

**The Hydrothermal Precipitation of  
Arsenical Solids in the  
Ca-Fe-AsO<sub>4</sub>-SO<sub>4</sub> System  
at Elevated Temperatures**

by

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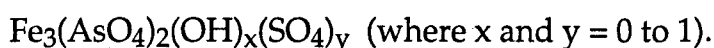
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## Abstract

Hydrothermal precipitation experiments were carried out in sealed test tubes to investigate the characteristics of solids precipitated from Ca-Fe-AsO<sub>4</sub>-SO<sub>4</sub> solutions at temperatures up to 225°C. The solids precipitated from solutions were examined by studying the individual Fe-AsO<sub>4</sub>, Ca-AsO<sub>4</sub> and Fe-Ca-AsO<sub>4</sub> systems at low (<1) and at elevated pHs (>3).

Precipitation of solids in the Fe-AsO<sub>4</sub>-SO<sub>4</sub> system at pH<1 was carried out in the temperature range 150 - 225°C using solutions of 0.5M total ionic concentration. The phases which were identified were hematite, scorodite, arsenical ferrihydrite, and two unknown compounds which have been designated the Type-1 and Type-2 compounds. The scorodite and Type-2 compounds were found to have very low solubilities (<5mg As/L by the US EPA criterion) and such materials may be considered suitable for disposal as wastes.

Scorodite (FeAsO<sub>4</sub>.2H<sub>2</sub>O) is usually light to apple green in colour and is found as crystals up to 20µm. It is formed at temperature above 150°C, from solutions with Fe:As ratios of >1:1. The family of Type-2 compounds show close similarities and are usually produced from starting solutions with Fe:As >1:1 at temperatures >175°C. These compounds are light brown in colour and are composed of crystals up to 50µm, they easily accommodate sulphate into their lattice and have compositions which approximate to:-



The formation of the Type-1 compound is common in the temperature range 150 - 225°C from solutions with ratios of Fe:As of <1:1. Type-1 compounds often have high solubilities and are found as white, fine grained solids (<2µm), usually having an Fe:As ratio of 0.7 to 0.9 with a stoichiometry approximating to:-



The overall results of the hydrothermal precipitation experiments, using simulated hydrometallurgical process solutions in test tube experiments and in a 4L autoclave, have shown that it is possible to precipitate >95% of the contained arsenic from solution. High temperatures are preferable (>175°C) as this promotes the growth of crystalline arsenical compounds. For

optimum conditions the Fe:As ratio in the solution must be around 1:1 to satisfy the Fe:As requirements of the precipitated compound (scorodite or the Type-2 compound, 1:1 or ~1.5:1 respectively) and most of the arsenic is removed within 30 minutes. When higher Fe:As ratios are used, the rate at which the compounds are precipitated is reduced.

In the Fe-AsO<sub>4</sub> system at pH5 using an Fe:As ratio of ~1:1, a crystalline compound; designated Type-3 (approximating to Fe<sub>2</sub>(HAsO<sub>4</sub>)<sub>x</sub>(AsO<sub>4</sub>)<sub>y</sub>), is precipitated from arsenical-ferrihydrite sludges at temperatures above 125°C. Only at elevated pHs (>3) do calcium arsenate compounds begin to precipitate, and during neutralisation of iron-rich solutions arsenic preferentially combines with iron rather than calcium. In sulphate-rich solutions calcium will precipitate as gypsum rather than combine with arsenate to produce calcium arsenate compounds.

From precipitation work carried out in the calcium-arsenate system, it was found that at temperatures below 100°C, the solids are partly hydrated and are usually composed of one of the following:- pharmacolite, haidingerite, or guerinite (CaHAsO<sub>4</sub>·2H<sub>2</sub>O, CaHAsO<sub>4</sub>·H<sub>2</sub>O and Ca<sub>5</sub>H<sub>2</sub>(AsO<sub>4</sub>)<sub>4</sub>·9H<sub>2</sub>O, respectively). In the temperature range 100 - 200°C at pH's < 8, the solids contain only constitutional water and are composed of a weilite-type compound (CaHAsO<sub>4</sub>). Solids precipitated at pH's above 8 and at temperatures above 100°C precipitated johnbaumite (Ca<sub>5</sub>(AsO<sub>4</sub>)<sub>3</sub>OH). Above 200°C, the predominant solid approaches a Ca<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub> composition which contains only minor amounts of constitutional water. This work has examined a wide range of solution compositions and it has been found that all the hydrothermally prepared calcium arsenate-type compounds have very high apparent solubilities (>1000mg/L)

Through experimental observation and consideration of some theoretical concepts a preliminary assessment of the long term behaviour of crystalline arsenic bearing metallurgical wastes in the environment has been made. Through empirical solubility testing and comparison with natural analogues it can be predicted that crystalline scorodite should have a low solubility for prolonged periods of time. Since scorodite is commonly found in many weathering zones and in most climatic regions of the world it is considered to be the most stable arsenate compound formed in nature and may be suitable for arsenic disposal purposes.

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**"Youth is wasted on youth"**

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# **Chapter 1**

## **Introduction**

## 1.1 Background

Arsenic is a toxic and carcinogenic element which presents major problems to the metallurgical industries of the world mainly due to its overproduction, and to the tightening of environmental legislation regarding its disposal into the environment. Industry is acutely aware of the problems of heavy metals and is realising that technology and research must be targeted so as to minimise any long term global risks.

In the processing of arsenical wastes numerous methods have been proposed for the stabilisation of arsenic to minimise its release into the environment. The ideal arsenic compound for disposal must be highly insoluble and have long term stability and its formation must be practical and cheap. A totally insoluble arsenical compound is obviously an unobtainable ideal, therefore a realistic compromise must be identified to confine any soluble arsenic to metallurgical dumps and protect ground and surface water from contamination.

The conventional methods for disposing of arsenic from hydrometallurgical solutions include: i) coprecipitation as arsenical ferrihydrite and ii) precipitation as calcium arsenites and arsenates. The long term stabilities of these compounds are in doubt as they can undergo physical and chemical changes with time [1, 2]. An alternative route for the formation of stable arsenic compounds is hydrothermal precipitation and this is the reason for this present study on the Fe-Ca-AsO<sub>4</sub>-SO<sub>4</sub>-H<sub>2</sub>O system at elevated temperatures (>150°C).

Arsenical solutions which are of hydrometallurgical interest often also contain iron and sulphate. However, despite the industrial importance of the Fe-AsO<sub>4</sub>-SO<sub>4</sub>-H<sub>2</sub>O system there is only limited published information at elevated temperatures. It is the aim of this work to examine the precipitation conditions, characteristics and solubility behaviour of the solids that can be precipitated from these solutions.



## 1.2 Objectives of the research

The objectives of this work are primarily to increase our knowledge and understanding of the structure and solubility behaviour of arsenic-containing compounds, and to examine hydrothermal precipitation as a method for the incorporation of arsenic into crystalline compounds. The systematic characterisation and solubility testing of precipitated compounds should allow the most insoluble arsenic compounds to be identified and these may be potential compounds for disposal as waste. The work should give an understanding of the long term stability of these compounds in the natural environment and guide industrial practice with regard to hydrothermal precipitation.

## 1.3 Arrangement of the research

The research covers three main aspects:

- Investigation into the precipitation conditions of arsenical solids at elevated temperatures (up to 225°C) under hydrothermal conditions,
- Characterisation of the compounds in the precipitates, and
- Solubility testing of the arsenical solids to determine their relative solubilities.

The experiments in the laboratory were conducted at two different scales:

- Hydrothermal precipitation of solids in test tubes (20mL), and
- Hydrothermal precipitation of solids in a large autoclave (4000mL)

The results of hydrothermal work carried out on a test tube scale allowed an understanding of the Ca-Fe-AsO<sub>4</sub>-SO<sub>4</sub>-H<sub>2</sub>O system at elevated temperatures and enabled identification of the least soluble arsenate compounds.

The precipitation conditions for the formation of low solubility solids were established on a small scale and this information helped guide and direct the larger scale precipitation test programme. The solutions used during the

course of the work were intended to simulate hydrometallurgical liquors from which arsenic can be removed and stabilised as a low solubility material.

## 1.4 Arrangement of the thesis

A literature review is given in Chapter 2, describing the main environmental and metallurgical problems with arsenic. The current disposal options are outlined with emphasis placed on ambient temperature lime neutralisation and the hydrothermal processing of arsenical solutions and dusts.

Chapter 3 covers the methodology and equipment used in the hydrothermal precipitation study. Attention is drawn to the precipitation techniques to produce the solids and to the characterisation procedures on the solids. The solubility testing methods used to assess the relative solubility of the samples are also discussed.

Chapter 4 introduces the main characteristics of the synthetic compounds precipitated from Fe-AsO<sub>4</sub>-SO<sub>4</sub> solutions. Attention is drawn to scorodite and to three important new arsenical compounds designated Type-1, -2 and -3. Aspects of synthetic iron arsenates and their relationship to the naturally occurring iron arsenate minerals are discussed. Information derived from infra-red spectroscopy is used in conjunction with other techniques for characterisation and structural examination.

Chapter 5 covers the precipitation conditions and characteristics of the arsenical solids precipitated from Fe-AsO<sub>4</sub>-SO<sub>4</sub> solutions at low pH(<1). The conditions of formation for the iron arsenate compounds were investigated.

Chapter 6 covers the results of the precipitation of the arsenical solids formed from Fe-AsO<sub>4</sub>-SO<sub>4</sub> solutions at pH5. The conditions of precipitation of the Type-3 compound is described. The 2- and 6-line arsenical ferrihydrites formed during hydrothermal precipitation are also examined.

Chapter 7 covers the results on the conditions and characteristics of the arsenical solids precipitated from Ca-Fe-AsO<sub>4</sub>-SO<sub>4</sub> solutions. The solids produced in the individual Ca-AsO<sub>4</sub> and Fe-AsO<sub>4</sub> systems at various pH's

are described. Attention is drawn to the comparison of the precipitated Ca-AsO<sub>4</sub> compounds with naturally occurring minerals. The range of compounds formed under different temperature and pH conditions were determined by IR spectroscopy.

**Chapter 8** summarises the solubility test results on a range of Ca-Fe-AsO<sub>4</sub>-SO<sub>4</sub> solids using the US EPA TCLP and MARG tests; these are evaluated and important interpretations made. The solids precipitated under different conditions are examined and the lowest solubility compounds empirically identified.

**Chapter 9** covers results on the autoclave scale precipitation (4000mL) of arsenic from simulated hydrometallurgical solutions. Experimental results indicate the optimum conditions for the formation of scorodite and the Type-2 compound; the work also clearly shows the influence of temperature and Fe:As ratio on precipitation.

**Chapter 10** is a discussion of the results and the environmental implications of the work. The chapter attempts to integrate all the available experimental and geological evidence to indicate and justify that scorodite and the Type-2 compound are suitable for disposal as industrial waste. The long term stability of the compounds are addressed and it is suggested how hydrothermal precipitation could be used on a commercial scale to remove arsenic from solution and produce disposable residues. A brief comparison between the different treatment options is made with emphasis placed on the processing and long term stability of the residues.

Finally in **Chapter 11**, major conclusions are presented and suggestions for further work discussed.

# **Chapter 2**

## **Literature survey**

## 2.1 Environmental and health aspects

Inorganic arsenic compounds are substantially more toxic than organo-arsenic compounds, and animal experimentation data indicate that trivalent arsenic is marginally more toxic than the pentavalent form [3 - 7]. Arsenic is absorbed through the respiratory and gastrointestinal tract and an oral consumption of 70 to 180mg is sufficient to cause chronic if not fatal poisoning to human life. The body can extract significant amounts of inorganic arsenic from solid and fluid intakes with only minor amounts (10 - 30%) discharged. Absorption through the skin has also been documented [4, 8].

The toxic and carcinogenic properties of arsenic are well known. However, extrapolation of the incidence of cancer from the extreme cases of long term exposure to high levels of arsenic in drinking water (e.g. Taiwanese, Chinese, Mexican, Chilean occurrences) [9, 10] to very low concentrations of arsenic (e.g. California) may not necessarily be valid. For this reason long term epidemiological and biochemical studies need to be carried out to quantify the influence of low arsenic levels on flora, fauna and human life. People are exposed to arsenic via air, water and food and a reduction of arsenic into the ecocycle, especially the inorganic form, is warranted, as it may have long term effects (see Table 2.1). While the organic form has not been shown to be deleterious to human life (based on fish consumption) [3 - 6] high quantities may be harmful in the long term. The long term effects of the introduction of arsenic into the ecocycle and the subsequent effects on man and the environment is unknown. To minimise any future risk the disposal option should be in as safe a manner as possible so as not to endanger the flora, fauna and ecosystems of our planet.

Table 2.1 Toxicity threshold levels for arsenic emissions [6, 11, 12]

Type of arsenic emission	USA	FRG	USSR	GB
Air (mg/Nm <sup>3</sup> )	0.01		0.003	0.2
Industrial waters (mg/L)		1.0		
Domestic water (mg/L)	0.01		0.05	
Solid waste (after TCLP mg/L)	5.0			

The mining industry has conventionally exploited those mineral deposits which were high grade, near surface and those requiring simple metallurgical processing and has left the more refractory and metallurgically complex ores for future generations. Those more complex ores can contain high levels of arsenic. Yet in future environmental regulations will force the metallurgical industries to reduce the levels of heavy elements in flue off-gases and minimise the wastes and effluents entering streams and ground waters. This could make the exploitation of these ores prohibitively expensive. Environmental constraints may also become of such a major cost that in future these may dictate the viability of mining operations and influence the choice of metallurgical process routes.

The health and environmental concerns over the use of arsenic has given rise to restrictive legislation and regulatory criteria and this will reduce the consumption of arsenic as used in: wood preservatives, fungicides, glass, ceramics, non-ferrous alloys and other lesser uses (see Table 2.2) [5, 6]. This will further exacerbate the problems of oversupply of arsenic and its eventual disposal.

**Table 2.2** Estimated US demand for arsenic [13]

Use	1971*	1981*	1991*
Agricultural chemicals (herbicides and desiccants)	15600	8900	5000
Glass	2000	1000	900
Industrial Chemicals (wood preservatives)	970	9100	14300
Non-ferrous alloys and electronics	570	600	1000
Other	500	400	400
<b>Total</b>	<b>19640</b>	<b>20000</b>	<b>21600</b>

\*(Metric tons of contained arsenic)

The supply and demand of arsenic is difficult to estimate [13], the largest producers are China and Chile (each around 10 000 tons of arsenic oxide per year) both of which are likely to increase production over the next decade. Estimates for the world arsenic oxide production are about 50 000 to 100 000

tons mainly derived from the processing of copper, lead and zinc ores. However, during processing about 10 000 tons are released into the environment either as tailings, slags or particulate materials formed during pyrometallurgical operations [13]. Arsenic oxide that is not sold is stored until suitable markets become available or suitable technology for its disposal is developed.

In the USA the Environmental Protection Agency (EPA) insists that industrially derived waste solids are tested by a toxicity characterisation leach procedure (TCLP) [14]. The test (Chapter 3) assesses the solubility by contacting the solid with a buffered pH acetate solution (pH 4.93, S:L - 1:20). This is agitated for 20 hours and the filtrate from the test must be below a 5mg As/L toxicity threshold, otherwise the material cannot be considered safe for disposal. Due to the limitations of this test procedure it can only be realistically viewed as a screening test, to separate the soluble from the low solubility solids. The 5mg As/L is an arbitrary value determined from practical evaluation of a wide variety of metallurgical samples and consideration of effluents and drinking water standards. In future this threshold limit may be reduced even further.

Current arsenical sludge disposal options include: tailings ponds, sludge ponds, marine and lake disposal and landfill. The long term stability of these sludges will depend on a number of factors including: disposal site characteristics; presence of oxygen; organics and sulphides; in-place permeability; pore water characteristics; leaching kinetics; solubility of arsenical waste products, coupled with the site-specific geologic and hydrologic data. These parameters and their possible variation with time all require to be quantified and are essential requirements for assessing any impact on the environment. Studies of this nature are necessary and will ultimately help develop waste management practices and technologies to minimise dissolution and migration of toxic elements and will ultimately help predict arsenic mobilisation from industrial wastes.

## 2.2 Geochemistry of arsenic

Arsenic is ubiquitous and owing to its chalcophile nature tends to concentrate in a wide range of sulphides and for this reason occurs in many types of

precious and base metal deposits world wide. The sulphosalts are the most important source of arsenic and are usually composed of As, Sb and Bi, linked with sulphur together with Cu, Ag and Pb (see Table 2.3). The arsenites and arsenate minerals can be considered to be secondary minerals derived from the oxidation of the primary arsenic bearing minerals. The secondary minerals often contain hydroxyl or water of crystallisation which would appear to help stabilise the compounds under environmental conditions. A comprehensive listing of the 196 documented arsenic minerals is given in a paper by Gonzalez [15].

**Table 2.3** Common arsenic bearing minerals [15]

Mineral	Formula
<b>Arsenides</b>	
Loellingite	FeAs <sub>2</sub>
Safflorite	(Co,Fe,Ni)As <sub>2</sub>
Skutterudite	CoAs <sub>3</sub>
<b>Sulphides and Sulphosalts</b>	
Arsenopyrite	FeAsS
Cobaltite	CoAsS
Enargite	Cu <sub>3</sub> AsS <sub>4</sub>
Glaucodot	(Co,Fe)AsS
Orpiment	As <sub>2</sub> S <sub>3</sub> (yellow)
Realgar	As <sub>4</sub> S <sub>4</sub> (orange-red)
Tennantite	(Cu,Fe) <sub>12</sub> As <sub>4</sub> S <sub>13</sub>
Arsenical Pyrite	Fe(As,S) <sub>2</sub>
<b>Oxides</b>	
Arsenolite	As <sub>2</sub> O <sub>3</sub>
Claudite	As <sub>2</sub> O <sub>3</sub>
<b>Arsenates</b>	
Erythrite	Co <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> .8H <sub>2</sub> O
Olivenite	Cu <sub>2</sub> (AsO <sub>4</sub> )OH
Pharmacosiderite	Fe <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH)3.5H <sub>2</sub> O
Scorodite	FeAsO <sub>4</sub> .2H <sub>2</sub> O

Arsenic is classified chemically as a non-metal or metalloid, although it is grouped with the metals for most environmental purposes. Arsenic is a member of the Group VB elements (P, As, Sb, Bi) in the periodic table and the ground-state electronic structure of arsenic, as with all Group VB elements features 3 unpaired electrons  $ns^2 np^3$ . and its chemistry is similar to phosphorus and antimony. It occurs as the valency states of -III, 0, III, and V.



The oxide is amphoteric showing ionic and covalent characteristics, and thus soluble in both acids and bases [123]. Arsenic combines readily with carbon and can be incorporated into many organic metallic compounds in both the +III and +V states. The organoarsines are derived from arsine ( $\text{AsH}_3$ ), by replacement of one to three hydrogen atoms by alkyl, cycloalkyl, aryl, or heterocyclic groups. The tertiary arsines have the most importance and are widely used as ligands in co-ordination chemistry. The arsenic acids,  $\text{R}_2\text{AsO}(\text{OH})$ , are important commercially, especially the dimethyl compound (cacodylic acid).

Arsenic chemistry is complex, involving a variety of valency states, anionic and cationic species, and it occurs as both inorganic and organic compounds and these are all commonly found in solid arsenic wastes, often at the same time. To further complicate the issue, the valency changes easily and reversibly with redox potentials [16].

While the predominant form of arsenic in natural waters is arsenate, arsenic may also be found as arsenite, arsine, monomethylarsenate, dimethylarsenate, dimethylarsine, trimethylarsenate and trimethylarsine. In geothermal fluids arsenic is transported mainly as the arsenite, but at elevated temperatures the As(III) oxidises to As(V) [17].

Arsenic speciation has been investigated in a number of studies [18, 19, 20] and has allowed Pourbaix (or  $E_h$ -pH) diagrams to be generated which enable predictions to be made on the stable species in aqueous systems. A lot of thermodynamic data exist for low temperature solutions and realistic assessments of effluents can therefore be made. The  $E_h$ -pH diagram (Figure 2.1) for the As- $\text{H}_2\text{O}$  system shows the stability of the various species at different pH's.

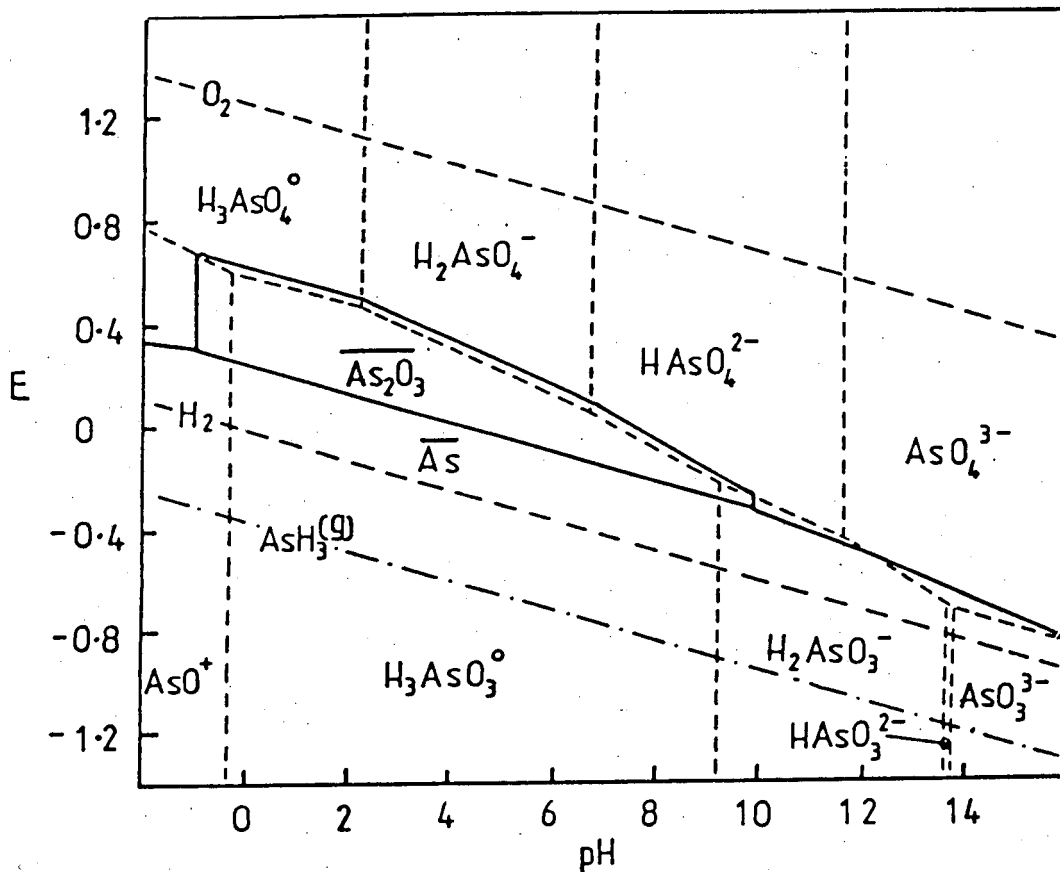


Figure 2.1 The Potential - pH equilibrium diagram for the system arsenic - water at 25°C and at unit activity of all species [20]

## 2.3 Arsenic in metallurgical processing

### 2.3.1 Arsenical dusts

The metallurgical treatment route for an ore or concentrate dictates the types of arsenical wastes and effluents that are produced. Smelting and roasting operate usually at temperatures  $>700^{\circ}\text{C}$  and this easily volatilises the arsenic, which moves as the As(III) oxide with the exhaust gases (mainly  $\text{SO}_2$ ). It is captured in bag houses and electrostatic precipitators as flue dusts (up to 30wt% arsenic) and is recovered as  $\text{As}_2\text{O}_3$ , and may also contain minor amounts of  $\text{As}_2\text{S}_3$  and  $\text{As}_2\text{O}_5$ . Significant amounts can also be recovered in the acid plant (As(III)) with sulphuric acid.

The recycling of arsenic dusts (which can contain significant amounts of base metals) to the smelter is often practised in an attempt to recover the base metals and to incorporate some of the arsenic into the slags. The dusts may also contain minor amounts of selenium, bismuth, mercury, antimony and thallium which may be detrimental to the quality of the final metal product. Recycling of these dusts can also ultimately increase the concentration of arsenic in anode copper destined for refining [21, 22]. This may in turn build up in the refinery electrolyte solutions (up to 20g/L) and may have a deleterious effect on the operation, therefore removal of arsenic from the smelting - refining cycle is often recommended [23 - 27].

### 2.3.2 Arsenical slags

Although very little quantitative published information is available on the arsenic content of base metal slags, only minor amounts of arsenic ( $\ll 0.5\%$ ) are likely to become incorporated into the slag, this is because arsenic oxide has only limited solubility in conventional silicate slags at normal operating conditions [28]. The distribution of arsenic between matte, slag and vapour can differ according to the operating conditions, also much of the arsenic is recycled [29] estimates of 80% of the total arsenic moving with the vapour phase have been reported, the remainder is partitioned equally between matte and slag (i.e.  $\sim 10\%$ ). How much of this arsenic is retained in the siliceous matrix and how much entrained in matte droplets within the slag is not known.

Testwork conducted at small scale [30 and 31] has shown that up to 10% arsenic can be incorporated into the slag in the form of calcium arsenate,

which is preferred due to its higher thermal stability as compared to that of iron arsenate. When the slags are slowly cooled, crystals of calcium arsenate-type phases nucleate and grow, these compounds are reasonably soluble as determined from solubility tests and may not be suitable for disposal. However, if the calcium arsenate can be incorporated into a quenched slag the arsenic is incorporated into the glassy matrix and has been found to have very low arsenic solubilities. The long term stability of this glass is unknown and the possibility exists that the glass may devitrify with time [28, 32]. When this happens the calcium arsenate may recrystallise from the glassy matrix and its arsenic solubility will increase.

### 2.3.3 Arsenical cements

Solidification/stabilisation is used for the disposal of some types of hazardous waste. The method involves mixing arsenical sludges and wastes (up to 70%) with a cement binder to produce a solid which is structurally sound and relatively impermeable [33 - 38]. The solutions filling the pores in the cement will have high pH and calcium ion activity, under such conditions the arsenic is expected to be combined with calcium and be immobilised. In the cement ionic transport is decreased as the porosity and permeability are reduced on hardening. The arsenic in the cement is retained by physical encapsulation and through incorporation into alumino-silicate compounds, however, the actual distribution of arsenic in the cements has not been fully quantified. During solubility testing of arsenical cements the high levels of lime and calcium compounds act to increase the calcium content and pH of test solutions and this helps prevent arsenic dissolution and leads to low arsenic levels in the filtrate [36].

### 2.3.4 Miscellaneous

Arsenic from some metallurgical operations can be efficiently concentrated into a speiss (essentially an Fe-arsenide) which is material that has been considered for disposal. However, as with all other arsenides and sulphides, with time speisses will undergo chemical and bacteriological breakdown [37, 39]. The ferrihydrite that forms from the breakdown of the speiss can reabsorb the released arsenic from solution and can act to partially stabilise the material.

Storage of arsenic in the metallic or oxide form has also been suggested, however, arsenic is unlikely to find a major use in the future and therefore

storage in underground cavities can only be considered as a temporary solution [39, 40]. The concerns with storage underground are the possible penetration by ground waters, and the necessity of upkeep and monitoring of the site in perpetuity so as to guarantee safety and security.

#### **2.3.4 Oxidation of arsenic trioxide**

Usually it is desirable to have arsenic in the pentavalent form since this is more easily precipitated e.g. ferrihydrite, jarosite, calcium arsenate, and the pentavalent form has been shown to be the more stable form of arsenic [26]. For arsenic fixation as ferric arsenate, the conversion of As(III) to As(V) in solution is a requisite and is possible by using a number of strong oxidants [41 - 44]. Oxidation can be achieved using oxygen at 90°C, the conversion is almost complete within 3 hours, however small residual amounts of As(III) (0.1g/L) can still remain in solution. Air is even less effective with only about 50% conversion after 3 hours. For more complete conversion, ozone, H<sub>2</sub>O<sub>2</sub>, oxygen gas, chlorine gas, or nitric acid, potassium permanganate and ammonium persulphate can be used [26]. Of these oxidants chlorine was considered by Harris and Monette [26] to be the most efficient and cost effective for their particular application.

Various methods have been proposed for the removal of arsenic from process solutions and effluents, including: electrolysis, solvent extraction, ion exchange, membrane separation, precipitate flotation, ion flotation and biological processes [20, 45 - 50]. The processing of an arsenical effluent is solution dependent and may require oxidation, but for high grade effluents where arsenic can be measured in g/L, lime neutralisation is the favoured route. The arsenic being conventionally precipitated as either calcium arsenite or arsenate or adsorption onto ferrihydrite.

## **2.4 Low temperature precipitation**

### **2.4.1 Lime neutralisation**

During hydrometallurgical and pyrometallurgical treatments of arsenic containing ores and concentrates some of the arsenic inevitably reports to the final effluents. These process solutions are required to be treated to remove the toxic elements before they are released into rivers or recycled back to the plant. The arsenic is conventionally removed from acidic solutions by a

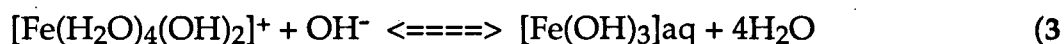
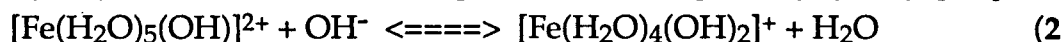
neutralisation process [34], the addition of lime or limestone or a combination of both is the most common practice. The arsenic is removed by coprecipitation with available iron(III) in solution, if iron levels are low arsenate will combine with calcium to form calcium arsenate compounds. As indicated in Figures 2.2 and 2.3 arsenical ferrihydrite precipitates preferentially to calcium arsenates, the arsenic containing ferrihydrite starts to precipitate at a significantly lower pH (1 - 2) than the calcium arsenates (3 - 4). Arsenites (As(III)), are not sufficiently stable for disposal purposes [51] and for this reason arsenic must be converted to the pentavalent form otherwise soluble residues will result.

During neutralisation iron(III) undergoes hydrolysis (see reaction 1), the actual mechanism of the reaction is very complex even though the overall reaction may look simple [52]. First the hexa-aquo ferric iron starts to hydrolyse as the pH is increased. The hydrolysis continues as successive aquo molecules are replaced by hydroxyl groups [52]. These reactions are very pH dependent and also some polymerisation takes place during the reaction, with hydroxyl groups behaving as bridges between iron atoms (reaction 4) (Figure 2.4). These polymeric molecules are important for the stabilisation of the colloidal particles where the charge on the particles is partly or completely neutralised so that they may coalesce as the iron precipitate starts to flocculate. The rate of transition from the aquatic ferric ion to the hydrated ferric oxide depends on the pH, the concentration of ferric ion, the alkalinity, and the number of nuclei in the system [52].

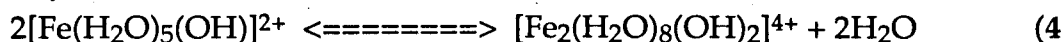
Hydrolysis



Hydrolysis continues as successive aquo molecules are replaced by hydroxyl groups



Polymerisation



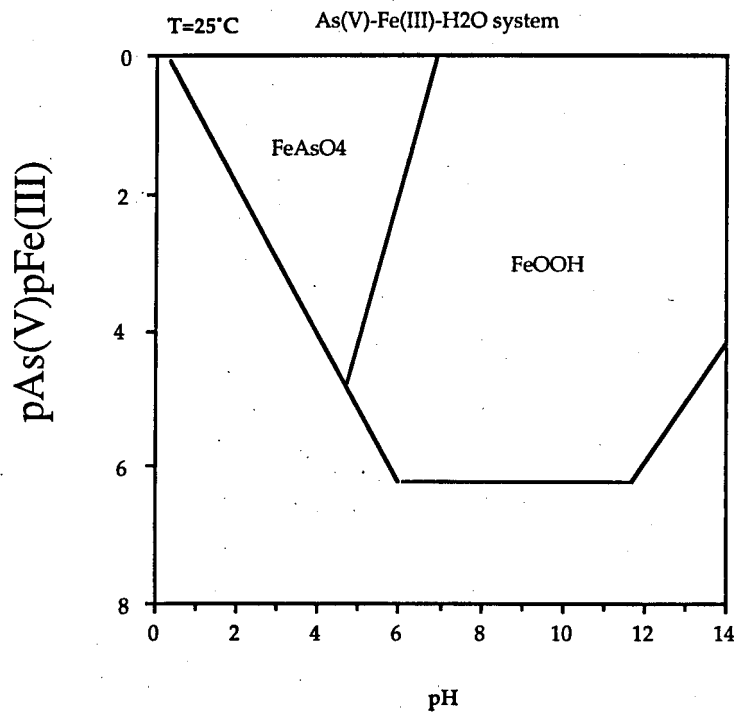


Figure 2.2 The stability regions of the solids in the Activity ( $p_{As(V)}$ ,  $p_{Fe(III)}$ ) - pH diagram for the iron(III)-arsenic(V)-water system [53]

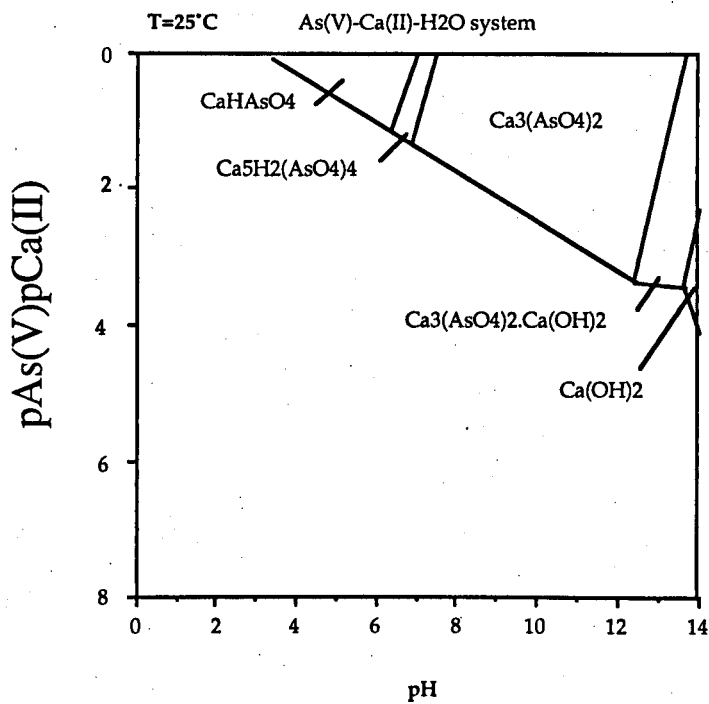


Figure 2.3 The stability regions of the solids in the Activity ( $p_{As(V)}$ ,  $p_{Ca(II)}$ ) - pH diagram for the calcium-arsenic(V)-water system [53]

The extent of polymerisation becomes more pronounced as the charge density of the iron species decreases. This polymerisation is important for the finer particles in effluents in that they can promote the adsorption of a coagulant onto the colloids [52]. In the presence of arsenic or other adsorbates the anions are effectively bound by the complex.

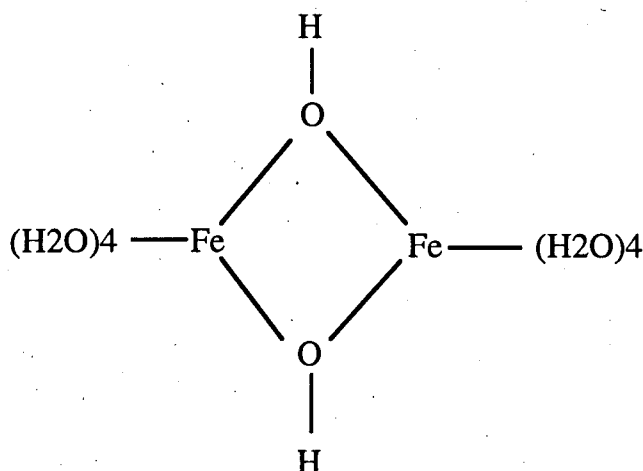


Figure 2.4 Polymerisation of a simple iron aquo-complex (see reaction 4)

Tozawa et al [47] have shown the coprecipitation of arsenic with iron is more complete when arsenic is in its pentavalent oxidation state. Coprecipitation of As(V) was maximised at pH~4 - 5 while As(III) reached its maximum at ~pH8. The coprecipitation of arsenic was shown to improve appreciably when the Fe:As molar ratio was increased above 2 [47]. If the arsenic in solution is not present in the As(V) form it may not be readily precipitated. Such a situation can arise from the bacterial leaching of arsenical concentrates where all the arsenic in the final leach residue may not have been fully oxidised during leaching and may lead to the leach residues having unacceptably high arsenic solubilities [54, 55]. From the knowledge that arsenic must be in the As(V) state and iron in the Fe(III) the detoxification of arsenical effluents with iron sulphate and hydrogen peroxide has been suggested [42].

#### 2.4.2 Stability of residues

Krause and Ettel [56] showed the effect of molar Fe:As ratio on the solubility of precipitated arsenic containing ferrihydrites (see Figure 2.5). The solids



used in their studies were precipitated using caustic soda solutions for pH control, and the subsequent solubility data showed that a minimum molar Fe:As ratio of 4 was required in the solids to maintain an arsenic concentration of less than 5mg/L in the pH range 3 - 6.5 (see Figure 2.5). It was also reported [57] that the presence of CO<sub>2</sub> and reactive solids, such as pyrrhotite and pyrite, do not increase the solubility of arsenic and that the accelerated ageing of the iron-arsenate precipitate does not significantly affect the arsenic dissolution. They also established that the solubility of natural crystalline scorodite is two orders of magnitude lower than the one reported in the literature for the apparent amorphous iron-arsenate (see Figure 2.6).

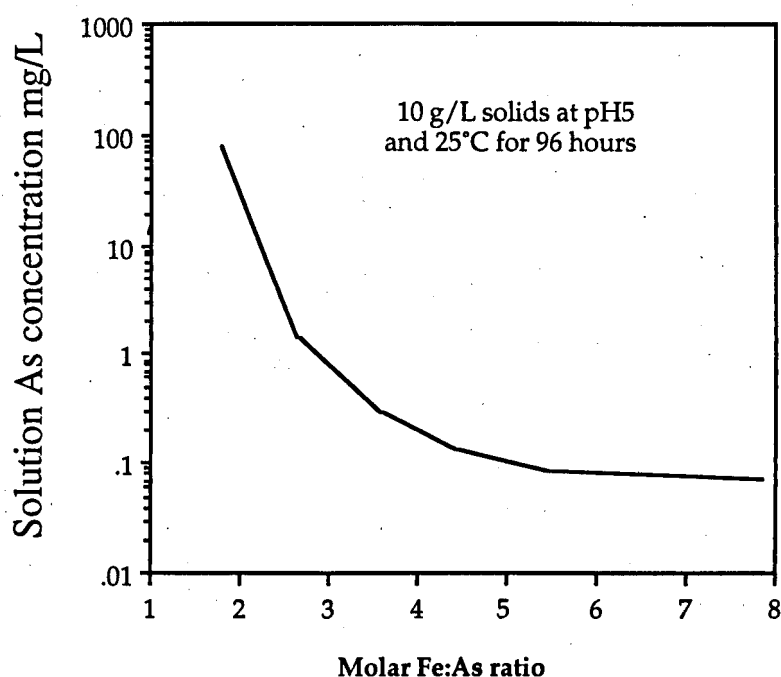


Figure 2.5 Solubility as a function of molar Fe:As ratio [56]

Until only recently there was some controversy on the structure of the precipitated solids formed during lime neutralisation. Robins [58] considered unlikely the existence of the basic ferric iron arsenates proposed by Krause and Ettel [56], and indicated that the only stable solid phases in the Fe(III)-As(V)-H<sub>2</sub>O are scorodite and Fe(OH)<sub>3</sub> and suggested that adsorption of arsenic onto the hydroxide will occur [59]. Robins also reported that the extent of arsenate incorporation into the ferric hydroxyl polycations was solution concentration dependent and concluded that amorphous ferric

hydroxide is a very effective material for binding and removing most As(V) from solution at pH=4. It has now become accepted that arsenate is adsorptively bound to ferrihydrite and is termed arsenical ferrihydrite (see also Section 2.5.7).

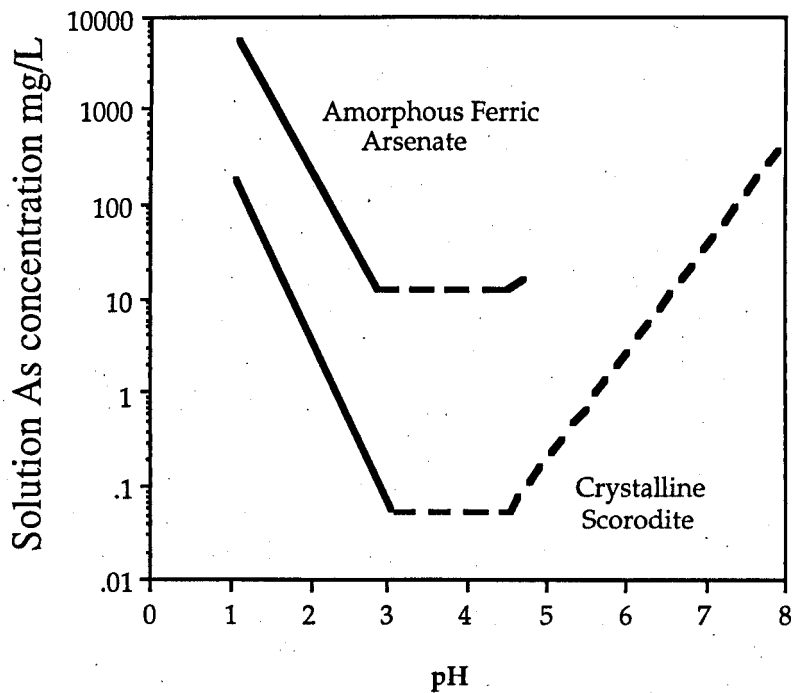


Figure 2.6 Solubility of amorphous and crystalline FeAsO<sub>4</sub> at 23°C [56]

A number of workers have noted that the presence of calcium, sulphate or gypsum has a stabilising effect on arsenical ferrihydrites, and for this reason solubility tests conducted at different pH's using lime usually showed lower arsenic values in solution as compared to those using sodium hydroxide. Khoe et al [34] studied the effect of calcium on the adsorption of arsenic on ferrihydrite by adding calcium in the form of calcium nitrate. They showed that increasing the initial calcium concentration consistently lowered the dissolved arsenate levels in alkaline conditions, they found that sulphate did not play a significant role. Using calcium nitrate they found that calcium tends to adsorb on to the ferrihydrite at elevated pH's and inferred that when using lime the calcium ions may behave similarly. They found that lead, magnesium, strontium and cadmium are as effective as calcium at reducing

dissolved arsenic concentrations at high pH when they are present at equal total concentrations (mole ratio of cation/Fe, i.e. M/Fe of 0.2). On investigating the influence of silicic acid on arsenical ferrihydrite, they [36] found that it was adsorbed by the ferrihydrite and if the silicic acid was adsorbed first then the amount of arsenic adsorbed was substantially reduced. Therefore silicate ions reduce the adsorptive capacity of ferrihydrite.

Harris and Monette [37] reported that co-adsorbed metal ions such as Cd, Pb and Zn enhanced the stability of dissolved arsenic by iron precipitation. The presence of small amounts of coprecipitated base metals, notably Cd+Zn+Cu extended the pH stability region from 4 - 7 to 4 - 10. Chemical analysis of test solutions taken over 8 years of continuous monitoring showed no indication that the residues were beginning to lose arsenic to solution. However different mechanisms may be involved in the reduction of residual dissolved arsenate depending on whether heavy metals or alkaline earth metals are coprecipitated. Khoe et al [34] supported these findings and found that sulphate ions have a minimal effect on the residual dissolved arsenate concentration.

The long term stability of the residues following neutralisation can be studied using thermodynamic behaviour assuming equilibrium conditions. The theoretical models can indicate the ultimate fate of a residue provided the parameters that could influence the system are predictable and quantifiable. Robins [58] suggested that arsenic-bearing ferrihydrite may be unstable over long periods because of its possible conversion to a more crystalline iron oxide phase such as goethite [34]. Since these crystalline materials have a lower specific surface area than the original ferrihydrite phase, arsenic could be released into solution during the transformation processes. Emmet and Khoe [36] have however suggested that adsorbed species tend to stabilise the ferrihydrite and slow down the transformation.

Overall the work by Robins [60] and other investigators [26, 56, 57] has shown that arsenical ferrihydrites with Fe(III):As(V) molar ratios of 3:1 and above are sufficiently stable for disposal on dumps or as landfill. Solubility data for arsenical residues derived from existing metallurgical plants given in the literature show very low solubilities and this further supports the stability of these compounds. Often the resultant contaminant-bearing ferric sludge is

disposed of in dams or ponds without further treatment [34]. At the optimal neutralisation pH of 4 - 5, residual dissolved arsenate levels as low as 20µg/L can be achieved with high Fe:As ratios in the initial solution. However, the adsorbed arsenate species will be released if the solution pH is raised from the optimal value.

## 2.5 Hydrothermal precipitation

### 2.5.1 Theory

The solubilities of compounds have been found to be a function of their crystallinity with amorphous solids having higher solubilities than their crystalline counterparts [61]. This is due to the higher surface area exposed to solution (kinetic effects) and to the influence of stronger bond energies in the crystalline compounds (thermodynamic effects). Therefore it is necessary to study the nature and structure of a compound to understand its solubility which can in turn have a bearing on its long term stability.

If the concentration of a solution exceeds the solubility product with respect to a solid phase, the new phase is not formed until a certain amount of supersaturation has been achieved. Stable nuclei can only be formed after an activation energy barrier has been surmounted. Small crystallites are more soluble than larger crystals and hence the energy barrier is related to the additional free energy needed to form the nuclei and is due to the surface energy of these small particles. Once nuclei of critical size have been formed, crystallisation is spontaneous. If the nucleus is smaller than one unit cell, the growing crystallite produced initially is most likely to be amorphous [62]. A critical number of ions are required to form clusters and an induction period is necessary for incorporation of a constant fraction into crystallites. For solutions at elevated temperatures nucleation is actually promoted, the reason being the supply of energy into the system allows for the formation of an interface between the crystalline cluster and the solution/amorphous matrix. This energy fixes the atoms and forms a more chemically stable material than the more disordered amorphous material. The growth of crystals will occur in a number of successive steps:

- a/ the transport of solute to the crystal solution interface,
- b/ the adsorption of solute at the surface, and

c/the incorporation of the chemical constituents into the crystalline lattice. An equilibrium will be established between growth and dissolution of the crystal which will be taking place simultaneously.

Thermal precipitation in acidic aqueous solutions involves the formation of a solid phase simply by heating the solution to higher temperatures. This is a result of a reaction or series of reactions where a final solid product is formed and for which the equilibrium constant for the overall reaction increases with temperature. However, investigations of high temperature aqueous systems have been impeded by the lack of high temperature data. Much work has been directed to obtaining this data either by experiment or by the use of various empirical methods of estimation (heat capacities). The most satisfactory extrapolation of data to high temperatures can be obtained by using the entropy correspondence principle of Criss and Cobble [63, 64] or a similar method proposed by Khodakovskiy [65].

Kwok and Robins [66] studied a number of simple base metals aqueous systems for which there were some published high temperature data and demonstrated that the conditions for thermal precipitation can be fairly accurately predicted and the results of these systems used as a basis for showing regions where high temperature separations are feasible.

### 2.5.2 Nucleation and growth

The formation of new crystals may take place either in the bulk of the solution (homogeneous nucleation) or on surfaces already present (heterogeneous nucleation). Much more frequently the formation of a new solid is governed by the presence of another solid phase within the system, the new phase therefore appears as a result of heterogeneous nucleation. The rate of homogeneous nucleation is low compared to heterogeneous nucleation, due to the higher energy requirements necessary for the formation of the nuclei. For this reason the presence of seed materials can reduce the activation barrier and speed up the kinetics of precipitation. When the two types of crystallisation occur in series an induction period is observed. While such processes can both occur, the macroscopic rates as measured in the tests reflect the predominant process which is most likely to be heterogeneous nucleation [67]. At a high degree of supersaturation poor crystals form due to the formation of many crystal nuclei few of which grow large, at low

supersaturation crystal growth will dominate over nucleation and result in few but larger crystals.

The shape and size of the particles are due to a combination of nucleation, growth and aggregation phenomena. During crystallisation there will be the gradual attachment of separate molecules to the cluster with the ordering and organising of the molecules into well defined structures which will become the crystal structure. The nucleation rate increases with increasing temperature and may limit the average size to which the crystals grows, this may be due to changes in the relative rates of diffusion and surface alteration steps. The rate of precipitation also increases at higher temperatures while the crystal size, shape and crystal modifications take place [67].

The Gibbs-Thomson equation links crystal size with the equilibrium solubility, the smaller the crystal, the more concentrated is the corresponding equilibrium solution. Predictably the solubility of a substance increases with decreasing grain size, mainly through the increasing surface area [67].

$$\ln\left[\frac{c(r)}{c^*}\right] = \frac{2M\gamma}{vRT\rho r}$$

Where  $c(r)$  is the solubility of particles of size (radius)  $r$  (in  $\text{nm } 10^{-9}$ ),  $c^*$  is the normal equilibrium solubility of the substance,  $\gamma$  is the interfacial tension of the solid in contact with solution (in  $\text{Jm}^{-2}$ ),  $T$  is temperature (in K),  $R$  is the gas constant ( $8.31 \times 10^3 \text{ Jkmol}^{-1}\text{K}^{-1}$ ),  $\rho$  is the density of the solid ( $\text{Kgm}^{-3}$ ),  $M$  is the molar mass of the solid in solution ( $\text{Kgkmol}^{-1}$ ). The quantity  $v$  represents the number of moles of ions formed from one mole of electrolyte, for a non-electrolyte,  $v = 1$  [67].

The implications of this equation is that different sized crystals can give different apparent solubilities. With some solution compositions exceeding the normal equilibrium saturation value if the excess solute particles dispersed in the solution are very small. The equation postulates an exponential increase in solubility with a reduction in particle size to zero. However, for most solutes in water, the solubility increase only starts to become significant for particle sizes smaller than about  $1\mu\text{m}$  (see also Section 2.6) [67]. During precipitation this could mean that on cooling some ultrafine compounds may reequilibrate with its solution more readily than others. The

size of some crystals that nucleate and grow from solution will increase with increasing temperature and this may avoid their reequilibration on cooling.

### 2.5.3 Hematite

From a consideration of the literature, a number of compounds can be expected to precipitate from Fe-AsO<sub>4</sub>-SO<sub>4</sub> solutions at elevated temperature. These are given in Table 2.4 [68]. Amongst these hematite, which is often the result of the transformation of goethite/ferrihydrate (see Figure 2.7) and its formation is promoted at elevated temperatures (>120°C). Hematite is generally one of the most dominant phases precipitated from iron-containing solutions and liquors at elevated temperatures.

