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ABSTRACT

Arsenic is one of the most problematic impurities in the metallurgical industry. Because of the small market for arsenical products and the ever increasing amounts processed in the industry most of the arsenic must be disposed of. This must be performed in an environmentally responsible manner, which is becoming technically more and more challenging because of the strict legislation towards arsenic emissions from effluents.

Arsenic extraction and immobilization from hydrometallurgical solutions and effluents is usually achieved by means of ferric arsenate precipitation. The industry produces amorphous high Fe(III):As(V) sludges by lime neutralization of these often acidic solutions. The long-term stability and general characteristics of these precipitates has been questioned by various researchers. An alternative vehicle for arsenic immobilization is proposed in the form of crystalline ferric arsenate, or the mineral scorodite (FeAsO₄.2H₂O).

The precipitation of scorodite from sulphate-based effluents at ambient pressure (95°C) was investigated in this work using a supersaturation controlled precipitation technique. This technique was used in previous work to successfully precipitate scorodite from chloride-based solutions at temperatures as low as 80°C. Prior to that work it was possible to precipitate scorodite only at elevated temperatures in an autoclave (>150°C).

Initial test work using NaOH as base showed that amorphous ferric arsenate precipitation was avoided even at very high supersaturation levels (>70). This feature was in sharp contrast with the results obtained in the chloride system (supersaturation <10) and is probably caused by the formation of inert ferric sulphate complexes in solution. The use of NaOH resulted in very slow precipitation kinetics and a low yield of arsenic precipitation but nevertheless scorodite was produced at 95°C. Particle growth through seed recycling was demonstrated, as was the moderate negative effect of increased sulphate concentration on the

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precipitation kinetics. By replacing NaOH with Mg(OH)₂ much improved precipitation kinetics were obtained. Magnesium ions are inert to the formation of scorodite as opposed to sodium ions which tend to instigate the formation of jarosite precursors in solution which are competing with scorodite for ferric ions.

The slow addition of ferric ions to sulphate solutions containing arsenic was found to be another method to control the supersaturation level and thus to precipitate scorodite. Decreasing pH values resulted in faster Fe(III) addition rates, and below the induction pH (pH_{ind}) for amorphous ferric arsenate (i.e. the pH corresponding to homogeneous nucleation onset), all Fe(III) could be added at once while still achieving only scorodite production. Higher seed concentrations below pH_{ind} led to much improved scorodite precipitation kinetics and yield. By supplying sufficient seed material (50g/L) 90% of all arsenic from an initial 10g/L As(V) solution could be precipitated within 2 hours as scorodite. Increased Fe:As ratios in solution were shown to have a strong negative effect on the kinetics and yield of scorodite precipitation.

The use of hydrated lime $(Ca(OH)_2)$ induces the simultaneous precipitation of gypsum and scorodite. Gypsum crystals tend to initially remove a small part of the As(V) from solution via adsorption but this is subsequently released back slowly into the solution during the remainder of the test. This results in slightly slower precipitation kinetics.

The scorodite samples produced in this work exhibit slightly higher solubilities (0.7 ppm [As] at pH=5 versus 0.1 ppm[As]) compared to what was found for scorodite produced from chloride and nitrate solutions. This is probably caused by the incorporation of small amounts of sulphate ($\approx 0.3\%$) into the scorodite crystal lattice.

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RESUME

L'arsenic est une des impuretés les plus problématiques dans l'industrie métallurgique. Compte tenu de l'étroitesse du marché des produits utilisant l'arsenic et des taux d'arsenic traités dans l'industrie toujours plus importants, la plupart de l'arsenic doit être rejetée. Ca doit être réalisé sans nuire à l'environnement, une tâche qui devient techniquement de plus en plus difficile en raison de la législation stricte sur l'emission d'arsenic provenant d'effluents.

L'extraction et l'immobilisation de l'arsenic de solutions hydrométallurgiques sont généralement réalisés par précipitation d'arsénate ferrique. L'industrie produit des boues de haute Fe(III):As(V) amorphe par neutralisation de la chaux de ce solutions souvent acides. La stabilité à long terme et les caractéristiques générals de ces précipités ont été remisès en question par divers chercheurs, et une alternative µour l'immobilisation de l'arsenic a été proposée sous forme d'arsénate ferrique crystalline, ou de minéral scorodite (FeAsO₄.2H₂O). La précipitation du scorodite des effluents à base de sulphate à pression ambiante (95°C) a été étudiée en utilisant une technique de précipitation par supersaturation controllée. Cette technique a été utilisée avec succès. Lors d'un travail précédent visant à précipiter du scorodite à partir de solutions à base de chlore à des températures aussi basses que 80°C. Avant cette étude il était suelement possible de précipiter du scorodite à températures élevées dans une autoclave (>150°C).

Un test initial utilisant NaOH en tant que base a montré que la précipitation d'arsénate ferrique amorphe était évitée même pour de très hauts niveaux de supersaturation (>70). Cette caractéristique a été un net contraste par rapport aux résultats obtenus dans les systèmes chlorydrique (supersaturation <10) et est probablement causé par la formation de complexes inertes de sulphate ferrique en solution. L'utilisation de la soude a abouti à une cinétique de précipitation très lente et à une précipitation d'arsenic ayant un faible rendement, mais néanmoins de la scorodite a été produite à 95°C. La grossisement des particles lors le recyclement

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des germes a été démontré, et est apparu comme étant l'effet modèremment néfaste de l'augmentation de concentration de sulphate sur la cinétique de précipitation. En remplaçant NaOH par Mg{OH}₂, le cinétiques de précipitation étaient grandement améliorisées. Les ions de magnésium sont inertes à la formation de scorodite contrairement aux ions de sodium qui ont tendance à provoquer la formation de précurseurs de jarosite en solution, ces derniers étant en concurrence avec la scorodite pour les ions ferriques.

L'addition lente d'ions ferriques aux solutions de sulphate contenant de l'arsenic a été trouvé comme étant une autre méthode pour controler le niveau de supersaturation et ainsi pour précipiter la scorodite. Réduire les valeurs de pH a abouti à des additions de Fe(III) plus rapids, et au dessous du pH d'induction (pH_{ind}) pour l'arsenate ferrique amorphe (c'est à dire le pH correspondant au début de la nucléation homogène), tout le Fe(III) pouvait être ajouté en une fois tout en acclompissant la production de scorodite. Des concentration plus élevées en germes au dessous du pH_{ind} ont conduit à une cinétiques et un rendement de précipitation de scorodite nettement améliorés. En fournissant suffisamment de germes (50g/L) 90% de l'arsenic total à partir d'une solution de 10g/L As(V) a pu être précipité en scorodite en 2 heures. Les augmentation du rapport Fe:As en solution sont apparus comme ayant un effet très négative sur la cinétique et sur le rendement de précipitation de scorodite.

