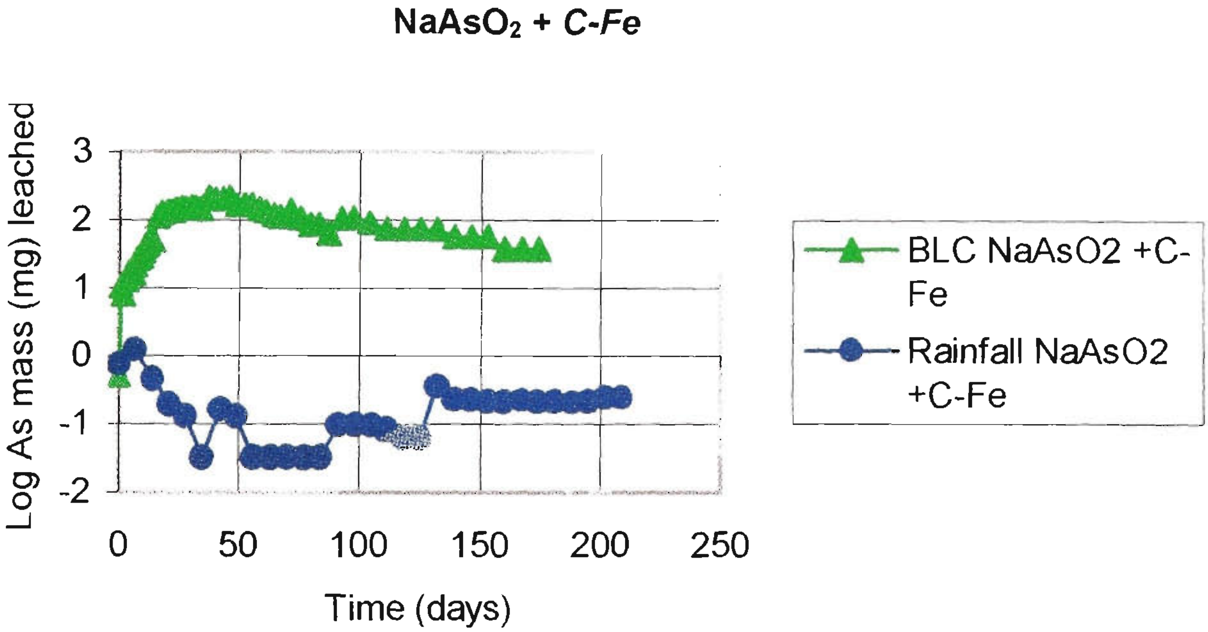
Log As mass (mg) leachec
3
2
1
0
-1
-2
-3
-4
0
50
100
150
200
250
Time (days)
Rainfall As2O5 +C-L
BLC As2O5 +C-L

Figure 4.39 – Comparison between the masses of arsenic leached from the column(rainfall) and column (BLC) leaching tests

Sodium Arsenite formulations



$NaAsO_2$ + *C*



$NaAsO_2$ + *C-Fe*

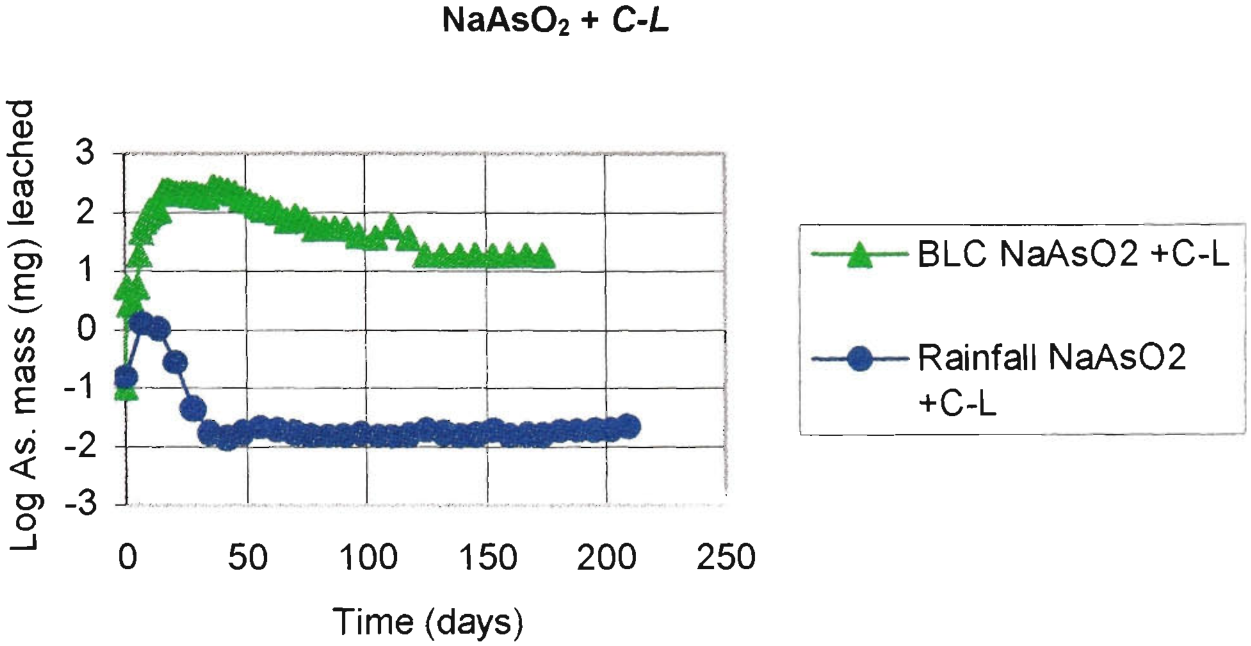
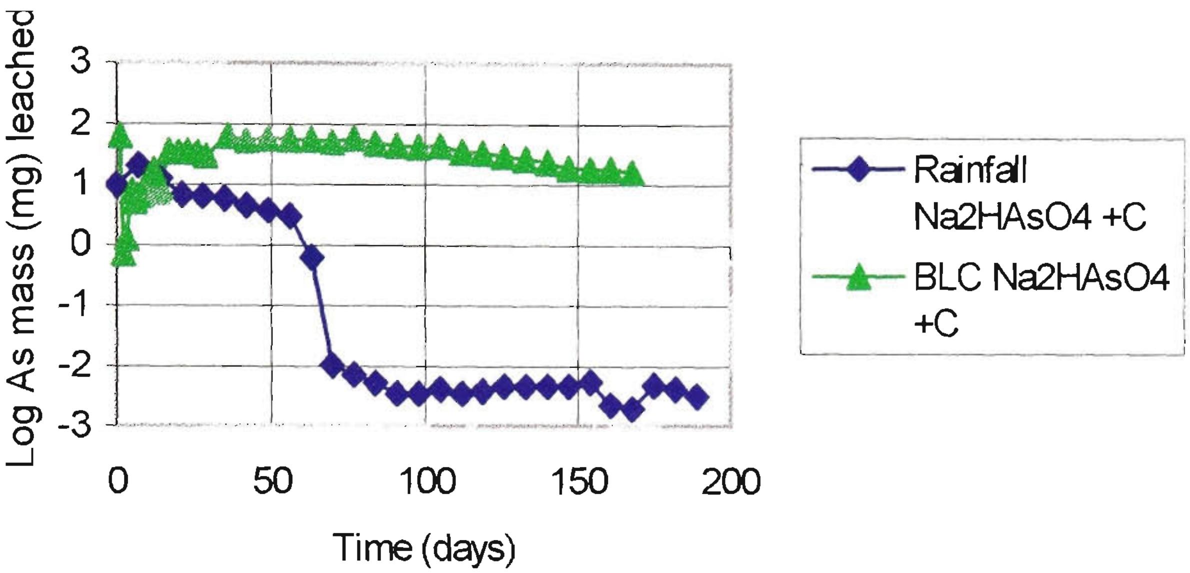

NaAsO$_2$ + *C-L*
Log As. mass (mg) leached
3
2
1
0
-1
-2
-3
0
50
100
150
200
250
Time (days)
BLC NaAsO2 +C-L
Rainfall NaAsO2 +C-L

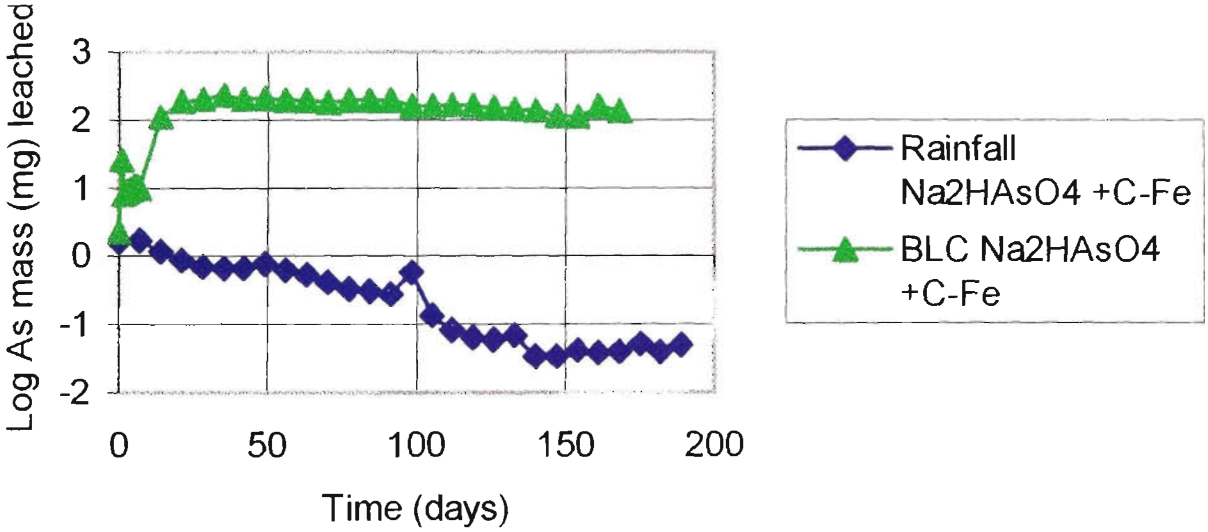
Figure 4.40 – Comparison between the masses of arsenic leached from the column (rainfall) and column (BLC) leaching tests

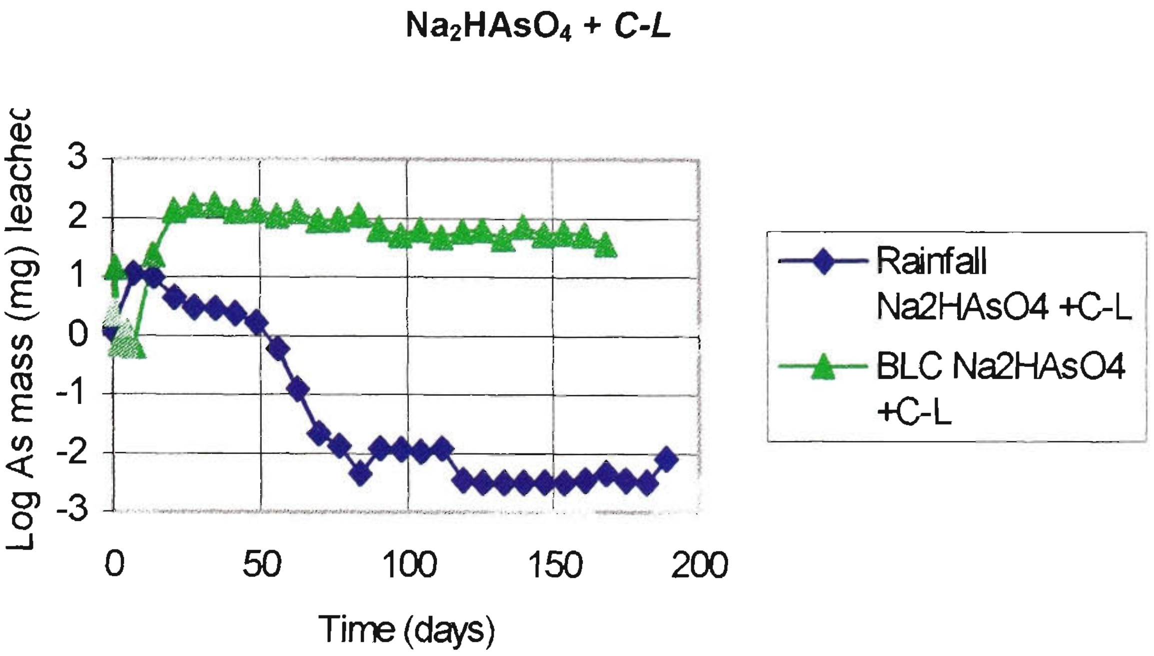
Sodium Arsenate formulations

Na_2HAsO_4 + *C*



Na_2HAsO_4 + *C-Fe*





From figure 4.40 and the Na_2HAsO_4 + *C* and the Na_2HAsO_4 + *C-L* formulations, it was evident that during the commencement of the column leaching tests, the column (rainfall) leaching tests leached arsenic masses which were approximately equal to the masses of arsenic leached from the column (BLC) leaching tests. While the arsenic masses leached from the two column leaching tests may have been comparable, there was a large discrepancy in the calcium masses leached as can be observed from table 4.2 which displays the total cumulative mass of calcium leached after 14 days of column leaching. Hence it is more than feasible that the Column (BLC) leaching tests would have leached substantially more arsenic as well. The larger calcium content of the column (BLC) leachates would have aided in the reduction of the arsenic leachate concentration after filtration due to the formation of the insoluble calcium-arsenic precipitate.

Table 4.2 - Comparison between the cumulative calcium masses (mg) leached from the column (rainfall) leaching tests and the column (BLC) leaching tests for the Na_2HAsO_4 + C formulation

Time	Ca mass (mg) Column (rainfall)	Ca mass (mg) Column (BLC)
7 days	0.8352	3900
14 days	0.8704	5166

4.2.3 Column (Rainfall) leaching versus Batch Leaching

Figures 4.41 through to 4.44 compare the total cumulative masses of arsenic leached from the Column (rainfall) leaching tests, which had a duration of 6 months, with the Australian Bottle Leaching Procedure (AS 4439.3), which consisted of a mere 18 hours of leaching. From figures 4.41, 4.42 and 4.43, which compare the masses of arsenic leached from the two leaching tests for the arsenic trioxide, arsenic pentoxide, and sodium arsenite salts respectively, an assessment can be made of the leaching severity of the current Australian Regulatory leaching test, the Australian Bottle Leaching Procedure (AS 4439.7). In general, the total cumulative mass of arsenic leached from six months of continual column leaching is less than the total arsenic mass leached from the 18 hour ABLP. However, due to the large masses of arsenic leached initially, the reverse of this scenario was true for the sodium arsenate salts. For the sodium arsenate salts, the column (rainfall) leaching tests leached a considerably larger mass of arsenic than did the Australian Bottle Leaching Procedure (AS 4439.3). However, although figure 4.44 suggests that the column (rainfall) leaching tests leached considerably larger masses of arsenic, the opposite is more likely the case. Agitated systems, where the particles remain in suspension and do not settle, usually result in very high degrees of mixing and mass transfer. Consequently, it is expected that the batch leaching tests would have leached larger quantities of arsenic as well as calcium, thereby allowing for the formation of an insoluble calcium-arsenic compound and resulting in a lower arsenic leachate concentration after filtering.

Figure 4.41 – Total mass of arsenic leached (mg) for the Arsenic Trioxide formulations

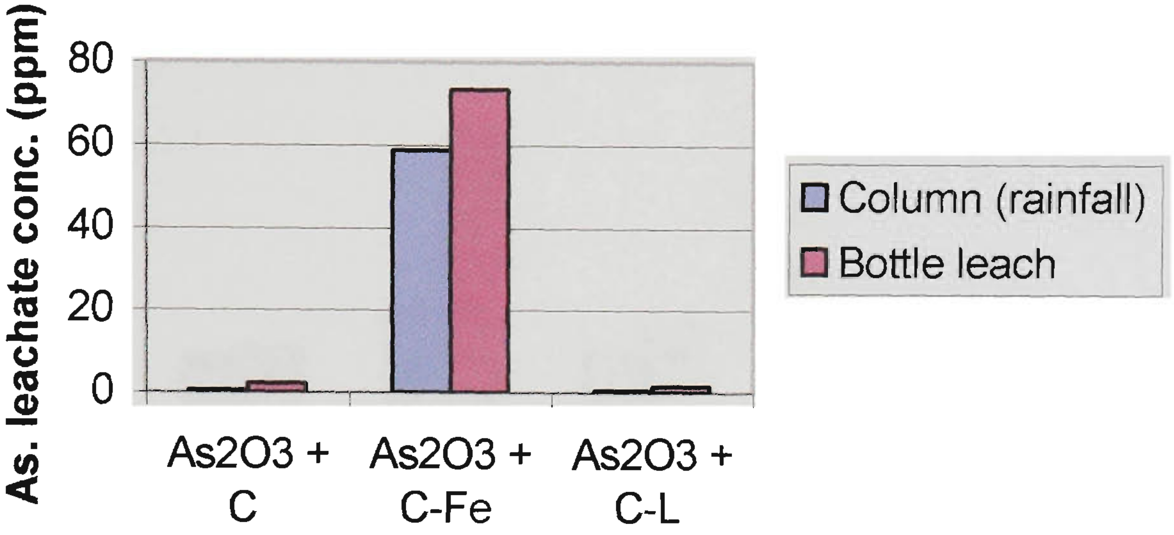


Figure 4.42 – Total mass of arsenic leached (mg) for the Arsenic Pentoxide formulations

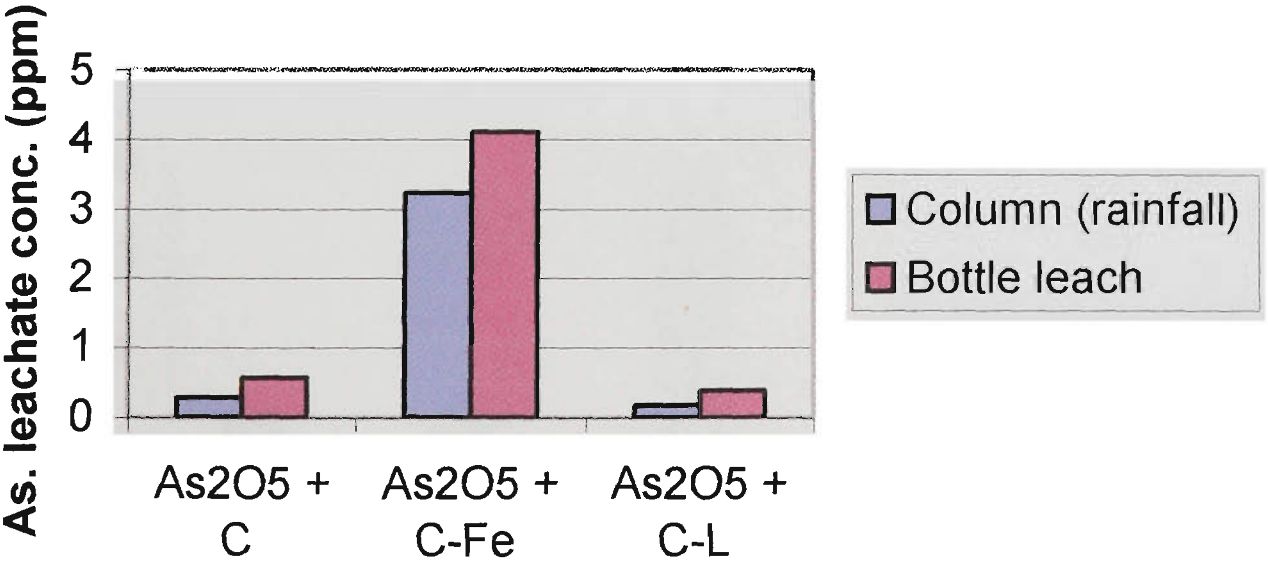


Figure 4.43 – Total mass of arsenic leached (mg) for the Sodium Arsenite formulations

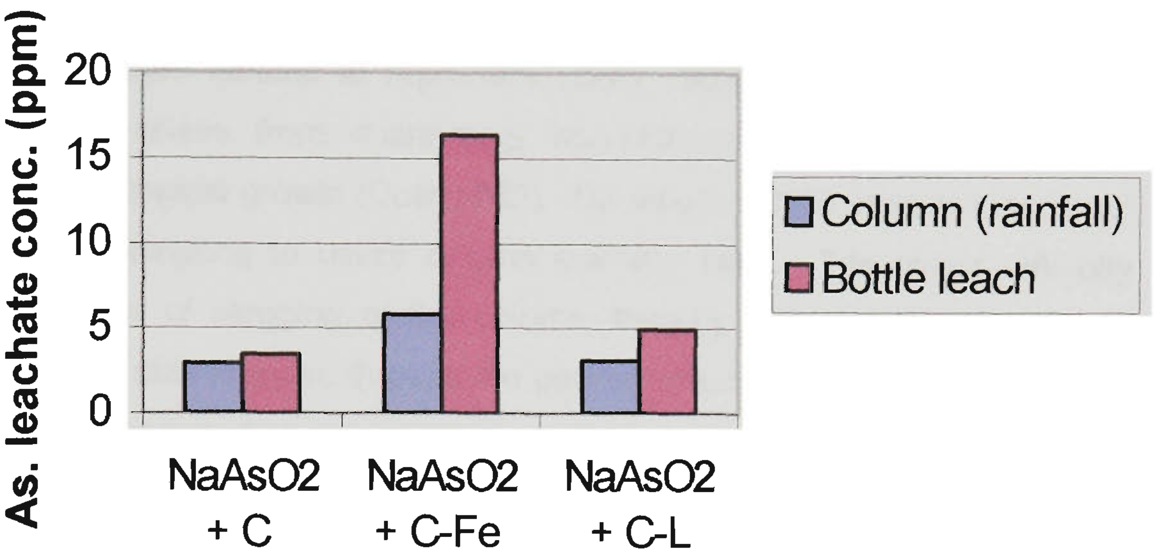
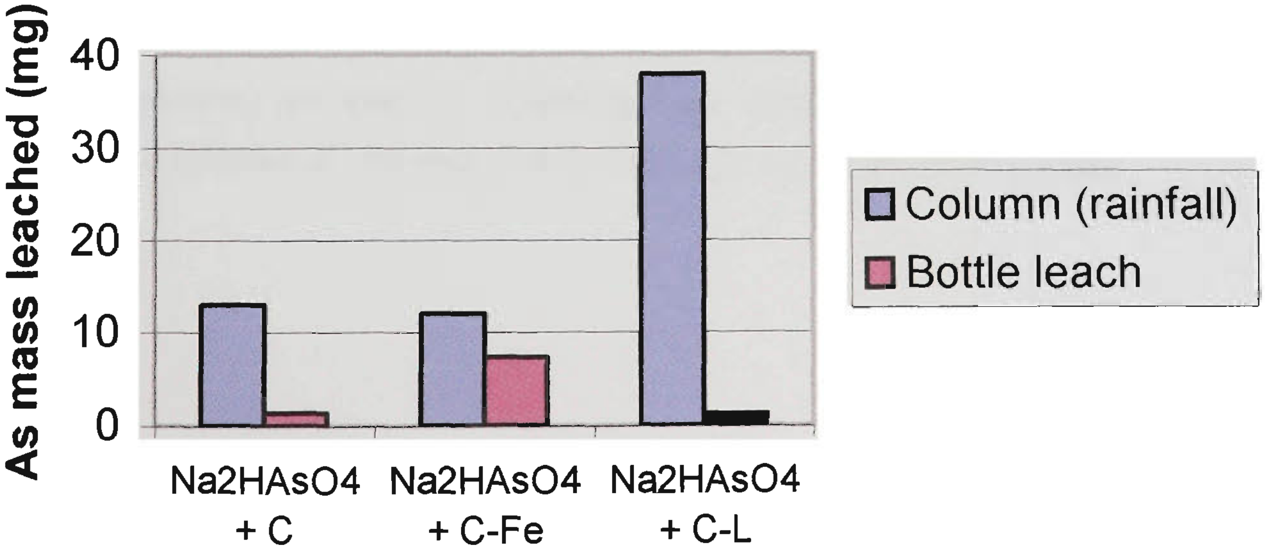


Figure 4.44 – Total mass of arsenic leached (mg) for the Sodium Arsenate formulations



4.3 Column Leaching Precision

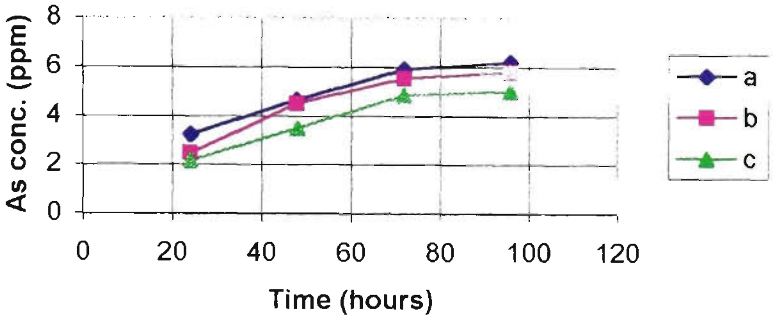
Although column tests are often considered to be more representative of field conditions than batch tests, they have often been criticized because the results generated are often difficult to reproduce (Cote 1982). The problem of poor precision often arises from channeling, non-uniform packing of the waste, clogging and biological growth (Cote 1982). De Villers (1995) encountered great difficulties in attempting to utilize column leaching tests. The major difficulty encountered was of clogging of the column, thereby reducing the amount of liquid which was able to move through the packed column. The flow rate through the column was reduced to an extremely small throughput within a few days. No such problems were encountered with the simpler but yet still effective column leaching setups that were utilized in this study (chapter 2).

Figures 4.45 through to 4.50 display the reproducibility obtained for the Column (BLC) leaching tests. While the precision exhibited is, perhaps, poorer than that exhibited by the sequential leaching (water) tests, it is still adequate to identify the leaching trends exhibited by the various S/S formulations.

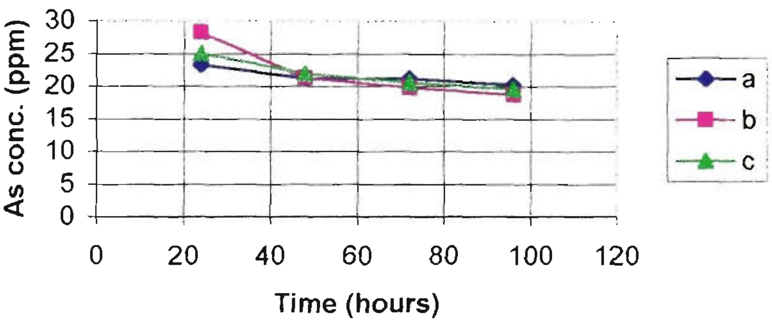
The precision exhibited by the column (rainfall) leaching tests, (figures 4.51, 4.52, 4.53 and 4.45) was more-than-pleasing, given that these tests employed a 'down-flow' scheme in place of the preferred 'up-flow' mode. The 'up-flow' mode allows for a more thorough dispersion of the leachant throughout the waste sample, thereby ensuring an adequate waste/leachant interface is established, and minimizing the chances of channels forming through the length of the waste column.

Figure 4.45 - Precision of the Column (BLC) leaching tests
Arsenic Trioxide formulation

As_2O_3 + *C*



As_2O_3 + *C-Fe*



As_2O_3 + *C-L*

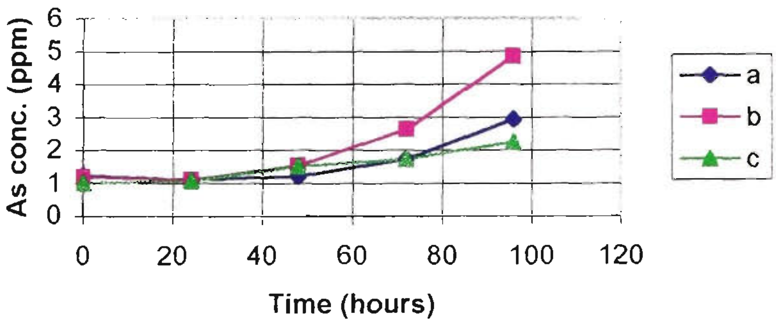
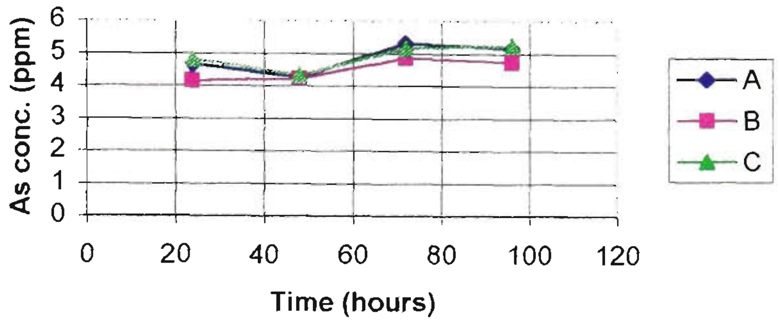
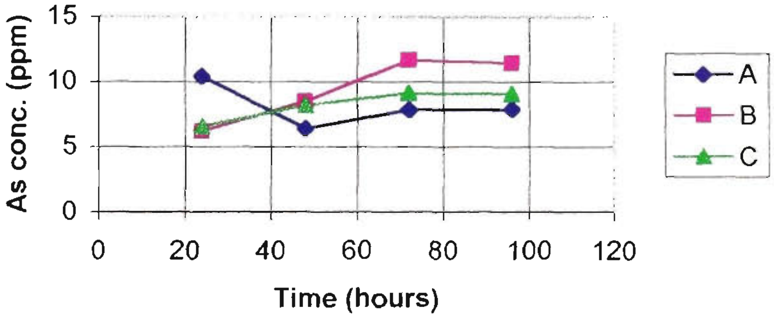


Figure 4.46 - Precision of the Column (BLC) leaching tests Sodium Arsenite formulation

$NaAsO_2$ + *C*



$NaAsO_2$ + *C-Fe*



$NaAsO_2$ + *C-L*

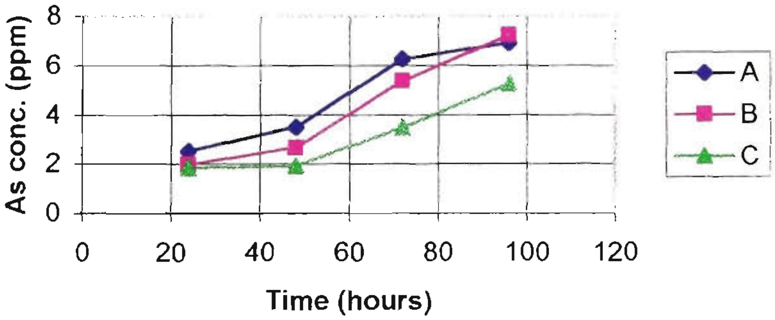
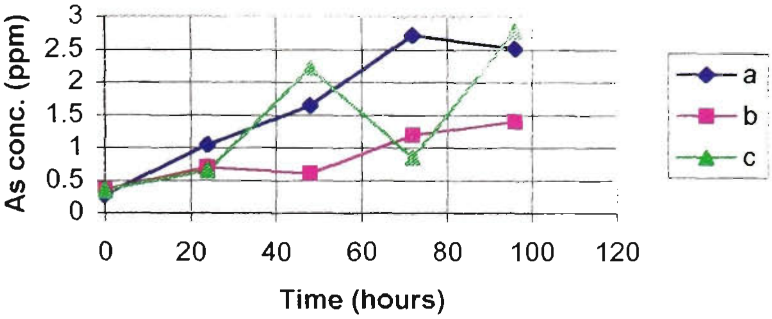


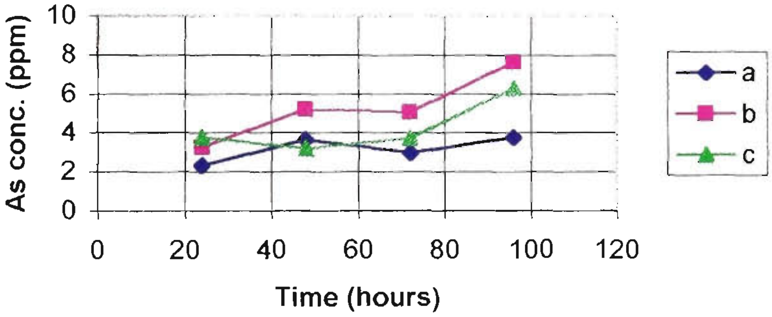
Figure 4.47 - Precision of the Column (BLC) leaching tests

Arsenic Pentoxide formulation

As_2O_5 + *C*



As_2O_5 + *C-Fe*



As_2O_5 + *C-L*

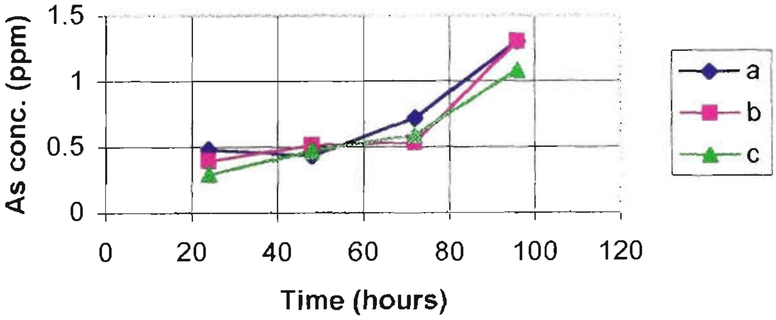
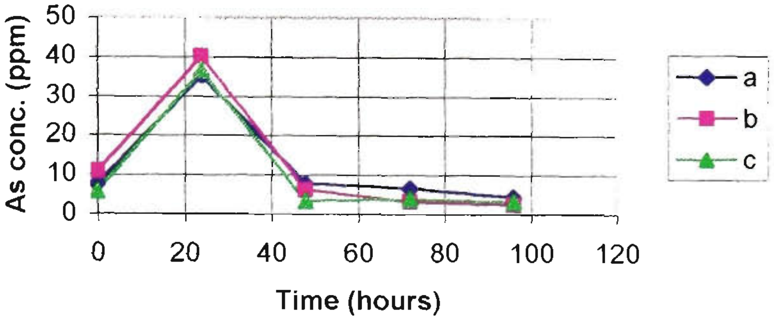
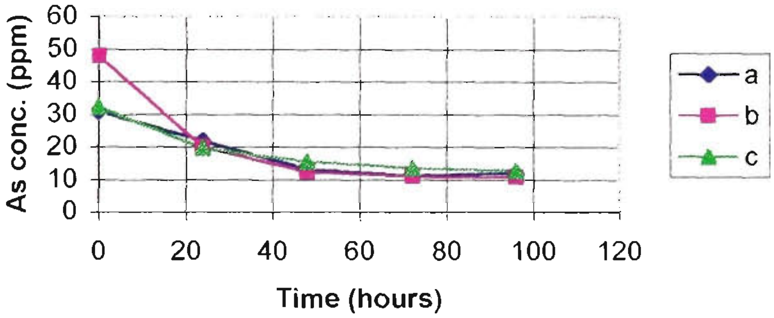


Figure 4.48 - Precision of the Column (BLC) leaching tests Sodium Arsenate formulation