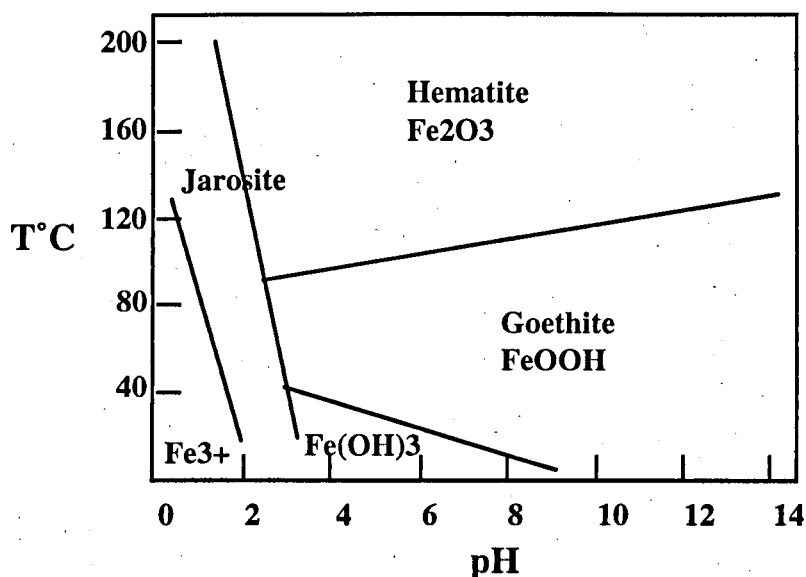


Figure 2.7 Stability fields for iron compounds as a function of pH and temperature from 0.5M Iron(III) sulphate solution [68]

### 2.5.4 Jarosite

Substitution of arsenate into the beudantite - crandallite group of minerals (notably jarosite) is possible. Jarosite has been quoted by Dutrizac [69] to contain up to 4% arsenic. Chemical and X-ray diffraction data suggest that arsenic is structurally incorporated into the lattice of jarosite, the arsenate substituting for sulphate with charge neutrality maintained by the incorporation of OH into the structure.

For charge balance in the jarosite structure  $\text{AsO}_4^{3-} + \text{OH}^- = 2\text{SO}_4^{2-}$

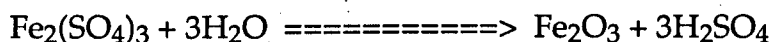
**Table 2.4** Compounds reported to be formed during hydrothermal precipitation from Fe-AsO<sub>4</sub>-SO<sub>4</sub> solutions

Compound type	Chemical composition
Hematite	Fe <sub>2</sub> O <sub>3</sub> [68]
Hydronium jarosite	(H <sub>3</sub> O)Fe <sub>3</sub> (OH) <sub>6</sub> (SO <sub>4</sub> ) <sub>2</sub> [68, 69]
Basic iron sulphate	Fe(OH)(SO <sub>4</sub> ) [70 - 74]
Arsenical ferrihydrite	Fe <sub>2</sub> O <sub>3</sub> .xH <sub>2</sub> O + arsenate [56 - 59, 75 - 79] (ferrihydrite onto which AsO <sub>4</sub> is adsorbed)
Scorodite	FeAsO <sub>4</sub> . 2H <sub>2</sub> O [79, 51]
Arsenic-rich Fe(III) compounds	Fe(H <sub>2</sub> AsO <sub>4</sub> ) <sub>3</sub> . 3H <sub>2</sub> O or FeAs <sub>3</sub> O <sub>9</sub> .6H <sub>2</sub> O [80 - 83]
Phase X	Fe <sub>4</sub> (AsO <sub>4</sub> ) <sub>3</sub> (SO <sub>4</sub> )(OH).15H <sub>2</sub> O [84] Fe <sub>2</sub> (AsO <sub>4</sub> )(SO <sub>4</sub> )(OH) [85] Fe <sub>2</sub> (AsO <sub>4</sub> )(SO <sub>4</sub> )(OH).nH <sub>2</sub> O [86] Fe <sub>5</sub> (AsO <sub>4</sub> ) <sub>4</sub> (SO <sub>4</sub> )(OH) [87]

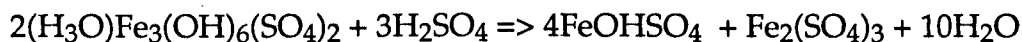
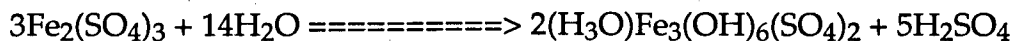
### 2.5.5 Basic iron sulphate

For solutions enriched in iron and sulphate (sulphuric acid) it has been shown [70 - 72] that the iron concentration reaches a constant value in the leach solution due to the hydrolysis of ferric iron at elevated temperatures (200°C) (see **Figure 2.8**). Changing the acidity from low through to high will change the major iron compound precipitated from hematite to basic iron sulphate. It has also been reported that the hydrolysis at elevated temperatures proceeds in one of three ways depending on the amount of free acid in the solution:

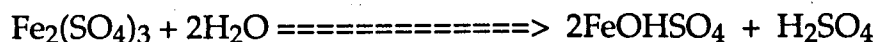
*a/ Low acidity (hematite)*



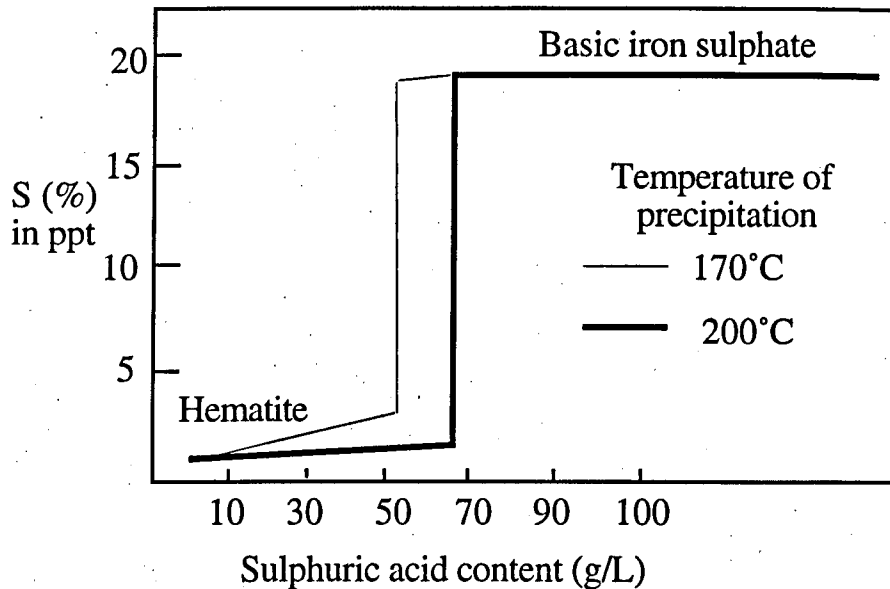
*b/ Moderate acidity (jarosite + basic iron sulphate)*



*c/ High acidity (basic iron sulphate)*







**Figure 2.8** Relationship between sulphur content in precipitates and concentration of free sulphuric acid in the absence of other metal sulphates [71]

### 2.5.6 Apatite minerals

The apatite group has also been studied as potential compounds for arsenic disposal [88], solubility tests on these compounds have shown that they all release arsenic into solution in amounts greater than 5mg/L and are therefore not a suitable option.

### 2.5.7 Arsenical ferrihydrite

Disordered poorly crystallised hydrous iron oxide, called ferrihydrite ( $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ), is often the initial precipitate that results from rapid hydrolysis of Fe(III) solutions. The compound can be formed by either heating Fe(III) solutions to above 80°C which results in the so called 6-line ferrihydrite (brown), or at lower temperatures by raising the pH above pH3 to produce the 2-line variety which is dark brown in appearance (almost X-ray amorphous). The ferrihydrites are so called because the structure of the compound shows 6 or 2 distinct peaks in their X-ray pattern; the 6-line variety having a more crystalline and ordered structure. Ferrihydrite readily transforms to goethite and/or hematite if stored under water especially at higher pH's(>8). This transformation can be blocked by small amounts of

adsorbates such as silicate, phosphate, coprecipitated aluminium and a range of organics [78].

The composition of the low temperature ferrihydrite is assumed to be roughly comparable to that of the high temperature variety which appears to be more structurally ordered. It is however, more reactive as it has a larger specific surface area. Low temperature ferrihydrite which has primary particle sizes in the 80 - 400nm range is an important adsorbent for many heavy elements including arsenic. The colloidal particles can form larger floccules or aggregates of particles under certain conditions. Numerous workers [51, 56, 57, 75] have reported that precipitates with Fe:As ratios greater than 3:1 are highly insoluble with arsenic EPA TCLP solubilities (buffered at pH4.93) as low as 0.05mg/L. Due to the importance of ferrihydrite as a potential adsorbent for arsenic, a significant amount of work has been carried out on this material and its behaviour. Harris and Monette [37] found that even after 3 years the solids with Fe:As greater than 3 still showed very low solubilities. The solubilities of arsenical compounds are strongly influenced by the pH of the contacting solution, with higher solubilities occurring at higher pH's (>8), complete dissolution of the materials also occurring at pH's below 2.

If the metals attached to the ferrihydrite were in the form of a chemical precipitate there would be a three dimensional arrangement of molecular units whereas with adsorption there would be an accumulation of solute species on the surface of a solid phase without the three dimensional molecular arrangement. No evidence exists to support surface precipitation or clustering. Coprecipitation and adsorption appear to be the main mechanisms by which arsenic is removed from solution as iron(III) is hydrolysed. The arsenic is adsorbed onto the iron-rich flocs, the flocs grow and attach to others and precipitate from solution. Interference may occur due to the presence of other anions and cations which may compete for sites on the ferrihydrite [58, 59, 75 - 77].

Numerous workers [60, 76, 89 - 96] have studied the characteristics of the 2-line arsenical ferrihydrites precipitated at ambient temperature mainly because they are analogous to the solid precipitates formed during the neutralisation of metallurgical effluents. The characterisation and solubility

behaviour of the crystalline 6-line variety produced at higher temperatures (>80°C) have not been examined in detail.

Kontopolous [45] reported that ferric arsenates formed at ambient temperatures were more stable than those formed at elevated temperatures, whereas other workers have found that the higher temperature compounds are the most stable [37]. Papassiopi et al [79] studied the effect of temperature of formation and found that in the range 30 - 80°C at pH 3 and 5 the solubility of the compounds increases.

### 2.5.8 Scorodite

Crystalline scorodite has been successfully produced by numerous workers [56, 57, 97 - 103] mostly from mixtures of iron(III) nitrate, chloride or sulphate and As(V) in solution. Scorodite is produced at temperatures above 125 and up to 180°C; the solids are pale green to apple green with characteristic IR and XRD patterns. The patterns of scorodite do show some anomalies which are thought to be related to the incorporation of slightly excess amounts of water or to protonation of the arsenate functional group. Scorodite may structurally accommodate up to 1% sulphate in the lattice with the amount of sulphate incorporation decreasing with increasing pH. Scorodite has been precipitated from solution temperatures as low as 80°C after prolonged periods of nucleation and growth [104 and 105].

A study of iron arsenic compounds formed during acidic pressure oxidation of arsenopyrite by Carageorgos [106] found that scorodite forms at temperatures below 175°C and can form within 15 minutes in some conditions. The scorodite formed in this manner, while having the correct IR and X-ray patterns contained only one water molecule of hydration (i.e.  $\text{FeAsO}_4 \cdot \text{H}_2\text{O}$ ).

$E_h$ -pH and stability diagrams for the Fe-AsO<sub>4</sub>-H<sub>2</sub>O and Fe-AsO<sub>4</sub>-SO<sub>4</sub>-H<sub>2</sub>O systems at 25°C are available from the literature [107]. The low temperature data on aqueous solutions cannot be realistically extrapolated to higher temperatures due to the non-linearity of activity relationships in solution and to the unknown nature of the compounds formed at the higher temperatures. Experimentation must be carried out at elevated temperatures to generate such data on these systems which are likely to be very specific to the solution

compositions used. Some data for this system are available at 170°C [108] and scorodite is considered to precipitate at pH's above 1.

### 2.5.9 Arsenic-rich Fe(III) compounds

A number of studies have been carried out on the Fe-AsO<sub>4</sub>-H<sub>2</sub>O system at low temperatures 25 - 60°C [80]. The characterisation of the compounds was not systematically carried out and relied on bulk analysis. Compounds that do appear to form in numerous experiments include an amorphous scorodite-type (Fe:As 1:1) and an unknown compound with a composition Fe(H<sub>2</sub>AsO<sub>4</sub>)<sub>3</sub>.H<sub>2</sub>O or Fe(H<sub>2</sub>AsO<sub>4</sub>)<sub>3</sub>.5H<sub>2</sub>O [80]. An assortment of other compounds have been tentatively identified although their structures have not been fully determined, and it is possible that these may actually be arsenical ferrihydrite-type compounds rather than chemically distinct compounds.

D'Yvoire and Ronis [81, 82] prepared a compound at 110°C with a formula Fe<sub>1-x</sub>H<sub>3x</sub>AsO<sub>4</sub>.2H<sub>2</sub>O where x = 0 to 0.07. This was similar to the mineral Kaatialaite identified by Raade [83] which had the formula Fe(H<sub>2</sub>AsO<sub>4</sub>)<sub>3</sub>.5H<sub>2</sub>O. The IR spectrum of the synthetic compound showed distinct bands at 2380 and 1225cm<sup>-1</sup> which are characteristic of strong hydrogen bonds and indicate the presence of the As-OH group. The compound was reported to have a 1:3 Fe:As ratio and a unique XRD pattern. The precipitation work by D'Yvoire and Ronis yielded a solid with a slightly lower water content than Kaatialaite. Further precipitation work is required to examine the compounds in the arsenic-rich region of the Fe-AsO<sub>4</sub> system.

### 2.5.10 Phase X

Ugarte and Monhemius [84] identified an unknown arsenate compound formed in a number of high temperature hydrometallurgical precipitates. The compound formed at temperatures above 200°C was shown to resemble the naturally occurring mineral zykaite (Fe<sub>4</sub>(AsO<sub>4</sub>)<sub>3</sub>(SO<sub>4</sub>)(OH). 15H<sub>2</sub>O).

The chemical analysis and characterisation of arsenical residues following pressure oxidation of pure arsenopyrite (FeAsS) have been examined by Carageorgos [87 and 106]. Scorodite compounds were formed at temperatures lower than 175°C which had an approximate formula of FeAsO<sub>4</sub>(SO<sub>4</sub>)<sub>x</sub>. yH<sub>2</sub>O where x = 0.02 - 0.04 and y = 0.8 - 1.0. At temperatures above 200°C a compound identical to those found by Ugarte and Monhemius

[84] and Stefanakis et al. [109] was identified, the formula of the compound approximated to  $\text{Fe}(\text{AsO}_4)_a(\text{SO}_4)_b(\text{OH})_c$  where  $a = 0.8$ ,  $b = 0.04 - 0.06$  and  $c = 0.3 - 1.3$ . Leach tests on these latter compounds found that they were of a low solubility and a suitable compounds for arsenic disposal. This compound would therefore appear to be common to higher temperature precipitation from Fe-AsO<sub>4</sub>-SO<sub>4</sub> solutions. Interestingly the high temperature phases formed above 175°C, after short heating periods contained significant amounts of As(III) (up to 30% of total arsenic) and were thought to represent intermediate arsenopyrite breakdown products [106].

Papassiopi et al. [85] carried out hydrothermal precipitation and also identified the unknown Phase X. The aim of their work was to produce crystalline ferric arsenates under controlled conditions to enable their structures and stoichiometry to be studied and allow their stabilities (solubility) to be individually assessed. The unknown phase precipitated at elevated temperatures was considered to represent a compound whose stoichiometry approximated to  $\text{Fe}_2(\text{AsO}_4)(\text{SO}_4)(\text{OH})$ . The XRD corresponds identically to the compound identified by Ugarte and Monhemius [84] and other workers [84 - 86, 109]. In the work of Passiopi et al. arsenic solutions were heated in a autoclave and when the target temperature was reached iron solution was injected. In this way the precipitation of intermediate products during the temperature increase were avoided. The heating was of the order of 1 hour at a temperature of 180°C. Basic iron sulphate and hydronium jarosite were also tentatively identified in their work.

### 2.5.11 Calcium-arsenate system

A lot of work that has been used to help understand the precipitation of calcium and arsenic from waste solutions has been based on thermodynamic data alone. Using equilibrium solubility the simple boundary conditions at ambient temperature can be established [88]. It is apparent that in any assessment of the calcium arsenate system, the influence of carbon dioxide must also be considered. Nishimura et al. [110, 111] found higher values for the solubilities of the tricalcium arsenate in the presence of CO<sub>2</sub>. This was used by Robins [112] to derive a stability diagram for the system. Robins and Tozawa [112] considered the influence of carbon dioxide on the solubility of tricalcium arsenates and they concluded that atmospheric carbon dioxide enhances the solubility of tricalcium arsenates due to the formation of calcium carbonate. Further work on the calcium arsenate system and calcium-

arsenate-water-carbonate system at 25°C was also done by Nishimura et al. [110, 111]. Similar compounds to those identified by Nelson and Harding [113] were found, however two dicalcium arsenates, and the two pentacalcium arsenates that were identified were found in different hydration states. They found experimentally that the arsenic solubility of the tricalcium arsenate and of the basic tricalcium arsenate is enhanced by CO<sub>2</sub> by approximately five orders of magnitude.

In studies of calcium arsenate compounds [113 - 118] the system was only studied at temperatures below 100°C. In these studies the addition of lime to arsenic acid was made, and on characterisation it was found that a number of the calcium arsenate compounds resembled naturally occurring minerals. Five calcium arsenate compounds were identified these include:-

Monocalcium arsenate	$\text{CaH}_4(\text{AsO}_4)_2$
Dicalcium arsenate	$\text{CaHAsO}_4$
Pentacalcium arsenate	$\text{Ca}_5\text{H}_2(\text{AsO}_4)_4$
Tricalcium arsenate	$\text{Ca}_3(\text{AsO}_4)_2$
Basic calcium arsenate	$(\text{Ca}_3(\text{AsO}_4)_2)_3 \cdot \text{Ca}(\text{OH})_2$

Of all the compounds only dicalcium arsenate and pentacalcium arsenate showed distinct crystalline structures under the microscope. Tricalcium arsenate was mainly amorphous with few crystals and the so-called basic calcium arsenate was almost entirely amorphous. It was noted that during precipitation some variation in the composition of the precipitates occurred and it was suggested that the variation was due to the formation of metastable compounds [114 - 116].

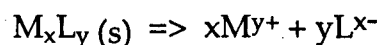
Guerin [117] studied the system at 17°C, 40°C, 60°C and 90°C. He also found the formation of metastable compounds which appear to be more important at low temperatures and pH. Some of the calcium arsenates formed especially those with compositions resembling minerals were characterised by Pierrot [118] using X-ray and thermal analysis.

## 2.6 Solubility of arsenical solids

On dissolution of a solid in an aqueous solution the energy of the system is lowered and the disorder of the system is maximised (i.e. the entropy). It is therefore necessary to supply energy into the system in order to break the lattice bonds before the atoms become soluble. The crystallinity and type of compound (i.e. bond energies) can therefore influence the solubility of the compound [62].

Finely divided solids have a greater apparent solubility than large crystals mainly due to a higher surface area of active solid which is able to equilibrate with a contacting solution (see also Section 2.5.2). As a consequence small crystals are thermodynamically less stable and should recrystallise into larger ones. For particles smaller than 1µm or of specific surface area greater than a few square metres per gram surface energy may become sufficiently large to influence surface properties [62]. For very fine crystalline phases (<100nm) the solubility can vary according to the Gibbs-Thomson effect [105] with large crystallites (>200nm) producing lower solubilities. For this reason the coarse crystalline compounds have much lower apparent solubilities and this is a highly desirable characteristic as the material will release arsenic very slowly to any contacting solution. Kinetics control the rate at which equilibrium is approached and hence the time required for the reactions to go to completion, for these larger crystals it will mean that it will take longer to reach the equilibrium situation.

For sparingly soluble compounds the solubility product is a constant at equilibrium and is independent of the saturation state of the solution. When a solid ( $M_xL_y$ ) dissolves in aqueous solution an equilibrium is established, which is a function of the solubility of the solid and the extent of the dissociation of dissolved species:



The equilibrium constant or solubility product  $K_s$  is defined as:

$$K_s = a_M^x \cdot a_L^y$$

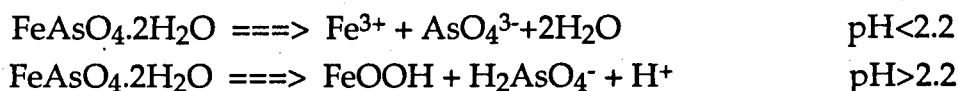
Where  $a$  is the activity of the ion in solution. The activity of water in a solution containing a sparingly soluble substance at equilibrium is equal to

unity as is the activity of the pure solid  $M_xL_y$ . The analytical solubility product is obtained if the activities in the equation are replaced by the concentrations of ions in solution (in molarities). The expression for the solubility product can therefore be given as:  $K_s = [M^{y+}]^x[L^{x-}]^y$ . The analytical solubility product is not constant at a constant pressure and temperature but is dependant on, for example, the composition and ionic strength of the equilibrium solution.

The solubility products of several metal arsenates published by Chukhlansev in 1956 [119 - 121] initially indicated that some arsenates were more insoluble than others. Later workers [122, 123] recognised that these results were only valid within a limited range of pH and cannot be extrapolated to higher pH's [60, 124]. The work does however give an indication of the relative stabilities between the different base metal arsenate compounds.

In amorphous materials the atoms are more disordered and have low amounts of energy binding the atoms together, for this reason the atoms will be more readily released to solution, whereas crystalline species have their atoms tightly bound and this confers more stability to the material which consequently should have a lower solubility.

Scorodite dissolves congruently at  $\text{pH} < 2.2$  and incongruently above 2.2 (see Figure 2.8) the departure from the 1:1 Fe:As ratio in the solution following the solids dissolution at  $\text{pH} > 2.2$  is due to the precipitation of iron as ferrihydrite/goethite ( $\text{FeOOH}$ ) [92, 125] whereas most of the arsenic remains in solution.



Note - the reaction is pH dependent

In the natural environment it is possible for Fe(III) and As(V) to be partially reduced if suitable conditions prevail with the conversion to Fe(II) and As(III) respectively. Such a transformation could also occur in metallurgical waste dumps and promote the prolonged release of arsenic bound onto ferrihydrite. For the long term testing ideally there is the need to know the behaviour of the compounds under simulated environmental conditions such



as redox conditions, prolonged rainfall, influence of CO<sub>2</sub>, variable pH, marine conditions and temperature [104].

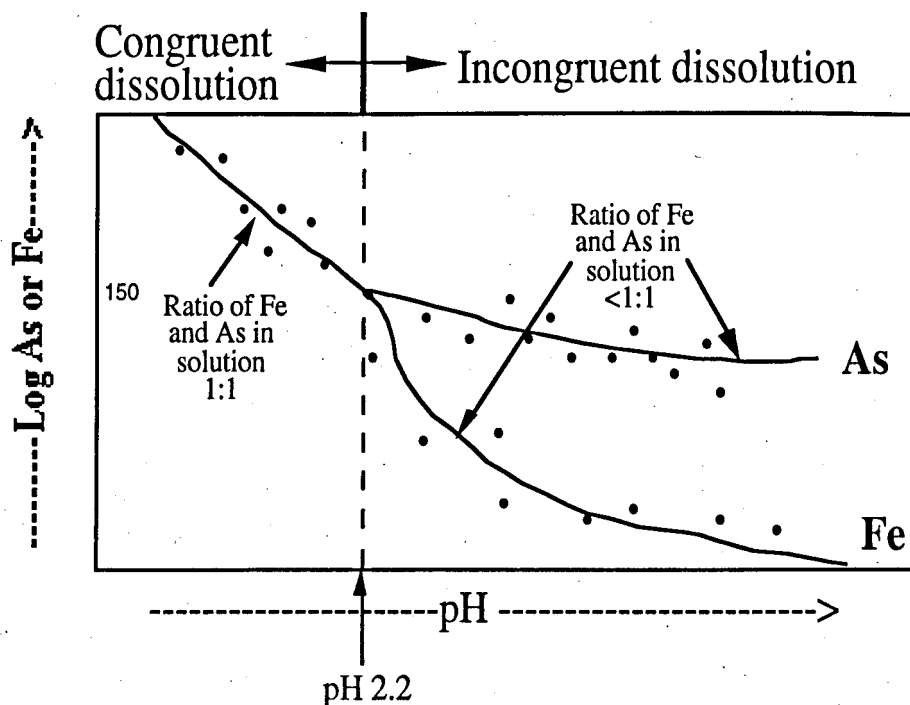


Figure 2.9 Stability regions for ferric arsenate and amorphous ferric hydroxide showing the point of incongruent solubility at about 150mg/L arsenic [76]

## 2.7 Concluding comment

Arsenic is found in numerous metallurgical operations world wide (Appendix 1) and presents a major challenge in determining the most suitable method for its disposal. There has been no consensus on how to dispose of arsenical wastes, however a number of workers have recently advocated crystalline materials as potential options [58, 105].

Due to the lack of basic knowledge on crystalline arsenic phases that can be produced hydrometallurgically it was considered necessary to examine the Fe-Ca-AsO<sub>4</sub>-SO<sub>4</sub> system at elevated temperatures. The conditions of formation of the crystalline compounds, namely scorodite and Phase X were examined. The information has industrial importance and has direct

application in the understanding of hydrothermal processing of arsenical wastes and effluents.

# **Chapter 3**

## **Experimental methods**

## 3.1 Precipitation

### 3.1.1 Test tube scale

As a source of iron and sulphate two different solution types were used: i) mixed ferric nitrate and lithium sulphate solutions, and, ii) ferric sulphate solutions (Table 3.1); these were used at their natural pH (<1). The compositions of the solutions used are given in the ternary diagrams of Figure 3.1. 0.5M solutions of  $\text{Li}_2\text{SO}_4 \cdot 9\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$  and 0.25M solutions of  $\text{As}_2\text{O}_5$  (i.e.  $\text{SO}_4$ , Fe(III) and As(V)) were prepared (see Appendix 2). In the preparation of solutions molar proportions were used throughout the work. 20mL aliquots of the mixtures were prepared and sealed in medium-walled Pyrex glass test tubes. The pH's of the mixed solutions were usually <0.9. The sealed test tubes were placed in a water-filled autoclave and heated at the required temperature for 24hrs, this time period was used throughout the test tube runs to enable the solutions reach equilibrium with the precipitated solids. The autoclave took ~1hr to reach temperature and 4 - 6hrs to cool down to room temperature. The heating temperature was usually in the range 150 to 225°C, i.e. within the range of existing hydrometallurgical operations.

In some tests the solutions were adjusted to pH5 prior to heating. In these test cases lithium hydroxide was used in the adjustment of the pH. Lithium is not a jarosite forming element and mainly remains in solution, as does nitrate. Sodium and calcium hydroxide solutions were avoided as they would precipitate other compounds and complicate the characterisation and solubility testing of the solids.

Other tests were carried out with solutions prepared by using 0.25M solutions of iron(III) sulphate ( $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ ) and  $\text{As}_2\text{O}_5$  (i.e. 0.5M Fe(III) and 0.5M As(V)); such solutions were considered to be closer analogues to hydrometallurgical solutions (see Figure 3.1). For calcium containing solution compositions, calcium nitrate  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  was used as the source of calcium in the individual Ca-Fe- $\text{AsO}_4$  and Ca- $\text{AsO}_4$  hydrothermal systems examined.

Table 3.1 Chemicals and conditions used in the precipitation programme

Described in Chapter	System Examined	Chemicals used
5 5 and 8	pH<1 Fe-AsO <sub>4</sub> -SO <sub>4</sub> pH<1 Fe-AsO <sub>4</sub> -SO <sub>4</sub>	Fe(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O + As <sub>2</sub> O <sub>5</sub> + Li <sub>2</sub> SO <sub>4</sub> .9H <sub>2</sub> O Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .xH <sub>2</sub> O + As <sub>2</sub> O <sub>5</sub>
6 and 7 6 and 7	pH5* Fe-AsO <sub>4</sub> -SO <sub>4</sub> pH5* Fe-AsO <sub>4</sub> -SO <sub>4</sub>	Fe(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O + As <sub>2</sub> O <sub>5</sub> + Li <sub>2</sub> SO <sub>4</sub> .9H <sub>2</sub> O Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .xH <sub>2</sub> O + As <sub>2</sub> O <sub>5</sub>
7	pH* 1 - 12 Ca-AsO <sub>4</sub>	Ca(NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O + As <sub>2</sub> O <sub>5</sub>
7	pH* 1 - 12 Fe-Ca-AsO <sub>4</sub> -SO <sub>4</sub>	Fe(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O + Ca(NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O + As <sub>2</sub> O <sub>5</sub> + Li <sub>2</sub> SO <sub>4</sub> .9H <sub>2</sub> O

\* pH adjustment using LiOH.H<sub>2</sub>O

The sealed tubes were removed from the autoclave and visually examined before opening. The solids were subsequently filtered using Whatman 542 and 0.45µm membrane filters, the mother liquor (i.e. the filtrate) was collected and its pH taken. The solids were usually repulped and washed with excess distilled water to remove any entrained liquor.

The more gelatinous/fine grained, iron-rich samples were centrifuged and the mother liquors decanted. The remaining solids were repulped, washed and the liquid decanted, this process was repeated where necessary. The washed solid was left in the polythene bottles and the remaining water was allowed to evaporate. As an alternative, filtration using 0.45µm membrane filters also proved to be successful on a number of occasions. The samples were air dried in a desiccator and their weights recorded. A minimum of 1.5g of sample was required for characterisation, chemical analysis and solubility testing.

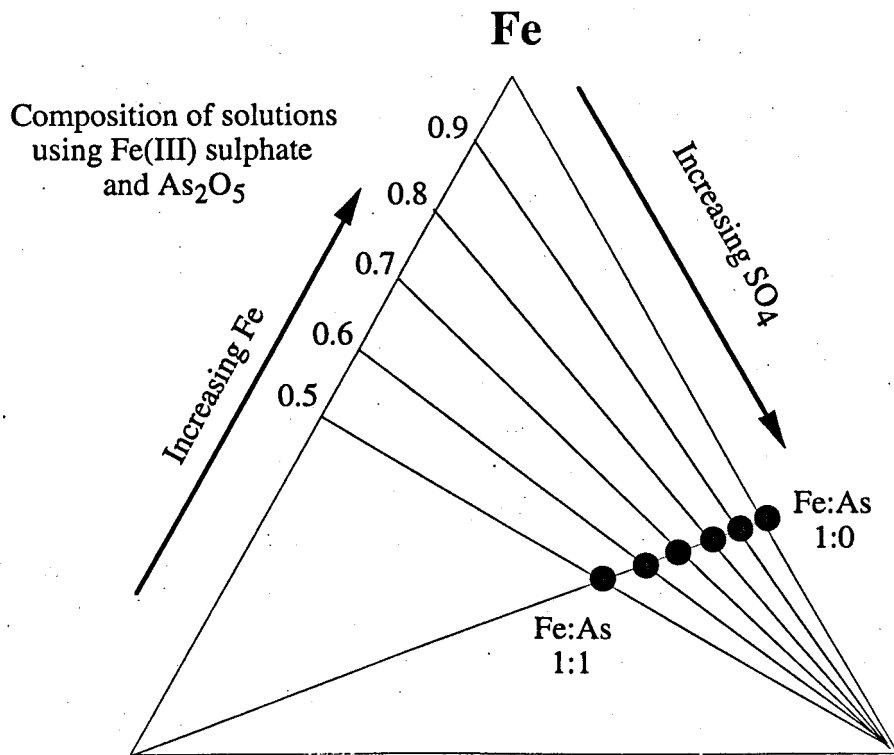
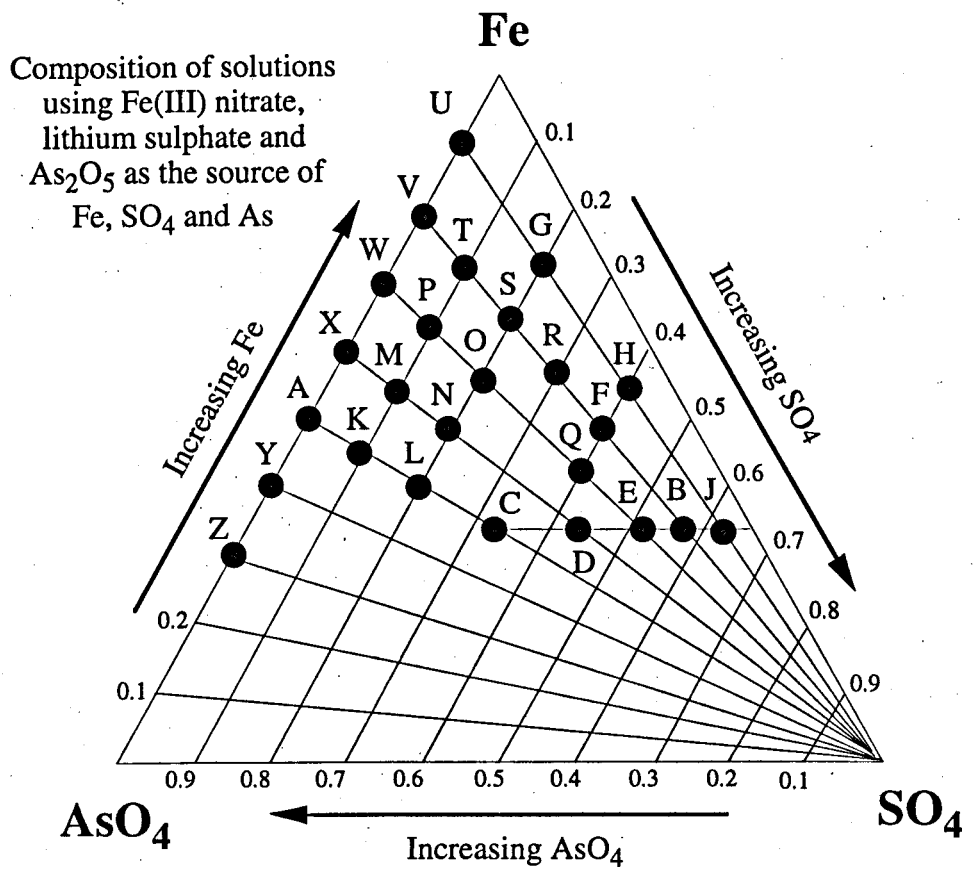
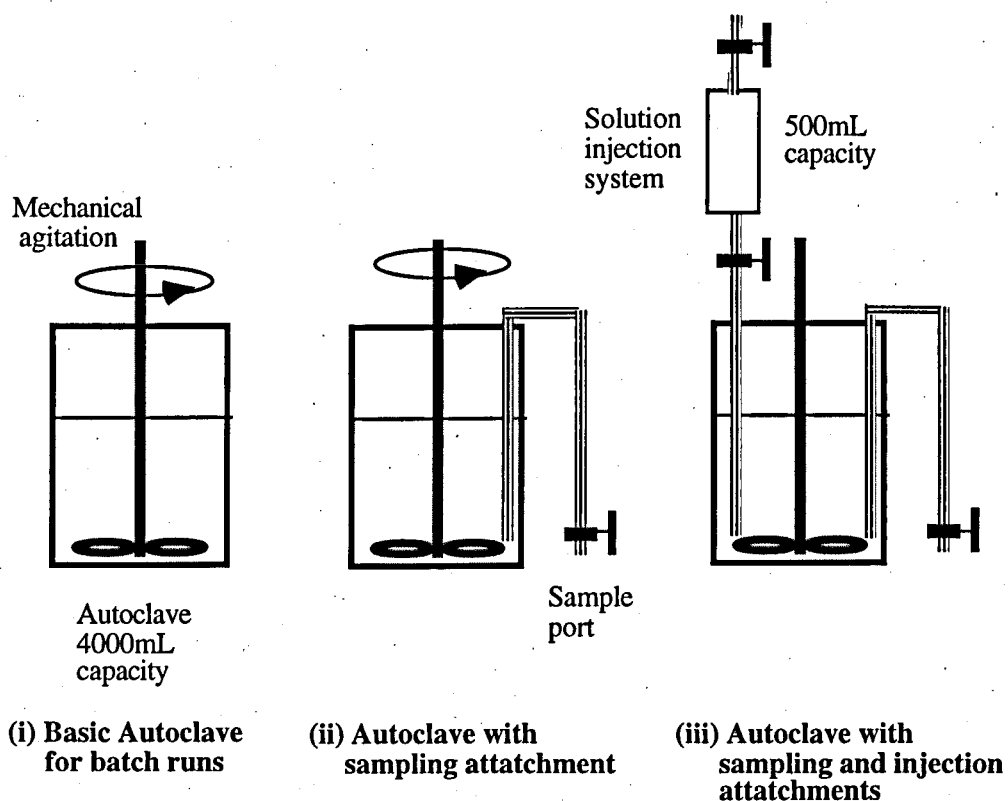


Figure 3.1 Composition of starting solutions used in the hydrothermal precipitation experiments

### 3.1.2 Autoclave experiments

The work was conducted using an oil heated, glass-lined, 4000mL Pfaudler autoclave, which has a maximum operating temperature of 200°C. The temperature of the solution inside the autoclave was monitored by a thermocouple in a thermal well in the body of the autoclave. Initially the autoclave was used in a batch mode and the experiments were carried out for up to 600 minutes (**Figure 3.2(i)**). These tests showed that monitoring the behaviour of the solution inside the autoclave was necessary and a sampling port was installed to sample the solution at defined intervals (**Figure 3.2(ii)**). The solution compositions were monitored during heating and the dip tube was back-flushed with nitrogen before every sample was taken to avoid cross contamination. Finally, to avoid the precipitation of iron-arsenate compounds during the heating-up period, it was necessary to adopt a different practice. Arsenical solutions were heated up in the autoclave to the selected reaction temperature (150 - 190°C), and when the temperature had stabilised, concentrated iron solution (4M) was injected from an auxiliary reservoir pressurised with nitrogen, to start the precipitation reaction (**Figure 3.2(iii)**).

The compositions of the solutions used during the course of these experiments are detailed in **Table 3.2** and **3.3**. The solutions were chosen to evaluate the influence of Fe:As molar ratio and temperature; in the short term experiments arsenic levels were initially 6 - 7g/L. In the longer duration tests (e.g. runs 34 - 44) increased concentrations were required (13g As/L) so that sufficient solids could be sampled during a run for solubility testing. The compositions of the initial arsenical solutions were known from analysis, whereas the concentrated iron solution (4M) injected into the autoclave was only measured volumetrically (see **Table 3.4**).



- Agitation in 4 litre autoclave at 375rpm (6.8cm propeller radius = 2.7m/s tip speed)
- Vessel cooled to below 100°C in 30 mins
- Iron added as Fe(III) sulphate
- Arsenic added as As<sub>2</sub>O<sub>5</sub>
- Arsenic removal based on the analysis of starting and final solutions

Figure 3.2 Development of the Phaudler autoclave during the course of the study

Table 3.2 Arsenical solution compositions used in the initial hydrothermal precipitation runs

Temp	Fe:As 1:2	Fe:As 1:1	Fe:As 2:1	Fe:As 3:1
150	•	•	•	•
170	nd	•	•	•
190	•	•	•	•

nd - not determined



**Table 3.3** Summary of conditions used during the autoclave arsenic precipitation runs

Run No.	Temp °C	Time mins	Fe:As (M)	H <sub>2</sub> SO <sub>4</sub> g/L	Fe inject	From ambient	Remarks
1	150	15	1.5	0	Yes		Examine the influence of time and Fe:As ratio
2	190	120	1.5	0	Yes		
3	150	120	2	0	Yes		
4	185	60	2	0	Yes		
34	190	600	1	0		Yes	Long duration precipitation runs
35	190	600	1.5	0		Yes	
36	190	600	2	0		Yes	
37	150	600	1	0		Yes	
38	150	600	1.5	0		Yes	
39	150	600	2	0		Yes	
40	190	600	1	0	Yes		Long duration precipitation runs
41	190	600	1.5	0	Yes		
42	150	600	1	0	Yes		
43	150	600	1.5	0	Yes		
44	190	600	2	0	Yes		
48	190	400	1	0	Yes		Inject As into Fe soln after 2hrs
49	190	400	1.5	0	Yes		
50	190	400	2	0	Yes		
55	190	400	1.5	0	Yes		Using FeCl <sub>3</sub> as the source of Fe

**Table 3.4** Solutions compositions used in the iron-injection experiments

Target Fe:As (M)	As mg/L in starting solution@	mL of 4M Fe(III) stock solution# injected into 3L of solution	Estimated* Fe mg/L in starting solution
1:2	~6500	38	2800
1:1	~6500	75	5500
2:1	~6500	150	11000
3:1	~6500	225	16500

@ based on analysis at time zero, # 220g/L from analysis

\*based on addition of Fe(III) to 3000mL of solution,

## 3.2 Characterisation

### 3.2.1 Thermal analysis

The precipitated solids were examined using differential thermal analysis (DTA - TG), 15 to 25mg of the solids were placed in quartz crucibles and heated using a Stanton Redcroft STA-700 Differential Thermal Analyser. The conditions used were the same for all the tests - rate of heating: 10°C/minute, temperature range: 20 to 900°C, air flow: 43.5mL/min. The output from the equipment gave valuable quantitative information on the samples with regard to water of hydration and constitutional water, allowing estimations to be made of the solids compositions. Chemical and physical transformations were represented as mass losses at well defined temperatures in the thermogravimetry (% mass loss versus temperature) and peaks in the differential thermal analysis (differential change in temperature with respect to an inert standard ( $\text{Al}_2\text{O}_3$ ) versus temperature).

The thermal analysis (DTA - TG) work yielded important information about the structures of the compounds. Changes such as mass loss, in conjunction with the presence of endothermic and exothermic peaks, were diagnostic for the individual compounds and reflected their structural characteristics. The phases that were identified in this study have distinctive DTA - TG patterns. For the samples containing lattice bound water, or constitutional water, the water was released usually over a limited temperature range.

### 3.2.2 Infrared spectroscopy

Pressed 7mm KBr discs were scanned using a DIR Perkin Elmer PE599 spectrophotometer over the range 200 - 4000 $\text{cm}^{-1}$ . The pellets were routinely prepared by the addition of 2mg of arsenical solid to 250mg of KBr and pressed at 8 tons pressure for one minute. When the solid yielded a poor spectrum the pellet was repeated using higher or lower amounts of solids. In the spectrum the individual peaks correspond to energies of vibrational and rotational transitions within the sample. These peaks are associated with the presence of particular functional groups. The spectrum is dependent on the inter-atomic forces, length of interatomic bonds, structural setting and the co-ordination of the elements. The change in symmetry of a tetrahedral arsenate group may be the result of bonding to a metal ion or through protonation of the arsenate tetrahedral group. Interpretation of the IR spectra can therefore give information on the type of bonding within a unknown solid. For further

details on the standard mineral samples used during the infra-red spectroscopy study see **Appendix 3**.

### **3.2.3 X-ray diffraction analysis**

Precipitated solids were examined by X-ray diffraction (XRD) to assess whether the individual solids were crystalline or amorphous, known or unknown. The equipment used throughout the work was a Phillips 1710 spectrophotometer using Cu K $\alpha$  radiation and with a setting of 40kV and 40mA.

### **3.2.4 Chemical analysis**

Solids, liquors and solubility test solutions were analysed mainly with a Perkin Elmer Model 1100B atomic absorption spectrophotometer. Single element hollow cathode lamps were used with an air-acetylene flame. The detection limits using AA were respectively 1mg/L and 2mg/L for iron and arsenic. For arsenic levels less than 2mg/L an atomic absorption hydride generation method was used with a Varian hydride generator (see **Appendix 4**). The solids were analysed by dissolving 0.1g of solid in 5ml of concentrated HCl and making up to 100mL. Sulphate in the solids was measured by inductively coupled plasma (ICP) spectroscopy.

### **3.2.5 Electron microscopy**

For detailed examination of the morphology of arsenical precipitates, a JOEL JSM T220A scanning electron microscope was used. For the electron diffraction work a JOEL 2000FX Mk1 Transmission electron microscope was used in an attempt to examine the unit cell of the Type-2 compound. An Olympus Optical Microscope was also used for a preliminary examination of the solids and to study the sizes and morphologies of the compounds. With this technique average crystal sizes, shapes and verification of the purity of the compounds were ascertained. This information often helped support previous XRD, IR and DTA - TG findings on the compounds.

### **3.2.6 Particle size determination**

Particle size determinations were made by direct observation using optical microscopy and SEM. A Malvern particle size analyser was also used to measure particle size distributions.

### 3.3 Solubility testing

#### 3.3.1 MARG solubility test

A solubility test procedure developed by the MIRO Arsenic Research Group (MARG) was used to evaluate the relative solubility of the solids. In the MARG static bottle test a solid to liquid ratio of 1:500 (0.1g in 50 mL) and test solutions of pH's 3, 5, 7, 9, 11 were used (early work used pH's 3, 5, 7 and 10). The pH 3 and 5 samples were adjusted with sulphuric acid, and pH's above 7 adjusted with NaOH. A typical testing campaign is given below:-

Mon	Tues	Wed	Thurs	Friday	Sat	Sun	Mon
Prepare sample bottles	Sample Day 1	Sample Day 2		Sample Day 4			Sample Day 7

The sample bottles were typically prepared on a Monday and the first 5 mL solution aliquots removed on the following day from the plastic bottles which were shaken prior to sampling. The pH was readjusted after each sample removal and solutions of the relevant pH added to the individual bottles to make up to the initial starting volume (mass). Four samples were taken from each bottle during the first 7 days, further samples were taken at 28 day intervals thereafter, with the sample bottles being shaken intermittently. Filtrate solutions from the solubility tests were analysed by AA or ICP for arsenic.

#### 3.3.2 US EPA TCLP test

The test solution (extraction fluid) consists of a buffered acetic acid solution (using 5.7 mL of glacial acetic acid and 64.3 mL of 1.0M NaOH made up to 1 litre) at pH 4.93, for a period of 20hrs agitated at 30rpm (end-over-end bottle agitation). Due to the limited amounts of precipitated solids that were available only 0.1 to 0.5g were used in the test procedure, L:S - 20:1 (EPA standard conditions require 100g of solid for the test). After agitation a 5mL aliquot of solution was removed and filtered through a 2.5cm GFF filter. The filtrate was analysed by AA or ICP for arsenic.

The TCLP test is considered to be the industrial standard and is used throughout the minerals and metals industry to evaluate metallurgical wastes. For arsenical solids to pass the test, the filtrates from the test must

have arsenic levels below 5mg As/L otherwise the solids can not be considered as non-toxic industrial waste. The 5mg/L arsenic limit is derived empirically and based on many tests and observations by the US EPA.

The two test procedures only screen the materials with no fundamental intention to define absolute solubility and in this work they were used empirically to establish the relative solubilities of the individual arsenical solids. For realistic solubility testing the solids must be tested appropriately for local conditions taking into consideration climate, permeability etc. To date no long term stability test has been devised. Some general test work relating to the technique is given in **Appendix 5**.

### **3.4 Errors and precision**

A large number of samples were systematically prepared and examined during the course of the work, this practice allowed important trends in composition and solubility to be established. The individual compounds that were tested in detail were usually chosen for their apparent purity following XRD examination, this allowed the solubility of the solids to be realistically interpreted.

Reproducibility of the arsenic solubility tests results was <1mg/L and considered to be acceptable for the purposes of this work. Analytical errors were thought by the investigator to be insignificant next to preparation procedures. For example different cooling rates of the sealed test tubes containing various compositions (air cooled vs slow cooling in an autoclave) allowed different degrees of reequilibration of the iron compounds in solution. Drying of the gelatinous materials also resulted in some degree of error in that water content varied with time and temperature of drying, the Fe:As ratio of the solid products did remain constant.

During the autoclave precipitation experiments the method of injection of Fe(III) solution was adopted to allow direct comparisons between experimental runs to be carried out for the different temperatures and solution compositions. Errors in the measurement of the volume of the 4M iron(III) solution (220g/L) injected into the autoclave were considered to be of significance, especially in the 1:1 and 1:2 Fe:As solution compositions

where the amount of iron solution used was only small (75 and 37.5 mL respectively). Small volumes (<3mL) of the viscous iron solution remaining in the injection bomb would have had an effect on the Fe:As ratio in the starting solution. Errors in the Fe:As ratios of these solutions following injection are considered to be less than 5%.

# **Chapter 4**

## **Characterisation of arsenate compounds**

## 4.1 Introduction

The solids produced during high temperature (150 - 225°C) hydrothermal precipitation were characterised using a combination of XRD, chemical analysis, IR, DTA - TG and SEM. A high percentage of the samples consisted mostly of crystalline components and for this reason XRD was very useful for their characterisation. X-ray examination revealed the presence of a limited number of distinct crystalline phases; these included arsenical ferrihydrite, scorodite, hematite, basic iron sulphate and three unknown crystalline compounds designated as the Type-1, Type-2 and Type-3 compounds (see Appendix 6 and 7). A fourth compound was also identified (Type-4), this is a Ca-Fe arsenate, of lesser importance than Types-1 to -3, and is introduced later in Chapter 7. Each compound has a distinctive X-ray pattern, the minor variations in peak broadening, peak intensity and peak position apparent from sample to sample represent variations in sulphate content, crystallinity or compositional differences.

Interpretation of the IR spectra of the iron arsenate compounds was possible following comparison with those of naturally occurring minerals of known composition and structure. In this chapter some of the IR characteristics of the synthetic arsenate compounds are examined and the contribution to their structural interpretation outlined.

## 4.2 Naturally occurring iron arsenate minerals

A number of naturally occurring iron arsenate minerals exist, as detailed in Table 4.1. Most of these contain water in their structure and are usually formed as a result of weathering of primary sulphide minerals. The arsenate minerals predominate over arsenite compounds and this is reflected in the list of common arsenic containing minerals [15]. For a number of minerals e.g. bukovskyite, sarmientite and zykaite, sulphate and hydroxyl are substituted into the arsenate lattice. The IR spectra for these compounds contain peaks that can be ascribed to the presence of a number of simple structural units including arsenate, sulphate, hydroxyl and water of hydration.