L'utilisation de chaux hydratée (Ca(OH)₂) implique la précipitation simultanée du gypse et de la scorodite. Les crystaux de gypse ont tendance à supprimer initiallement une partie de l'As(V) de la solution par adsorption, mais le dernier est ultérieurement libéré lentement dans la solution pendant le reste du test. Cá mène à une cinétique de précipitation légèrement plus lente.

Le scorodite que était produit dans ce thésis montre une solubilitée un peu plus haute que lesquelles qui était produit des solutions chloryhdrique et nitrique. Il est possible que cet effet soit causé par incorporation des petites quantités de sulphate dans la lattice crystallique de scorodite.

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CHAPTER 1 INTRODUCTION

Arsenic imposes one of the most important environmental problems in the metallurgical industry. The problem of arsenic disposal has intensified in recent years due to the increasing volume of As-containing low grade and complex ores processed by the industry. The markets for arsenical products like arsenic trioxide and arsenic metal have not grown in a similar manner, thus creating a surplus of arsenic production. This is particularly true in the copper, gold, lead and uranium industries.

During hydrometallurgical processing at least part of the arsenic goes into solution from which it ultimately must be removed. The environmental legislations regarding arsenic content in water are becoming increasingly stringent. For example in the USA, industrial waste water may contain only 1.0 mg/L As and domestic water 0.05 mg/L As¹¹. On the other hand, in Canada the arsenic limits for metallurgical effluents are 0.05 mg/L for As⁵⁺ and 0.01 mg/L for As³⁺. The lower limits for trivalent arsenic are imposed because of its higher toxicity and carcinogenicity¹²¹.

Many industrial solutions contain arsenic at concentrations above the limits and are thus considered to be toxic. The arsenic must therefore be removed before effluents are emitted. Among the various methods used for the removal of arsenic from process solutions and waste streams, the precipitation of arsenic as an insoluble arsenical compound seems to be the technically and economically preferred option. The precipitation methods are based upon the limited solubility of compounds of arsenic with specific metals, such as Ca, Pb, Cu and Fe^[3,4]. Specifically the precipitation of As⁵⁺ with Fe³⁺ as "ferric arsenate" has become the most important avenue of arsenic fixation and as such has been the subject of a multitude of published works. A lot of attention has been given in particular to the solubility of ferric arsenate and other metal arsenate compounds that are known to form upon neutralization of acidic effluents.

As a result of neutralization of this type of effluents, thousands of tons of arsenical compounds are produced worldwide and are usually disposed in tailings areas. Up to 15 years ago, the precipitated disposed arsenical compounds, regardless of their processing conditions, were thought to be practically environmentally stable, i.e. sufficiently insoluble. However, work done over the past 10-15 years has showed this not to be the case. Currently the best method of As removal (immobilization) is in the form of a high Fe/As ratio(>4) amorphous Fe(III)-As(V) precipitate¹⁵¹. The exact nature of this precipitate is the subject of a controversy. Some attribute the low solubility of As to a complex "basic ferric arsenate" type structure and others to adsorption of As(V) on the surface of amorphous ferric oxyhydroxide. Alternatively, the crystalline structure of ferric arsenate (FeAsO₄.2H₂O, or scorodite) offers equally low solubilities of As. compared to the high Fe:As precipitates, thus meeting the environmental discharge regulations. Scorodite would be preferred to the other compounds for its lower (Fe/As)-ratio and thus for its lower tonnage, i.e. dumping cost, and Fe(III)-salt consumption, not to mention the question over the long-term stability of the amorphous high Fe/As precipitates.

The problem with scorodite production is that it cannot be readily produced by ambient pressure neutralization, i.e. at T < 100°C. It must be produced in a high temperature autoclave system, which of course is economically prohibitive. The \sim situation changed though in 1993 when this author^[6] showed that crystalline scorodite could be produced at ambient pressure ($\approx 90°C$) from chloride solutions after developing and employing a controlled precipitation procedure. This method was based on supersaturation control by controlled neutralization and seeding. The successful findings of this work led to the start of the current work, which has as objective to develop a similar precipitation method for arsenic from sulphate-based solutions. Sulphate-based solutions were studied because they are, as opposed to chloride solutions, much more widely used in the metallurgical industry.

This thesis consists of the following chapters: Literature Review (Chapter 2); Crystallization and Solution Equilibria (Chapter 3); Experimental (Chapter 4); Results and Discussion (Chapter 5); Practical Implications (Chapter 6); Conclusions and Further work (Chapter 7).

In Chapter 2 a review is given of the arsenic aqueous chemistry, the arsenic disposal problem and the precipitation of ferric arsenate. The crystallization theory underlying this novel precipitation method developed in the present work is described in Chapter 3, as well as an overview of the relevant sulphate solution equilibria. In Chapter 4 the materials, equipment and experimental techniques used are elaborated. The experimental results are described and discussed in Chapter 5 in terms of the effect several process variables have on the production of crystalline scorodite. The findings from Chapter 5 are discussed in terms of their potential for industrial implementation in Chapter 6. Finally, Chapter 7 summarizes the conclusions of the thesis and offers recommendations for further work.

CHAP7ER 2 LITERATURE REVIEW

2.1 ARSENIC SOURCES

Arsenic occurs in low concentrations almost everywhere in nature. The overall average concentration in the earth's crust is approximately 5 ppm. It is widely found in many types of mineral deposits and it tends to concentrate in sulphide deposits, and is a minor or trace constituent of a great number of sulfides, sulfosalts and secondary oxidation minerals⁽¹¹⁾. Arsenic associates with iron, copper, nickel, cobalt, lead, antimony, silver and gold as arsenic-bearing minerals or is contained within sulphides in solid solutions.(e.g. As-content in pyrite commonly ranges between 0.02 to 0.5%)⁽¹⁾

A list of some industrially important As-containing minerals is given below:^(1,7)

arsenopyrite	FeAsS
enargite	Cu₃AsS₄
tennantite	Cu ₁₂ As ₄ S ₁₃
niccolite	NiAs
gersdorffite	NiAsS
rammelsbergite	NiAs₂
cobaltite	(Co,Fe)AsS
safflorite	CoAs ₂
proustite	Ag ₃ AsS ₃

The major economically significant arsenic-bearing metalliferous deposits are the enargite-bearing Cu-Zn-Pb-deposits, arsenopyrite-bearing pyritic Cu-deposits, Ag-deposits, Ni-Co-arsenide deposits and arsenical refractory gold deposits.^[1,7]

2.2 THE ARSENIC DISPOSAL PROBLEM

As was indicated in the introduction, the metallurgical industry is faced with a major disposal problem for arsenic and this problem will only become larger in the future, as the environmental regulations and legislations imposed on arsenic disposal become more and more strict. Especially in third world countries where no environmental control was practiced until now, these regulations will cause for some major process and policy changes in industry. In order to get a better comprehension of the arsenic disposal problem, the different types of arsenic wastes generated by the metallurgical industry will be described.