Na_2HAsO_4 + *C*



Na_2HAsO_4 + *C-Fe*



Na_2HAsO_4 + *C-L*

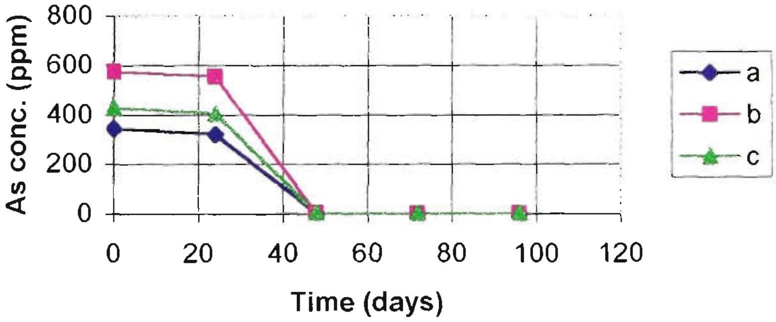
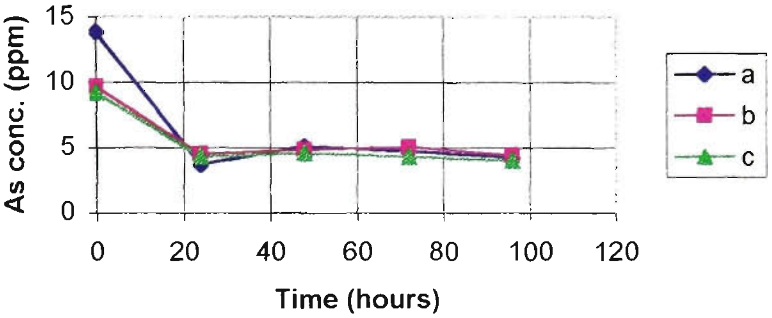
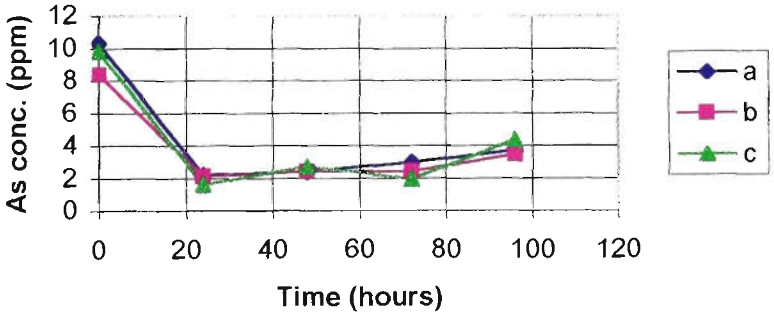


Figure 4.49 - Precision of the Column (BLC) leaching tests
Lead Arsenate formulations – *Arsenic concentrations*

$PbHAsO_4$ + *C*



$PbHAsO_4$ + *C-Fe*



$PbHAsO_4$ + *C-L*

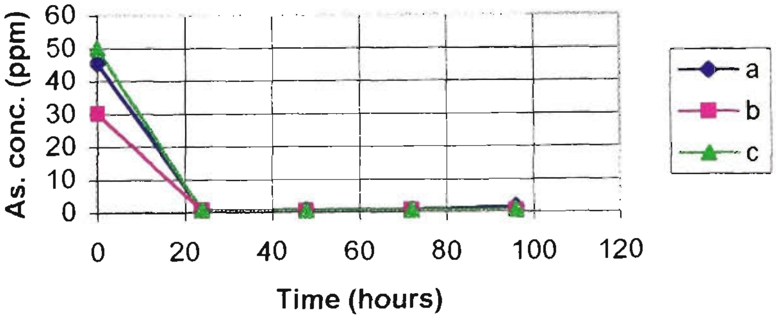
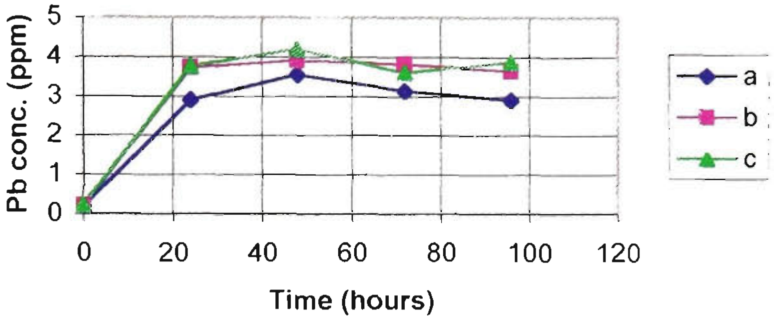
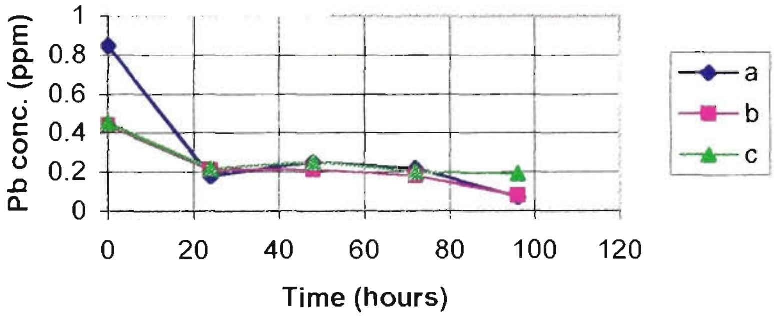


Figure 4.50 - Precision of the Column (BLC) leaching tests Lead Arsenate formulations – *Lead concentrations*

$PbHAsO_4$ + *C*



$PbHAsO_4$ + *C-Fe*



$PbHAsO_4$ + *C-Fe*

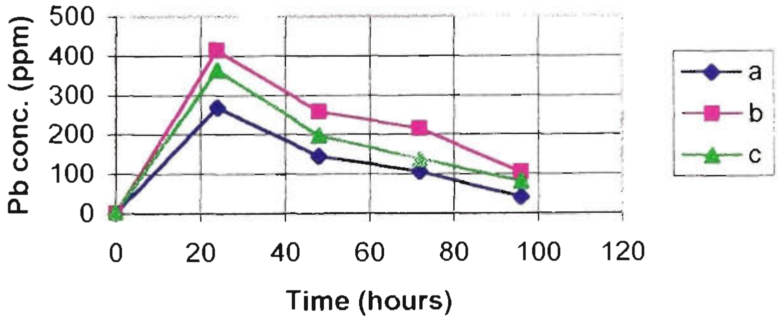
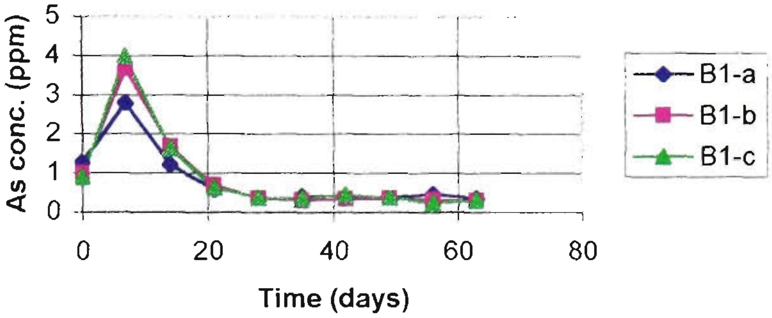
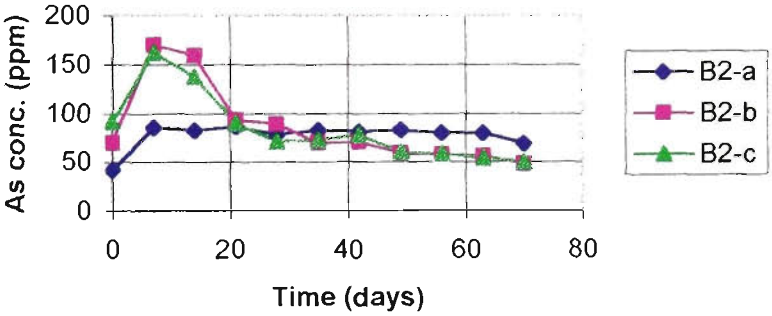


Figure 4.51 - Precision of the Column (Rainfall) leaching tests
Arsenic Trioxide formulation

As_2O_3 + *C*



As_2O_3 + *C-Fe*



As_2O_3 + *C-L*

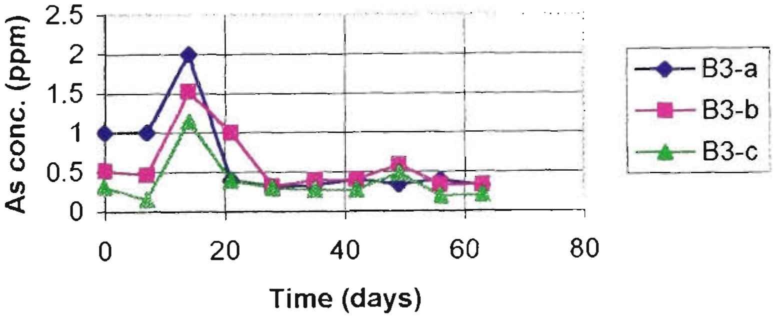
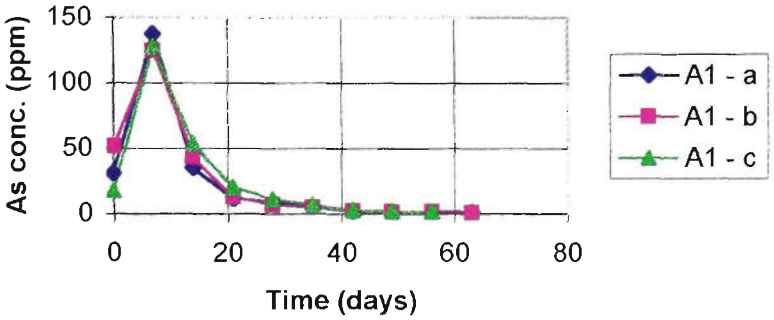
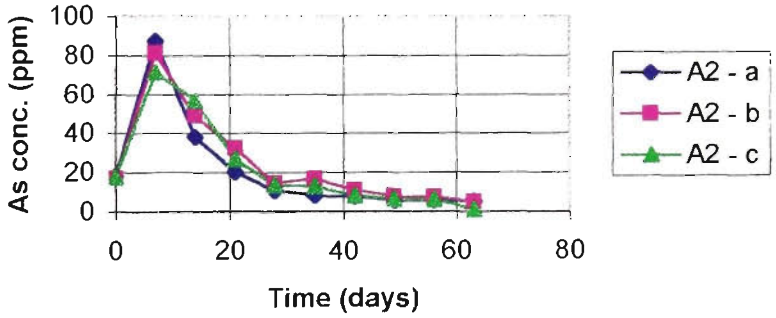


Figure 4.52 - Precision of the Column (Rainfall) leaching tests
Sodium Arsenite formulation

$NaAsO_2$ + *C*



$NaAsO_2$ + *C-Fe*



$NaAsO_2$ + *C-L*

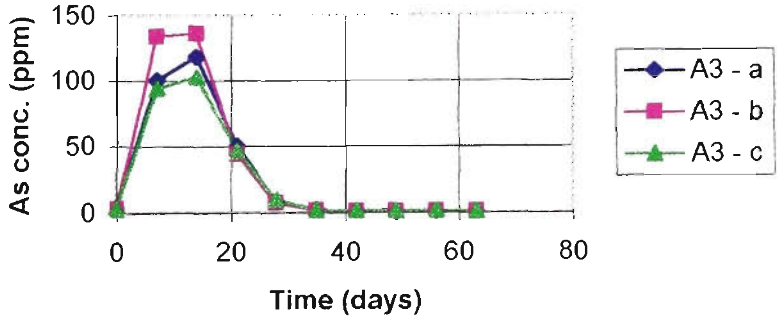
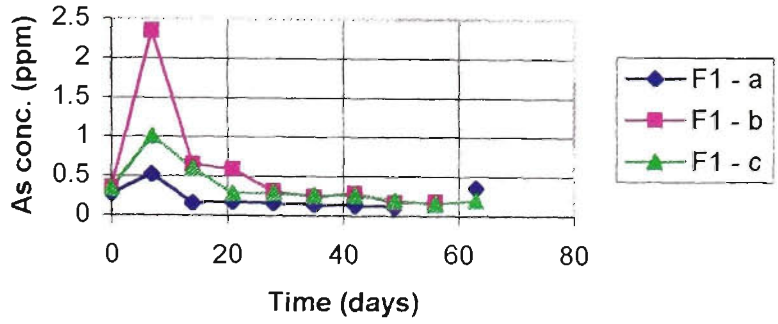
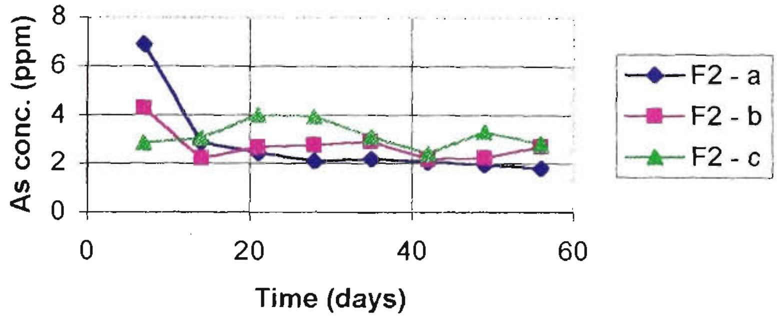


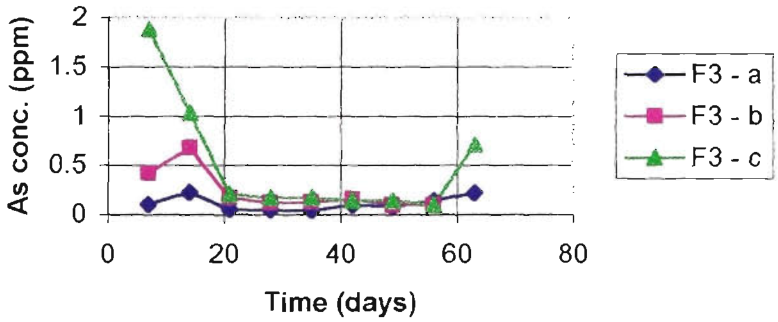
Figure 4.53 - Precision of the Column (Rainfall) leaching tests Arsenic Pentoxide formulation



As_2O_5 + *C*



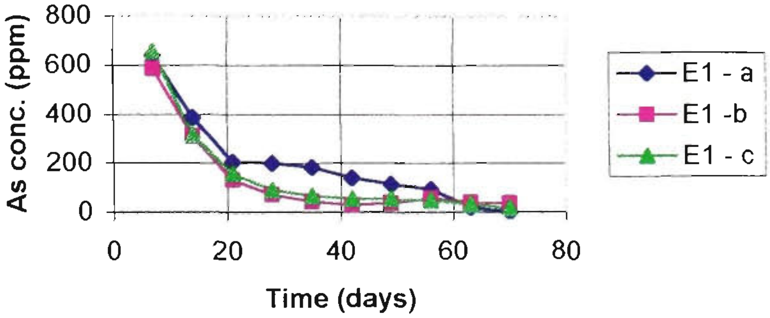
As_2O_5 + *C-Fe*



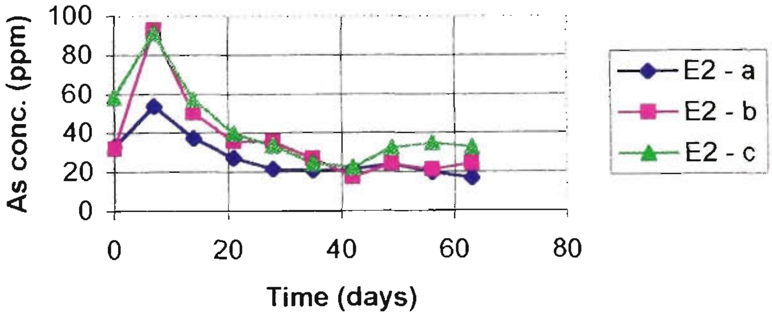
As_2O_5 + *C-L*

Figure 4.54 - Precision of the Column (Rainfall) leaching tests
Sodium Arsenate formulation

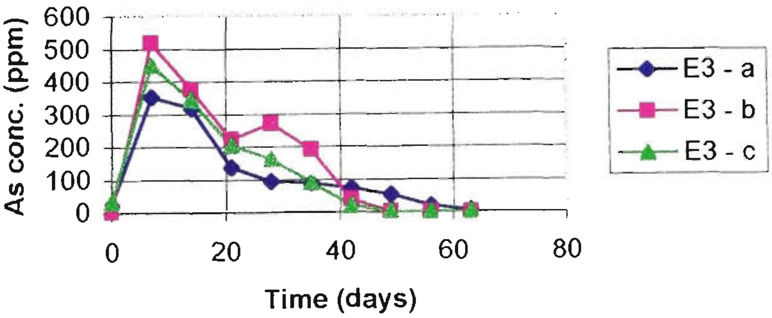
Na_2HAsO_4 + *C*



Na_2HAsO_4 + *C-Fe*



Na_2HAsO_4 + *C-L*



4.4 pH

Figures 4.55 to 4.58 indicate that the pH values for the leachates collected from the column (BLC) leaching tests, for any given arsenic compound are similar, despite the varying initial calcium contents of the S/S formulations. The similarity of the pHs of the leachates that were collected from the column (BLC) leaching tests may be partly attributable to the comparable calcium concentrations that were leached by all three formulations for any of the arsenic compounds. The similarity between the calcium concentrations leached can be seen in figure 4.59, which displays the calcium concentrations leached by the As_2O_5 + *C,* As_2O_5 + *C-Fe* and As_2O_5 + *C-L* formulations when subjected to the column (BLC) leaching tests.

The leachates collected for the various S/S formulations from the column (rainfall) leaching tests exhibited clear differences in pH, unlike the leachates collected from the column (BLC) leaching tests. As can be observed in figures 4.60, 4.61, 4.62 and 4.63, the leachates collected from the [cement + iron(II)] samples had a noticeably lower pH than the other two formulations, i.e. either the cement only, or the cement + lime formulations. Not surprisingly, given the relationship that is known to exist between the calcium levels and pH for both the column (BLC) leaching tests and the batch leaching tests (Chapter 3), the [cement + iron] formulations that exhibited distinctively lower pHs also yielded lower calcium concentrations as can be observed from figure 4.64.

Figure 4.55 - pH values recorded for the sodium arsenate leachates collected from the column (BLC) leaching tests

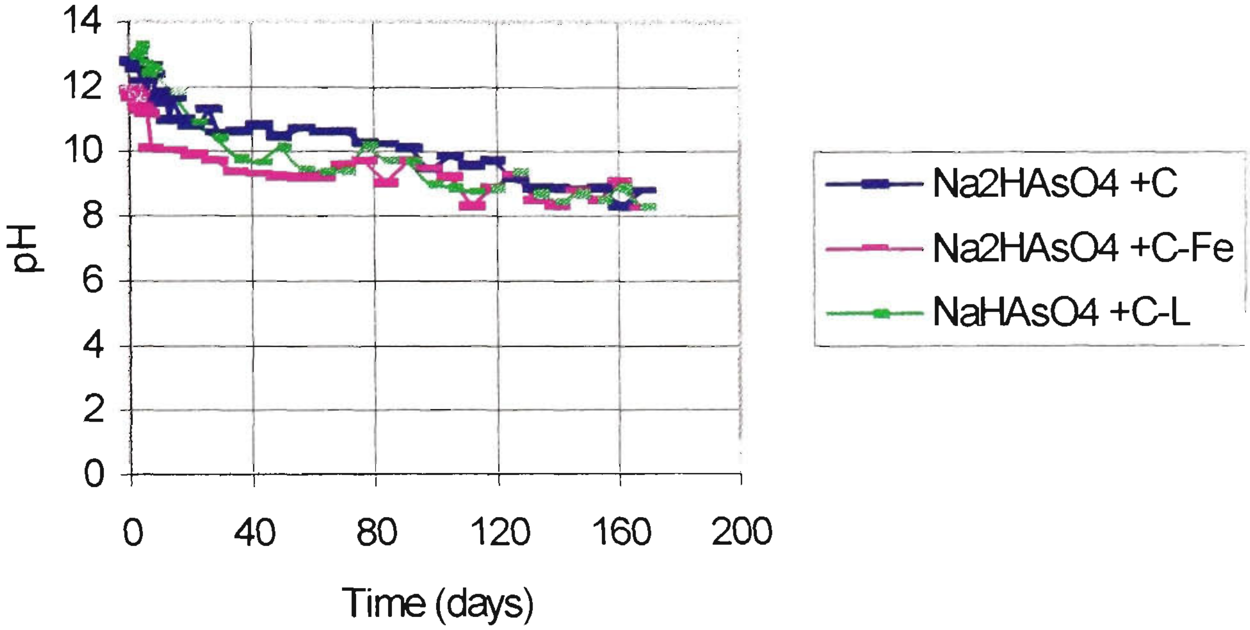


Figure 4.56 - pH values recorded for the sodium arsenite leachates collected from the column (BLC) leaching tests

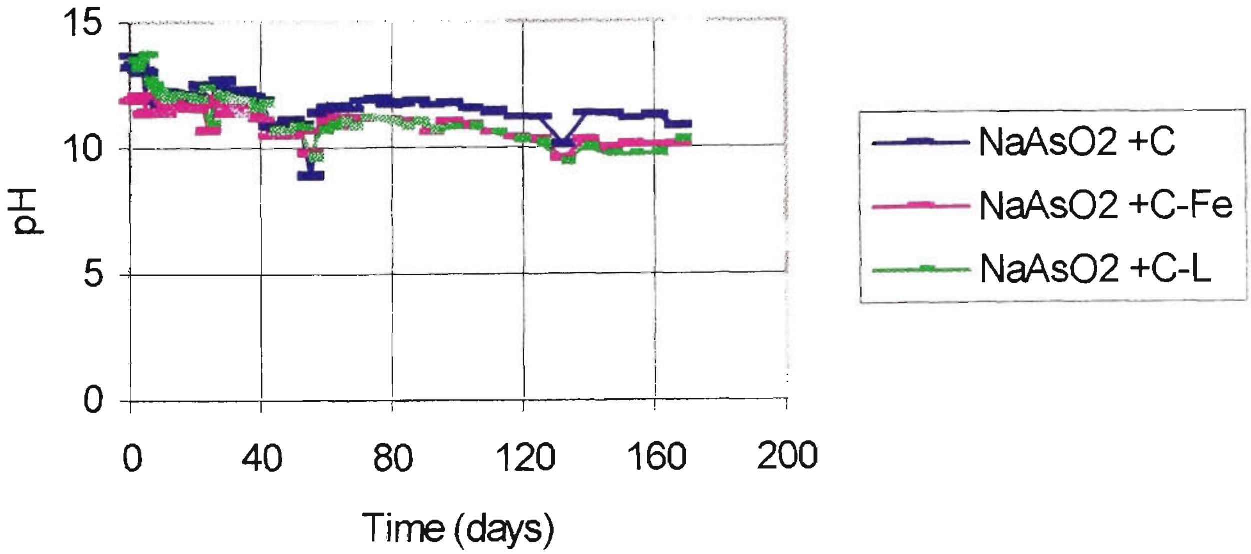


Figure 4.57 - pH values recorded for the arsenic trioxide leachates collected from the column (BLC) leaching tests

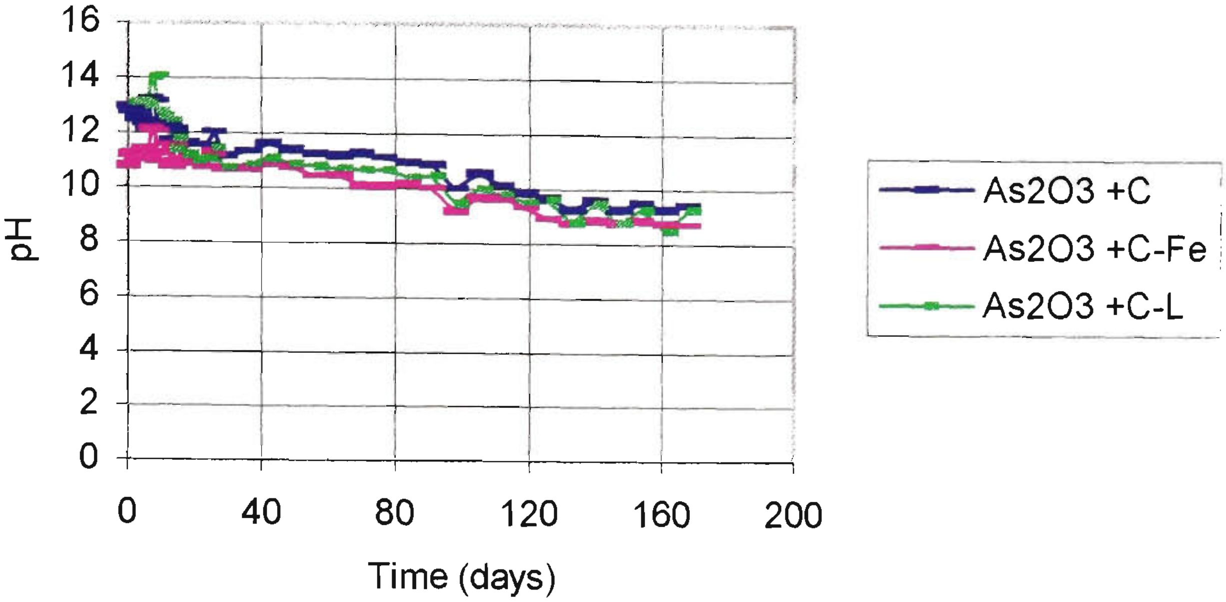


Figure 4.58 - pH values recorded for the arsenic pentoxide leachates collected from the column (BLC) leaching tests

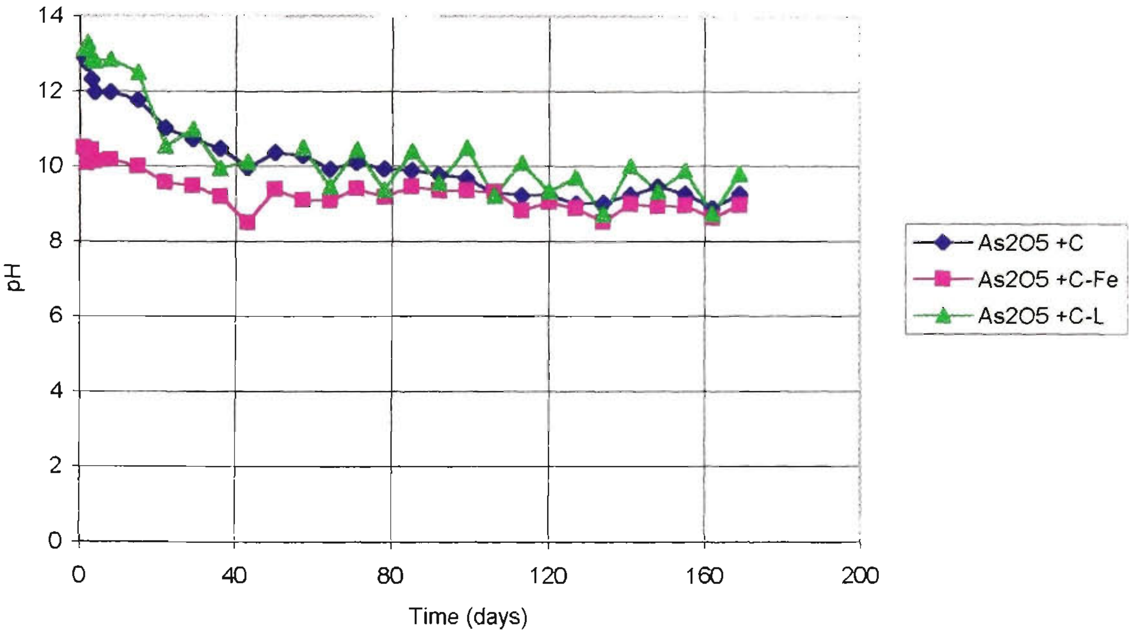


Figure 4.59 – Calcium leachate concentrations for the arsenic pentoxide formulations when subjected to the Column (BLC) leaching tests

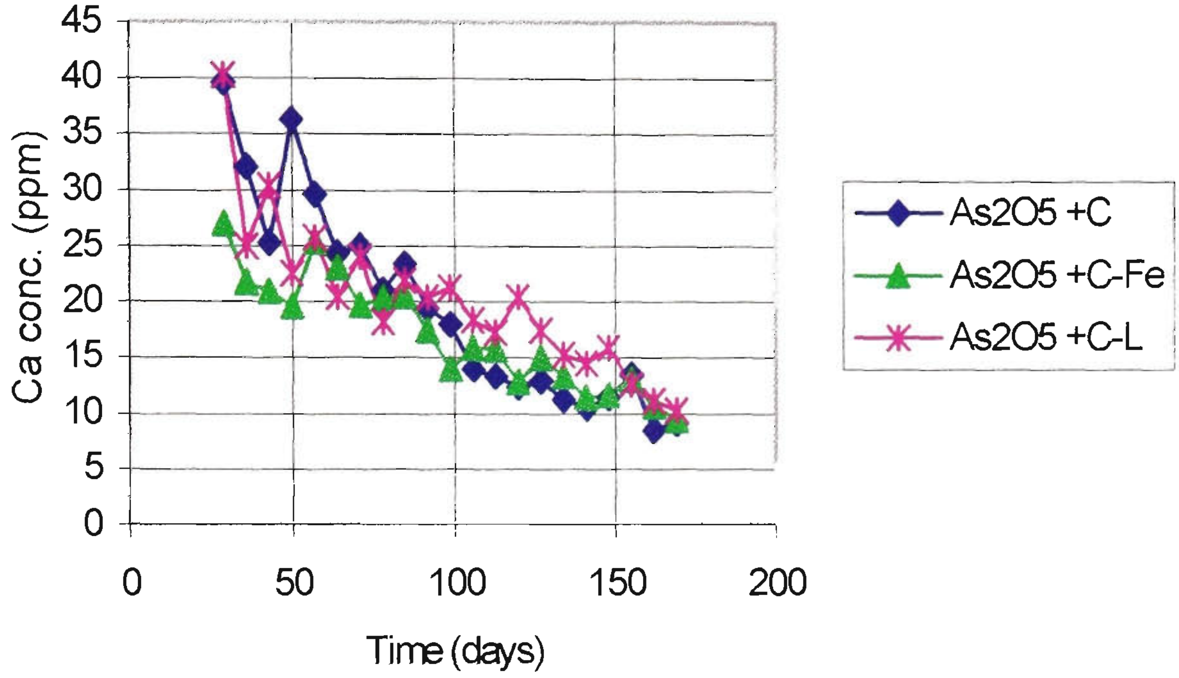


Figure 4.60 - pH values recorded for the sodium arsenate leachates collected from the column (Rainfall) leaching tests

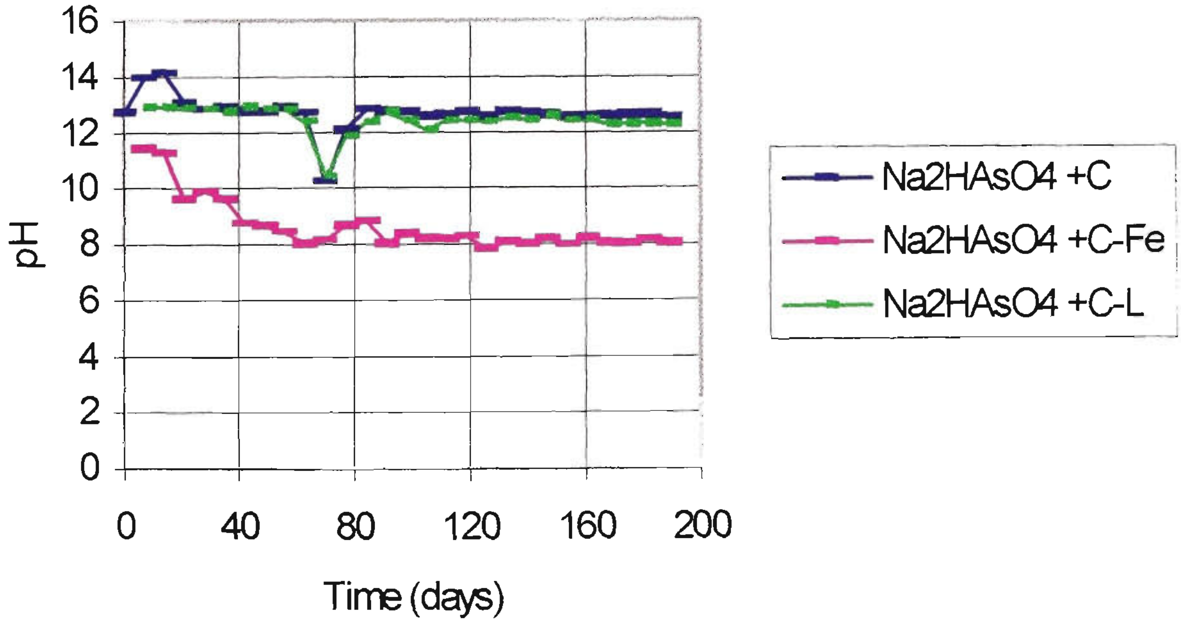


Figure 4.61 - pH values recorded for the sodium arsenite leachates collected from the column (Rainfall) leaching tests

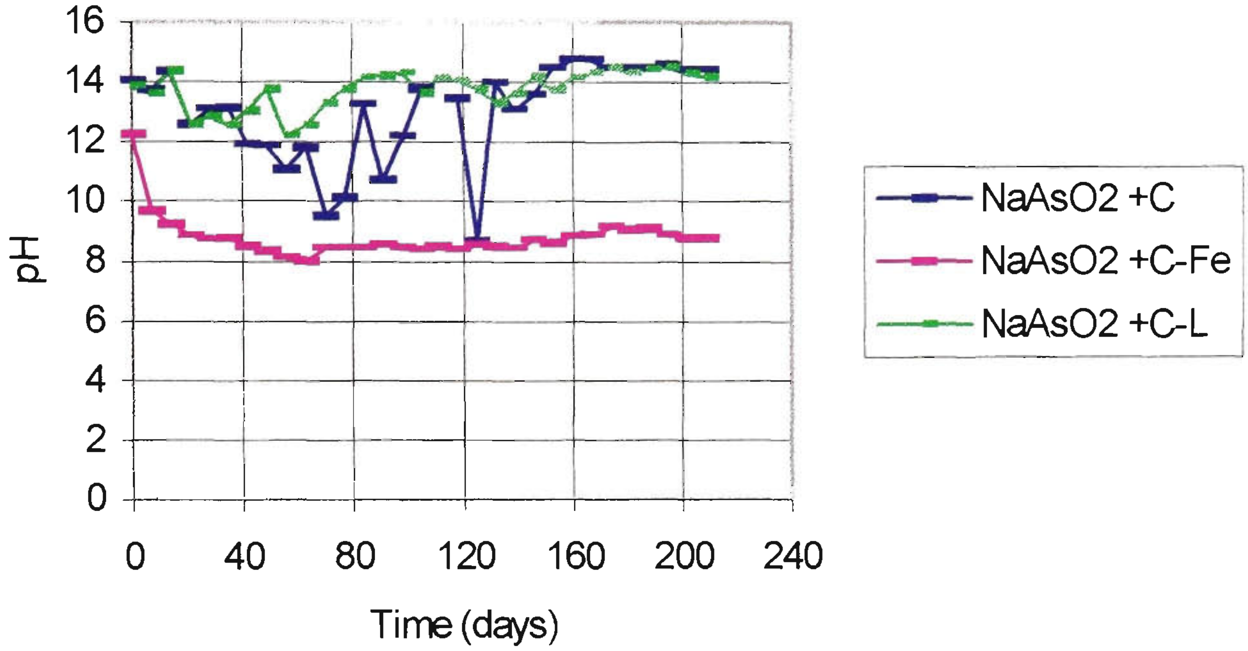


Figure 4.62 - pH values recorded for the arsenic trioxide leachates collected from the column (Rainfall) leaching tests