**Table 4.1** List of iron-arsenic containing minerals [15]

Mineral	Formula
Angelellite	$\text{Fe}_4(\text{AsO}_4)_2\text{O}_3$
Arseniosiderite	$\text{CaFe}_9(\text{AsO}_4)_6(\text{OH})_9 \cdot 18\text{H}_2\text{O}$
Arsenical-ferrihydrate	$\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O} + \text{arsenate}$
Bukovskyite	$\text{Fe}_2\text{AsO}_4\text{SO}_4\text{OH} \cdot 7\text{H}_2\text{O}$
Kaatiatite	$\text{Fe}(\text{H}_2\text{AsO}_4)_3 \cdot 5\text{H}_2\text{O}$
Kankite	$\text{FeAsO}_4 \cdot 3.5\text{H}_2\text{O}$
Limonite	mixture of hydrous iron oxides (mainly goethite + ferrihydrate)*
Pharmacosiderite	$(\text{K},\text{H}_3\text{O})\text{Fe}_4(\text{OH})_4(\text{AsO}_4)_3 \cdot 6\text{H}_2\text{O}$
Pitticite	$\text{Fe}_2\text{O}_3\text{As}_2\text{O}_5 \cdot (9-10)\text{H}_2\text{O}$
Sarmientite	$\text{Fe}_2\text{AsO}_4\text{SO}_4\text{OH} \cdot 5\text{H}_2\text{O}$
Scorodite	$\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$
Symplesite (Fe(II))	$\text{Fe}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$
Zykaite	$\text{Fe}_4(\text{AsO}_4)_3\text{SO}_4\text{OH} \cdot 15\text{H}_2\text{O}$

\* material may be arsenical

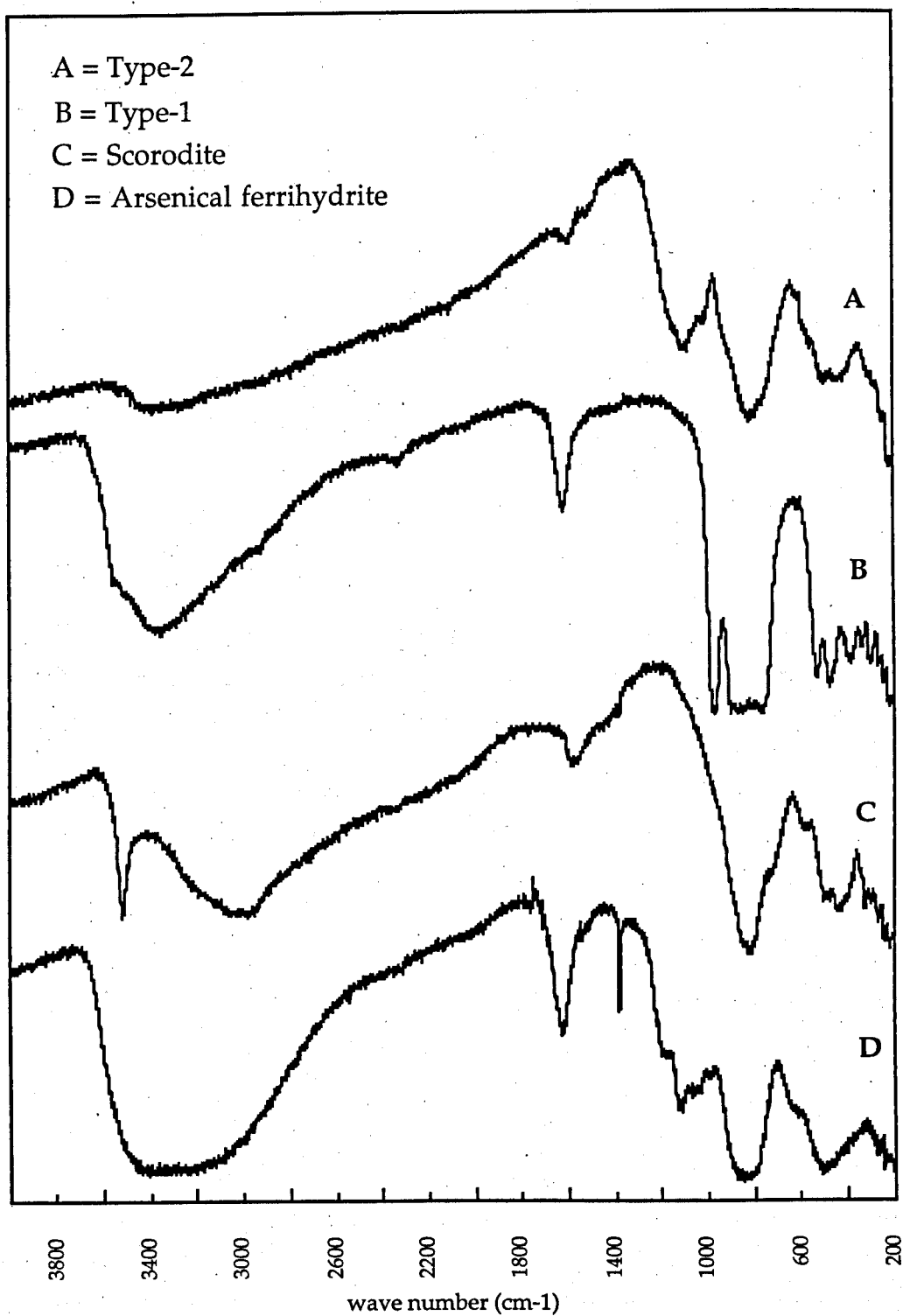
### 4.3 Infrared spectroscopy of synthetic arsenate compounds

Infrared analysis used in conjunction with other analytical techniques can yield important information about the molecular structure and chemical bonding characteristics of both crystalline and amorphous compounds. Following bulk chemical analysis (for determination of the Fe:As ratio, and sulphate content) and DTA - TG (water of hydration and constitutional water) IR enables the structure of the compound to be investigated. The techniques have made an invaluable contribution to the understanding of the iron arsenate solids. In the analysis of a completely unknown arsenic-containing compound, comparisons are made with similar and related compounds. For example scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ) contains chemically bound water and its structure and character can be compared to related mineral species such as kankite ( $\text{FeAsO}_4 \cdot 3.5\text{H}_2\text{O}$ ), and others with known structure and symmetry from which IR relationships can be empirically derived.

The bending mode for the scorodite compounds occurs in the  $1600\text{cm}^{-1}$  region (Figure 4.1). The HO..H peaks of the precipitated samples appear at higher wave numbers (up to  $3600\text{cm}^{-1}$ ) than natural scorodite ( $3508\text{cm}^{-1}$ ), indicating that the interaction between the O-H groups in the lattice is weaker in the former. This suggests an expansion of the unit cell was probably due to the incorporation of hydrogen or sulphate from solution. Furthermore, the peak intensities of the water bands are significantly reduced when compared to natural scorodite mineral.

The bands in the region of  $800$  and  $450\text{cm}^{-1}$  are assigned to the tetrahedral arsenate structure. The tetrahedral symmetry of the arsenate ion gives rise to four vibrational bands, of which only two are infrared active and these appear at  $887$  and  $463\text{cm}^{-1}$ . When distortion of the tetrahedra occurs due to for example co-ordination with metals, or hydrogen, the symmetry of the arsenate group becomes distorted, with a splitting of the bands and the appearance of other bands, which become infrared active, at  $725\text{cm}^{-1}$  and around  $350\text{cm}^{-1}$ . In scorodite, splitting at  $900$ ,  $892$  and  $828\text{cm}^{-1}$  and  $496$ ,  $441$  and  $400\text{cm}^{-1}$  of the asymmetric  $\nu_3$  stretching mode and  $\nu_4$  bending mode respectively are observed. The appearance of the  $\nu_1$  mode at  $728\text{cm}^{-1}$  and  $\nu_2$  at  $350\text{cm}^{-1}$  is also seen. The band at  $594\text{cm}^{-1}$  can be attributed to O-As-O bonding. The symmetric  $\nu_1$  and  $\nu_2$  peaks represent the As-O stretch and the O-As-O bending modes are not strongly IR active and were also examined by Raman spectroscopy, the technique is complimentary and shows that stretching and bending modes were coincident using the two techniques. The bands due to Fe-O bonding occur at wave numbers lower than  $300\text{cm}^{-1}$  but these were not clearly observed in the KBr pellets that were used. Comparison of the spectrum of well-crystallised natural scorodite with the synthetic scoroditic compounds have shown that the spectra of the latter are not as well resolved as that of the mineral. The bands at  $1230$ ,  $1700$  and in the interval  $2700 - 2900\text{cm}^{-1}$  shows that there are acidic As-O-H groups ( $\text{HAsO}_4$ ) in some of the synthetic compounds.

The new compound designated as Type-1 that was identified during the course of this work was characterised by IR peaks around  $3550 - 3000$  and  $1600\text{cm}^{-1}$ , these are similar to scorodite and are assigned to water of crystallisation. It also shows a series of peaks at between  $1000 - 700\text{cm}^{-1}$  and  $530 - 330\text{cm}^{-1}$ . Peaks at  $974$  and  $750\text{cm}^{-1}$  are characteristic of acidic arsenates ( $\text{HAsO}_4$ ) and can be assigned to the As-O-H group (Figure 4.1).



**Figure 4.1** IR spectra of the most important arsenical compounds

The new compound designated as Type-2 has broad arsenate bands at 850 and 520 $\text{cm}^{-1}$  and a weak peak at 1030 $\text{cm}^{-1}$ , which is characteristic of O-H bonding and could indicate the presence of the hydroxyl radical in the structure of this compound. For Type-2, the distinct peaks observed at 1150 and 850 $\text{cm}^{-1}$  and the shape of the spectrum are characteristic (Figure 4.1). However, in a number of cases, the IR spectra of Type-2 samples appeared relatively flat and featureless, with no distinct peaks present, despite the samples showing clear Type-2 XRD patterns. In the examination of high temperature hydrometallurgical residues and in the pressure oxidation of arsenopyrite at elevated temperatures, compounds identical to those of the Type-2 have also been identified by other workers [84 - 87]. However, the actual composition and structure of the material has not been conclusively resolved.

The most conspicuous formula units that are present in the IR spectra of arsenical ferrihydrite include OH,  $\text{SO}_4$ ,  $\text{AsO}_4$  and water of hydration. The  $\nu$  O-H stretching peaks are immediately apparent in most of the spectra (3300 and 1630 $\text{cm}^{-1}$  regions); these can represent either water of hydration, or weakly adsorbed water that has not been completely removed on drying.

As the temperature of precipitation is raised, the solids become more crystalline and hematite becomes an important component. This is most apparent in the 225°C samples that have Fe:As ratios >3. When the IR spectrum of pure hematite is compared to those of the arsenic-rich hematite samples, no major spectral differences can be observed, apart from the appearance of a distinct arsenate band in the 800 $\text{cm}^{-1}$  region. It is unlikely that arsenic is held in the hematite lattice, as distortion of the lattice would be expected to cause significant changes in the hematite spectrum, which are not apparent. When hematite occurs in a mixture, it can be characterised by the overall shape of the spectrum and the distinct peak at 350 $\text{cm}^{-1}$ , due to Fe-O bonding. It is observed that as the arsenic content of the hematitic solids increases, distortion of the hematite peak at 550 $\text{cm}^{-1}$  may occur. This peak starts to broaden and other bands at 800, 1025, and 3200 $\text{cm}^{-1}$  appear, which are more characteristic of arsenate and O-H, respectively. The broadening of the 550 $\text{cm}^{-1}$  peak may be due to a change in the crystal lattice, or to a superimposition of the arsenate band, or both. The main band at 350 $\text{cm}^{-1}$  is also observed to decrease as the arsenic content increases. Ferrihydrite is also still likely to be present in the iron-rich solids onto which the arsenic will be adsorbed.

The presence of sulphate functional groups are shown by the presence of distinctive peaks at 1100, 1150 and 1200 $\text{cm}^{-1}$ . The sulphate peak intensities in IR spectra are usually found to be proportional to the sulphate content and can be used in the absence of analytical data as a rough guide to the amount of sulphate in the compounds. From analytical data [Appendix 7] the sulphate levels in the solids precipitated at pH5 are relatively low (< 0.8% sulphate) throughout and this is supported by the absence of sulphate peaks in their IR spectra.

The IR spectrum of the arsenate functional group commonly has a characteristic shape and peak position, as in scorodite and in the arsenical ferrihydrite. However, the new compound designated as Type-3 has a very broad arsenate peak in the 800 $\text{cm}^{-1}$  region. The broadening is mainly due to the development of two distinct peaks at 1020 $\text{cm}^{-1}$  and 740 $\text{cm}^{-1}$  adjacent to the 800 $\text{cm}^{-1}$  peak of arsenate. Both of these distinct peaks are assigned to O-H, in the HAsO<sub>4</sub> functional group which is present in high levels in the Type-3 compound (see Section 4.4.4 for spectrum of the Type-3 compound).

## 4.4 Synthetic arsenate compounds

### 4.4.1 Scorodite

Precipitation experiments at pH<1 in the Fe-AsO<sub>4</sub>-SO<sub>4</sub> system (Chapter 5) commonly produced a pure scorodite [126], this has a distinct apple green colour, which may be discoloured to a bluish-tinge when other impurities are present. The compound is usually restricted to the solids derived from solutions with initial Fe:As molar ratio's of >1:1 and is usually formed at temperatures above 125°C. Optical microscopy (transmitted mode) was used for rapid evaluation of the crystallite size and shape, usually scorodite particles were crystalline and less than 20 $\mu\text{m}$  in size. SEM photomicrographs (Figure 4.2) show the scorodite to vary from discrete grains to spherulitic aggregates.

Bulk chemical analysis of the scorodite precipitates showed that they usually had an Fe:As molar ratio of 1, and sulphate levels usually less than 5% (see Table 4.2 and Appendix 7). The thermal analysis (DTA - TG) work showed that for scorodite (FeAsO<sub>4</sub>.2H<sub>2</sub>O) the lattice water is released at 210 - 230°C, (~220°C) (Figure 4.3) and constitutes usually less than 17%. The scorodite

compounds usually had the typical scorodite XRD pattern with only slight variation in X-ray peak intensities which were not considered significant.

The orthorhombic crystal structure of scorodite has been extensively studied and consists of  $\text{AsO}_4$  tetrahedra and  $\text{FeO}_4(\text{OH}_2)_2$  octahedra connected alternatively at vertices [127]. None of the water participates in this linkage. The structure has wide channels and during its nucleation and growth prolonged exposure to sulphate in solution may lead to sulphate incorporation in the structure.

The precipitated scorodite-type compounds show infrared spectra which resemble natural scorodite. They show two distinctive peaks in the region of  $3600 - 3000\text{cm}^{-1}$ , one sharp "spike" at about  $3500\text{cm}^{-1}$  and a broad peak centred at  $3000\text{cm}^{-1}$ . These bands have been assigned to the stretching mode of the HO..H bonding of water of crystallisation and represent the two crystallographic environments that water occupies in the structure (Figure 4.1).

**Table 4.2** Composition of a typical synthetic scorodite

Sample*	Fe (%)	AsO <sub>4</sub> (%)	SO <sub>4</sub> (%)	H <sub>2</sub> O (%)	Total (%)	Fe:As (M)
W175	24.37	57.51	0.0	17.70	99.6	1.1
FeAsO <sub>4</sub> ·2H <sub>2</sub> O (theoretical)	24.2	60.2	0	15.6	100	1

\* (for further scorodite analyses see Appendix 8)

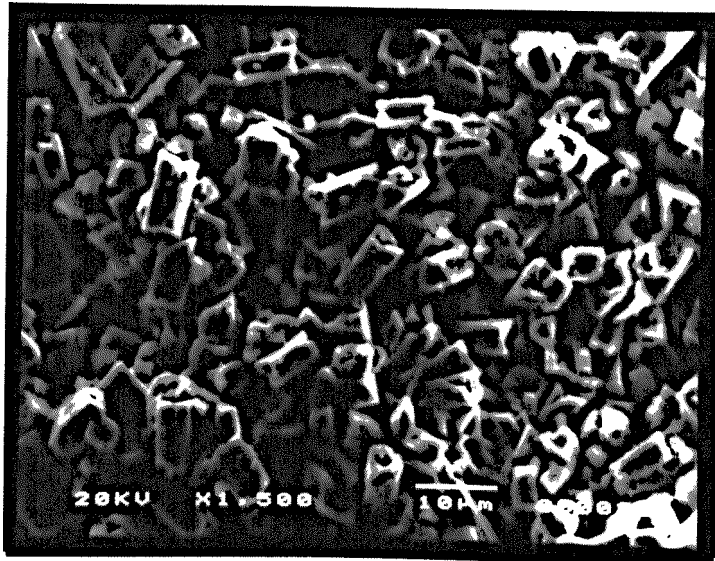


Figure 4.2a SEM photomicrograph showing scorodite crystals



Figure 4.2b SEM photomicrograph showing spherulitic aggregates of scorodite

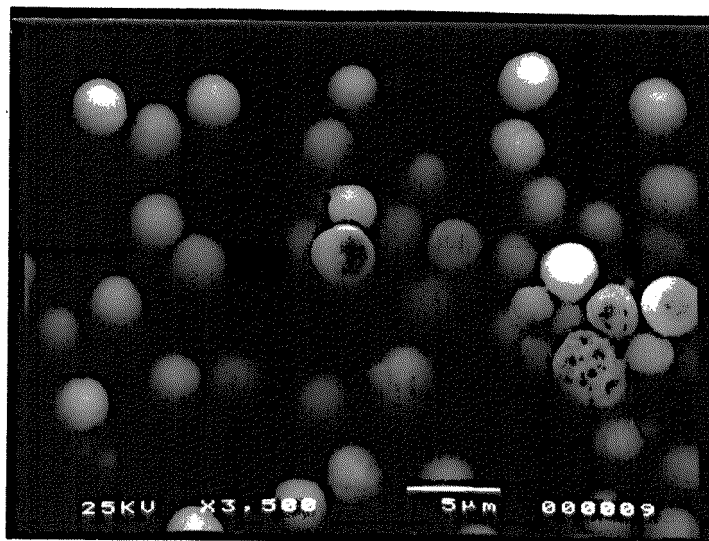
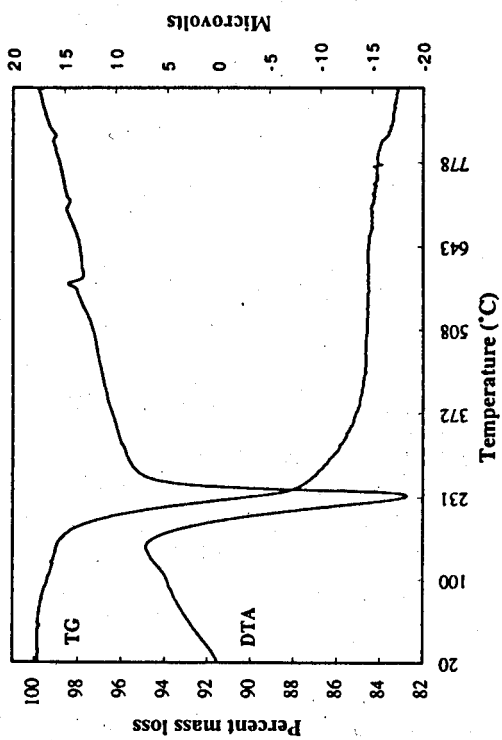
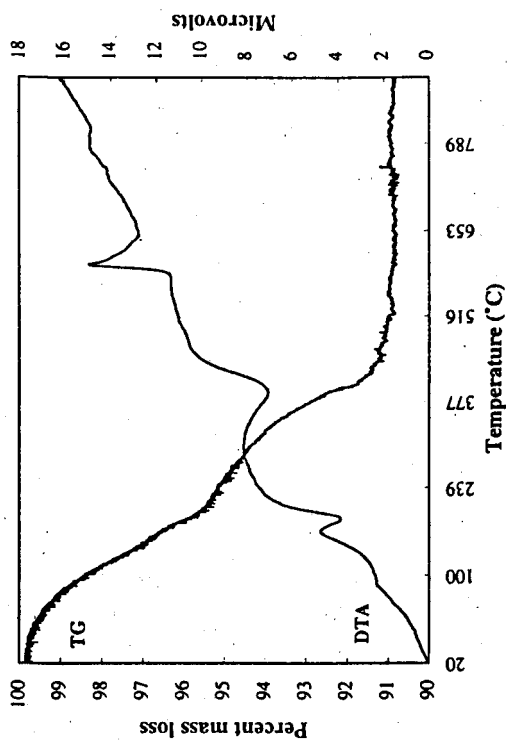


Figure 4.2c SEM photomicrograph showing the morphology of the Type-1 compound

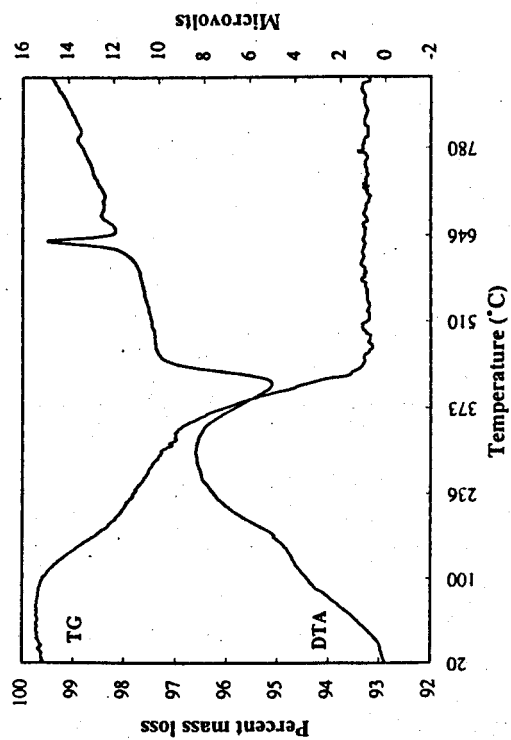
a) Scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ )



b) Type-1 (hydrated  $\text{Fe}_2(\text{HAsO}_4)_3 \cdot x\text{H}_2\text{O}$ )



c) Type-1 (unhydrated -  $\text{Fe}_2(\text{HAsO}_4)_3 \cdot x\text{H}_2\text{O}$ )



d) Type-2 ( $\text{Fe}_4(\text{AsO}_4)_3(\text{SO}_4)x(\text{OH})_y$ )

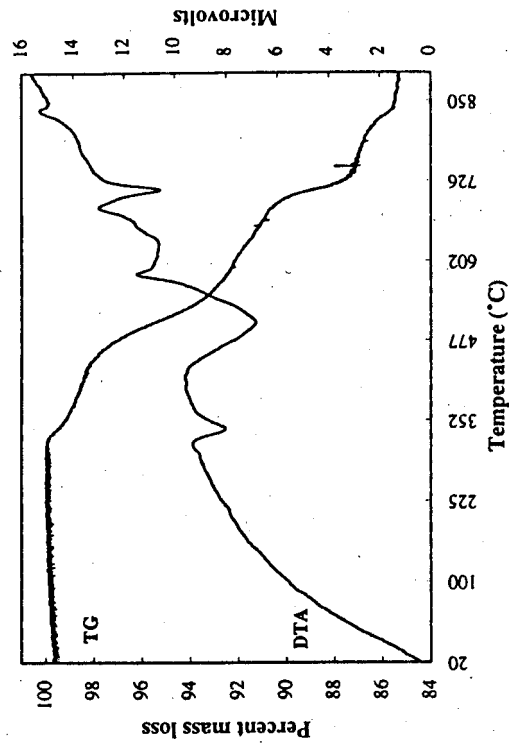


Fig 4.3 DTA-TG of the important arsenical compounds.



#### 4.4.2 Type-1 compound

In the solids derived from precipitation experiments at  $\text{pH} < 1$  in the  $\text{Fe-AsO}_4\text{-SO}_4$  system (Chapter 5) a distinctive white powder is formed. This compound is usually restricted to the solids derived from the arsenic-rich solutions, with Fe:As compositions of  $< 1:1$  and is usually formed at temperatures above  $125^\circ\text{C}$ . This has been designated the Type-1 material and is generally composed of very fine grained aggregates ( $< 2\mu\text{m}$ ). Transmission electron microscopy (TEM) was used to examine the Type-1 compound and showed that the spherical aggregates were made up of smaller equidimensional crystallites  $< 0.1\mu\text{m}$  (see Figure 4.4). The almost amorphous nature of the material would explain the poor XRD patterns obtained from these compounds.

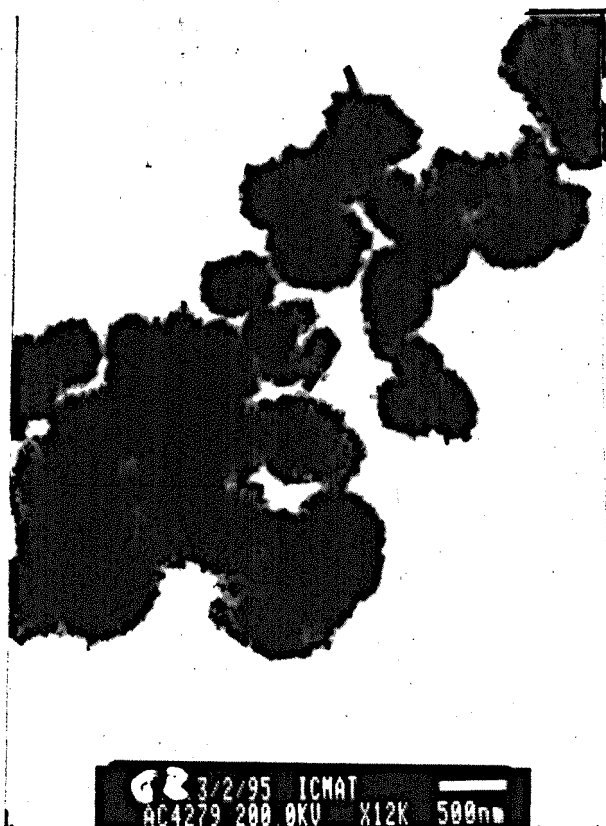
During thermal analysis the Type-1 compound has a mass loss at  $\sim 420^\circ\text{C}$  (Figure 4.3). Samples of Type-1 formed at lower temperatures ( $< 200^\circ\text{C}$ ) showed peaks at both  $220^\circ\text{C}$  and  $420^\circ\text{C}$ ; these represent the Type-1 compound that contains constitutional water from the acid salt and variable amounts of water of hydration. All such Type-1 compounds, independent of their hydration state, yielded identifiable X-ray patterns and usually had Fe:As ratios of less than 1 (Table 4.3 and Appendix 8).

Table 4.3 Composition of a typical Type-1 compound

Sample	Fe (%)	AsO <sub>4</sub> (%)	SO <sub>4</sub> (%)	H <sub>2</sub> O (%)	Total (%)	Fe:As (M)
Y200	27.8	75.64	0.00	1.5	104.94	0.91

\* (for further analyses of Type-1 see Appendix 8)

From consideration of the available information on the compound and the Fe:As ratio of 0.7 - 0.9, it is considered that the compound has a composition which approaches  $\text{Fe}_2(\text{HAsO}_4)_3 \cdot x\text{H}_2\text{O}$ , where  $x$  is usually less than 4. The crystal structure may consist of  $\text{AsO}_3(\text{OH})$  tetrahedra and  $\text{FeO}_4(\text{OH}_2)_2$  octahedra connected at oxygens atoms provided by the  $\text{AsO}_3(\text{OH})$  tetrahedra. The presence of the As-O-H bonding could give rise to the distinct IR pattern in the  $800 - 1000\text{cm}^{-1}$  region. None of the water (when present) participates in this linkage, the similarity in the IR patterns in the water region ( $\sim 3300\text{cm}^{-1}$ ) of the Type-1 and scorodite structure is apparent and is due to a similar structural arrangement of the water molecules.



**Figure 4.4a - c**  
 TEM photomicrographs showing the fine structure of the Type-1 spherules. The small spherules (see also Figure 4.2c) are themselves composed of ultra-fine crystals ( $<0.01\mu\text{m}$ ) from which single crystal diffraction patterns are difficult to obtain.  
 (100nm =  $0.10\mu\text{m}$ )

#### 4.4.3 Type-2 compound

The Type-2 compound is sandy-brown in colour, crystalline in appearance and is produced from hydrothermal precipitations at  $\text{pH} < 1$  in the  $\text{Fe-AsO}_4\text{-SO}_4$  system (Chapter 5). The compound is usually found in solids derived from solutions with Fe:As compositions greater than 1:1 and is usually formed at temperatures above  $175^\circ\text{C}$ . When the Fe:As ratios of the solutions are increased well above 1:1, the colour of the precipitates progressively changes towards dark brown, reflecting the increased amounts of hematite or ferrihydrite in the solids. Crystalline Type-2 grains were 5 -  $50\mu\text{m}$  in size; SEM photomicrographs show the nature of the compound (Figure 4.5). The compound varies in composition but it is apparent from bulk chemical analysis on a number of solids that the Fe:As ratio is relatively constant at around 1.5:1 with some variation in sulphate and water content (see Table 4.4).

Table 4.4 Composition of a typical Type-2 compound

Sample*	Fe (%)	AsO <sub>4</sub> (%)	SO <sub>4</sub> (%)	H <sub>2</sub> O (%)	Fe:As (M)
N225	30.51	50.32	9.69	0.0	1.51

\* Microprobe analysis of individual grains ( $50\mu\text{m}$ ) by the Natural History Museum showed comparable results Fe - 31.8%, AsO<sub>4</sub> - 52.6%, SO<sub>4</sub> - 6.3%.

\* (for further analyses of Type-2 see Appendix 8)

Some Type-2 compounds contain constitutional water which is released at  $\sim 500^\circ\text{C}$ . Other DTA peaks are found at a temperature of  $710^\circ\text{C}$  and are due to the release of a sulphur species and the mass loss reflects the amount of sulphate present in the structure of the compound (Figure 4.3). During heating it is possible that sulphate is removed from the structure at a number of distinct stages, notably at  $500$  and  $710^\circ\text{C}$  as sulphur dioxide. From the available chemical and structural information the compound has an idealised composition of  $\text{Fe}_3(\text{AsO}_4)_2(\text{OH})(\text{SO}_4)$  or  $\text{Fe}_3(\text{AsO}_4)_{0.33(9-x-2y)}(\text{OH})_x(\text{SO}_4)_y$  (where  $x \leq 1$  and  $y \leq 1$ ), this latter formula takes into account the compositional variations.



Figure 4.5a SEM photomicrograph showing the nature of the Type-2 compound

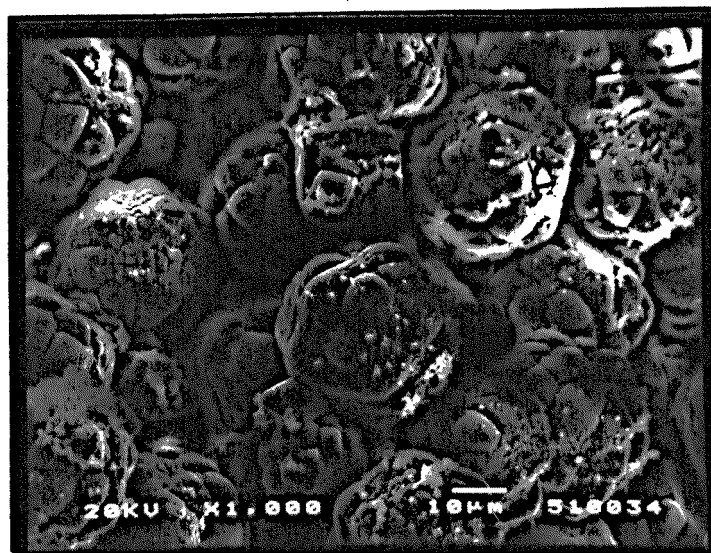


Figure 4.5b SEM photomicrograph showing the nature of the Type-2 compound



Figure 4.5c SEM photomicrograph showing the nature of the Type-2 compound

Transmission electron microscopy (TEM) was used to examine the Type-2 compound, which was found up to 50µm in size and usually consisted of intertwined crystals. Cross sections of the 50µm grains showed that they are composed of crystallites radiating from a central core. For this reason it makes them unsuitable for single crystal X-ray examination. When pulverised to less than 5µm, single untwinned fragments of crystals could be isolated by TEM from which clear electron diffraction patterns could be produced. The data derived from electron diffraction (TEM) and X-ray diffraction data were compared (Table 4.5). The d-spacings using the two methods were similar and allowed the patterns to be partially indexed (hkl). Interpretation of the TEM crystallographic data and X-ray diffraction data indicates monoclinic or triclinic symmetry. This is different to scorodite and basic iron sulphate, which are both considered to be orthorhombic in structure.

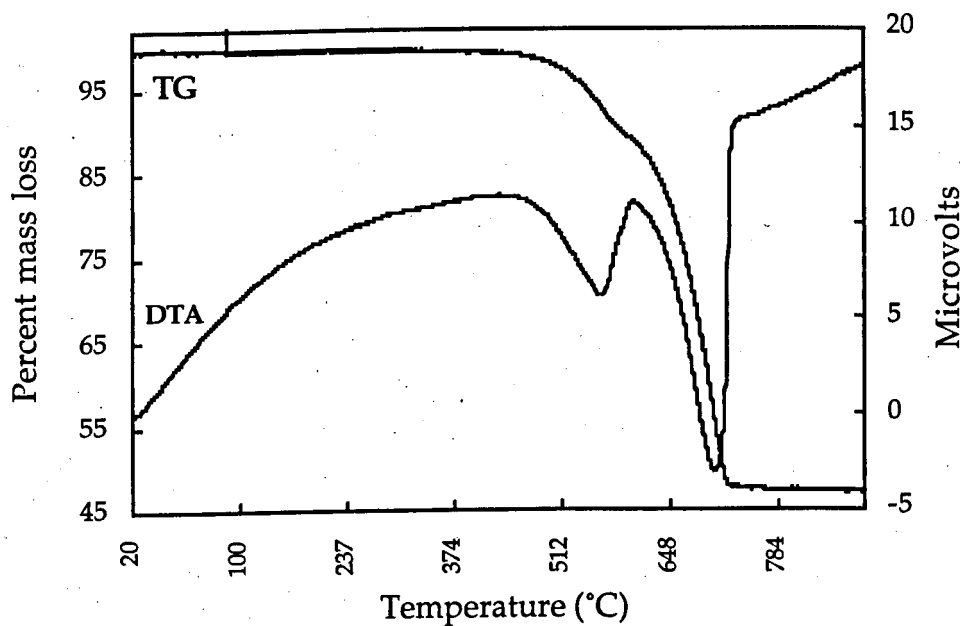
**Table 4.5** Composition of a typical basic iron sulphate

Sample	Fe (%)	SO <sub>4</sub> (%)	H <sub>2</sub> O* (%)
Iron sulphate soln. 28g Fe/L	57	31	12

\* by difference (100 - Fe - SO<sub>4</sub>)

A basic iron sulphate (Fe(OH)SO<sub>4</sub>) is formed under similar conditions to the Type-2 compound (Table 4.5). This has very characteristic IR and DTA - TG pattern (Figure 4.6). The simple IR spectrum shows the presence of sulphate and hydroxyl structural units. From the literature [72] structural studies of similar basic iron sulphate polymorphs have shown that each iron atom in the structure is octahedrally coordinated with two hydroxyl groups and four sulphate oxygens so that each iron atom is octahedrally surrounded by six oxygen atoms. Two of these oxygens are shared between two octahedra. The remaining four oxygens belong to sulphate. The four H atoms in the unit cell are probably associated with the bridging oxygens. The metals are therefore joined by single hydroxyl bridges. Despite the apparently simple formula for the basic iron sulphate (Fe(OH)(SO<sub>4</sub>)) and its documentation in a number of papers, the crystalline polymorph is not referred to in the X-ray JCPDS file index [72, 128]. However the atomic structure of this unknown basic iron sulphate is likely to be similar to the known polymorph.

DTA - TG pattern of the basic iron sulphate



IR spectrum of the basic iron sulphate compound

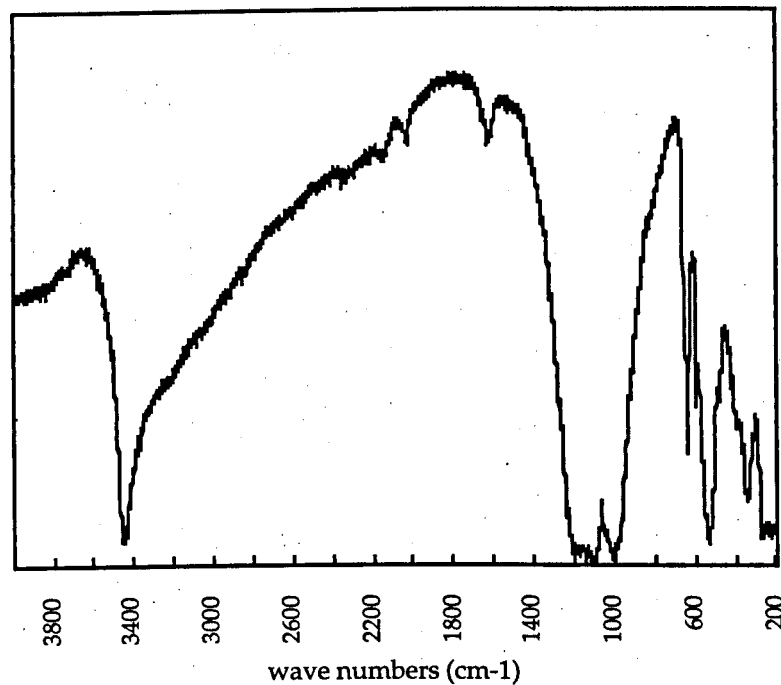
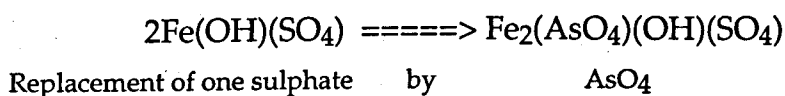


Figure 4.6 Thermal data and IR spectrum of the basic iron sulphate

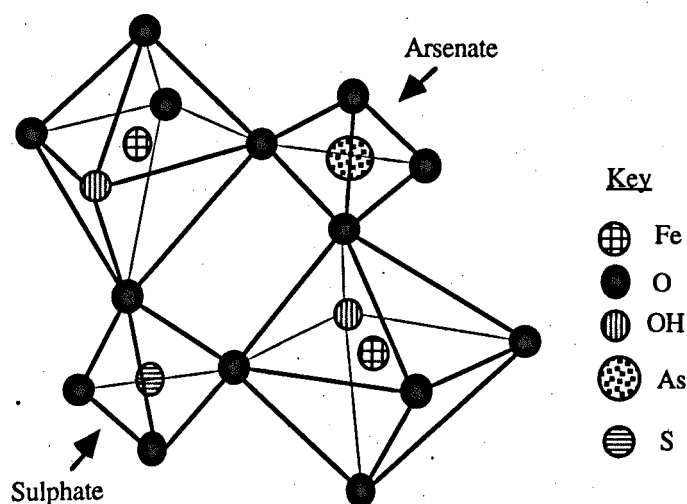
It was found by experimentation that a sulphate free Type-2 compound can exist and therefore the Type-2 compounds do not always contain sulphate; any deficiency in charge would be balanced by excess hydroxyl or arsenate in the structure. Generally it has been found that the Fe:As ratio in the compound is ~3:2 and it contains variable amounts of sulphate and hydroxyl. However, the simplified formula for the Type-2 compound given by Papassiopi et al [85] of  $\text{Fe}_2(\text{AsO}_4)(\text{OH})(\text{SO}_4)$  is used here as a starting point in the structural investigation of this new arsenate compound.

The Type-2 compound is precipitated under identical conditions as the basic iron sulphate and it is conceivable that only the substitution of sulphate by arsenate is required to achieve this new structure. The suggested structure of the compound is also only a slight deviation from the scorodite structure with incorporation of sulphate and hydroxyl. The actual compositional variation and structure requires further verification and investigation.



On an atomic scale if the structure of the Type-2 compound is isostructural with basic iron sulphate [72] each Fe will be octahedrally coordinated with two sulphate and two arsenate oxygen atoms, the remaining oxygens being contributed by hydroxyl groups (see **Figure 4.7**). The metal atoms will be joined by oxygen or single hydroxyl units.

While the structure of the basic iron sulphate and scorodite is orthorhombic the different sizes of the arsenate and sulphate tetrahedral groups would distort such a structure and form possibly the monoclinic or triclinic structure as indicated by crystallographic work (TEM and XRD) (**Table 4.6**).



**Figure 4.7** Suggested structure of the Type-2 compound (viewed along the b-axis)

#### 4.4.4 Type-3 compound

In the solids derived from precipitation experiments at pH5 in the Fe-AsO<sub>4</sub>-SO<sub>4</sub> system (Chapter 6), the Type-2 structure was not observed and Type-1 was only present as a subordinate phase (<10%). However, a third unknown compound was observed and designated the Type-3 compound (see Table 4.7). This compound is usually restricted to the solids derived from the arsenic-rich solutions, with Fe:As compositions of <2:1 and is usually formed at temperatures above 125°C. One of the most diagnostic features of the compound comes from its IR spectrum (Figure 4.8). The presence of OH in the structure of the Type-3 compound creates a distinct spike at 3300cm<sup>-1</sup> and an equally distinct peak at 1020cm<sup>-1</sup>. This may be due to the presence of a hydroxyl unit in the HAsO<sub>4</sub> functional group rather than to a separate hydroxyl grouping (Figure 4.9). Comparison of its IR spectrum with that of the Type-1 compound, which contains the HAsO<sub>4</sub> unit, shows similar spectral characteristics yet is laterally displaced (Figure 4.10). Nevertheless the IR spectra of the Types-1 and -3 compounds are similar in the 800cm<sup>-1</sup> region and they may have similar structural characteristics. Thermal data indicates a consistent weight loss of around 4% at around 450 - 550°C which is consistent with loss of constitutional water from a HAsO<sub>4</sub> structural unit in the Type-3 structure (Figure 4.7). The compound has distinct XRD, IR and thermal signatures and has a formula considered to be Fe<sub>2</sub>(AsO<sub>4</sub>)<sub>0.33(6-2x)</sub>(HAsO<sub>4</sub>)<sub>x</sub> (Fe:As ~1:1 and where x<1) (Appendix 8).



Table 4.6 Electron and X-ray diffraction data for the Type-2 compound

Diameter from TEM photo's (cm)	d-spacing from TEM•	d-spacing from XRD	Intensity relative values	hkl
0.80	6.30	6.36	<2	001
1.03	4.89	4.89	5	010
1.50	3.36	3.35	100	100
1.55	3.26	3.26	64	002
1.90	2.65	2.63	19	210
2.06	2.45	2.44	<2	020
2.10	2.40	2.35	6	022
2.15	2.34	2.32	20	not indexed
2.35	2.14	2.08	15	122
2.40	2.10	2.05	9	003
2.65	1.90	1.89	9	not indexed
2.70	1.87	1.87	<2	not indexed
2.85	1.77	1.76	2	222
3.00	1.68	1.69	8	004/200
3.09	1.63	1.64	<2	030
3.14	1.61	1.63	11	not indexed
3.20	1.58	1.62	28	004
3.40	1.48	1.47	9	330
3.45	1.46	1.45	3	322
3.60	1.40	1.39	<2	005/420
4.12	1.22			not indexed
4.20	1.20			006
4.50	1.12			600
4.70	1.07			not indexed
4.80	1.05			007

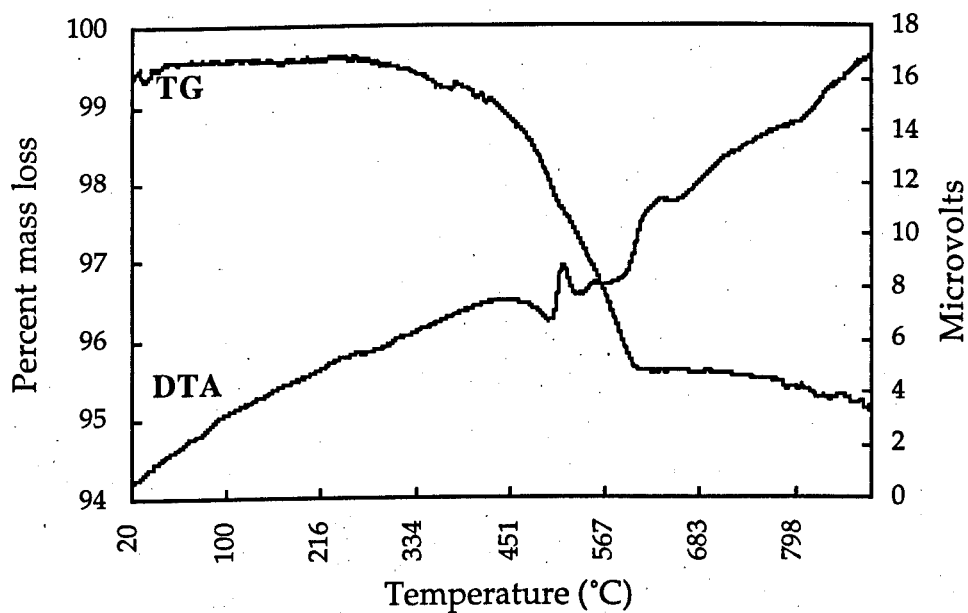
- using the relationship  $d \cdot \text{diameter} = 2\lambda l$  to solve for the d-spacing (d), ( $2\lambda l = 5.04$  at 100cm camera distance using the Joel 2200 TEM)

Table 4.7 Composition of a typical Type-3 compound

Sample	Fe (%)	AsO <sub>4</sub> (%)	SO <sub>4</sub> (%)	H <sub>2</sub> O (%)	Total (%)	Fe:As (M)
C225	27.8	69.9	<0.01	5.0	102.7	0.99

\* (for further analyses see Appendix 8)

DTA - TG pattern of the Type-3 compound



IR spectrum of the Type-3 compound

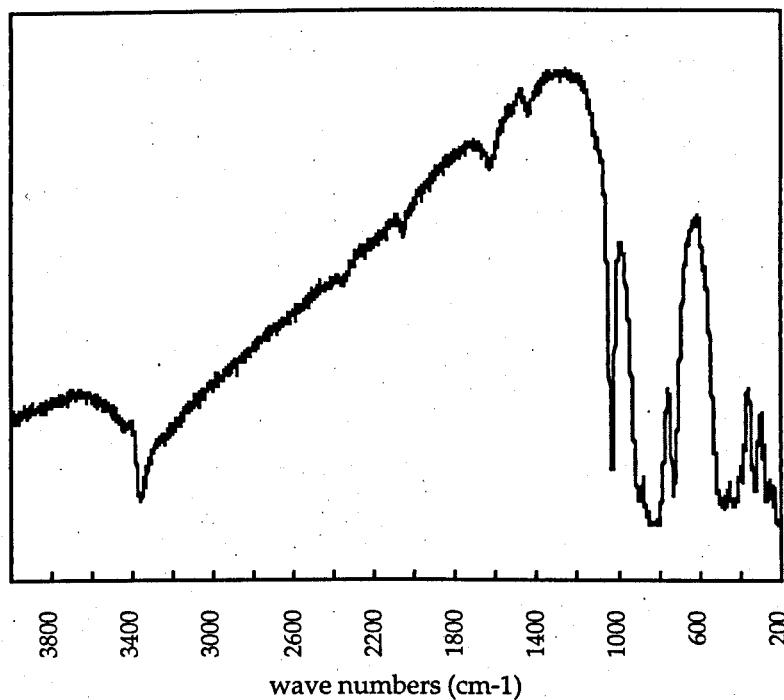
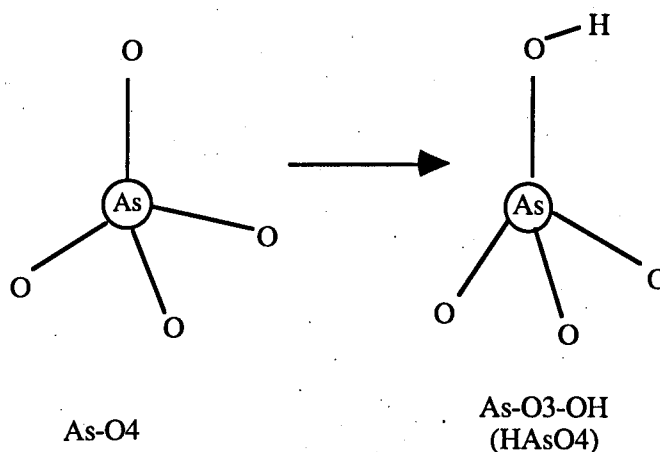


Figure 4.8 Thermal data and IR spectrum of the Type-3 compound



**Figure 4.9** Protonation of the arsenate tetrahedral group

Through a study of the IR spectra of a number of naturally occurring minerals and synthetic products, the basic structural units in the Type-3 compound can be identified by simple comparison. The crystal structure is likely to consist of either  $\text{AsO}_4$  or  $\text{AsO}_3(\text{OH})$  tetrahedra and  $\text{FeO}_6(\text{OH})_2$  octahedral groups, possibly connected at OH groups provided by the  $\text{AsO}_3(\text{OH})$  tetrahedra. No water exists in the structure, the water has been replaced by OH. The IR spectral features for the Type-1 and Type-3 (see Figure 4.10) are very similar in the  $1000 - 800\text{cm}^{-1}$  region which suggests similar structures. In the Type-1 compound it is suggested that the hydroxyl from the  $\text{HAsO}_4$  unit does not participate in the bonding, while in the Type-3 it does and the OH acts as the bridge between octahedral and tetrahedral groups. This would explain the difference between the compounds especially with regard to the presence of the distinct OH peak in the IR spectrum of the Type-3. This suggests that hydroxyl may be supplying oxygens for bridging and participating in the tetrahedral-octahedral linkage.

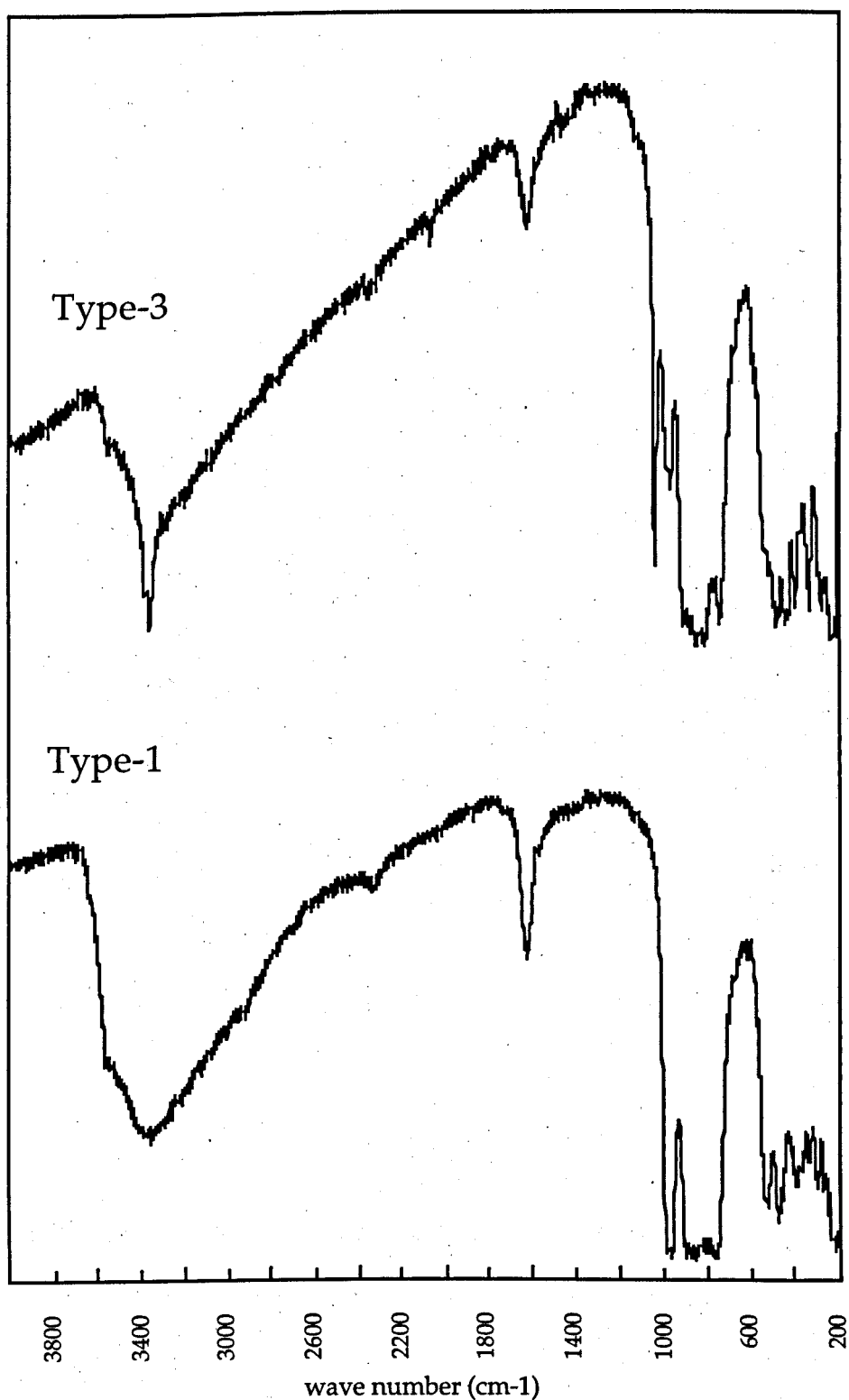


Figure 4.10 Comparison between the IR spectra of the Type-1 and the Type-3 compounds

#### 4.4.5 Arsenical ferrihydrite

Hematite and ferrihydrite when present were found finely intergrown with each other forming a translucent orange-red product. These compounds were formed from iron-rich solution compositions (Fe:As >3:1) and hematite was preferentially formed by the conversion of ferrihydrite at higher temperatures >175°C. Mixtures of amorphous and crystalline materials were occasionally present and required a combination of techniques for their full identification.