Arsenic containing wastes from the metallurgical industry can be divided into two groups: pyrometallurgical wastes and hydrometallurgical wastes. When arsenical ores are subjected to roasting or smelting processing, most of the arsenic will be volatilized and will report to the roaster off-gas. When this gas is cooled down in contact with air, arsenic trioxide (As_2O_3) is formed. Commercial grade 1 As_2O_3 is produced in this manner in some copper, gold and lead plants, but in general most plants produce a flue dust with a highly complex composition making the dust non-marketable. These flue dusts must subsequently be disposed of as toxic waste or treated to immobilize the toxic As_2O_3 .

Arsenic from ores that are subjected to hydrometallurgical processing will either completely or partially go into solution. This arsenic is sometimes removed from the solution because it will interfere with subsequent stages of the process. However, in some processes the arsenic is not removed during the process and thus reports to the process waste streams, which have to be cleaned prior to disposal or recycling. Extraction of arsenic from such solutions is usually achieved through precipitation.

The precipitation of arsenic metal compounds is presently used to remove As from solution. In the past arsenic compounds were precipitated by adding lime (CaO or Ca(OH)₂) to the solution, via which acid was neutralized and arsenate was induced to precipitate as calcium arsenate according to the following reaction:

$3CaO(s) + 6H^{+} + 2AsO_4^{3.} = = > Ca_3(AsO_4)_2(s) + 3H_2O(1)$

Recently, the stability of these calcium arsenate compounds has been questioned⁽³⁾ because they tend to convert to calcium carbonate which is, from a thermodynamic point of view, more stable than calcium arsenate. According to this reasoning atmospheric CO_2 dissolved in water gives rise to CO_3^{2} anions which in turn react with calcium arsenate to form the more stable calcium carbonate, thereby releasing arsenic into solution (see reaction 2).

$Ca_{3}(AsO_{4})_{2}(s) + 3CO_{3}^{2} = = > 3CaCO_{3}(s) + 2AsO_{4}^{3}$ (2)

This was actually observed in industry, where high As run-off waters were collected from tailings ponds containing calcium arsenate precipitates¹³¹.

After the realization that calcium arsenate was not a stable arsenic carrier industry focussed on the immobilization of arsenic in the form of more stable "ferric arsenates". Two kinds of "ferric arsenates" have been found to meet the environmental legislations. The first kind has the empirical formula $Fe_xAsO_4(OH)_{3(x-1)}$ where x has to be 4 or more in order to have an insoluble compound. Precipitates with an x less than 4 have shown to be less stable. All these precipitates are called "basic ferric arsenates" (see section 2.4.1) and they are amorphous. The second "ferric arsenate" is the mineral $FeAsO_4.2H_2O$, scorodite, which is crystalline and has a Fe/As ratio of 1.0 (see section 2.4.2). At present the industry has adopted the method of arsenic disposal involving the high Fe:As "ferric arsenates" due to the ease of process implementation. Over the long run, however, one may argue that crystalline scorodite may be the preferred vehicle of arsenic immobilization (at least for the bulk of it) for both economic and environmental reasons. This study was undertaken to explore the option of processing waste arsenic as scorodite.

2.3 ARSENIC CHEMISTRY

Arsenic, with an atomic number of 33, is a member of the group VB elements of the Periodic Table together with nitrogen, phosphorous, antimony and bismuth. In solution the arsenic ion exists in the -3, +3 and +5 oxidation states. Its aqueous chemistry is similar to that of antimony and bismuth, and its +5 oxidation state closely resembles that of the phosphate ion. Speciation in non-complexing solutions is described most conveniently by means of the Eh-pH diagram shown in figure 1¹⁷¹. The aqueous species which are relevant to the hydrometallurgical precipitation of arsenic compounds are those in the upper left quarter of the diagram (i.e the acidic to neutral oxidizing quarter). These are $H_3AsO_3^{\circ}$ and AsO^+ for As(III) and $H_3AsO_4^{\circ}$ and $H_2AsO_4^{-}$ for As(V).

Two oxides of arsenic will crystallize from aqueous solution: As_2O_3 and the two hydrates of As_2O_5 . The difference in solubility between As_2O_3 and As_2O_5 (the former is the least soluble) is the basis for the reduction of As^{5+} to As^{3+} solutions in order to recover As_2O_3 in a number of industrial processes. On the other hand oxidation of As^{3+} to As^{5+} is very important in hydrometallurgical processes. Air and oxygen are good oxidizing agents only at elevated temperatures^[8] and neutral to alkaline pH. Fe³⁺ can not oxidize As^{3+} even at high temperatures. Strong oxidants are necessary to oxidize acidic solutions of As^{3+} to As^{5+} like NaClO₃, MnO₂, $K_2Cr_2O_7$, H_2O_2 cr HNO₃. Fe³⁺ and As^{5+} form a very insoluble compound FeAsO₄.2H₂O (scorodite), visualized in the Eh-pH diagrams of the Fe-As-H₂O system (figures 2 and 3). These figures show that scorodite is thermodynamically stable in the pH-range of 0 to 6 at 25°C and at potential above 0.5V.

Ferrous arsenates have also shown to be very insoluble but due to the eventual oxidation of Fe^{2+} to Fe^{3+} by O_2 from the air and the difficulty of producing them, do not seem to offer a particular advantage over scorodite as a solid waste compound¹⁷¹. Ferric and ferrous arsenides do not appear to be environmentally inert, from the solubility and stability point of view.



FIG.1 The Eh-pH diagram of the As-H₂O system at 25°C and at unit activity for all species¹⁷¹.



FIG.2 The Eh-pH diagram of the Fe-As- H_2O system showing iron compounds at 25°C and at unit activity for all species¹⁷³.



FIG.3 The Eh-pH diagram of the Fe-As-H₂O system showing arsenic compounds at 25°C and at unit activity for all species¹⁷¹.



FIG.4 As(V) and Fe(III) concentrations, produced upon precipitation or dissolution of ferric arsenate (amorphous scorodite) at 25°C⁽¹¹⁾.

2.4 SOLUBILITIES AND STABILITIES OF FERRIC ARSENATE

As previously stated, the solubilities of ferric arsenates have recently attracted the attention of a large number of papers. This was due to the environmental focus of ferric arsenate on one hand and on the other due to considerable disagreement among various research groups. Here follows a short review of these papers.