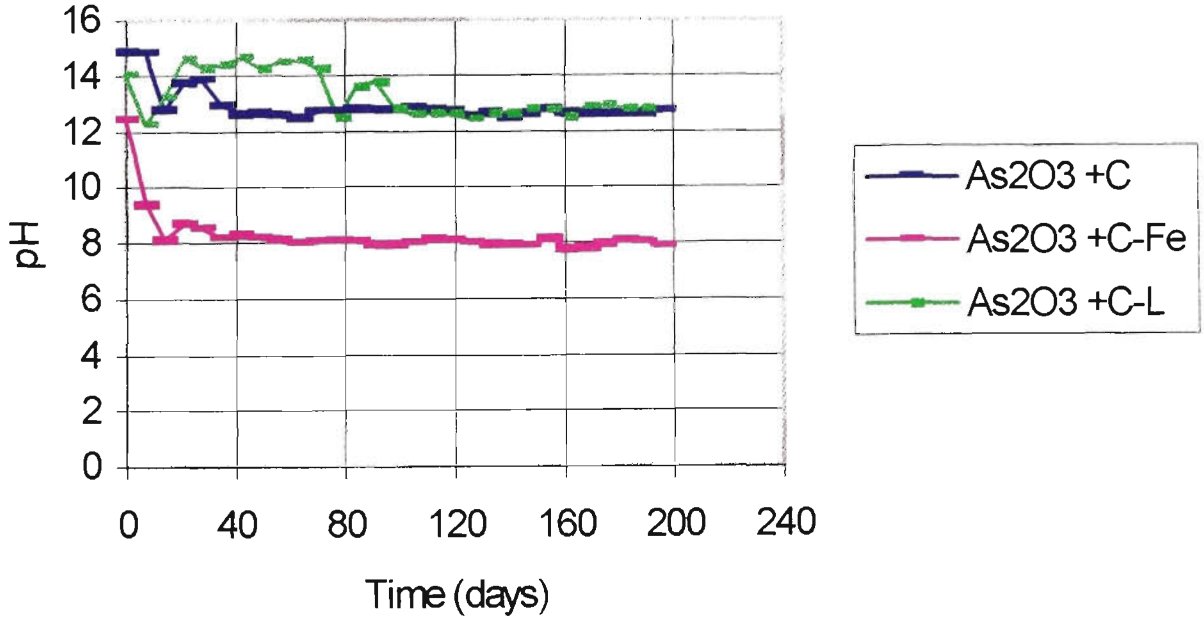


Figure 4.63 - pH values recorded for the arsenic pentoxide leachates collected from the column (Rainfall) leaching tests

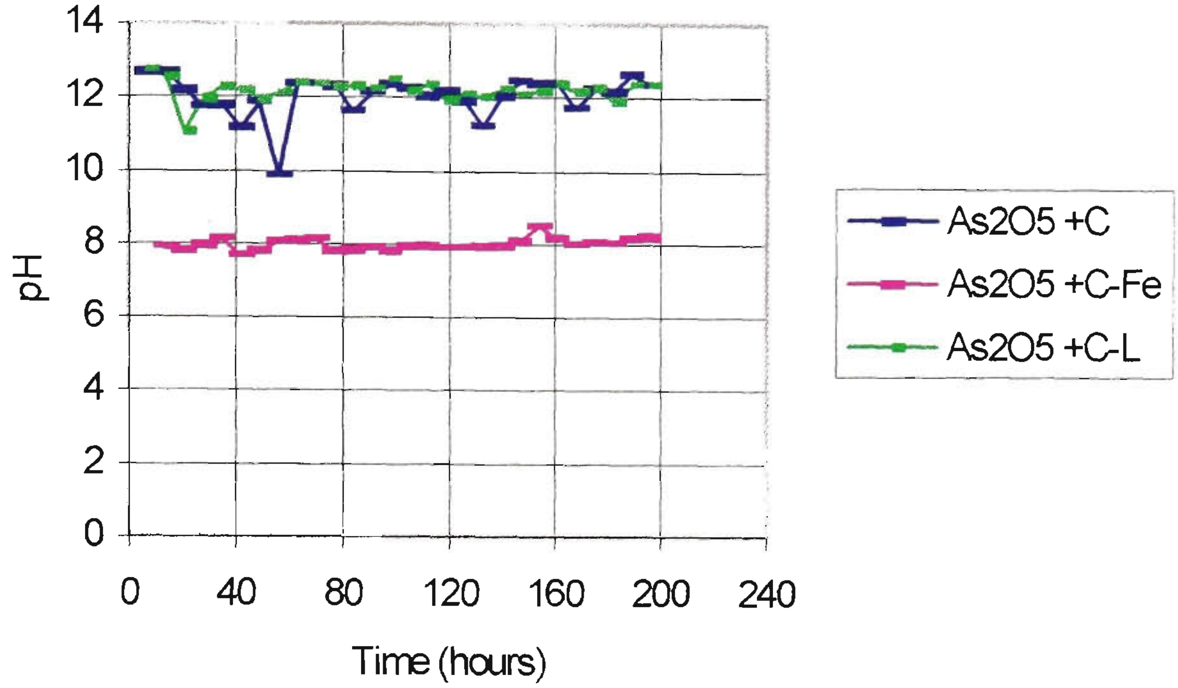
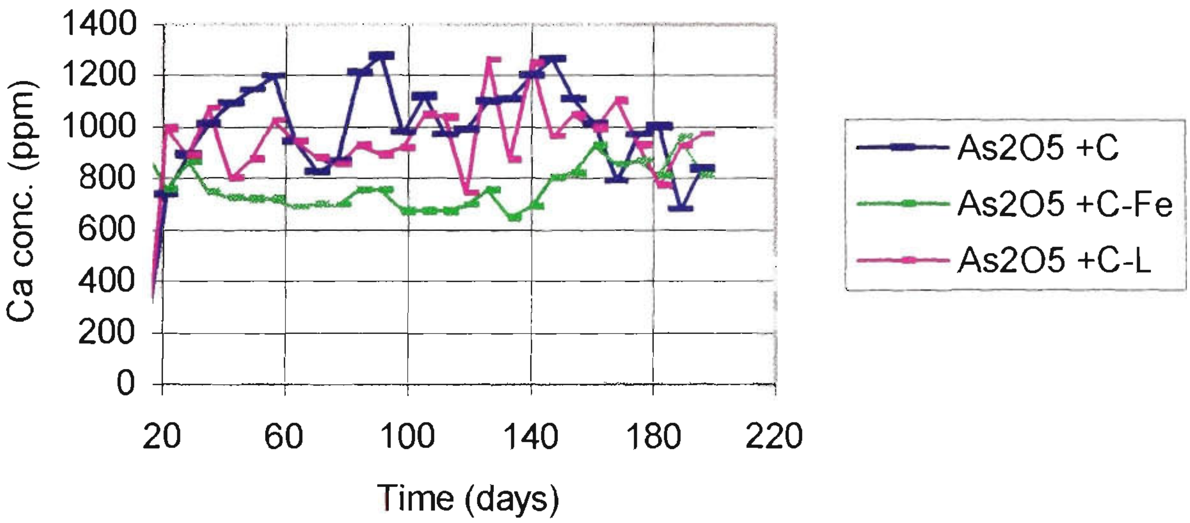


Figure 4.64 – Calcium leachate concentrations for the arsenic pentoxide formulations



4.5 Redox potential

In Chapter 3, the relationship between the Calcium concentration, pH and redox potential for the leachates collected from the batch leaching tests was highlighted. Not surprisingly, the same principles appear to apply to the leachates collected from the column leaching tests. The redox potentials recorded for various formulations for leachates collected from the column (BLC) leaching tests were similar for each arsenic compound (figures 4.65 to 4.68), while for the leachates collected from the column (rainfall) tests, the [cement + iron] formulations exhibited a clearly different redox potential from that exhibited by the other two formulations (figures 4.69 to 4.72). This pattern is exactly the same as that demonstrated by the recorded pHs.

Figure 4.65 - Redox potential recorded for the sodium arsenate formulations, Column (BLC) leaching

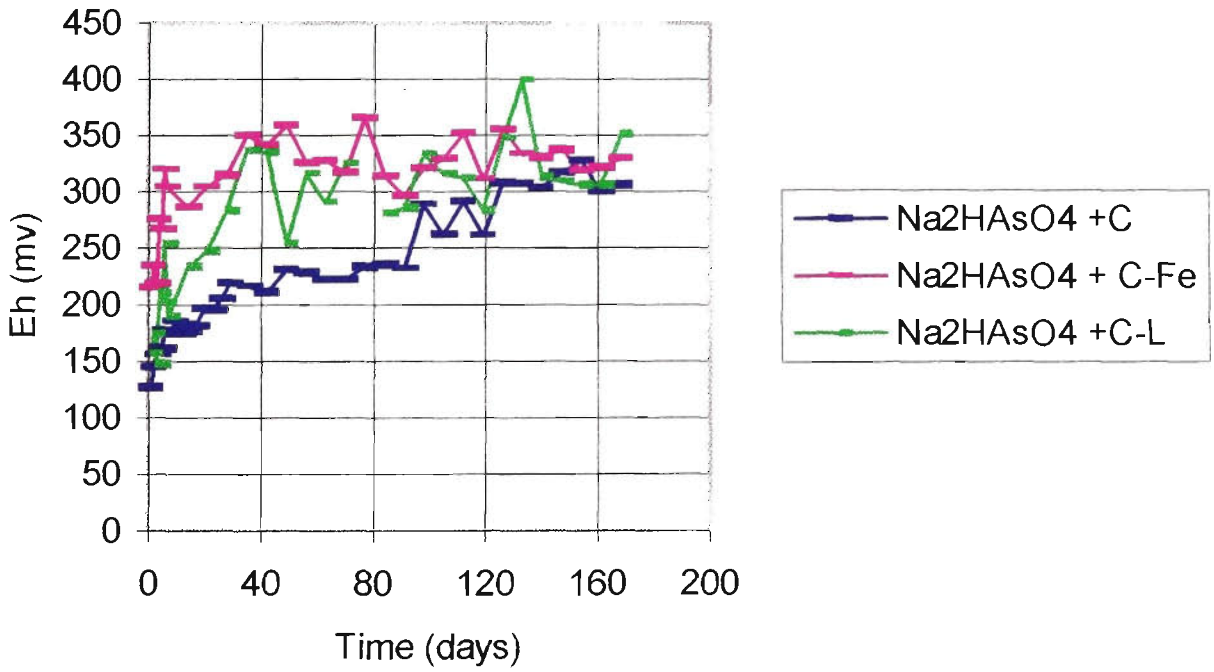


Figure 4.66 - Redox potential recorded for the sodium arsenite formulations, Column (BLC) leaching

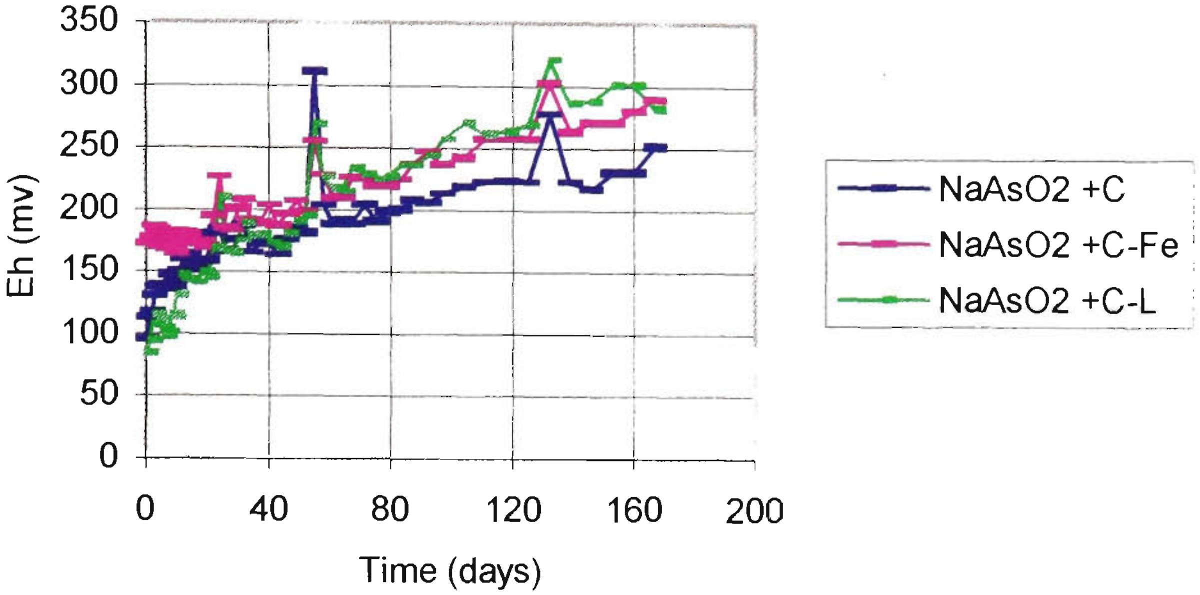


Figure 4.67 - Redox potential recorded for the arsenic trioxide formulations, Column (BLC) leaching

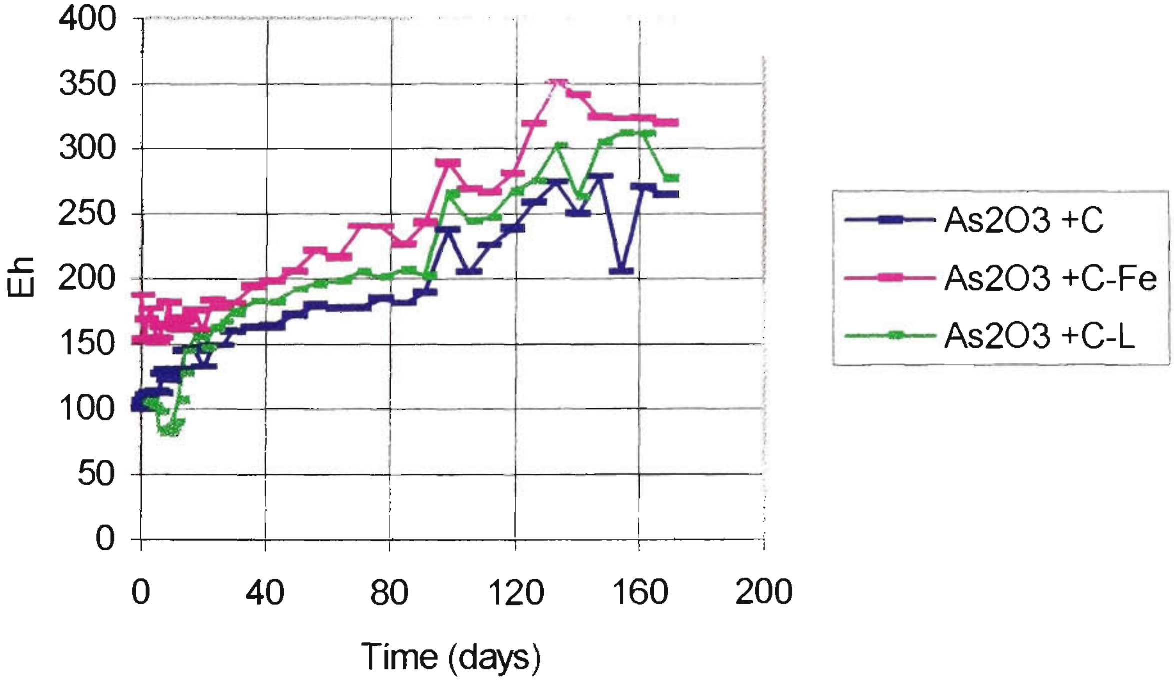


Figure 4.68 - Redox potential recorded for the arsenic pentoxide formulations, Column (BLC) leaching

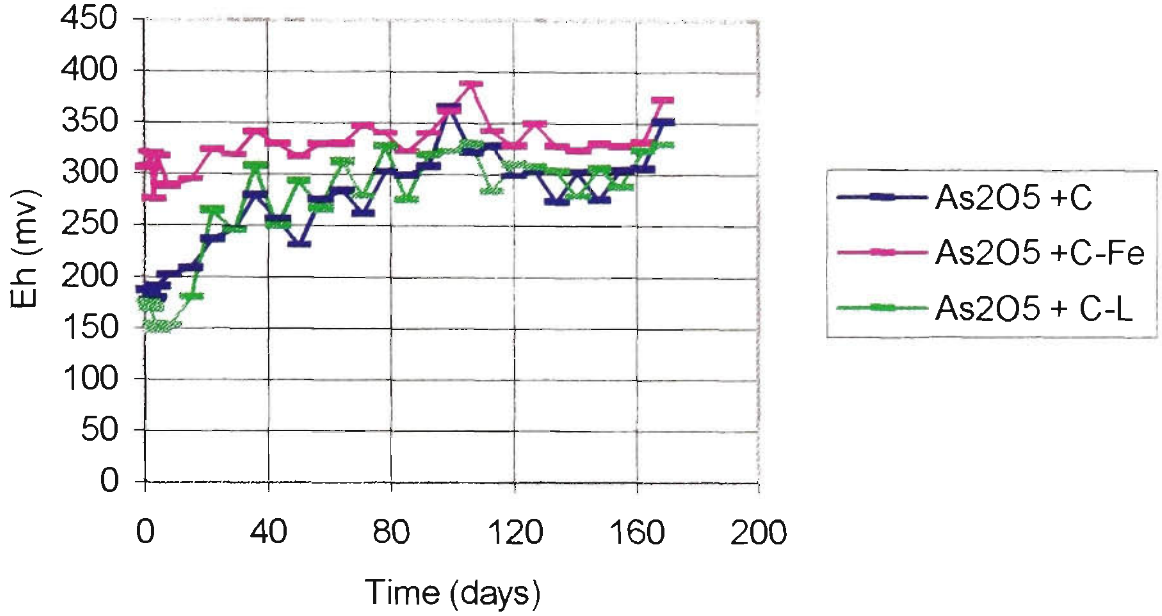


Figure 4.69 - Redox potential recorded for the sodium arsenate formulations, Column (Rainfall) leaching

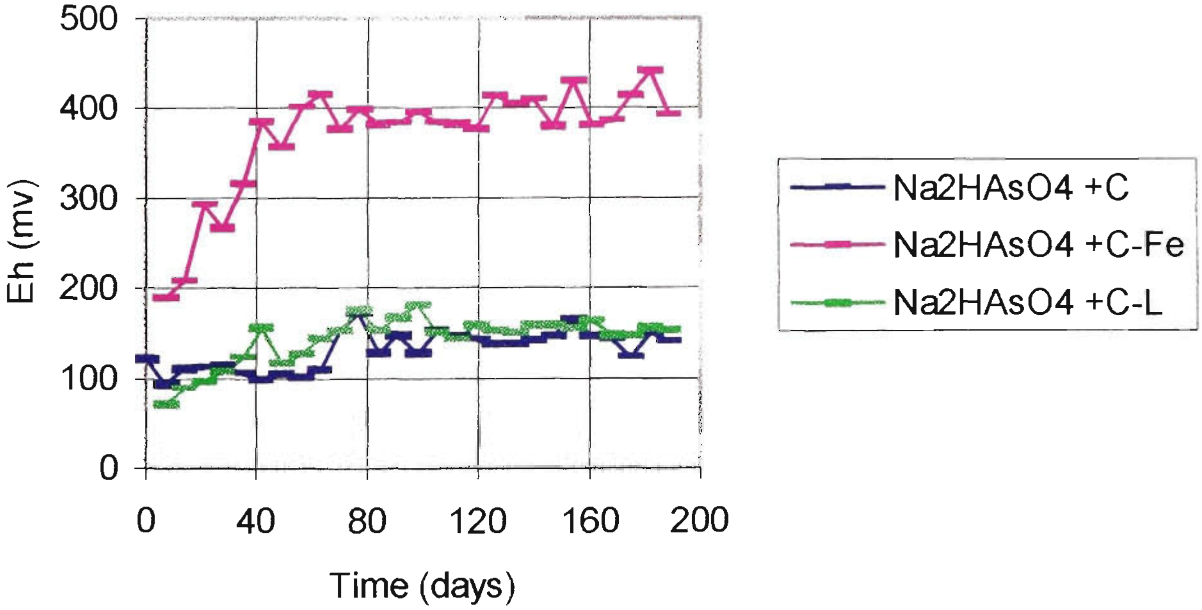


Figure 4.70 - Redox potential recorded for the sodium arsenite formulations, Column (Rainfall) leaching

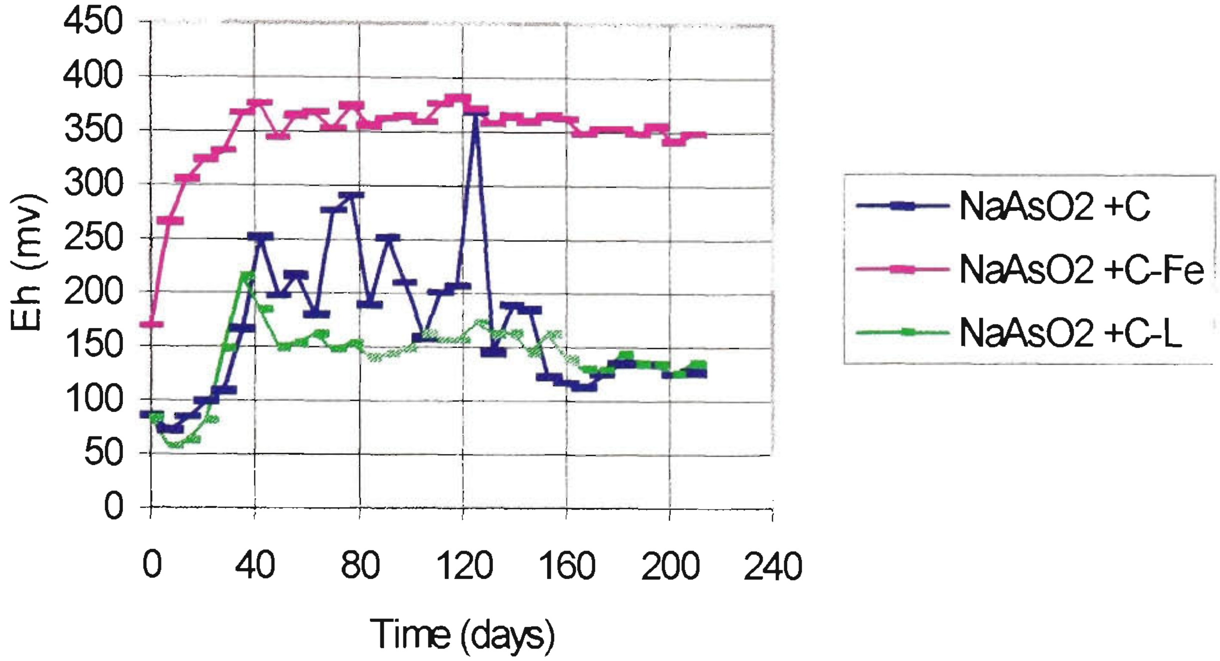


Figure 4.71 - Redox potential recorded for the arsenic trioxide formulations, Column (Rainfall) leaching

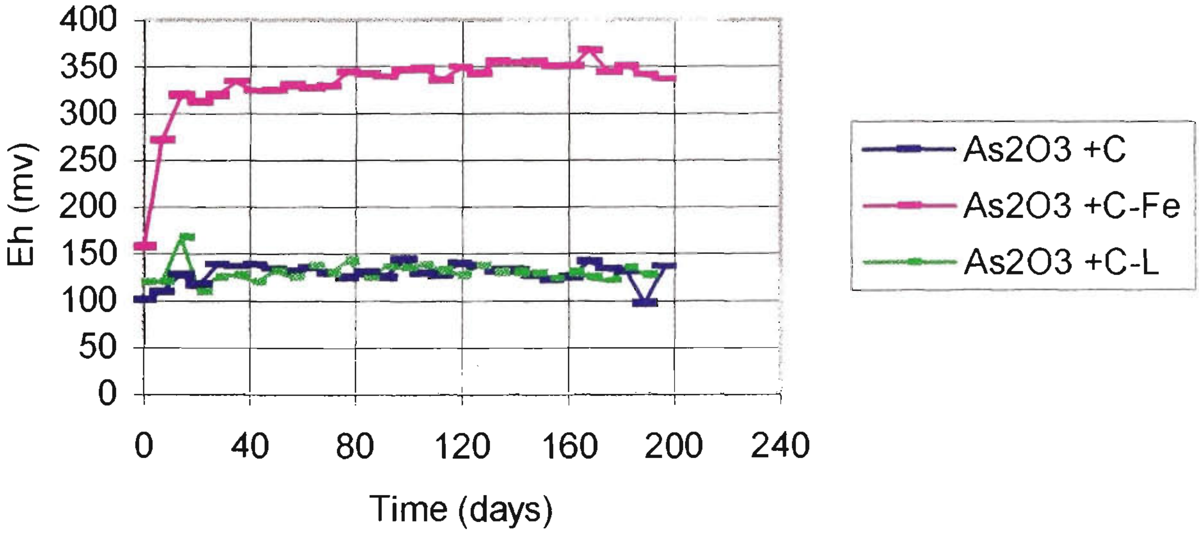
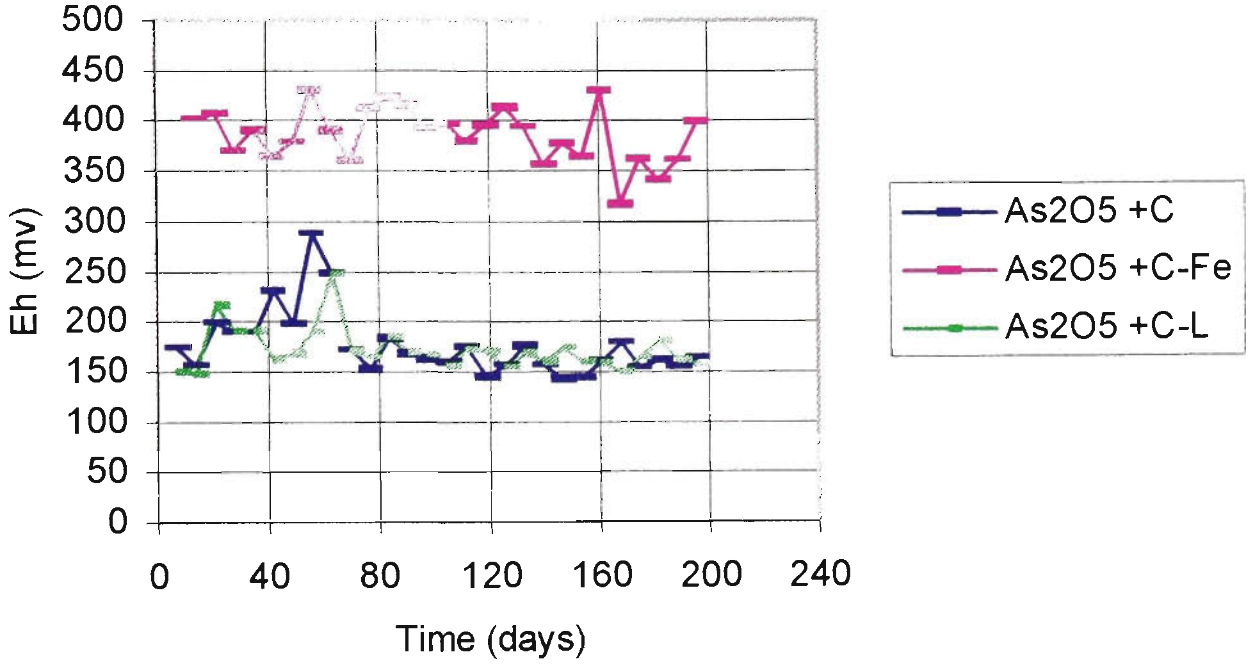


Figure 4.72 - Redox potential recorded for the arsenic pentoxide formulations, Column (Rainfall) leaching

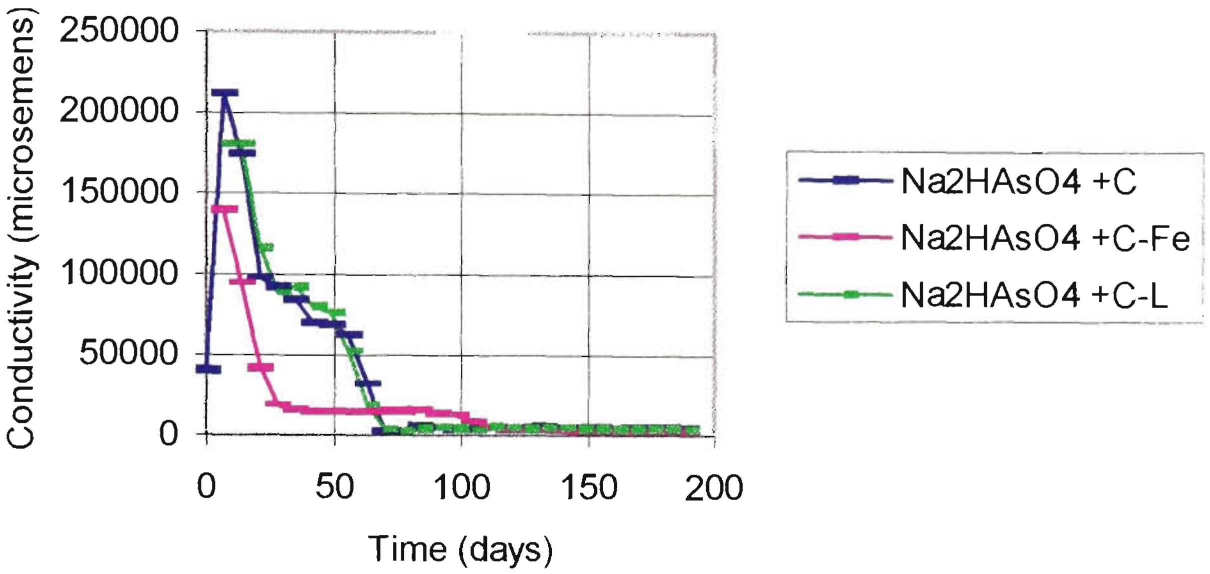


4.6 Conductivity

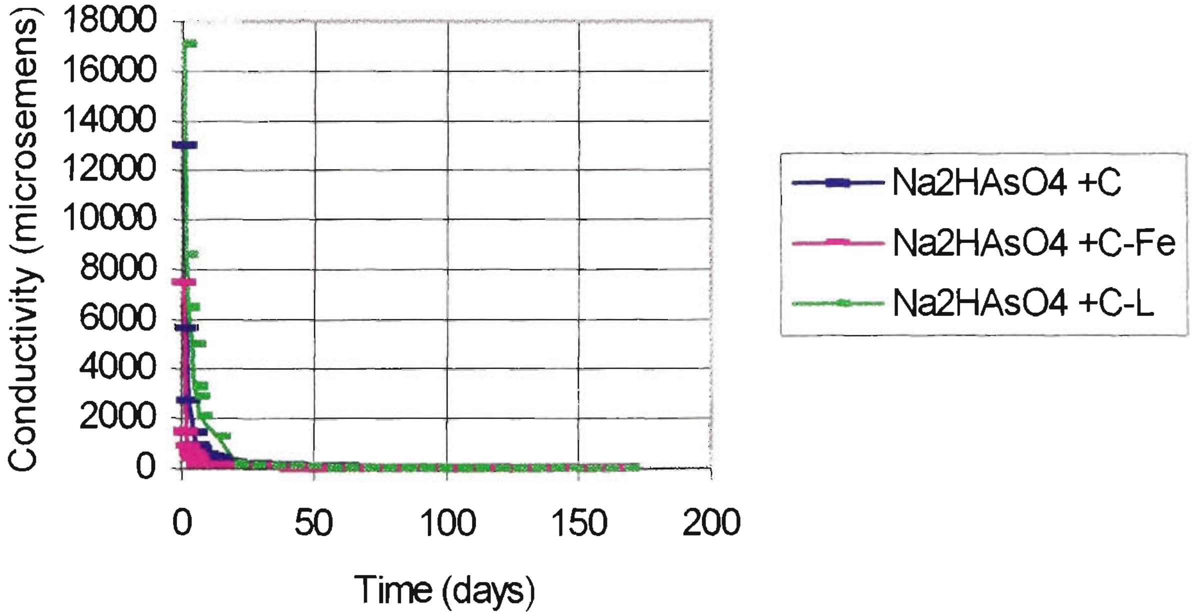
The conductivities recorded from the column (BLC) and column (rainfall) leaching tests are displayed in figures 4.73 through to 4.76. The large conductivities at the commencement of the column leaching tests are, no doubt, influenced by the presence of residual ions on the surface of the particles. Their magnitude, and the length of time during which the column (rainfall) leaching tests exhibited large conductivity readings when compared to the column (BLC) leachates, would be a result of the reduced flow rate. The higher flow rate employed in the column (BLC) tests was capable of reducing quantities of the ions on the surface particles far more quickly and, hence, the conductivity reduced far more quickly.

In Chapter 3, it was shown that, for the sequential batch leaching tests, rises or falls in the recorded conductivities do not appear to correlate with changes in the arsenic leachate concentration. Not surprisingly, this was found to be also the case for the column leaching tests. For example, changes in the arsenic leachate concentrations for the arsenic pentoxide formulations from the column (rainfall) and column (BLC) leaching tests, figures 4.77 and 4.78 respectively, do not correlate with the changes observed in the recorded conductivities (figure 4.75).