Ferrihydrite (6-line variety) was present in samples precipitated at 200 and 225°C. X-ray diffraction on solids derived from iron-rich starting solutions showed that hematite is the dominant phase, however, these iron-rich solids were found by chemical analysis (Appendix 7) to contain up to 10% arsenic, with arsenic most probably being adsorbed onto a coexisting amorphous ferrihydrite compound which is not revealed on the X-ray patterns.

The iron-rich compounds are mostly ultra-fine grained and of high surface area. These solids have a large quantity of adsorbed water (Table 4.8) and their TG curves show a slow progressive mass loss through release of this loosely bound water. The curves have a distinct endothermic peak at 100°C which approximates to the boiling point of water. Small extraneous endothermic peaks are also occasionally observed at ~325°C which possibly represent weakly adsorbed sulphuric acid (boiling point of H<sub>2</sub>SO<sub>4</sub>). More commonly in the DTA curves, exothermic peaks are observed; these are mainly due to energy released during recrystallisation of the arsenates, usually at temperatures above 600°C. Quantitative estimations of water content were also determined from the TG curves and were found to be highly dependent on the drying procedure used for the sample.

Table 4.8. Composition of a typical arsenical ferrihydrite

Sample	Fe (%)	AsO <sub>4</sub> (%)	SO <sub>4</sub> (%)	H <sub>2</sub> O (%)	Fe:As (M)
U175	54.6	10.3	0.0	<20	13

## 4.5 Summary

The IR technique was used to study both amorphous and crystalline arsenical solids, and in combination with XRD, DTA - TG and chemical analysis, allowed a more complete characterisation of the materials. A number of distinct crystalline iron arsenate compounds were formed during hydrothermal precipitation. Table 4.9 summarises some of their important characteristics.

**Table 4.9** Chemical compositions of the arsenical compounds produced during precipitation

Compound	Fe (%)	AsO <sub>4</sub> (%)	SO <sub>4</sub> <sup>1</sup> (%)	Average Fe:As (M)	H <sub>2</sub> O <sup>2</sup> (%)	Size (µm)
<b>Scorodite</b> FeAsO <sub>4</sub> .2H <sub>2</sub> O	20 to 29	45 to 70	up to 5	1	11 to 17	up to 20
<b>Type-1</b> Fe <sub>2</sub> (HAsO <sub>4</sub> ) <sub>3</sub> .zH <sub>2</sub> O where z<4	21 to 27	63 to 75	<1.0	0.7 - 0.9	<5	up to 5
<b>Type-2</b> Fe <sub>3</sub> (AsO <sub>4</sub> ) <sub>0.33(9-x-2y)</sub> (OH) <sub>x</sub> (SO <sub>4</sub> ) <sub>y</sub> where x≤1 and y≤1	29 to 38.0	41 to 52	up to 18.0	1.50	up to 4	up to 50
<b>Type-3</b> Fe <sub>2</sub> (AsO <sub>4</sub> ) <sub>0.33(6-2x)</sub> (HAsO <sub>4</sub> ) <sub>x</sub> where x <1	25 to 28	61 to 72	<0.01	0.95	4 to 6	~25µm
<b>Arsenical ferrihydrite</b> Fe <sub>2</sub> O <sub>3</sub> .xH <sub>2</sub> O + arsenate	<65	<20	usually <0.1	variable	<40	«0.01

<sup>1</sup> Sulphate content variable dependent on the initial solution composition.

<sup>2</sup> Mass loss determined by DTA-TG,

# Chapter 5

## The hydrothermal Fe-AsO<sub>4</sub>-SO<sub>4</sub> system at pH<1

## 5.1 Introduction

The Fe-AsO<sub>4</sub>-SO<sub>4</sub> solution compositions are considered to be the most important hydrometallurgically as these represent common effluents and solutions derived from the leaching and processing of arsenical materials. The arsenical solutions used during the course of this work were prepared initially using ferric nitrate and lithium sulphate as the source of iron and sulphate, following these experiments iron(III) sulphate was used. It was found that the two different solution compositions produced a marginally different assemblage of solids.

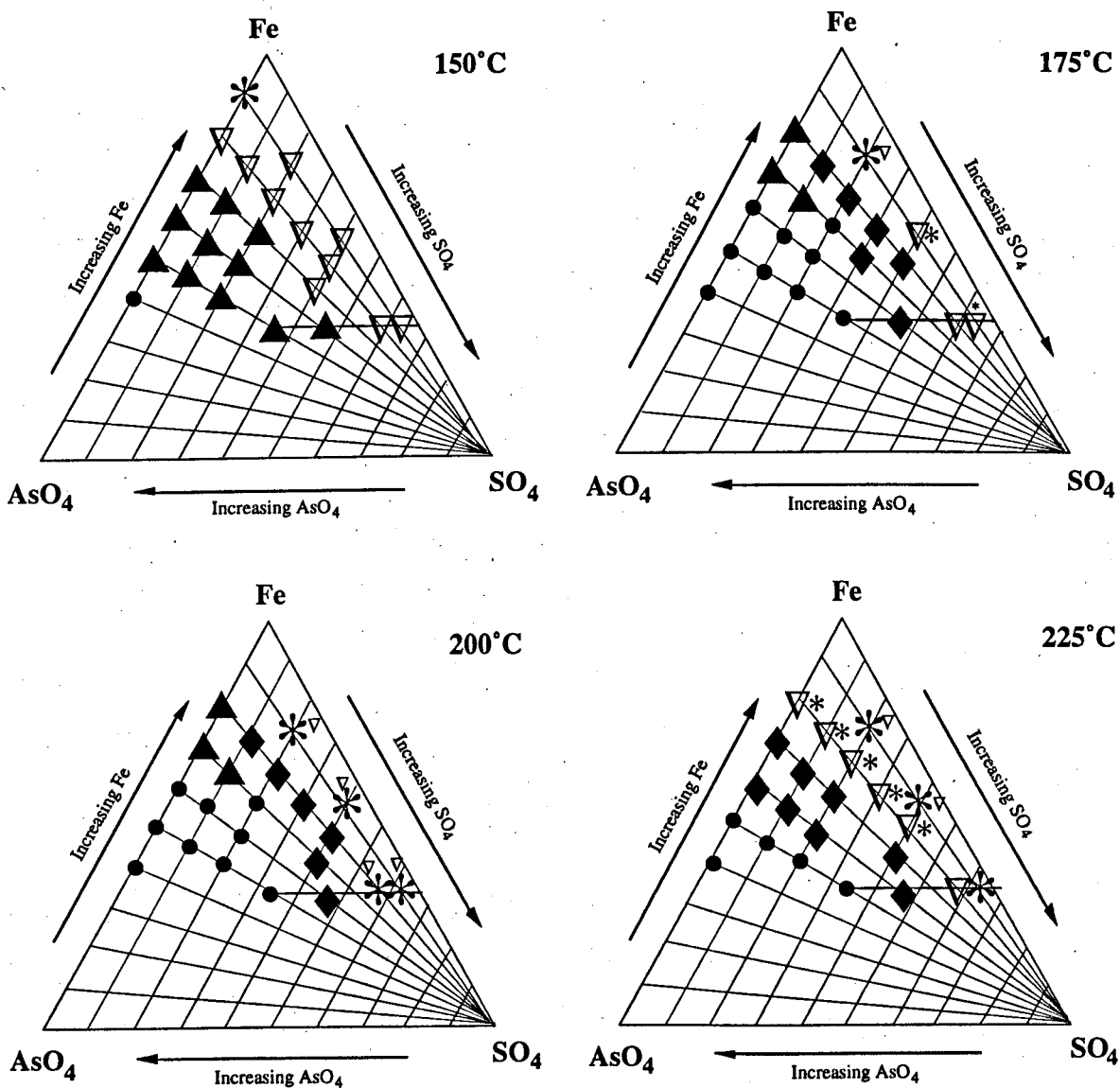
An understanding of the behaviour of this system at elevated temperature was considered to be necessary to help identify the temperatures and solution compositions required for the formation of stable crystalline compounds. The advantages of crystalline compounds over gelatinous arsenical ferrihydrites will be examined and compared to assess their relative merits in later chapters.

## 5.2 Precipitation of Fe-AsO<sub>4</sub>-SO<sub>4</sub> solids

### 5.2.1 Using ferric nitrate and lithium sulphate at pH<1

Each characterisation method (XRD, IR, DTA, SEM, TEM and chemical analysis) has individually contributed to the evaluation of the solids. Integration of all the available information by plotting the structure of the solids according to their initial solution compositions is given in **Figure 5.1**. The main species that can be identified include scorodite, hematite, ferrihydrite, Type-1 and Type-2 compounds. Each of these compounds forms under a relatively distinct set of conditions, which are summarised in **Table 5.1**. From the information in **Figure 5.1** and **Table 5.1** it is clear that there is strong control by the Fe:As ratio of the starting solutions on the type of compound precipitated.





Key to compounds - Type-2 compound (◆), Type-1 compound (●),  
Hematite (\*), Ferrihydrite (▽), Scorodite (▲)

**Figure 5.1** Distribution of compounds at 150 - 225°C relative to the starting composition of the pH<1 solutions

For the 150°C set of precipitations, scorodite is the dominant compound, although the Y and Z samples (see Figure 3.1 for solution compositions) contain only minor scorodite (<10%) and consist mainly of hydrated Type-1. The amorphous samples V to F consist of scorodite and the partly crystalline ferrihydrite.

**Table 5.1** Conditions for the formation of the compounds in the Fe-AsO<sub>4</sub>-SO<sub>4</sub> system at natural pH(<1) using lithium sulphate and iron nitrate

Compound -type	Example@	Temperature of formation	Fe:As range* of solutions	Remarks on solids
Hematite	U225	>200	>3:1	•Usually formed in the high iron region.
Ferrihydrite (6-line)	F150	>150	>1:1	•Solids are ultra fine and vary from gelatinous to crystalline.
Scorodite	X150	150 - 200	>1:1	•Usually crystalline with characteristic apple green colour
Type-1	Y200	150 - 225	<1:1	•Solids may be partially mixed with scorodite.
Type-2	N225	175 - 225	>1:1	•Solids may be intimately intergrown with hematite and ferrihydrite.

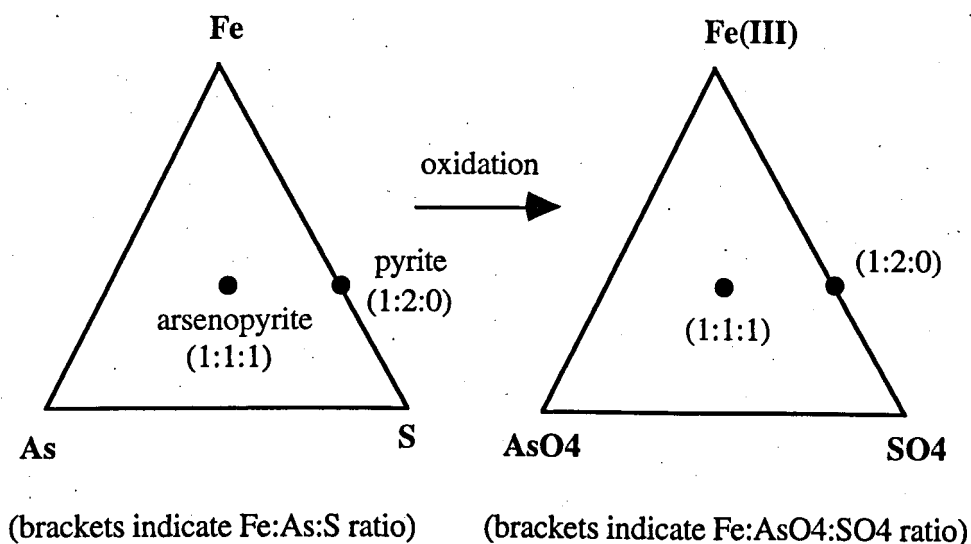
@ Solids considered to be composed of a single compound \* Initial solution composition

The 175°C samples contain only minor scorodite and have Type-1 as the dominant arsenate-type, except for the higher iron content solution compositions (Fe:As >4:1) which yield the Type-2 compound. The distribution of phases in the 200°C set of precipitations is identical to that of the 175°C set. The ferrihydrite in the iron-rich samples in the 175 and 200°C samples is often associated with the Type-2 compound.

When the temperature of precipitation was increased to 225°C, higher yields of solids were obtained. As the temperature was increased from 150 to 225°C the Type-1 compounds progressively lost their water of hydration. For this reason as the water content of the compound progressively decreased, the iron and arsenic contents increased, yet the Fe:As ratio stayed relatively constant.

Solids derived from solution compositions (C, D, B, E and J) (see Figure 3.1) are considered to represent analogues to those that arise from the oxidative dissolution of arsenopyrite and pyrite mixtures (Fe:2S and Fe:As:S) (Figure 5.2). The resulting idealised aqueous solutions, assuming no precipitation, would have identical molar compositions to those of the digested sulphide

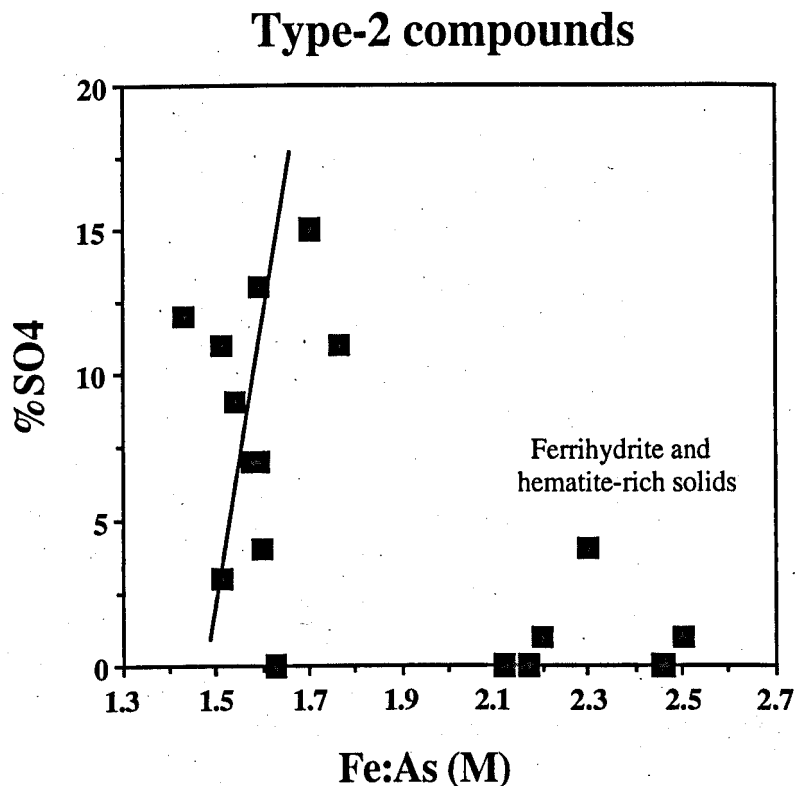
concentrate. Consideration of the distribution of compounds on the diagram (Figure 5.1) shows that the sulphate does not have a major influence on the solids that crystallise from solution. The assemblages of compounds include Type-1, Type-2, hematite and ferrihydrite and are identical to those formed from the lower sulphate compositions. In general the Fe:As ratio controls the distribution of the phase types, although minor anomalies do occur, such as the Type-2 phase produced from the solution of composition D(175 to 225°C). From the oxidative dissolution of arsenopyrite-pyrite mixtures (Py>Asp) it would be predicted using information from Figure 5.1 that at temperatures >175°C the precipitating solids would consist of Type-2, ferrihydrite and hematite, whereas the more arsenic compositions would possibly yield a higher percentage of the Type-2 compound.



**Figure 5.2** Idealised compositions of common sulphides and the solutions derived from the oxidation of the sulphides

The sulphate analyses of the various precipitates show that the Type-2 compounds are the most sulphate-rich, containing up to 12 - 13% sulphate, while those solids containing scorodite, or the Type-1 compound, are mostly low in sulphate, less than 4%. The iron-rich solids (G, H, J and B) (see Figure 3.1) produced at 150°C contain high sulphate levels, up to 19% (B150). The actual mode of occurrence of the sulphate in the ferrihydrite solids cannot be easily determined but it is thought that it occurs as an amorphous basic iron sulphate or jarosite-type compound. At higher temperatures (>150°C) the

iron-rich solids crystallise as ferrihydrite and hematite and incorporates only minimal amounts of sulphate.



**Figure 5.3** Composition of solids as they relate to the arsenical compound-type

For the purpose of plotting the analytical data on the solids (**Appendix 7**) the Fe, AsO<sub>4</sub>, SO<sub>4</sub> and H<sub>2</sub>O mass percentages were totalled and the data normalised to 100% and plotted (see **Figure 5.3** and **5.4**). The scorodite-type and Type-1 compounds usually have a limited compositional range and contain only low levels of sulphate (<<4%). Examination of the Type-2 compound compositions (**Figure 5.3**) shows the Fe:As ratio remains relatively constant (Fe:As ratio of 1.4 to 1.6). However, an increasing sulphate content does lead to an increased Fe:As ratio due to arsenic being replaced by sulphate in the Type-2 structure. The high sulphate levels in the solids (up to 18%) relate to high sulphate contents of the initial solutions and vice-versa. Departure away from this trend indicates the presence in the solid of an extra iron containing phase, either hematite, or ferrihydrite (e.g. Fe:As 2.1 - 2.5).

In Figure 5.4, compositional data are replotted to show the variation in the hydration of the compounds. It may be seen that the scorodite and Type-1 compounds show two distinct trends reflecting two distinct Fe:As ratios (1 and 0.7 - 0.9 respectively). The apparent presence of water (up to 5%) in the Type-2 compounds, may be partially associated with the presence of ferrihydrite, which can contain weakly adsorbed water.

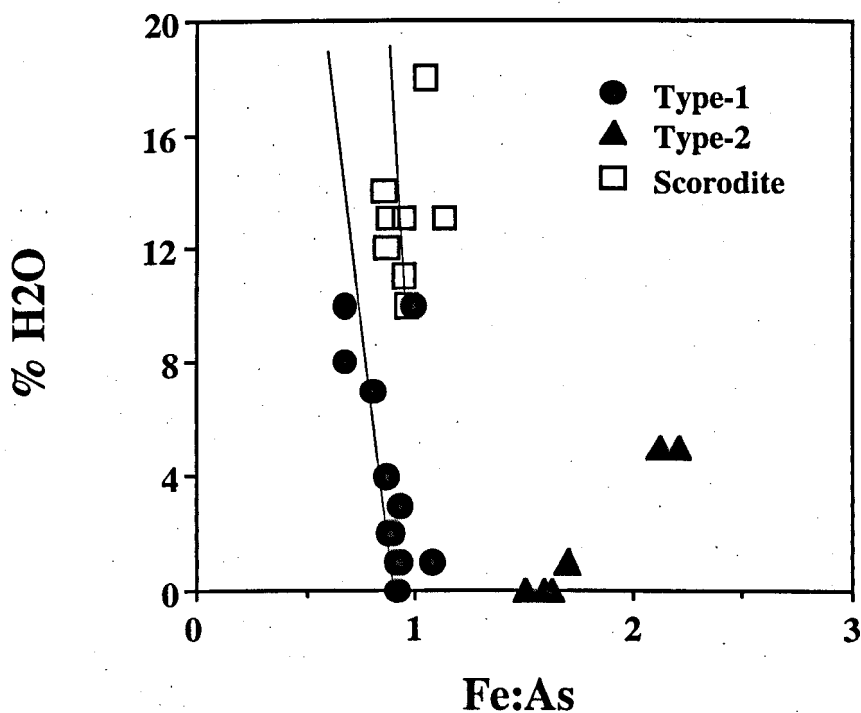


Figure 5.4 Fe:As vs %H<sub>2</sub>O diagram showing the variation in the water content of the arsenical solids

Mass balance calculations using the chemical analyses of the liquors at the start and finish of the experiments (Table 5.2) showed that 90% or more of the arsenic was precipitated during high temperature precipitation. The Fe:As molar ratio of the solution must be at least 1:1 to enable the arsenic to combine with iron and therefore be removed from solution. In initial starting solutions with Fe:As <1:1 there would be an insufficient amount of iron to combine with all the arsenic and for this reason any excess would remain in solution, giving low arsenic yields, e.g. composition Z, Fe:As 0.4:1. The mass balance calculations show that higher temperatures of hydrothermal precipitation yield greater arsenic removal from solution. The precipitation behaviour of iron from solution can be explained by its combination with

available arsenic to precipitate scorodite. Excess iron (Fe:As >1:1) is not precipitated at 150°C while at higher temperatures (>150°C) the excess iron may be precipitated as ferrihydrite or hematite and more fully removed from solution.

**Table 5.2** Mass balance calculations for the pH<1 precipitations at 150 to 225°C

Soln. Sample	Fe:As (M) soln	Removal of Fe and As from solutions at different temperatures of precipitation*							
		150°C		175°C		200°C		225°C	
		Fe(%)	As(%)	Fe(%)	As(%)	Fe(%)	As(%)	Fe(%)	As(%)
Z	0.4:1	97.1	46.6	98.6	37.1	>100	41.4	99.0	48.1
Y	0.7:1	98.0	72.7	98.6	51.9	74.5	52.6	98.9	72.4
A	1:1	91.7	96.0	98.6	84.4	79.3	55.6	98.3	99.1
K	1:1	94.4	99.0	97.6	83.4	105.4	51.9	97.0	99.0
L	1:1	93.6	98.2	97.7	83.2	>100	57.3	96.2	97.8
M	1.5:1	61.4	98.5	97.7	75.4	107.8	76.0	97.7	98.1
N	1.5:1	64.2	99.0	97.2	77.5	109.7	78.3	97.0	98.1
X	1.5:1	62.3	97.8	98.1	76.6	82.3	78.8	95.7	97.8
O	2.3:1	nd	nd	87.7	95.6	70.8	96.1	89.9	96.7
P	2.3:1	84.9	95.3	86.4	95.6	84.6	98.3	88.6	95.8
W	2.3:1	nd	nd	83.2	99.6	84.8	97.6	91.1	95.6
F	4:1	nd	nd	71.4	91.7	104.3	93.3	91.8	91.7
R	4:1	47.9	91.4	73.4	93.3	79.6	90.9	92.2	91.9
S	4:1	32.0	38.3	73.7	94.2	nd	85.8	90.5	89.2
T	4:1	nd	nd	67.0	65.9	79.5	91.1	90.8	87.8
V	4:1	nd	nd	66.7	84.0	79.9	93.0	92.0	93.0
U	9:1	nd	nd	72.8	94.7	76.6	81.3	96.3	89.3

nd - not determined, \* sealed test tube kept at temperature for 24hrs

### 5.2.2 Using ferric sulphate at pH5

Solutions prepared using iron(III) sulphate as the source of both iron and sulphate produced a different assemblage of compounds to those produced using iron nitrate and lithium sulphate. This suggests that the presence of lithium and nitrate does have an influence on the solids that precipitate. The Fe:As ratios as determined from the chemical analyses on the solids are summarised in Table 5.3. Comparison of the Fe:As ratios of the solids with

those of the starting solutions indicates that more iron than arsenic precipitates as the precipitation temperature is increased.

**Table 5.3** Fe:As molar ratio's of solids precipitated from Fe(III) sulphate and As<sub>2</sub>O<sub>5</sub> solutions at their natural pH.

Ppt T (°C)	Initial starting solution compositions (Fe:As)						
	0.44:1	0.66:1	1:1	1.5:1	2.3:1	4:1	9:1
150	nd	nd	1.08	nd	nd	nd	nd
175	0.93	0.91	1.37	1.33	nd	nd	nd
200	0.89	0.91	1.69	2.15	3.11	5.54	10.28
225	0.87	0.93	nd	nd	nd	nd	nd

nd - not determined

This precipitation behaviour is slightly different from the solution compositions containing nitrate and lithium in that any excess iron is precipitated as a basic iron sulphate-type solid, whereas for the nitrate containing solutions ferrihydrite can form and under certain conditions may reequilibrate in the acidic liquor and give rise to a lower apparent removal of iron.

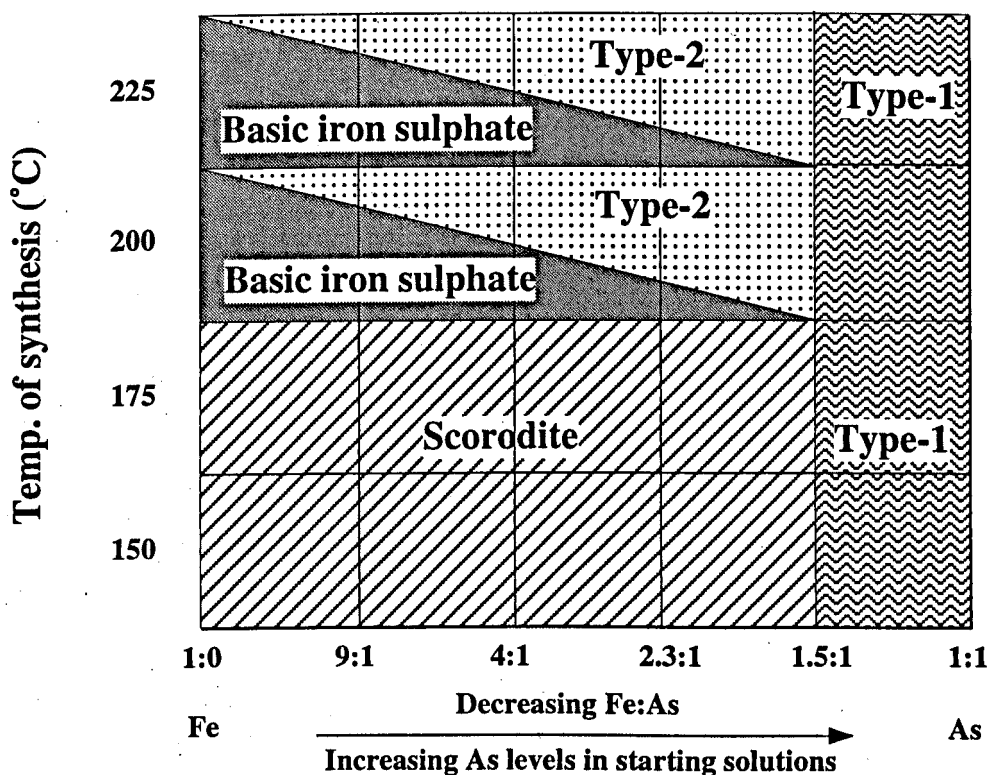
When ferrihydrite does form, the gelatinous, high surface area, material can adsorb arsenate, whereas the basic iron sulphate compound is crystalline and unlikely either to adsorb or to incorporate any arsenic into its structure.

**Table 5.4** Arsenic mass balance, indicating the amount of arsenic (%) reporting to the precipitate

Precipitation Temp (°C)	Arsenic precipitation (%) from different Fe:As solution compositions* (Fe(III) sulphate used)				
	1:1	1.5:1	2.3:1	4:1	9:1
225	93.2	90.9	94.1	99.9	53.9
200	94.2	96.4	96.9	100.0	87.5
175	93.9	97.2	92.4	99.8	63.2
150	92.7	93.2	62.2	99.1	nd
125	91.3	73.2	19.5	99.1	nd

(\* using the analysis of the final liquor and the composition of the starting solutions)

The arsenic analyses on the mother liquors before and after hydrothermal precipitation allowed a mass balance on the individual systems to be calculated. It can be seen (Table 5.4) that high temperature precipitation usually removes well over 90% of the arsenic from solution. Removal of arsenic from solution increases with increased temperature of precipitation and increased levels of iron.



E.g. A solid precipitated from a 9:1 solution at 225°C yields ~90% basic iron sulphate and ~10% Type-2

**Figure 5.5** Distribution of compounds formed from Fe-AsO<sub>4</sub>-SO<sub>4</sub> solutions (pH<1) (using Fe(III) sulphate) at different temperatures

The XRD patterns of the solids precipitated at low pH(<1) showed the existence of scorodite, Type-1, Type-2 and basic iron sulphate. The distribution of the phases formed at various temperatures is given in Figure 5.5. Above 175°C the basic iron sulphate and Type-2 form, whereas below this temperature scorodite predominates. The composition of solids are also controlled by the Fe:As ratio of the starting solutions, when this is <1.5:1, the Type-1 compound is most likely to form, whereas when >1.5:1, scorodite or Type-2 will form. The proportion of basic iron sulphate increases with increased Fe:As ratio (i.e. from 1:1 to 1:0). The 100% Fe solutions yield 100%



basic iron sulphate. From the limited amount of information available the basic iron sulphate shows some variation in the OH content which appears to decrease with increasing temperature. At temperatures below 175°C other iron sulphate compounds are certain to form [73] but in the experimental set up used they must readily reequilibrate or were washed away following separation. Solutions with low iron levels (<5g/L) precipitate any excess iron as hematite in preference to the basic iron sulphate [71] which is favoured where the solutions contain higher free sulphuric acid levels.

### 5.3 Conclusions

Precipitation experiments at  $\text{pH} < 1$  have revealed a number of distinct compounds, the most important of which are scorodite, Type-1, Type-2 and the basic iron sulphate. Most of these compounds have not been described extensively in the literature yet they can be easily prepared experimentally. One complication with the compounds is that they appear to have variable compositions which are dependent on temperature of formation and on the initial solution compositions. However, the precipitation programme has allowed a wide range of compounds to be produced and the general characteristics have emerged.

The Type-1 compound is an acid salt of composition  $\text{Fe}_2(\text{HAsO}_4)_3 \cdot z\text{H}_2\text{O}$ , (where  $z = 0$  to 4) with the water of hydration varying from 0% to 11%, the higher amount being comparable to the levels of water found in precipitated scorodite. The formula of the Type-2 compound appears also to be equally complex and approaches the composition  $\text{Fe}_3(\text{AsO}_4)_{0.33(9-x-2y)}(\text{OH})_x(\text{SO}_4)_y$ , (where  $x \leq 1$  and  $y \leq 1$ ). Hydrothermal experiments have enabled the conditions of formation of these compounds to be more clearly defined.

# Chapter 6

## The hydrothermal Fe-AsO<sub>4</sub>-SO<sub>4</sub> system at pH5

## 6.1 Introduction

The work in this chapter investigates the precipitation of solids from arsenical solutions at pH5 following the hydrolysis of iron(III) in solution. In the hydrothermal experiments conducted at low pH<1, and elevated temperatures (>150°C) crystalline compounds precipitated from clear solutions. At pH's above 2 the iron(III) is hydrolysed and precipitated as a ferrihydrite sludge, the arsenic coprecipitates with the ferrihydrite and is strongly adsorbed onto the compound.

Iron-arsenate solution compositions were adjusted to pH5 to investigate the nature of solids which can grow from gelatinous ferrihydrite sludges. Investigations into the nature of gelatinous materials can be difficult as the solids can vary according to the preparation procedure and may be contaminated with other compounds which complicate their characterisation. A range of solution compositions were prepared using lithium hydroxide to adjust pH and these were heated at various temperatures from ambient to 225°C. The initial gelatinous precipitates underwent solid transformations into a number of different compounds. The changes in the solid and solution characteristics with temperature were examined and conclusions drawn.

## 6.2 Fe-AsO<sub>4</sub>-SO<sub>4</sub> system at pH5

### 6.2.1 Using ferric nitrate and lithium sulphate at pH<1

In the solids derived from precipitation experiments at pH5 in the Fe-AsO<sub>4</sub>-SO<sub>4</sub> system from solutions containing also lithium and nitrate, the Type-2 structure was not observed and Type-1 was only present as a subordinate phase (<10%). However, a third unknown compound was observed and this has been designated as the Type-3 compound. This compound is usually restricted to the solids derived from the arsenic-rich solutions, with Fe:As compositions of <2:1 and is usually formed at temperatures above 125°C.

The distributions of phases observed show that the samples which have Fe:As ratios of less than 2:1 contain the Type-3 compound, which is rarely admixed with the Type-1 compound. As the iron levels are increased, ferrihydrite and hematite become progressively more abundant. The presence of minor

amounts of the Type-3 compound in some of the iron-rich solids suggests that arsenic is precipitated partially as this compound while the remainder is adsorbed onto ferrihydrite.

High levels of iron in the solids result from the presence of major amounts of hematite and ferrihydrite, while lower iron and higher arsenic levels are due to the presence of the Type-3 phase. The occurrence of the Type-3 compound in the solids is often indicated by a green to light brown product with rhombohedral crystals up to 20 $\mu$ m, while the iron-rich varieties give rise to darker brown coloured solids.

The sulphate contents of all of the crystalline compounds precipitated at pH5 were very low (< 0.8%); the reason for these low levels is thought to be that the solids grew from the gelatinous precipitates which contained only minimal amounts of sulphate. However, those solids precipitated at low temperatures (<150°C) and at low pH(<1) contained significant amounts of sulphate (up to 20%) through adsorption onto a gelatinous-type phase.

### 6.2.2 Using ferric sulphate at pH5

Precipitation of solids at pH5 using solutions made from ferric sulphate, with lithium hydroxide used for pH adjustment, produced a similar set of compounds to those formed when iron nitrate and lithium sulphate solutions were used. The X-ray diffraction data (Table 6.1) showed that the solids formed at lower temperatures (<125°C) are amorphous and most probably consist of poorly-crystalline arsenical ferrihydrite (2-line). Increased precipitation temperatures resulted in the reorganisation and ordering of the atoms into more crystalline compounds and, for the more iron-rich solutions, hematite, and crystalline ferrihydrite (6-line) are formed. At a Fe:As ratio of 1:1, the precipitate that is formed at 225°C is composed mainly of the Type-3 compound with subordinate amounts of the Type-1 compound. As the iron content of the solutions is increased, arsenic does not precipitate as a distinct phase, but is most likely to be adsorbed onto the ferrihydrite. Hematite is precipitated from the iron-rich solution compositions and it is likely that poorly crystalline ferrihydrite is also present, resulting in some adsorption of arsenic. From the chemical compositions of the solids (Table 6.2) it appears that the Fe:As ratios of the solids precipitated at pH5 approach those of the initial solution compositions. This is thought to be due to high product yields resulting from the nucleation and growth from the initial gelatinous solids

which precipitate prior to heating (i.e. during the pH adjustment to pH5) and which contain most of the arsenic and iron.

**Table 6.1** Distribution of phases formed from Fe-AsO<sub>4</sub>-SO<sub>4</sub> solutions (pH5) (using Fe(III) sulphate) at different temperatures as determined by XRD

Ppt Temp (°C)	Fe:As ratio of solutions used for precipitated at pH5				
	1:1	1.5:1	2.3:1	4:1	9:1
20	Amorphous	Amorphous	Amorphous	Amorphous	Amorphous
75	Amorphous	Amorphous	Amorphous	Amorphous	Amorphous
125	Amorphous	Amorphous	Amorphous	Amorphous	Hematite
175	Type-3 + Type-1	Type-3 + Ferrihydrite	Hematite + Ferrihydrite	Hematite + Ferrihydrite	Hematite
225	Type-3 + Type-1	Type-3 + Ferrihydrite	Hematite + Ferrihydrite	Hematite + Ferrihydrite	Hematite

Note: The quantification of a crystalline component in an amorphous matrix is very difficult, the amorphous solids are considered to be the 2-line ferrihydrite

**Table 6.2** Fe:As molar ratio of solids precipitated from Fe(III) sulphate and As(V) solutions at pH5

Precipitation Temp.(°C)	Fe:As ratio of precipitated solids				
	1:1	1.5:1	2.3:1	4:1	9:1
20	1.11	1.49	2.44	4.11	9.51
75	1.21	1.60	2.48	4.09	9.79
125	1.24	1.57	2.31	3.70	8.51
175	1.11	1.60	2.45	3.69	9.63
225	1.06	1.58	2.53	4.34	11.21

A ferrihydrite sample was prepared at ambient temperatures when the pH of a ferric sulphate solution was adjusted to pH8 with lithium hydroxide. The

gelatinous sludge was allowed to stand, and after a period of five weeks a transformation occurred with the discoloration of the dark brown ferrihydrite to light brown goethite. The XRD of the dark brown material with the two broad peaks characteristic of 2-line ferrihydrite changed through polymerisation and crystallisation to goethite. However, when small amounts (~2%) of arsenic was coprecipitated with the ferrihydrite the arsenic was strongly adsorbed and this prevented the mineralogical transformation from taking place. Phosphates, silica and organic reagents [78] interact with ferrihydrite in a similar manner and the compound will remain as the partially stabilised 2-line ferrihydrite. At elevated temperatures (>100°C) in the presence of arsenic the more distinctive 6-line ferrihydrite forms and, as there is no evidence for any other arsenic compound, the arsenic must be adsorbed or weakly incorporated into the ferrihydrite structure. During preparation of numerous arsenical sludges at elevated temperatures no goethite was ever identified, at lower temperatures (100 - 150°C) ferrihydrite predominated whereas at higher temperatures (>150°C) the ferrihydrite becomes less stable and is converted to hematite.

### 6.3 Conclusions

The reasons for the pH5 solutions precipitating a different assemblage of phases at elevated temperatures compared with the natural pH (<1) solutions is that the mechanism of formation of the solids is very different; for the pH5 solids the crystallisation occurs from an initial gelatinous, hydrated, sulphate deficient, iron-arsenate-hydroxide mixture, whereas those compounds formed from the natural pH solutions (<1) nucleate and grow from initially clear, sulphate-rich solutions. This latter growth mechanism allows well-formed, more clearly defined, arsenical phases to develop.

At elevated temperatures a crystalline compound designated as the Type-3 compound crystallises from gelatinous arsenical-ferrihydrite (Fe:As <2:1). X-ray diffraction, IR and DTA - TG show that the Type-3 compound is distinct and is considered to be a new compound. At elevated temperatures the 2-line arsenical ferrihydrite crystallises mostly into the 6-line arsenical ferrihydrite with minor amounts of arsenic occurring partially as the Type-3 compound.

The presence of arsenic in the structure of the ferrihydrite appears to inhibit the transformation of the compound to goethite. During the course of the hydrothermal precipitation experiments using arsenical solutions, no goethite was observed which supports the idea that adsorbed arsenic can stabilise the ferrihydrite structure and prevents its transformation to goethite from taking place.

# Chapter 7

## The hydrothermal Ca-Fe-AsO<sub>4</sub> system



## 7.1 Introduction

In the metallurgical processing of arsenic-bearing solutions, precipitation of arsenical compounds is usually brought about by neutralisation with lime. If the process liquor contains iron in addition to arsenic, then arsenical ferrihydrite compounds will be precipitated; otherwise, calcium arsenate compounds will be formed. The solubilities and stabilities of these two groups of compounds differ widely and the work reported in this chapter was carried out to try to understand the precipitation behaviour in the Ca-Fe-AsO<sub>4</sub> system.

A range of Fe-Ca-AsO<sub>4</sub> compounds was precipitated at temperatures ranging from ambient to 225°C. The solids were characterised by various techniques, including XRD, IR, DTA - TG. Supporting data for the study were obtained by investigation of the individual Fe-AsO<sub>4</sub> and Ca-AsO<sub>4</sub> hydrothermal systems, mostly at elevated temperatures (125 - 225°C). As calcium arsenate compounds only begin to precipitate at pH's > 3, the Fe-AsO<sub>4</sub> system at pH 5 was considered to be most relevant in the interpretation of the Ca-Fe-AsO<sub>4</sub> system at elevated pH.

## 7.2 Characterisation of Fe-AsO<sub>4</sub>-SO<sub>4</sub> solids

Previous work (Chapter 5) has shown that the compounds precipitated at elevated temperatures from solutions in the Fe-AsO<sub>4</sub>-SO<sub>4</sub> system at low pH's (<1) include scorodite, hematite, ferrihydrite and two compounds designated Type-1 and Type-2. In Chapter 6 it was shown that if Fe:As solutions are initially adjusted to pH 5, prior precipitation of gelatinous ferrihydrite occurs before the hydrothermal treatment. Under these conditions, the compounds found after the heat treatment included ferrihydrite, hematite, Type-1 and another unknown crystalline phase which was designated the Type-3 compound.

X-ray diffraction data show that solids formed at lower temperatures (<125°C) are amorphous and consist primarily of poorly-crystalline (2-line) ferrihydrite. Increased precipitation temperatures resulted in the reorganisation and ordering of the atoms into more crystalline compounds,

with the more iron-rich solutions forming mainly hematite and the crystalline (6-line) form of ferrihydrite. At a Fe:As ratio of ~1:1, the precipitate that formed at 225°C was composed of the Type-3 compound with subordinate amounts of the Type-1 compound. The presence of minor amounts of the Type-3 compound in some of the iron-rich solids suggests that arsenic may precipitate partially as this compound, with the remainder adsorbed onto ferrihydrite.

### 7.3 Ca-AsO<sub>4</sub> system

A range of calcium arsenate solids was precipitated at different pH's and temperatures, as listed in Table 7.1, from solutions initially containing 0.5M Ca<sup>2+</sup> and 0.5M AsO<sub>4</sub><sup>3-</sup>. At low temperatures (<100°C) and pH's of 7 and below, the precipitated solids were comprised of partially hydrated CaHAsO<sub>4</sub>-type compounds. These compounds are crystalline and commonly have a relatively small number of XRD peaks, yet these are undocumented (see Appendix 6) and have no comparable natural mineral analogue; however their IR spectra match those of natural calcium arsenate minerals, in particular weilite (CaHAsO<sub>4</sub>), haidingerite (CaHAsO<sub>4</sub>·H<sub>2</sub>O) and guerinite (Ca<sub>5</sub>H<sub>2</sub>(AsO<sub>4</sub>)<sub>4</sub>·9H<sub>2</sub>O) (see Table 7.2 and Figure 7.1). The extra peaks in the haidingerite mineral sample (around 2800cm<sup>-1</sup>) suggests contamination or a mixture of compounds. However, these peaks were not observed in the IR spectrum of another pure sample analysed by the Natural History Museum. At pH8 and in the temperature range 20 - 75°C, the precipitated compounds have a different Ca:As ratio and are comparable to the mineral guerinite. At precipitation temperatures above 100°C, the solids have little water of hydration and the predominant compound is similar to the mineral weilite (CaHAsO<sub>4</sub>). At 225°C, the solids precipitated have distinct IR patterns and their DTA-TG patterns show negligible levels of constitutional water and a composition of Ca<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>·xH<sub>2</sub>O is inferred, solids precipitated at higher pH's (8) at temperatures above 100°C also show a similar compound, although this is more likely to be the basic calcium arsenate (Johnbaumite (Ca<sub>5</sub>(AsO<sub>4</sub>)<sub>3</sub>OH)) (see Table 7.1).

**Table 7.1** Characteristics of precipitated calcium arsenate compounds

Mineral-type	Composition	Ca:As (M)	Precipitation conditions
Haidingerite	CaHAsO <sub>4</sub> .H <sub>2</sub> O	1:1	Ca:As 1:1, pH6, 50°C*
Pharmacolite	CaHAsO <sub>4</sub> .2H <sub>2</sub> O	1:1	Ca:As 1:1, pH6, 20°C*
Guerinite	Ca <sub>5</sub> H <sub>2</sub> (AsO <sub>4</sub> ) <sub>4</sub> .9H <sub>2</sub> O	5:4	Ca:As 1:1, pH8, 50°C*
Weilite	CaHAsO <sub>4</sub>	1:1	Ca:As 1:1, pH7, 200°C*
Ca-arsenate	Ca <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> .xH <sub>2</sub> O	3:2	Ca:As 1:1, pH5, 225°C*
Basic Ca-arsenate	Ca <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> . Ca(OH) <sub>2</sub>	>2:1	Ca:As 1:1, pH11, 100°C
Ferrarisite	Ca <sub>5</sub> H <sub>2</sub> (AsO <sub>4</sub> ) <sub>4</sub> .9H <sub>2</sub> O	5:4	Ca:As 1:1, pH9, 20°C
Johnbaumite	Ca <sub>5</sub> (AsO <sub>4</sub> ) <sub>3</sub> OH	5:3	Ca:As 1:1, pH10, 150°C

\* see IR patterns (Figure 7.1) which are identical to the naturally occurring minerals

**Table 7.2** Distribution of phases in the Ca-AsO<sub>4</sub> system precipitated at different temperatures and initial solutions pH's

Precipitation Temp. (°C)	pH									
	3	4	5	6	7	8	9	10	11	
20	P	P	P	P	H	G	G/F	G?	G?	
50	nd	nd	H	H	H	G	G	G	G	
75	nd	nd	H	H	H	G	G	G	G	
100	nd	nd	W	W	W	W	G?	G	JB	
125	nd	W	W	W	W	W	JB	JB	JB	
150	nd	W	W	W	W	W	JB	JB	JB	
175	W	W	W	W	W	W	JB	JB	JB	
200	W	W	W	W	W	W	JB	JB	JB	
225	CA	CA	CA	CA	CA	CA	JB	JB	JB	

W - weilite, G - guerinite, P - pharmacolite, H - haidingerite, JB - Johnbaumite

CA - Ca-arsenate, F - Ferrarisite, nd - not determined,

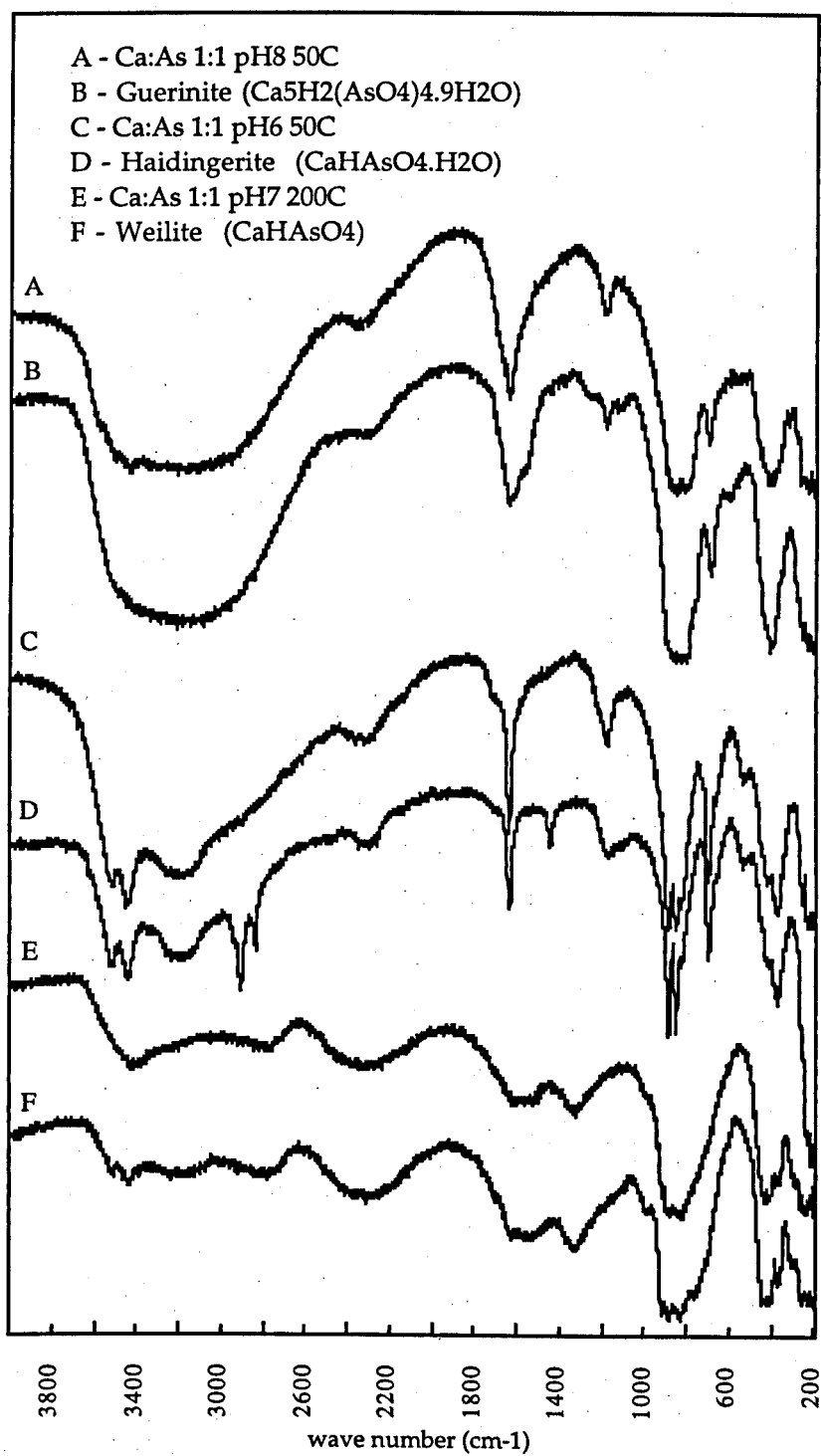


Figure 7.1 IR spectra of natural and precipitated calcium arsenates

## 7.4 Ca-Fe-AsO<sub>4</sub> system

For the precipitation of solids in the ternary system a set of three solution compositions were used which had Ca:Fe:As ratios of 3:1:4, 1:1:2 and 1:3:4. The solution compositions were chosen to have cation:anion ratios of one ( $[Ca + Fe] = [As] = 1$ ) and to show a variation of calcium:iron ratios. The initial pH's of these solutions were adjusted in the range 1 to 7 and hydrothermal precipitations were carried out over the temperature range 150 - 225°C. A study of the characteristics of the precipitated solids gave some understanding of the precipitation processes operating during the thermal treatment of Ca-Fe-AsO<sub>4</sub> solutions.

At pH1 all of the solution compositions precipitated either scorodite (FeAsO<sub>4</sub>·2H<sub>2</sub>O) or the Type-1 compound, depending on the temperature. As the pH was increased, calcium started to precipitate as a coprecipitated Ca-arsenate phase, with the solids derived from the higher Ca:Fe ratio solutions having higher calcium contents (see Table 7.3). The overall distribution of solid compositions is strongly controlled by the preferential precipitation of the iron with arsenic as a Type-1 or a scorodite-type compound (Fe:As ratio ~1:1); these compounds precipitate in preference to the calcium arsenate phases from solutions with initial pH's below 5. Some anomalies in the XRD patterns of scorodite and the Type-1 compound were found and it is thought that these compounds contain minor amounts of calcium in their crystal lattices. Increasing the precipitation temperature (150 - 225°C) has a negligible effect on the Ca:Fe ratio, indicating that the compositions of the precipitated solids are virtually independent of temperature and are controlled mainly by the pH of the starting solutions.