In 1956 Chukhlantsev^[9] was the first researcher to perform a comprehensive study on the solubility of ferric arsenate and, unfortunately, his results are still used as a source of solubility product and free energy of formation data. He determined the solubility by measuring only the Fe(III)-ion concentrations. This introduced a large error, as was shown later by Nishimura and Tozawa^[10] who determined the solubility of scorodite by measuring both Fe³⁺ and As⁵⁺ concentrations. They showed that the Fe:As ratio deviated from unity above pH \approx 2 (see figure 4). This was subsequently described by Robins^[11] as being due to incongruent dissolution and the formation of ferric oxyhydroxide. Thus at pH lower than 2 the following equilibrium would occur:

$FeAsO_4.2H_2O(s) + 3H^+ \rightleftharpoons Fe^{3+} + H_3AsO_4 + 2H_2O(3)$

From $pH \approx 2$ to $pH \approx 6$ this reaction will shift to:

$$FeAsO_4.2H_2O(s) \rightleftharpoons H_2AsO_4 + FeOOH(s) + H^+$$
 (4)

On the basis of thermodynamic data (which is derived from solubility data of amorphous ferric arsenate) and the above incongruent dissolution mechanism (equation 4) Robins⁽¹²⁾(1985) suggested that ferric arsenate is not a viable vehicle for the disposal of arsenic. He made this suggestion because:(1) ferric arsenate as it was produced then was quite soluble, much above the allowed limits (see figure

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5) and (2) because over the long term the (amorphous) ferric arsenate compound will be converted to ferric oxyhydroxide with the concomitant release of all its arsenic into the environment (see equation 4).



FIG.5 Solubility regions for amorphous ferric arsenate and amorphous ferric hydroxide^[12].



FIG.6 Arsenic solubility as a function of molar Fe/As ratio in amorphous ferric arsenate, at pH = 5 and $25^{\circ}C^{(18)}$.

At the same time, Krause and Ettel⁽¹³⁾ (1985) found that the solubility of ferric arsenate precipitates decreases enormously (2-3 orders of magnitude lower, i.e below the permissible level of approx. 1 mg/l) if the Fe/As ratio in the starting solution and the resultant precipitate was more than 4:1 (see figure 6). The same authors called these high Fe/As ratio precipitates "basic ferric arsenates" ,in analogy to the basic ferric sulphates, with the formula FeAsO₄.3Fe(OH)₃ or $Fe_4(AsO_4)(OH)_9$. These compounds could not be confirmed, however, by XRD analysis or any other characterization method as they were amorphous compounds. Harris and Monette^(14,15) (1987,1989) and Kontopoulos et al^(16,17) (1987,1989), via independent investigations, confirmed that high Fe/As ratio ferric arsenates are highly insoluble and thus suitable for environmental disposal.

Later (1989), Krause and Ettel⁽¹⁸⁾ demonstrated that all previous studies on the solubility of scorodite were not reproducible as they were done with amorphous material and reported the true solubility of natural and synthetic crystalline scorodite to be at least two orders of magnitude lower than previously published (see figure 7). This means that, at pH = 5, crystalline scorodite is as stable as the amorphous material with an Fe:As ratio>4, called "basic ferric arsenate". Measurements on the solubility of crystalline scorodite were later made by Robins⁽¹¹⁾ as well and he confirmed the low solubility of this material versus the amorphous 1:1 product. Robins^[12,19] (1987 and 1992) in a different line of thought questioned the existence-formation of the so-called "basic ferric arsenate" and attributed the very low solubility of As(V) in the high Fe:As precipitates to its adsorption on the huge surface area of the amorphous ferric oxyhydroxide which is the bulk precipitated phase. He called this high Fe/As ratio precipitate As-bearing ferrihydrite (this is the name commonly used by colloid chemists to refer to amorphous ferric oxyhydroxide). Some typical adsorption data of As(V) on coprecipitated ferric oxyhydroxide are shown in figure 8.

Moreover, Robins^[11,19] has proposed that both crystalline scorodite and the amorphous As-bearing ferrihydrite material are expected to decompose in contact with water in the neutral pH region over the long term and slowly release As ions.



FIG.7 Comparison of arsenic solubility data for crystalline and amorphous scorodite^[18].



FIG.8 Arsenic removal from 300mg/L As(V) solutions with 6 different levels of Fe/As due to adsorption of As(V) on co-precipitated ferric oxyhydroxide^[12].



FIG.9 Solid-liquid equilibria in the Fe(III)-As(V)-H₂O system (adapted from data taken from Robins⁽¹¹⁾ and Krause and Ettel⁽¹⁸⁾).

This can be seen for the case of scorodite by examining the equilibrium data of figure 9. The solubility of As increases above pH=4-5. At pH=7 the equilibrium As concentration is at least 25 ppm, while the corresponding one at $pH\approx3$ is only 0.2 ppm. However, this decomposition of crystalline scorodite, especially when it is in the form of well grown crystals, is expected to be extremely slow resulting in very low (at any given time) As concentrations, always below the permissible levels^[20]. The size of the individual particles in fact directly influences the solubility of small crystalline particles according to the Gibbs-Thomson effect^[20]. In the range of 10-100 nm the solubility increases towards lower particle size and these particles generally give higher solubility than well grown coarse crystals (see calculations in reference 20).

The fate of the As-bearing ferrihydrite is less predictable. Over the long term ferrihydrite is expected upon aging to transform to crystalline ferric oxyhydroxide (*a*-goethite). What will happen to the adsorbed arsenic remains a question. It might be incorporated into the new formed goethite structure, i.e. immobilized, or simply be released to the environment due to the decreasing adsorptive capacity of the crystalline goethite. In any case this release process is expected to be slow as well^[19].

It can be concluded that amorphous ferric arsenates with Fe:As ratio <4 are quite soluble and, therefore, not useful as a disposal option. Material with Fe:As ratio >4 has been shown to be very insoluble and stable. CO_2 in solution (in equilibrium with air) was also shown not to increase the solubility and neither did long term exposure to water with moderate pH^[18]. Crystalline scorodite has also been shown to be a good disposal carrier for arsenic and has the advantage over the stable high Fe/As ratio amorphous material because of its lower volume and higher As content and consequently lower dumping costs. In situations where there is simply no excess of Fe in the solution to confer stability to the amorphous product, scorodite production instead of high Fe:As precipitates could lead to a considerable cost reduction, not to mention the enhanced long term environmental stability of a crystalline compound over an amorphous counterpart.

2.5 SCORODITE PRECIPITATION

Precipitation of crystalline scorodite has been reported by various researchers and in different chemical environments. In 1988 Dutrizac and Jambor⁽²¹⁾ published a paper on the synthesis of crystalline scorodite in a NO₃· solution. 0.3 *M* Fe(NO₃)₃ and 25 g/l As⁵⁺ solutions were mixed at pH = 7 and then heated up to 160°C for 24 hours in an autoclave. According to the authors As⁵⁺ concentrations greater than 15 g/l were needed to ensure a pure product. Papangelakis and Demopoulos⁽²²⁾ reported the formation of scorodite during acid pressure oxidation of arsenopyrite in a 0.5 *M* H₂SO₄ medium. Conditions favouring the build-up of Fe³⁺ and As⁵⁺ in solution (160°C or more and high slurry-densities) led to fast precipitation of well-grown scorodite crystals with a diameter of more than 20 μ m.