Figure 4.73 - Conductivities recorded for the Sodium arsenate formulations

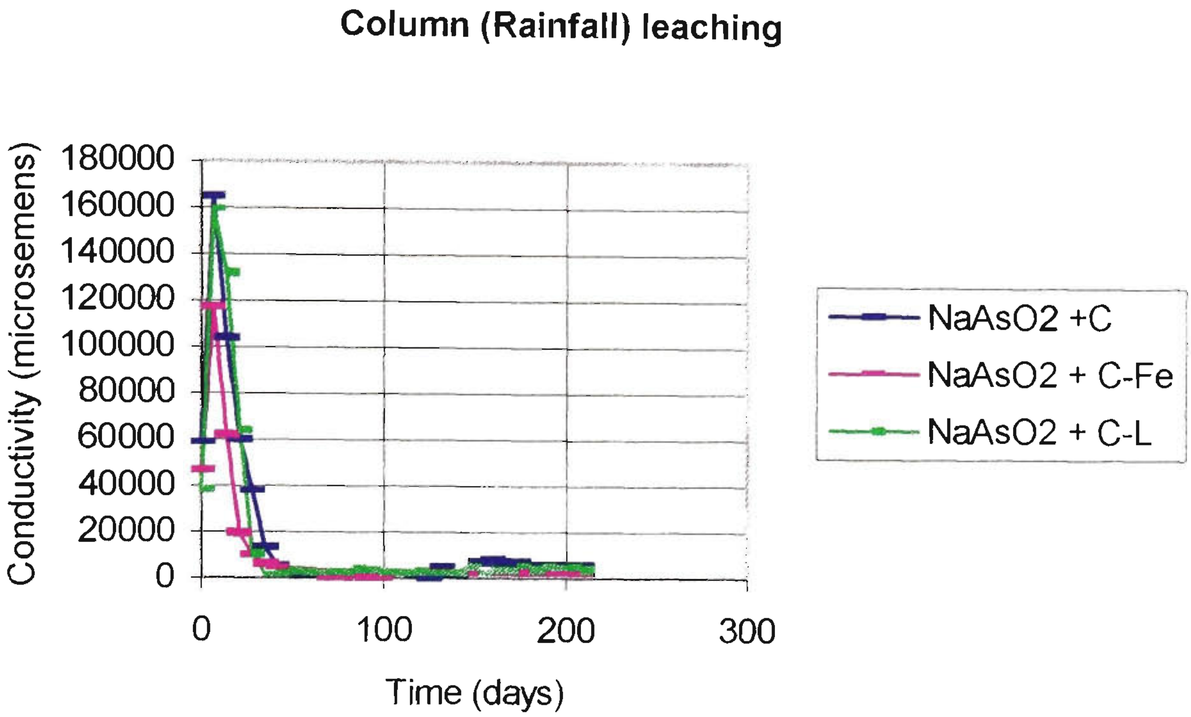


Column (Rainfall) leaching



Column (BLC) leaching

Figure 4.74 - Conductivities recorded for the Sodium arsenite formulations



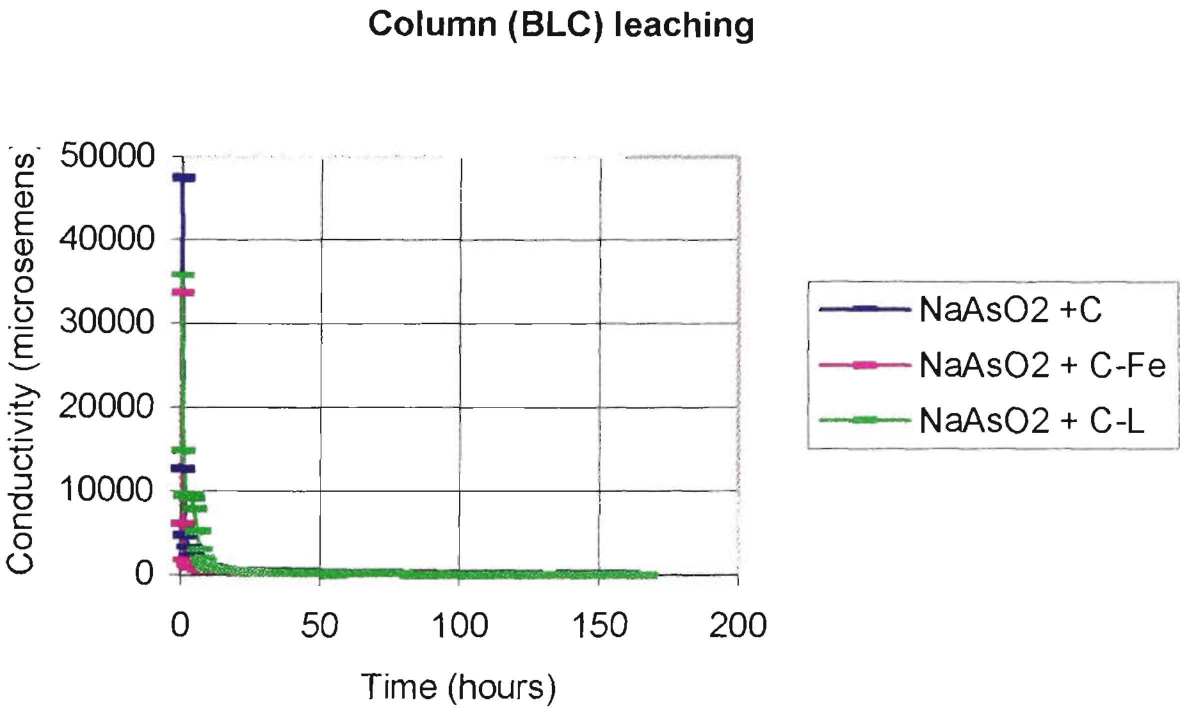
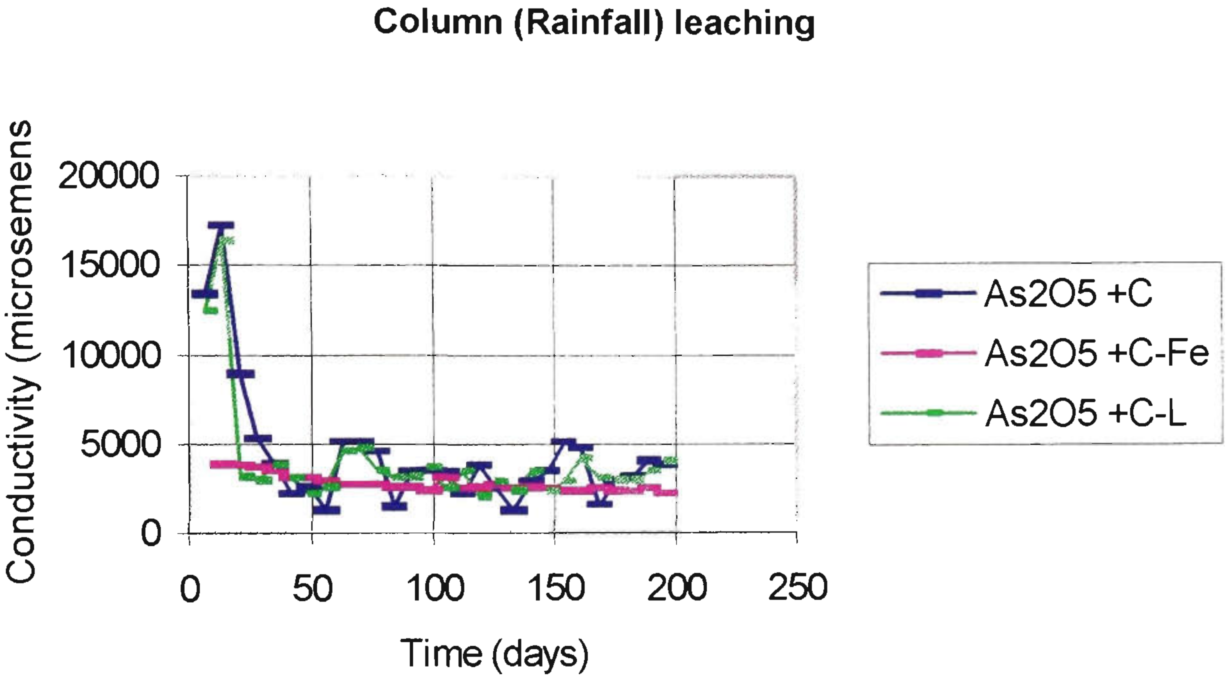


Figure 4.75 - Conductivities recorded for the Arsenic Pentoxide formulations



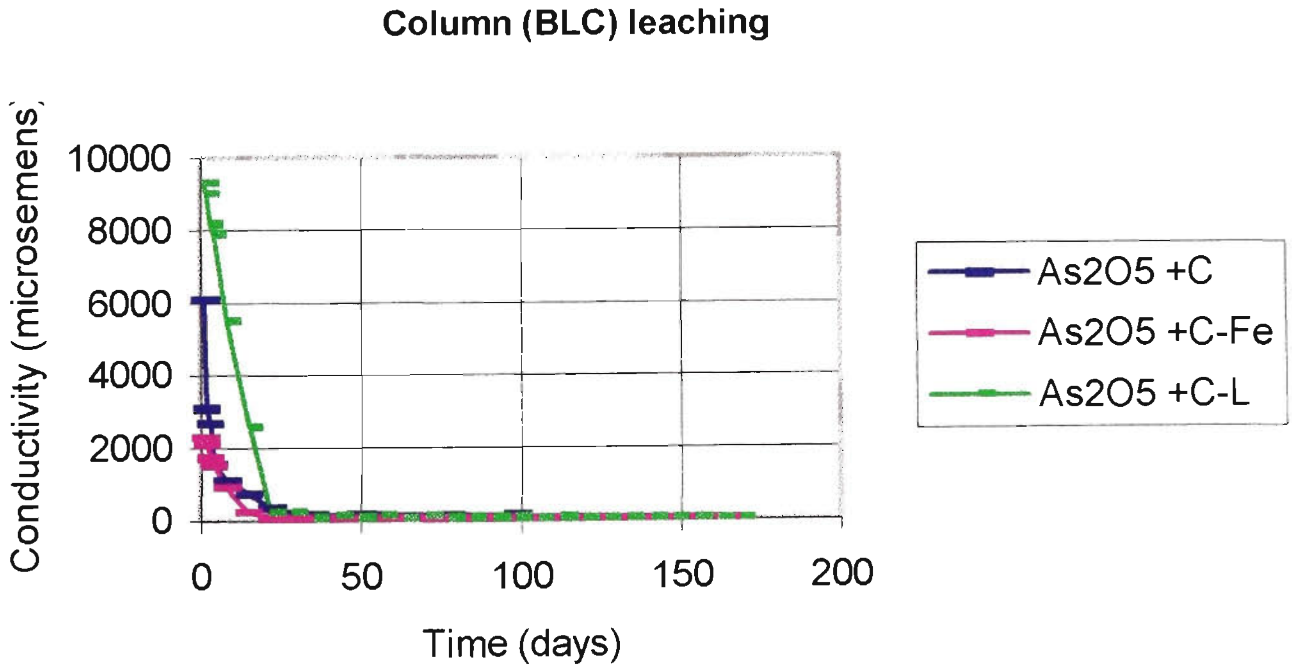
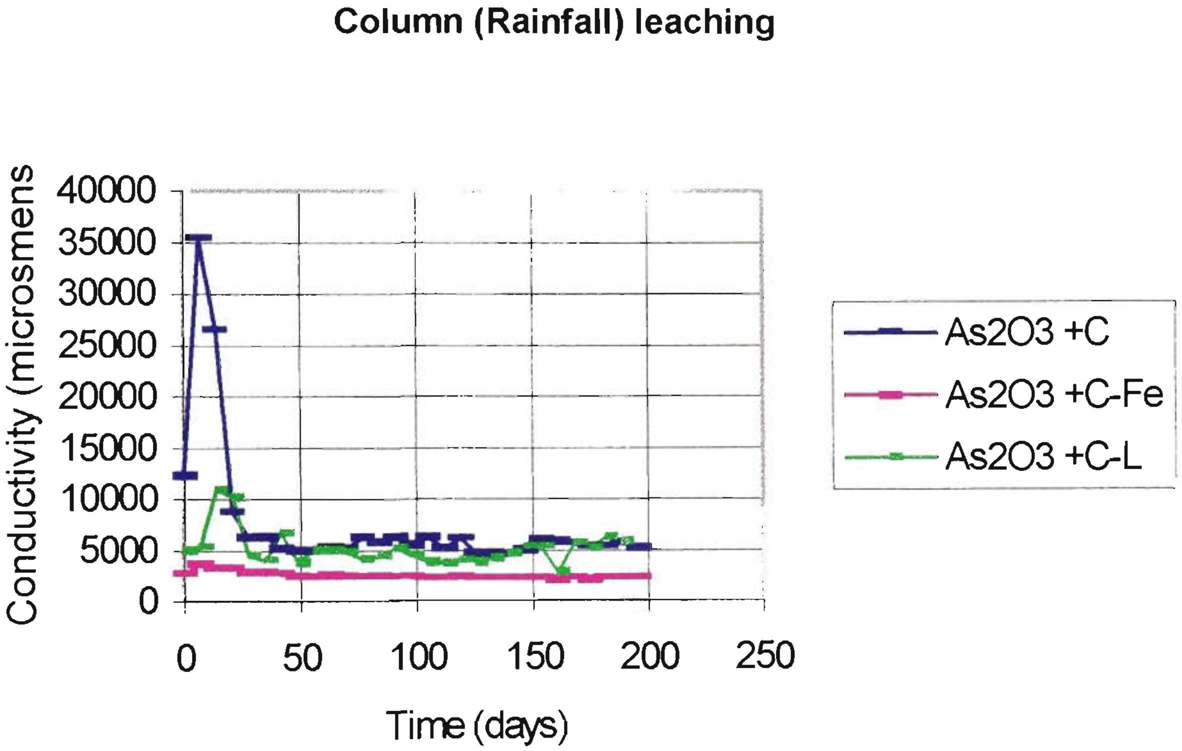


Figure 4.76 - Conductivities recorded for the Arsenic Trioxide formulations



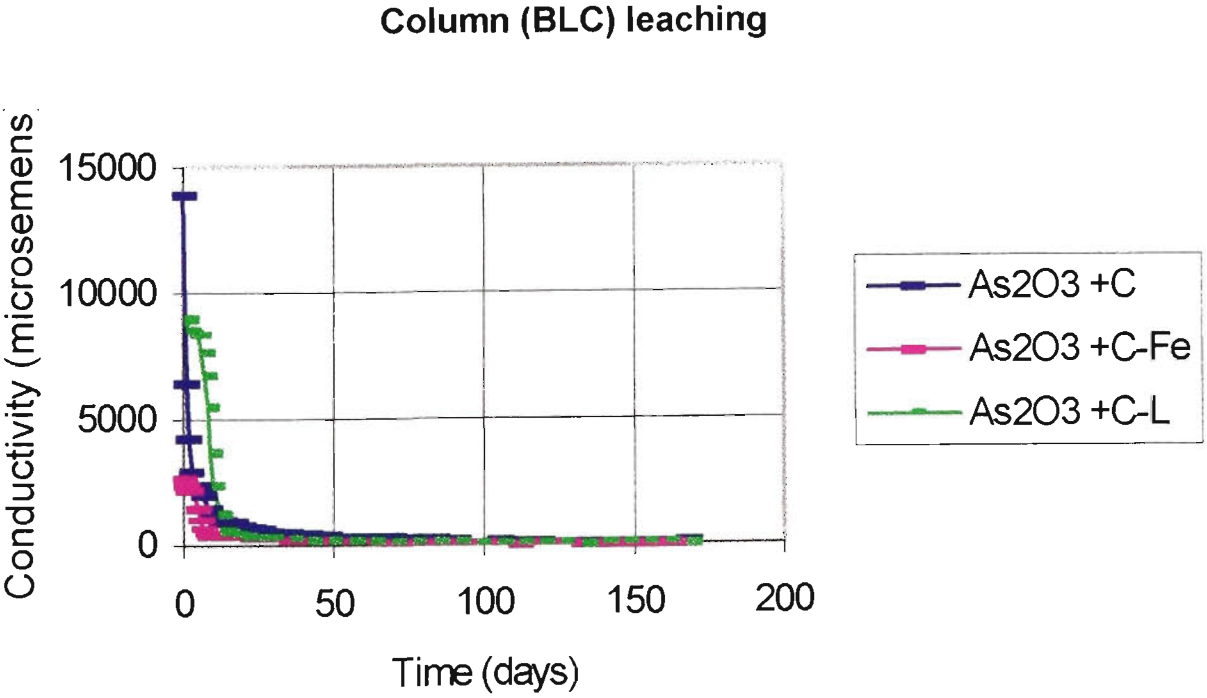


Figure 4.77 - Arsenic leachate concentrations for the arsenic pentoxide formulations, Column (BLC) leaching tests

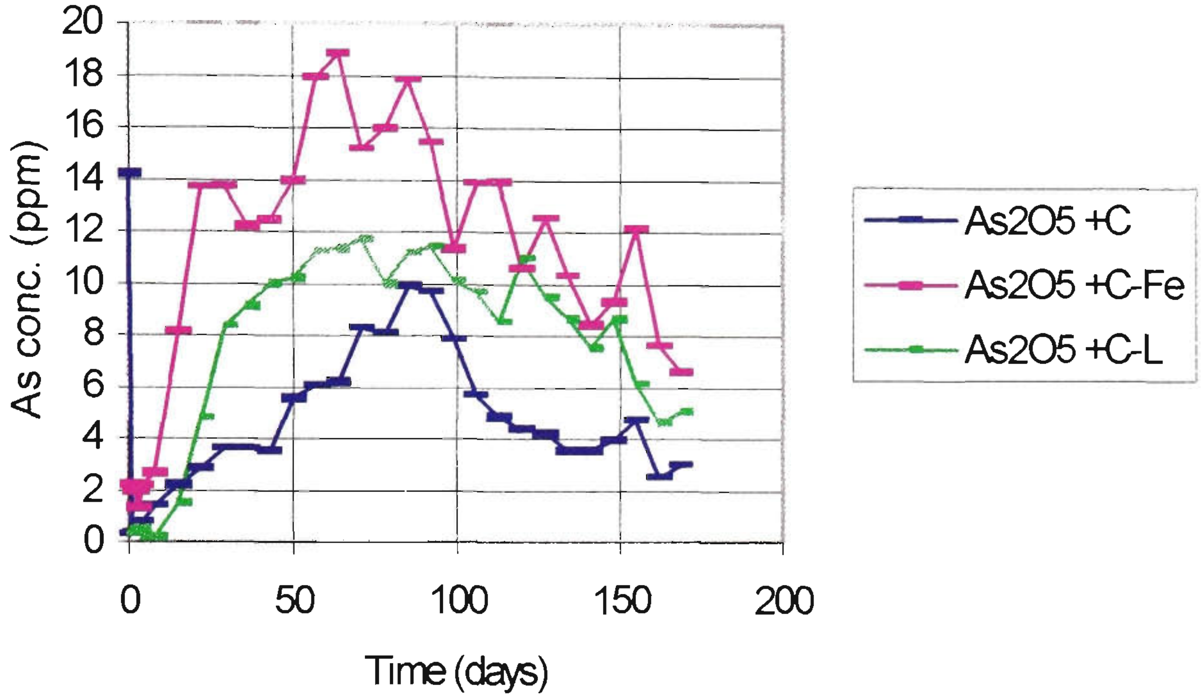
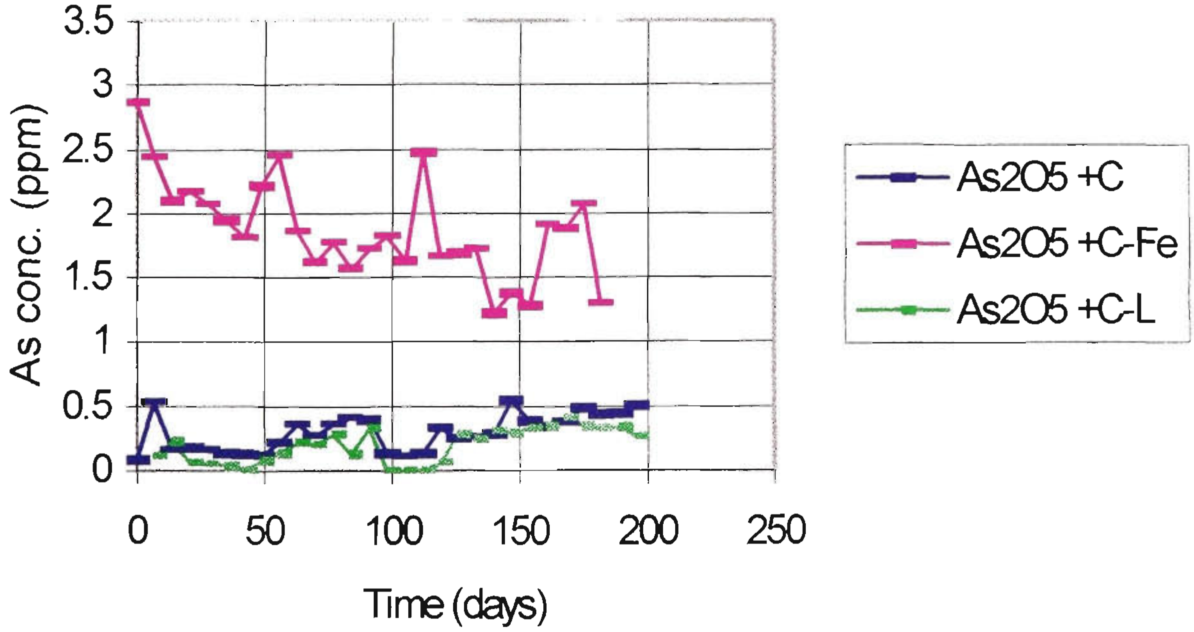


Figure 4.78 - Arsenic leachate concentrations for the arsenic pentoxide formulations, Column (Rainfall) leaching tests



4.7 Column leaching overview

Column leaching tests, the subject of this chapter, as opposed to batch leaching tests, provide insight into the long term leaching behavior of stabilized wastes. The results presented in this chapter show that a good measure of the success of a S/S formulation can be easily identified during the initial periods of the investigation. Towards the latter stages of both column leaching protocols, the leachate concentrations did not differ greatly from one week to another, suggesting a steady state had been attained. That is, the dissolution of arsenic species at the internal leaching boundary and their subsequent transport through the particle had reached a constant rate.

The sodium arsenate formulations were prime examples of formulations whose failure to satisfactorily immobilize arsenic could be readily observed during the early stages of the leaching tests. The sodium arsenate formulations are also reminders of how it is not possible to predict the behavior of a particular arsenic waste based on the results of a different arsenic containing waste, even if it was of the same oxidation state. The column leaching results for the sodium arsenate formulations bear little resemblance to those obtained for the other arsenate containing formulation, arsenic pentoxide. The results obtained were also significantly different from those obtained for the sodium arsenite formulations.

This chapter has also compared and contrasted the results obtained from column leaching tests with:

- Column leaching tests which employed a different leaching regime;
- Sequential batch leaching tests.

The magnitude of the differences in the amounts of arsenic leached from the two column leaching setups varied greatly, both across wastes and between formulations. Despite a difference in the liquid-to-solid ratio between the two tests of 573:1, the masses leached from the two column leaching tests were shown to differ by margins both significantly greater and lower than this value. For the sodium arsenite formulations, the difference in the arsenic levels leached approached a factor of 10,000:1. For the sodium arsenate formulations, the difference between the two setups in terms of the masses of arsenic leached was as low as a factor of 20 during the initial periods of the investigation.

The large differences that exist between the leaching methodologies of the column and batch leaching tests were not reflected in the results obtained from the two types of tests. However, variability which did exist between the two tests was sufficiently large that those formulations which performed most favorably in the batch tests did not always perform so well in the column leaching tests. From chapter 3, those formulations containing the largest Ca:As mole ratios performed the best. However for the Column (BLC) leaching tests the [cement – only] formulations constantly leached the lowest levels of arsenic. The leaching of arsenic however, was still shown to be influenced by the leaching of calcium.

This chapter has demonstrated, for the less aggressive column leaching setups, that the positive or negative influences exhibited by the arsenic wastes and/or additives on the setting of cement have had a significant impact on the leaching performance. The cement-only formulation, which during the crushing process was noted to have the greatest strength, performed the best during the Column (BLC) leaching tests. The variation in the effects that the combinations of the arsenic compounds and additives have had on the cement matrix also explains why in some instances, the differences in the arsenic masses leached by the two column leaching setups sometimes differed by margins both greater or lower than the difference in the liquid to solid ratio.

The effects of the additives on the cement matrix were not so noticeable in the sequential batch leaching tests due to the aggressiveness of these tests. The batch tests appear capable of breaking down even the strongest of the matrices.

Chapter 5

5.0 MATRIX CHARACTERIZATION

The effects which the inclusion of the additives, i.e. lime or iron and/or the arsenic wastes, have had upon the hydration of Portland cement have been investigated using Fourier Transform Infrared Spectroscopy (FTIR) and, to a lesser extent, Scanning Electron Microscopy (SEM). Following a brief introduction (section 5.1), this chapter details and discusses the results of the experimental study described in sections 2.6 and 2.7 of chapter 2 (pages 70 to 72).

5.1 Molecular Characterization

Molecular characterization is provided by FTIR, which, through vibrational modes, provides insight into molecular structure. The major performance objectives of cement based S/S treatments are to reduce the mobility of contaminants, by both physically and chemically retaining the contaminants in a monolithic matrix. The solid matrix forms because of hydration of silicates in the cement, yielding calcium-silicate hydrate. Cementation of the waste-binder mixture begins once water is added. Once the cement powder contacts water, tricalcium aluminate immediately hydrates, causing the rapid setting which produces a rigid structure. In an idealized setting, the water hydrates the calcium silicates and aluminates in the cement to form calcium-silicate-hydrate (Means et al 1995). Thin, densely-packed fibrils of silicate grow out from the cement grains and interlace to harden the mixture and entrap inert materials (Means et al 1995).

Waste constituents, such as arsenic, can exhibit positive, negative, or inert contributions to the strength forming reactions, thus affecting the ability of the S/S process to render these hazardous constituents "safe". Studies of the effect of metals and organic additives on cement hydration have generated considerable interest (Mollah et al 1995a, Mollah et al 1995b). Through the monitoring of vibrational frequencies, Fourier transform infrared spectroscopy (FTIR) can provide both molecular characterisation and insight into molecular structures. During the hydration of cement, the vibrational spectra are known to change with time.

5.1.1 FTIR Analysis of dry and hydrated Portland cement

The hydration of Portland cement involves dicalcium silicate (belite) and tricalcium silicate forming $CaO.SiO_2.H_2O$ (C-S-H). The major infrared band oberved for both dry and hydrated cement is the $\nu3$ (asymmetrical Si-O stretch) vibrations located between 960 –1000 cm^{-1}. Figure 5.0 and 5.1 illustrate that upon hydration of cement, the Si-O asymmetric stretching band ($\nu3$) is shifted to higher frequencies (921 to 965 cm^{-1}). This has also been shown elsewhere (Mollah et al 1998, Ortego et al 1991, Ortego et al 1989). Other main bands which can be observed in the hydrated cement (figure 5.1) are the stretching vibration of the SO_4^{2-} group at 1112 cm^{-1}, while the water bands appear at approximately 3440 cm^{-1} (stretching) and 1650 cm^{-1} (bending) respectively. The OH band from $Ca(OH)_2$ appears at 3641 cm^{-1}. The peaks associated with the mineral oil are those located at approximately 1376 cm^{-1} and 1460 cm^{-1} as well as the broad absorption at 2900 cm^{-1}. The small peak located at approximately 721 cm^{-1} can also be attributed to the mineral oil.

5.1.1.1 Arsenic Doped Cement

The incorporation of arsenic and/or additives into the cement matrix has had little effect upon the shifting of the Si-O asymmetric band ($\nu 3$) when compared to that of cement alone (965 cm^{-1}) as shown in Table 5.0, which lists the frequency of the Si-O band ($\nu 3$) for each of the solidification/stabilization formulations

Those solidification/stabilization formulations incorporating cement-arsenic sample-lime, exhibited the smallest shift of the $\nu 3$ band. These formulations were also generally the best performing of those investigated, resulting in the lowest arsenic leachate concentrations, as is shown in Table 5.2. Silicate hydration in Portland cement occurs under highly basic conditions due to the formation of $Ca(OH)_2$. The reaction between the orthosilicate ion and water also produces OH^-. The degree of polymerization, therefore, is restricted by the high hydroxide ion concentration. Those formulations which do not present conditions as alkaline as the cement-arsenic sample-lime formulations, exhibited a larger shift in the $\nu 3$ band. The pHs of the various solidification/stabilization formulations, as determined by the Australian Bottle Leaching Procedure, are listed in table 5.1. For all five of the arsenic compounds investigated, $\nu 3$ is shifted to the highest frequencies in those formulations consisting of cement-arsenic sample-ferrous sulfate, which were the least successful solidification/stabilization formulations in terms of the amount of arsenic leached (table 5.2).

Figure 5.0 – FTIR spectrum of unhydrated cement

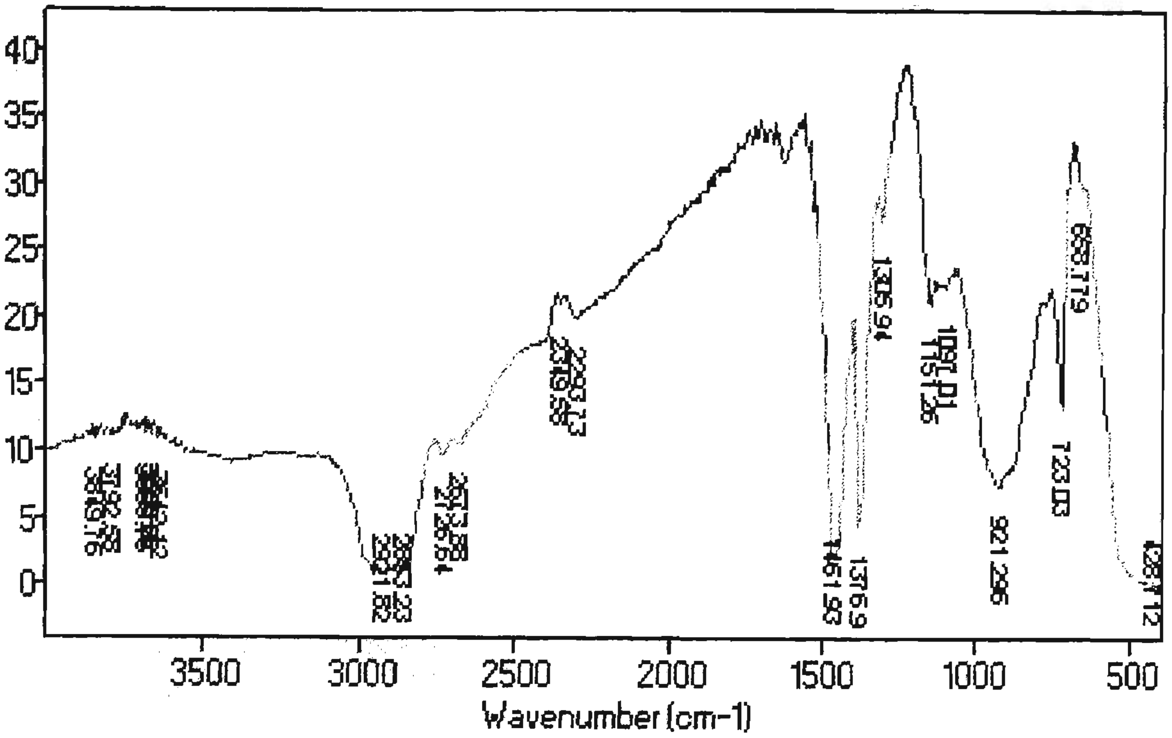


Figure 5.1 – FTIR spectrum of hydrated cement

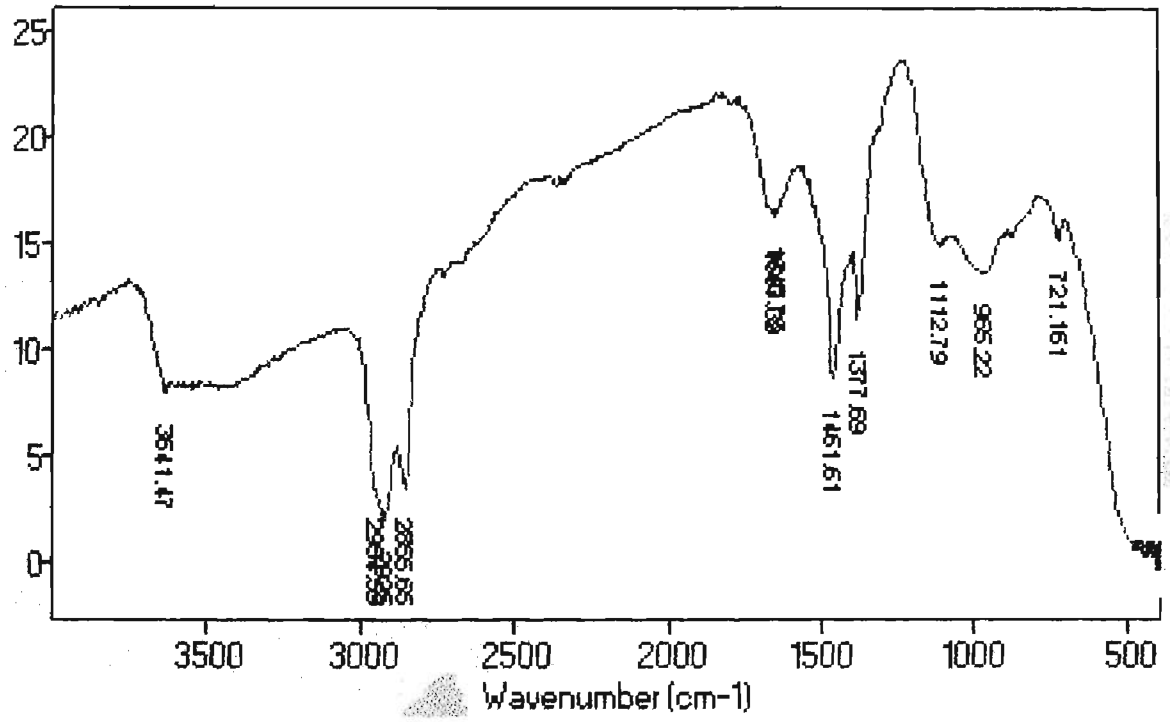


Table 5.0 – Frequency of the Si-O band ($v3$) for arsenic doped cement

Formulation	Frequency of Si-O band ($v3$)
$NaAsO_2$ + *C*	966 cm^{-1}
$NaAsO_2$ + *C-Fe*	976 cm^{-1}
$NaAsO_2$ + *C-L*	943 cm^{-1}
As_2O_3 + *C*	972 cm^{-1}
As_2O_3 + *C-Fe*	masked by sulfate band
As_2O_3 + *C-L*	966 cm^{-1}
Na_2HAsO_4 + *C*	958 cm^{-1}
Na_2HAsO_4 + *C-Fe*	983 cm^{-1}
Na_2HAsO_4 + *C-L*	938 cm^{-1}
As_2O_5 + *C*	994 cm^{-1}
As_2O_5 + *C-Fe*	1008 cm^{-1}
As_2O_5 + *C-L*	958 cm^{-1}
$PbHAsO_4$ + *C*	927 cm^{-1}
$PbHAsO_4$ + *C-Fe*	984 cm^{-1}
$PbHAsO_4$ + *C-L*	974 cm^{-1}

Table 5.1 – pHs of the various Solidification/Stabilization formulations as determined by the Australian Bottle Leaching Procedure (AS 4439.3)

S/S Formulation	pH
$NaAsO_2$ + *C*	12.52
$NaAsO_2$ + *C-Fe*	11.51
$NaAsO_2$ + *C-L*	12.83
As_2O_3 + *C*	12.68
As_2O_3 + *C-Fe*	9.74
As_2O_3 + *C-L*	12.76
Na_2HAsO_4 + *C*	12.38
Na_2HAsO_4 + *C-Fe*	10.70
Na_2HAsO_4 + *C-L*	12.54
As_2O_5 + *C*	12.35
As_2O_5 + *C-Fe*	10.05
As_2O_5 + *C-L*	12.98
$PbHAsO_4$ + *C*	11.74
$PbHAsO_4$ + *C-Fe*	9.97
$PbHAsO_4$ + *C-L*	12.55

Table 5.2 – Australian Bottle Leaching Procedure arsenic leachate concentrations

S/S formulation	Deionized water leachant [As]/mg L^{-1}	Acid leachant [As]/mg L^{-1}
$NaAsO_2$ + *C*	1.73 ± 0.40	1.80 ± 0.01
$NaAsO_2$ + *C-Fe*	8.15 ± 0.21	144 ± 8.78
$NaAsO_2$ + *C-L*	2.48 ± 0.06	1.40 ± 0.07
As_2O_3 + *C*	1.04 ± 0.13	1.97 ± 0.09
As_2O_3 + *C-Fe*	36.61 ± 0.73	407 ± 27
As_2O_3 + *C-L*	0.79 ± 0.01	1.17 ± 0.02
$NaHAsO_4$ + *C*	0.73 ± 0.03	2.54 ± 0.17
$NaHAsO_4$ + *C-Fe*	3.63 ± 0.18	525 ± 68.30
$NaHAsO_4$ + *C-L*	0.10 ± 0.02	0.40 ± 0.03
As_2O_5+ *C*	0.29 ± 0.02	2.09 ± 0.04
As_2O_5+ *C-Fe*	2.05 ± 0.10	1036 ± 69.78
As_2O_5+ *C-L*	0.20 ± 0.01	0.58 ± 0.04

Chemical incorporation of the lead arsenate insecticide into the cement matrix does not appear to have been achieved. The ftir spectrum of the lead arsenate doped cement (Figure 5.3) does not differ greatly from that of the lead arsenate insecticide (Figure 5.2), with the band at ~ 800 cm^{-1} from the lead arsenate still clearly evident in the stabilized formulation, suggesting there is little interaction between the sample and the cement. The $\nu3$ Si-O band appears at only 927 cm^{-1} indicative of little, if indeed any, cement hydration. Lead has been identified as a substance found to affect cement reactions (Conner 1990, Means 1995). Butler et al (1992) found that lead salts caused extreme retardation of the hydration reactions that applied to the aluminate phases as well as the silicate phases. Cheeseman and Asavapisit (1999) found that the cement stabilization of a synthetic lead hydroxide waste, incorporated at a dosage of 10% (by weight) delayed the heat of hydration curve from 8.7 to 172 hours. Wang and Vipulanandan (1996) found that the cement setting times for formulations containing lead nitrate were significantly affected. The change in the initial and final setting times were very much dependent upon the initial lead nitrate concentrations. In the study conducted by Wang and Vipulanandan (1996) the control cement (no lead addition) reached initial set in 3 hours and final set in 4.5 hours. In the presence of 0.5% lead, the initial and final setting times were 35 and 80 hours respectively. For 10% lead nitrate containing formulations, the time to initial set was 100 hours and time to final set was 260 hours. The lead contents of formulations investigated in this study ranged between 9.5 and 13% (the exact composition of the S/S formulations was provided in Table 2.4, Chapter 2, p.53). From Table 5.0 it is evident that the other two lead arsenate formulations i.e. those involving the use of either lime or ferrous sulfate, did not exhibit the same lack of hydration. This is a direct result of the addition of these additives, i.e. lime or iron. Both of these additives have been found to be useful for countering the inhibitory effects presented by constituents of wastes (Conner 1990). For example, iron compounds have been found useful for the co-precipitation of interfering metals, such as lead (Conner 1990) and, indeed, have been found useful for precipitating the lead in this study as well.