**Table 7.3** Chemical analyses of precipitated Ca-Fe-AsO<sub>4</sub> solids

T°C Ppt	pH	Ca:Fe:As 3:1:4			Ca:Fe:As 1:1:2			Ca:Fe:As 1:3:4		
		Fe (%)	AsO <sub>4</sub> (%)	Ca (%)	Fe (%)	AsO <sub>4</sub> (%)	Ca (%)	Fe (%)	AsO <sub>4</sub> (%)	Ca (%)
150	pH1	23.8	63.9	0.0	24.0	62.9	0.0	23.9	62.1	0.0
150	pH3	12.1	60.9	5.4	20.9	61.0	1.2	23.3	60.8	0.1
150	pH5	11.5	64.2	7.8	14.8	57.4	5.8	21.1	57.4	2.9
150	pH7	10.5	69.7	16.6	19.8	54.4	9.6	22.7	52.1	4.9
175	pH1	24.1	63.8	0.0	23.4	61.1	0.0	23.8	61.8	0.0
175	pH3	12.6	63.9	5.8	21.0	62.9	1.5	24.1	62.5	0.0
175	pH5	11.0	63.4	7.5	20.3	60.2	8.1	21.5	58.3	2.9
175	pH7	11.1	65.6	16.5	20.6	55.6	10.0	22.7	52.3	4.9
200	pH1	25.2	66.4	0.0	26.3	67.9	0.0	23.4	60.7	0.0
200	pH3	13.1	64.9	5.8	22.7	62.5	1.2	24.0	61.9	0.4
200	pH5	11.3	63.9	7.8	22.8	60.5	8.8	23.9	61.0	3.7
200	pH7	10.2	66.1	17.5	21.0	56.2	10.1	23.4	52.6	5.1
225	pH1	25.7	67.4	0.0	26.9	69.4	0.0	26.5	67.9	0.0
225	pH3	13.1	62.3	7.2	24.8	64.3	4.2	24.9	64.1	0.9
225	pH5	11.6	64.6	8.0	22.9	60.5	8.7	24.7	61.0	4.3
225	pH7	9.7	66.9	17.7	20.9	58.2	10.8	23.9	52.1	5.1

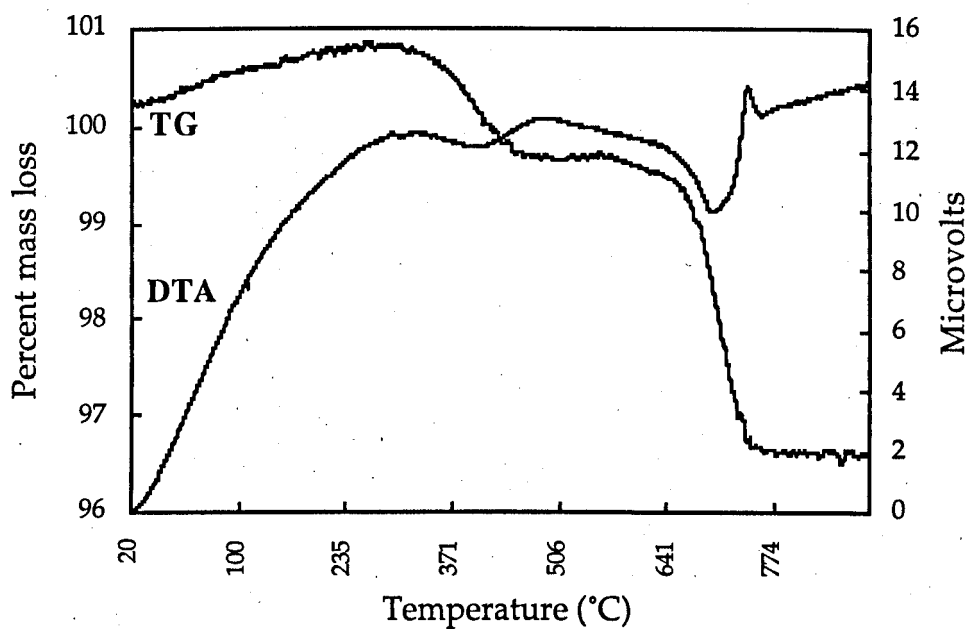
In the 1:1:2 solutions (i.e. intermediate Fe:Ca) at pH5, a crystalline Ca-Fe-arsenate phase was produced. The compound has a Ca:Fe ratio of 0.54 and a (Ca + Fe)/As ratio of 1.44 and it has a stoichiometry that approaches  $\text{CaFe}_2(\text{AsO}_4)_{0.33(8-2x)}(\text{HAsO}_4)_x$  (where  $x < 1$ ) (see Table 7.4). This light brown compound, which has distinct IR, XRD and DTA - TG patterns, has been designated the Type-4 compound. The Type-4 compound is the least clearly defined of the new arsenate compounds found during the course of this work due to its very fine grain size (<2 $\mu\text{m}$ ) and its intimate mixture with the other coprecipitated compounds which interfere with its characterisation. Thermal data on the compound suggests constitutional water loss at ~360°C, the compound does not contain any sulphate and the mass loss at 710°C would also appear to be consistent with hydroxyl or constitutional water (HAsO<sub>4</sub>). The IR spectrum of the Type-4 compound (see Figure 7.2) does not show any significant hydroxyl peaks, and it appears to be quite different from the compounds formed in the individual Ca-AsO<sub>4</sub> and Fe-AsO<sub>4</sub> systems at pH5, which were CaHAsO<sub>4</sub> (weillite) and  $\text{Fe}_2(\text{AsO}_4)_{0.33(6-2x)}(\text{HAsO}_4)_x$  (Type-3), respectively. The compound is also very different to the two naturally occurring Ca-Fe arsenate minerals: arseniosiderite and yukonite

( $\text{Ca}_3\text{Fe}_4(\text{OH})_6(\text{AsO}_4)_4 \cdot 3\text{H}_2\text{O}$  and  $\text{Ca}_3\text{Fe}_4(\text{AsO}_4)_2(\text{OH})_6 \cdot 5\text{H}_2\text{O}$  respectively) [15]. The XRD data on the Type-4 compound is given in Appendix 6.

**Table 7.4** Ca:Fe and (Fe + Ca):As ratios of solids formed during syntheses at various temperatures and pH's

		Ca:Fe ratio (M) of solids							(Fe + Ca)/As (M) of solids				
Solution Compn.		T°C	pH1	pH3	pH5	pH7	Solution Compn.		T°C	pH1	pH3	pH5	pH7
Ca:Fe:As 3:1:4		150	0.00	0.62	0.94	nd	Ca:Fe:As 3:1:4		150	0.93	0.80	0.87	nd
		175	0.00	0.64	0.94	2.06			175	0.94	0.81	0.84	1.29
		200	0.00	0.62	0.96	2.38			200	0.95	0.81	0.86	1.30
		225	0.00	0.77	0.96	2.54			225	0.95	0.92	0.88	1.28
Ca:Fe:As 1:1:2		150	0.00	0.08	0.58	0.67	Ca:Fe:As 1:1:2		150	0.95	0.92	0.96	1.51
		175	0.00	0.10	0.55	0.67			175	0.95	0.91	1.30	1.55
		200	0.00	0.07	0.54	0.67			200	0.96	0.97	1.44	1.56
		225	0.00	0.24	0.53	0.72			225	0.97	1.19	1.44	1.54
Ca:Fe:As 1:3:4		150	0.00	0.00	0.19	0.30	Ca:Fe:As 1:3:4		150	0.96	0.96	1.09	1.41
		175	0.00	0.00	0.19	0.30			175	0.96	0.96	1.09	1.41
		200	0.00	0.02	0.21	0.30			200	0.96	0.98	1.18	1.44
		225	0.00	0.05	0.24	0.29			225	0.97	1.01	1.25	1.48

DTA - TG pattern of the Type-4 compound



IR spectrum of the Type-4 compound

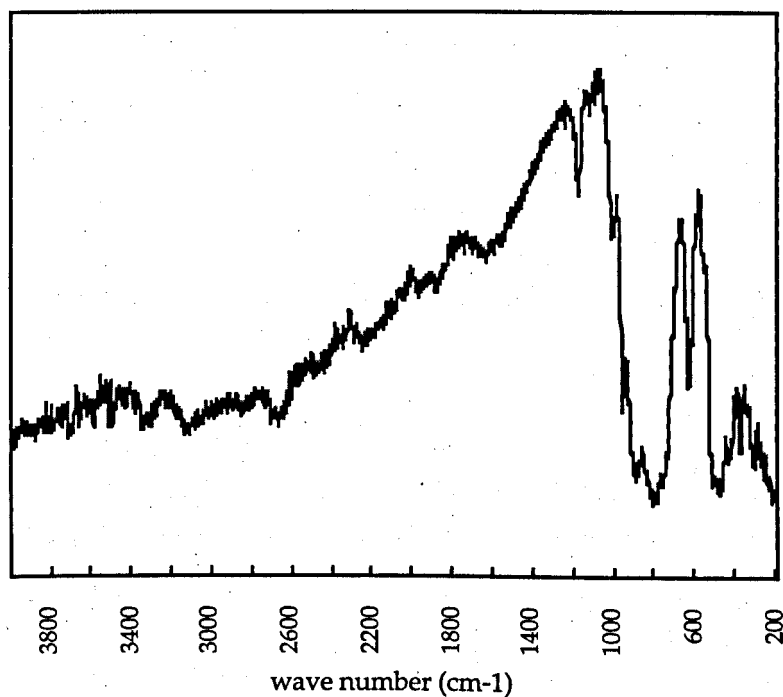


Figure 7.2 Thermal data and IR spectrum of the Type-4 compound



## 7.5 Conclusions

A detailed hydrothermal synthesis study of the Ca-Fe-AsO<sub>4</sub> ternary system was carried out with the aim of understanding the system at temperatures up to 225°C. Although the Fe-AsO<sub>4</sub> binary system is reasonably simple, the Ca-AsO<sub>4</sub> system is significantly more complex and so this was further investigated to supplement the work on the ternary system.

From precipitation work carried out in the calcium-arsenate system, it was found that at temperatures below 100°C, the solids are partly hydrated and are usually composed of one of the following:- pharmacolite, haidingerite, or guerinite (CaHAsO<sub>4</sub>·2H<sub>2</sub>O, CaHAsO<sub>4</sub>·H<sub>2</sub>O and Ca<sub>5</sub>H<sub>2</sub>(AsO<sub>4</sub>)<sub>4</sub>·9H<sub>2</sub>O, respectively). In the temperature range 100 - 200°C at pH's < 8, the solids contain only constitutional water and are composed of a weilite-type compound (CaHAsO<sub>4</sub>). Solids precipitated at pH's above 8 and at temperatures above 100°C precipitated johnbaumite (Ca<sub>5</sub>(AsO<sub>4</sub>)<sub>3</sub>OH). Above 200°C, the predominant solid approaches a Ca<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub> composition which contains only minor amounts of constitutional water. The type of Ca-As compound that is precipitated is dependent on the pH of the initial solution, with precipitation only occurring at pH 3 and above.

Characterisation of the compounds formed in the binary Ca-AsO<sub>4</sub> and Fe-AsO<sub>4</sub> systems has enabled the ternary system to be more fully understood. At pH 1 and 3 the solids precipitated from the Ca-Fe-AsO<sub>4</sub> solutions resemble scorodite and the Type-1 compound (Fe<sub>2</sub>(HAsO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O), the latter forming at higher temperatures (>175°C). The incorporation of small amounts of calcium into the structure of these two compounds is reflected by changes in their X-ray line intensities. At pH 5 the solids that form appear not to be a physical mixture of calcium and iron arsenates, but rather a mixed Ca-Fe arsenate compound with distinct X-ray, IR and DTA - TG patterns. This compound has been designated Type-4 and has a composition, CaFe<sub>2</sub>(AsO<sub>4</sub>)<sub>0.33(8-2x)</sub>(HAsO<sub>4</sub>)<sub>x</sub> (where x < 1) and is likely to be admixed with the Type-1 compound. The solids synthesised at pH 7 appear to be mixtures of crystalline calcium and iron arsenates.

The study has indicated the importance of solution pH and how calcium is not easily incorporated into any distinct Fe-Ca arsenate compounds. During hydrothermal precipitation at elevated temperatures and low initial pH's (< 1)

iron can stoichiometrically remove arsenic from Fe-Ca-AsO<sub>4</sub> solutions. It is only at pH's greater than 3 that calcium starts to precipitate and where it may exist only as physical mixtures with amorphous ferrihydrite.

The experimental data on the Ca-AsO<sub>4</sub> system has provided a better understanding of the likely precipitation behaviour during the neutralisation of iron-arsenic effluents with lime. The compounds most likely to precipitate include: CaHAsO<sub>4</sub>.xH<sub>2</sub>O, Ca<sub>5</sub>H<sub>2</sub>(AsO<sub>4</sub>)<sub>4</sub> or a basic calcium arsenate-type compound. At low temperatures during neutralisation of arsenical liquors by the addition of excess lime, any sulphate present will preferentially combine with calcium to form gypsum, removing most of the sulphate from solution. At pH1 - 3, arsenical ferrihydrite will begin to form, which will remove most of the arsenic from solution, if sufficient iron is present. Only if the Fe:As ratio in the liquor is low will arsenic be left in solution to combine with the lime to form calcium arsenates, which will begin to precipitate at pH3 - 4. While it has been shown experimentally that a Ca-Fe-As compound does exist (Type-4), this is produced under rather specific conditions and hence it is unlikely this compound will form during ambient temperature neutralisation.

# Chapter 8

## The solubilities of the Ca-Fe-AsO<sub>4</sub>-SO<sub>4</sub> solids

## 8.1 Introduction

The relative solubilities of the arsenical compounds precipitated during the course of the work (Chapters 5 to 7) were assessed by the MARG and EPA TCLP tests (Chapter 3). As the solids were fully characterised, reasonably pure samples of the individual compounds could be tested and their relative solubilities were empirically assessed. While the solubility of a compound is no real indicator of its long term stability, it is an important parameter in the assessment of the solid and gives some indication of the likely behaviour of that compound in the environment.

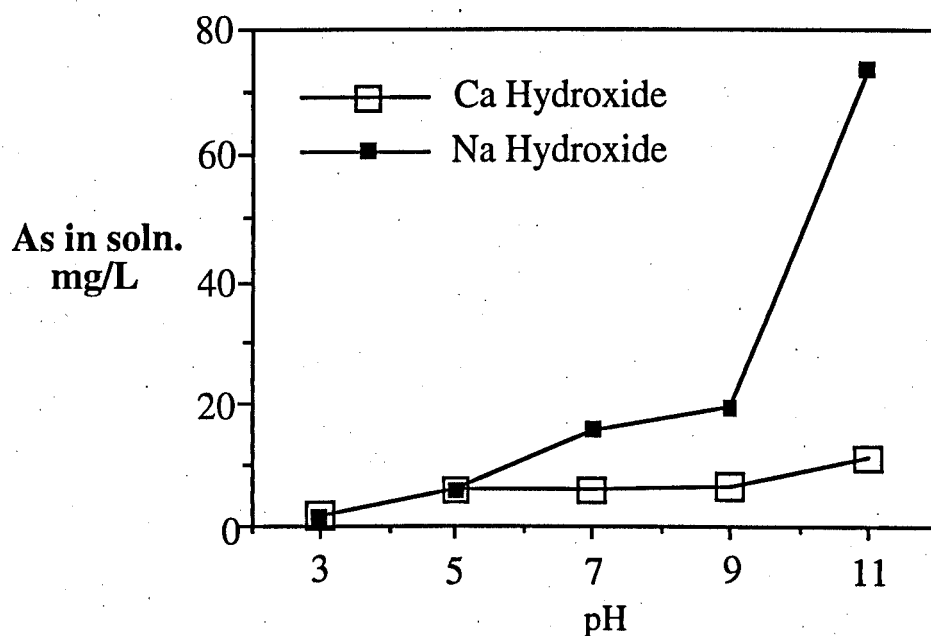
No attempt was made to determine the absolute solubility of the precipitated solids. The tests allowed the relative solubilities to be determined and from this work the least soluble compound was identified. After identifying the least soluble arsenate compound larger scale tests could then be focused on producing such material, with the possibilities of treating real arsenical effluents and dusts.

## 8.2 Solubility of the Fe-AsO<sub>4</sub> solids (pH<1)

During initial solubility test trials using the MARG test, when Ca(OH)<sub>2</sub> was used in place of NaOH for the adjustment of the pH of the test solutions, major differences in the soluble arsenic levels were observed in the pH 7 - 11 solutions (see Figure 8.1). The reasons for these differences are thought to be due to the influence of calcium in solution which seems to lower the apparent solubility of arsenic. Reduced levels of soluble arsenic were also found in EPA TCLP tests when gypsum and calcium nitrate were deliberately added to test the influence of the presence of calcium (Appendix 5). In the determination of the solubilities of arsenical compounds, the interaction of arsenic with calcium adds complications to the interpretation of the results. For this reason it was found preferable to use NaOH to control the pH in solubility tests rather than lime and so avoid these interference effects.

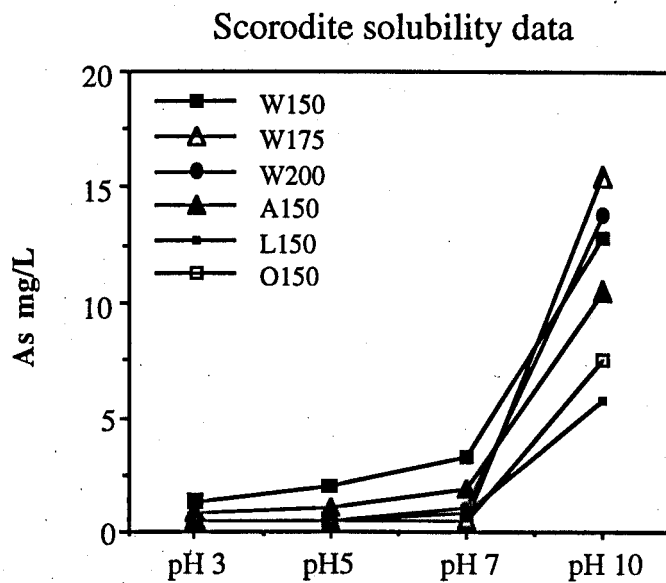
The solubility test results showed that the relative solubilities of the individual solids measured after 7 days were comparable to those found after 180 days. Representative solubility data of the precipitated compounds are

given in Figure 8.2 - 8.4, which illustrates the behaviour of scorodite, Type-1 and Type-2 compounds as a function of pH. These compounds were precipitated at various solution compositions and temperatures. For each compound type, a range of solubilities is apparent. This is most pronounced for the Type-1 compounds, where the solubility varies according to the hydration state of the solid, with the more hydrated solids being more soluble. It is evident that in all cases, arsenic solubility increases with pH, with relatively high solubilities occurring at pH 10 and above.



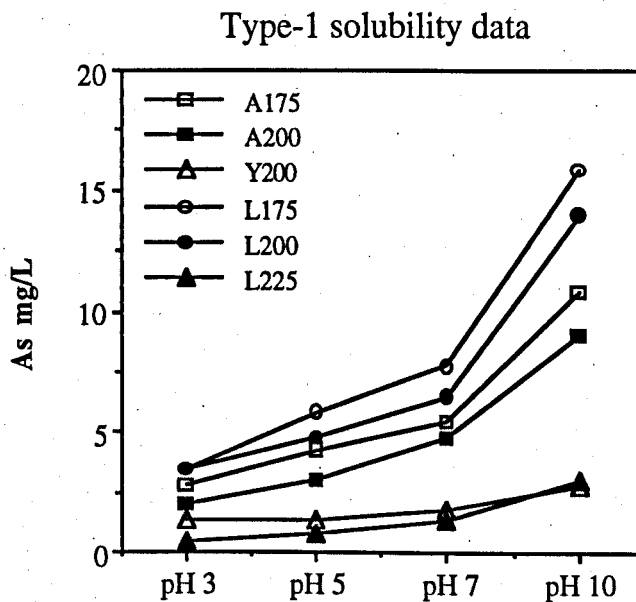
The tested solid was precipitated from a solution of Fe:As 2.3:1 at a temperature of 150°C and pH 5.

Figure 8.1 The influence of calcium and sodium hydroxide used for pH adjustment in the MARG static bottle test solutions



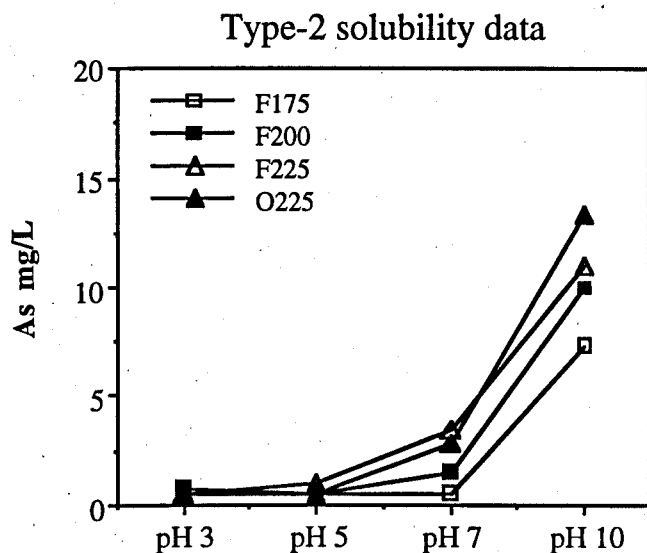
Note - Letters denote the composition of the starting solution (see Figure 3.1) and the numbers indicate the temperature of precipitation

Figure 8.2 Solubility plots of the scorodite compounds



Note - Letters denote the composition of the starting solution (see Figure 3.1) and the numbers indicate the temperature of precipitation

Figure 8.3 Solubility plots of the Type-1 compounds



Note - Letters denote the composition of the starting solution (see Figure 3.1) and the numbers indicate the temperature of precipitation

Figure 8.4 Solubility plots of the Type-2 compounds

In the EPA TCLP test the solution conditions are more aggressive and a lower liquid to solid ratio (20:1) is used compared with the MARG procedure (500:1). These differences result in higher apparent solubilities in the EPA tests due mainly to the nature of the buffered solution, however, the trends are the same as those determined by the MARG tests. The scorodite and Type-2 compounds are of relatively low solubility (<5mg/L) and are considered to be non-toxic according to the EPA criterion. The Type-1 compound is, however, generally more soluble over the range of pH's examined. The solids formed during high temperature precipitation using solutions of iron(III) sulphate and  $As_2O_5$  were solubility tested using the EPA TCLP method, the results of which are given in Table 8.1. For solutions with a Fe:As ratio >1.5:1 scorodite or the Type-2 compound is precipitated, which have low solubilities, whereas the solids formed from solutions of Fe:As <1.5:1 precipitate the Type-1 compound which accounts for their higher solubilities.

The EPA TCLP solubility data for the high temperature crystalline compounds are compared with those for Fe:As solids precipitated at ambient temperatures (20°C) and pH5 in Table 8.2, the latter solids being analogous to those formed during the neutralisation of arsenical liquors in commercial operations. The high Fe:As ratio (>2.3:1), gelatinous, low temperature solids

show lower solubilities than the high temperature crystalline solids precipitated from low pH(<1) solutions. However, low temperature solids precipitated from solutions with Fe:As <2.3:1 show much higher solubilities than the corresponding high temperature precipitates.

**Table 8.1** EPA test results on Fe:As compounds precipitated using solutions of iron(III) sulphate and arsenic(V) at the natural pH(<1)

Precipitation Temp (°C)	EPA TCLP filtrate - As (mg/L)				
	9:1	4:1	2.3:1	1.5:1	1:1
225	<0.10	1.04	0.44	4.70	11.90
200	nd	1.58	0.34	4.90	16.70
175	0.14	1.14	0.74	1.50	24.10
150	nd	nd	0.80	1.06	30.60

nd - not determined, \* the phases present in the solids can be found from Figure 5.5

**Table 8.2** Solubilities of high and low temperature precipitates measured by the EPA TCLP method

Precipitation Conditions	Sample (conditions of precipitation)*	EPA TCLP filtrate@ (As mg/L)
pH Natural (<1) High Temperature	Scorodite (Fe:As 2.3:1, 150°C)	<0.80
	Type-2 (Fe:As 2.3:1, 200°C)	<0.34
	Type-1 (Fe:As 1:1, 225°C)	11.9
pH 5 Low Temperature	Ferrihydrite (Fe:As - 9:1, 20°C)	0.4
	Ferrihydrite (Fe:As - 2.3:1, 20°C)	1.2
	Ferrihydrite (Fe:As - 1.5:1, 20°C)	50.2

\* starting solutions of iron(III) sulphate and As(V) @ 20hrs end-over-end agitation



### 8.3 Solubility of the Fe-AsO<sub>4</sub> solids (pH5)

The EPA TCLP results for the solids precipitated at pH5 at low temperatures show that in general the compounds have a lower solubility as the Fe:As ratio increases, i.e. 1:1 to 9:1 (Table 8.3 and summarised in Figure 8.5). However, at high temperatures (225°C) the reverse situation prevails, in that the lower the Fe:As ratio, the lower the solubility. The solids precipitated at low temperature are composed of ferrihydrite, the more arsenic-rich solids (1:1) are composed of amorphous light brown coloured material, while the more iron-rich are dark brown in colour. At elevated temperatures, the more arsenic-rich solids (1:1) are less soluble because they are composed of the crystalline Type-3 compound. The elevated temperatures allow the nucleation and growth of the Type-3 compound from the amorphous Fe-As gelatinous material and the structural reorganisation and reduction in surface area produces a less soluble compound. Figure 8.5 shows the general solubility changes as a function of temperature and molar Fe:As ratio, the reasons for the changes are identified on the diagram.

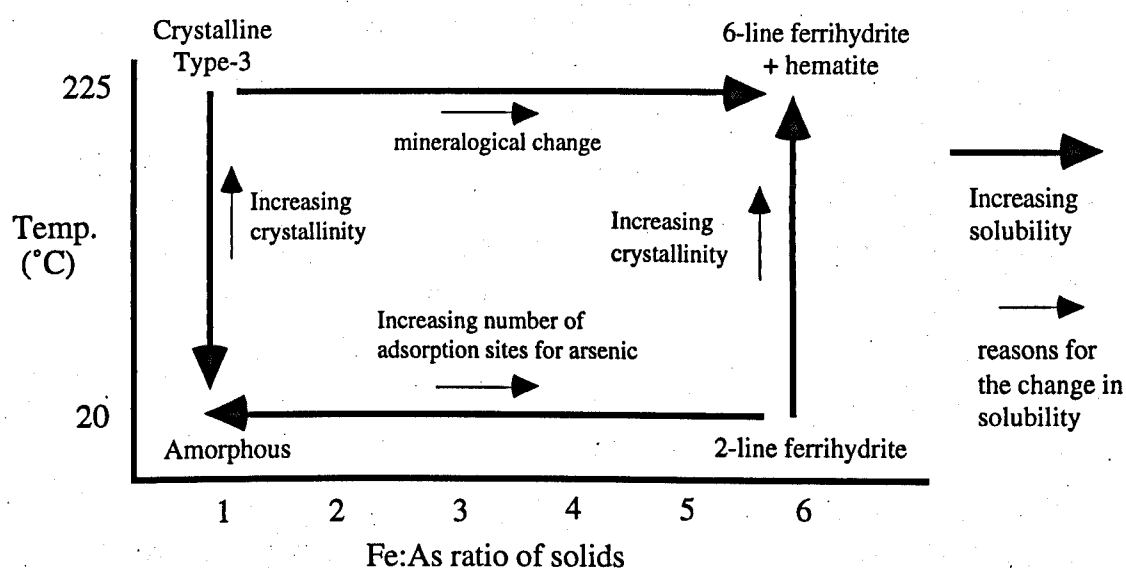


Figure 8.5 Solubility behaviour of solids precipitated from pH5 solutions at different temperatures and Fe:As ratios

**Table 8.3** EPA TCLP test results on Fe:As solids precipitated using solutions of Iron(III) sulphate and As(V) at pH5 (summarised in Figure 8.5)

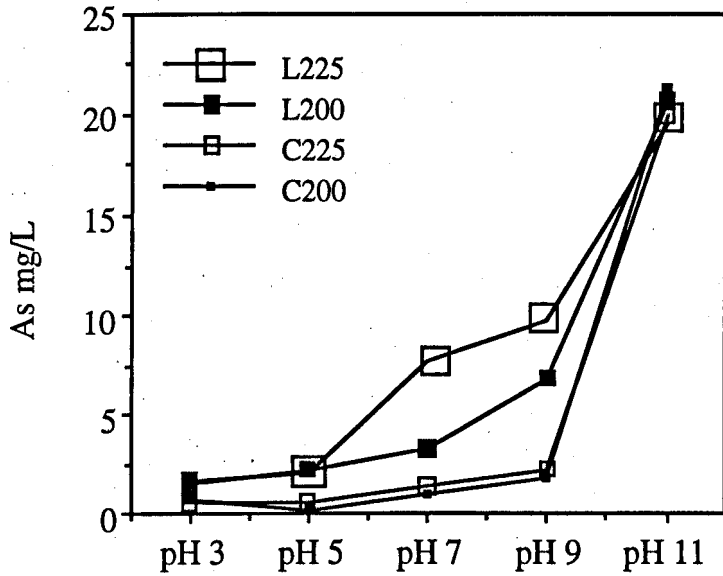
Precipitation Temp. (°C)	As mg/L in filtrate				
	1:1	1.5:1	2.3:1	4:1	9:1
225	19.6	56.3	82.8	116.0	51.7
175	67.9	71.1	58.8	11.8	34.4
125	192	56.1	20.1	3.1	<0.1
75	267	43.6	0.75	0.29	<0.1
20	350	35.6	0.5	<0.1	<0.1

The Type-3 compound as measured by the TCLP test has a solubility of 19.6mg/L, this is however, more soluble than the low temperature, high Fe:As, ferrihydrite-containing solids, which have arsenic solubilities of <0.1mg/L. The more iron-rich solutions yield solids which become more soluble at higher precipitation temperatures. In these solutions the character of the ferrihydrite changes at elevated temperatures with the conversion of the 2-line ferrihydrite into a mixture of 6-line ferrihydrite and hematite. These latter compounds do not adsorb arsenic as effectively as the less ordered, low temperature precipitates, which accounts for the greater arsenic solubility shown by the higher temperature precipitates. The reverse of this behaviour is shown by precipitates whose Fe:As ratios are <2 (Table 8.3). For these materials arsenic solubilities decrease with increasing precipitation temperature as a more crystalline solid is formed (Figure 8.5).

Figure 8.6 shows the solubility of a number of Type-3 compounds using the MARG test. In general the Type-3 compounds are more soluble than the scorodite and Type-2 compounds (Figures 8.2 and 8.4).

During the MARG solubility testing it was found that when the test solution was at pH3 which is close to the pH of ferrihydrite precipitation (~2.2), most of the arsenical solids undergo only minimal dissolution. This is possibly related to the fact that the arsenic is not easily released as ferrihydrite can reprecipitate immediately and simultaneously re-adsorb any arsenic from solution.

### Type-3 solubility data



Note - Letters denote the composition of the starting solution (see Figure 3.1) and the numbers indicate the temperature of precipitation

Figure 8.6 Solubility plots of the Type-3 compounds

#### 8.4 Solubility of the Ca-AsO<sub>4</sub> solids

The relative solubilities of the individual calcium-arsenate solids (see Chapter 7), as indicated by the EPA TCLP tests, are shown in Table 8.4. Their solubilities are compared with the various iron arsenate compounds in Table 8.5. It may be seen that the calcium compounds are significantly more soluble than the iron compounds at all temperatures and precipitation pH's. The arsenic levels in solution for the calcium compounds fall in the range 900 - 4400mg/L, while the iron arsenates, such as scorodite, show solubilities which are generally at least two orders of magnitude lower.

**Table 8.4 EPA TCLP results on Ca-AsO<sub>4</sub> solids (as shown in Table 7.2) precipitated at various pH's and temperatures**

Precipitated Temp(°C)	As mg/L in filtrate following solubility testing of solids precipitated at different pH's				
	pH6	pH7	pH8	pH9	pH10
20	3400	3150	950	1010	1220
50	nd	3120	2990	nd	2160
75	4355	3740	3686	nd	2375
100	nd	2190	2260	2945	3595
125	3280	nd	2615	2715	3555
150	3610	2870	2710	nd	2230
175	3330	2800	2485	1650	2650
200	nd	2170	3010	nd	2110
225	2535	2865	2360	nd	2020

nd - not determined

**Table 8.5 Relative solubilities of the calcium and iron arsenates**

Precipitation mineral-type	Relative solubility (As mg/L in filtrate )*
Scorodite	<5
Type-1	5 - 85
Type-2	<5
Type-3	<30
Haidingerite   Pharmacolite	3120 - 4360
Guerinite	950 - 3680
Weilite	2170 - 3610
Ca-arsenate	1650 - 3600

\* relative solubility using the US EPA TCLP test on precipitated compounds

## 8.5 Solubility of the Ca-Fe-AsO<sub>4</sub> solids

### 8.5.1 High temperature

The results of the EPA TCLP testing on the Ca-Fe-arsenates (see Chapter 7) show that the higher the calcium content of the solution (Ca:Fe:As - 3:1:4) and hence that of the precipitate, the more soluble is the compound (Table 8.6). The more iron-rich solids, produced from the 1:3:4 solutions are significantly less soluble, with the higher temperature solids being the least soluble. The intermediate solution compositions yield solids with intermediate solubility (1:1:2). Solids formed at pH1 and 3 (125 - 225°C) from all solution composition ratios are predictably of relatively low solubility because they are composed of either scorodite or the Type-1 compound. The incorporation of trace amounts of calcium in these compounds does however yield solubilities which are higher than those of the pure iron(III) arsenate compounds. The progressive increase in solubility as the pH of precipitation is increased reflects the higher amount of calcium that has been precipitated. Increasing the temperature of precipitation has the effect of making the solids less soluble (e.g. Ca:Fe:As 1:3:4, pH5, 20 to 225°C), possibly due to the formation of more crystalline phases which dissolve more slowly than their finer-grained amorphous counterparts. The influence of crystal grain size is a kinetic effect which does not necessarily imply greater stability, but which is clearly a beneficial characteristic for the slow release of arsenic.

### 8.5.2 Low temperature

A range of Ca-Fe-AsO<sub>4</sub> solid compositions was produced by precipitation at 20°C using calcium hydroxide in the adjustment of the pH of precipitation (3 to 12). These solids were subjected to the EPA TCLP test and the results are given in Figure 8.7. The more iron-rich compounds are the least soluble (i.e. Ca:Fe:As 1:3:4), the arsenic being mainly adsorbed onto ferrihydrite, with any remaining arsenic combined with calcium to form the hydrogen arsenate compound (see Table 8.6). The solids are most soluble when precipitated from pH6 - 7 solutions. As the precipitation pH is increased above 7, the excess calcium in solution combines with any available arsenic and leads to lower apparent solubilities.

**Table 8.6** EPA TCLP testing results on Ca-Fe-AsO<sub>4</sub> solids formed at various pH's and temperatures

	Precipitation Temp.(°C)	As mg/L in TCLP filtrate				
		pH1	pH3	pH5	pH7	pH9
<b>Ca:Fe:As</b> <b>3:1:4</b>	20	nd	1215	1490	3205	1760
	50	nd	790	980	2650	2680
	75	nd	920	890	2250	3625
	100	nd	760	1110	2180	2590
	125	nd	595	880	2745	2220
	150	nd	nd	845	nd	2375
	175	nd	880	1065	3050	2380
	200	nd	710	1445	2735	2310
	225	nd	180	625	2200	1445
<b>Ca:Fe:As</b> <b>1:1:2</b>	20	nd	510	676	1010	245
	50	nd	545	620	1160	420
	75	nd	495	564	1000	2335
	100	nd	325	373	456	2320
	125	nd	375	341	215	2080
	150	nd	330	375	200	2315
	175	nd	360	298	105	2390
	200	23.1	430	68	62	2240
	225	nd	1.1	7.0	87	2020
<b>Ca:Fe:As</b> <b>1:3:4</b>	20	nd	510	410	280	230
	50	nd	375	430	550	1160
	75	nd	375	75	105	2115
	100	nd	275	nd	nd	3165
	125	nd	130	25	nd	3580
	150	12.6	48.4	170	205	3215
	175	6.9	31.4	180	290	3200
	200	6.9	7.4	65	215	3350
	225	nd	3.7	3.0	2.5	3770

\* pH of the initial solution prior to hydrothermal precipitation nd - not determined

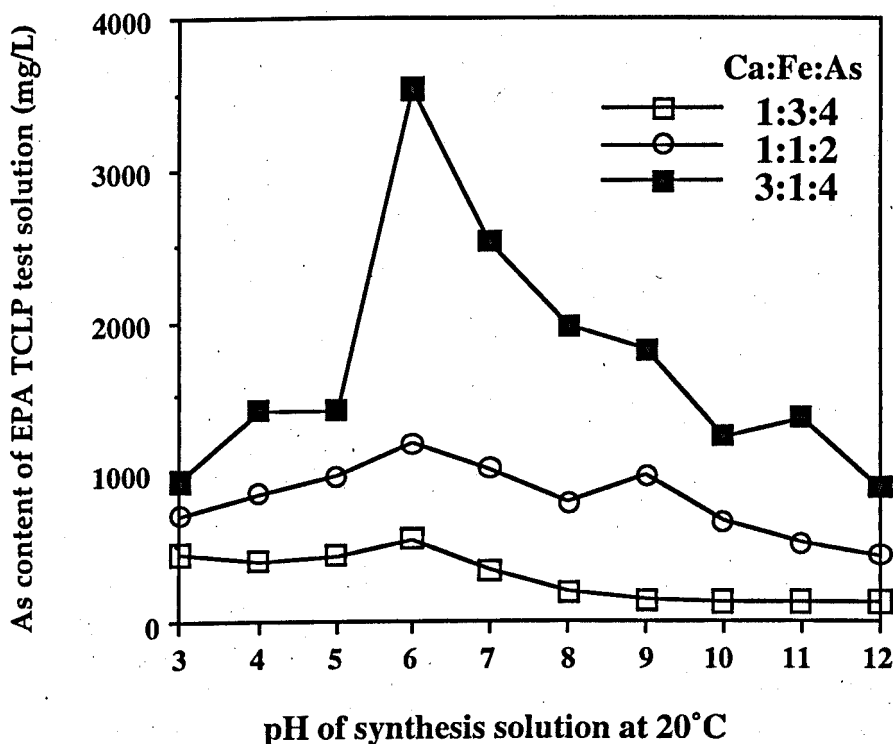


Figure 8.7 EPA TCLP solubility plots of the Ca-Fe-As solids stabilised at various pH's with calcium hydroxide at 20°C

### 8.6 Solubility of some naturally occurring arsenate minerals

Finely milled samples of individual arsenate minerals, which were obtained from the Natural History Museum, were solubility tested using the MARG test procedure, the results are given in Table 8.7. The minerals show similar behaviour to the synthetic solids in that they are highly soluble at high pH(11) and are mostly of low solubility at low pH(<5). An anomalous result is the solubility of the crystalline scorodite and kankite samples at pH3, where the solubility starts to increase. The other arsenate mineral samples also show this trend but to a lesser extent. A number of the synthesised crystalline compounds have a similar solubility to those of the natural minerals (Table 8.8).

**Table 8.7** MARG solubility test results (As mg/L) on finely milled naturally occurring mineral samples (100% <38 $\mu$ m)

Mineral Name	Ideal Formula	Solubility data (As mg/L)*				
		pH3	pH5	pH7	pH9	pH11
Bukovskyite	Fe <sub>2</sub> AsO <sub>4</sub> SO <sub>4</sub> OH .7H <sub>2</sub> O	0.19	0.10	0.07	0.51	84.30
Kankite	FeAsO <sub>4</sub> .3.5H <sub>2</sub> O	3.10	0.11	0.94	1.79	44.30
Scorodite#	FeAsO <sub>4</sub> .2H <sub>2</sub> O	4.60	0.10	0.07	0.08	2.05
Scorodite°	FeAsO <sub>4</sub> .2H <sub>2</sub> O	0.57	0.40	1.80	2.25	93.50
Scorodite\$	FeAsO <sub>4</sub> .2H <sub>2</sub> O	0.12	0.04	0.62	1.85	61.00
Pitticite	Fe-Zn-Co-As .xH <sub>2</sub> O	0.47	0.10	0.10	5.80	137.20
Yukonite	CaFe <sub>5</sub> (AsO <sub>4</sub> ) <sub>6</sub> (OH) <sub>9</sub> .18H <sub>2</sub> O	21.60	2.01	2.36	4.10	18.50
Arsenosiderite	Ca <sub>3</sub> Fe <sub>4</sub> (OH) <sub>6</sub> (H <sub>2</sub> O) <sub>3</sub> (AsO <sub>4</sub> ) <sub>4</sub>	2.16	0.40	0.62	0.71	2.17
Symplesite	Fe <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> .8H <sub>2</sub> O	nd	nd	nd	2.42	50.50

\* test solution compositions after 7 days, nd - not determined  
 \$ scorodite-sericite schist, # crystalline scorodite, ° porous scorodite,

**Table 8.8** MARG solubility test results on typical precipitated compounds

Compound -Type	Temperature of precipitation	Solubility test data (As mg/L)*			
		pH3	pH5	pH7	pH10
Type-2	175°C	<0.5	0.8	<0.5	7.3
Scorodite	150°C	<0.5	<0.5	0.8	5.8
Type-1	200°C	3.5	4.8	6.5	14.0

\* test solution compositions after 7 days

## 8.7 Solubility of dehydrated arsenical ferrihydrite

Pure ferrihydrite is thermodynamically unstable compared to most of the other iron hydroxide-type phases, and with time it is predicted that it will transform into goethite, hematite or a mixture of the two. The transformation can be blocked by small amounts of adsorbates such as silica, phosphates, coprecipitated aluminium and a range of organics [78]. However, from X-ray



diffraction results on arsenic-rich ferrihydrite it has been found in this work that arsenate also blocks this transformation. On examining the influence of drying on the solubility of arsenical ferrihydrites (Table 8.9) it was found that the solubility of the materials increased with increased dehydration. Accelerated ageing tests (i.e. drying) converts the ferrihydrite into a more dense dehydrated form and reduces the active surface area that can adsorb arsenic. The compound can be considered to be a hydrated form of hematite ( $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ) and may be identical in character to limonite formed in gossans, these natural amorphous iron oxides possibly also remain as non-crystalline compounds due to the influence of adsorbates. The widespread existence of limonite in the geological record indicates that such compounds have long term stability in the environment. In soils and gossans, the ferrihydrite may retain its characteristics and efficiently adsorb and extract arsenate from migrating solutions.

**Table 8.9** The influence of drying temperature on the solubility of arsenic from amorphous ferrihydrite-type compounds

Drying temperature (°C)	EPA TCLP test results (As mg/L)		
	Fe:As ratio of ferrihydrite		
	1.5:1	2.3:1	9:1
20	35.6	0.5	<0.10
60	50.7	6.3	0.32
100	59.3	8.9	0.28

\* Duration of drying - 5 days

Arsenical ferrihydrite will remain insoluble as long as it remains moist since it will retain its high surface area and adsorptive properties. However, if arsenical ferrihydrite becomes dehydrated, arsenic solubility will increase, as shown by accelerated dehydration experiments, see Table 8.9. To some extent this simulates the natural drying of ferrihydrite materials in arid climatic conditions and shows that arsenical ferrihydrite becomes more soluble with time. The apparent increase in solubility of the arsenical ferrihydrite on drying also explains differences in solubilities between ferrihydrite-rich samples that have been dried and those tested wet (see Appendix 1, example 6).

## 8.8 Conclusions

The solubilities of the scorodite and Type-2 compounds precipitated from low pH solutions (<1) are by far the lowest in all of the crystalline compounds examined. These are comparable to the high Fe:As arsenical ferrihydrites precipitated at ambient temperatures. This suggests that they are suitable candidates for disposal. The crystalline nature of the compounds and their large grain size up to 20 - 50 $\mu$ m appears to be an important characteristic which should slow any release of any arsenic to ground waters.

The solubility test results on the precipitated solids from Fe-AsO<sub>4</sub> solutions at pH5 show that the temperature of precipitation appears to have an important influence on the stability of the solids. It is inferred that the main effect of temperature is on the crystallinity of the compounds rather than on the formation of different compounds. In the samples precipitated at pH5, ferrihydrite is formed and its presence helps stabilise the arsenic. However, the ferrihydrite formed at higher temperatures (6-line form) is significantly more crystalline and therefore likely to have a lower surface area than the amorphous low temperature ferrihydrite (2-line form). The increased crystallinity of the 6-line ferrihydrites apparently weakens the binding of the adsorbed arsenic, since they show higher arsenic solubilities than the low temperature, 2-line ferrihydrites.

EPA TCLP testing of the calcium-arsenate phases precipitated under a range of conditions showed that they are considerably more soluble than the iron arsenate phases. The calcium-arsenate solids precipitated at higher temperatures, while being more crystalline and of different compositions, have similar solubilities to those formed at lower temperatures. Furthermore, variations in the pH of the solutions do not have a major influence on the solubilities of the calcium arsenate compounds. This work has examined a wide range of solution compositions and it has been found that all the hydrothermal calcium arsenate-type compounds that were produced had high apparent solubilities.

The solubility results on the solids formed during the hydrothermal treatment of Ca-Fe-AsO<sub>4</sub> solutions show that these are significantly more soluble than the corresponding calcium-free ferric arsenates. The presence of even small amounts of calcium in the crystal structure of scorodite and the Type-1

compounds exerts a destabilising influence and makes the solids more soluble than the pure Fe(III) arsenates. Hydrothermal processing of arsenical ferrihydrites (produced at elevated pH) at temperatures above 150°C has shown that these compounds can be converted to a crystalline Type-3 phase, but even this compound is considered toxic by the US EPA criterion (>5mg As/L). It would therefore appear that only those crystalline compounds precipitated at low pH (<1) are of a sufficiently low solubility to be considered for disposal.

# **Chapter 9**

## **Larger scale hydrothermal precipitation**

## 9.1 Introduction

Larger scale hydrothermal precipitation experiments using a 4 litre autoclave were conducted in order to validate the finding of the test tube experiments. While the test tube scale experiments were carried out over a 24 hour period shorter duration runs were carried out using the autoclave to establish the rates at which arsenic and iron are removed from solution. The work was designed to show the viability of hydrothermal precipitation as a potential method for the removal and stabilisation of arsenic from solutions.

While the precipitation of arsenic from solution as crystalline iron arsenate compounds is not novel, the understanding and control of the reactions has not been examined in any great detail. The current experimental work examines some of the parameters that govern precipitation and will help in the understanding of arsenic behaviour during hydrothermal processing.

## 9.2 Autoclave results

### 9.2.1 Initial precipitation experiments

A sequence of exploratory batch experiments were conducted in which solution were heated from ambient and samples were taken during the experimental runs (see Chapter 3). The precipitation results showed that temperature has an important influence on the rate at which arsenic was removed from solution. However, in these batch runs no clear relationship could be established between the arsenic removal and starting solution compositions. The rate at which the arsenic was removed was also found to be some function of the Fe:As ratio of the solution, with rapid precipitation being favoured by lower Fe:As ratios (1:1), while higher Fe:As ratios (>1:1) slowed the rates of precipitation. All of these experiments showed very high levels of arsenic removal (>90%). From the initial set of batch experiments to assess the influence of temperature, and Fe:As ratio it was clear that it was necessary to inject iron solutions into arsenic solutions that were stabilised at various temperatures so that important kinetic data could be obtained.

### 9.2.2 Batch and iron injection experiments

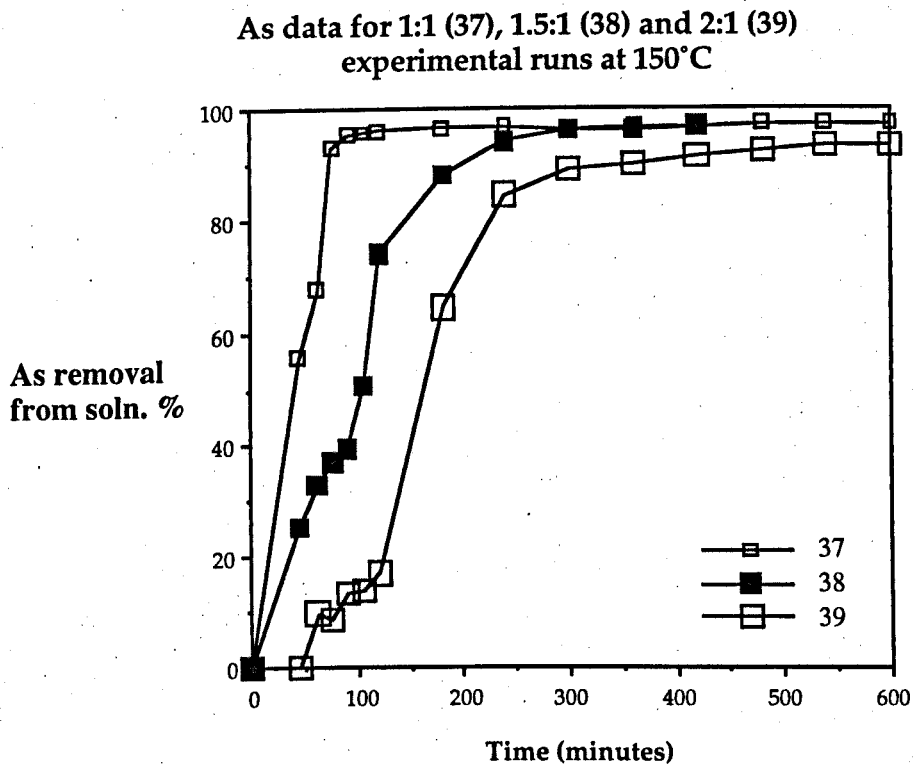
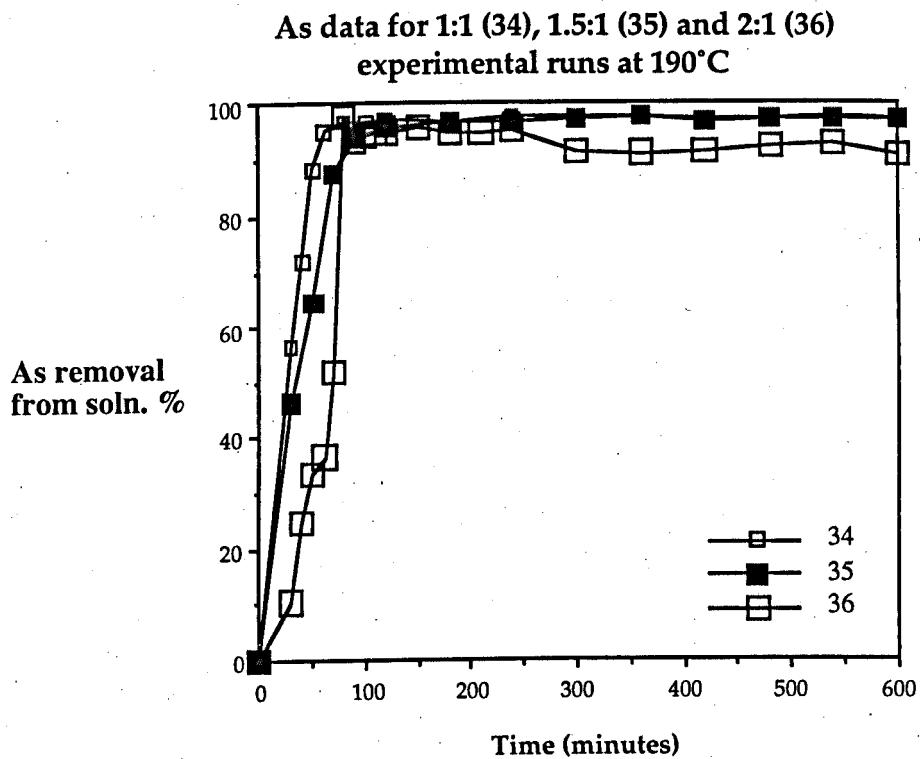
Long duration precipitation experiments (10hrs) in the autoclave were carried out at temperatures of 150 and 190°C, with Fe:As ratios in the starting liquors

of 2:1, 1.5:1 and 1:1 (21, 16 and 10.5g/L Fe, using 13g/L As throughout). Increasing iron levels in solution showed an appreciable influence on the precipitation of the arsenic as illustrated in **Figure 9.1**. The high iron containing solutions (>2:1) show slower rates of precipitation than those of lower Fe:As ratio (1:1). At lower temperatures (150°C) precipitation of arsenate from solution was reduced owing to slower rates of nucleation and mineral growth. Precipitation of iron from solution (**Figure 9.2**) is strongly influenced by temperature and Fe:As ratio with increased iron removal at higher temperatures (190°C) due to its precipitation from solution.