Dutrizac, Jambor and Chen⁽²³⁾ produced crystalline scorodite during jarosite precipitation (24 hours) at 150°C from 0.6 M SO₄² solutions containing 5 g/l As⁵⁺ at initial pH = 1.3. The same authors^[24] found that at 97°C amorphous scorodite was co-precipitated with jarosite in 0.6 M SO42 solutions, but in 4.5 M Cl solutions at initial pH=1 (24 hours) the precipitated scorodite was identified by XRD as crystalline. Dove and Rimstidt⁽²⁵⁾ also synthesized scorodite in a Cl solution. They mixed ferric chloride and sodium arsenate at ~100°C and let it age for 14 days resulting in a precipitate, showing a distinct X-ray diffraction pattern of scorodite (the actual solution composition was not reported). Kunter and Bedal⁽²⁰⁾ also made reference to possible precipitation of crystalline scorodite from a chloride-process (Cashman process) during treatment of arsenic containing smelter flue dusts. However, no additional information on the conditions of the formation and characterization of the formed scorodite were given in this paper. The precipitation of crystalline scorodite during pressure chloride leaching (170-200°C, H2SO4/NaCl medium) of a refractory gold arsenical concentrate was also reported by Demopoulos and co-authors^[27].

Robins^[11], for his work on the solubility of scorodite, prepared crystalline

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scorodite in a SO₄² solution. He synthesized the scorodite by adding 0.1 *M* $Fe_2(SO_4)_3$ to 0.1 *M* H_3AsO_4 at pH = 1 and refluxing the solution at a not reported temperature for several days, presumably at ambient pressure. This resulted in very fine scorodite crystals of approx. 60nm.

More recently, a detailed study was conducted at the Imperial College in London^[28,29] and in Greece^[30] on the structure and stability of crystalline ferric arsenates produced from autoclave precipitation. They used synthetic solutions made up of Fe₂(SO₄)₃ and H₃AsO₄ and heated these to temperatures ranging from 140°C to 200°C. They found that crystalline scorodite precipitates at temperatures between 140°C and 170°C. Above that temperature and at Fe:As ratios > 3, arsenic precipitated as different crystalline ferric arsenate-sulphate compounds with the composition Fe₂(HAsO₄)₃.zH₂O or Fe₄(AsO₄)₃(OH)_x(SO₄)_y. The first compound was found to have a solubility similar to scorodite, while the second compound showed much higher solubility. When lower Fe:As ratios were used above 170°C, a mixture of scorodite and ferric arsenate-sulphate was formed.

Demopoulos and co-workers⁽³¹⁾ described a novel precipitation technique with which crystalline scorodite could be precipitated at ambient pressure and lower temperatures (80°C<T<95°C) from chloride-based Fe(III)-As(V) solutions. The precipitation method was based on strict supersaturation control in combination with scorodite seeding. This method was tested for solutions containing 2g/L As(V); a typical precipitation test is presented in figure 10. The resulting precipitates were characterised by XRD, XRF, SEM, and their solubility was determined. The results proved to be the same as the results of the crystalline scorodite samples described by the above mentioned researchers.

The current work is a direct consequence of the encouraging results obtained by Demopoulos et al. The same supersaturation-controlled precipitation technique (as described in chapter 3) was applied to precipitate arsenic as crystalline scorodite from sulphate based solutions. Sulphate solutions were chosen due to the fact that these are the solutions predominantly used in industry. The significant difference in solution chemistry between chloride solutions and sulphate

solutions, however, called for significant modifications in the original procedure. In view of the key roles that crystallization theory and the solution chemistry of ferric sulphate solutions play in this work, a brief overview of the two is presented in the following chapter.





CHAPTER 3 CRYSTALLIZATION AND SOLUTION EQUILIBRIA

In this chapter the basic principles of aqueous crystallization are reviewed with the objective of defining the underlying theoretical formulations on which the present work is based. In particular, emphasis is given on the definition and role of supersaturation in controlling the crystallization process. In the second part of the chapter the ferric sulphate complexation equilibria are reviewed and the concentration/activity of protons in sulphate media is discussed from the standpoint of experimental control of the ferric sulphate + arsenic acid precipitation reaction. The ferric sulphate complexation equilibria data will aid the interpretation of the experimental findings of the work.

3.1 THEORY OF CRYSTALLIZATION (32,33)

Crystallization and precipitation from solutions dates back to the beginning of time. In nature many examples illustrate the complexity and ingenuity of these processes. One such example is the manner in which mollusks precipitate calcium carbonate from the surrounding seawater as a highly organized structure: its shell. We still have much to learn from nature in the way nucleation is controlled and the localized level of supersaturation around a growing crystal is regulated. In this chapter the fundamentals of crystallization are reviewed in an effort to gain a better understanding of what steps must be taken in controlling the crystallinity of the precipitated ferric arsenate compound

3.1.1 Supersaturation

Crystallization or precipitation out of a solution involves the nucleation and growth of particles from a supersaturated solution. Supersaturation is the concentration of component ions in excess of the saturated concentration and is expressed by the difference from the saturation concentration or the ratio to the saturation concentration. The supersaturated solution is composed of two zones, the metastable and the unstable or labile zone, as shown in figure 11¹³⁴¹.



Temperature ----→

Figure 11. Solubility-supersaturation diagram explaining the stable, metastable and labile zones^[34].

There are several ways to induce supersaturation in a solution. For systems in which the solubility is not a strong function of temperature evaporation is used to induce supersaturation. Cooling is used when the solubility increases with temperature and heating is used when the solubility decreases with temperature. Elevated pressures can supersaturate solutions that contain a particular crystal phase which is not stable at atmospheric pressure, but the most common method used is that of a chemical reaction resulting in the production of an insoluble species. This is usually done by adding another reagent (for example acids or bases) to the solution so as to reduce the solubility of the solute. Reactive crystallization is traditionally referred to as <u>precipitation</u>.

The phase change A(aq) + B(aq) \Rightarrow AB(s) during precipitation can be explained thermodynamically^(32,33). The reaction can only occur when the Gibbs free energy(Δ G) for the transformation is negative. Δ G can be expressed in terms of activity as:

$$\Delta G = -RT \ln(\frac{a}{a_0}) = -RT \ln(S) \tag{5}$$

- R = universal gas constant.
- T = absolute temperature.
- a = activity of the solute.
- a_0 = activity of the pure solute in equilibrium with a macroscopic crystal.
- S = supersaturation.

When activity coefficients are assumed to be 1, then:

$$\frac{a}{a_0} = \frac{C}{C_{aq}} = S \tag{6}$$

C = solute concentration.