Figure 5.2 – FTIR spectrum of lead arsenate insecticide

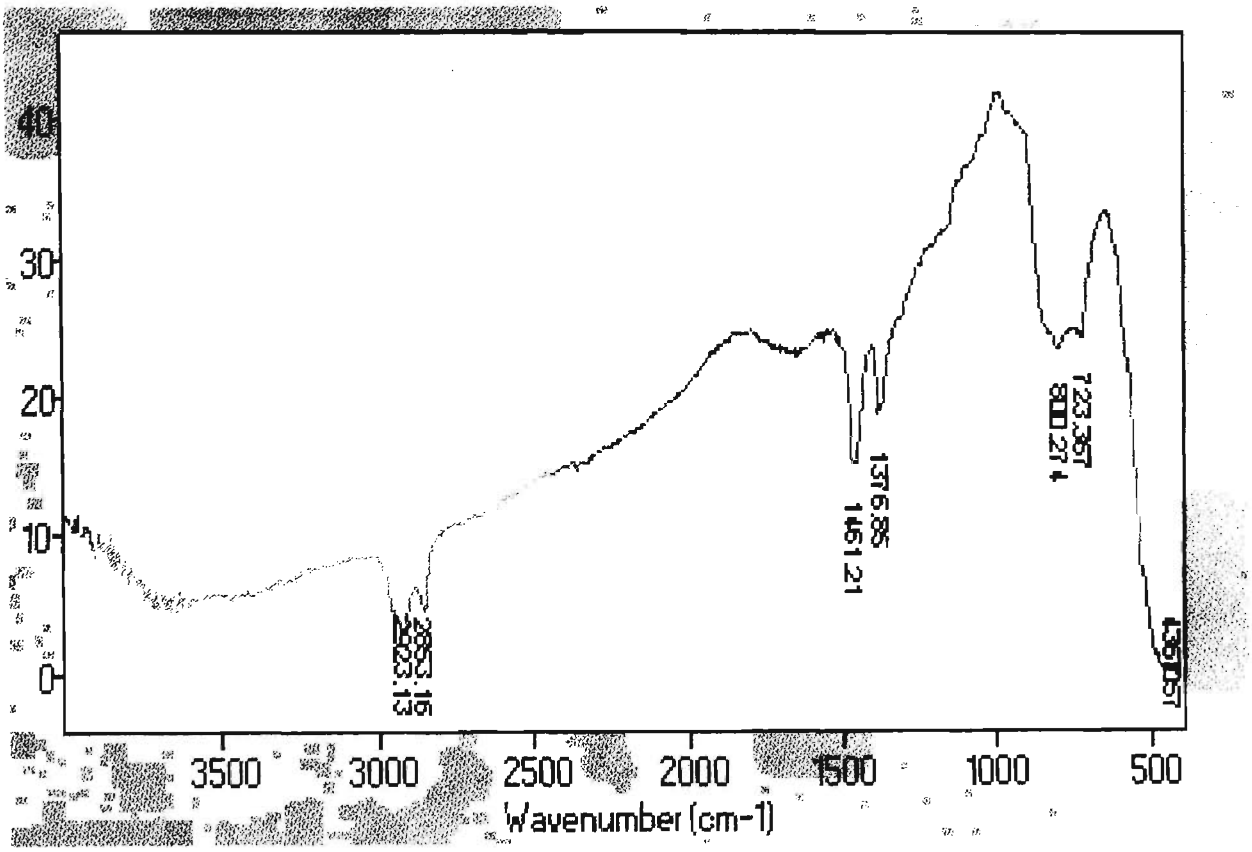
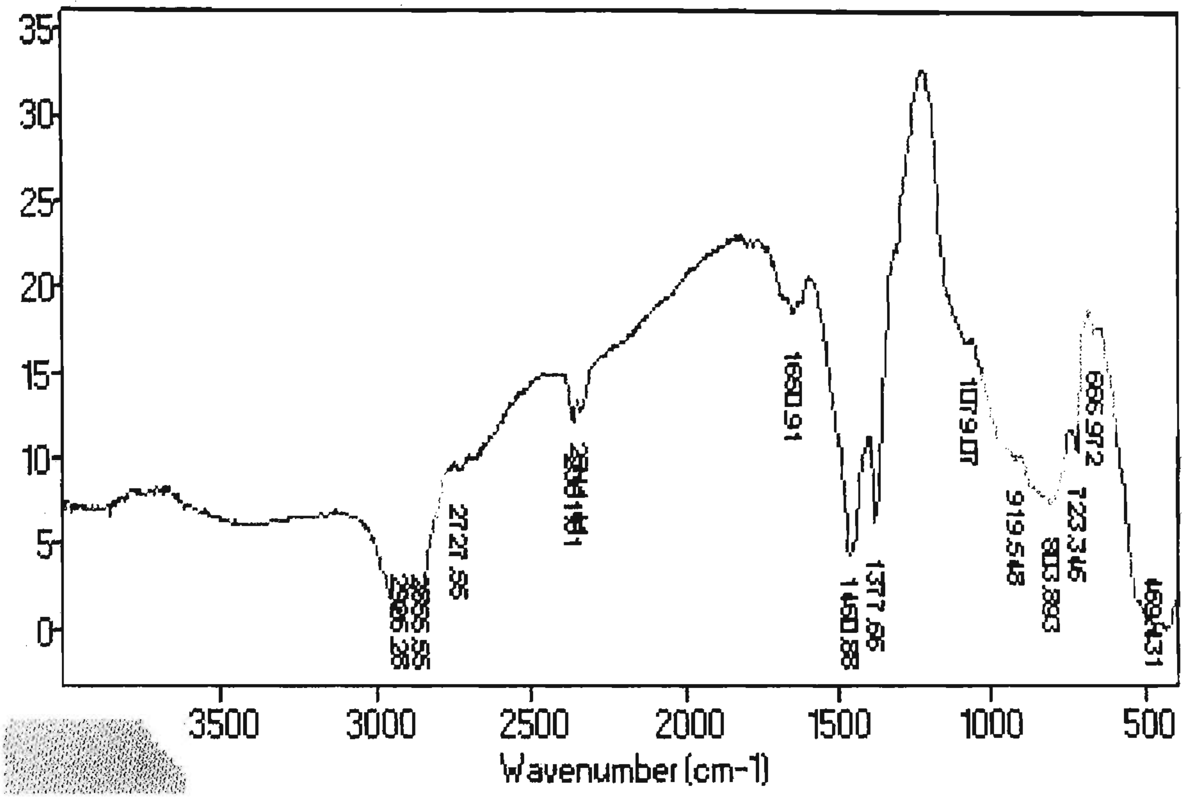


Figure 5.3 – FTIR spectrum of lead arsenate doped cement



5.1.1.2 The leaching of the stabilized wastes

Table 5.3 displays the shift of the ν3 peak in stabilized wastes following sequential leaching using both deionized water and an acidic leaching fluid (5.7 mL of acetic acid per litre), as well as after the six month column leach tests. The acidic leaching fluid has resulted in a significant shift in ν3 to higher energies, while the use of deionized water has resulted in little shift, in either the sequential leach tests, or the column leach tests. As the sequential leaching tests, utilizing the acidic leaching fluid, yielded a significantly greater shift in the ν3 peak, the most important factor in determining the shift of the ν3 peak after leaching is the type of leaching fluid and not the duration of the leaching tests. The duration of the sequential leaching test was a mere 144 hours as opposed to the 6 months for the column leach tests.

Table 5.3 – Effect of the leaching scenario on the shift *v*3

S/S Formulation	Sequential leaching – Deionized water	Sequential leaching – acetic acid (5.7mL/litre)	Column (Rainfall) Leaching	Column (BLC) Leaching
As_2O_3 + *C*	970 cm^{-1}	1048 cm^{-1}	968 cm^{-1}	u.t.b.d
As_2O_3 + *C-Fe*	1018 cm^{-1}	1117 cm^{-1}	997 cm^{-1}	1009 cm^{-1}
As_2O_3 + *C-L*	970 cm^{-1}	1034 cm^{-1}	965 cm^{-1}	965 cm^{-1}
Na_2HAsO_4 + *C*	966 cm^{-1}	1060 cm^{-1}	967 cm^{-1}	u.t.b.d
Na_2HAsO_4 + *C-Fe*	997 cm^{-1}	1046 cm^{-1}	1004 cm^{-1}	1003 cm^{-1}
Na_2HAsO_4 + *C-L*	966 cm^{-1}	1068 cm^{-1}	963 cm^{-1}	963 cm^{-1}
As_2O_5 + *C*	970 cm^{-1}	1060 cm^{-1}	967 cm^{-1}	1017 cm^{-1}
As_2O_5 + *C-Fe*	1011 cm^{-1}	1032 cm^{-1}	1013 cm^{-1}	1023 cm^{-1}
As_2O_5 + *C-L*	967 cm^{-1}	1071 cm^{-1}	964 cm^{-1}	971 cm^{-1}

Key to above table u.t.b.d.= unable to be determined (S/S material unable to be removed from column, consequently no FTIR analysis was able to be performed)

When the solidification/stabilization formulations are contacted by acid, calcium hydroxide is neutralized and dissolved, exposing the silicates to aqueous hydrogen ion. The reactive silanol groups so formed then condense, producing longer and/or branched silicate structures as illustrated (Ortego 1991):

$$SiOX + H^{+} (aq) \rightarrow SiOH + X^{+}$$

Where X is calcium, potassium, sodium or toxic metal ions.

Then

$Si(OH)_x \rightarrow$ branched and cross linked silicates

The latter process destroys the cement matrix. Thus, the effectiveness of the immobilization process is compromised in two respects (Ortego 1991):

1. The chemistry of the system is now that characteristic of an acidic medium where most toxic metals are soluble and;
2. Any encapsulation effects associated with the cement matrix are drastically reduced.

5.2 Physical/Bulk Characterization

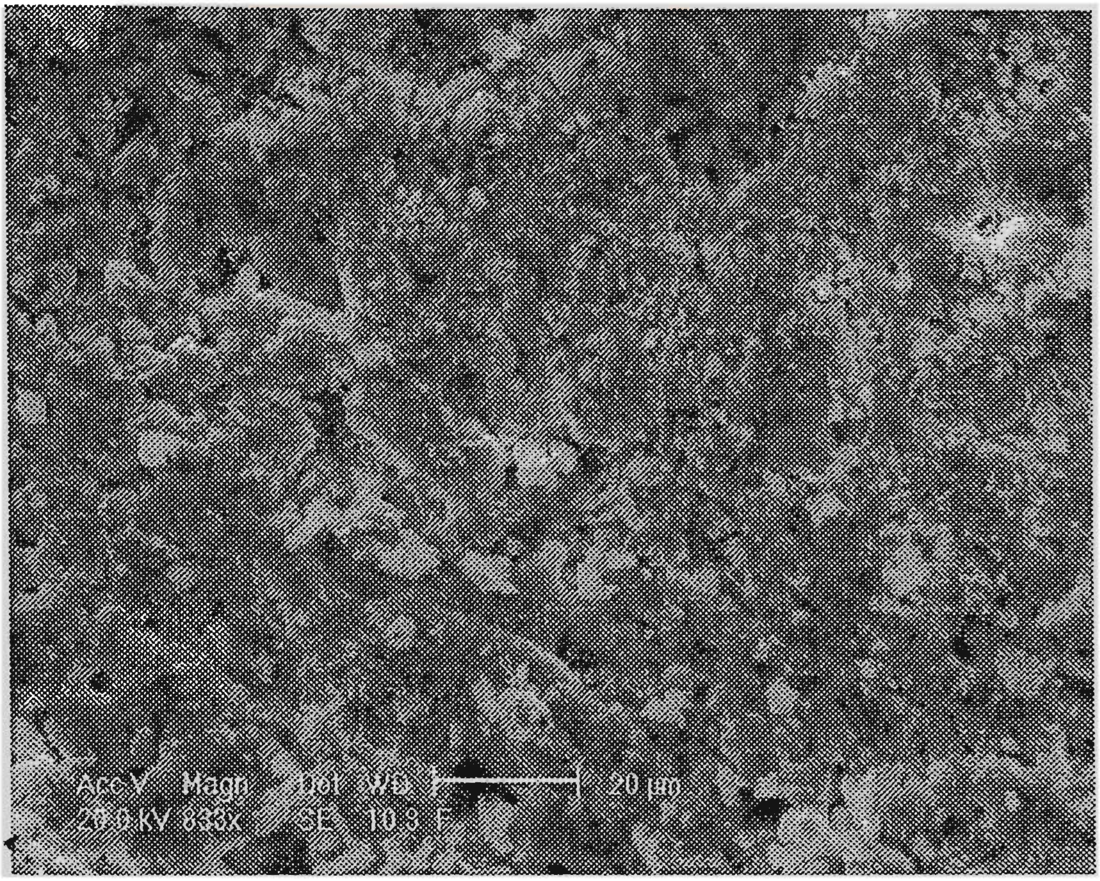
Physical characterization involves determining the macroscopic, microscopic, and morphological structure of the material. SEM can provide valuable insight into the microstructure and morphology.

5.2.1 Scanning Electron Microscopy (SEM)

A SEM investigation of the fixed arsenic pentoxide samples was undertaken, and has highlighted notable discrepancies between the various S/S formulations. Of the S/S formulations, it was not surprising that the cement only formulation had the least effect upon the cement matrix as can be observed by comparing the SEM Image of the As_2O_5 + *C* formulation (figure 5.5) with that of the OPC hydrated cement (figure 5.4). From the SEM image of the cement + lime formulation, additional $Ca(OH)_2$ crystals could be readily observed (figure 5.6). The cement + ferrous sulfate formulation has resulted in a large difference in the appearance of the cement matrix (figure 5.7). The As_2O_5 + *C-Fe* matrix has a very fibrous appearance, suggestive of ettringite formation.

Inspection of the EDXA spectra associated with the SEM images shows no unexpected differences. A notable decrease in the silicon intensity could be observed between the EDXA spectrums of the [cement + iron] and [cement + lime] formulations when compared to either the cement only formulations or the unadulterated hydrated cement. This is attributable to the dilution of the cement by inclusion of either the ferrous sulfate or lime.

Figure 5.4 - SEM image of OPC hydrated cement



EDXA Spectrum

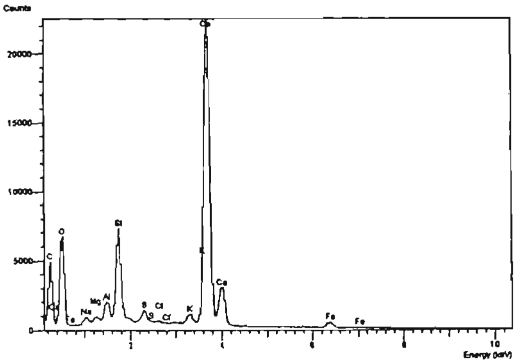
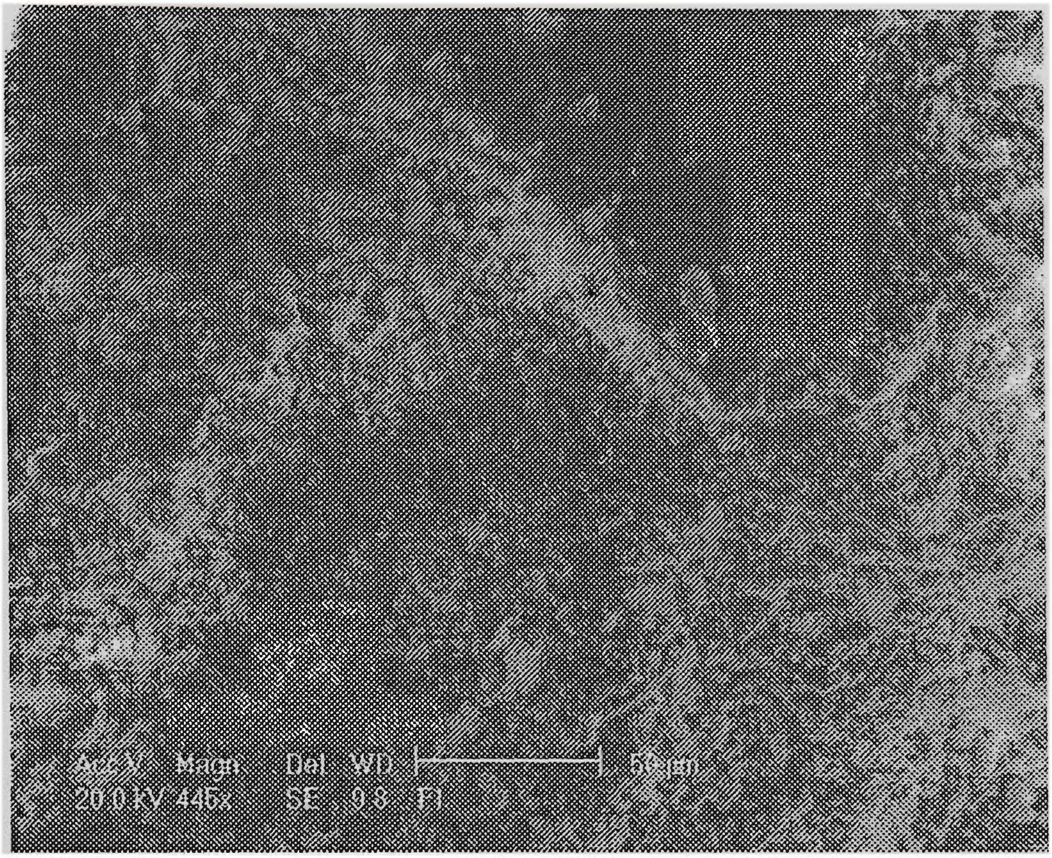


Figure 5.5 - SEM image of As_2O_5 + *C*



EDXA spectrum

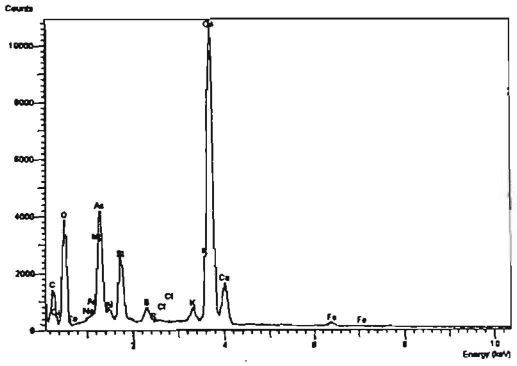
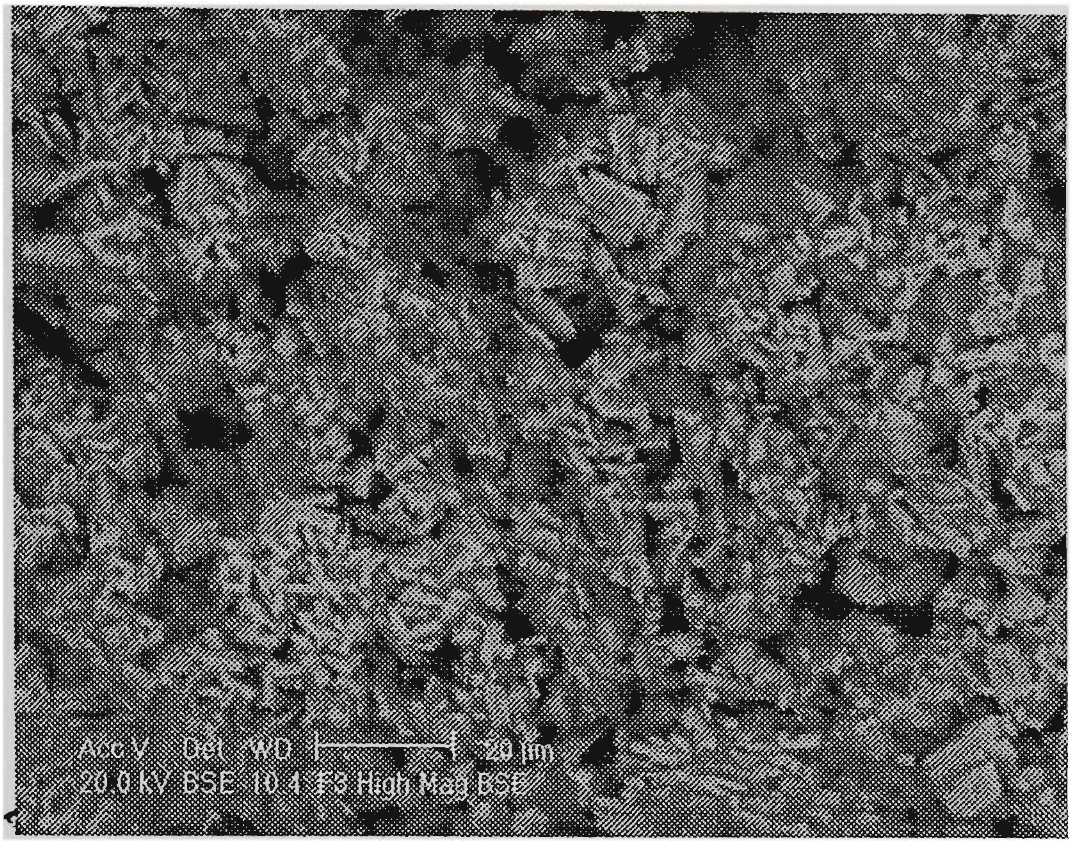


Figure 5.6 - SEM image of As_2O_5 + *C-L*



EDXA Spectrum

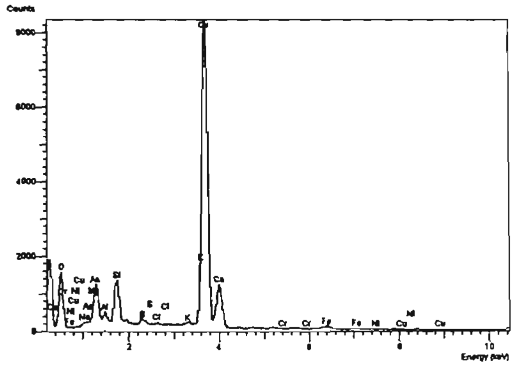
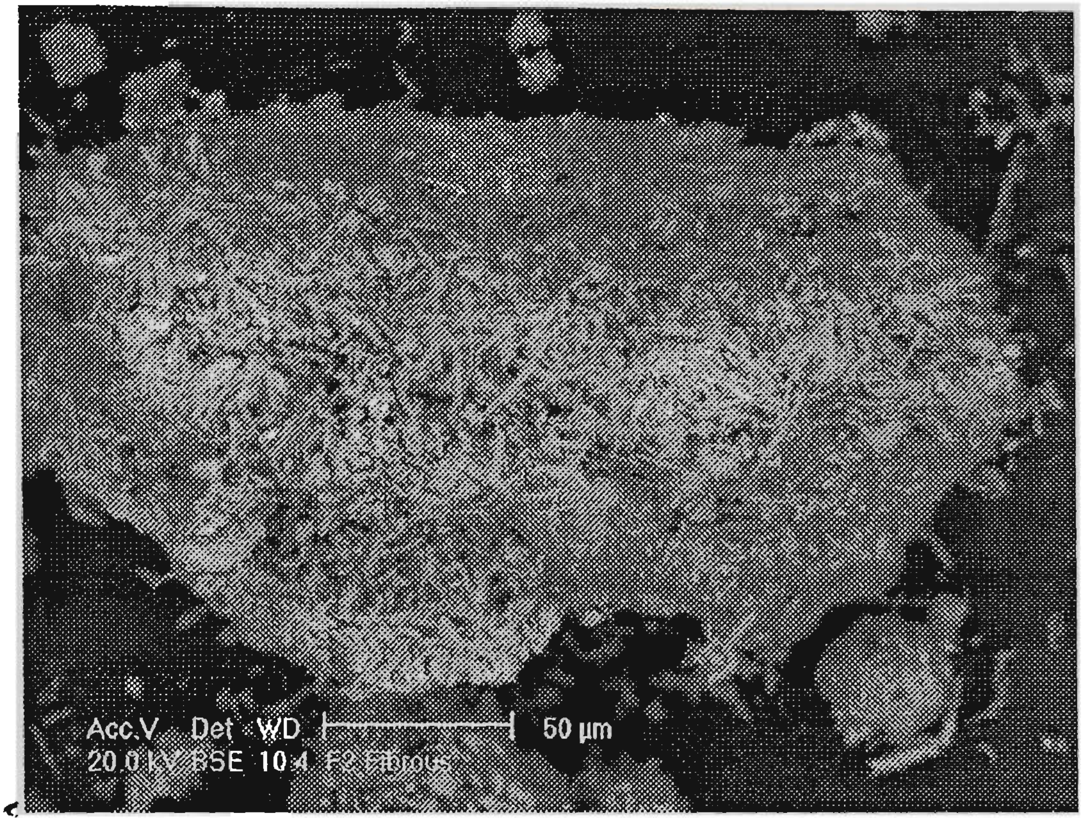
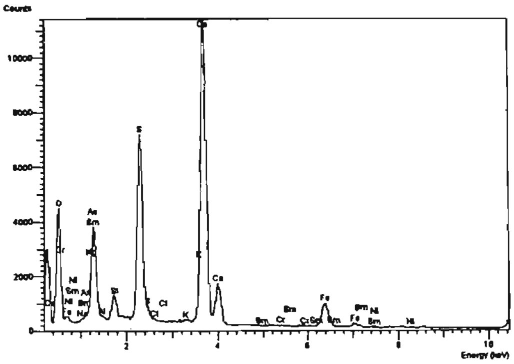


Figure 5.7 - SEM image of As_2O_5 + *C-Fe*



EDXA Spectrum



5.2.1.1 The effect of sulfate addition

Given the success of arsenic fixation which was achieved by Taylor and Fuessle (1994) and Fuessle and Taylor (2000) using ferrous sulfate, trials using this salt were also widely used in this study (chapters 3 and 4). The disadvantage of using this salt, however, is the addition of sulfate to the cement matrix. The effect of sulfate on cement-based S/S is chemically similar to sulfate attack in concrete. Large excesses of sulfate lead to the formation of calcium aluminate sulfate hydrate (i.e. ettringite). The hexagonal unit cell of ettringite contains two molecules of $3CaO.Al_2O_3.3CaSO_4.31H_2O$.

Formation of ettringite is typically required early in the curing process to control setting rate. Subsequently, the ettringite then dissolves and reprecipitates as calcium sulfate. However, a large presence of sulfate, for example from ferrous sulfate, allows ettringite to be re-formed.

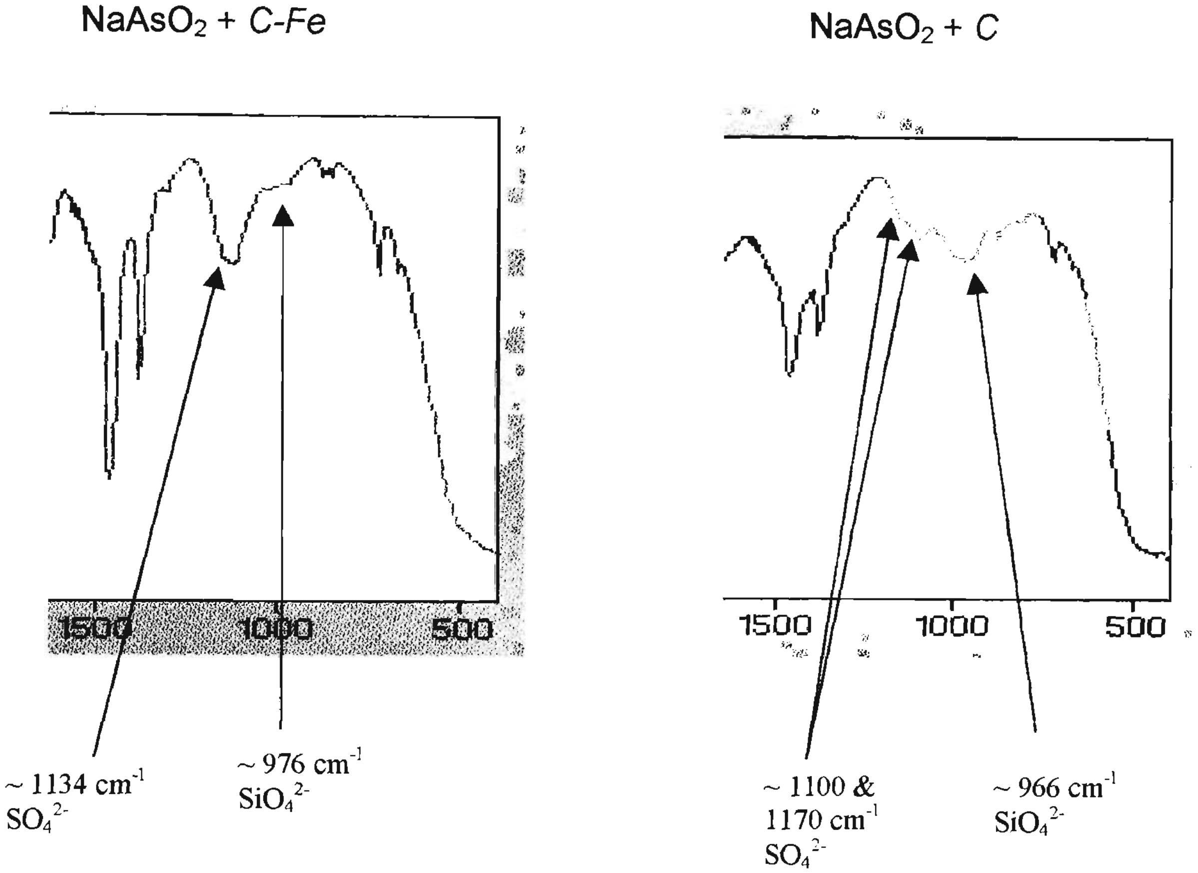
If the ettringite is formed while the S/S treated waste is still plastic, the material can accommodate the expansive salt. However, if the ettringite forms after the grout has become rigid, cracking can occur and will reduce the strength of the product. The formation of this salt, with its large amount of water of crystallization and consequently large increases in volume, can be destructive to the S/S treated product, increasing porosity and causing cracking.

Ettringite is suggested to be contained in the As_2O_5 + *C-Fe* formulations.. The extremely fibrous appearance of the As_2O_5 + *C-Fe* formulation is easily observable with the use of scanning electron microscopy as shown in figure 5.7. The presence of ettringite in the cured S/S formulations was also confirmed by FTIR. The sulfate peak from the cement + ferrous sulfate formulations was clearly evident as a strong singlet at 1130 cm^{-1}, the approximate wavenumber at which the sulfate from the ettringite is known to appear (Cocke et al 1992). Replacement of ettringite by monosulfate causes the sulfate band to move to lower wavenumbers (~ 1110 cm^{-1}) with a weaker sulfate band observable at approximately 1170 cm^{-1}. The difference in the location of the sulfate bands for the cement only and cement + ferrous sulfate stabilization of sodium arsenite is presented as figure 5.8.

The formation of ettringite can be an additional factor explaining the poor performance of the ferrous sulfate formulations. The problem of ettringite formation would have been largely avoided in the work highlighted by Taylor & Fuessle (1994) and Fuessle & Taylor (2000) for two reasons;

1. Their S/S formulations contained a lower percentage of arsenic therefore lower dosages of ferrous sulfate were required;
2. The arsenic waste used in the aforementioned research papers contained large quantities of Barium which would have reacted with the sulfate, forming $BaSO_4$. This, therefore, would have significantly reduced the quantities of excess sulfate contained in the S/S formulations.

Figure 5.8 – The difference in the location of the Sulfate peak between cement only and cement + ferrous sulfate formulations



$NaAsO_2$ + *C-Fe*

$NaAsO_2$ + *C*

~ 1134 cm^{-1} SO_4^{2-}

~ 976 cm^{-1} SiO_4^{2-}

~ 1100 & 1170 cm^{-1} SO_4^{2-}

~ 966 cm^{-1} SiO_4^{2-}

5.3 Matrix Characterization overview

The aim of this chapter was to highlight any discrepancies that may be present between the cement matrices of the various S/S formulations, which may hinder their performance when subjected to a variety of leaching scenarios. Discrepancies between the numerous S/S matrices may be as a result of the inclusion of various additives, namely ferrous sulfate or lime, or simply a result of the inclusion of the arsenic wastes.

FTIR analysis of the cement matrices was able to identify that the v3, asymmetrical Si-O stretch was found at the highest frequencies in the [cement + ferrous sulfate] formulations. The frequencies which the Si-O group was present at in the [cement + iron] formulations is suggestive of longer and/or branched silicate structures, the formation of which is known to be destructive to the cement matrix.

The addition of sulfate through the inclusion of ferrous sulfate to the cement matrix has resulted in the formation of etttringite. The presence of ettringite could be identified from the fibrous appearance of the As_2O_5 + *C-Fe* matrix when viewed with the Scanning Electron Microscope, and the higher frequency of the SO_4^{2-} group in the [cement + iron] formulations. The presence of ettringite can be destructive to the cement matrix by increasing its porosity

Throughout this thesis, in particular chapters 3 and 4, it has been repeatedly shown that those S/S formulations containing additional iron (ferrous sulfate) have been generally the worst performing formulations. In previous chapters, the poorer performance of these formulations has been shown to be partly attributable to the lower calcium content that the iron formulations contained. Iron, when used at identical arsenic mole ratios is generally less effective than calcium for the precipitation of arsenic (chapter 3 page 121). This chapter has highlighted further reasons which may have contributed to the poor performance of the ferrous sulfate containing formulations; principally the effect which the inclusion of ferrous sulfate has had on the cement matrix.

Chapter

6

6.0 CONCLUSION

Contamination of the environment is an issue of growing public concern, due to its possible impact upon human health. Concern over arsenic contamination of the environment is justified, given that exposure to arsenic is linked to a variety of health disorders and can ultimately result in death and also given the large extent of the problem.

Solidification/Stabilization or fixation, is widely applied to waste streams and contaminated soils and in this thesis has shown it can be capable of significantly reducing the arsenic leachate concentration. The most common form of this technology using a cement or pozzolanic binder to convert the waste to a monolithic waste form that limits contaminant mobility due to its low permeability and small surface area, has been extensively studied in this thesis.

Solidification/Stabilization technology has been demonstrated in this work to be capable of significantly reducing the leachability of arsenic (Leist et al 2000). Unfortunately, factors including additive-to-waste ratios, arsenic oxidation states, and the type of leaching tests that have been utilized have often differed in previous research. This has made it impossible to make any definitive conclusions about what form of the S/S technology is the most effective in reducing the leachability of arsenic.

This thesis has successfully addressed this important shortcoming by comparing and contrasting the efficacy of three Solidification/Stabilization (S/S) processes involving use of:

- Cement only,
- Cement + iron,
- Cement + lime,

All three S/S formulations had similar arsenic loadings (less than 10% by mass) and were evaluated using identical batch and column leaching tests.

While it may certainly not be clear which S/S processes are the most effective for the stabilization of arsenic, the use of iron appears to have been favored. Many researchers, including Artiola et al (1990), and Fuessle and Taylor (2000) have successfully used iron to stabilize arsenic containing wastes. Iron stabilization appears favored for two main reasons:

1. Iron arsenate is less soluble than calcium arsenate (Ksp for calcium arsenate is 6.8×10^{-19}, while the Ksp of iron arsenate is 5.1×10^{-21} at 25°C (Artiola et al 1990)).
2. Concerns over the stability of calcium arsenate. Calcium arsenates have been known to decompose in the presence of atmospheric carbon dioxide, consequently releasing arsenic back into the environment (Robins 1981, Robins and Tozawa 1982).