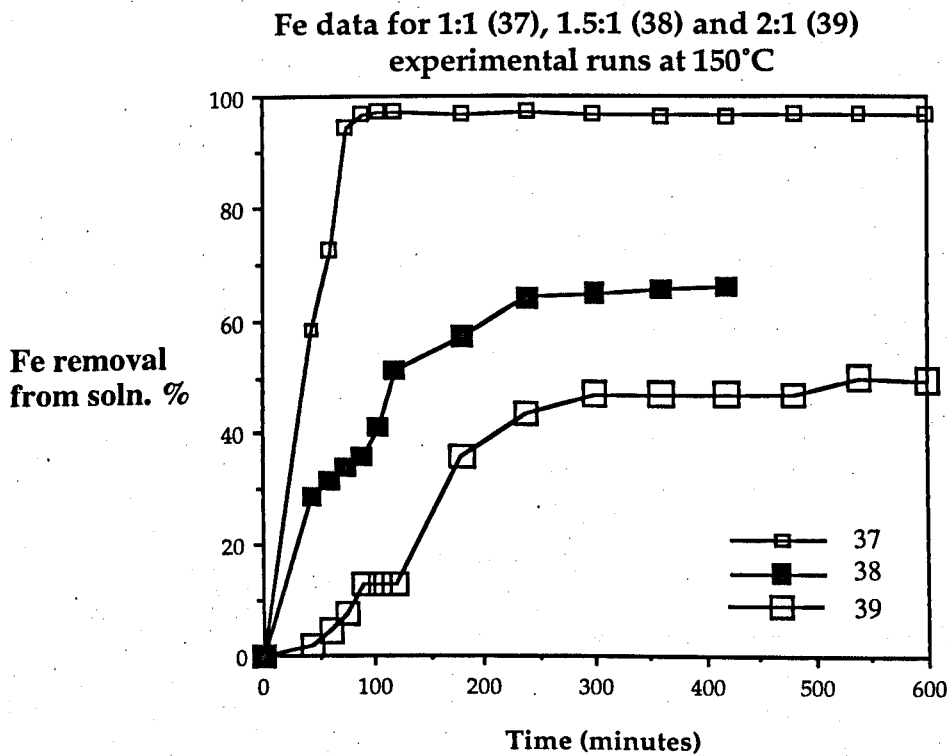
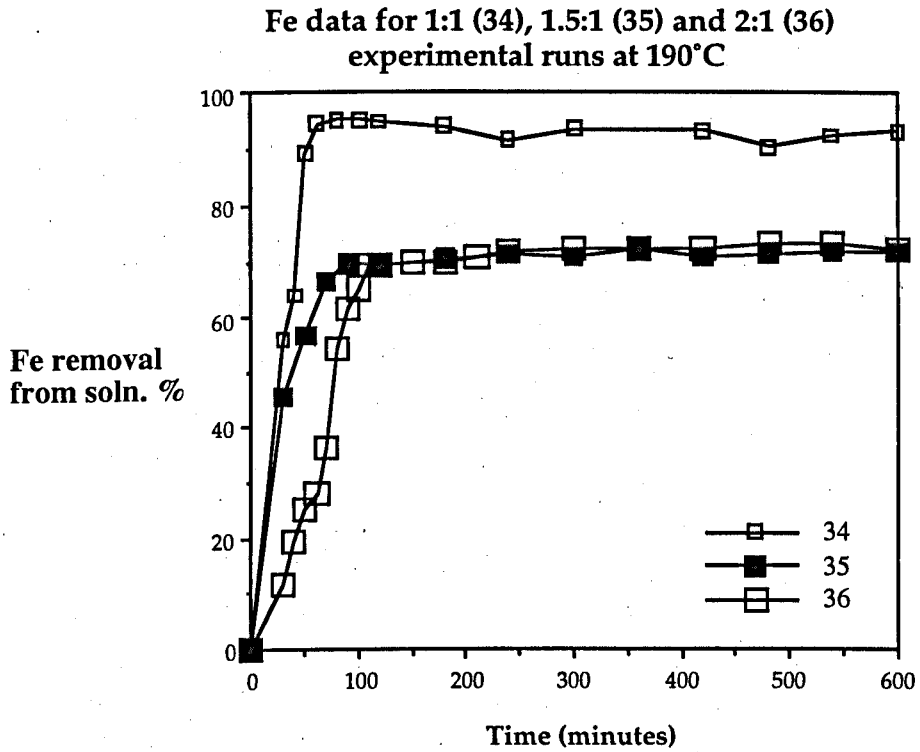
For the 150°C batch runs (**Figure 9.2**) the iron recoveries reach apparent equilibrium values of ~50%, ~66% and ~100%, respectively, for the Fe:As ratio 2:1, 1.5:1 and 1:1 solution compositions. This would be expected if part of the iron combined with available arsenate and precipitated as a scorodite (Fe:As 1:1) compound, with the remaining iron being left in solution. The slower rates of precipitation from the high iron solutions indicate chemical interference during the nucleation and growth of the scorodite compound. At higher temperatures (190°C) iron recoveries were very high and this was considered to be due to coprecipitation of amorphous iron compounds with the scorodite. Chemical analysis of the solid precipitates also reflect the higher iron and sulphate levels above those expected for pure scorodite or Type-2 components. In general the rates of precipitation of the iron and arsenic are very similar and this supports the idea of the formation of a gelatinous precursor from which the crystalline compounds ultimately grow.

For the iron injection runs (**Figure 9.3**) the precipitation of the iron and arsenate appeared to be very rapid, with almost total removal occurring during the first 25 minutes. The lower initial Fe:As solution composition (1:1) showed the most rapid removal of iron and arsenate from solution.

The solutions heated from ambient temperature and those runs where iron was injected into solutions held at high temperatures identified temperature, and Fe:As ratio as the most important controlling factors (**Figures 9.1 to 9.3**). The results showed that usually greater than 95% of the arsenic can be removed from solution by using temperatures greater than 150°C.



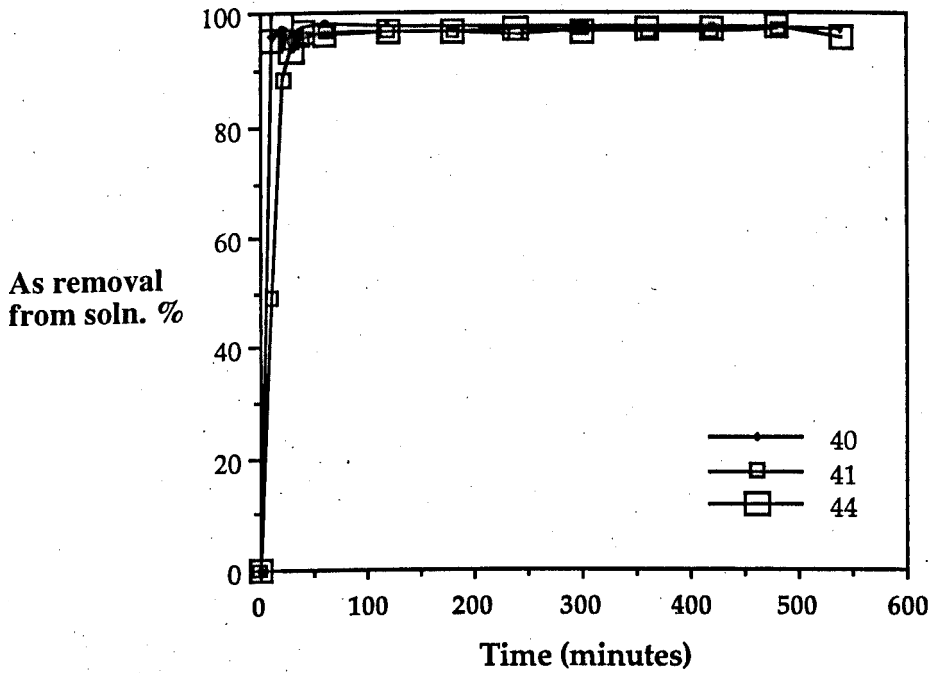
**Figure 9.1** Arsenic precipitation curves for the 190 and 150°C experimental runs (heating solutions from ambient temperature)



**Figure 9.2** Iron precipitation curves for the 190 and 150°C experimental runs (heating solutions from ambient temperature)



As data for 1:1 (40), 1.5:1 (41) and 2:1 (44)  
experimental runs at 190°C



As data for 1:1 (42) and 1.5:1 (43)  
experimental runs at 150°C

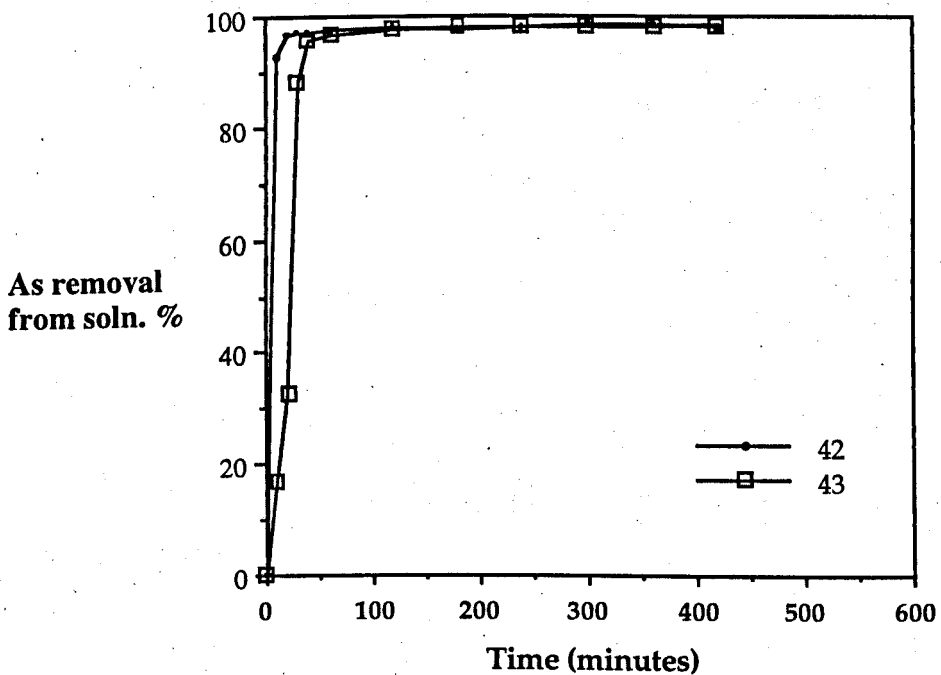


Figure 9.3 Arsenic precipitation curves for the 190 and 150°C experimental runs (Injecting iron solutions at elevated temperature)

From the one experimental run where ferric chloride was used as the source of iron (run 55) the arsenate was almost totally (97%) precipitated during the first five minutes. Precipitation and removal of arsenate from solution would appear to occur at a significantly faster rate than for the sulphate solutions (runs 40 - 44) which usually took ~25 minutes for a comparable removal of arsenate. The faster kinetics are explained by the absence of any gelatinous iron sulphate complex which would not normally form in chloride or nitrate media.

The settling of crystalline scorodite (generally  $<20\mu\text{m}$ ) in water was usually complete within less than ten minutes with only the ultra-fine particles remaining in suspension. The Type-2 compound tended to be coarser in grain size (up to  $50\mu\text{m}$ ) and settled faster than scorodite.

### 9.2.3 Arsenic injection

Iron arsenate precipitation was examined by the injection of an arsenate solution into an iron solution held at an elevated temperature ( $190^\circ\text{C}$ ). On heating an iron sulphate solution the iron is precipitated and undergoes a phase change, this was initially investigated by injecting 400 mL of iron(III) sulphate solution (210g Fe/L) into 3000mL of water at  $190^\circ\text{C}$ . The X-ray diffraction patterns of the precipitates removed from the autoclave during heating clearly showed the progressive change from a jarosite compound through to hematite after about 2 hours (Table 9.1 and Figure 9.4).

**Table 9.1** Semi-quantitative estimation of compounds in precipitates

Time (mins)	Compounds	Content*	Sample No.
1	Jarosite	100%	379
5	Jarosite	100%	380
15	Jarosite	100%	382
30	Jarosite + Hematite	~90% + ~10%	384
60	Jarosite + Hematite	~50% + ~50%	386
120	Hematite	100%	387

\* Semi-quantitative estimate based on XRD (see Figure 9.4)

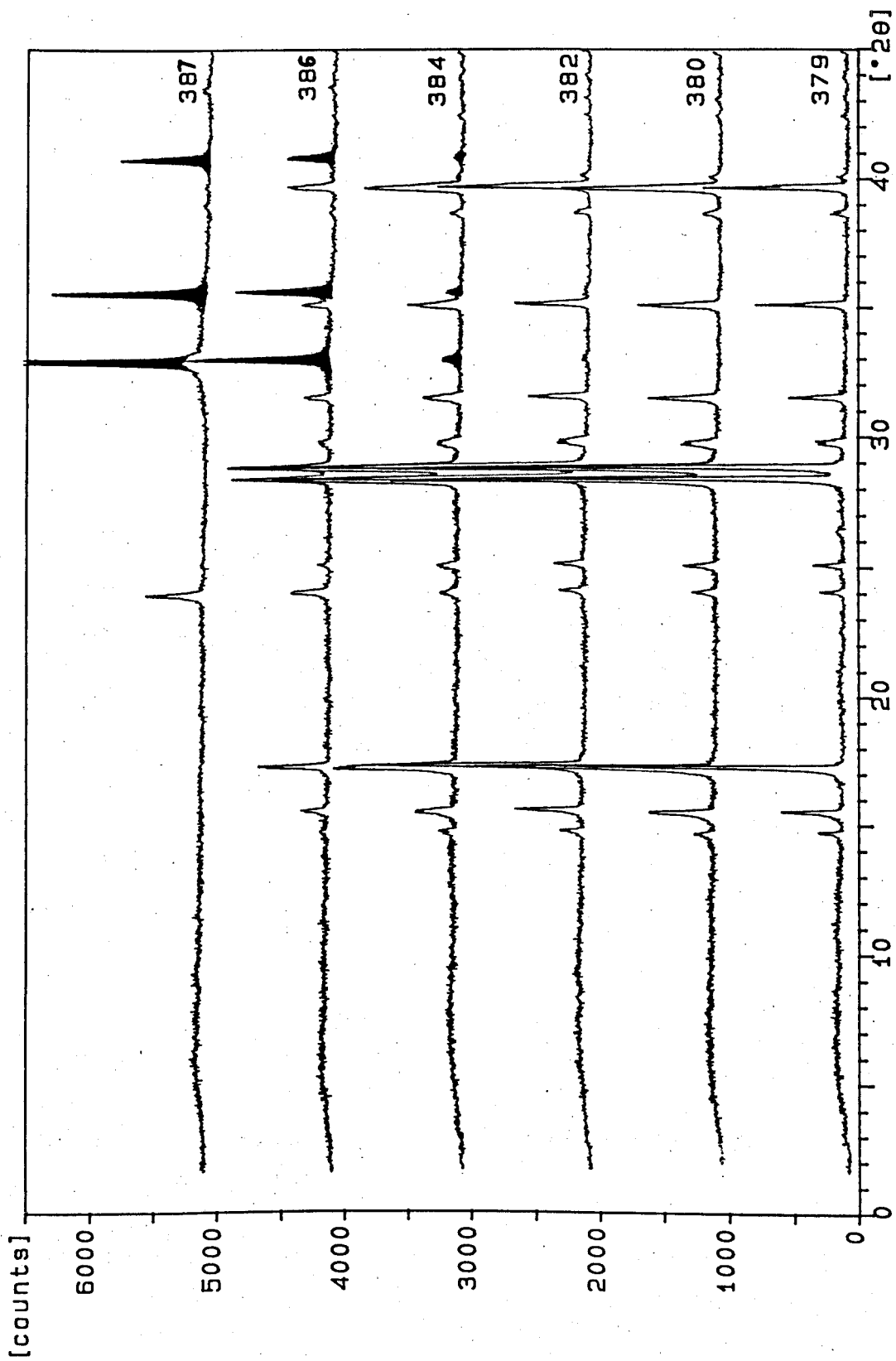
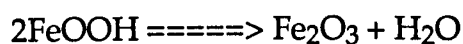
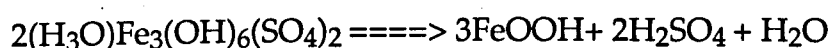


Figure 9.4 Transformation of hydronium jarosite to hematite over a 2hr period (shaded peaks represent hematite)

Injection of iron solution into hot water at 190°C initially formed a light brown solid which was found to be hydronium jarosite ((H<sub>3</sub>O)Fe<sub>3</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub>). Only after 30 minutes did hematite begin to form and total conversion to hematite occurred after 120 minutes (see also Section 2.5.3). The jarosite-hematite transformation required an induction period prior to the precipitation of a stable component, the conversion to an intermediate ferrihydrite or goethite possibly takes place which finally breaks down to hematite. No basic iron sulphate was formed in this experiment and this possibly suggests low levels of free sulphuric acid in the solution (<60g/L).

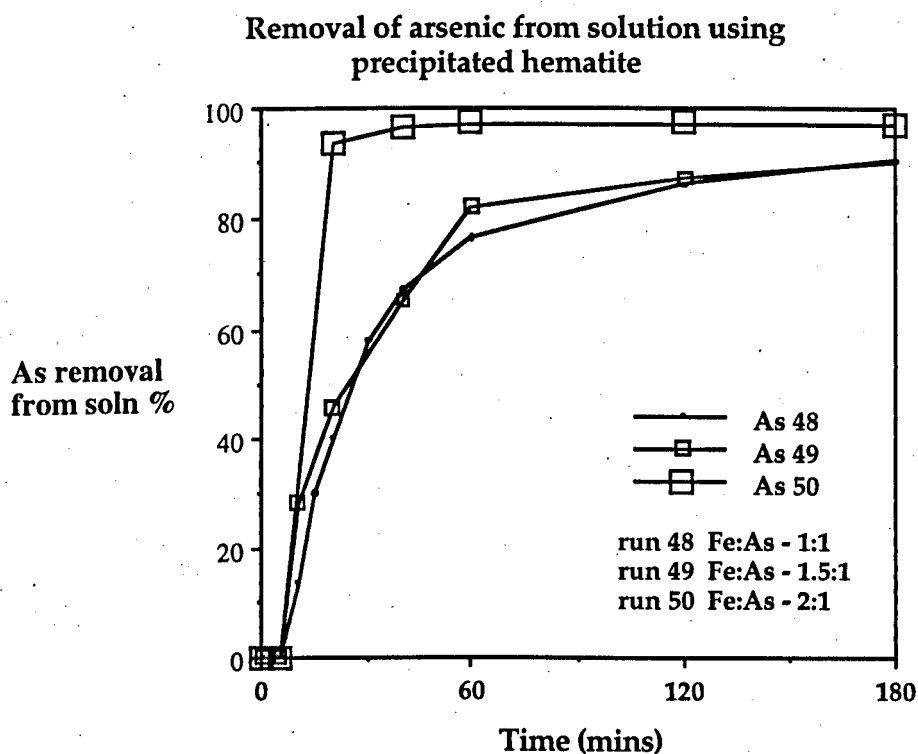


When arsenic was present in solution no evidence for the presence of the jarosite phase was found in the precipitated solids. This was possibly due to interference in the nucleation and growth of this phase and to the low pH of the solution (0.5 - 1.0). On comparing the solids from test tube experiments (24hrs) and large scale experiments it appears that those heated for a longer time have equilibrated, while those heated for only 2 - 3 hours may not necessarily represent a stable mineral assemblage. The type of solid precipitated hydrothermally will therefore be a function of time as well as temperature, pH and possibly iron, sulphate and arsenate concentration. The runs carried out at higher temperatures would favour an equilibrium assemblage.

Ferric sulphate containing solutions do appear to behave differently to the ferric nitrate and chloride based systems. The latter do not easily form complexes, such as the basic iron sulphate and jarosite compounds and for this reason the iron stoichiometrically can react with arsenic or simply form hematite or goethite when heated in the absence of arsenic.

The injection of an arsenate solution into an iron solution which has been heated for two hours simulates the reaction of arsenate (AsO<sub>4</sub>) with crystalline hematite. In Figure 9.5 the arsenate was introduced at time zero when most of the iron originally in solution was precipitated as hematite (runs 48, 49 and 50). Removal of arsenic from solution (6g/L) took place by

reaction of the hematite with dissolved arsenate to produce scorodite (as determined by XRD). The solid residues were still red in colour which indicated the presence of unreacted hematite in the solids. The higher amounts of hematite present in solution (Fe:As 3:1) removed arsenic faster than the low (Fe:As 1:1). Results indicated that the reaction preferably requires the hematite to be finely divided and agitated for the liquid-solid reaction to proceed.



**Figure 9.5** Arsenic removal from solution by precipitated hematite at 190°C

### 9.2.4 XRD examination of solids

An X-ray examination of selected solids removed from the autoclave following Fe(III) injection into arsenic solutions (Section 9.2.2) showed that crystalline scorodite precipitated within 5 minutes in the higher temperature runs (190°C). However, despite the obvious presence of scorodite in the X-ray pattern, a large portion of the solid was still amorphous. The solid precipitates taken from the lower temperatures injection runs (150°C) at 5 minutes were found to be totally amorphous. Above 170°C and with longer equilibration times, either scorodite or the Type-2 compound was formed.

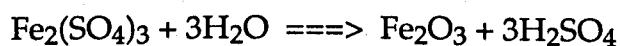
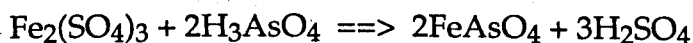
X-ray diffraction of the precipitated solids showed that the Type-2 compound ( $\sim\text{Fe}_3(\text{AsO}_4)_2(\text{SO}_4)(\text{OH})$ ) was only precipitated at temperatures of  $>175^\circ\text{C}$  when the Fe:As ratio of the solution was  $>1.5:1$ . This stoichiometry appears to be an important control on the solids that are precipitated from solution with scorodite being formed at Fe:As  $<1.5:1$ . During the heating of the solutions the solids changed directly from an amorphous compound into either crystalline scorodite or the Type-2 compound, depending on the temperature and solution composition; no intermediate compounds appear to exist.

### 9.2.5 Chemical analysis of solids

Solids from the hydrothermal precipitation experiments conducted at 150 and  $190^\circ\text{C}$  were chemically analysed and the compositions are given in Table 9.2. It can be seen that at the higher temperatures ( $190^\circ\text{C}$ ) greater amounts of sulphate were incorporated into the solid precipitates. The reason for this is that at higher temperatures the Type-2 compound develops, which can accommodate up to 18% sulphate, while at lower temperatures scorodite forms which has been shown to accommodate a maximum of only 5% sulphate in its structure. The high levels of sulphate in some of the scorodite-containing samples can be explained by the presence of an amorphous phase which contains high amounts of sulphate and iron. Higher Fe:As ratios than expected ( $<1.5:1$  for scorodite at  $150^\circ\text{C}$ , and  $>1.5:1$  for the Type-2 compound at  $190^\circ\text{C}$ ) and reduced levels of arsenate in the solids also suggest dilution caused by the presence of an amorphous phase which is not shown in the X-ray diffraction patterns.

### 9.2.6 Solution pH

The pH's of the solutions (at ambient temperature) removed from the autoclave following precipitation from Fe-AsO<sub>4</sub>-SO<sub>4</sub> solutions were taken. The pH's at ambient temperature are usually  $<1$  and the data show a predictable decrease with time. This reduction in pH correlates with the hydrolysis of iron from solution and the generation of free sulphuric acid (see equations below).



**Table 9.2** Chemical analyses of selected final solids precipitated during Fe(III) injection experiments at different temperatures

Precipitation conditions		Solids analyses			
Fe:As soln.	Temp (°C)	Fe (%)	AsO <sub>4</sub> (%)	SO <sub>4</sub> (%)	Fe:As (M)
1	150	15.0	38.30	3.33	1.0
1	190	23.0	57.17	2.34	1.0
2	150	24.8	53.84	7.35	1.1
2	190	30.1	41.26	17.07	1.8

### 9.2.7 Solubility of the precipitates

The larger scale precipitation experiments were conducted for a much shorter time than the initial test tube scale experiments (24hrs) and the solutions were also agitated continuously by a stirred propeller. From the experimental runs the precipitated solids were mostly crystalline scorodite and generally had low solubilities (<5mg/L) (Table 9.3).

From the solubility data on precipitates it was clear that the solids in the early stages of the experiments (10 - 60 mins) had higher than normal solubilities (>2mg/L As in TCLP filtrates). The colour (light brown) and the poor settling characteristics of these solids indicated that they were of low crystallinity, whereas the samples taken after 120 minutes were generally green in colour and settled very quickly. Therefore with prolonged heating the soluble solids appeared to crystallise and yield solids with significantly lower solubilities (Figure 9.6).

The erratic nature of some of the analytical results for the solubility tests suggests that washing was an important part of the solid preparation method and the higher than expected solubility of some of the final residues is explained by incomplete washing prior to the EPA TCLP tests. The amount of soluble amorphous solid in the samples was estimated to be in trace quantities (<0.2%) yet such a component could result in residues having solubilities as high as 30mg/L as measured by the EPA TCLP test.

Based on the experience from previous test tube experiment, highly crystalline compounds were mostly found to have low solubilities. It would therefore be expected that elevated temperatures (>190°C) or longer heating times should maximise the conversion of any trace amounts of amorphous materials into a low solubility crystalline form.

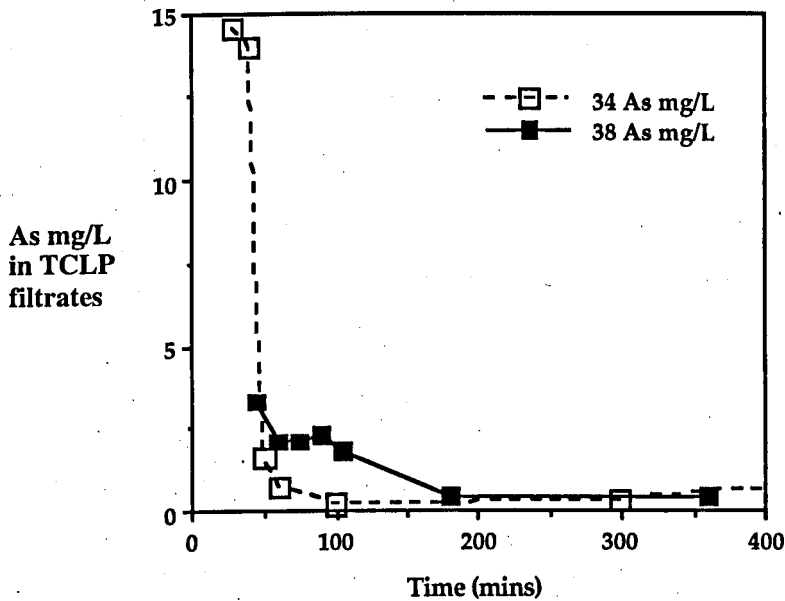
**Table 9.3** EPA TCLP solubility test results on solids taken during the long term precipitation experiments

Run No.	Time taken (mins)	As mg/L in filtrate*	Run No.	Time taken (mins)	As mg/L in filtrate*
Run 34	30	14.5	Run 39	45	<2
	40	14.0		60	2.2
	50	1.6		75	<2
	60	0.7		90	<2
	100	0.2		105	<2
	300	0.3		300	<2
	660	1.5	Run 40	10	0.9
Run 35	30	2.0		20	0.4
	50	<2		30	0.2
	70	3.9		40	0.1
	90	<2		60	0.2
	120	<2		180	0.1
	360	<2	540	1.9	
	480	<2	Run 41	10	2.0
660	<2	20		1.2	
Run 37	45	10.1		30	3.3
	60	1.7		40	2.4
	75	0.7		60	0.8
	90	2.1		120	0.2
	180	0.4	300	0.1	
	480	0.5	480	0.1	
	660	0.4	Run 42	10	0.2
Run 38	45	3.3		20	0.2
	60	2.1		30	0.4
	75	2.1		40	0.5
	90	2.3		120	0.5
	105	1.8		300	0.8
	180	0.4	480	0.7	
	360	0.4			

\* Lower limit of detection by AA for As <2mg/L, below LLD this is done by the hydride generation technique



### Influence of time on solubility of precipitate



(run 34 Fe:As 1:1, 190°C, run 38 Fe:As 1.5:1 150°C both heating from ambient)

**Figure 9.6** Solubility of arsenical solids as a function of time

### 9.3 Conclusions

The results of the hydrothermal precipitation experiments have shown that it is possible to precipitate >95% of the contained arsenic from solution by controlling temperature and Fe:As solution ratios. Higher temperatures are preferable as this promotes the growth of crystalline compounds from solution. For optimum conditions, the Fe:As ratio in the solution should be around 1:1. The compounds that are precipitated include scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ) and the Type-2 compound ( $\sim\text{Fe}_3(\text{AsO}_4)_2(\text{OH})(\text{SO}_4)$ ). Variations in the sulphate content of the scorodite-containing solids can be explained by the presence of an amorphous solid which may contain significant amounts of sulphate.

The presence of high Fe:As ratios in solution has a detrimental effect on the precipitation of arsenical compounds at elevated temperatures. It is evident that the Fe:As ratio in solution should approach 1:1 for optimum precipitation. Although higher Fe:As solutions can yield arsenic recoveries of

>90%, they require longer heating times due to slower rates of nucleation and growth.

Injection of Fe(III) into As(V) solution at 190°C resulted in the instantaneous formation of scorodite crystals. At lower temperatures the rates of nucleation and growth of crystalline arsenate compounds are slower and this accounted for the reduced arsenic precipitation. X-ray diffraction of solids removed from the autoclave after 5 mins at 190°C showed they were composed of crystalline scorodite plus an amorphous phase, whereas solids taken from solutions heated to lower temperatures were totally amorphous.

Precipitation experiments at elevated temperatures (>150°C) showed the important control of Fe:As ratio of the solution on the composition of the precipitated product. An Fe:As ratio of >1.5:1 ratio was required for the formation of the Type-2 compound while lower Fe:As ratios (<2:1) produce scorodite.

Heating solutions of iron sulphate to 190°C initially caused precipitation of hydronium jarosite, which in turn was transformed into hematite after a heating period of two hours. Injection experiments were conducted to contact arsenate with hematite. The work showed that arsenate slowly reacts with hematite to form crystalline scorodite.

From numerous experiments and from the erratic nature of some of the solubility test results, it was concluded that inadequate washing of the solids can lead to the presence of minor amounts of highly soluble arsenical compounds remaining in the solids. Higher processing temperatures (>200°C) may well be a suitable substitute for long processing times (>4 hrs at 190°C) and should fully convert any amorphous component into crystalline scorodite or Type-2.

# **Chapter 10**

## **General discussion and environmental considerations**

## 10.1 Hydrothermal precipitation

Hydrothermal arsenate precipitates are crystalline and have been shown to have low solubilities compared to solids produced by other treatment options. However, despite its low solubility Robins [58] has shown that even crystalline scorodite may not be perfectly stable in the neutral pH region and over several thousands of years it too will slowly decompose so that arsenic will enter the solution phase. The arsenic would therefore be released only slowly to ground waters.

In treatments of arsenical dusts and effluents containing high levels of arsenic, hydrothermal precipitation is a realistic process option. The requirements are only an Fe:As ratio of ~1:1, whereas arsenical ferrihydrite requires the presence of significantly higher levels of iron (Fe:As >3:1). Hydrothermal precipitation can be considered to be a clean and safe technology and it also has a number of other processing advantages in the removal of arsenic including:-

- Process is simple (Autoclave or pipe reactor),
- Simultaneous conversion of As(III) to As(V) is possible,
- Low solubility solid produced,
- Low volume of solid residue,
- Good filtration characteristics,
- High arsenic content product, and
- Reduced lime consumption.

While hydrothermal precipitation is a feasible process option the problem is how to integrate the process into existing circuits in a practical and cost effective manner. For the treatment of arsenical dusts, sludges and sulphides, the use of pyrite as the source of Fe(III) could be considered. Simultaneous oxidation of the pyrite and As(III) could take place with the formation of a crystalline scorodite.

In highly acidic solutions where the Fe:As composition can be controlled to around 1:1 the possibility exists for using an adapted Hematite Process, similar to that used in the zinc industry, to bring about the formation of scorodite. Reduction of iron and arsenic using sulphur dioxide could be used prior to removal of acid by lime or limestone addition. The Fe(II) and As(III)

would not be precipitated during neutralisation and the solution would form a low acid content feed for hydrothermal treatment in a multi-compartment autoclave.

The more complex solution compositions such as those coming from the treatment of flue dusts and refinery bleeds may require more complex treatment with the selective removal of arsenic by solvent extraction. The arsenical pregnant strip liquor could generate a suitable feed solution for hydrothermal treatment with the addition of iron to meet the stoichiometric requirements for the formation of crystalline iron arsenate.

## 10.2 Long term stability of arsenical wastes

Conventional thermodynamics provides a sound theoretical framework to examine and theoretically predict the behaviour of materials in the environment. Solubility depends on the solubility product of the solid phase containing the arsenic and the equilibrium distribution of aqueous solutes containing arsenic. Equilibrium solubilities can be predicted with confidence for varying environmental situations. The main practical limitation in using such data is the unknown rates of reaction (kinetics) especially when these solid-solution reactions are very slow. Extrapolation of data measured over a very short time to a longer time scale may not be valid [129] due to the complex chemical reactions and changing environmental conditions.

A totally insoluble arsenical compound is obviously an unobtainable ideal; therefore a realistic and practical compromise must be identified. Solubility is not necessarily indicative of long term stability, cognisance must also be taken of the physical and chemical changes that the compounds can undergo with time. Pure ferrihydrite is thermodynamically unstable compared to most of the other iron hydroxide-type phases, and with time will transform into goethite, hematite or a mixture of the two [78]. Eventually transformation of the arsenical ferrihydrite should occur, leading to the release of arsenic, which is not incorporated into the crystalline goethite lattice. Kinetic data for the rates of polymerisation and recrystallisation of ferrihydrite with different adsorbates are currently not available, and the lack of this data has put into doubt the long term stability of these materials. However, from X-ray diffraction results on dried arsenic-rich ferrihydrite, it has been found during

the course of this study, and also recognised by other workers [36], that arsenate and other species blocks or severely retards this mineralogical transformation.

During lime neutralisation of arsenical effluents, arsenate is coprecipitated with ferrihydrite and the arsenate is adsorbed onto the solid. While such solids have low solubilities when moist, the rate at which arsenic can be released will change if the ferrihydrite undergoes dehydration which converts the ferrihydrite into a more dense dehydrated form. It is probable that if arsenical ferrihydrites remain moist, they will retain their surface areas and adsorptive properties. Such conditions will prevail if the climatic conditions provide sufficient rainfall to avoid the dehydration of the ferrihydrite. For mixtures of arsenical ferrihydrite with gypsum some workers [34, 36] have suggested the participation of calcium in the complexation with the arsenic adsorbed onto the ferrihydrite and this could further stabilise the material.

Another treatment route for arsenical effluents is to precipitate the arsenic as a calcium arsenite or arsenate compound. High concentrations of calcium, and high pH's (12.5) can reduce the concentrations of As(III) and As(V) in solution to below 0.5mg/L through the precipitation of  $\text{Ca}(\text{AsO}_2)_2 \cdot \text{Ca}(\text{OH})_2$  and  $\text{Ca}_3(\text{AsO}_4)_2 \cdot \text{Ca}(\text{OH})_2$  compounds (see Appendix 9). Speciation of the arsenic has been shown to be of importance with As(III) being more difficult to remove from solution than As(V) [130]. Thermodynamically such calcium-arsenic compounds are unstable in the presence of carbon dioxide and, in the long term these compounds can transform through carbonation (action of  $\text{CO}_2$ ) to calcium carbonate and release the chemically bound arsenic [35, 110, 121]. A number of workers have bubbled air (0.3%  $\text{CO}_2$ ) through alkaline solutions containing solid calcium arsenate compounds and have shown that the dissolved arsenic in solution increases while the pH and dissolved calcium decreases (see Figure 10.1) [35, 44, 110, 131 - 133]. Carbonation would also contribute to the conversion of any excess lime ( $\text{Ca}(\text{OH})_2$ ) which would otherwise temporarily maintain a high pH (~12.5) in a metallurgical dump. A lowering of the pH of the ground and pore waters would lead to the conversion of the basic calcium arsenate and arsenite to more soluble intermediate products [ $\text{Ca}_3(\text{AsO}_4)_2$  and  $\text{Ca}(\text{AsO}_2)_2$  -type compounds respectively]. The new calcium arsenate compounds are appreciably more soluble (Table 10.1) as the buffering capacity at higher pH will be insufficient

to maintain their stability and this will promote the release of arsenic to solution.

The lime-stabilised calcium arsenate materials do give stability to arsenical materials on exposure to the environment therefore this demonstrates the effectiveness of lime in removing arsenic from waste effluents. However, the high solubility of calcium hydroxide (1.85g/L) indicates it could easily be washed out of a dump with time. Also it can be shown that the carbonation of the material is possibly even more important when considering the long term equilibrium assemblage. Regarding predictions on the long term stability of lime stabilised calcium arsenate dumps, no quantitative kinetic data is currently available on the transformation to calcite. However, some evidence for this comes from the study of mortars and cements in which free lime is a main component.

Carbon dioxide present in the atmosphere reacts, in the presence of moisture, with lime-bearing cement to form calcite. Complete decomposition of calcium compounds in hydrated cements is chemically possible if the cement is sufficiently porous, but in compacted cements carbonation penetrates beyond the exposed surface only very slowly (<2mm following many years of exposure). If diffusion of water and CO<sub>2</sub> into the cement paste is retarded the reaction is practically stopped. As calcite grows by carbonation this seals the micropores in the cement and inhibits mass transport by reducing the permeability [134]. In the case of old fashioned lime mortars, it is carbonation that hardens the material. But again CO<sub>2</sub> is impeded from penetrating into the interior of the mortar because of the carbonate crust that is formed on the mortar surface. Evidence of free lime hydrate in the interior of mortars that are hundreds of years old is common [135].

The available evidence on the exposure of lime to the atmosphere indicates that it can in certain circumstances be stable. Therefore the stabilisation of calcium arsenate compounds with lime may provide some degree of long term stability. The rates of carbonation and dissolution due to environmental action cannot be easily quantified but will have an important bearing on the chemical fixation of the arsenic.

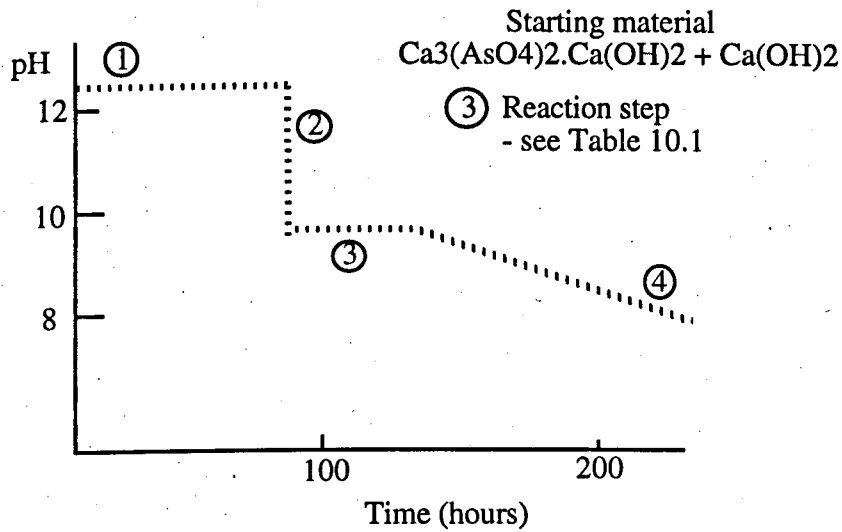


Figure 10.1 Influence of carbon dioxide on calcium arsenate - lime mixtures [110]

Table 10.1 Influence of carbon dioxide on calcium arsenate - lime mixtures [110]

Step	pH	Reaction
1	12.7	$\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightleftharpoons \text{CaCO}_3$
2	12.7 to 9.9	$\text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CaCO}_3 + 2\text{H}^+$
3	9.9	the basic calcium arsenate breaks down $\text{Ca}_3(\text{AsO}_4)_2 \cdot \text{Ca}(\text{OH})_2 + \text{CO}_2 \rightleftharpoons \text{Ca}_3(\text{AsO}_4)_2 + \text{CaCO}_3 + \text{H}_2\text{O}$
4	9.9 to 8.3	$\text{CO}_2$ depresses pH $\text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CaCO}_3 + 2\text{H}^+$
5	below 8.3	$\text{Ca}_3(\text{AsO}_4)_2 + 3\text{HCO}_3^- \rightleftharpoons 3\text{CaCO}_3 + 2\text{HAsO}_4^{2-} + \text{H}^+$

Step 1. Removal of any excess lime from solution by calcite precipitation

Step 2. pH is depressed by the influence of  $\text{CO}_2$

Step 3. Conversion of soluble basic calcium arsenate to calcium arsenate

Step 4. pH is depressed further by atmospheric  $\text{CO}_2$

Step 5. Eventual adjustment of pH to pH of natural waters (~6). Calcium arsenate and calcite coexist as stable solid phases at pH 8.3



In industry the formation of arsenical ferrihydrites and calcium arsenates and arsenites are considered as low cost operations [125] when compared to the arsenical slag, arsenical cements and hydrothermal precipitation routes. However, if one considers the long term stability of the different arsenical products the more expensive processing alternatives should be able to yield products that are significantly more stable.

In the uranium industry where radioactive wastes are disposed of, they too have investigated the long term stabilisation of toxic wastes. Their predictions also rely on solubility concepts and long term predictions are qualitative at best and often assume worse case scenarios [129]. Their view of the long time scales over which predictions are required is that it is impossible to validate any models by comparing prediction with observation. However it is possible to test and build confidence into models through quantitative and qualitative ideas developed through the study of field and natural analogues. For deep repositories (below the water table) in which a high pH is maintained around the wastes by cement, hydrolysis reactions can reduce the solubility and therefore retard the migration of toxic elements. The time over which containment will be effective is related to ground water flow because of the potential for leaching out of cementitious materials. For this reason the hydrogeological conditions below the water table are very important. Surface deposits can be considered to be open systems and may well behave very differently especially when exposed to oxygen-enriched waters and high throughputs of atmospheric carbon dioxide [129].

Quantitative long term stability data on the behaviour of most waste material are not available due to the difficulties in carrying out such experiments, so qualitative predictions must be made to assess the behaviour of the material under conditions which may promote the breakdown of the material in the long term. For long term stability predictions standard solubility testing in conjunction with detailed characterisation of the residue and associated compounds can be considered to be the only realistic procedure. Judgements should also be based on comparisons with geological and archaeometallurgical materials and rely heavily on basic scientific principles and the aqueous geochemistry of related inorganic and organic solutions.

While conventional solubility testing always uses solutions which are oxygen saturated, natural ground waters could be very different in composition and

contain high amounts of dissolved carbon dioxide and other organic acids making some solubility tests almost meaningless.

Long term predictions on the chemical stability can only be guesses at best, even when taking into consideration thermodynamic principles and comparisons with natural analogues. Physical coverings as barriers against wind and rain erosion are equally as important and also have got to be considered. Containment is very crucial and prevents wastes from being widely dispersed, the problems of arsenic dusts are often rarely addressed in discussions on toxic waste stability but these possibly present an even greater hazard than arsenic released to ground waters.

### 10.3 Geological evidence

The disposal and long term stability of arsenical materials can be examined indirectly by the study and examination of naturally occurring arsenic minerals and weathering products under natural environment conditions. Such work has important implications in that arsenical compounds in geological systems can be considered to be analogues of metallurgically derived arsenical compounds on mine dumps (**Appendix 1**) and can thus give information on the long term behaviour of such compounds.

The states of the system may depend on pressure, temperature and chemical composition [62] and the thermodynamic equilibria will proceed toward an equilibrium state. In an open system, as in an oxidised ore zone or in a metallurgical dump, the system can constantly change due to the permeability of the material with the ingress of gas and liquid [62]. This can move the equilibrium position of the mineral system and accelerate its breakdown.

The production of arsenical compounds with similar structures to those of low solubility natural minerals would be obvious materials for the disposal of arsenic, as such minerals have reached equilibrium with the environment over a prolonged duration. Scorodite is the most common arsenate mineral [136] and can be considered to be one of the most stable arsenic bearing compounds. The broad range of climates in which scorodite is found, together with the wide range of geological environments, reflects its stability.

The compound has stabilised arsenic which has usually been released from the oxidative breakdown of arsenical sulphides. Hydrothermal precipitation can simulate natural processes and can potentially stabilise metallurgical sources of arsenic.

The secondary minerals which form as the result of contact between arsenic and the environment are either kinetically stable compounds or are actually in a thermodynamically stable state. They are most probably intermediate breakdown products when considered over geological time where the equilibrium conditions cannot easily be measured or established. In general it can be said the relative rarity of other Fe-arsenates and Ca-Mg-arsenates indicates that they are much less stable than scorodite. Secondary arsenate minerals which have formed at low temperatures include those of Fe, Ca, Cu, Pb, Mg, Mn, Ni and U [15]. A large number of the arsenate minerals contain hydroxyl, or are hydrated, and this appears to stabilise the compounds in their natural environment.

From a consideration of As(III) and As(V) pH vs log activity diagrams [20, 89, 60, 132, 133, 137] it is clear that As(III) compounds are very soluble compared with equivalent As(V) compounds. This is also reflected in the mineral record by the predominance of As(V) over As(III) mineral species, which suggests that the latter are much less stable. Localised conditions can change the  $E_h$ -pH regime and may dramatically influence arsenical mineral assemblages. For example, in alkaline conditions such as those close to limestone host rock, the dissolution of calcium carbonate can raise the pH of natural waters well above neutral, where scorodite is more soluble. Yet under these pH conditions the formation of calcium arsenates are favoured and would form preferentially.

The valency of arsenic in fact can change easily and reversibly with redox potential, and in sulphide-rich waste dumps [16], where reducing conditions prevail, As(V) could be reduced to form arsenite or maybe even organo-arsenides. Arsenic loosely bound to ferrihydrite in waste dumps may therefore be susceptible to reduction, leading to increased levels of As(III) in ground water over time.

Paragenetic study of arsenates in a number of geological conditions [136] has allowed the relative stabilities of the secondary arsenates to be empirically

established. Figure 10.2 shows a schematic mineral paragenesis diagram which is based on observed mineral assemblages of the phases in the Fe-AsO<sub>4</sub>-SO<sub>4</sub>-H<sub>2</sub>O system. With increasing stability the arsenates have lower water of hydration and have simpler chemical compositions, and removal of sulphate and hydroxyl from the structure. The final arsenical compound is arsenical ferrihydrite which eventually converts to goethite or hematite depending on the E<sub>h</sub>-pH conditions.

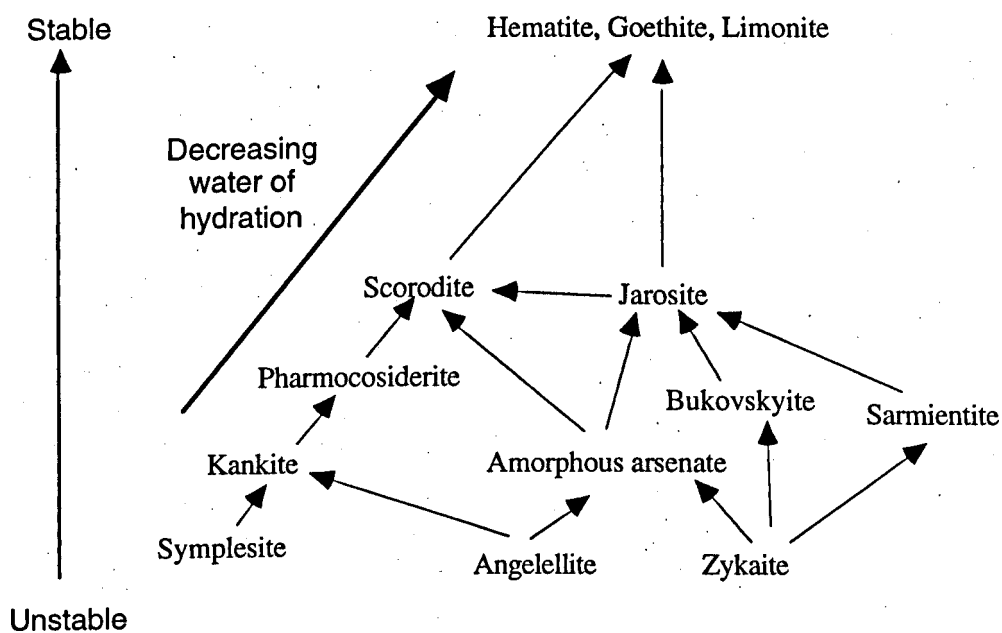


Figure 10.2 Schematic stability of secondary Fe(III) arsenate minerals in the natural environment (adapted from Bowell [136])

The predominance of iron arsenates over calcium arsenates in the geological record reflects the greater stability of the former. This is supported by the solubility test data on precipitated calcium and iron arsenate compounds (Chapter 8) and is also predicted from consideration of published thermodynamic data on the solubility of arsenical solids precipitated at 25°C. The influence of carbon dioxide on calcium arsenates will play an important role on the survival of these minerals in the natural environment and explains their apparent low abundance in arsenical weathering products. Carbon dioxide not only lowers the pH of alkaline solutions but also combines with the calcium in calcium-arsenate compounds to form calcite which is a more stable calcium compound.

The study of mineral interactions such as mineral solubility, complexation, precipitation, oxidation-reduction, arsenic adsorption etc., can have important implications and may allow processes operating inside metallurgical dumps to be better understood. In the assessment of the long term stability of arsenate precipitates the biogeochemistry and geology of the dump site must also be taken into account as well as the solubility of the precipitates.