 C_{eq} = equilibrium solubility of the solute at the temperature and pressure of the system.
For ionic crystal precipitation the solubility of a compound can be represented in terms of the solubility product as shown here below.

$$A^{+}(aq) + B^{-}(aq) \Rightarrow AB(s)$$
(7)

$$K_{p} = [A^+]_{q} [B^-]_{q}$$
(8)

S can be re-defined as:

$$S = \frac{[A^{\cdot}] [B^{\cdot}]}{K_{sp}}$$
(9)

[A⁺] and [B⁻] are ionic concentrations in supersaturated solution; for simplicity concentrations are considered to be equivalent to activities.

These thermodynamic considerations show that the supersaturation (S) is the driving force for the precipitation reaction and that when S > 1, ΔG will be <0.

3.1.2 Nucleation

The crystallization of a new solid phase out of solution involves the following, sequential phenomena:

NUCLEATION = = > GROWTH = = > AGGREGATION

The rate of nucleation plays an important role in controlling the final particle size distribution. This is explained by the three different modes of nucleation that can occur during precipitation:

- Primary homogeneous nucleation
- Primary heterogeneous nucleation
- Secondary nucleation

- <u>Primary homogeneous nucleation</u> occurs in the absence of a solid surface. Due to local static fluctuations of concentration and temperature, molecules or ion pairs cluster together forming "embryos" of 10-1000 molecules. With the supersaturation as driving force these embryos keep growing and form stable nuclei as soon as they are above a minimum critical size, r°. The overall free energy of the embryos is the sum of two terms: ΔG_v due to the formation of new volume and ΔG_v due to the creation of new surface.

$$\Delta G_{\text{ambryo}} = \Delta G_{\text{v}} + \Delta G_{\text{a}}$$
(10)
$$\Delta G_{\text{v}} \text{ is } <0 \text{ and } \Delta G_{\text{a}} \text{ is } >0$$







Figure 13. Critical nuclei size as a function of supersaturation⁽³²⁾.

Plotting ΔG_{embryo} against the nuclei size shows a curve with a maximum value, ΔG_{max} , which is the activation energy for nucleation at a critical nuclei size r^{*} (see figure 12). Embryos larger than r^{*} will further decrease their free energy by growth, giving stable nuclei which grow to form macroscopic particles. Embryos smaller than r^{*} cannot grow further and redissolve into solution. The critical nuclei size r^{*} is usually between 40 and 200 Å and is a function of supersaturation (figure 13).

When S increases, the critical nuclei size decreases and the number of nuclei increase. This means in reality that at high S a large population of ultra fine colloidal particles will form at a very fast rate. The minimum S required for this condition is termed $S_{cr,homo}$ (figure 14). This graph shows that at $S_{cr,homo}$ the nucleation rate increases exponentially with S. For ferric hydroxide precipitation it was determined $S_{cr,homo}$ to be relatively low (<10)^[35]. For other compounds like BaSO₄ $S_{cr,homo}$ was shown to be as high as 1000^[32].

- <u>Heterogeneous nucleation</u> is induced by surfaces of a different material than the one which is precipitated (for instance the reactor's walls or the stirring equipment). Nucleation is induced due to the lower surface energy of these surfaces than that of a newly forming particle. The difference between homogeneous and heterogeneous nucleation is that once hetero-nuclei are consumed, heterogeneous nucleation stops, thus limiting maximum possible heterogeneous nucleation rate. The critical supersaturation($S_{cr,het}$) is lower than the corresponding one($S_{cr,hom}$) for homogeneous nucleation (see figure 15).

- <u>Secondary nucleation</u> occurs in the presence of crystal surfaces with the same composition as the material that precipitates. These particles have to be present in solution and can be added as seed. Secondary nucleation can be divided into 3 separate categories:

1: Apparent secondary nucleation is a somewhat limited case occuring mostly in

physical crystallization processes, i.e. not in precipitation, and refers to small fragments breaking from longer crystals.





:



Figure 15. Generalized nucleation rate diagram showing the dominant areas for homogeneous, heterogeneous and surface nucleation^[32].

2: True secondary nucleation (or surface nucleation) involves the deposition of fresh material on an existing crystal surface of the same material. The seed crystals facilitate surface nucleation of newly deposited material due to lower activation energy barriers.

3: Contact secondary nucleation occurs when a growing particle collapses on the walls of the reactor due to the hydrodynamic stirring force, thus leaving behind residual solute particles. This mechanism is also known as "plastering".

Surface nucleation occurs at a lower critical value of S, $S_{\alpha,aurf}$, than heterogeneous and homogeneous nucleation, i.e. $S_{\alpha,aurf} < S_{\alpha,het} < S_{\alpha,hetero}$. This is

shown in figure 15 where S is plotted against the nucleation rate, J. Contact nucleation, and to a lesser degree heterogeneous nucleation, are primarily responsible for scaling problems in conventional crystallization systems that are not carefully controlled. An empirically derived equation shows that the rate of contact nucleation depends on the stirrer rotation speed (RPM), particle mass density or solids loading(M,) and the supersaturation^[32].

 $J_{cont,nucl} \alpha (S-1)^{b} (M_{t}) (RPM)^{h}$ (11) 0.5<b<2.5 and 2<h<4

3.1.3 Growth

After the nuclei are formed, the particles grow according to two main mechanisms: "epitaxial" growth and/or "aggregational" growth. Figure 16 shows the characteristic differences between the two growth mechanisms. During epitaxial growth a new layer is continuously deposited onto an individual particle, hereby increasing the diameter of the particle. During aggregational growth two or more individual particles are clustered together and the freshly deposited material cements the particles and cause for an irregular morphology of the particle. These two mechanisms often occur simultaneously, where at lower S values epitaxial growth dominates and at higher S values aggregation becomes the dominant mechanism.

The growth kinetics of epitaxial growth is best explained by figure 17⁽³⁶⁾. Solute diffusion or surface reaction may be the rate determining step, yielding a surface growth rate of⁽³⁶⁾:

$$\frac{dr}{dt} = k V_m C_{eq} (S-1)$$
(12)

 \mathbf{r} = radius of a spherical particle.

k = mass transfer coefficient or rate constant.

 C_{n} = equilibrium concentration.

 $V_m = molar volume of solid.$



Figure 16. Simplified illustration of the two growth mechanisms.





This equation shows that the growth rate G(=dr/dt) is proportional to the supersaturation. This feature was elegantly visualized by Demopoulos^[36] (see figure 18). This figure shows that as long as the growth rate is larger than the nucleation rate the solution will be in a regime of growth, providing that seed material is present. When the nucleation rate becomes larger than the growth rate, homogeneous nucleation will occur and growth of the particles will stop. Under the homogeneous nucleation regime of precipitation colloids are formed instead of well-grown particles; This is a situation that must be avoided when scorodite precipitation is desired.