Despite this apparent preference for iron-arsenic stabilization, the results generated using the rapid regulatory leaching tests (ABLP or TCLP) (Chapter 3), or the longer term column leaching tests (Chapter 4), have generally shown, quite clearly, that those formulations to which the additional iron (ferrous sulfate) had been added, were clearly the least effective in immobilizing arsenic. When containing nearly identical arsenic loadings and assessed using the ABLP, the iron containing formulations were shown to give arsenic leachate concentrations anywhere up to 36 times larger than those obtained using either the [cement only] or the [cement + lime] formulations.

One factor that may have contributed to the poorer performance of the iron containing formulations, is the relative low Fe:As mole ratio used in this study (between 1.31 and 2.05). Arsenic solubility has been shown to decrease with increasing Fe:As mole ratios (Krause et al 1989), as predicted by the common ion effect. However, given that Artiola et al (1990) had success in reducing the arsenic leachability using an Fe:As ratio of 1.2, the low ratios used in this study can hardly be solely responsible for the dire performances exhibited.

Through microstructural analyses using FTIR and SEM, substantial changes could be identified to the microstructures of the iron formulations. Increased silicate polymerization and the compound ettringite were identified in these matrices. Both of these are known to increase the porosity and be generally detrimental to the overall performance of cement. Previous successful studies, such as those conducted by Artiola et al (1990), and Fuessle and Taylor (2000) using iron, in particular ferrous sulfate, have dealt with the disposal of wastes with relatively low arsenic contents when compared to the arsenic compounds used in this study. For example, the work conducted by Artiola et al (1990) involved the stabilization of a soil which contained a mere 1.8% As. Given the higher arsenic concentrations of the compounds that have been used in this study, larger masses of additives such as ferrous sulfate have been used. From this study it appears that, for highly concentrated arsenic wastes, the large masses of any additives such as ferrous sulfate that are required have a very pronounced detrimental effect upon the cement matrix, more so than the arsenic wastes themselves.

Given the large $Ca(OH)_2$ content of cement, it is not surprising that the leachates collected from the cement based stabilization procedures are very alkaline. For example, the pH of the leachate collected from the ABLP (deionized water) testing of the As_2O_3 + *C-Fe* formulation was 11.50. These high pHs are also where ferric arsenates are the most soluble. For example, work conducted by Papassiopi et al (1994) has shown that the solubilities of ferric arsenates increase considerably over a pH of 7.5. Hence it appears that cement based S/S will never provide the most suitable means for the further stabilization of ferric arsenates.

Unlike the iron formulations, those formulations containing additional calcium were shown to be very successful. Calcium appears to not only reduce the arsenic leachability by the formation of insoluble calcium arsenites or arsenates within the S/S matrix, but may also form them in the leachate. Regardless of the type of leaching test conducted, high calcium leachate concentrations often resulted in low arsenic leachate concentrations. As soon as the quantities of calcium in the leachate decreased, the arsenic leachate concentrations were shown to increase just as suddenly. Despite all the indications that the reduction in the arsenic leachate concentration is linked to the calcium content of the formulations, definitive characterization techniques such as XRD are required to prove this beyond doubt

In those rare instances during which the [cement + lime] formulations produced higher leachate concentrations than the [cement + iron] formulations, such as during the commencement of the column leaching tests, the increased arsenic leachate concentration was shown not to be attributable to exposure of the formulation to CO_2 and hence dissolution of the calcium arsenates or arsenites. Instead, the increase in the arsenic leachate concentrations of the [cement + lime] formulations are suggested to be a result of the reduced strength of these matrices. Not on any single occasion throughout the entire six month duration of the column leaching tests, could the release of arsenic from any of the S/S formulations be found to be attributable to the dissolution of calcium arsenites or arsenates, resulting from exposure to carbon dioxide.

Though not always the case prior to fixing, this thesis has also shown that the lowest leachate concentrations were always obtained when the arsenic was present in the +5 or arsenate form. This is not surprising considering calcium appears to dictate the leaching of arsenic and $Ca_3(AsO_4)_2$ (Ksp = 6.8×10^{-19}) is less soluble than $CaHAsO_3$ (Ksp = 1.07×10^{-7}).

Arsenic is significantly affected by redox potential, which causes changes in oxidation state and speciation. Under mildly reducing conditions As(III) is present, while at higher Eh conditions As(V) is predominant. From the measurement of the leachate redox potentials, it is suggested that the arsenic primarily stays in the same oxidation state as it was when originally introduced, since the arsenate containing formulations always exhibited higher leachate redox potentials than those obtained from the arsenite containing formulations.

As a result of the work described in this thesis, it is now possible to identify which of the formulations investigated ([cement only], [cement + iron], [cement + lime]) offers the most promise for dealing with arsenic wastes. The [cement only] or the [cement + lime] formulations were shown to be the most effective. While the [cement + lime] formulation generally yielded the lowest leachate concentrations, the difference between the results obtained from either the [cement only] or the [cement + lime] formulations were often not substantial, as increasing the Ca:As mole ratio above 7 was shown to return diminished benefits. Just whether the [cement only] or the [cement + lime] formulations are chosen will ultimately be dependent upon what other components are present in the waste. For example in the stabilization of the lead arsenate formulation, the [cement only] formulation would be a more appropriate choice, given that lead solubility increases with leachate pH. The exact nature of the leaching process used to determine the efficacy of the stabilization process will also aid in the choice of which of the two formulations is more appropriate. Batch tests such as the current regulatory tests, the TCLP and ABLP would favor the choice of the [cement + lime] formulations, as the batch tests provide greater opportunities for re-precipitation. For this scenario, the formulation that contains larger calcium quantities, [cement + lime] would be a more appropriate choice.

An additional aim of this thesis was to compare and contrast the results generated from the regulatory leaching methodologies with the conceptually more realistic column leaching setups. While it is widely appreciated that the current regulatory leaching tests are very severe in terms of the masses they leach, it is not so well known just how severe they are, or whether indeed those formulations that behave the most satisfactorily with the regulatory leaching tests will also behave as favorably when subjected to more realistic leaching scenarios.

Both of the current regulatory tests, i.e., TCLP and ABLP, were shown to yield similar arsenic leachate concentrations when using the same leachant. It was also found, somewhat surprisingly, that despite their harsh extraction processes these tests can result in lower arsenic masses in the leachate. This was achieved due to the severity of these batch tests producing high concentrations of both arsenic and calcium in the leachate. This allowed for the formation of insoluble calcium-arsenic precipitates and subsequent lower arsenic concentrations once filtered.

As alluded to previously, regardless of the leaching scenario that was utilized, it was clear that the leaching of arsenic was related to the leaching of calcium. However, those S/S formulations with the highest Ca:As mole ratios, i.e., the [cement + lime] formulations, were not always the best performers. While the [cement + lime] formulations may have been the most successful for the aggressive regulatory tests, they were not always so successful initially in column tests, such as the column (BLC) tests. The results obtained from the less aggressive column leaching tests were shown to be greatly affected by the negative influences of either the arsenic compounds or additives upon the cementation reactions. The poorer performance of the [cement + lime] formulations when accessed with the column (BLC) tests can be attributed to the reduced physical strength of these matrices, a result of the large lime additions. The [cement + lime] and [cement only] formulations containing sodium arsenate initially produced results that were worse than those formulations that contained lower Ca:As mole ratios. This was proposed to be a result of the negative influences that sodium arsenate exhibited upon the cementation reactions.

Increasing environmental awareness by communities will undoubtedly cause industry and regulatory bodies to continually strive to improve ways in which hazardous materials are handled and disposed. As they stand, the current regulatory tests are flawed because they do not represent real landfill conditions. This thesis, however, has reinforced the notion that no one leach test can ever possibly hope to replicate conditions that a waste may encounter when disposed of in a landfill. Even when using the same type of leaching tests, column tests, which are conceptually more realistic than the current regulatory batch leaching tests, those S/S formulations that behaved most favorably at one particular flow rate did not always perform so favorably at a different flow rate. Hence, careful selection of flow rates is required. Even if, as in this thesis, flow rates are based on actual rainfall data, the masses that would be leached using these tests would still possibly bear little resemblance to those that would be leached in a landfill situation. Hence, those S/S formulations that behaved most favorably using these tests may still not be those that will behave the best when finally disposed of, since the column (rainfall) tests used a constant flow rate. However, in landfill conditions, the S/S material would be submitted to intermittent leachant. This could possibly consist of periodic rainfall followed by extended dry periods or, perhaps, heavy rainfall which may result in flooding, in which case the waste may be inundated with stagnant leachant for extended periods of time. Hence, any attempts to accurately predict the levels of hazardous components that may be leached seems futile. At best, leaching tests can be used as guide to what formulations may behave the most favorably when subjected to either a worst case or best case scenario. However, if the option taken is to try to endeavor to mimic a worst case scenario, care must be taken that this aim is, indeed, achieved. The results contained in this thesis illustrate that the "worst case scenario" (batch leaching) can, on occasions, yield results that are more favorable than the intended "best case scenario" (column leaching). It appears that this danger will always be present if the leaching test is capable of releasing into solution large quantities of elements that are likely to form insoluble precipitates, such as calcium and arsenic.

6.1 Future Work

The management and disposal of arsenic wastes is a large problem, and consequently it is not surprising that there are still areas for further research.

It is recommended that the following research areas be considered for furhter study:

- *Refining the Solidification/Stabilization formulations investigated in this thesis.*

  The main aim of investigating the S/S processes in this thesis was to enable the effectiveness of the formulations to be compared and contrasted with one another at equal arsenic dosages. While this has been achieved, work has not been undertaken to determine the maximum arsenic loadings that the S/S formulations can contain and still meet regulatory obligations. If any of the S/S formulations investigated in this thesis were to be used commercially, such trials would have to be undertaken.

  The S/S of arsenic wastes has been shown to be clearly most effective when arsenic was present in the pentavalent state. Therefore, trials are required to investigate the most efficient and effective means of oxidizing As(III) to As(V).

- *Developing other options, apart from the cement based S/S for the safe disposal of arsenic wastes.*

  Alternatives to cement based S/S could include the incorporation of arsenic into waste smelter slags, thus providing the opportunity to safely dispose of two waste streams at the one time. The only down side of such a process would be that the success of the process would be highly dependent upon the individual chemistry of both the arsenic waste and the slag, not just the waste system as was the case in this present study. The possible success of the process may become even harder to predict than cement based S/S.

Another possible, and perhaps more attractive alternative, may see arsenic wastes encapsulated into post-consumer "mixed plastics". Presently, as a result of kerbside recycling there is an enormous glut of "mixed plastic". Thus the low cost of "mixed plastics" coupled with its poor biodegradability may result in plastics being a viable alternative for the stabilization or arsenic wastes. However significant research will have to be undertaken before this can be determined.

- *Work on the isolation or recovery of arsenic.*

  From the work carried out in this study, it is clear that the arsenic leachate concentrations obtained varied between the arsenic compounds investigated, even if they were initially present in the same oxidation state. For example, sodium arsenate yielded significantly larger arsenic leachate concentrations than arsenic pentoxide. Therefore, work on the isolation or recovery of arsenic from the other components may be of great use e.g. volatizing the arsenic as AsH_3 and devaporising it as As metal. Such a process would not be undertaken with the aim of recycling or reusing the arsenic, as the demand for arsenic today is too low. The aim, however would be to make Solidification/Stabilization a more predictable science for the disposal of arsenic. In isolating the arsenic there would be concurrent removal of possible interferents to the cementation reactions.

Removal of arsenic, or perhaps "soil washing" would also reduce the bulking factor, resulting in a smaller portion of material having to be disposed of in secure landfills. The majority of the arsenic contaminated sites in Australia are a result of former agricultural uses (e.g. sheep and cattle dips). There are in excess of a thousand such sites in the state of Queensland alone (Chappell et al 1992). Hence the volume of contaminated soil that would have be removed and

> disposed of in secure landfills would be prohibitively large (even more so considering that Solidification/Stabilization typically increases the mass to be disposed of by a factor of 10). Soil washing would allow as much clean soil to be recovered as possible, allowing for the soil contaminants (e.g. arsenic) to be concentrated. The recovered, or clean soil would then be ideally kept at the site of origin, or at least beneficially reused/recycled in some other way.

While much work on the disposal of arsenic wastes is still required, this thesis has contributed significantly to knowledge of cement based S/S. This thesis has been able to prove that cement based S/S can offer positive solutions to the large predicament of disposing safely of arsenic wastes. Regardless of the initial oxidation state, [cement + lime (calcium)] formulations have been shown to offer the most promise in dealing with arsenic wastes. Light has also been shed on the leaching tests used to determine the efficacy of the stabilization processes. Unless leaching tests are performed in situ, and for longer durations the numbers generated are merely that, numbers.

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Appendix A

Molar compositions of the S/S formulations

Arsenic Trioxide S/S formulations

Molar compositions	Arsenic	Calcium	Iron
Cement only	9.7×10^{-4}	7.4×10^{-3}	2.5×10^{-4}
Cement + iron	1.3×10^{-3}	4.3×10^{-3}	1.7×10^{-3}
Cement + lime	2.1×10^{-3}	8.7×10^{-3}	1.8×10^{-4}

Arsenic Pentoxide S/S formulations

Molar compositions	Arsenic	Calcium	Iron
Cement only	8.4×10^{-4}	8.5×10^{-3}	2.6×10^{-4}
Cement + iron	9.5×10^{-4}	4.4×10^{-3}	1.4×10^{-3}
Cement + lime	7.7×10^{-4}	8.4×10^{-3}	1.4×10^{-4}

Sodium Arsenite S/S formulations

Molar compositions	Arsenic	Calcium	Iron
Cement only	9.9×10^{-4}	8.1×10^{-3}	3.4×10^{-4}
Cement + iron	1.1×10^{-3}	5.0×10^{-3}	1.9×10^{-3}
Cement + lime	1.1×10^{-3}	9.0×10^{-3}	1.9×10^{-4}

Sodium Arsenate S/S formulations

Molar compositions	Arsenic	Calcium	Iron
Cement only	7.8×10^{-4}	6.7×10^{-3}	2.2×10^{-4}
Cement + iron	8.2×10^{-4}	3.6×10^{-3}	1.2×10^{-3}
Cement + lime	6.4×10^{-4}	6.8×10^{-3}	1.2×10^{-4}

Lead Arsenate S/S formulations

Molar compositions	Lead	Arsenic	Calcium	Iron
Cement only	6.2×10^{-4}	6.6×10^{-4}	7.2×10^{-3}	2.1×10^{-4}
Cement + iron	6.3×10^{-4}	6.5×10^{-4}	3.5×10^{-3}	1.3×10^{-3}
Cement + lime	4.6×10^{-4}	4.5×10^{-4}	5.6×10^{-3}	1.5×10^{-4}

Appendix B

Australian Bottle Leaching Procedure (ABLP)

Australian Standard 4439.3 - 1997

STANDARDS AUSTRALIA

Australian Standard
Wastes, sediments and contaminated soils

Part 3: Preparation of leachates-Bottle leaching procedure

1 SCOPE This Standard provides a method for the preparation of leachates from liquid and solid wastes, sediments, sludges and soils for assessing the potential of inorganic and semivolatile organic contamination of groundwater, in a variety of disposal-to-land scenarios. It deals only with the preparation of the leachate and does not describe procedures prior to submitting samples to the laboratory for analysis or sub-sampling. The range of analyte compounds includes, but is not limited to, those compounds with a vapour pressure in the range IO~1 mm Hg to iO~^{7} mm Hg and with a boiling point greater than 150^{0}C.

The procedure is not applicable to encapsulated wastes which cannot be reduced to the specified maximum particle size without breaking the integrity of encapsulation.

The pH and the oxidation-reduction (redox) potential, or Eh, of a leaching fluid may vary with each disposal environment and is known to affect the leaching of metals and possibly some organic species. No provision is made in this procedure, however, to control pH and Eb during leaching. As an aid to interpretation of results, it is recommended that the Eh of the extracted sample liquid and the solids leachate be measured and reported.

2 REFERENCED DOCUMENTS The following documents are referred to in this Standard:

AS	
1152	Specification for test sieves
2162	Verification and use of volumetric apparatus
2162.1	Part 1: General-Volumetric glassware
2163	Laboratory glassware Measuring cylinders
2243	Safety in laboratories
2243.1	Part 1: General
2243.2	Part 2: chemical aspects
4439	Wastes sediments and contaminated soils
4439.2	Part 2: Preparation of leachates-Zero headspace procedure

AS/NZS	
2243	Safety in laboratories
2243.3	Part 3: Microbiology

ISO	
3696	Water for analytical laboratory use-Specification and test methods

ASTM	
D1498	Practice for oxidation-reduction potential of water

3 DEFINITIONS For the purpose of this Standard, the definitions below apply.

3.1 **Laboratory sample**-a sample as received by the laboratory from the field and intended for inspection or testing.

3.2 **Leaching fluid**-the solution produced in the laboratory to be used for the leaching of the test sampTe.

3.3 **Percentage solids**-that amount of a test portion remaining after aTT liquids have been expelled by pressure filtration under a pressure of 350 kPa, expressed as a percentage.

3.4 **Sample**-one or more items taken from a lot and intended to provide information about the lot and, possibly, to serve as the basis for a decision on the lot or on the process which has produced it.

3.5 **Sample liquid-the** liquid which is separated from a test sample by pressure filtration as described in Clause 8.3.

3.6 **Solids leachate-the** liquid produced by treatment of the solids with the leaching fluid and subsequent filtration.

3.7 **Test portion-the** quantity of material taken from the test sample (or, if both are the same, from the laboratory sample) and on which the test or observation is actually carried out.

3.8 **Test sample-a** sample prepared from the laboratory sample and from which test portions will be taken.

4 PRINCIPLE The percentage solids is determined by pressure filtering a weighed portion and weighing the extracted sample liquid. A second test portion is subjected to pressure filtration and the sample liquid collected and stored. The solids remaining are reduced in particle size if necessary and leached by agitation with a selected leaching fluid. The solids leachate is recovered by pressure filtration through a glass fibre filter with 0.6 ~m to 0.8 ~m effective pore size. The sample liquid and solids leachate thus obtained are then analysed by appropriate test methods.

5 REAGENTS

5.1 **General requirement** Unless otherwise specified, all reagents shall be of analytical reagent grade. All containers should meet requirements of Clause 6.1.

5.2 **Reagent water Water of laboratory Grade** 1 as defined in ISO 3696 shall be used.

5.3 Leaching fluid

5.3.1 *General* The leaching fluid shall be tested immediately before use to ensure ~onformit~ to the specified pH value. Leaching fluids not prepared immediately prior to use shall also be examined for indication of contamination or deterioration. In the presence of microbial growth, colouration, solid or suspended matter, the solution shall be discarded and fresh leaching fluid prepared.

5.3.2 *Leaching fluid pH 2.9* Add 5.7 mL of glacial acetic acid (P20 = 1.01 g/mL) to 900 mL of water. Dilute to 1 L with water. The pH of this fluid should be 2.8 to 3.0 and adjustment of pH is not permitted.

5.3.3 *Leaching fluid pH 5.0* Add 5.7 mL of glacial acetic acid (P20 = 1.01 g/mL) to approximately 900 mL of water. Add 64.3 mL of 1 mole/L sodium hydroxide solution, dilute to 1 L with water and mix well. If the pH is not 4.9 to 5.1, adjust by dropwise addition of 1 mol/L acetic acid or 1 mol/L sodium hydroxide solution as appropriate. Store in an airtight container.

5.3.4 *Leaching fluid pH 9.2* Dissolve 38.2 g of sodium tetraborate decahydrate (borax, $Na_2B_4O_7.10H_20$) in approximately 900 mL of water, dilute to 1 L and mix well. The pH of this fluid shall be 9.1 to 9.3, otherwise it should be discarded. Adjustment of pH is not permitted. Store in an airtight container.

5.4 Compressed gas Pressure controllable up to *350* kPa, free of partic~ate and organic contaminants.

6 APPARATUS

6.1 General All devices with which the sample or leaching fluids come into contact shall be made of a material(s) which will not leach or adsorb analytes such as-

(a) glass;

(b) polytetrafluoro ethylene (PTFE);

(c) stainless steel Type 316; or

(d) polyethylene, polypropylene or polyvinyl chloride when only inorganic analytes will be determined.

These components shall be cleaned so that they do not contribute significantly to the level of analyte being determined.

6.2 Glassware Graduated measuring cylinders shall comply with AS 2163. The use of volumetric glassware shall comply with AS 2162.1.

6.3 pH Meter Accurate to +0.05 pH units at *25^0C.*

6.4 Laboratory balance Accurate to +~0.1 g.

6.5 Filters Filter disks to suit devices specified in Clause 6.6 and made of borosilicate glass fibres, not containing binder materials and with an effective pore size of 0.6 ~m to 0.8~m or equivalent, are suitable.

6.6 Pressure filtration device Any filter holder capable of supporting a 0.6 µm to 0.8 µm glass fibre filter membrane with a minimum of 47 mm in diameter, with the ability to withstand a pressure of 350 kPa or more and a capacity of at least 300 mL is suitable. An example of a suitable pressure filtration device is shown in Figure 1.

NOTE:The recommended device has a capacity of 1.5 L and 142 mm diameter.

6.7 Liquid collection vessels Containers for collection and storage of sample liquid and solids leachate prior to analysis must be composed of any of those materials listed in Clause 6.1.

6.8 Agitation apparatus Capable of rotating extraction bottles in an end-over-end fashion at 30 ±2 revolutions per minute.

6.9 Extraction bottles Capable of containing up to 100 g of sample and up to 2000 g of leaching fluid, with at least 100 mL of headspace.

6.10 Sieve Plate or mesh sieve with an aperture dimension of approximately 2.4 mm and complying with AS 1152.

7 SAMPLING AND SAMPLE PREPARATION

7.1 Collection Samples shall be large enough to support all the requirements of this method. There shall be sufficient sample to perform, where required, the following-

(a) preliminary determination of total analytes, if necessary;

(b) preliminary evaluation of the solids content (Clause 7.3);

(c) preliminary screening of waste pH (Clause 7.5);

(d) leaching of solids for determination of metals;

(e) leaching of solids for determination of semi-volatile compounds;

(f) leaching of solids for determination of volatile organic compounds; and

(g) any repeat analyses.

WARNING: APPROPRIATE SAFETY PRECAUTIONS AS DEFINED IN AS 2243, PARTS 1, 2 AND 3 SHOULD BE TAKEN.

7.2 Storage Samples shall be stored at 2^0C to 6^0C, in a manner to prevent change in content or leachability of analytes, in vessels specified in Appendix C. Sample vessels should be filled to capacity and only opened immediately prior to leaching. Leaching of samples shall be carried out as soon as possible, but within the maximum holding times specified in Table 1. They should be stored in accordance with Appendix C.

TABLE 1

MAXIMUM SAMPLE HOLDING TIMES (DAYS)

Analyte	**Maximum sample holding time prior to bottle leaching** **days**
Inorganics	
Metals (all)	28
Anions (Cr, F~, 1-, $S0_4^{2}$-, S^{2} -, CN~, NO_{2}~, **NO_{3}~, PO4~**)	7
Nitrogen (total Kjeldahl, NH_3INH_4+)	7
Phosphorus (all forms)	7
Organics	
Hydrocarbons (including total petroleum hydrocarbons, PARs)	7

Pesticides, organochiorine (OCs)	28
Pesticides, other	7
Phenolics	7
Polychlorinated biphenyls (PCBs)	28
Other	14

7.3 Determination of percentage solids The percentage solids in the sample shall be determined as follows:

(a) Weigh the vessel that is to receive the filtrate (m_1).

(b) Weigh approximately 100 g of the test sample into a beaker and record the combined weight. Transfer as much as possible to the pressure filtration device (6.6), fitted with a filter (6.5). Spread the waste sample evenly over the surface of the filter. Reweigh the beaker and calculate the mass of waste transferred (m_2) by difference.

WARNING: SUITABLE CONTAINMENT PROCEDURES SHALL BE IN PLACE TO ISOLATE FLYING PARTS IN THE EVENT OF OVER PRESSURE EXPLODING THE DEVICE.

(c) Apply a pressure of 50 kPa to the pressure filtration device, and maintain it until liquid ceases to pass through the filter. Gradually increase the pressure, in 50 kPa increments, to 350 kPa.

(d) When filtration is complete (i.e. when no liquid has passed during the previous I mm period). Weigh the receiving vessel plus filtrate (m_3).
NOTE: If the sample liquid Contains volatile solvents, then either the receiving vessel is designed to prevent loss of volatiles (e.g. narrow neck flask) or the pressure filtration device is weighed before and after to determine the mass of liquid collected.

(e) Calculate the percentage solids from the following equation:

$$\text{Percentage solids} = 100 - \frac{(m_3 - m_1) \times 100}{m_2}$$

where

m_3 = mass of the receiving vessel plus filtrate, in grams

m_1 = mass of the empty receiving vessel, in grams

m_2 = *mass of sample transferred, in grams*

NOTE: For testing metals and semi-volatile organic compounds, it is allowable to use the solid portion from this preliminary evaluation for subsequent leaching as described in Clause 8, provided that no particle size reduction is required (see Clause 7.4), and the sample liquid is collected and. It may be necessary, however, to filter more than 100 g of waste, as some solids may be used for other preliminary tests.

7.4 Reduction of sample particle size

7.4.1 *General* To ensure that test portions adequately represent the laboratory sample, all particles in a test sample of at least 250 g mass shall be reduced if necessary to pass through a 2.4 mm aperture sieve (6.10). The sample shall be chilled to 1^0C-4^0C prior to particle size reduction and care taken during the process to prevent the generation of heat.

NOTE: Percentage solids are to be determined before particle size reduction.

7.4.2 *Large particles* If the sample is predominantly greater than 2.4 mm particle size, or if the larger particles are not significantly different from the bulk of the material, then the whole test sample should be reduced to pass through a sieve (6.10) in such a way as to minimize any loss of analytes of interest.

If a relatively small proportion of material is greater than 2.4 mm maximum particle size, and is significantly different in type from the bulk of the material, then this fraction should be removed from any test sample, discarded and this noted in the report.

7.5 Selection of leaching fluid The leaching fluid selected shall be appropriate to the landfill category and selected from Table 2. If the proposed landfill category is such that an acidic leaching fluid is specified, the following preliminary procedure shall be performed:

(a) Weigh out a small subsample of the solid phase of the waste, reduce the solid, if necessary, to a particle size of approximately 1 mm in diameter or less. Transfer 5.0 g of this solid phase of the waste to a 500 mL beaker or erlenmeyer flask.

(b) Add 100 mL of water to the beaker, cover with a watchglass, and stir vigorously for 5 mm using a magnetic stirrer. Measure and record the pH.

(c) If the pH is less than *5.0,* then use leaching fluid (5.3.3) and proceed to Clause 8.

(d) If the pH is greater than *5.0,* add 3.5 mL of 1 mol/L HCl, slurry briefly, cover with a watchglass, heat to 50^0C to 60^0C and hold at this temperature for 10 mm.

(e) Let the solution cool to room temperature and record the pH. If the pH is less than 5.0, use leaching fluid (5.3.3); if the pH is greater than *5.0,* use leaching fluid (5.3.2).

TABLE 2

SUGGESTED LEACHING FLUIDS

Class	Landfill category	Leaching fluid
CLASS 1	In situ–to be left undisturbed at the site	Reagent water
CLASS 2	Monofilled	
	2a Putrescible material	Acetate buffer pH 5.0
	2b Non-putrescible material	Reagent water
CLASS 3	Co-disposed with	
	3a Putrescible material	Acetate buffer pH 5.0 or pH 2.9
	3b Non-putrescible material	Acetate buffer pH 5.0 or pH 2.9 and Tetraborate buffer pH 9.2 (i.e. two leaches)
CLASS 4	Disposed of without confinement e.g. dispersed over land	Reagent water

NOTES:

1. Subject to regulatory approval for a specific site assessment, other appropriate leaching fluids, such as local groundwater or seawater, may be used in place of those above. Use of groundwater as a leaching fluid may prove difficult as it would need to be maintained in the same chemical, physical and biological environment from which it was obtained up to and during the extraction process. It may also be difficult to interpret data unless the complete chemical composition of the groundwater is known due to analytical interferences and chemical speciationl precipitation reactions.
2. Some losses of cyanide, fluoride, iodide and sulfide may be experienced where non-alkaline leach fluids are used. If these leach fluids must be used, see AS 4439.2 for requirements for the zero headspace procedure.

8 PROCEDURE

8.1 Number of determinations Using the procedure described in Clause 8.3, a single test portion from each test sample shall be leached. In addition, duplicate test portions shall be leached from selected test samples at a rate not less than one duplicate leach in every 10 test portions or one duplicate leach for each batch of samples, whichever is the greater rate.

8.2 Blank test A blank test shall be run in parallel with the test samples using the same procedure and reagents in the same quantity but omitting the sample. A blank test shall be run with each batch or at a rate of at least one in every 10 samples processed.

Should the level of analyte determined in the blank be greater than 20% of the appropriate regulatory limit, the source of contaminants shall be determined and rectified before any further samples are processed.

8.3 Preparation of sample liquid The procedure for preparing sample liquid and solids leachate as shall be as foTlows:

(a) Weigh out the mass of test portion, as determined from the following equation into a beaker or similar vessel and record the weight:

$$\text{Mass of test portion, (grams)} = \frac{100 \times 100}{\text{percentage solids}}$$

Notes:

1 The purpose in using the amount of sample calculated as above is to provide a mass of approximately 100 g of solids for leaching. For samples with low solids content, the mass calculated above may exceed the amount of sample available or the volume of the pressure filtration unit. In this case, a smaller sample may be filtered, provided it is derived by filtration of at least 100 g of sample, not less than 5 g of solids are obtained and the leachate derived is sufficient to support all of the analyses required. Should this not be possible, additional sample must be obtained or multiple filtrations must be performed.

2 For samples of high percentage solids content, the amount of liquid obtainable by filtration of 100 g may not be sufficient to support its separate analysis. In this case, a larger sample, up to 500 g, should be filtered. Should this still produce insufficient liquid for separate analysis, the liquid derived may be combined with the solids leachate obtained in Clause 8.4(a) to (f) for analysis.

3 If particle size reduction is required, at least 250 g of sample is to be filtered (see Clause 7.4.1).

(b) Weigh an empty liquid collection vessel (6.7) for collection of sample liquid. Record this mass (m_4) and place the vessel beneath a pressure filtration device (6.6).

(c) Quantitatively transfer the test portion to the pressure filtration device (6.6) with a filter *(6.5)* installed. Reweigh the beaker and calculate the mass transferred *(m_5)* by difference. Spread the waste evenly over the surface of the filter.

(d) Seal the pressure filtration device and then apply gentle pressure of up to 50 KPa. Maintain this pressure for 2 mm, then increase the pressure in 50 kPa increments, holding at each pressure for 2 mm, up to 350 KPa. Collect the filtered sample in a preweighed liquid collection vessel (6.7).
NOTE: Instantaneous application of high pressure can degrade the glass fibre filter or may cause premature plugging or rupture.

(e) Hold the pressure at 350 kPa until no further liquid flow is detected during any 1 mm period; then shut off the gas pressure and reweigh the liquid collection vessel. Calculate the mass of liquid collected *(m_6)* by difference.

NOTE: If the sample liquid contains volatile solvents, then either the receiving vessel is designed to prevent loss of volatiles (e.g. narrow neck flask) or the pressure filtration device is weighed before and after to determine the mass of liquid collected.

(f) Remove a small portion of the collected sample liquid and measure and record its pH. Store the remaining liquid prior to analysis

NOTE: If redox potential is to be measured using ASTM D1498, a small portion of the leachate should be removed for this purpose at this stage and the measurement made within 5 mm of the portion being withdrawn.

(g) Remove the filter and the material remaining ('the solids') from the pressure filtration device. Clean the filtration device before re-use.

8.4 Leaching of solids The procedure shall be as follows:

(a) Reduce the particle size of the solids (see Clause 7.4) if necessary.

(b) Place the solids, derived from Clause 8.3(a) to (g), together with the filter used, into an extraction bottle. Calculate the mass of leaching fluid required to be added to the solids from the following equation:

$$\text{Mass of leaching fluid, (grams)} \quad 20 \times (m_5 - m_6)$$

where

20 = ratio of leaching solution to solids
m_5 = mass of test sample transferred, in grams
m_6 = mass of sample liquid collected, in grams

(c) Slowly add the amount of appropriate leaching fluid selected in Clause 7.5 to the extraction bottle and seal tightly.

CAUTION: AT INTERVALS, SUCH AS 15 MIN, 30 MIN AND 60 MIN AFTER COMMENCING THE AGITATION, ANY PRESSURE BUILT UP SHALL BE VENTED INTO A FUMEHOOD.

(d) Place the extraction bottle on the rotator, suitably counterbalanced and rotate the extraction bottle for 18 ±2 h at 30 ±2 revolutions per minute at an ambient temperature in the range of 22 ±5°C.

CAUTION: UNLESS CORRECTLY COUNTERBALANCED, THE ROTATION APPARATUS WILL BE SUBJECT TO SEVERE VIBRATIONS WHICH WILL CAUSE WEAR OF THE BEARING, OVERHEATING OF THE MOTOR, AND MAY CAUSE THE APPARATUS TO MOVE ALONG THE BENCH. IF A SECOND EXTRACTION BOTTLE IS USED AS A COUNTERBALANCE, IT MAY CONTAIN WATER OR LEACHING FLUID, WITH OR WITHOUT ANOTHER SAMPLE. HOWEVER, IT IS DESIRABLE TO MATCH THE WEIGHTS AS CLOSELY AS POSSIBLE.

(e) Remove the extraction bottle from the agitator. Place a fresh glass fibre filter into the cleaned, dry, pressure filtration device and filter the solids leachate using the method described in Clause 8.3(e).

NOTE: If the filtered liquid contains multiple phases, it is most convenient to collect the whole of the filtrate in a single container.

(f) Remove a small portion of the filtered solids leachate and measure and record its pH. Store the remaining liquid prior to analysis as described in Appendix C.

NOTE: If redox potential is to be measured using ASTM D1498, a small portion of the leachate should be removed for this purpose at this stage and the measurement made within 5 mm of the portion being withdrawn.

9 ANALYSIS AND REPORTING All sample liquid and leachate phases should be analysed separately using appropriate analytical methods for the required analytes. The results should be reported separately.

With multiphasic samples, more than one phase may result from either the sample liquid(s) or leachate. A mass averaged value shall also be reported with the separate phase results. For each analyte, this is calculated from the general equation:

$$C_{calc} = \frac{\Sigma (c_i \times m_i)}{\Sigma m_i}$$

where

C_{calc} = calculated mass averaged value for the analyte in sample liquid(s) and leachate, in milligrams per kilogram

c_i = concentration of analyte measured in the sample liquid or leachate phase i, in milligrams per kilogram

m_i = mass of sample liquid or leachate phase i, in grams

Appendix C

TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP)

1.0 *Scope and application.*

1.1 The TCLP is designed to determine the mobility of both organic and inorganic contaminants present in liquid, solid, and multiphasic wastes.

1.2 If a total analysis of the waste demonstrates that individual contaminants are not present in the waste, or that they are present, but at such low concentrations that the appropriate regulatory thresholds could not possibly be exceeded, the TCLP need not be run.

2.0 *Summary of method.*

2.1 For wastes containing less than *0.5* percent solids, the waste, after filtration through a 0.6-0.8-~m glass fiber filter, is defined as the TCLP extract.

2.2 For wastes containing greater than *0.5* percent solids, the liquid phase, if any, is separated from the solid phase and stored for later analysis. The particle size of the solid phase is reduced (if necessary), weighed, and extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatiles (See Table 1). Following extraction, the liquid extract is separated from the solid phase by 0.6-0.8-~m glass fiber filter filtration.

2.3 If compatible (e.g., precipitate or multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract and these liquids are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield volume weighted average concentration.