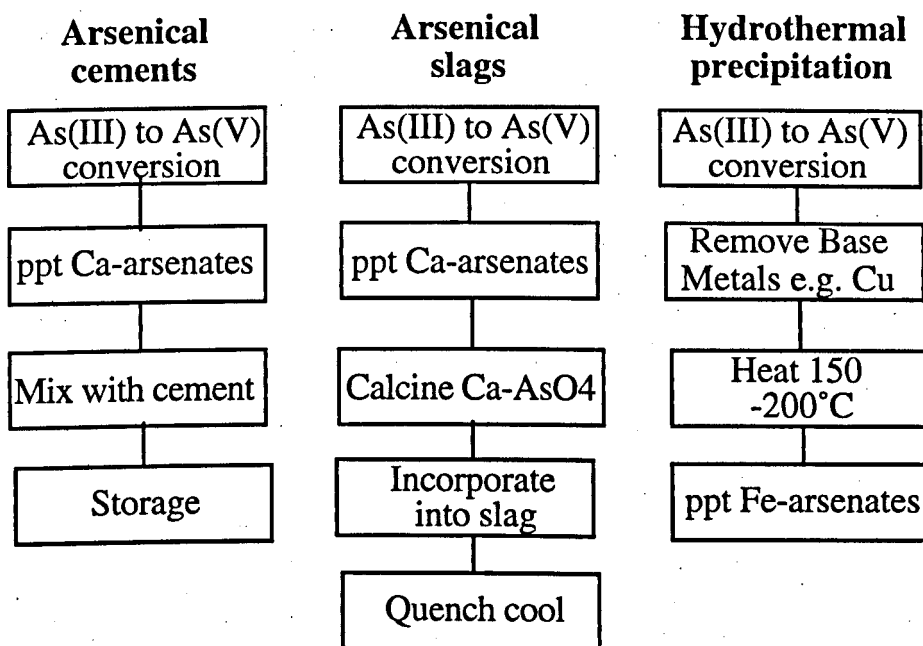
While synthetic scorodite has a naturally occurring analogue, the Type-2 compound does not. This suggests that the Type-2 structure may have bonding insufficiently stable to allow its survival under environmental conditions. The experimental finding that Type-2 is formed at higher temperatures than scorodite infers that when removed from the high temperature equilibrium conditions, at which it was formed, it may be more unstable than the synthetic scorodite. Conventional solubility testing may not be able to identify any significant differences in solubility between the two compounds. Yet it would be predicted that scorodite would be marginally more stable under environmental conditions.

#### **10.4 Comparison between disposal options**

The possible alternatives for arsenic disposal together with considerations of the long term stability of the arsenical products are given below in **Table 10.2**. The formation of arsenical ferrihydrites and calcium arsenates and arsenites are attractive options to industry in that they are cheap and require very simple technology when compared to the arsenical slag, arsenical cements and hydrothermal precipitation routes. The three processing routes are schematically illustrated in **Figure 10.3**.

While the incorporation of arsenical wastes (calcium arsenates) into cement would appear to be the simplest and possibly the cheapest option of the three, the arsenic is mostly physically encapsulated with possibly some incorporated into the cement-type phases [34 - 36]. The calcium arsenate compounds as shown in this current work and by Robins et al [112] are highly soluble and in time the ingress of moisture and CO<sub>2</sub> will eventually promote their breakdown and slowly release the enclosed arsenic. The slag option [30,

31] may well produce an arsenical glass with ultra low solubility but technologically the process has not been demonstrated on a significantly large scale and may not even be practical. Concern over the possible recrystallisation or devitrification of the glassy phase is of importance as such material may mechanically breakdown and the arsenic may crystallise as highly soluble compounds and thus making the material environmentally unsuitable. Other calcined arsenate compounds (e.g.  $\text{FeAs}_2\text{O}_7$ ) could be considered for incorporation into slags, arsenic-rich viscous glasses as well as other materials could also be introduced as pellets immediately prior to cooling. The latter may avoid the need to quench the slag, however the arsenate would be encapsulated rather than chemically incorporated into the crystalline phases or glassy matrix.



Schematic diagram showing the processing of arsenical dusts and effluents

**Figure 10.3** Treatment technologies - options to meet tighter regulatory criteria

**Table 10.2** Long term stability considerations for the various arsenic disposal options

Arsenical compound	Long term disposal considerations
<p><b>Arsenical ferrihydrite (Fe:As &gt;3:1) ambient temperature precipitation</b></p>	<ul style="list-style-type: none"> <li>• Dehydration leading to a more unstable compound</li> <li>• Recrystallisation to goethite?</li> <li>• Possibility of biochemical reduction of As(V) to As(III) and Fe(III) to Fe(II)</li> <li>• Dilute, voluminous material</li> </ul>
<p><b>Calcium-arsenates</b> + <b>Calcium-arsenites</b></p>	<ul style="list-style-type: none"> <li>• High intrinsic solubility.</li> <li>• Ca-arsenates converted to CaCO<sub>3</sub> with release of arsenic (influence of atmospheric CO<sub>2</sub>).</li> <li>• High lime levels in the precipitated solids result in high pH's (11 - 12). With time the lime is converted to CaCO<sub>3</sub> - this leads to a reduced pH and an increased solubility of the calcium arsenate compounds.</li> </ul>
<p><b>Crystalline ferric arsenates (Scorodite or the Type-2 crystalline phase)</b></p>	<ul style="list-style-type: none"> <li>• Compact, high grade arsenic materials of low solubility</li> <li>• In comparison with other arsenical compounds they are considered to undergo little physical or chemical change</li> <li>• The low solubility suggests that the solids should have reasonably long term stability?</li> </ul>
<p><b>Arsenical slags (up to 10% arsenic)</b></p>	<ul style="list-style-type: none"> <li>• Long term stability unknown - quenched slags show low solubility.</li> <li>• Require highly specific conditions for incorporation into slag</li> <li>• Recrystallisation - devitrification</li> </ul>
<p><b>Arsenical cements</b></p>	<ul style="list-style-type: none"> <li>• If calcium compounds are fully carbonated this may reduce the buffering action and lead to reduced pH and arsenic precipitation.</li> <li>• The arsenic may be chemically bound as calcium arsenate phases which are highly soluble.</li> </ul>

The various disposal options for arsenical waste have been briefly reviewed with emphasis placed on the long term stability of the arsenical materials in the environment. The costs for the production of stabilised waste is obviously of importance to industry but this factor must be balanced against

the long term stability of the material. In future if the material becomes unsafe and a hazard to man it will require further reprocessing and incur further costs which may be many times that of the initial stabilisation step. Diluting arsenic wastes into slags, cements and tailings may also need to be reassessed as these become more expensive to reprocess at a later date. Keeping the solid as a high grade crystalline material of low solubility certainly would appear advantageous over time so long as the compounds do not undergo any major mineralogical transformations.

Lime neutralisation of effluents is designed to eliminate acidity, precipitate heavy metals and 'fix' any deleterious substances into a stable waste that can be readily disposed of. The toxic compounds are diluted in the waste making it almost impossible to re-treat, recover or stabilise the entrained toxic elements. In the treatment of some base metals there is a trend towards hydrometallurgical operations in preference to pyrometallurgical processes, this is partially environmentally driven in the belief that the toxic elements can be diluted into such residues. Changes in environmental legislation could well change these long held views by requiring that the toxic elements be recovered and disposed of separately where they can be stored and monitored.

While chemical containment of arsenic is often utilised for long term stability the engineering of the physical containment is often not considered in enough detail. In the Uranium industry toxic wastes are stored in deep repositories and perhaps arsenic should also be stored in a similar manner as shallow surface deposits cannot be considered safe [129]. This is because of the uncertainties with regard to mans future activities, hydrogeology, and some of the more extreme factors such as: climatic change, earthquakes, sea level changes, permafrost, glacial loading, erosion, and even meteorite impacts! Based on the past recent history of our planet the ownership of mining and metallurgical companies, governments and country boundaries all have changed considerably over the last century and who will take responsibility for toxic wastes in future will be open to debate. The toxicity of arsenic does not disappear with age and future generations will insist on cleaning up all dumps containing toxic elements.

Continuous monitoring of a waste site after the solids have been disposed of will be inevitable and the mining company who initially exploited the deposit



will be responsible. The idea that a mining company can walk away from a deposit after the reserves have been depleted will be a thing of the past. The dumps will clearly require care so as to reduce any mobilisation and dispersal of pollutants. This will involve long term management to ensure environmental security and acceptability to government and local communities. Prevention is better than cure and finding the most convenient compromise for arsenic's disposal will be required, hence the move towards clean and safe technologies in the treatment of arsenic. For this reason it is predicted that hydrothermal precipitation of stable iron arsenate compounds will be seriously considered by industry and may well become incorporated into precious and base metal processing operations in the near future.

# **Chapter 11**

## **Conclusions and recommendations**

## 11.1 Summary and Conclusions

- The main objective of the investigation was to precipitate, characterise and solubility test a wide range of arsenical compounds comparable to those produced during metallurgical processing. This work has increased the knowledge and understanding of the structure and behaviour of arsenic-containing materials and has allowed suitable candidates for disposal as waste to be identified. The most suitable compounds are those with the lowest solubility and which have long term chemical and physical stability under environmental conditions. The test tube scale work allowed suitable precipitation conditions to be established for the production of environmentally stable arsenical materials and guided the larger scale precipitation experiments.
- During the course of the precipitation and characterisation work a number of new arsenate compounds have been identified and these have been designated Type-1, -2, -3 and -4 and have formulae which correspond respectively to :-  
$$\text{Fe}_2(\text{HAsO}_4)_3 \cdot x\text{H}_2\text{O}$$
$$\text{Fe}_3(\text{AsO}_4)_{0.33(9-x-2y)}(\text{OH})_x(\text{SO}_4)_y$$
$$\text{Fe}_2(\text{AsO}_4)_{0.33(6-2x)}(\text{HAsO}_4)_x$$
$$\text{CaFe}_2(\text{AsO}_4)_{0.33(8-2x)}(\text{HAsO}_4)_x$$
- Hydrothermal precipitation diagrams have been generated for Fe-AsO<sub>4</sub>-SO<sub>4</sub> solutions at pH<1. These show the distribution of compounds formed at various temperatures and Fe:As ratio's allow in the iron arsenate system at elevated temperatures (150 - 225°C).
- Systematic hydrothermal precipitation experiments using Ca-Fe-AsO<sub>4</sub>-SO<sub>4</sub> solutions at different temperatures and pH's has produced a wide range of solids which were characterised and solubility tested. The data have contributed towards an understanding of the system at elevated temperatures.
- It was found that the most insoluble compounds that can be formed from Fe-AsO<sub>4</sub>-SO<sub>4</sub> solutions at pH<1 are the Type-2 (formed at temperatures above 175°C) and scorodite (formed at temperatures below 175°C). While the crystalline materials have a low solubility the long

term stability of the compound cannot be predicted with any degree of accuracy.

- Empirical evidence for the stability of scorodite is provided by the study of secondary arsenate minerals, which are compounds that have been formed by the oxidative breakdown of arsenical sulphides. These have been formed as the result of contact between arsenic and the environment and this indicates that they are either kinetically stable compounds or are actually in a thermodynamically stable state. When considered over geological time; equilibrium cannot easily be measured or established as the environment can be considered to be an open system and can constantly change. The low solubility compounds are likely to remain as such and undergo only minimal change with time. Since scorodite is commonly found in many weathering zones and in most climatic regions of the world it is considered to be the most stable arsenate compound formed in nature and may also be suitable for arsenic disposal purposes.
- Through experimental observation and consideration of some theoretical concepts a preliminary assessment of the long term behaviour of crystalline arsenic bearing metallurgical wastes in the environment has been made. Through empirical solubility testing and comparison with natural analogues it can be predicted that crystalline scorodite should have a low solubility for prolonged periods of time.
- A preliminary assessment of the high temperature precipitation process for the stabilisation of arsenical effluents and dusts was made using the small scale precipitation testwork. This provided valuable technical and operating information for the larger scale precipitation work.
- The basic information determined during the course of the test tube scale experiments with regard to precipitation conditions and the characteristics of the solids and the solubility were verified by the autoclave scale experiments. During the course of the larger scale experiments, removal of over 95% arsenic was achieved from simulated hydrometallurgical solutions. The solids precipitated were found to be composed of scorodite, the Type-2 compound, or a mixture of the two compounds. The solubility of the compounds were found to pass the US

EPA TCLP test and were considered to be of a low enough solubility to be safe for disposal.

- Scorodite and the Type-2 compound have a comparable arsenic solubility to arsenical ferrihydrite produced during low temperature neutralisation. The larger scale testwork has established that hydrothermal precipitation is a realistic disposal option in the removal and immobilisation of arsenic from metallurgical dusts and liquors and could in future be incorporated into metallurgical operations as a unit process operation.

## 11.2 Suggestions for further work

While hydrothermal precipitation can be used successfully on simulated hydrometallurgical analogues, it has to be shown to work on actual effluent compositions found in the metallurgical industries. During the course of the current investigations the arsenic was used in the As(V) form, yet in many hydrometallurgical liquors arsenic is most likely to be in the As(III) form and therefore the oxidation of the arsenic must be examined and optimised with respect to temperature, pH, Fe:As and arsenic concentration. The form of iron to be added to the system also needs to be examined with the possibility of using pyrite ( $\text{FeS}_2$ ) as a source of iron.

Repetition of some of the experimental runs and accurate definition of the behaviour of the solutions with respect to temperature and Fe:As ratio is warranted to simulate solution compositions similar to effluents from acid plants, copper refineries and dust leaching operations.

There is the need to examine the structure of the Type-1, -2, -3 and -4 compounds in further detail using conventional TEM as well as XRD unit cell determinations on single crystals. More detailed test tube scale hydrothermal precipitation work is required to ascertain the compositional variations in the Type-2 structure with regard to sulphate and hydroxyl substitution.

Thermodynamic data on the compounds at elevated temperatures needs to be determined and may allow the processes to be evaluated from a thermodynamic point of view. If such a process reaches commercialisation mathematical modelling may be necessary to simulate the process.

Mechanistic models may also be needed so as to completely describe the system in terms of the physical and chemical laws that govern the precipitation reactions. Such models would account for variations in temperature, Fe:As ratio, acid concentration, base metal content and time.

Examination of the hydrothermal Ca-Fe-AsO<sub>4</sub>-SO<sub>4</sub> system at elevated temperatures has shown that the system, despite its complexity, can be studied and understood. From the literature there is a lack of data on hydrothermal precipitation at elevated temperatures and it is considered by the investigator that other systems of similar importance to the arsenate system could also be examined using identical methods and techniques. Further studies could investigate the characteristics of the solids precipitated from solutions of phosphates, molybdenates, selenates, bismuthates, tellurates, antimonates and tungstates.

# Appendices 1 - 10

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## Appendix 1

### Examination of arsenical metallurgical products

During the course of the study a number of arsenical metallurgical products were characterised and solubility tested (Table A1). These samples showed the wide variation of arsenical products produced by industry. Summaries and interpretations of the examinations are given below:-

**Table A1.** Index of metallurgical samples examined during the study

Sample No.	Nature of sample	Origin	As content (%)
1	Gypsum sludge	USA	~2
2	Scorodite-rich cake (from a dump)	Zimbabwe	12
3	Autoclave residue (pilot plant)	Canada	22
4	Lime precipitate	Brazil	<2
5	Autoclave discharge	PNG	<0.3
6	Autoclave discharge and tailings samples	PNG	<0.3
7	Lime stabilised Ca-arsenate	Europe	<15
8	Bioleach residue (pilot plant)	RSA	<6
9	Arsenical cement	Europe	5
10	Autoclave discharge	Canada	13
11	Scorodite precipitate (high temp.)	Canada	~30
12	Scorodite precipitate (ambient)	Canada	~30

#### *1. Examination of a soluble arsenical precipitate from a copper refining operation.*

The sample contained ~1.75% arsenic and the bulk of the material was gypsum with minor amounts of calcite. The sample was analysed and found to contain a high proportion of As(III) (0.57%), also iron levels (2.02%) in the sample were low, making the Fe:As ratio low (<3:1). It can be inferred that the iron or calcium arsenites that are present are likely to be soluble or at least metastable and are the cause of the high arsenic solubility.

For minimum solubility the contained arsenic should be in the As(V) form and there should be an Fe:As ratio of >3. Therefore it was recommended that

an oxidising agent and extra iron should be added to the effluent for the formation of a low solubility arsenic product.

## *2. Examination of an arsenical dump material containing old flotation concentrates*

The sample consisted of quartz, pyrite and scorodite and assayed at 12.7% arsenic. Although arsenopyrite may be reasonably stable in the short term oxidation of the arsenopyrite may form scorodite.



The compound in the sample was crystalline and gave a moderately strong scorodite XRD pattern. The sample was EPA TCLP tested and found to have a very low solubility with <0.1mg/L arsenic in the filtrate solution; this is well below the EPA toxicity limit. Samples consisting almost wholly of scorodite have been reported from this locality, these samples possibly represent crusts or precipitates which have resulted from the evaporation of arsenic-rich liquors derived from a dump. Precipitation of scorodite from saturated iron-arsenate solution is being examined by Demopolous and Droppert in McGill University, Canada [105] and the sample represents a comparable mode of formation from saturated solutions formed during evaporative enrichment (see example 12).

## *3. Examination of a Sherrit Gordon autoclave residue.*

EPA TCLP and MARG solubility testing of the residue (21.7% arsenic, Fe:As ~1:1) showed that the sample was soluble and was not considered suitable for disposal. On examination of XRD, IR and DTA-TG information, the sample was found to be composed of the  $\text{Fe}_2(\text{HAsO}_4)_3 \cdot x\text{H}_2\text{O}$  (Type-1 compound) and scorodite. The material could be more efficiently and completely converted to scorodite in the autoclave if higher iron levels are added to the autoclave feed to increase the Fe:As ratio. Scorodite is substantially less soluble than the Type-1 compound (see Chapter 8) and overall would be a better compound for disposal.

#### *4. Examination of a neutralisation precipitate sample from Brazil*

An arsenical sample from Brazil contained <2.0% arsenic and was composed mainly of a gypsum matrix. Mineralogical identification and isolation of the arsenical component was impossible to achieve. The arsenic is most likely to be present as an amorphous arsenic-containing ferrihydrite, since the preferential precipitation as the iron compound over the calcium arsenates can be predicted from consideration of the available calcium and iron solubility diagrams (see Chapter 3). The calcium arsenates only begin to precipitate at about pH3-4 while the iron-arsenates start to precipitate at pH2.2. When iron is present in sufficient amounts in the effluent it will combine with most of the arsenic and remove it from solution, assuming that the iron and arsenic are in their highest oxidation states i.e. (III) and (V) respectively.

#### *5. Examination of arsenical autoclave residues (~0.27% As) from an operating plant.*

EPA TCLP and MARG solubility testing of the residue showed that the material had very low solubilities by both test methods. The characterisation of the arsenical component was very difficult owing to the residue being a mixture of gangue and arsenical material. The arsenical compound in the residue was tentatively considered to be amorphous in character from consideration of IR, DTA-TG, and XRD data. It is considered that the arsenic is held in the sample as arsenical ferrihydrite.

#### *6. Examination and testing of 12 arsenical solids from PNG.*

A number of metallurgical products from PNG were solubility tested using the EPA TCLP test procedure. The samples examined included:- Autoclave Discharge (CD), Precipitation Tailings (PT), CIP Tailings (CIP) and Flotation Tailings (FT).

The samples were tested wet (as received) and dry to assess the influence of drying (dried at 50°C for 24hrs). For the wet samples the water contents were determined by calculating the mass loss on drying which allowed an equivalent mass of wet solid to be used in the tests. The equivalent of 50g of the wet and dried samples were tested in 1 litre of EPA test solution (20:1, L:S ratio).

**Table A2. Results of the EPA TCLP solubility tests on PNG samples**

Sample	EPA TCLP test results (As mg/L in solution)	
	Samples Tested Dry	Samples Tested Wet
CD 24	0.50	<0.1
CD 25*	0.76	0.15
CD 26	1.00	<0.1
PT 24	0.18	<0.1
PT 25	<0.10	0.61
PT 26	0.15	<0.1
CIP 24	1.14	0.08
CIP 25	0.89	0.11
CIP 26	0.52	0.24
FT 24	0.56	<0.1
FT 25	1.01	0.95
FT 26	<0.1	<0.1

\* Chemical analysis of the solid indicated a arsenic content of 0.27%

All of the samples tested (Table A2) are well below the EPA TCLP toxicity limit (5mg/L arsenic in solution). The CIP Tailings, Precipitation Tailings and Autoclave Discharge are most likely to contain ferrihydrite (~Fe<sub>2</sub>O<sub>3</sub>. xH<sub>2</sub>O) onto which the arsenic is adsorbed. For this reason the solids are stable with the low levels of arsenic strongly bound to the ferrihydrite.

The dry samples are on average marginally more soluble than the wet samples. It would be expected that if the majority of the arsenic in the solids is adsorbed onto ferrihydrite, the drying of such samples at 50°C would cause some dehydration and change the character of the solid. The arsenic on the surface of the material could therefore be partially released on rehydration during the solubility testing and hence account for the solubility difference between the dry and wet samples.

#### **7. Examination of a neutralised calcium arsenate material**

The solid contained around 15% arsenic. The solid was EPA TCLP tested and found after testing to have a filtrate containing <0.10mg/L arsenic; which is below the EPA toxicity threshold. The pH of the solution after testing was found to have increased from 4.9 to 11.8.

X-ray diffraction showed that the solid was composed of a number of components. Estimates of their content in the solids are given below:

Ca(OH) <sub>2</sub>	Major >40%
CaCO <sub>3</sub>	Minor <10% (Checked using HCl)
Ca <sub>5</sub> (AsO <sub>4</sub> ) <sub>3</sub> (OH). xH <sub>2</sub> O	Medium 20 - 40%
Ca <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> .xH <sub>2</sub> O	Minor <10%

The reason for the increased pH is the large amounts of free lime in the sample. The high levels of lime and the high pH promote the precipitation of any arsenic from solution as an apparently stable (i.e. insoluble) arsenate compound.

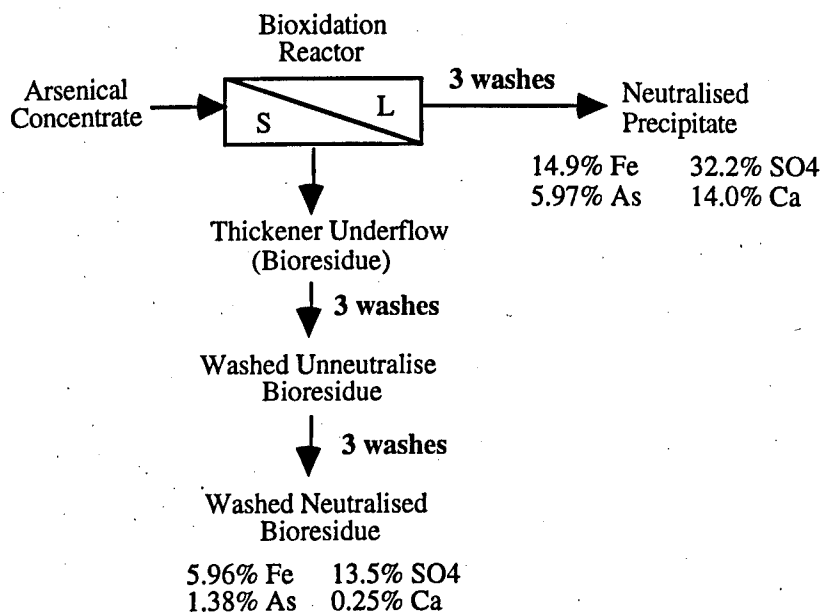
The solid when placed on a dump will eventually slowly change, the pH of the fluid phase filling any pore volume will eventually be lowered and a reduction in the free lime content will also take place. The reduction in lime will occur either by washing away of the soluble lime or through carbonation of the lime to form calcium carbonate.

If sufficient amounts of free lime are retained in the dump over a prolonged duration the calcium arsenate compounds will be buffered at high pH and calcium ion saturation, this will stabilise the arsenates with minimal release of arsenic to the ground waters (see also Chapter 10).

#### **8. Examination of bioleach residue samples to assess their stability.**

Four samples were submitted from a three stage bioleach pilot plant operation (see Figure A1) these were :-

- Neutralisation Precipitate (from bioliquor),
- Thickener Underflow (unwashed),
- Washed Unneutralised Bioresidue, and
- Neutralised Bioresidue.



**Figure A1.** Biooxidation samples that were examined from a small scale pilot plant

The following information was supplied on the samples:- The Thickener Underflow was washed three times which released successive arsenic levels of 624, 105 and 44mg/L to solution (L:S ~8:1), after the individual washing of the Neutralised Bioresidue, the washings gave arsenic levels of 6.7, 14.0, and 13.0mg/L. Washing of the Neutralisation Precipitate gave arsenic values of 0.10, 0.12 and 0.09mg/L. EPA TCLP testing of the Neutralisation Precipitate and the washed Neutralised Bioresidue gave arsenic levels in the EPA TCLP extract of 1.3 and 12 respectively. The bioresidue sample clearly does not pass the EPA regulatory levels.

From the data supplied the arsenic in the bioresidue samples is still apparently soluble, presumably on account of the presence of gelatinous arsenical-ferrhydrite-sulphate compounds formed during arsenical sulphide breakdown. These compounds are intermediate products before the arsenic is oxidised and enters the bioleach solution, they will have low Fe:As ratios (comparable to arsenopyrite 1:1?) and will be moderately soluble. Those gelatinous breakdown products formed from arsenical pyrite (Fe:As >3:1) may be less soluble as they have higher Fe:As ratios.

Non-sulphide arsenic was determined by heating the solid with a 4M solution of NaOH at 50°C for 30mins (L:S ratio 40:1), the "oxide" arsenic (i.e. non-sulphide) enters the solution, whereas the sulphide arsenic remains in the residue as the solid form. The high levels of arsenic in the liquids derived from the washing of the residue samples indicates that the "oxide" arsenic is not readily washing out from the sample. Even after neutralisation the Bioresidue samples still release arsenic on washing, this is possibly promoted by the higher pH of the solids which may aid the breakdown of the gelatinous arsenical solids. During washing and solubility testing whether the arsenic is released to solution as the As(III) or the As(V) form needs to be examined.

The characteristics of the intermediate breakdown products are of great importance especially with regard to the presence of As(III) in the structural framework as the As(III) does not form stable iron or calcium compounds except at very high pH (>11).

Of the arsenic present in the Thickener Underflow (Table A3) 32% occurs as the "oxide" (non-sulphide) form. In the final bioresidue samples (Washed Unneutralised and Neutralised Bioresidues) the "oxide" arsenic levels have been reduced by 4 to 7% after washing of the solid. The "oxide" arsenic is probably the cause of the arsenic solubility in the residues.

To explain the As(III) levels the bioresidues may contain minor amounts of ferric-arsenites as intermediate breakdown products of arsenopyrite, these are likely to have low Fe:As ratios (~1:1) and will be found on the surfaces of partially undigested sulphides and as unassimilated gelatinous material (Figure A3). For the total oxidation and dissolution into the bioleach solution of the "oxide" arsenic prolonged agitation may be required. Work carried out by the Natural History Museum [136] examining the oxidation of arsenopyrite in the presence of steam also indicates that the intermediate break-down products are As(III) compounds which further supports this mechanism. Work on the stability of arsenical bacterial oxidation products by Adam et al. [54] also showed the presence of significant amounts of As(III) in the bio-oxidation residues.

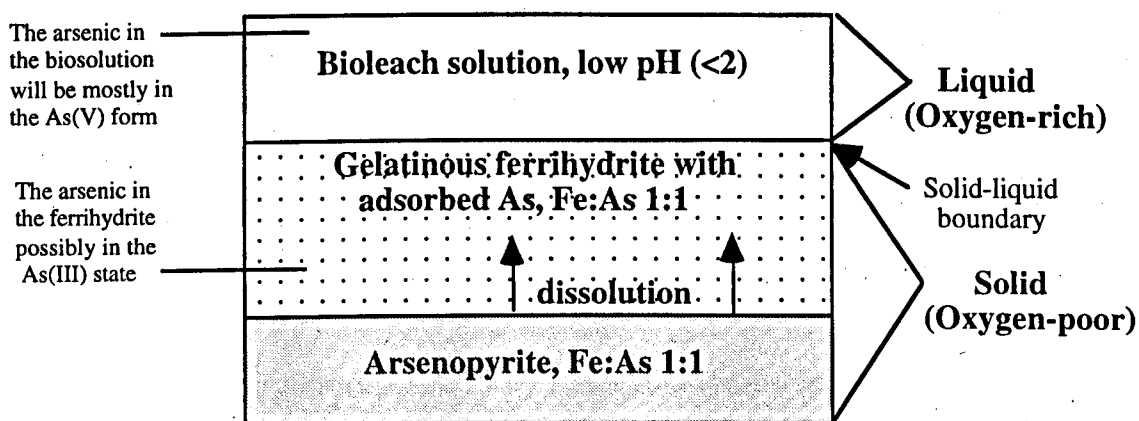
**Table A3.** Arsenic analyses on arsenical bio-oxidation residues and precipitates

Sample	Mineralogical composition (% in residues)	Total As (%)	Non-Sulphide ("oxide") As(%)* (% of total As)	Sulphide As(%) - by difference (% of total As)
Neutralisation Precipitate	Mostly gypsum	6.22	assumed to be 6.22 (100)	assumed to be 0 (0)
Thickener Underflow	Quartz (>65%)	1.97	0.63 (32)	1.34 (68)
Washed Unneutralised Bioresidue	minor - Pyrite (<5%) Arsenopyrite (<1%)	1.35	0.34 (25)	0.99 (75)
Washed Neutralised Bioresidue	Chlorite (<5%) Muscovite (<5%)	1.34	0.38 (28)	0.96 (72)

Provisional As(V)/As(III) determinations on the 4M NaOH solution extracts showed that the majority of the arsenic in the Neutralisation Precipitate is in the As(V) state, whereas the arsenic in the Thickener Underflow and Washed Unneutralised Bioresidue was partially in the As(III) state (As(V):As(III) ~ 4:3). The existence (by smell) of H<sub>2</sub>S in the analytical solution indicates partial dissolution of arsenical sulphides from the residues and makes the accurate department of the As(III) in the solid bioresidue questionable.

During neutralisation of the bioliquor the arsenic from solution is coprecipitated with iron as the pH of the solution is raised above 2.2, the arsenic precipitates as ferrihydrite (Fe:As ratio of 3.3:1) which has low solubility. The arsenic in the solid (Neutralisation Precipitate) suggests that the bioliquor is sufficiently rich in oxygen to convert all of the As(III) to As(V).





**Figure A2.** Hypothetical solid:liquid interface of an arsenopyrite grain during bio-oxidation and the formation of a soluble intermediate breakdown product

### 9. Examination of arsenical cement samples

A number of arsenical concrete samples and arsenical products supplied by an industrial company were examined. The encapsulation of arsenical wastes in concrete is considered as a possible arsenic disposal option, but such a process needs extensive testing and evaluation especially with regards to the long term stability of the material.

#### Results and discussion

The main advantage of using the scanning electron microscope on concrete samples is that a detailed study of individual areas can be made. The high resolution as well as the back scattered electron image allowed the high atomic numbered elements (e.g. arsenic, atomic number 33) to be more easily located and studied.

The cements show typical hydration features such as hydration rims around the concrete grains and partial reaction of the slag-type phases (up to 10% of the concrete). In general the concretes show recognisable microstructures, although some anomalies are apparent and need further examination. The pores within the samples are found as rare isolated macro-pores (<200µm), micropores (<2µm) and larger interconnected pores. SEM photomicrographs of a concrete sample showed the presence of equidimensional particles of slag and the more elongated particles of gypsum in a fine cement matrix.

From a cursory examination of polished sections of the concrete, the arsenical products can be found as discrete particles  $<3\mu\text{m}$  encapsulated in the cement phases, and may also be partially incorporated into the hydrated crystalline cement phases. The actual distribution of the arsenic cannot easily be determined and it is likely to be very dependent on the physical mixing of the arsenical products with the cement and lime. Incomplete mixing will inhibit the homogenisation of arsenical components into the cement and reduce the capacity of the compound to be assimilated into the hydrated cement phases.

The arsenical compounds occur only in limited amounts in the concretes and their actual distributions cannot easily be quantified. To assess whether the arsenic is incorporated either as ultrafine particles ( $<5\mu\text{m}$ ) or chemically combined into the different hydrated calcium-silicate phases in the cements requires more detailed examinations. While cement preparation method A appears to be preferable to B1 and B2, the reasons for the measured differences in solubility are not known.

The incorporation of arsenic into cement has been studied by a number of workers, but they have concentrated more on the leachability of concretes rather than on microstructures and how they relate to stability.

The concrete acts to protect the incorporated arsenic by two main mechanisms, namely a) physical encapsulation into the cement, and b) incorporation into the structure of the newly hydrated calcium-silicate crystallised phases. The high pH of any internal pore waters may promote precipitation of any arsenate as calcium arsenates from the calcium-saturated waters. The long term effectiveness of the porous cement in actually immobilising the arsenic cannot easily be assessed without resorting to a major testwork campaign.

#### Concrete preparation methods

*Method A* Used on samples 2, 5, 8, 11 and 14  
The method uses Ordinary Portland Cement (OPC) 325 with a water-to-cement mixture of 0.65 and the arsenical material is blended into the paste.

*Method B1* Used on samples 3, 6, 12, and 15  
1 step process -1 part arsenical product ( $\sim 50\% \text{H}_2\text{O}$ )(50%)  
+ 0.7 part slag (35%)  
+ 0.1 part cement P40 (5%)  
+ 0.1 part lime (5%)  
+ 0.1 part  $\text{H}_2\text{O}$  (5%)

The samples are mixed manually and stored for 8 days.

- Method B2*      Used on sample 9 only  
2 step process - (a) + (b)
- (a) 1 part wet arsenical product  
+ 1.6 part slag  
+ addition of HCl and H<sub>2</sub>O to make a dense slurry at pH 2  
- 8hr reaction
  - (b) 0.88 part cement (P40)  
+ 0.55 part Ca(OH)<sub>2</sub>  
+ ~2 parts H<sub>2</sub>O to get pH >12.5

**10. Examination of an autoclave discharge sample from an operating Canadian mine.**

In the pressure oxidation of arsenical flotation concentrates (~195°C, 305 psi ~13% As, 15 - 19% S, Fe ~20%) the sulphides are digested in an autoclave leaving in the residue the inert gangue phases and any precipitates formed from the breakdown of the pyrite and arsenopyrite. An examination of a residue from an autoclave from an operating mine has shown that the extra phases in the residues consist of the so called Type-2 compound (Fe<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>(OH)(SO<sub>4</sub>) and a jarosite or basic iron sulphate-type compound, this would be in agreement with work from the hydrothermal precipitation experiments and from pressure oxidation of pure arsenopyrite concentrates [87]. The arsenic held within the crystalline Type-2 compounds is considered to be stable and test work on the compound has shown it to pass the EPA solubility threshold (5mg/L).

**11. Examination of a stabilised arsenical solid produced by the pressure oxidation of a mixture of arsenic oxide and pyrite .**

On the suggestion by the investigator a Canadian company reacted arsenic oxide and pyrite in an autoclave at elevated temperature. The work was carried out at 210°C and 100psi oxygen over pressure for 2 hours. The arsenic was found to have been converted to scorodite this was verified by XRD. Chemical analysis of the residue showed no As(III) suggesting total conversion of the arsenic to the As(V) state. An EPA TCLP test on the residue was found to have low solubility <0.4mg/L.

## *12. Comparison of two low temperature scorodite compounds produced using sulphate and chloride media.*

Two samples of crystalline scorodite were submitted for examination, these samples were precipitated from respectively: sulphate and chloride media at McGill University by D. Droppert. The compounds were precipitated at atmospheric pressure at temperatures in the range 80 - 95°C, employing a supersaturation controlled procedure [105]. Acidic chloride solutions contained 2g/L As(V), the procedure involved the step-wise neutralisation under a low supersaturation environment in the presence of seed.

The IR spectra of the two samples both show typical scorodite features. The distinct spike in the 3300cm<sup>-1</sup> region corresponds to the two water molecules in the crystalline scorodite. Amorphous iron arsenate with an Fe:As ratio 1:1 does not show this peak and it can therefore be used as an index of crystallinity. The less distinct spike in the sulphate spectrum therefore suggests that it has a marginally lower crystallinity than the sample prepared in the chloride medium. The scorodite produced from the sulphate medium shows the presence of sulphate (1000 - 1200 cm<sup>-1</sup>). However, whether this is actually in the lattice of the scorodite or is present in a separate phase cannot easily be determined. The inflection of the spectra around the 2300cm<sup>-1</sup> region possibly indicates the presence of an HAsO<sub>4</sub> functional group.

The DTA-TG data of the two samples are almost identical and show features typical of scorodite with an endothermic peak at ~220°C, which relates to a 16 - 17% mass loss (removal of water of hydration in FeAsO<sub>4</sub>.2H<sub>2</sub>O) and an exothermic peak at ~550°C which relates to a recrystallisation event. The mass loss appears to take place over a greater temperature range (200 - 400°C) than in more crystalline varieties of scorodite, which suggests that the samples may be fine grained and of a lower crystallinity.

An anomalous endothermic peak is observed on the patterns around 330°C, this is not found with hydrothermally prepared scorodite (>150°C). The mass loss (<1%) at around 770°C is also anomalous and may correspond to water loss from a ferrihydrite-type compound in the solid.

## Appendix 2

### Hydrothermal precipitation

#### 2.1 Method of small scale precipitation in Pyrex test tubes

1. 0.5M solutions of  $\text{Li}_2\text{SO}_4 \cdot 9\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and a 0.25M solution of  $\text{As}_2\text{O}_5$  (i.e.  $\text{SO}_4$ , Fe(III) and As(V)) were prepared (see Table A4). The lithium is not a jarosite forming element and remains in solution, as does the excess nitrate. If sodium or calcium hydroxide were used these would precipitate other compounds and complicate the characterisation and solubility testing of the solids.
2. Sulphate containing solutions were also prepared using 0.5M solutions of  $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$  and As(V). These solutions were considered to be closer hydrometallurgical analogues than those containing lithium and nitrate (see above).
3. Lithium hydroxide was used for the pH adjustment of the arsenical solutions.
4. Using molar proportions the composition of solutions were calculated and 20mL aliquots of the mixture were prepared and sealed in medium-walled Pyrex glass test tubes. The pH of the mixed solutions were usually  $< 0.7$ .
5. The sealed test tubes were placed in a water-filled autoclave and heated at the required temperature for 24hrs. The autoclave took  $\sim 1$ hr to reach temperature and 5 - 6hrs to cool to room temperature, prior to opening.
6. The sealed tubes were removed from the autoclave and visually examined before opening. The solids were subsequently filtered using Whatman 542 and  $0.45\mu\text{m}$  membrane filters, the mother liquor (i.e. the filtrate) was collected and its pH taken (usually  $< 0.5$ ). The solids were usually repulped and washed with excess amounts of distilled water to remove any soluble salts. Nevertheless, in some compounds, IR analysis revealed the presence of nitrate which has a distinctive peak at  $1390\text{ cm}^{-1}$ .

7. The more gelatinous/fine grained, iron-rich samples were centrifuged and the mother liquors decanted. The remaining solids were repulped, washed and the liquid decanted, this process was repeated where necessary. The washed solid remained in the polythene bottles and the remaining water was allowed to evaporate. Filtration using 0.45 $\mu$ m membrane filters also proved to be successful on a number of occasions.
8. The samples were air dried in a desiccator and their weights recorded. A minimum of 1.5g of sample was required for characterisation, chemical analysis and solubility testing. The precipitation procedure was repeated if an insufficient amount of sample was obtained.
9. During the course of the precipitations some preparations were carried out both in the autoclave and in an oven. Characterisation of the solids from the two methods showed them to be similar. However, iron-rich samples produced in the autoclave at 150°C were fine grained and the solids appeared to have partially reequilibrated on cooling (up to 6 hours), whereas the samples produced in the oven (cooling time <1 hour) were essentially quenched and retained their crystallite size and composition.

## 2.2 Composition of precipitation solutions

Table A4. Compositions of solutions used in the hydrothermal precipitations. These compositions are given in the ternary diagram of Figure 3.1 (main text).

Soln Compn.	0.5M Fe sol.(%)	0.5M AsO <sub>4</sub> sol.(%)	0.5M SO <sub>4</sub> sol.(%)	Fe:As (M)	Solution pH
A	50	50	0	1:1	0.36
B	33.3	8.3	58.4	4:1	1.10
C	33.3	33.3	33.3	1:1	0.81
D	33.3	22.2	44.5	1.5:1	0.83
E	33.3	14.3	52.4	2.3:1	0.95
F	48	12	40	4:1	0.64
G	71.1	8.9	20	9:1	0.71
H	53.4	6.6	40	9:1	0.89
J	33.3	3.7	63	9:1	1.29
K	45	45	10	1:1	0.48
L	40	40	20	1:1	0.49
M	55	36	9	1.5:1	0.48
N	50	33	17	1.5:1	0.53
O	56	24	20	2.3:1	0.35
P	64	27	9	2.3:1	0.49
Q	42	18	40	2.3:1	0.81
R	62	15	23	4:1	0.66
S	67	17	16	4:1	0.54
T	73	18	9	4:1	0.54
U	90	10	0	9:1	0.58
V	80	20	0	4:1	0.47
W	70	30	0	2.3:1	0.06
X	60	40	0	1.5:1	0.40
Y	40	60	0	0.7:1	0.42
Z	30	70	0	1:2.3	0.58

## Appendix 3 Infra-red spectroscopy

### 3.1 Naturally occurring arsenate minerals examined by IR

Table A5. Mineral samples used from the Natural History Museum

BM number	Mineral	Formula	locality
34336	Arseniosiderite	$\text{Ca}_3\text{Fe}_4(\text{OH})_6(\text{H}_2\text{O})_3(\text{AsO}_4)_4$	Romaneche, near Macon
1916 454	Arseniosiderite	$\text{CaFe}_9(\text{AsO}_4)_6(\text{OH})_9.18\text{H}_2\text{O}$	Daulton mine, Yukon, Canada
1936 1457	Scorodite	$\text{FeAsO}_4.2\text{H}_2\text{O}$	Britch-Mulla, Siberia
1950 286	Scorodite	$\text{FeAsO}_4.2\text{H}_2\text{O}$	Gold Hill, Tooele Co. Utah
1968 265	Bukovskyite	$\text{Fe}_2\text{AsO}_4\text{SO}_4\text{OH}.7\text{H}_2\text{O}$	Kank, Bohemia, Czechoslovakia
1974 371	Arseniosiderite	$\text{Ca}_3\text{Fe}_4(\text{OH})_6(\text{H}_2\text{O})_3(\text{AsO}_4)_4$	Las Animas, Sonora Mexico
1975 242	Scorodite	$\text{FeAsO}_4.2\text{H}_2\text{O}$	Tsumeb, Namibia
1976 344	Symplesite	$\text{Fe}_3(\text{AsO}_4)_2.8\text{H}_2\text{O}$	Ojuela mine, Mapimi, Mexico
1979 259	Kankite	$\text{FeAsO}_4.3.5\text{H}_2\text{O}$	Kank, Bohemia, Czechoslovakia.
1985 643	Kaatiatite	$\text{Fe}(\text{H}_2\text{AsO}_4)_3.5\text{H}_2\text{O}$	locality unknown
1979 259	Kankite	$\text{FeAsO}_4.3.5\text{H}_2\text{O}$	Kank, Kutna Hora Prazska zup.
1975 242	Scorodite	$\text{FeAsO}_4.2\text{H}_2\text{O}$	Tsumeb, Namibia
1977 40	Symplesite	$\text{Fe}_3(\text{AsO}_4)_2.2\text{H}_2\text{O}$	Mapimi, Mexico
1968 206	Bukovskyite	$\text{Fe}_2\text{AsO}_4\text{SO}_4\text{OH}.7\text{H}_2\text{O}$	Kank, Kutna Hora, Czechoslovakia
99345	Pitticite	$\text{Fe}_2\text{O}_3\text{As}_2\text{O}_5.(9-10)\text{H}_2\text{O}$	St Just, Cornwall
AG1	Haidingerite	$\text{CaHAsO}_4.\text{H}_2\text{O}$	Wittchen, Baden, Germany.
AG2	Pharmacolite	$\text{CaHAsO}_4.2\text{H}_2\text{O}$	Saint-Marie-aux mines, France
1965 303	Weilite	$\text{CaHAsO}_4$	Gabe-Gottes as above
1966 446	Saintfeldite	$\text{Ca}_5\text{H}_2(\text{AsO}_4)_4.4\text{H}_2\text{O}$	Gabe-Gottes as above
1972 221	Guerinite	$\text{Ca}_5\text{H}_2\text{AsO}_4.9\text{H}_2\text{O}$	Friedrich-Wilhelm mine, Hessen.
1984 81	Phaunouxite	$\text{Ca}_3(\text{AsO}_4)_2.11\text{H}_2\text{O}$	Bauhaus, Richelorf, Hessen.
1984 82	Ferrarisite	$\text{Ca}_5\text{H}_2(\text{AsO}_4)_4.9\text{H}_2\text{O}$	Bauhaus, Richelorf, Hessen



## Appendix 4

### Arsenic analytical methods

#### 4.1 Hydride generation method

A hydride generation method was used when the normal flame AAS method indicated that the arsenic concentration of a sample solution was 3mg/L or less. When the method is applied as detailed below, the analytical range covered is 0.2 - 4.0 mg/L arsenic.

1. The sample solution A is diluted 10 times with 1% HCl to give solution B (i.e. 0.5ml sample +4.5ml of 1% HCl)
2. Solution B is diluted 20 times with 1% KI solution in 5M HCl to give solution C (i.e. 0.5 mL solution B + 9.5 mL KI solution).
3. Solution C is allowed to stand for 50 minutes in order for the complete reduction of As(V) to As(III) to take place. This reduction is essential otherwise low arsenic levels will be obtained.
4. Standard solutions in the range 5 - 20 ppb ( $\mu\text{g/L}$ ) arsenic are prepared in the KI solution and treated as in 3/ above.
5. Solution C is then reacted with 0.6% sodium borohydride solution in 0.5% NaOH solution and 5M HCl in the hydride generator. The resulting arsine ( $\text{AsH}_3$ ) is flushed with nitrogen into a heated silica cell in the light path of the AA.

## 4.2 The molybdenum blue photometric method for As(III) determination (heteropoly - blue method)

### Introduction

The arsenic(III)/(V) ratio of metallurgical sample is often necessary before any detailed assessment can be made. This is because As(III) compounds (arsenites) are invariably soluble at pH's less than ~pH8 and the arsenic cannot easily be coprecipitated as a solid phase. The recommended analytical method used in the determination of As(III) is detailed below:-

Molybdic acid forms yellow heteropoly acids with As(V), phosphorus, silicon and germanium. The molybdenum combined in these heteropoly acids is more easily reducible than the uncombined molybdate, and a blue substance of undetermined composition is formed by various reductants. In this method ascorbic acid is the reducing agent. As(III) must be oxidised to As(V) before colour development, and in this method sodium hypochlorite solution is used for this purpose. Finally the absorbance of the developed colour is measured on a suitable UV/VIS spectrophotometer.

### Reagents

1. Sulphuric acid - 2.5M
2. Antimony Potassium Tartrate - 0.45wt % in H<sub>2</sub>O
3. Ammonium Molybdate - 5.0wt % in H<sub>2</sub>O. Stand for 24hrs then filter before use.
4. Ascorbic acid - 2.5wt % in H<sub>2</sub>O. Prepare fresh just before use.
5. Sodium Hypochlorite solution - 10% with H<sub>2</sub>O

Mixture A Mix together the following reagents and store in a polythene bottle:-

Sulphuric acid 2.5M - 50mL  
Antimony Potassium Tartrate 0.45wt % - 5.0mL  
Ammonium Molybdate 5.0wt % - 15.0mL  
Ascorbic acid - 2.5wt % - 30.0mL  
(prepare fresh just before use)

### Calibration

Take aliquots of an arsenic standard solution such that the arsenic concentration of the final developed solutions cover the range 0.5 - 5.0mg/L arsenic. Place in 50mL standard flasks. If an As(III) standard is used add 1ml of the sodium hypochlorite solution and allow to stand for 15 mins. If an As(V) standard solution is used this step is omitted.

Add a little water to the flask followed by 8.0ml of mixture A, dilute to the mark with water, mix and then allow the colour to develop for 30 minutes before measuring. Measure the absorbance of the standards using a suitable spectrophotometer at a wavelength of 880nm using 1cm cells. The reference solution should be pure water treated as above.

#### Determination of As(III)

1. Take an aliquot of the sample solution such that the arsenic concentration falls in the range 0.5 - 5mg/L arsenic.
2. Place in a 50ml standard flask and proceed as for the calibration with As(III) standards.
3. The absorbance measured is then compared to the standard calibration to obtain the concentration of arsenic.

#### Notes

- If the sample also contains As(V) this will have been measured so a total arsenic figure has been obtained. Repeating the above procedure but omitting the oxidation step with sodium hypochlorite solution will give a result for As(V) only - hence the As(III) may then be obtained from the difference between the total arsenic and the As(V) results.
- Appropriate blanks should be carried through the whole of these procedures and deducted from the results obtained.
- Note the possible interference from phosphorus, silicon and germanium.

## Appendix 5

### General testwork on the EPA TCLP method

To test the reproducibility of the EPA TCLP test (L:S 20:1, buffered at pH4.93, using an end-over-end agitation for a 20 hour period) a 5g sample of precipitated solids was divided into two halves; one half was finely milled before testing and the other half was tested unmilled. Five tests on each sample were carried out and the results are given in Table A6. The two sets of samples displayed similar results and showed that for the purposes of the study the test is reproducible.

**Table A6.** Results of multiple EPA TCLP testing on a single sample

Sample	As content of EPA TCLP test solution (mg/L)	Mean (Std. Deviation.)
Milled - Fe:As 1.5:1 25°C pH5	49.6 50.2 50.1 49.4 51.4	50.14 (±0.78)
Unmilled - Fe:As 1.5:1 25°C pH5	48.6 50.3 51.2 51.9 49.7	50.34 (±1.29)

While the EPA TCLP test recommends the testing of 100g samples, such quantities were not available in the current precipitation work. In order to test its validity on smaller samples comparative tests were carried out using a liquid:solid ratio of 20:1 on 5g and 100g of an arsenical solid. The results were similar (see Table A7). The use of even smaller amounts of solid is likely to be valid especially when the sample is finely divided and homogeneous.

The EPA TCLP testing of numerous samples precipitated at pH<1 and pH5 has been shown by the MIRO Arsenic Research Group that a positive correlation does exist between the solubility as determined by the MARG test and the EPA TCLP test. In agreement with the relative solubility determinations of previous MARG testwork, the EPA TCLP tests indicate that

the Type-2 and scorodite are the least soluble compounds (with soluble arsenic levels mostly in the 1 to 4mg/L range).

**Table A7. Influence of sample size on the EPA TCLP test results**

Arsenical sample (11.1% As)	L:S ratio (20:1) Sample test size	As content of solution (mg/L)
1	100ml : 5g	0.60
	2000ml : 100g	0.77
2	100ml : 5g	2.50
	2000ml : 100g	2.49
3	100ml : 5g	0.96
	2000ml : 100g	0.91

Arsenical solids precipitated at high temperatures using iron sulphate and As(V) were tested and compared to the low temperature (20°C) Fe:As >2.3:1 precipitates. It was found that the low temperature, high Fe:As varieties were the least soluble of the arsenical compounds examined so far, with arsenic levels in solution usually well below 1.5 mg/L, while the scorodite and Type-2 phases showed arsenic levels in solution usually less than 2 mg/L (Table A8).