3.1.4 Attainment of crystallinity: application to this work

Production of crystalline as opposed to amorphous compounds can be favoured by either applying a high temperature or a lower supersaturation. In the case of scorodite precipitation (see section 2.5) it has already been concluded that it could only be produced in the past via the use of autoclaves (T>160°C). This is in agreement with the statement that high T favours the attainment of crystallinity. The latter result can also be attained if S is controlled below $S_{cr,homo}$. This is derived from Stranski's rule^[36] which states that "When homogeneous nucleation prevails at low temperatures, the least stable phase will precipitate first". In the ferric arsenate system the least stable phase is amorphous ferric arsenate as was shown in figure 7. In other words when S is controlled below $S_{cr,homo}$ the formation of amorphous ferric arsenate is avoided and the production of crystalline scorodite is favoured.



Figure 18. Growth regimes and nucleation regimes as a function of nucleation rate and S^[34].



Figure 19. Supersaturation controlled precipitation strategy⁽³¹⁾.

The validity of the low supersaturation approach to attainment of crystallinity in the case of the ferric arsenate system was experimentally demonstrated by Demopoulos et al.^[6]. According to that work, which is the precursor of the present thesis, crystalline scorodite was produced from chloride so⁺utions at temperatures as low as 80°C by controlling supersaturation below S_{cr,homo} via a staged neutralization procedure. This procedure is described schematically in figure 19. According to this procedure the solubility line, C_E, is first determined experimentaly, and then various supersaturation levels are tested. This is done as follows: Supersaturation lines are drawn as, C=S.C_E. For every S curve a solution with composition C₀ is neutralized in steps from pH₀ to pH₁. Each neutralization step is not supposed to exceed the pH defined by the S line. At the end of each step the solution is left to equilibrate prior to the next step. During the first step seed material is added to the solution to induce growth and to avoid homogeneous nucleation. In this fashion S is maintained at a sufficient low value, i.e. below S_{cr home}, throughout the whole test.

A S_{cr,homo} of ≈ 8 was found experimentally for the precipitation of scorodite from chloride solutions at 95°C. It was also found that the addition of sulphate ions in the chloride solution had a retarding effect on the precipitation kinetics of scorodite and an adverse effect on the attainment of crystallinity. This suggested that the current work involving 100% sulphate solutions would become more difficult and thus more challenging than the previous chloride-based work.

3.2 SULPHATE SOLUTION EQUILIBRIA

Most industrial hydrometallurgical processes practiced today are based on sulphate solutions. Hence the interest of this work was to focus on the ambient pressure precipitation of crystalline scorodite from such solutions. Since the precipitation of scorodite involves on one hand the reaction of ferric species with As(V), and on the other the control of pH as way of favouring the attainment of crystallinity, it is considered appropriate to look at the existing

 $Fe_2(SO_4)_3/H_2SO_4$ solution equilibria (the respective As(V) equilibria were already analyzed in section 2.3).

3.2.1 Thermodynamic equilibria of the Fe(III)-SO₄-H₂O system

Sulphuric acid is unique among the family of strong acids because of the formation of the bisulphate ion which is responsible for the relative decrease of proton activity with increasing acid concentration. This is better seen by considering the following equilibra.

$$H_2SO_4 = HSO_4 + H^+$$
(13)

$$HSO_{4}^{\cdot} = SO_{4}^{2 \cdot} + H^{+} \qquad (14)$$

The first dissociation of sulphuric acid is generally considered to be complete. The second dissociation (reaction 14), on the other hand, is not complete and occurs only in dilute sulphuric acid solutions, generally at pH>2 at $25^{\circ}C^{1371}$.

Recently at McGill University, a new method was developed for the estimation of the activity of H⁺ in mixed metal sulphate solutions^[38]. The method makes use of the "extended Debye-Hückel" equation that was originally used by $Das^{[39]}$ for pure sulphuric acid solutions at ambient temperature. The treatment of mixed metal sulphate solutions was made possible by combining that equation of Das with a speciation algorithm which calculates the abundance of all species formed. The developed method takes into account ionic strength and temperature effects, and it can be used to calculate proton activities and speciation data for the Fe(III)-SO₄-H₂O system. This speciation system is of particular interest to this work because ferric sulphate complexes in solution could affect the precipitation of scorodite. Arsenic speciation is of much less importance because it is well known that arsenic does not form any complexes in sulphate solutions.

Figure 20 and 21 show the speciation diagram of ferric sulphate solutions as a function of pH at 25°C and 100°C. It is interesting to see that the proportion of

Fe³⁺ ions is very low at 25°C and is almost negligible at 100°C. Ferric sulphate species dominate the lower pH region and ferric hydroxide species start to form slowly above pH 1.5. This feature is more apparent at higher temperatures, and this is shown with the data of figure 22, which refer to speciation of ferric sulphate solutions at 150°C. At this temperature free Fe(III) ions are below the detection limit and the concentration of ferric sulphate complexes decreases in favour of partially hydrolyzed Fe(III) species above pH = 1.5.



Figure 20. Ferric sulphate speciation diagram at 25°C. The total ferric concentration is 0.5M and the pH is adjusted by sulphuric acid additions. Species that do not appear on the diagram exist in negligible concentrations⁽³⁸⁾.



Figure 21. Ferric sulphate speciation diagram at 100°C. The total ferric concentration is 0.5M and the pH is adjusted by sulphuric acid additions. Species that do not appear on the diagram exist in negligible concentrations⁽³⁸⁾.



Figure 22. Ferric sulphate speciation diagram at 150°C. The total ferric concentration is 0.5M and the pH is adjusted by sulphuric acid additions. Species that do not appear on the diagram exist in negligible concentrations^[38].

3.2.2 Monitoring pH in strong sulphuric acid solutions

In most hydrometallurgical processes the H^{*} concentration, or more correctly the proton activity (a_{H+}), is a key parameter that may determine equilibria in precipitation reactions, or dissolution rates of certain compounds. This is also the case during scorodite precipitation. In dilute acidic solutions (<0.1M) the activity of H⁺ is generally considered equal to its analytical concentration and therefore direct pH measurements can be used to monitor the proton activity. However, in more concentrated acidic solutions (>0.1M) the proton activity starts to deviate from the concentration with increasing acidity, resulting in pH measurements which differ significantly from the value expected from the analytical determination. In chloride solutions, for example, this deviation is quite dramatic as was shown by Jansz^[40]. However, in sulphuric acid solutions this feature is much less significant.

It has always been an unwritten law not to use direct pH measurements in highly concentrated sulphuric acid solutions because the measurements would not be stable and/or reproducible, and even if a stable measurement could be achieved, the obtained pH value would only be a relative indicator of acidity and not necessarily will reflect the value of -log(a_{H+}). However, it was possible in this work to measure pH in sulphuric acid solutions using a standard Orion Ross combination glass electrode, and to successfully correlate the measured values to proton activities estimated by the computer algorithm^[38]. This finally made possible the subsequent control of the precipitation system via the continuous monitoring of pH. In this way the need for time consuming acid titrations, as was done in the chloride system^[6], was avoided. This was accomplished with the determination of calibration curves that allowed for a direct conversion of the pH readings into the analytical acid concentration.