3.0 *Interferences.*

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 *Apparatus and materials.*

4.1 Agitation Apparatus: An acceptable agitation apparatus is one which is capable of rotating the extraction vessel in an end-over-end fashion at 30 ~ 2 rpm. Suitable devices known to the EPA are identified in Table 2.

TABLE 1 Volatile Contaminants~

Compound	CASNO
Acetone	67-64-1
Acrylonitrile	107-13-1
Benzene	71-43-2
n-Butyl alcohol	71-36-6
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3

I ,2-Dichloroethane	107-06-2
I, l-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-I
1,1,1 ,2-Tetrachloroethane	630-20-6
1,1 ,2,2-Tetrachloroethane	79-34-5
Tetrachloroethylene	127-18-4
Toluene	108-88-3
I ,l,l-Trichloroethane	71-55-6
1,1 ,2-Trichloroethane	79-00-5 79-01-6
Trichloroethylene	
Trichlorolluoromethane	75-69-4
1,1 2-Trichloro- 1 2,2-trilluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

Includes compounds identified in both the Land Disposal Restrictions Rule and the Toxicity Characteristic.

TABLE 2 Suitable Rotary Agitation Apparatus

Company	Location	Model
Associated Design and Manufacturing Co.	Alexandria, Virginia (703) 549-5999	4-vessel device 6-vessel device
Lars Lande Manufacturing	Whitmore Lake, Michigan (313) 449-4116	10-vessel device
IRA Machine Shop and Laboratory	Santurce, Puerto Rico (809) 752-4004	16-vessel device
EPRI Extractor		6-vessel device[5]

Any device that rotates the extraction vessel in an end-over-end fashion at 30 ± 2 rpm is acceptable.

Although this device is suitable, it is not commercially made. It may also require retrofitting to accommodate ZIIE devices.

4.2 Extraction vessel:

4.2.1 Zero -Headspace Extraction Vessel (ZHE). When the waste is being tested for mobility of any volatile contaminants (See Table 1), an extraction vessel which allows for liquid/solid separation within the device, and which effectively precludes headspace, is used. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without having to open the vessel (See Section 4.3.1). These vessels shall have an internal volume of 500 to 600 ml and be equipped to accommodate a 90-mm filter. Suitable ZHE devices known to EPA are identified in Table 3. These devices contain viton 0-rings which should be replaced frequently.

4.2.2 When the waste is being evaluated for other than volatile contaminants, an extraction vessel which does not preclude headspace (e.g., 2-1 bottle) is used. Suitable extraction vessels include bottles made from various materials, depending on the contaminants to be analyzed and the nature of the waste (See Section 4.3.3). These bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Section 4.3.2 is used for initial liquid-solid separation and final extract filtration.

4.3 Filtration devices:

4.3.1 Zero-Headspace Extractor Vessel: When the waste is being evaluated for volatiles, the zero-headspace extraction vessel is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter, must be able to withstand the pressure needed to accomplish separartion (50 psi).

TABLE 3 Suitable Zero-Headspace Extractor Vessels

Company	Location	Model Number
Associated Dcaign and	Alexandria, Virginia	3740-ZHB
Manufacturing Co.	(703) 549-5999	
Millipore Corp.	Bedford, Massachusetts	SDIPS8ICS
	(800) 225-3384	

Note.-When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the extract.

4.3.2 Filter Holder. When the waste is being evaluated for other than volatile compounds, a filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation is used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressure up to 50 psi and more. The type of filter holder used depends on the properties of the material to be filtered (See Section 4.3.3). These devices shall have a minimum internal volume of 300 ml and be equipped to accommodate a minimum filter size of 47 mm. Filter holders known to EPA to be suitable for use are shown in Table 4.

4.3.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb waste components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high-density polyethylene (HDPE), polypropylene, or polyvinyl chloride may be used when evaluating the mobility of metals.

4.4 Filters: Filters shall be made of borosilicate glass fiber, contain no binder materials, and have an effective pore size of 0.6-0.8 ~m, or equivalent. Filters known to EPA to meet these specifications are identified in Table 5. Prefilters must not be used. When evaluating the mobility of metals, filters shall be acid washed prior to use by rinsing with 1.0 N nitric acid followed by three consecutive rinses with deionized distilled water (minimum of 500 ml per rinse). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters: Any of the commonly available pH meters are acceptable.

4.6 ZHE extract collection devices: TEDLAR® bags or glass, stainless steel, or PTFE gas-tight syringes are used to collect the initial liquid phase and the final extract of the waste when using the ZHE device.

TABLE 4 Suitable Filter Holders~

Company	Location	Model	Size (mm)
Nuclepore Corp.	Pleasanton, California	425910	142
	(800) 882-7711	410400	47
Micro Filtration	Dublin, California (415)	302400	142

Systems.	828-6010		
Millipore Corp.	Bedford, Massachusetts	YT30142HW	142
	(800) 225-3384	XX1004700	47

Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that is is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic Cont5minants are of concern.

TABLE 5 Suitable Filter Media

Company	Location	Model	Size[1]
Whatman	Clifton, New Jersey	6FF	0.7
Laboratory	(201) 773-5800		
Products,			
Inc.			

[1] Nominal pore size.

4.7 ZHE extraction fluid collection devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g., a constant displacement pump, a gas-tight syringe, pressure filtration unit (See Section 4.3.2), or another ZHE device).

4.8 Laboratory Balance: Any laboratory balance accurate to within +0.01 grams may be used (all weight measures are to be within + 0.1 grams).

5.0 Reagents.

5.1 Water: ASTM Type 1 deionized, carbon treated, decarbonized, filtered water (or equivalent water that is treated to remove volatile components) shall be used when evaluating wastes for volatile contaminants. Otherwise, ASTM Type 2 deionized distilled water (or equivalent) is used. These waters should be monitored periodically for impurities.

5.2 1.0 N Hydrochloric acid (HCI) made from ASC Reagent grade.

5.3 1.0 N Nitric acid (HNO_3) made from ACS Reagent grade.

5.4 1.0 N Sodium hydroxide (NaGH) made from ACS Reagent grade.

5.5 Glacial acetic acid (HOAc) made from ACS Reagent grade.

5.6 Extraction fluid:

5.6.1 Extraction fluid #1: This fluid is made by adding 5.7 ml glacial HOAc to *500* ml of the appropriate water (See Section 5.1), adding 64.3 ml of 1.0 N NaOH, and diluting to a volume of 1 liter. When correctly prepared,

the pH of this fluid will be 4.93 + 0.05.

5.6.2 Extraction fluid #2: This fluid is made by diluting 5.7 ml glacial HOAc with ASTM Type 2 water (See Section 5.1) to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88 + 0.05.

Note.-These extraction fluids shall be made up fresh daily. The pH should be checked, prior to use to insure that they are made u~ accurately, and these fluids should be monitored frequently for impurities.

5.7 Analytical standards shall be prepared according to the appropriate analytical method.

6.0 *Sample Collection, preservation, and handling.*

6.1 All samples shall be collected using a sampling plan that addresses the consideration discussed in "Test Methods for Evaluating Solid Wastes" (SW-846).

6.2 Preservatives shall not be added to samples.

6.3 Samples can be refrigerated unless it results in irreversible physical changes to the waste.

6.4 When the waste is to be evaluated for volatile contaminants, care must be taken to insure that these are not lost. Samples shall be taken and stored in a manner which prevents the loss of volatile contaminants. If possible, any necessary particle size reduction should be conducted as the sample is being taken (See Step *8.5).* Refer to SW-846 for additional sampling and storage requirements when volatiles are contaminants of concern.

6.5 TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. If they need to be stored, even for a short period of time, storage shall be at 4^0C and samples for volatiles analysis shall not be allowed to come into contact with the atmosphere (i.e., no headspace).

7.0 *Procedure when volatiles are not involved.*

Although a minimum sample size of 100 g is required, a larger sample size may be necessary, depending on the percent solids of the waste sample. Enough waste sample should be collected such that at least *75* g of the solid phase of the waste (as determined using glass fiber filter filtration) is extracted. This will ensure that there is adequate extract for the required analyses (e.g., semivolatiles, metals, pesticides, and herbicides).

The determination of which extraction fluid to use (See Step 7.12) may also be conducted at the start of this procedure. This determination shall be on the solid phase of the waste (as obtained using glass fiber filter filtration).

7.1 If the waste will obviously yield no free liquid when subjected to pressure filtration, weigh out a representative subsample of the waste (l00-g minimum) and proceed to Step 7.11.

7.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device discussed in Section 4.3.2, and is outlined in Steps 7.3 to 7.9.

7.3 Preweigh the filter and the container which will receive the filtrate.

7.4 Assemble filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (See Section 4.4).

7.5 Weigh out a representative subsample of the waste (l00-g minimum) and record weight.

7.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration.

7.7 Transfer the waste sample to the filter holder.

> Note.-If waste material has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.5, to determine the weight of the waste sample which will be filtered. Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if additional liquid has passed through the filter in any 2-mm interval, slowly increase the pressure in lO-psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-mm interval, proceed to the next 10-psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., does not result in any additional filtrate within any 2-mm period), filtration is stopped.
>
> Note.-Instantaneous application of high pressure can degrade the glass fiber filter, and may cause premature plugging.

7.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

Note.-Some wastes, such as oily wastes and some paint wastes, will obviously contain some material which appears to be a liquid-but even after applying vacuum or pressure filtration, as outlined in Step 7.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid, and is carried through the extraction as a solid.

7.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (See Step 7.3) from the total weight of the filtrate-filled container. The liquid phase may now be either analyzed (See Step *7.15)* or stored at 4^0C until time of analysis. The weight of the solid phase of the waste sample is determined by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in Step 7.5 or 7.7. Record the weight of the liquid and solid phases.

Note.-If the weight of the solid phase of the waste is less than 75 g, review Step 7.0.

7.10 The sample will be handled differently from this point, depending on whether it contains more or less than *0.5* percent solids. If the sample obviously has greater than 0.5 percent solids go to Step 7.11. If it appears that the solid may comprise less than *0.5* percent of the total waste, the percent solids will be determined as follows:

7.10.1 Remove the solid phase and filter from the filtration apparatus.

7.10.2 Dry the filter and solid phase at 100~20^0C until two successive weighings yield the same value. Record final weight.

7.10.3 Calculate the percent solids as follows:
Weight of dry waste and filters minus tared weight of filters divided by initial weight of waste (Step 7.5 or 7.7) multiplied by 100 equals percent solids.

7.10.4 If the solid comprises less than 0.5 percent of the waste, the solid is discarded and the liquid phase is defined as the TCLP extract. Proceed to Step 7.14.

7.10.5 If the solid is greater than or equal to 0.5 percent of the waste, return to Step 7.1, and begin the procedure with a new sample of waste. Do not extract the solid that has been dried.

Note.-This step is only used to determine whether the solid must be extracted, or whether it may be discarded unextracted. It is not used in calculating the amount of extraction fluid to use in extracting the waste, nor is the dried solid derived from this step subjected to extraction. A new sample will have to be prepared for extraction.

7.11 If the sample has more than 0.5 percent solids, it is now evaluated for particle size. If the solid material has a surface area per gram of material equal to or greater than 3.1 em^2, or is capable of passing through a 9.5-mm (0.375-in.) standard sieve, proceed to Step 7.12. If the surface area is smaller or the particle size is larger than that described above, the solid material is prepared for extraction by crushing, cutting, or grinding the solid material to a surface area or particle size as described above. When surface area or particle size has been appropriately altered, proceed to Step 7.12.

7.12 This step describes the determination of the appropriate extracting fluid to use (See Sections 5.0 and 7.0).

7.12.1 Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer a 5.0-g portion to a 500-mi beaker or erlen-meyer flask.

7.12.2 Add *96.5* ml distilled deionized water (ASTM Type 2), cover with watchglass, and stir vigorously for 5 mm using a magnetic stirrer. Measure and record the pl1. If the pl1 is <5.0, extraction fluid #1 is used. Proceed to Step 7.13.

7.12.3 If the PH from Step 7.12.2 is > 5.0, add 3.5 ml 1.0 N HC¾ slurry for
30 5, cover with watchglass, heat to 50^0C, and hold for 10 mm.

7.12.4 Let the solution cool to room temperature and record pH. If pH is <5 0 use extraction fluid #1. If the pH is >*5~0~* extraction fluid #2 is used.

7.13 Calculate the weight of the remaining solid material by subtracting the weight of the subsample taken for Step 7.12, from the original amount of solid material, as obtained from Step 7.1 or 7.9. Transfer remaining solid material into the extractor vessel, including the filter used to separate the initial liquid from the solid phase.

Note.-If any of the solid phase remains adhered to the walls of the filter holder, or the container used to transfer the waste, its weight shall be determined, subtracted from the weight of the solid phase of the waste, as determined above, and this weight is used in calculating the amount of extraction fl~iid to add into the extractor bottle.

Slowly add an amount of the appropriate extraction fluid (See Step 7.12) into the extractor bottle equal to 20 times the weight of the solid phase that has been placed into the extractor bottle. Close extractor bottle tightly, secure in rotary extractor device and rotate at 30 + 2 rpm for 18 h. The temperature shall be maintained at 22 + 3 ^{0}C during the extraction period.

Note.-As a the extractor bottle (Due to the evolution of gasses such as carbon dioxide). To relieve these pressures, the extractor bottle may be periodically opened and vented into a hood.

7.14 Following the 18-h extraction, the material in the extractor vessel is separated into its component liquid and solid phases by filtering through a new glass fiber filter as outlined in Step 7.7. This new filter shall be acid washed (See Section 4.4) if evaluating the mobility of metals.

7.15 The TCLP extract is now prepared as follows:

7.15.1 If the waste contained no initial liquid phase, the filtered liquid material obtained from Step 7.14 is defined as the TCLP extract. Proceed to Step 7.16.

7.15.2 If compatible (e.g., will not form precipitate or multiple phases), the filtered liquid resulting from Step 7.14 is combined with the initial liquid phase of the waste as obtained in Step 7.9. This combined liquid is defined as the TCLP extract. Proceed to Step 7.16.

7.15.3 If the initial liquid phase of the waste, as obtained from Step 7.9, is not or may not be compatible with the filtered liquid resulting from Step 7.14, these liquids are not combined. These liquids are collectively defined as the TCLP extract, are analyzed separately, and the results are combined mathematically. Proceed to Step 7.16.

7.16 The TCLP extract will be prepared and analyzed according to the appropriate SW-846 analytical methods identified in Appendix III of 40 CFR 261. TCLP extracts to be analyzed for metals shall be acid digested. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to 0.1 ml), conduct the appropriate analyses, and combine the results mathematically by using a simple weighted average:

$$\text{Final contaminant concentration} \quad \frac{(V_1)(C_1)+(V_2)(C_2)}{VI+V_2}$$

Where

V_1 The volume of the first phase (1)
C_1 The concentration of the contaminant of concern in the first phase (mg/i)
V_2 ~= The volume of the second phase (1)
C_2 = The concentration of the contaminant of concern in the second phase (mg/l)

7.17 The contaminant concentrations in the TCLP extract are compared to the thresholds identified in the appropriate regulations. Refer to Section 9 for quality assurance requirements.

8.0 *Procedure when volatiles are involved.*
The ZHE device has approximately a 500-mi internal capacity. Although a minimum sample size of 100g was required in the Section 7 procedure, the ZHE can only accommodate a maximum 100 percent solids sample of 25 g, due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase. Step 8.4 provides the means of which to determine the approximate sample size for the ZHE device.
Although the following procedure allows for particle size reduction during the conduct of the procedure, this could result in the loss of volatile compounds. If possible, any necessary particle size reduction (See Step 8.5) should be conducted on the sample as it is being taken. Particle size reduction should only be conducted during the procedure if there is no other choice.
In carrying out the following steps, do not allow the waste to be exposed to the atmosphere for any more time than is absolutely necessary.

8.1 Preweigh the (evacuated) container which will receive the filtrate (See Section 4.6), and set aside.

8.2 Place the ZHE piston within the body of the ZHE (it may be helpful to first moisten the piston O rings slightly with extraction fluid. Secure (the gas inlet/ outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

8.3 If the waste will obviously yield no free liquid when subjected to pressure filtration, weigh out a representative subsample of the waste (25-g maximum-See Step 8.0), record weight, and proceed to 8.5.

8.4 This step provides the means by which to determine the approximate sample size for the ZHF device. If the waste is liquid or multiphasic, follow the procedure outlined in Steps 7.2 to 7.9 (using the Section 7 filtration apparatus), and obtain the percent solids by dividing the weight of the solid phase of the waste by the original sample size used. If the waste obviously contains greater than 0.5 percent solids, go to Step 8.4.2. If it appears that the solid may comprise less than 0.5 percent of the waste, go to Step 8.4.1.

8.4.1 Determine the percent solids by using the procedure outlined in Step 7.10. If the waste contains less than 0.5 percent solids, weigh out a new 100-g minimum representative sample, proceed to Step 8.7, and follow until the liquid phase of the waste is filtered using the ZHE device (Step 8.8). This liquid filtrate is defined as the TCLP extract, and is analyzed directly. If the waste contains greater than or equal to 0.5 percent solids, repeat Step 8.4 using a new 100-g minimum sample, determine the percent solids, and proceed to Step 8.4.2.

8.4.2 If the sample is <25 percent solids, weigh out a new 100-g minimum representative sample, and proceed to Step 8.5. If the sample is > 25 percent solids, the maximum amount of sample the ZHE can accommodate is determined by dividing 25 g by the percent solids obtained from Step 8.4. Weigh out a new representative sample of the determined size.

8.5 After a representative sample of the waste (sample size determined from Step 8.4) has been weighed out and recorded, the sample is now evaluated for particle size (See Step 8.0). If the solid material within the waste obviously has a surface area per gram of material equal to or greater than 3.1 cm^2, or is capable of passing through a 9.5-mm (0.375-in.) standard sieve, proceed immediately to Step 8.6. If the surface area is smaller or the particle size is larger than that described above, the solid material which does not meet the above criteria is separated from the liquid phase by sieving (or equivalent means), and the solid is prepared for extraction by crushing, cutting, or grinding to a surface area or particle size as described above.

Note.-Wastes and appropriate equipment should be refrigerated, if possible, to 4^{0}C prior to particle size reduction. Grinding and milling machinery which generates heat shall not be used for particle size reduction. If reduction to the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.
When surface area or particle size has been appropriately altered, the solid is recombined with the rest of the waste.

8.6 Waste slurries need not be allowed to stand to permit the solid phase to settle. Wastes that settle slowly shall not be centrifuged prior to filtration.

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8.7 Transfer the entire sample (liquid and solid phases) quickly to the ZHF. Secure the filter and support screens into the top flange of the device and secure the top flange to the Z1IE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/ outlet flange on the bottom). Do not attach the extract collection device to the top plate.

Note.-If waste material has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Step 8.4, to determine the weight of the waste sample which will be filtered.
Attach a gas line to the gas inlet/outlet valve (bottom flange), and with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to slowly force all headspace out of the ZHE device. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure.

8.8 Attach evacuated preweighed filtrate collection container to the liquid inlet/ outlet valve and open valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase into the filtrate collection container. If no additional liquid has passed through the filter in any 2-mm interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of
10 psi, if no additional liquid has passed through the filter in any 2-mm interval, proceed to the next 10 psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within any 2-mm period, filtration is stopped. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect the filtrate collection container.

Note.-Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

8.9 The material in the ZHE is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

Note.-Some wastes, such as oily wastes and some paint wastes, will obviously contain some material which appears to be a liquid-but even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid, and is carried through the TCLP extraction as a solid.
If the original waste contained less than 0.5 percent solids (See Step 8.4), this filtrate is defined as the TCLP extract, and is analyzed directly-proceed to Step 8.13.

8.10 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (See Step 8.1) from the total weight of the filtrate-filled container. The liquid phase may now be either analyzed (See Steps 8.13 and 8.14), or stored at 4°C until time of analysis. The weight of the solid phase of the waste sample is determined by subtracting the weight of the liquid phase from the weight of the total waste sample (See Step 8.4). Record the final weight of the liquid and solid phases.

8.11 The following details how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #1 is used in all cases (See Section *5.6).*

8.11.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the amount of fluid introduced into the device equals 20 times the weight of the solid phase of the waste that is in the ZHF.

8.11.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve, and disconnect the extraction fluid line. Check the ZHE to make sure that all valves are in their closed positions. Pick up the ZHE and physically rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Put 5-10 psi behind the piston (if necessary), and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Repressurize the ZHE with 5-10 psi and check all ZHE fittings to insure that they are closed.

8.11.3 Place the ZHE in the rotary extractor apparatus (if it is not already there), and rotate the ZHE at 30 + 2 rpm for 18 h. The temperature shall be maintained at 22 + + 3^0C during agitation.

8.12 Following the 18-hr extraction, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve, and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the device is leaking. Replace ZHE 0-rings or other fittings, as necessary, and redo the extraction with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR bag, gas-tight syringe) holding the initial liquid phase of the waste, unless doing so would create multiple phases, or unless there is not enough volume left within the filtrate collection container. A separate filtrate collection container must be used in these cases. Filter through the glass fiber filter, using the ZHE device as discussed in Step 8.8. All extract shall be filtered and collected if the extract is multiphasic or if the waste contained an initial liquid phase.

Note.-If the glass fiber filter is not intact following agitation, the filtration device discussed in the Note in Section 4.3.1 may be used to filter the material within the ZHF.

8.13 If the waste contained no initial liquid phase, the filtered liquid material obtained from Step 8.12 is defined as the TCLP extract. If the waste contained an initial liquid phase, the filtered liquid material obtained from Step 8.12, and the initial liquid phase (Step 8.8) are collectively defined as the TCLP extract.

8.14 The TCLP extract will be prepared and analyzed according to the appropriate SW-846 analytical methods, as identified in Appendix III of 40 CFR 261. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to 0.1 ml), conduct the appropriate analyses and combine the results mathematically by using a simple volume weighted average:

$$\text{Final contaminant concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where

V_1 = The volume of the first phase (1)
C_1 = The concentration of the contaminant of concern in the first phase (mg/l)
V_2 = The volume of the second phase (1)
C_2 = The concentration of the contaminant of concern in the second phase (mg/l)

8.15 The contaminant concentrations in the TCLP extract are compared to the thresholds identified in the appropriate regulations. Refer to Section 9 for quality assurance requirements.

9.0 *Quality assurance requirements.*

9.1 All data, including quality assurance data, should be maintained and available for reference or inspection.

9.2 A minimum of one blank for every 10 extractions that have been conducted in an extraction vessel should be employed as a check to determine if any memory effects from the extraction equipment is occurring. One blank shall also be employed for every new batch of leaching fluid that is made up.

9.3 All quality control measures described in the appropriate analytical methods shall be followed.

9.4 The method of standard addition shall be employed for each waste type if: (1) recovery of the compound from spiked splits of the TCLP extract is not between 50 and 150 percent, or (2) if the concentration of the constituent measured in the extract is within 20 percent of the appropriate regulatory threshold. If more than one extraction is being run on samples of the same waste, the method of standard addition need only be applied once and the percent recoveries applied to the remainder of the extractions.

9.5 TCLP extracts shall be analyzed within the following periods after generation: volatiles-14 days, semivolatiles-10 days, mercury-28 days, and other metals-180 days.

Appendix D

DETERMINATION OF METALS *(ICP-AES)*

1.0 INTRODUCTION

This method is suitable for the determination of dissolved metals and trace elements in water and wastewaters. Table 1 lists the elements for which this method applies.

Element	Suggested wavelength	Estimated detection limit	Alternate wavelength *nm*
Aluminum	308.22	40	237.32
Antimony	206.83	30	217.58
Arsenic	193.70	50	189.04
Barium	455.40	2	493.41
Beryllium	313.04	0.3	234.86
Boron	249.77	5	249.68
Cadmium	226.50	4	214.44
Calcium	317.93	10	315.89
Chromium	267.72	7	206.15
Cobalt	228.62	7	230.79
Copper	324.75	6	219.96
Iron	259.94	7	238.20
Lead	220.35	40	217.00
Lithium	670.78	4	-
Magnesium	279.08	30	279.55
Manganese	257.61	2	294.92
Molybdenum	202.03	8	203.84
Nickel	231.60	15	221.65
Potassium	766.49	100	769.90
Selenium	196.03	75	203.99
Silica	212.41	20	251.61
Silver	328.07	7	338.29
Sodium	589.00	30	589.59
Strontium	407.77	0.5	421.55
Thallium	190.86	40	377.57
Vanadium	292.40	8	-

2.0 REAGENTS/EQUIPMENT

ICP-AES

Appropriate analytical standards

- *Nitric acid 1 + 1*: Add 500 mL of HNO_3 to 400 mL of milli Q water and dilute to 1 L
- *Hydrochloric acid 1 + 1*: Add 500 mL of HCl to 400 mL of milli Q water and dilute to 1 L
- *Calibration blank:* Add 20 mL of (1+1) nitric acid and 20 mL of (1+1) hydrochloric acid to 500 mL using milli Q water.

3.0 PROCEDURE

To all standards and samples add 2 mL of (1+1) nitric acid and 1 mL of (1+1) hydrochloric acid per 100 mL

3.1 Calibrate the instrument according to the manufacturer's recommended procedure.

3.2 Aspirate each standard or blank for a minimum of 15 s after reaching the plasma before beginning signal integration.

3.3 Rinse with calibration blank for at least 60 s between each sample to eliminate any carryover.

4.0 CALCULATIONS and CORRECTIONS

4.1 Subtract the value obtained for the sample blank from the sample results.

4.2 If the sample was diluted in preparation, multiply the results by a dilution factor as follows:

$$DF = \frac{\text{final weight or volume}}{\text{Initial weight or volume}}$$

5.0 QUALITY CONTROL REQUIREMENT

Instrument Quality Control

- Analyze instrument check standard once per 10 samples to determine if significant instrument drift has occurred. If agreement is not within ± 5% of the expected values, terminate analysis of samples, correct problem and recalibrate instrument.

Test for matrix interference

- When analyzing a new or unusual sample matrix verify that neither a positive or negative non linear interference effect is operative, by using the method of standard additions. Recovery of the addition should be either between 95% and 105%.

6.0 REFERENCES

APHA-AWWA-WPCF (1989). *Standard Methods for the Examination of Water and Wastewater, 17th Edition, method 3120 B,* American Public Health Association, Washington.

Methods for the determination of metals in environmental samples, US EPA Method 200.7

Appendix
E

ARSENIC DETERMINATION *(Hydride Generation AA)*

1.0 INTRODUCTION

To analyze As by hydride generation AA, the solution is aspirated into the vapor generation unit where it is mixed with the reductant (4g L^{-1} $NaBH_4$) and carrier (100 mL L^{-1} HCl) solution in a reaction loop. The gaseous As hydride (AsH_3) thus formed was separated by a gas-liquid unit and swept into the quartz cell where it is decomposed by the surrounding heat to yield atomic arsenic.

The quartz cell attached to the vapor generation unit is mounted on a single slot burner head. The instrument and the attachments were adjusted as described in the operating manuals (Rothery, 1989).

The sensitivity of the vapor generation technique restricts the analytical range to relatively low concentrations of arsenic. Typically the concentrations of the working standards are between 10 and 100 ppb.

2.0 EQUIPMENT

Varian model 1475 Atomic Absorption Spectrometer
Varian VGA-76 Vapor Generation Accessory

3.0 REAGENTS

- Arsenic standard

A 1000 ppm As(III) standard was used to prepare working solutions of 5, 10, 15, 20 and 25 ppb

- Hydrochloric Acid solution

Carrier. 100 mL hydrochloric acid diluted to 1 litre using milli Q water.

- Sodium Borohydride solution

Reductant. 4g of sodium borohydride and 18 mL of 0.5 M NaOH made up to a litre with milli Q water

- Potassium Iodide - Ascorbic Acid Solution

50 g of potassium iodide and 50 g of ascorbic acid made up to 1L with milli Q water.

All plastic and glassware was soaked in 10% HNO_3 for a minimum of 24 hours before use.

4.0 PREPARATION OF STANDARDS

Add 1 mL of the 1000 ppm As(III) standard to a 100 mL volumetric flask and 1 mL of concentrated sulfuric acid. Dilute to the mark with milliQ water
= 10ppm

Preparation of working standards between 5 and 25 ppb
Add 5 mL of 10 ppm standard into a 100 mL volumetric flask and add 1 mL of conc. HCl = 500ppb

1. Add 1 mL of 500 ppb st. into a 100 mL volumetric = 5 ppb
2. Add 2 mL of 500 ppb st. into a 100 mL volumetric = 10 ppb
3. Add 3 mL of 500 ppb st. into a 100 mL volumetric = 15 ppb
4. Add 4 mL of 500 ppb st. into a 100 mL volumetric = 20 ppb
5. Add 5 mL of 500 ppb st. into a 100 mL volumetric = 25 ppb

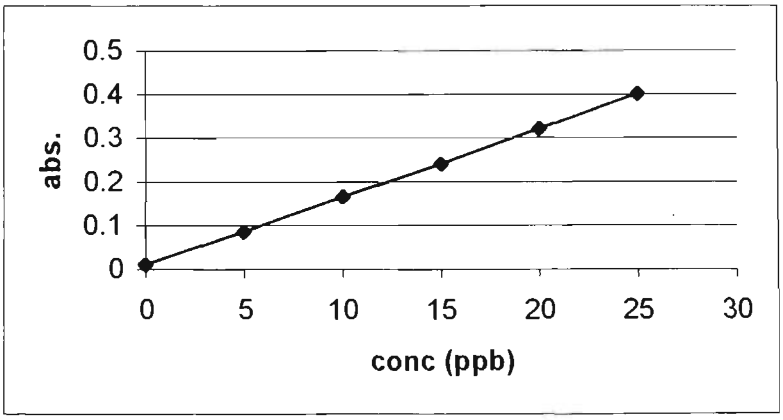
5.0 OPERATIONAL PARAMETERS

The Hydride Generation Atomic Absorption working conditions are outlined in table 1. A typical calibration curve is displayed as figure 1.

Table 1 – HG-AAS Operating Conditions

Parameter	Value
Wavelength	193.7 nm
Lamp current	7 mA
Slit width	1
Flame type	Air/acetylene
Air flow rate	20 L/min
Acetylene flow rate	8 L/min
Reductant	4g L^{-1} $NaBH_4$
Carrier	100 mL L^{-1} HCl
Reductant flow rate	1 mL/min
Carrier flow rate	1 mL/min
Sample flow rate	6 mL/min

Figure 1 – Typical arsenic calibration curve



6.0 REFERENCES

- Rothery, E., 1989, *Vapor Generation Accessory Operation Manual,* Varian Pty. Ltd.

- Zhu, B., Tabatabai, M., 1995, "An alkaline oxidation method for determining total arsenic and selenium in soils", *Soil Science Society of America Journal,* vol. 59, pp. 1564-1569.