Surprisingly, a comparison of the standard EPA TCLP (20:1 L:S) results with unagitated tests (Table A8) showed that agitation (20 hours) does not influence the results to any great extent. Changing the L:S ratio of the EPA TCLP test solution (to 40:1) does yield different results which are on average ~30% higher than expected if one considers that twice the liquid volume is used.

In some tests gypsum was added to the test solids (solid:gypsum ratio - 1:1 and 1:2) as a source of calcium in order to simulate the behaviour of lime-neutralised arsenical solids (Table A9). Soluble arsenic levels in the presence of gypsum usually fell to less than 50% of the conventional EPA TCLP test levels. The addition of even greater amounts of gypsum would depress arsenic levels even further. These results support the view that the presence of gypsum has a passivating effect by precipitating the arsenic as a calcium

arsenate: probably at pH4 - 7 as  $\text{CaHAsO}_4 \cdot x\text{H}_2\text{O}$  and  $>\text{pH}7$  as a  $\text{Ca}_5\text{H}_2(\text{AsO}_4)_4$  or  $\text{Ca}_3(\text{AsO}_4)_2$  compound. It is therefore recommended that if arsenical precipitates are to be tested, where possible they should be free from gypsum, in order to evaluate the true solubility of the arsenate by removing the influence and interference of calcium ions. In process samples this is often not possible due to gypsum being in intimate contact with the arsenate compounds and unfortunately there is no practical means of concentrating the arsenical component in such samples.

Table A8. EPA TCLP results on selected iron-arsenate samples

Solid - type	Conditions of precipitation (T°C, Fe:As, pH)	TCLP 20:1		TCLP 20:1	TCLP 40:1
		Test 1 As (mg/L)	Test 2 As (mg/L)	No agitation As (mg/L)	Test 1 As (mg/L)
Type-1	Y#200°C pH<1	84.60	80.80	97.60	50.10
Type-1	225°C 1:1 pH<1	18.50	16.60	18.00	12.90
Type-3	225°C 1:1 pH5	3.20	2.48	3.00	2.20
Type-1	150°C 1:1 pH<1	34.70	34.2	35.40	26.60
Type-2	200°C 3:1 pH<1	1.30	0.24	0.6	0.12
Type-2	200°C 1.5:1 pH<1	1.52	1.49	0.75	0.85
Scorodite	150°C 3:1 pH<1	1.36	1.29	1.51	<0.1
Scorodite	150°C 1.5:1 pH<1	2.00	2.23	0.88	1.43
Ferrihy.*	20°C 9:1 pH5	0.39	0.08	0.30	0.20
Ferrihy.*	20°C 4:1 pH5	6.10	4.80	4.80	4.10
Ferrihy.*	20°C 2.3:1 pH5	1.21	0.91	1.50	1.60
Ferrihy.*	20°C 1.5:1 pH5	50.20	46.8	56.20	54.10

# Composition Y (see Figure 3.1)

\* Arsenic adsorbed onto amorphous ferrihydrite solid

The testing of a Type-1 compound gave an EPA TCLP solubility result of 14.9mg/L arsenic in solution. The addition of calcium to the test (solid: calcium compound of 1:1) in the form of calcite, gypsum or calcium nitrate gave arsenic levels of 1.69, 5.3 and 2.67mg/L arsenic respectively, indicating the apparent stabilisation of the arsenic by the presence of calcium. The arsenic may be precipitated on the surface of the grains or precipitated from solution.

The influence of the L:S ratio on the final arsenic concentration in solution was tested by end-over-end agitation of various volumes of pH5 solution (adjusted using H<sub>2</sub>SO<sub>4</sub>, Table A10). As would be expected the arsenic levels progressively increase as the liquid content decreases (i.e. lower liquid:solid ratio), but dissolution does not appear to proceed in any systematic fashion, although a greater proportion of the solids dissolves in the higher L:S tests.

**Table A9.** Influence of gypsum during EPA TCLP testing

Solid -Type	Conditions of precipitation (T°C, Fe:As, pH)	EPA TCLP*		
		no gypsum added As (mg/L)	1:1 gypsum As (mg/L)	2:1 gypsum As (mg/L)
Type-1	Y200°C pH<1	84.6	46.1	40.3
Type-1	225°C 1:1 pH<1	18.5	7.8	6.1
Type-3	225°C 1:1 pH5	3.2	3.5	2.5
Type-1	150°C 1:1 pH<1	34.7	12.8	11.7
Type-2	200°C 1.5:1 pH<1	1.52	1.41	1.26
Scorodite	150°C 1.5:1 pH<1	2.00	1.01	1.09
Ferrihy.	25°C 9:1 pH5	0.39	2.1	0.13
Ferrihy.	25°C 4:1 pH5	6.1	1.8	1.88
Ferrihy.	25°C 2.3:1 pH5	1.21	1.5	1.23
Ferrihy.	25°C 1.5:1 pH5	50.2	33.9	29.1

\* 0.5g solid added to 10ml EPA TCLP solution

**Table A10.** Influence of the liquid:solid ratio on the arsenic concentration of the contacting solution

Sample	As concentration (mg/L) in pH5 solutions* adjusted with H <sub>2</sub> SO <sub>4</sub> (variable L:S ratio)				
	50000:1	5000:1	500:1	50:1	5:1
Fe:As 1.5:1 20°C pH5	0.52	3.50	35.2	107.8	50.3
Type-1 Y200 pH<1	0.25	0.71	6.8	34.5	240.0
Fe:As 1:1 150°C pH<1	0.19	0.89	5.2	18.7	50.4

\* 20hr end-over-end agitation

## Appendix 6 X-ray diffraction data

### 6.1 X-ray diffraction data on precipitated compounds

**Table A11.** X-ray diffraction data for the Types 1 to 4 compounds formed during hydrothermal precipitation using iron sulphate and As(V) solutions. The conditions of formation are given below.

Type-1 compound		Type-2* compound		Type-3 compound		Type-4 compound	
d-spacing	Peak Intensity	d-spacing	Peak Intensity	d-spacing	Peak Intensity	d-spacing	Peak Intensity
8.77	42	4.89	5	4.88	35	8.92	100
6.42	63	3.38	100	4.76	25	4.88	56
5.08	12	3.25	64	3.52	18	3.47	47
4.02	23	2.64	19	3.36	38	3.38	25
3.83	14	2.35	6	3.33	29	3.17	62
3.67	22	2.32	20	3.26	43	3.03	21
3.39	13	2.06	15	3.08	100	3.00	57
3.27	11	1.89	9	2.60	25	2.98	60
3.23	24	1.76	2	2.53	35	2.96	65
3.16	100	1.69	8	2.52	19	2.92	68
3.09	43	1.63	11	2.42	17	2.77	22
2.97	69	1.62	28	2.38	20	2.69	41
2.96	48	1.47	9	1.96	20	2.51	62
2.91	63	1.45	3	1.87	12	2.50	50
2.87	17			1.70	18	2.22	33
2.84	13			1.68	16	2.17	20
2.77	6			1.63	21	1.77	33
2.71	16			1.59	43	1.69	28
2.62	27					1.65	31
2.59	18					1.58	24
2.53	9					1.53	28
2.41	11						
2.39	12						

\* see also Table 4.6, Chapter 4

Compound	Temperature of formation (°C)	Composition of starting solution
Type-1	200	Composition Y 22g/L As, 11g/L Fe
Type-2	225	Composition N 12g/L As, 13g/L Fe
Type-3	225	20g/L As, 15g/L Fe Composition C Solution adjusted to pH5 with lithium hydroxide
Type-4	200	5g/L Ca, 17g/L As, 7g/L Fe Solution adjusted to pH5 with lithium hydroxide



**Table A12.** X-ray diffraction data for ferrihydrite, hematite, jarosite and the basic iron sulphate compounds formed during hydrothermal precipitation. The conditions of formation are given below.

Ferrihydrite		Hematite		Hydronium jarosite		Basic iron sulphate	
d-spacing	Peak Intensity	d-spacing	Peak Intensity	d-spacing	Peak Intensity	d-spacing	Peak Intensity
2.51	100	14.71	11	5.98	8	4.79	13
2.21	70	6.30	5	5.66	24	3.58	9
1.97	30	3.69	29	5.10	100	3.27	5
1.70	35	2.70	100	3.69	5	3.22	100
1.51	100	2.52	65	3.54	7	2.29	2
1.46	90	2.29	2	3.14	75	2.23	9
1.05	10	2.20	22	3.09	79	2.05	21
0.97	10	2.08	2	3.00	5	2.00	2
		1.84	35	2.99	6	1.84	2
		1.69	74	2.83	12	1.78	2
		1.60	10	2.55	16	1.64	4
		1.48	40	2.27	23	1.60	14
		1.45	39	1.99	22	1.59	13
				1.98	10	1.56	5
				1.93	9	1.44	13

Compound	Temperature of formation (°C)	Composition of starting solution
Ferrihydrite	175	Composition U 5g/L As 15g/L Fe
Hematite	225	Iron nitrate 4g/L As 25g/L Fe
Hydronium jarosite	190	Fe(III) sulphate solution only, before 1hr (24g/L Fe) Agitated in autoclave
Basic iron sulphate	225	Fe(III) sulphate solution only, after 24hrs (29g/L Fe) Not agitated in test tubes

## 6.2 X-ray diffraction results on precipitated solids

**Table A13.** Results of the XRD analysis on the solids precipitated at pH5 showing the major phases in the samples.

Sample	Precipitation Temperature (°C)				
	125	150	175	200	225
Y	S	S+T3	S+T3	T3+T1	T3+T1
A	A	A	T3	T3+T1	T3+T1
L	A	A	T3	T3	T3
C	A	S+T3	T3	T3	T3
W	A	F	F+H	F	F
O	nd	F	F	F	F+T3
Q	F	F	F+T3	F+T3	F+T3
U	A	H	nd	nd	H+F
F	F	F	F	F+H	F+H

Key A - Amorphous, F - Ferrihydrite compound, H - Hematite, T3 - Type-3, T1 - Type-1 compound, S - Scorodite, nd - not determined,

**Table A14.** XRD analyses on the solids precipitated at the natural pH showing the major phases in the samples.

Sample	Precipitation temperature (°C)				
	125	150	175	200	225
D	nd	S	T2	T2	T2
B	nd	x+y	F	H+F	H+T2+F
J	nd	F+x+y	H+F	H+F	H+F
Q	nd	F+x	T2+F	F+T2	F+T2
C	nd	S+T1	T1+S	T1	T1
G	nd	F	H+F	H+F	H+F
H	nd	F+x+y	H+F	H+F	H+F

Key F - Ferrihydrite compound, T1 - Type-1 compound, T2 - Type-2 compound, H - hematite, nd - not determined. Anomalous compounds (x and y) appear in the 150°C precipitation samples.

### 6.3 X-ray diffraction data on unknown calcium arsenate compounds

**Table A15.** X-ray diffraction data for the unknown synthetic calcium arsenate compounds precipitated using calcium nitrate, arsenic acid and lithium hydroxide in the pH adjustment.

Weilite-type (1)		Weilite-type (2)		Haidingerite-type (3)		Pharmacolite-type (4)	
d-spacing	Peak Intensity	d-spacing	Peak Intensity	d-spacing	Peak Intensity	d-spacing	Peak Intensity
6.53	11	6.93	9	8.21	87	14.19	14
6.47	7	3.47	100	8.09	100	7.71	96
5.21	7	3.43	5	4.04	65	5.34	6
4.49	5	2.84	7	3.21	19	5.11	26
4.41	7	2.31	18	3.20	15	4.28	100
3.97	13	2.11	2	2.96	8	3.85	9
3.96	14	1.78	3	2.69	7	3.81	14
3.46	16	1.73	9	2.62	8	3.08	66
3.45	8	1.59	2	2.51	15	3.06	18
3.25	10			2.39	11	3.03	47
3.14	12			1.94	9	2.92	9
3.12	15			1.88	11.3	2.84	6
3.06	35			1.80	5	2.71	31
3.03	14			1.69	4	2.67	34
2.97	100			1.59	4	2.57	10
2.86	22			1.54	6	2.51	18
2.81	12			1.49	2	2.44	13
2.6	7					2.22	10
2.52	6.83					2.01	7
2.01	9					1.91	12
1.91	7					1.91	16
1.85	11					1.86	16
1.75	16					1.83	9

#### Synthesis conditions of compounds

- 1) Ca:As 1:1, pH8, solution heated to 125°C (and Ca:As 1:1, pH6, 175°C)
- 2) Ca:As 1:1, pH4, solution heated to 125°C (and Ca:As 1:1, pH8, 175°C)
- 3) Ca:As 1:1, pH6, solution heated to 75°C
- 4) Ca:As 1:1, pH6, solution heated to 25°C

Solids 1) to 4) show IR spectra comparable to known naturally occurring calcium arsenate minerals

**Table A15(cont.)** X-ray diffraction data for the unknown synthetic calcium arsenate compounds precipitated using calcium nitrate, arsenic acid and lithium hydroxide in the pH adjustment

Ca-arsenate-type (5)		Ca-arsenate-type (6)		Ca-arsenate-type (7)		Guerinite-type (8)	
d-spacing	Peak Intensity	d-spacing	Peak Intensity	d-spacing	Peak Intensity	d-spacing	Peak Intensity
6.31	7	3.46	7	8.44	5	14.16	34
4.69	18	3.34	87	4.88	6	11.68	8
4.66	27	3.12	100	4.00	17	10.67	23
3.46	25	2.80	5	3.65	8	8.88	6
3.38	37	2.80	5	3.49	9	8.10	100
3.35	80	2.78	23	3.38	100	5.36	15
3.15	18	1.80	5	3.34	23	5.31	13
3.14	16	1.73	7	3.19	5	4.83	9
3.11	16	1.55	8	3.11	30	4.05	50
3.08	8			3.07	6	3.75	11
2.98	24			2.97	16	3.57	8
2.84	8			2.90	53	3.47	11
2.78	100			2.83	20	3.44	12
2.77	69			2.83	18	3.27	33
2.59	6			2.81	33	3.26	10
2.35	6			2.78	7	3.08	5
2.33	8			2.69	8	3.05	17
2.24	34			2.34	7	2.91	9
2.19	5			2.21	8	2.86	7
2.09	13			2.20	8.09	2.82	16
1.93	5			2.09	19	2.81	9
1.89	13			1.99	32	2.70	31
1.86	11			1.88	7	2.67	26
1.72	36			1.86	7	2.66	9
1.66	24			1.72	25	2.58	5
1.64	15			1.69	9	2.57	6
1.64	50			1.67	5	2.48	16
				1.62	16	2.42	7
				1.59	13	2.41	11

**Synthesis conditions of compounds**

- 1) Ca:As 1:1, pH4, solution heated to 225°C
- 2) Ca:As 1:1, pH6, solution heated to 225°C
- 3) Ca:As 1:1, pH8, solution heated to 225°C
- 4) Ca:As 1:1, pH8, solution heated to 75°C

Solids 5) to 8) show IR spectra comparable to known naturally occurring calcium arsenate minerals

## Appendix 7

### Chemical analyses of solids

**Table A16.** Chemical analyses of iron-arsenate solids precipitated at 150 and 175°C (pH<1)

Sample 150°C	Mass percentage (%)				
	Fe	AsO <sub>4</sub>	SO <sub>4</sub>	H <sub>2</sub> O	Total
U150	nd	nd	nd	nd	nd
V150	nd	nd	nd	nd	nd
W150	20.70	59.49	0.00	13.60	93.79
X150	24.59	70.12	0.00	13.40	108.11
A150	23.40	65.85	0.00	12.90	102.15
Y150	23.55	72.34	0.00	6.90	102.79
Z150	26.16	79.48	0.00	7.40	113.04
T150	nd	nd	0.00	15.20	nd
P150	22.18	57.51	1.11	9.20	90.00
M150	24.71	64.69	3.51	11.10	104.01
I150	22.46	53.02	3.87	9.70	89.05
F150	22.68	45.61	5.73	nd	74.02
R150	37.39	49.45	3.39	9.70	99.93
K150	23.51	61.22	1.92	12.90	99.55
N150	24.50	63.22	4.05	10.60	102.37
O150	21.39	50.10	2.43	nd	73.92
L150	22.43	65.54	2.52	nd	90.49
S150	21.95	44.66	4.23	nd	70.84
C150	24.8	66.97	1.31	nd	93.07
D150	23.5	60.13	5.18	nd	88.81
Q150	26.5	47.55	5.77	nd	79.82
B150	30.5	25.16	19.16	nd	74.82
H150	40.8	27.2	8.68	nd	76.67
J150	42.0	18.69	12.63	nd	73.31
G150	38.8	24.79	4.09	nd	67.67
U175	54.62	10.25	0.00	nd	64.87
V175	33.63	44.94	0.00	nd	78.57
W175	24.37	57.51	0.00	17.70	99.58
X175	25.55	68.58	0.00	nd	94.13
A175	25.63	60.48	0.00	6.00	92.11
Y175	24.54	89.08	0.00	9.40	123.02
Z175	21.31	77.87	0.00	10.70	109.88
T175	28.50	32.63	0.03	nd	61.16
P175	22.01	57.18	1.92	nd	81.11
M175	25.19	70.93	0.03	nd	96.15
I175	30.74	48.07	6.39	nd	85.20
F175	28.89	45.14	11.34	0.00	85.37
R175	27.47	47.61	10.53	nd	85.61
K175	23.48	59.81	0.12	nd	83.41
N175	24.17	64.65	0.06	nd	88.88
O175	23.13	57.66	1.83	8.90	91.52
L175	21.43	60.92	0.24	3.30	85.89
S175	29.50	47.52	7.86	nd	84.88
C175	25.6	66.42	0.77	nd	92.79
D175	28.7	52.91	9.15	nd	90.76
Q175	33.1	44.22	9.28	nd	86.60
B175	41.6	31.82	3.02	nd	76.44
H175	49	22.39	3.68	nd	75.07
J175	53.8	13.88	4.22	nd	71.90
G175	48.4	20.72	3.58	nd	72.70

Table A17. Chemical analyses of iron-arsenate solids precipitated at 200 and 225°C (pH<1)

Sample	Mass percentage (%)				
	200°C	Fe	AsO <sub>4</sub>	SO <sub>4</sub>	H <sub>2</sub> O
U200	44.35	22.71	0.00	10.10	77.16
V200	26.25	45.48	0.00	nd	71.73
W200	26.57	58.62	0.00	12.20	97.39
X200	21.44	62.74	0.00	nd	84.18
A200	25.91	71.68	0.00	2.30	99.89
Y200	27.80	75.64	0.00	1.50	104.94
Z200	27.90	75.46	0.00	0.00	103.36
T200	38.19	41.33	3.39	nd	82.91
P200	29.87	63.41	2.07	nd	95.35
M200	23.01	56.32	1.98	nd	81.31
I200	28.07	46.20	2.40	nd	76.67
F200	27.43	40.16	12.36	0.50	80.45
R200	31.81	44.74	9.42	nd	85.97
K200	22.85	69.77	0.03	nd	92.65
N200	23.38	68.60	0.09	nd	92.07
O200	24.05	64.02	1.62	2.80	92.49
L200	23.11	65.30	0.12	2.20	90.73
S200	26.15	40.57	2.88	nd	69.60
C200	26	68.45	0.43	nd	94.88
D200	29.7	52.36	11.54	nd	93.60
Q200	27.8	33.12	4.90	nd	65.82
B200	40.4	25.9	1.97	nd	68.27
H200	52.4	17.39	3.38	nd	73.17
J200	55.2	13.69	3.13	nd	72.02
G200	51.7	15.36	2.86	nd	69.92
U225	57.52	7.45	0.00	0.00	64.97
V225	46.31	28.90	0.00	nd	75.21
W225	35.27	41.31	0.00	4.10	80.68
X225	33.09	50.58	0.00	0.00	83.67
A225	27.29	63.04	0.00	0.90	91.23
Y225	26.43	70.45	0.00	0.90	97.78
Z225	24.70	74.38	0.00	nd	99.08
T225	45.02	28.48	1.38	nd	74.88
P225	38.74	38.43	0.90	nd	78.07
M225	32.94	51.78	6.60	nd	91.32
I225	46.13	46.55	0.03	nd	92.71
F225	46.68	28.33	1.89	nd	76.90
R225	45.88	25.96	2.43	nd	74.27
K225	25.58	66.21	0.15	nd	91.94
N225	30.51	50.32	9.69	0.00	90.52
O225	36.40	41.10	1.17	4.00	82.67
L225	25.47	63.52	0.33	nd	89.32
S225	39.65	27.68	1.11	nd	68.44
C225	25.6	70.3	0.64	nd	96.54
D225	29.9	53.1	10.42	nd	93.42
Q225	42.8	42.00	0.74	nd	85.54
B225	47.2	27.94	1.54	nd	76.68
H225	55.6	17.76	2.47	nd	75.83
J225	56.5	11.47	2.05	nd	70.02
G225	51.8	16.28	2.44	nd	70.52

Table A18. Chemical analyses of solids precipitated at pH 5

Sample	AsO <sub>4</sub> (%)	Fe (%)	SO <sub>4</sub> (%)	Li (%)	H <sub>2</sub> O (%)*	Total (%)	Fe:As Solid	Fe:As# S.Soln
Y125	48.1	18.6	0.009	0.55	30.0	97.26	0.96	0.66
Y150	62.35	21.4	0.018	1.41	18.0	103.18	0.85	0.66
Y175	62.53	25.1	0.006	1.83	8.0	97.47	1.00	0.66
Y200	71.41	25.6	0.012	2.02	6.0	105.04	0.89	0.66
Y225	66.42	25.4	0.009	2.02	5.5	99.35	0.95	0.66
A125	25.16	14.9	0.108	0.46	45.0	85.63	1.47	1
A150	51.06	23.3	0.012	1.38	20.0	95.75	1.13	1
A175	28.49	11.5	0.009	0.67	52.0	92.67	1.00	1
A200	69.19	26.7	0.006	1.47	7.4	104.77	0.96	1
A225	69.93	27.8	0.009	1.47	5.0	104.21	0.99	1
C125	55.13	25.5	0.027	0.62	16.0	97.28	1.15	1
C150	61.61	26.7	0.045	0.87	13.0	102.23	1.07	1
C175	68.64	26.5	0.369	1.95	5.0	102.46	0.96	1
C200	72.34	26.4	0.438	2.56	4.0	105.74	0.90	1
C225	65.49	26.1	0.342	2.81	4.0	98.74	0.99	1
L125	54.76	25.9	0.039	0.96	18.0	99.66	1.17	1
L150	53.47	24.7	0.021	0.93	22.0	101.12	1.15	1
L175	55.13	25.2	0.144	1.31	15.0	96.78	1.13	1
L200	71.78	26.4	0.108	2.47	5.5	106.26	0.91	1
L225	66.42	27.1	0.06	2.59	3.5	99.67	1.01	1
W125	32.93	30.1	0.006	0.18	28.0	91.22	2.27	2.33
W150	36.26	34.2	0.012	0.14	21.0	91.61	2.34	2.33
W175	30.16	35.2	0.006	0.26	20.0	85.63	2.89	2.33
W200	36.08	38.9	0.012	0.28	9.5	84.77	2.67	2.33
W225	44.4	40.9	0.012	0.27	9.0	94.58	2.28	2.33
Q125	43.48	36.0	0.102	0.16	16.0	95.74	2.05	2.33
Q150	39.78	38.2	0.024	0.06	13.0	91.06	2.38	2.33
Q175	40.7	39.2	0.039	0.18	14.0	94.12	2.39	2.33
Q200	37.56	41.2	0.126	0.25	30.0	109.14	2.72	2.33
Q225	39.59	38.7	0.753	0.56	10.0	89.60	2.42	2.33
O125	37.56	35.6	0.246	0.69	17.0	91.10	2.35	2.33
O150	33.86	37.0	0.027	0.42	16.0	87.31	2.71	2.33
O175	28.12	29.9	0.06	0.20	18.0	76.28	2.64	2.33
O200	38.85	37.5	0.021	0.42	13.0	89.79	2.39	2.33
O225	32.75	39.3	0.078	0.50	8.0	80.63	2.98	2.33
F125	28.49	43.1	0.111	0.03	14.5	86.23	3.75	4
F150	31.64	44.2	0.042	0.03	14.0	89.91	3.46	4
F175	25.16	39.7	0.039	0.05	21.0	85.95	3.91	4
F200	25.35	44.5	0.087	0.08	13.0	83.02	4.35	4
F225	28.12	50.4	0.015	0.05	7.0	85.59	4.44	4
U125	15.73	49.1	0.021	0.05	18.0	82.90	7.74	9
U150	10.92	48.8	0.018	0.02	17.0	76.76	11.08	9
U175	14.43	50.9	0.033	0.04	12.0	77.40	8.74	9
U200	14.8	56.3	0.021	0.01	6.0	77.13	9.43	9
U225	13.69	59.7	0.012	0.01	2.5	75.91	10.81	9

Solid - precipitate, S.Soln. - Starting solution

\* water content determined by DTA-TG

# Initial conditions

**Table A19.** Chemical Analyses of iron arsenates precipitated using iron sulphate and As<sub>2</sub>O<sub>5</sub> solutions at pH<1 (i.e. Natural (N) pH of the solutions)

Temp.°C ppt.	pH	Fe:As# soln (M)	Fe (%)	SO <sub>4</sub> (%)	AsO <sub>4</sub> (%)	Fe:As solid (M)
200	N	1:0	30.82	19.10	-	-
175	N	1:0	32.13	19.10	-	-
150	N	1:0	35.8	nd	-	-
200	N	9:1	30.66	16.84	7.42	10.28
200	N	4:1	30.11	14.83	13.52	5.54
200	N	2.3:1	30.28	12.05	24.18	3.11
200	N	1.5:1	29.15	9.01	33.71	2.15
175	N	1.5:1	26.01	3.80	48.50	1.33
200	N	1:1	27.49	6.09	40.45	1.69
175	N	1:1	27.42	3.82	49.65	1.37
150	N	1:1	23.26	1.95	53.38	1.08
225	N	0.7:1	26.30	nd	70.45	0.93
200	N	0.7:1	25.80	nd	70.82	0.91
175	N	0.7:1	25.80	nd	70.45	0.91
225	N	0.4:1	26.10	nd	74.72	0.87
200	N	0.4:1	25.50	nd	71.19	0.89
175	N	0.4:1	25.30	nd	67.86	0.93

# Initial conditions



**Table A20.** Chemical analyses of iron arsenates precipitated using iron sulphate and As<sub>2</sub>O<sub>5</sub> solutions at pH5

Temp. (°C) precipitation	pH	Fe:As# soln (M)	Fe (%)	AsO <sub>4</sub> (%)	Fe:As solid (M)
20	5	1:1	18.50	41.53	1.11
75	5	1:1	17.70	36.52	1.21
125	5	1:1	24.20	48.39	1.24
175	5	1:1	27.20	61.18	1.11
225	5	1:1	27.70	64.70	1.06
20	5	1.5:1	19.20	32.07	1.49
75	5	1.5:1	25.40	39.49	1.60
125	5	1.5:1	29.20	46.16	1.57
175	5	1.5:1	32.60	50.80	1.60
225	5	1.5:1	34.10	53.77	1.58
20	5	2.3:1	30.00	30.59	2.44
75	5	2.3:1	32.30	32.45	2.48
125	5	2.3:1	37.30	40.23	2.31
175	5	2.3:1	40.20	40.79	2.45
225	5	2.3:1	40.80	40.05	2.53
20	5	4:1	34.30	20.76	4.11
50	5	4:1	36.90	22.62	4.06
75	5	4:1	38.10	23.18	4.09
100	5	4:1	33.10	20.76	3.96
125	5	4:1	37.80	25.40	3.70
150	5	4:1	43.00	25.59	4.18
175	5	4:1	43.70	29.48	3.69
200	5	4:1	47.50	29.48	4.01
225	5	4:1	47.20	27.07	4.34
20	5	9:1	40.20	10.51	9.51
75	5	9:1	45.30	11.51	9.79
125	5	9:1	43.60	12.74	8.51
175	5	9:1	57.00	14.72	9.63
225	5	9:1	58.50	12.98	11.21

# Initial conditions

**Table A21. Chemical analyses of Ca:As compounds precipitated at various pH and temperatures from solutions with a Ca:As ratio of 1:1.**

Temp* ppt	pH	As (%)	Ca (%)	AsO <sub>4</sub> (%)	Total* (%)	Ca:As (M)
150	pH4	44.20	20.60	81.96	102.56	0.87
100	pH5	41.00	20.30	76.02	96.32	0.93
125	pH5	44.20	20.70	81.96	102.66	0.88
150	pH5	43.40	21.10	80.47	101.57	0.91
175	pH5	44.40	20.90	82.33	103.23	0.88
200	pH5	43.90	21.40	81.40	102.80	0.91
20	pH6	35.19	18.78	65.25	84.09	1.00
50	pH6	40.60	18.80	75.28	94.08	0.87
75	pH6	38.56	19.53	71.50	91.04	0.95
100	pH6	40.40	19.10	74.91	94.01	0.89
125	pH6	44.40	21.30	82.33	103.63	0.90
150	pH6	42.30	21.40	78.43	99.83	0.95
175	pH6	41.63	21.54	77.19	98.74	0.97
200	pH6	44.70	21.40	82.88	104.28	0.90
225	pH6	43.73	22.23	81.09	103.34	0.95
20	pH7	36.80	18.00	68.24	86.24	0.92
50	pH7	35.10	17.70	65.08	82.78	0.94
75	pH7	39.40	19.60	73.06	92.66	0.93
100	pH7	41.70	22.10	77.32	99.42	0.99
125	pH7	42.10	22.00	78.06	100.06	0.98
150	pH7	42.30	21.80	78.43	100.23	0.97
175	pH7	44.30	21.70	82.14	103.84	0.92
200	pH7	44.80	22.20	83.07	105.27	0.93
225	pH7	47.4	23.10	87.89	110.99	0.91
20	pH8	32.42	22.13	60.11	82.28	1.28
50	pH8	33.40	20.40	61.93	82.33	1.14
75	pH8	37.84	20.06	70.16	90.23	0.99
100	pH8	40.8	22.90	75.65	98.55	1.05
125	pH8	41.20	24.70	76.39	101.09	1.12
150	pH8	43.20	24.10	80.10	104.20	1.04
175	pH8	39.07	25.61	72.45	98.07	1.23
200	pH8	42.30	25.00	78.43	103.43	1.11
225	pH8	40.22	26.80	74.58	101.39	1.25

\* does not include constitutional water or water of hydration

Table A22. Chemical analyses of the precipitated Ca-Fe-AsO<sub>4</sub> solids from Ca:Fe:As solutions of various pH and temperatures.

T°C ppt.	Sample# (Ca:Fe:As)	pH	Fe (%)	AsO <sub>4</sub> (%)	Ca (%)	Total* (%)	Ca:Fe (M)	(Fe + Ca)/As (M)
150	CaFeAs 3:1:4	pH1	23.84	63.90	0.01	87.75	0.00	0.93
150	CaFeAs 3:1:4	pH3	12.07	60.91	5.40	78.38	0.62	0.80
150	CaFeAs 3:1:4	pH5	11.51	64.18	7.78	83.47	0.94	0.87
150	CaFeAs 3:1:4	pH7	10.50	69.71	16.6	96.30	0.84	1.23
175	CaFeAs 3:1:4	pH1	24.08	63.80	0.01	87.89	0.00	0.94
175	CaFeAs 3:1:4	pH3	12.63	63.95	5.80	82.38	0.64	0.81
175	CaFeAs 3:1:4	pH5	11.03	63.40	7.46	81.89	0.94	0.84
175	CaFeAs 3:1:4	pH7	11.13	65.62	16.47	93.22	2.06	1.29
200	CaFeAs 3:1:4	pH1	25.24	66.36	0.01	91.61	0.00	0.95
200	CaFeAs 3:1:4	pH3	13.07	64.90	5.83	83.80	0.62	0.81
200	CaFeAs 3:1:4	pH5	11.29	63.99	7.81	83.09	0.96	0.86
200	CaFeAs 3:1:4	pH7	10.24	66.14	17.53	93.91	2.38	1.30
225	CaFeAs 3:1:4	pH1	25.68	67.40	0.01	93.09	0.00	0.95
225	CaFeAs 3:1:4	pH3	13.05	62.27	7.20	82.52	0.77	0.92
225	CaFeAs 3:1:4	pH5	11.62	64.56	8.04	84.22	0.96	0.88
225	CaFeAs 3:1:4	pH7	9.68	66.92	17.68	94.28	2.54	1.28
150	CaFeAs 1:3:4	pH1	23.94	62.06	0.01	86.01	0.00	0.96
150	CaFeAs 1:3:4	pH3	23.34	60.82	0.05	84.21	0.00	0.96
150	CaFeAs 1:3:4	pH5	21.10	57.43	2.92	81.45	0.19	1.09
150	CaFeAs 1:3:4	pH7	22.68	52.10	4.88	79.66	0.30	1.41
175	CaFeAs 1:3:4	pH1	23.77	61.78	0.01	85.56	0.00	0.96
175	CaFeAs 1:3:4	pH3	24.05	62.47	0.03	86.55	0.00	0.96
175	CaFeAs 1:3:4	pH5	21.46	58.32	2.92	82.70	0.19	1.09
175	CaFeAs 1:3:4	pH7	22.74	52.31	4.90	79.95	0.30	1.41
200	CaFeAs 1:3:4	pH1	23.36	60.71	0.01	84.08	0.00	0.96
200	CaFeAs 1:3:4	pH3	24.01	61.95	0.35	86.31	0.02	0.98
200	CaFeAs 1:3:4	pH5	23.94	61.02	3.66	88.62	0.21	1.18
200	CaFeAs 1:3:4	pH7	23.37	52.55	5.06	80.98	0.30	1.44
225	CaFeAs 1:3:4	pH1	26.45	67.85	0.00	94.30	0.00	0.97
225	CaFeAs 1:3:4	pH3	24.95	64.14	0.87	89.96	0.05	1.01
225	CaFeAs 1:3:4	pH5	24.71	61.00	4.28	89.99	0.24	1.25
225	CaFeAs 1:3:4	pH7	23.95	52.12	5.05	81.12	0.29	1.48
150	CaFeAs 1:1:2	pH1	23.98	62.95	0.01	86.94	0.00	0.95
150	CaFeAs 1:1:2	pH3	20.89	60.99	1.15	83.03	0.08	0.92
150	CaFeAs 1:1:2	pH5	14.07	57.41	5.83	77.31	0.58	0.96
150	CaFeAs 1:1:2	pH7	19.76	54.35	9.56	83.67	0.67	1.51
175	CaFeAs 1:1:2	pH1	23.40	61.12	0.01	84.53	0.00	0.95
175	CaFeAs 1:1:2	pH3	21.00	62.90	1.48	85.38	0.10	0.91
175	CaFeAs 1:1:2	pH5	20.33	60.19	8.07	88.59	0.55	1.30
175	CaFeAs 1:1:2	pH7	20.64	55.57	9.97	86.18	0.67	1.55
200	CaFeAs 1:1:2	pH1	26.26	67.92	0.01	94.19	0.00	0.96
200	CaFeAs 1:1:2	pH3	22.74	62.54	1.22	86.50	0.07	0.97
200	CaFeAs 1:1:2	pH5	22.83	60.54	8.79	92.16	0.54	1.44
200	CaFeAs 1:1:2	pH7	21.02	56.15	10.13	87.30	0.67	1.56
225	CaFeAs 1:1:2	pH1	26.91	69.39	0.01	96.31	0.00	0.97
225	CaFeAs 1:1:2	pH3	24.79	64.29	4.24	93.32	0.24	1.19
225	CaFeAs 1:1:2	pH5	22.94	60.52	8.67	92.13	0.53	1.44
225	CaFeAs 1:1:2	pH7	20.90	58.22	10.80	89.92	0.72	1.54

\* Excludes constitutional water and water of hydration  
## Initial conditions

**Table A23. ICP analyses of arsenical solids from large scale precipitation runs (injecting iron solution into hot arsenic acid)**

Sample No*	T°C	Fe:As $\phi$ (M) liquor	Fe (%)	AsO <sub>4</sub> (%)	SO <sub>4</sub> (%)	H <sub>2</sub> O# (%)	Total (%)	Fe:As (M) solid	XRD data ID
1	170	1	24.5	60.9	2.4	<14	101.8	1.0	(S)
2	170	3	27.9	49.8	11.4	<14	103.0	1.4	S
3	170	2	26.6	49.2	9.5	<14	99.4	1.3	T2 + S
4	170	1.5	26.6	53.1	7.6	<14	101.3	1.2	S
5	190	2	30.1	41.3	17.1	<4	92.4	1.8	T2
7	150	2	24.8	53.8	7.4	<14	100.0	1.1	S
10	150	1	15.0	38.3	3.3	<14	70.7	1.0	S
11	190	3	17.3	25.3	12.8	<4	59.5	1.7	T2
12	150	3	21.8	32.4	13.5	<14	81.7	1.7	S + T1
13	150	0.5	22.6	57.4	1.2	<14	95.2	1.0	(S)
14	190	1	23.0	57.2	2.3	<14	96.5	1.0	S
15	190	0.5	24.1	60.5	1.4	<4	90.0	1.0	(T2)

# water estimate assuming scorodite - 14%, Type-2 - <4%, some low totals due to mixed compounds and therefore under-estimation of water of hydration (Type-1 compound also up to 16% water)

XRD - Brackets indicate visual identification only, either the brown Type-2 compound (T2), white to light green - Type-1 compound (T1) or the green scorodite (S)

$\phi$  Initial conditions

**Appendix 8**  
**Miscellaneous information on the new arsenate compounds**

**Table A24.** Theoretical (\*) and actual (#) compositions of calcium arsenates

Formula	Ca (%)	AsO <sub>4</sub> (%)	Ca:As (molar)	Constitutional Water (%)	Water of Hydration (%)
* CaHAsO <sub>4</sub>	22.2	77.2	1	5.0	0
# 175°C pH6	21.5	77.2	0.97	5.0	0
* CaHAsO <sub>4</sub> .H <sub>2</sub> O	20.2	70.2	1	4.5	9.1
# 75°C pH7	19.6	73.1	0.93	4.0	10.0
* CaHAsO <sub>4</sub> .2H <sub>2</sub> O	18.6	64.3	1	4.2	16.7
# 25°C pH6	18.8	65.3	0.87	2.5	16.5
* Ca <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub>	30.2	69.8	1.5	0	0
# 225°C pH7	26.8	74.6	0.91	1.2	0
* Ca <sub>5</sub> H <sub>2</sub> (AsO <sub>4</sub> ) <sub>4</sub>	26.4	73.3	1.25	2.3	0
# 25°C pH8	22.1	60.1	0.92	1.0	0

Table A25. Chemical composition of synthetic scorodite compounds

Sample	Fe (%)	AsO <sub>4</sub> (%)	SO <sub>4</sub> (%)	H <sub>2</sub> O (%)	Total (%)	Fe:As (M)
W150	20.70	59.49	0.00	13.60	93.79	0.9
X150	24.59	70.12	0.00	13.40	108.11	0.9
A150	23.40	65.85	0.00	12.90	102.15	0.9
P150	22.18	57.51	1.11	9.20	90.00	1.0
M150	24.71	64.69	3.51	11.10	104.01	0.9
K150	23.51	61.22	1.92	12.90	99.55	1.0
N150	24.50	63.22	4.05	10.60	102.37	1.0
O150	21.39	50.10	2.43	nd	73.92	1.1
L150	22.43	65.54	2.52	nd	90.49	0.9
C150	24.8	66.97	1.31	nd	93.07	0.9
D150	23.5	60.13	5.18	nd	88.81	1.0
W175	24.37	57.51	0.00	17.70	99.58	1.1
P175	22.01	57.18	1.92	nd	81.11	1.0
V200	26.25	45.48	0.00	nd	71.73	1.4
W200	26.57	58.62	0.00	12.20	97.39	1.1
P200	29.87	63.41	2.07	nd	95.35	1.2

Theoretical*	Actual (see above)#
Fe - 24.2%	Fe - 20 to 29%
AsO <sub>4</sub> - 60.2%	AsO <sub>4</sub> - 45 to 70%
H <sub>2</sub> O - 15.6%	H <sub>2</sub> O up to 17.7%
SO <sub>4</sub> - 0%	SO <sub>4</sub> up to 4%
Fe:As - 1:1	Fe:As - 0.9 to 1.1

\* based on the composition FeAsO<sub>4</sub>·2H<sub>2</sub>O

# based on bulk composition

Table A26. Chemical composition of Type-1 compounds

Sample	Fe (%)	AsO <sub>4</sub> (%)	SO <sub>4</sub> (%)	H <sub>2</sub> O (%)	Total (%)	Fe:As (M)	Remarks on ppt. conditions
225	26.3	70.5	nd	nd	nd	0.93	Fe:As 0.7:1 sol
200	25.8	70.8	nd	nd	nd	0.91	Fe:As 0.7:1 sol
175	25.8	70.5	nd	nd	nd	0.91	Fe:As 0.7:1 sol
225	26.1	74.7	nd	nd	nd	0.87	Fe:As 0.4:1 sol
200	25.5	71.2	nd	nd	nd	0.89	Fe:As 0.4:1 sol
175	25.3	67.9	nd	nd	nd	0.93	Fe:As 0.4:1 sol
Y150	23.5	72.3	0.0	6.9	102.8	0.81	
Y200	27.8	75.6	0.0	1.5	104.9	0.91	
Y225	26.4	70.5	0.0	0.9	97.8	0.93	
Z175	21.3	77.9	0.0	10.7	109.8	0.68	
Z200	27.9	75.5	0.0	0.0	103.3	0.92	
Z225	24.7	74.4	0.0	nd	99.1	0.83	
A200	25.9	71.7	0.0	2.3	99.9	0.90	
A225	27.3	63.0	0.0	0.9	91.2	1.08	
K200	22.9	69.8	0.03	nd	92.7	0.82	
K225	25.6	66.2	0.15	nd	91.9	0.96	
L200	23.1	65.3	0.12	2.2	90.7	0.88	
L225	25.5	63.5	0.33	nd	89.3	1.00	
C175	25.6	66.4	0.77	nd	92.8	0.96	
C200	26.0	68.5	0.43	nd	94.9	0.94	
C225	25.6	70.3	0.64	nd	96.5	0.91	

Theoretical*	Actual (see above)#
Fe - 21 to 19%	Fe - 21 to 27%
AsO <sub>4</sub> - 70 to 78%	AsO <sub>4</sub> - 63 to 75%
H <sub>2</sub> O up to 12%	H <sub>2</sub> O up to 11%
SO <sub>4</sub> - 0%	SO <sub>4</sub> up to 1%
Fe:As - 0.7	Fe:As - 0.7 to 0.9

\* based on range of composition Fe<sub>2</sub>(HAsO<sub>4</sub>)<sub>3</sub> to Fe<sub>2</sub>(HAsO<sub>4</sub>)<sub>3</sub>.4H<sub>2</sub>O

# based on bulk composition

Higher than expected iron levels due to possible coprecipitation of amorphous iron arsenate compound and/or scorodite

Table A27. Chemical composition of Type-2 compounds

Sample	Fe (%)	AsO <sub>4</sub> (%)	SO <sub>4</sub> (%)	H <sub>2</sub> O (%)	Total (%)	Fe:As (M)
D175	28.7	52.9	9.2	nd	90.7	1.3
S175	29.5	47.5	7.9	nd	84.9	1.5
R175	27.5	47.6	10.5	nd	85.6	1.4
F175	28.9	45.1	11.3	0.0	85.4	1.6
Q175	33.1	44.2	9.3	nd	86.6	1.9
D200	29.7	52.4	11.5	nd	93.6	1.4
T200	38.2	41.3	3.4	nd	82.9	2.3
R200	31.8	44.7	9.4	nd	86.0	1.8
D225	29.9	53.1	10.4	nd	93.4	1.4
W225	35.3	41.3	0.0	4.1	80.7	2.1
P225	38.7	38.4	0.90	nd	78.1	2.5
O225	36.4	41.1	1.17	4.0	82.7	2.2
X225	33.1	50.6	0.0	0.0	83.7	1.6
M225	32.9	51.8	6.6	nd	91.3	1.6
N225	30.5	50.3	9.7	0.0	90.5	1.5

Theoretical*	Actual (see above)#
Fe - 30%	Fe - 29 to 38%
AsO <sub>4</sub> - 50%	AsO <sub>4</sub> - 41 to 52%
H <sub>2</sub> O up to 12%	H <sub>2</sub> O up to 4%
SO <sub>4</sub> up to 17%	SO <sub>4</sub> up to 18%
Fe:As - 1.5:1	Fe:As - 1.3 to 1.8

\* based on a composition Fe<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)(OH)

# based on bulk composition

Higher than expected iron levels due to possible coprecipitation of amorphous arsenical ferrihydrite. High Fe:As ratio due to higher Fe.



Table A28. Chemical composition of Type-3 compounds

Sample	Fe (%)	AsO <sub>4</sub> (%)	SO <sub>4</sub> (%)	H <sub>2</sub> O (%)	Total (%)	Fe:As (M)	Remarks on ppt. conditions
L200	26.4	71.8	0.11	5.5	106.3	0.91	
L225	27.1	66.4	0.06	3.5	99.67	1.01	
C175	26.5	68.6	0.37	5.0	102.5	0.96	
C200	26.4	72.3	0.44	4.0	105.7	0.90	
C225	26.1	65.5	0.34	4.0	98.74	0.99	
225	27.2	61.2	nd	nd	nd	1.11	Fe:As 1:1 sol.
175	27.7	64.7	nd	nd	nd	1.06	Fe:As 1:1 sol.
Y200	25.6	71.4	0.01	6.0	105.0	0.89	
Y225	25.4	66.4	0.01	5.5	99.4	0.95	

Theoretical*	Actual (see above)#
Fe - 26%	Fe - 25 to 28%
AsO <sub>4</sub> - 74%	AsO <sub>4</sub> - 61 to 72%
H <sub>2</sub> O up to 2%	H <sub>2</sub> O up to 6%
Fe:As - 1.1	Fe:As - 0.9 to 1.1

\* based on a composition Fe<sub>2</sub>(AsO<sub>4</sub>)<sub>1.3</sub>(HAsO<sub>4</sub>)

# based on bulk composition

Higher than expected water levels due to possible coprecipitation of scorodite or Type-1 compounds

**Table A29. Chemical composition of Type-4 compounds**

Sample	Fe (%)	AsO <sub>4</sub> (%)	Ca (%)	H <sub>2</sub> O (%)	Total (%)	Fe+Ca /As	Fe:As (M)	Remarks on ppt. conditions
175	20.3	60.2	8.1	~4	92.6	1.30	0.84	Ca:Fe:As 1:1:2 pH5
200	22.8	60.5	8.8	~4	96.1	1.44	0.94	Ca:Fe:As 1:1:2 pH5
225	22.9	60.5	8.7	~4	96.1	1.44	0.94	Ca:Fe:As 1:1:2 pH5

Theoretical*	Actual (see above)#
Fe - 22.9%	Fe - 20 to 23%
AsO <sub>4</sub> - 65%	AsO <sub>4</sub> - 60.0 to 60.5%
H <sub>2</sub> O up to <3.4%	H <sub>2</sub> O up to <3%
Fe:As - 0.87	Fe:As - to 0.85 to 0.95

\* based on a composition of CaFe<sub>2</sub>(AsO<sub>4</sub>)(HAsO<sub>4</sub>)

# based on bulk analysis

Higher than expected water levels due to possible coprecipitation of scorodite or Type-1 compounds

## Appendix 9

### Influence of lime on arsenic precipitation

The solubility of arsenic oxide - lime solid mixtures was evaluated using the EPA TCLP test. The work showed that when excess lime was added to the mixture (>45%) the arsenic combined with the calcium and was precipitated yielding low apparent solubilities. At the higher lime additions, the pH of the EPA TCLP solution is 11 - 12 with obviously no further buffering action possible. At lower lime additions insufficient calcium was available to precipitate and immobilise the arsenic and hence the higher solubilities. This behaviour was the same for both As(III) and As(V) oxides and it illustrates the precipitating effect of high calcium levels in solution. The As(III) oxide when mixed with lime has a marginally higher solubility than the As(V) mixtures (see Table A30 and Figure A3).

**Table A30.** Apparent solubility of arsenical oxides (As<sub>2</sub>O<sub>3</sub> and As<sub>2</sub>O<sub>5</sub>) with the addition of lime (Ca(OH)<sub>2</sub>)

As(V) oxide As <sub>2</sub> O <sub>3</sub> (g)	Lime Ca(OH) <sub>2</sub> (g)	EPA TCLP filtrate As (mg/L)
0.60	0.40	2864
0.50	0.50	7.60
0.40	0.60	0.08
0.35	0.65	0.76
0.30	0.70	0.07
0.25	0.75	0.29
0.20	0.80	0.12
0.15	0.85	0.31
0.10	0.90	0.32
0.05	0.95	0.37
As(III) oxide As <sub>2</sub> O <sub>5</sub> (g)	Lime Ca(OH) <sub>2</sub>	EPA TCLP filtrate As (mg/L)
0.75	0.25	1491
0.60	0.40	394
0.50	0.50	0.48
0.45	0.55	0.43
0.40	0.60	0.53
0.35	0.65	0.54
0.30	0.70	1.65
0.20	0.80	0.46
0.15	0.85	0.77
0.10	0.90	0.53
0.05	0.95	1.4

This simple experiment illustrates the behaviour of arsenic and the ability of lime to combine with it and remove it from solution and temporarily stabilise it. Excess lime can however be washed away or may be carbonated if left in the atmosphere. Likewise the calcium arsenate precipitates can also react with carbon dioxide to form calcium carbonate. Such calcium arsenate compounds can only therefore be considered to have short term stability.

Solubility of oxide-lime mixtures using the EPA TCLP test

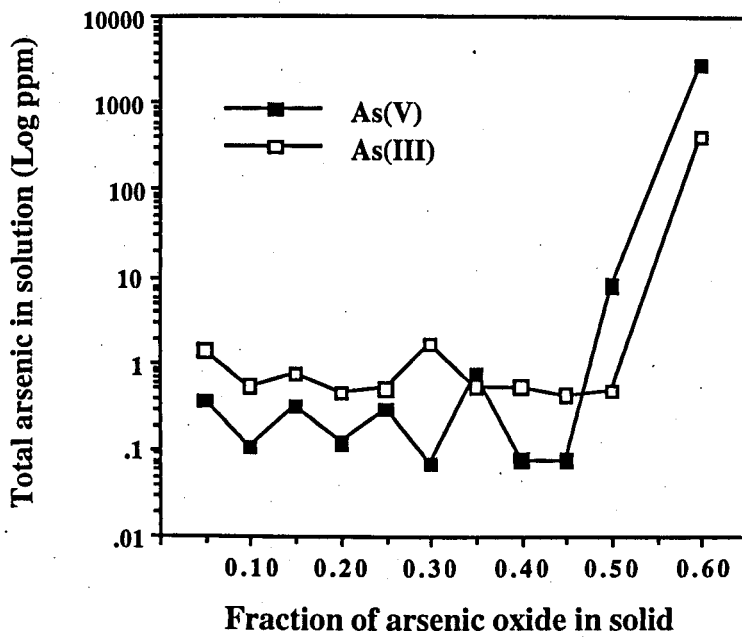


Figure A3. Solubility of lime - arsenic oxide mixtures by the EPA TCLP test

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