Appendix

F

PERCENT RECOVERIES

Arsenic Trioxide, As_2O_3 formulations

- **Sodium peroxide fusion**

S/S Formulation	Element	% Recovery
As_2O_3 + *C*	As	112%
As_2O_3 + *C*	As	103%
As_2O_3 + *C*	As	95%
As_2O_3 + *C*	Ca	93%
As_2O_3 + *C*	Ca	95%
As_2O_3 + *C*	Fe	86%
As_2O_3 + *C*	Fe	89%
As_2O_3 + *C-Fe*	As	96%
As_2O_3 + *C-Fe*	As	95%
As_2O_3 + *C-Fe*	As	95%
As_2O_3 + *C-Fe*	Ca	95%
As_2O_3 + *C-Fe*	Ca	92%
As_2O_3 + *C-Fe*	Ca	94%
As_2O_3 + *C-Fe*	Fe	108%
As_2O_3 + *C-Fe*	Fe	106%
As_2O_3 + *C-L*	As	97%
As_2O_3 + *C-L*	As	95%
As_2O_3 + *C-L*	As	91%
As_2O_3 + *C-L*	Ca	94%
As_2O_3 + *C-L*	Ca	92%
As_2O_3 + *C-L*	Ca	101%
As_2O_3 + *C-L*	Fe	89%
As_2O_3 + *C-L*	Fe	87%
As_2O_3 + *C-L*	Fe	90%

- **Column (rainfall) leaching**

S/S Formulation	Element	% Recovery
As_2O_3 + *C*	As	118%
As_2O_3 + *C*	As	96%
As_2O_3 + *C*	As	93%
As_2O_3 + *C*	As	103%

S/S Formulation	**Element**	**% Recovery**
As_2O_3 + *C*	As	109%
As_2O_3 + *C*	As	104%
As_2O_3 + *C*	Ca	90%
As_2O_3 + *C*	Ca	94%
As_2O_3 + *C*	Ca	111%
As_2O_3 + *C*	Fe	92%
As_2O_3 + *C*	Fe	97%
As_2O_3 + *C-Fe*	As	93%
As_2O_3 + *C-Fe*	As	105%
As_2O_3 + *C-Fe*	As	90%
As_2O_3 + *C-Fe*	As	87%
As_2O_3 + *C-Fe*	As	99%
As_2O_3 + *C-Fe*	Ca	97%
As_2O_3 + *C-Fe*	Ca	91%
As_2O_3 + *C-Fe*	Ca	97%
As_2O_3 + *C-Fe*	Fe	109%
As_2O_3 + *C-Fe*	Fe	103%
As_2O_3 + *C-Fe*	Fe	102%
As_2O_3 + *C-Fe*	Fe	98%
As_2O_3 + *C-L*	As	112%
As_2O_3 + *C-L*	As	96%
As_2O_3 + *C-L*	As	92%
As_2O_3 + *C-L*	As	94%
As_2O_3 + *C-L*	As	96%
As_2O_3 + *C-L*	As	98%
As_2O_3 + *C-L*	Ca	95%
As_2O_3 + *C-L*	Ca	97%
As_2O_3 + *C-L*	Ca	94%
As_2O_3 + *C-L*	Fe	95%
As_2O_3 + *C-L*	Fe	97%
As_2O_3 + *C-L*	Fe	100%

- **Column (BLC) leaching**

S/S Formulation	**Element**	**% Recovery**
As_2O_3 + *C*	As	99%
As_2O_3 + *C*	As	90%
As_2O_3 + *C*	As	102%
As_2O_3 + *C*	As	100%
As_2O_3 + *C*	As	105%
As_2O_3 + *C*	As	96%
As_2O_3 + *C*	Ca	96%
As_2O_3 + *C*	Ca	95%
As_2O_3 + *C*	Ca	103%
As_2O_3 + *C*	Ca	96%
As_2O_3 + *C*	Ca	105%
As_2O_3 + *C*	Fe	104%
As_2O_3 + *C*	Fe	98%
As_2O_3 + *C*	Fe	96%
As_2O_3 + *C-Fe*	As	100%
As_2O_3 + *C-Fe*	As	99%

S/S Formulation	**Element**	**% Recovery**
As_2O_3 + *C-Fe*	As	101%
As_2O_3 + *C-Fe*	As	101%
As_2O_3 + *C-Fe*	As	96%
As_2O_3 + *C-Fe*	As	96%
As_2O_3 + *C-Fe*	Ca	97%
As_2O_3 + *C-Fe*	Ca	106%
As_2O_3 + *C-Fe*	Ca	94%
As_2O_3 + *C-Fe*	Ca	85%
As_2O_3 + *C-Fe*	Ca	90%
As_2O_3 + *C-Fe*	Fe	103%
As_2O_3 + *C-Fe*	Fe	101%
As_2O_3 + *C-Fe*	Fe	101%
As_2O_3 + *C-L*	As	100%
As_2O_3 + *C-L*	As	92%
As_2O_3 + *C-L*	As	93%
As_2O_3 + *C-L*	As	106%
As_2O_3 + *C-L*	As	102%
As_2O_3 + *C-L*	As	95%
As_2O_3 + *C-L*	Ca	98%
As_2O_3 + *C-L*	Ca	93%
As_2O_3 + *C-L*	Ca	93%
As_2O_3 + *C-L*	Ca	98%
As_2O_3 + *C-L*	Ca	97%
As_2O_3 + *C-L*	Fe	107%
As_2O_3 + *C-L*	Fe	103%
As_2O_3 + *C-L*	Fe	98%

- **Sequential Leaching (water)**

S/S Formulation	Element	% Recovery
As_2O_3 + *C*	As	103%
As_2O_3 + *C*	As	107%
As_2O_3 + *C*	As	103%
As_2O_3 + *C*	Ca	104%
As_2O_3 + *C*	Ca	106%
As_2O_3 + *C*	Ca	101%
As_2O_3 + *C*	Fe	101%
As_2O_3 + *C*	Fe	101%
As_2O_3 + *C-Fe*	As	92%
As_2O_3 + *C-Fe*	As	98%
As_2O_3 + *C-Fe*	As	98%
As_2O_3 + *C-Fe*	Ca	100%
As_2O_3 + *C-Fe*	Ca	97%
As_2O_3 + *C-Fe*	Ca	99%
As_2O_3 + *C-Fe*	Fe	108%
As_2O_3 + *C-Fe*	Fe	85%
As_2O_3 + *C-L*	As	108%
As_2O_3 + *C-L*	As	101%
As_2O_3 + *C-L*	As	104%
As_2O_3 + *C-L*	Ca	95%

S/S Formulation	Element	% Recovery
As_2O_3 + *C-L*	Ca	97%
As_2O_3 + *C-L*	Ca	89%
As_2O_3 + *C-L*	Fe	102%
As_2O_3 + *C-L*	Fe	102%

- **Sequential Leaching (acid)**

S/S Formulation	Element	% Recovery
As_2O_3 + *C*	As	109%
As_2O_3 + *C*	As	94%
As_2O_3 + *C*	As	96%
As_2O_3 + *C*	As	97%
As_2O_3 + *C*	Ca	98%
As_2O_3 + *C*	Ca	96%
As_2O_3 + *C*	Ca	106%
As_2O_3 + *C*	Ca	95%
As_2O_3 + *C*	Fe	101%
As_2O_3 + *C*	Fe	104%
As_2O_3 + *C*	Fe	100%
As_2O_3 + *C-Fe*	As	98%
As_2O_3 + *C-Fe*	As	98%
As_2O_3 + *C-Fe*	As	101%
As_2O_3 + *C-Fe*	As	93%
As_2O_3 + *C-Fe*	Ca	95%
As_2O_3 + *C-Fe*	Ca	108%
As_2O_3 + *C-Fe*	Ca	92%
As_2O_3 + *C-Fe*	Ca	94%
As_2O_3 + *C-Fe*	Fe	107%
As_2O_3 + *C-Fe*	Fe	109%
As_2O_3 + *C-Fe*	Fe	111%
As_2O_3 + *C-L*	As	85%
As_2O_3 + *C-L*	As	90%
As_2O_3 + *C-L*	As	92%
As_2O_3 + *C-L*	As	93%
As_2O_3 + *C-L*	Ca	96%
As_2O_3 + *C-L*	Ca	97%
As_2O_3 + *C-L*	Ca	109%
As_2O_3 + *C-L*	Ca	101%
As_2O_3 + *C-L*	Fe	110%
As_2O_3 + *C-L*	Fe	107%
As_2O_3 + *C-L*	Fe	103%

Arsenic Pentoxide, As_2O_5, Formulations

- **Sodium Peroxide Fusion**

S/S Formulation	**Element**	**% Recovery**
As_2O_5 + *C*	As	82%
As_2O_5 + *C*	As	86%
As_2O_5 + *C*	As	90%
As_2O_5 + *C*	Ca	102%
As_2O_5 + *C*	Ca	114%
As_2O_5 + *C*	Ca	107%
As_2O_5 + *C*	Fe	90%
As_2O_5 + *C*	Fe	89%
As_2O_5 + *C*	Fe	88%
As_2O_5 + *C-Fe*	As	108%
As_2O_5 + *C-Fe*	As	101%
As_2O_5 + *C-Fe*	As	93%
As_2O_5 + *C-Fe*	Ca	92%
As_2O_5 + *C-Fe*	Ca	97%
As_2O_5 + *C-Fe*	Ca	94%
As_2O_5 + *C-Fe*	Fe	89%
As_2O_5 + *C-Fe*	Fe	83%
As_2O_5 + *C-Fe*	Fe	88%
As_2O_5 + *C-L*	As	102%
As_2O_5 + *C-L*	As	106%
As_2O_5 + *C-L*	As	112%
As_2O_5 + *C-L*	Ca	97%
As_2O_5 + *C-L*	Ca	100%
As_2O_5 + *C-L*	Ca	105%
As_2O_5 + *C-L*	Fe	83%
As_2O_5 + *C-L*	Fe	92%
As_2O_5 + *C-L*	Fe	90%

- **Column (Rainfall) leaching**

S/S Formulation	**Element**	**% Recovery**
As_2O_5 + *C*	As	99%
As_2O_5 + *C*	As	95%
As_2O_5 + *C*	As	93%
As_2O_5 + *C*	As	97%
As_2O_5 + *C*	As	97%
As_2O_5 + *C*	As	94%
As_2O_5 + *C*	Ca	96%
As_2O_5 + *C*	Ca	97%
As_2O_5 + *C*	Ca	93%
As_2O_5 + *C*	Ca	82%
As_2O_5 + *C*	Ca	84%
As_2O_5 + *C*	Fe	103%
As_2O_5 + *C*	Fe	102%
As_2O_5 + *C-Fe*	As	116%

S/S Formulation	Element	% Recovery
As_2O_5 + *C-Fe*	As	115%
As_2O_5 + *C-Fe*	As	98%
As_2O_5 + *C-Fe*	As	94%
As_2O_5 + *C-Fe*	As	105%
As_2O_5 + *C-Fe*	Ca	86%
As_2O_5 + *C-Fe*	Ca	88%
As_2O_5 + *C-Fe*	Ca	92%
As_2O_5 + *C-Fe*	Ca	96%
As_2O_5 + *C-Fe*	Ca	93%
As_2O_5 + *C-Fe*	Fe	98%
As_2O_5 + *C-Fe*	Fe	102%
As_2O_5 + *C-Fe*	Fe	103%
As_2O_5 + *C-L*	As	109%
As_2O_5 + *C-L*	As	103%
As_2O_5 + *C-L*	As	101%
As_2O_5 + *C-L*	As	108%
As_2O_5 + *C-L*	As	101%
As_2O_5 + *C-L*	As	108%
As_2O_5 + *C-L*	Ca	88%
As_2O_5 + *C-L*	Ca	93%
As_2O_5 + *C-L*	Ca	95%
As_2O_5 + *C-L*	Ca	89%
As_2O_5 + *C-L*	Ca	90%
As_2O_5 + *C-L*	Fe	97%
As_2O_5 + *C-L*	Fe	101%

- **Column (BLC) leaching**

S/S Formulation	Element	% Recovery
As_2O_5 + *C*	As	99%
As_2O_5 + *C*	As	99%
As_2O_5 + *C*	As	102%
As_2O_5 + *C*	As	98%
As_2O_5 + *C*	As	97%
As_2O_5 + *C*	As	101%
As_2O_5 + *C*	Ca	97%
As_2O_5 + *C*	Ca	108%
As_2O_5 + *C*	Ca	82%
As_2O_5 + *C*	Ca	98%
As_2O_5 + *C*	Ca	98%
As_2O_5 + *C*	Fe	97%
As_2O_5 + *C*	Fe	100%
As_2O_5 + *C*	Fe	102%
As_2O_5 + *C-Fe*	As	98%
As_2O_5 + *C-Fe*	As	99%
As_2O_5 + *C-Fe*	As	105%
As_2O_5 + *C-Fe*	As	96%
As_2O_5 + *C-Fe*	As	98%
As_2O_5 + *C-Fe*	Ca	95%
As_2O_5 + *C-Fe*	Ca	104%

S/S Formulation	**Element**	**% Recovery**
As_2O_5 + *C-Fe*	Ca	98%
As_2O_5 + *C-Fe*	Ca	97%
As_2O_5 + *C-Fe*	Fe	103%
As_2O_5 + *C-Fe*	Fe	101%
As_2O_5 + *C-Fe*	Fe	106%
As_2O_5 + *C-L*	As	101%
As_2O_5 + *C-L*	As	103%
As_2O_5 + *C-L*	As	98%
As_2O_5 + *C-L*	As	98%
As_2O_5 + *C-L*	As	93%
As_2O_5 + *C-L*	Ca	99%
As_2O_5 + *C-L*	Ca	98%
As_2O_5 + *C-L*	Ca	102%
As_2O_5 + *C-L*	Ca	105%
As_2O_5 + *C-L*	Ca	97%
As_2O_5 + *C-L*	Fe	93%
As_2O_5 + *C-L*	Fe	102%

- **Sequential Leaching (water)**

S/S Formulation	**Element**	**% Recovery**
As_2O_5 + *C*	As	106%
As_2O_5 + *C*	As	112%
As_2O_5 + *C*	As	105%
As_2O_5 + *C*	Ca	100%
As_2O_5 + *C*	Ca	110%
As_2O_5 + *C*	Ca	101%
As_2O_5 + *C*	Fe	107%
As_2O_5 + *C*	Fe	103%
As_2O_5 + *C-Fe*	As	95%
As_2O_5 + *C-Fe*	As	87%
As_2O_5 + *C-Fe*	As	107%
As_2O_5 + *C-Fe*	Ca	95%
As_2O_5 + *C-Fe*	Ca	90%
As_2O_5 + *C-Fe*	Ca	96%
As_2O_5 + *C-Fe*	Fe	98%
As_2O_5 + *C-Fe*	Fe	104%
As_2O_5 + *C-L*	As	100%
As_2O_5 + *C-L*	As	98%
As_2O_5 + *C-L*	As	96%
As_2O_5 + *C-L*	Ca	97%
As_2O_5 + *C-L*	Ca	102%
As_2O_5 + *C-L*	Ca	98%
As_2O_5 + *C-L*	Fe	105%
As_2O_5 + *C-L*	Fe	101%

- **Sequential Leaching (acid)**

S/S Formulation	**Element**	**% Recovery**
As_2O_5 + *C*	As	104%
As_2O_5 + *C*	As	102%
As_2O_5 + *C*	As	87%
As_2O_5 + *C*	As	97%
As_2O_5 + *C*	Ca	87%
As_2O_5 + *C*	Ca	106%
As_2O_5 + *C*	Ca	90%
As_2O_5 + *C*	Ca	94%
As_2O_5 + *C*	Fe	89%
As_2O_5 + *C*	Fe	99%
As_2O_5 + *C-Fe*	As	89%
As_2O_5 + *C-Fe*	As	99%
As_2O_5 + *C-Fe*	As	105%
As_2O_5 + *C-Fe*	As	101%
As_2O_5 + *C-Fe*	Ca	95%
As_2O_5 + *C-Fe*	Ca	102%
As_2O_5 + *C-Fe*	Ca	105%
As_2O_5 + *C-Fe*	Ca	100%
As_2O_5 + *C-Fe*	Fe	107%
As_2O_5 + *C-Fe*	Fe	103%
As_2O_5 + *C-L*	As	105%
As_2O_5 + *C-L*	As	92%
As_2O_5 + *C-L*	As	109%
As_2O_5 + *C-L*	As	99%
As_2O_5 + *C-L*	Ca	101%
As_2O_5 + *C-L*	Ca	109%
As_2O_5 + *C-L*	Ca	103%
As_2O_5 + *C-L*	Ca	99%
As_2O_5 + *C-L*	Fe	111%
As_2O_5 + *C-L*	Fe	105%

Sodium Arsenite, $NaAsO_2$, formulations

- **Sodium peroxide fusion**

S/S Formulation	Element	% Recovery
$NaAsO_2$ + *C*	As	82%
$NaAsO_2$ + *C*	As	95%
$NaAsO_2$ + *C*	As	82%
$NaAsO_2$ + *C*	Ca	94%
$NaAsO_2$ + *C*	Ca	101%
$NaAsO_2$ + *C*	Ca	90%
$NaAsO_2$ + *C*	Fe	83%
$NaAsO_2$ + *C*	Fe	89%
$NaAsO_2$ + *C*	Fe	93%
$NaAsO_2$ + *C-Fe*	As	89%
$NaAsO_2$ + *C-Fe*	As	91%
$NaAsO_2$ + *C-Fe*	As	92%
$NaAsO_2$ + *C-Fe*	Ca	91%
$NaAsO_2$ + *C-Fe*	Ca	93%
$NaAsO_2$ + *C-Fe*	Ca	94%
$NaAsO_2$ + *C-Fe*	Fe	89%
$NaAsO_2$ + *C-Fe*	Fe	93%
$NaAsO_2$ + *C-Fe*	Fe	93%
$NaAsO_2$ + *C-L*	As	82%
$NaAsO_2$ + *C-L*	As	86%
$NaAsO_2$ + *C-L*	As	88%
$NaAsO_2$ + *C-L*	Ca	89%
$NaAsO_2$ + *C-L*	Ca	92%
$NaAsO_2$ + *C-L*	Ca	103%
$NaAsO_2$ + *C-L*	Fe	84%
$NaAsO_2$ + *C-L*	Fe	84%
$NaAsO_2$ + *C-L*	Fe	84%

- **Column (Rainfall) leaching**

S/S Formulation	Element	% Recovery
$NaAsO_2$ + *C*	As	92%
$NaAsO_2$ + *C*	As	94%
$NaAsO_2$ + *C*	As	94%
$NaAsO_2$ + *C*	As	90%
$NaAsO_2$ + *C*	As	89%
$NaAsO_2$ + *C*	As	97%
$NaAsO_2$ + *C*	Ca	95%
$NaAsO_2$ + *C*	Ca	103%
$NaAsO_2$ + *C*	Ca	107%
$NaAsO_2$ + *C*	Ca	102%
$NaAsO_2$ + *C*	Ca	99%
$NaAsO_2$ + *C*	Fe	106%
$NaAsO_2$ + *C*	Fe	104%
$NaAsO_2$ + *C-Fe*	As	111%
$NaAsO_2$ + *C-Fe*	As	92%

S/S Formulation	**Element**	**% Recovery**
$NaAsO_2$ + *C-Fe*	As	97%
$NaAsO_2$ + *C-Fe*	As	96%
$NaAsO_2$ + *C-Fe*	As	104%
$NaAsO_2$ + *C-Fe*	As	99%
$NaAsO_2$ + *C-Fe*	Ca	93%
$NaAsO_2$ + *C-Fe*	Ca	97%
$NaAsO_2$ + *C-Fe*	Ca	96%
$NaAsO_2$ + *C-Fe*	Ca	99%
$NaAsO_2$ + *C-Fe*	Ca	101%
$NaAsO_2$ + *C-Fe*	Fe	92%
$NaAsO_2$ + *C-Fe*	Fe	93%
$NaAsO_2$ + *C-L*	As	105%
$NaAsO_2$ + *C-L*	As	103%
$NaAsO_2$ + *C-L*	As	97%
$NaAsO_2$ + *C-L*	As	90%
$NaAsO_2$ + *C-L*	As	92%
$NaAsO_2$ + *C-L*	As	92%
$NaAsO_2$ + *C-L*	Ca	109%
$NaAsO_2$ + *C-L*	Ca	103%
$NaAsO_2$ + *C-L*	Ca	103%
$NaAsO_2$ + *C-L*	Ca	100%
$NaAsO_2$ + *C-L*	Ca	99%
$NaAsO_2$ + *C-L*	Fe	89%
$NaAsO_2$ + *C-L*	Fe	95%

- **Column (BLC) leaching**

S/S Formulation	**Element**	**% Recovery**
$NaAsO_2$ + *C*	As	100%
$NaAsO_2$ + *C*	As	100%
$NaAsO_2$ + *C*	As	102%
$NaAsO_2$ + *C*	As	102%
$NaAsO_2$ + *C*	As	107%
$NaAsO_2$ + *C*	As	111%
$NaAsO_2$ + *C*	Ca	89%
$NaAsO_2$ + *C*	Ca	97%
$NaAsO_2$ + *C*	Ca	101%
$NaAsO_2$ + *C*	Ca	96%
$NaAsO_2$ + *C*	Ca	96%
$NaAsO_2$ + *C*	Fe	99%
$NaAsO_2$ + *C*	Fe	101%
$NaAsO_2$ + *C-Fe*	As	85%
$NaAsO_2$ + *C-Fe*	As	103%
$NaAsO_2$ + *C-Fe*	As	100%
$NaAsO_2$ + *C-Fe*	As	98%
$NaAsO_2$ + *C-Fe*	As	108%
$NaAsO_2$ + *C-Fe*	As	107%
$NaAsO_2$ + *C-Fe*	Ca	101%
$NaAsO_2$ + *C-Fe*	Ca	104%
$NaAsO_2$ + *C-Fe*	Ca	106%

S/S Formulation	**Element**	**% Recovery**
$NaAsO_2$ + *C-Fe*	Ca	101%
$NaAsO_2$ + *C-Fe*	Ca	99%
$NaAsO_2$ + *C-Fe*	Fe	105%
$NaAsO_2$ + *C-Fe*	Fe	105%
$NaAsO_2$ + *C-L*	As	100%
$NaAsO_2$ + *C-L*	As	95%
$NaAsO_2$ + *C-L*	As	96%
$NaAsO_2$ + *C-L*	As	100%
$NaAsO_2$ + *C-L*	As	108%
$NaAsO_2$ + *C-L*	As	100%
$NaAsO_2$ + *C-L*	Ca	102%
$NaAsO_2$ + *C-L*	Ca	108%
$NaAsO_2$ + *C-L*	Ca	106%
$NaAsO_2$ + *C-L*	Ca	104%
$NaAsO_2$ + *C-L*	Ca	102%
$NaAsO_2$ + *C-L*	Fe	103%
$NaAsO_2$ + *C-L*	Fe	105%

- **Sequential Leaching (water)**

S/S Formulation	**Element**	**% Recovery**
$NaAsO_2$ + *C*	As	99%
$NaAsO_2$ + *C*	As	95%
$NaAsO_2$ + *C*	As	104%
$NaAsO_2$ + *C*	Ca	100%
$NaAsO_2$ + *C*	Ca	97%
$NaAsO_2$ + *C*	Ca	99%
$NaAsO_2$ + *C*	Fe	99%
$NaAsO_2$ + *C*	Fe	101%
$NaAsO_2$ + *C*	Fe	105%
$NaAsO_2$ + *C-Fe*	As	108%
$NaAsO_2$ + *C-Fe*	As	96%
$NaAsO_2$ + *C-Fe*	As	92%
$NaAsO_2$ + *C-Fe*	Ca	95%
$NaAsO_2$ + *C-Fe*	Ca	100%
$NaAsO_2$ + *C-Fe*	Ca	94%
$NaAsO_2$ + *C-Fe*	Fe	101%
$NaAsO_2$ + *C-Fe*	Fe	109%
$NaAsO_2$ + *C-Fe*	Fe	105%
$NaAsO_2$ + *C-L*	As	98%
$NaAsO_2$ + *C-L*	As	98%
$NaAsO_2$ + *C-L*	As	99%
$NaAsO_2$ + *C-L*	Ca	96%
$NaAsO_2$ + *C-L*	Ca	101%
$NaAsO_2$ + *C-L*	Ca	99%
$NaAsO_2$ + *C-L*	Fe	96%
$NaAsO_2$ + *C-L*	Fe	96%
$NaAsO_2$ + *C-L*	Fe	105%

Sodium Arsenate, Na_2HAsO_4, formulations

- **Sodium Peroxide Fusion**

S/S Formulation	Element	% Recovery
Na_2HAsO_4 + *C*	As	89%
Na_2HAsO_4 + *C*	As	87%
Na_2HAsO_4 + *C*	As	85%
Na_2HAsO_4 + *C*	Ca	85%
Na_2HAsO_4 + *C*	Ca	92%
Na_2HAsO_4 + *C*	Ca	86%
Na_2HAsO_4 + *C*	Fe	90%
Na_2HAsO_4 + *C*	Fe	83%
Na_2HAsO_4 + *C*	Fe	89%
Na_2HAsO_4 + *C-Fe*	As	99%
Na_2HAsO_4 + *C-Fe*	As	94%
Na_2HAsO_4 + *C-Fe*	As	98%
Na_2HAsO_4 + *C-Fe*	Ca	87%
Na_2HAsO_4 + *C-Fe*	Ca	88%
Na_2HAsO_4 + *C-Fe*	Ca	89%
Na_2HAsO_4 + *C-Fe*	Fe	85%
Na_2HAsO_4 + *C-Fe*	Fe	85%
Na_2HAsO_4 + *C-Fe*	Fe	93%
Na_2HAsO_4 + *C-L*	As	97%
Na_2HAsO_4 + *C-L*	As	104%
Na_2HAsO_4 + *C-L*	As	101%
Na_2HAsO_4 + *C-L*	Ca	88%
Na_2HAsO_4 + *C-L*	Ca	85%
Na_2HAsO_4 + *C-L*	Ca	87%
Na_2HAsO_4 + *C-L*	Fe	83%
Na_2HAsO_4 + *C-L*	Fe	92%
Na_2HAsO_4 + *C-L*	Fe	87%

- **Column (Rainfall) leaching**

S/S Formulation	Element	% Recovery
Na_2HAsO_4 + *C*	As	106%
Na_2HAsO_4 + *C*	As	108%
Na_2HAsO_4 + *C*	As	107%
Na_2HAsO_4 + *C*	As	108%
Na_2HAsO_4 + *C*	As	106%
Na_2HAsO_4 + *C*	As	102%
Na_2HAsO_4 + *C*	As	99%
Na_2HAsO_4 + *C*	Ca	86%
Na_2HAsO_4 + *C*	Ca	100%
Na_2HAsO_4 + *C*	Ca	88%
Na_2HAsO_4 + *C*	Ca	94%
Na_2HAsO_4 + *C*	Fe	105%
Na_2HAsO_4 + *C*	Fe	104%
Na_2HAsO_4 + *C-Fe*	As	106%

S/S Formulation	**Element**	**% Recovery**
Na_2HAsO_4 + *C-Fe*	As	106%
Na_2HAsO_4 + *C-Fe*	As	92%
Na_2HAsO_4 + *C-Fe*	As	85%
Na_2HAsO_4 + *C-Fe*	As	89%
Na_2HAsO_4 + *C-Fe*	Ca	92%
Na_2HAsO_4 + *C-Fe*	Ca	95%
Na_2HAsO_4 + *C-Fe*	Ca	100%
Na_2HAsO_4 + *C-Fe*	Ca	102%
Na_2HAsO_4 + *C-Fe*	Ca	98%
Na_2HAsO_4 + *C-Fe*	Fe	98%
Na_2HAsO_4 + *C-Fe*	Fe	98%
Na_2HAsO_4 + *C-L*	As	106%
Na_2HAsO_4 + *C-L*	As	106%
Na_2HAsO_4 + *C-L*	As	100%
Na_2HAsO_4 + *C-L*	As	97%
Na_2HAsO_4 + *C-L*	As	95%
Na_2HAsO_4 + *C-L*	As	101%
Na_2HAsO_4 + *C-L*	Ca	94%
Na_2HAsO_4 + *C-L*	Ca	96%
Na_2HAsO_4 + *C-L*	Ca	99%
Na_2HAsO_4 + *C-L*	Ca	104%
Na_2HAsO_4 + *C-L*	Ca	102%
Na_2HAsO_4 + *C-L*	Fe	100%
Na_2HAsO_4 + *C-L*	Fe	101%

- **Column (BLC) Leaching**

S/S Formulation	**Element**	**% Recovery**
Na_2HAsO_4 + *C*	As	97%
Na_2HAsO_4 + *C*	As	101%
Na_2HAsO_4 + *C*	As	99%
Na_2HAsO_4 + *C*	As	102%
Na_2HAsO_4 + *C*	As	83%
Na_2HAsO_4 + *C*	As	97%
Na_2HAsO_4 + *C*	Ca	96%
Na_2HAsO_4 + *C*	Ca	102%
Na_2HAsO_4 + *C*	Ca	85%
Na_2HAsO_4 + *C*	Ca	107%
Na_2HAsO_4 + *C*	Ca	95%
Na_2HAsO_4 + *C*	Fe	107%
Na_2HAsO_4 + *C*	Fe	95%
Na_2HAsO_4 + *C-Fe*	As	92%
Na_2HAsO_4 + *C-Fe*	As	88%
Na_2HAsO_4 + *C-Fe*	As	87%
Na_2HAsO_4 + *C-Fe*	As	102%
Na_2HAsO_4 + *C-Fe*	As	99%
Na_2HAsO_4 + *C-Fe*	As	98%
Na_2HAsO_4 + *C-Fe*	Ca	101%
Na_2HAsO_4 + *C-Fe*	Ca	96%
Na_2HAsO_4 + *C-Fe*	Ca	98%

S/S Formulation	**Element**	**% Recovery**
Na_2HAsO_4 + *C-Fe*	Ca	107%
Na_2HAsO_4 + *C-Fe*	Ca	92%
Na_2HAsO_4 + *C-Fe*	Fe	98%
Na_2HAsO_4 + *C-Fe*	Fe	96%
Na_2HAsO_4 + *C-L*	As	97%
Na_2HAsO_4 + *C-L*	As	102%
Na_2HAsO_4 + *C-L*	As	102%
Na_2HAsO_4 + *C-L*	As	101%
Na_2HAsO_4 + *C-L*	As	101%
Na_2HAsO_4 + *C-L*	As	102%
Na_2HAsO_4 + *C-L*	Ca	89%
Na_2HAsO_4 + *C-L*	Ca	92%
Na_2HAsO_4 + *C-L*	Ca	99%
Na_2HAsO_4 + *C-L*	Ca	100%
Na_2HAsO_4 + *C-L*	Ca	98%
Na_2HAsO_4 + *C-L*	Ca	98%
Na_2HAsO_4 + *C-L*	Fe	100%
Na_2HAsO_4 + *C-L*	Fe	101%

- **Sequential Leaching (water)**

S/S Formulation	**Element**	**% Recovery**
Na_2HAsO_4 + *C*	As	110%
Na_2HAsO_4 + *C*	As	109%
Na_2HAsO_4 + *C*	As	108%
Na_2HAsO_4 + *C*	Ca	97%
Na_2HAsO_4 + *C*	Ca	99%
Na_2HAsO_4 + *C*	Ca	112%
Na_2HAsO_4 + *C*	Fe	107%
Na_2HAsO_4 + *C-Fe*	As	100%
Na_2HAsO_4 + *C-Fe*	As	96%
Na_2HAsO_4 + *C-Fe*	As	106%
Na_2HAsO_4 + *C-Fe*	Ca	93%
Na_2HAsO_4 + *C-Fe*	Ca	91%
Na_2HAsO_4 + *C-Fe*	Ca	97%
Na_2HAsO_4 + *C-Fe*	Fe	98%
Na_2HAsO_4 + *C-L*	As	108%
Na_2HAsO_4 + *C-L*	As	105%
Na_2HAsO_4 + *C-L*	As	106%
Na_2HAsO_4 + *C-L*	Ca	101%
Na_2HAsO_4 + *C-L*	Ca	97%
Na_2HAsO_4 + *C-L*	Ca	100%
Na_2HAsO_4 + *C-L*	Fe	96%

- **Sequential Leaching (acid)**

S/S Formulation	**Element**	**% Recovery**
Na_2HAsO_4 + *C*	As	109%
Na_2HAsO_4 + *C*	As	92%
Na_2HAsO_4 + *C*	As	87%
Na_2HAsO_4 + *C*	As	93%
Na_2HAsO_4 + *C*	Ca	98%
Na_2HAsO_4 + *C*	Ca	105%
Na_2HAsO_4 + *C*	Ca	102%
Na_2HAsO_4 + *C*	Ca	99%
Na_2HAsO_4 + *C*	Fe	97%
Na_2HAsO_4 + *C-Fe*	As	91%
Na_2HAsO_4 + *C-Fe*	As	94%
Na_2HAsO_4 + *C-Fe*	As	96%
Na_2HAsO_4 + *C-Fe*	Ca	97%
Na_2HAsO_4 + *C-Fe*	Ca	101%
Na_2HAsO_4 + *C-Fe*	Ca	100%
Na_2HAsO_4 + *C-Fe*	Fe	102%
Na_2HAsO_4 + *C-Fe*	Fe	103%
Na_2HAsO_4 + *C-Fe*	Fe	113%
Na_2HAsO_4 + *C-L*	As	110%
Na_2HAsO_4 + *C-L*	As	115%
Na_2HAsO_4 + *C-L*	As	100%
Na_2HAsO_4 + *C-L*	As	96%
Na_2HAsO_4 + *C-L*	Ca	89%
Na_2HAsO_4 + *C-L*	Ca	99%
Na_2HAsO_4 + *C-L*	Ca	101%
Na_2HAsO_4 + *C-L*	Ca	98%
Na_2HAsO_4 + *C-L*	Fe	103%

Lead Arsenate, $PbHAsO_4$, formulations

- **Sodium Peroxide Fusion**

S/S Formulation	Element	% Recovery
$PbHAsO_4$ + *C*	As	87%
$PbHAsO_4$ + *C*	As	90%
$PbHAsO_4$ + *C*	As	89%
$PbHAsO_4$ + *C*	Pb	106%
$PbHAsO_4$ + *C*	Pb	107%
$PbHAsO_4$ + *C*	Pb	102%
$PbHAsO_4$ + *C*	Ca	89%
$PbHAsO_4$ + *C*	Ca	87%
$PbHAsO_4$ + *C*	Ca	93%
$PbHAsO_4$ + *C*	Fe	94%
$PbHAsO_4$ + *C*	Fe	112%
$PbHAsO_4$ + *C*	Fe	111%
$PbHAsO_4$ + *C-Fe*	As	86%
$PbHAsO_4$ + *C-Fe*	As	100%
$PbHAsO_4$ + *C-Fe*	As	92%
$PbHAsO_4$ + *C-Fe*	Pb	99%
$PbHAsO_4$ + *C-Fe*	Pb	102%
$PbHAsO_4$ + *C-Fe*	Pb	97%
$PbHAsO_4$ + *C-Fe*	Ca	84%
$PbHAsO_4$ + *C-Fe*	Ca	85%
$PbHAsO_4$ + *C-Fe*	Ca	93%
$PbHAsO_4$ + *C-Fe*	Fe	107%
$PbHAsO_4$ + *C-Fe*	Fe	94%
$PbHAsO_4$ + *C-Fe*	Fe	106%
$PbHAsO_4$ + *C-L*	As	92%
$PbHAsO_4$ + *C-L*	As	94%
$PbHAsO_4$ + *C-L*	As	90%
$PbHAsO_4$ + *C-L*	Pb	95%
$PbHAsO_4$ + *C-L*	Pb	97%
$PbHAsO_4$ + *C-L*	Pb	95%
$PbHAsO_4$ + *C-L*	Ca	88%
$PbHAsO_4$ + *C-L*	Ca	88%
$PbHAsO_4$ + *C-L*	Ca	91%
$PbHAsO_4$ + *C-L*	Fe	101%
$PbHAsO_4$ + *C-L*	Fe	104%
$PbHAsO_4$ + *C-L*	Fe	112%

- **Continual Leaching**

S/S Formulation	Element	% Recovery
$PbHAsO_4$ + *C*	As	90%
$PbHAsO_4$ + *C*	As	95%
$PbHAsO_4$ + *C*	As	92%
$PbHAsO_4$ + *C*	As	88%

S/S Formulation	**Element**	**% Recovery**
$PbHAsO_4$ + *C*	As	88%
$PbHAsO_4$ + *C*	Pb	85%
$PbHAsO_4$ + *C*	Pb	83%
$PbHAsO_4$ + *C*	Pb	90%
$PbHAsO_4$ + *C*	Pb	94%
$PbHAsO_4$ + *C*	Pb	87%
$PbHAsO_4$ + *C*	Pb	92%
$PbHAsO_4$ + *C*	Ca	95%
$PbHAsO_4$ + *C*	Ca	101%
$PbHAsO_4$ + *C*	Ca	94%
$PbHAsO_4$ + *C*	Ca	87%
$PbHAsO_4$ + *C*	Ca	96%
$PbHAsO_4$ + *C*	Fe	101%
$PbHAsO_4$ + *C*	Fe	99%

- **Sequential Leaching (water)**

S/S Formulation	**Element**	**% Recovery**
$PbHAsO_4$ + *C*	As	103%
$PbHAsO_4$ + *C*	As	99%
$PbHAsO_4$ + *C*	As	97%
$PbHAsO_4$ + *C*	Pb	104%
$PbHAsO_4$ + *C*	Pb	100%
$PbHAsO_4$ + *C*	Pb	96%
$PbHAsO_4$ + *C*	Ca	95%
$PbHAsO_4$ + *C*	Ca	99%
$PbHAsO_4$ + *C*	Ca	98%
$PbHAsO_4$ + *C*	Fe	101%
$PbHAsO_4$ + *C-Fe*	As	114%
$PbHAsO_4$ + *C-Fe*	As	103%
$PbHAsO_4$ + *C-Fe*	As	102%
$PbHAsO_4$ + *C-Fe*	Pb	98%
$PbHAsO_4$ + *C-Fe*	Pb	11%
$PbHAsO_4$ + *C-Fe*	Pb	104%
$PbHAsO_4$ + *C-Fe*	Ca	101%
$PbHAsO_4$ + *C-Fe*	Ca	96%
$PbHAsO_4$ + *C-Fe*	Ca	94%
$PbHAsO_4$ + *C-Fe*	Fe	107%
$PbHAsO_4$ + *C-Fe*	Fe	101%
$PbHAsO_4$ + *C-L*	As	97%
$PbHAsO_4$ + *C-L*	As	95%
$PbHAsO_4$ + *C-L*	As	96%
$PbHAsO_4$ + *C-L*	Pb	106%
$PbHAsO_4$ + *C-L*	Pb	102%
$PbHAsO_4$ + *C-L*	Pb	96%
$PbHAsO_4$ + *C-L*	Ca	99%
$PbHAsO_4$ + *C-L*	Ca	86%
$PbHAsO_4$ + *C-L*	Ca	92%
$PbHAsO_4$ + *C-L*	Fe	104%

- **Sequential Leaching (acid)**

S/S Formulation	**Element**	**% Recovery**
$PbHAsO_4$ + *C*	As	87%
$PbHAsO_4$ + *C*	As	92%
$PbHAsO_4$ + *C*	As	99%
$PbHAsO_4$ + *C*	Pb	90%
$PbHAsO_4$ + *C*	Pb	89%
$PbHAsO_4$ + *C*	Pb	94%
$PbHAsO_4$ + *C*	Ca	106%
$PbHAsO_4$ + *C*	Ca	99%
$PbHAsO_4$ + *C*	Ca	97%
$PbHAsO_4$ + *C*	Fe	99%
$PbHAsO_4$ + *C-Fe*	As	106%
$PbHAsO_4$ + *C-Fe*	As	102%
$PbHAsO_4$ + *C-Fe*	As	102%
$PbHAsO_4$ + *C-Fe*	Pb	105%
$PbHAsO_4$ + *C-Fe*	Pb	106%
$PbHAsO_4$ + *C-Fe*	Pb	108%
$PbHAsO_4$ + *C-Fe*	Ca	105%
$PbHAsO_4$ + *C-Fe*	Ca	108%
$PbHAsO_4$ + *C-Fe*	Ca	98%
$PbHAsO_4$ + *C-Fe*	Fe	111%
$PbHAsO_4$ + *C-Fe*	Fe	108%
$PbHAsO_4$ + *C-Fe*	Fe	107%
$PbHAsO_4$ + *C-L*	As	101%
$PbHAsO_4$ + *C-L*	As	108%
$PbHAsO_4$ + *C-L*	As	98%
$PbHAsO_4$ + *C-L*	Pb	96%
$PbHAsO_4$ + *C-L*	Pb	90%
$PbHAsO_4$ + *C-L*	Pb	91%
$PbHAsO_4$ + *C-L*	Ca	89%
$PbHAsO_4$ + *C-L*	Ca	96%
$PbHAsO_4$ + *C-L*	Ca	95%
$PbHAsO_4$ + *C-L*	Fe	100%