The pH was measured with an Orion 720A pH-meter using an Orion Ross combination glass electrode. An Automatic Temperature Control probe (ATC) was used in all tests, even at room temperature, to allow for automatic temperature compensation. The Ross electrode offered stable pH readings within 30 seconds, independent of temperature, and was found to be 3 to 5 times faster than with

conventional electrodes. Calibration was performed with pH buffers 1.00 and 2.00 and obtained efficiency was always between 0.96 and 1.01.



Figure 23. Actual pH readings as a function of $[H_2SO_4]$ and temperature. Theoretical values are determined with speciation computer program¹³⁸¹.



Figure 24. pH as function of mL NaOH added. Starting conditions: 0.5M H_2SO_4 V=500 mL, T=25°C.



Figure 25. Influence of 0.04M Fe(III) on pH measurements. Theoretical values are determined with speciation computer program⁽³⁸⁾.

The pH of H_2SO_4 solutions with a known analytical concentration ranging from 0.1 to 1.0M was measured first at 25 and 90°C and the results are shown graphically in figure 23. In addition to the experimental values the computational estimates of pH obtained from the speciation computer program that was developed by Filippou et al⁽³⁸⁾ are plotted on figure 23 in the form of dashed lines for comparison purposes.

The most striking feature of the data of figure 23 is the good agreement between the measured values and the theoretical values obtained from the speciation program. It seems that the measured values start to deviate from the theoretical values only for $[H_2SO_4] > 0.8M$ or pH < 0.2. Another observation is the decreased acidity with increasing temperature. This can be explained by the fact that increasing temperature favours the formation of bisulphate ions⁽³⁷⁾. In other words, the equilibrium constant K of reaction 6 decreases with increasing temperature, hindering the second dissociation of H_2SO_4 . The measurements of Fig.14 were repeated 3 times at both temperatures and are shown in Table 1. The similar values of the individual series show that good reproducible results can be obtained from direct pH measurements in strong sulphuric acid solutions. No major changes, fluctuations or trends were observed.

	25°C			90°C		
[H₂SO₄]	Series 1	Series 2	Series 3	Series 1	Series 2	Series 3
1.0 M	-0.185	-0.200	-0.194	0.172	0.169	0.174
C.8 M	0.096	0.091	0.094	0.245	0.250	0.253
0.6 M	0.218	0.238	0.224	0.364	0.370	0.361
0.4 M	0.404	0.430	0.412	0.524	0.509	0.521
0.2 M	0.704	0.710	0.706	0.814	0.815	0.808
0.1 M	0.968	0.965	0.964	1.104	1.099	1.102

Table 1. Reproducibility of pH measurements at 25°C and 90°C.

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The influence of NaOH was tested by neutralizing step-wise a 500 mL, 0.5M H_2SO_4 solution with predetermined amounts of 1.0M NaOH solution. By addition of certain volumes of NaOH to the sulphuric acid solution the acidity was altered not only via neutralization but also via dilution. This effect was accounted for and is eliminated from the results shown in Fig.24. The dashed line shows the theoretical pH values if H_2SO_4 is assumed to be only half dissociated. This line starts to deviate significantly from the experimental values above pH \approx 0.8. Good reproducibility was obtained as proven by the nearly identical lines of series 1, 2 and 3.

Ferric ions may interfere with the pH measurements as they may form sulphato-complexes. To determine this effect, the same tests as described above were conducted at 25°C with a 0.04M Fe(III)-sulphate solution. The results are shown in figure 25. They show that in the presence of ferric ions the pH values are slightly higher in H_2SO_4 solutions than without Fe(III). This experimental trend is in agreement with the predictions of the speciation program of Filippou et al.^[39], although there is a modest discrepancy between the two sets of values. The most important conclusion is that again very stable and reproducible readings were obtained and overall there was good correspondence between theory and measurement.

Conductivity measurements were also conducted as an alternative approach to monitoring the acidity, but it was found that the addition of cations into the solution had a significant effect on the conductivity. This meant that for each solution composition different calibration curves were required. Another disadvantage was that stable readings could not be obtained when solids were present in solution. This is of course unacceptable for precipitation testwork where there are always solids present. This interference was not observed when the pH electrode was used. The latter method was, therefore used for monitoring and controlling the progress of the scorodite precipitation reaction.

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CHAPTER 4 EXPERIMENTAL

4.1 EXPERIMENTAL SET-UP AND PROCEDURE

The test solution was contained in a 1 litre Pyrex reaction kettle with a separate glass lid. The lid contained 4 holes; each hole plugged with rubber stoppers to prevent solution loss by evaporation or to allow insertion of a stirrer, pH meter, thermometer and a sampling pipet. The lid and kettle were held together by a metal ring with three clamps. The reaction kettle was immersed in a custom-made water bath. The water in the bath was mixed, heated and maintained at the desired temperature with two heater/circulators with an accuracy of approximately 1-2°C. Solution mixing was performed by a plastic propeller-shaped stirrer with a diameter of 4.5 cm (3 blades at a 45 degree angle) attached to a plastic-coated metal rod. A Cole Parmer agitator was used with variable speed control.

The pH was continuously monitored by an Orion Ross electrode and an Orion (model 720a) pH meter. In the last stages of the work the Orion Ross electrode was replaced by a Fischer Accu-pHast electrode because of its increased durability in hot acidic solutions. Both electrodes are especially designed for high temperature and quick response in acidic media (see section 3.2.1).

A typical controlled neutralization test procedure would proceed as follows: (1) Make up of solution from analytically pure chemicals (H_2SO_4, H_3AsO_4) and ferric sulphate salt). This solution was subsequently heated to 95°C in the waterbath. (2) The solution was neutralized by adding base $(NaOH, Mg(OH)_2, \text{ etc.})$ to the point where the solution was supersaturated, i.e. just below $S_{cr,homo}$ or below pH_{ind} . At that point scorodite seed material was added to the solution to induce the precipitation reaction. (3) More base was added at a constant rate and samples were taken as a function of time and pH. Samples were filtered while still hot using

a funnel and Whatman qualitative filterpaper number 1 (150 mm). The sample filtrate was analyzed by atomic absorption. (4) When the desired final pH was reached the precipitates were filtered and washed with distilled water using a Cole Parmer model 7050-00 aspirator pump and Whatman qualitative filter paper number 1 (18.5 cm). The solids were further dried for 24h in an oven at 50°C prior to analysis.

4.2 ANALYSIS

The arsenic content in solution was determined with an Atomic Absorption Spectrometer (AA, Perkin Elmer model 3100). The machine was fitted with a special EDL system because it was found that without this special modulated power source the arsenic lamp would not give a stable beam thus resulting in inaccurate and unstable readings. The linear range of this method was 1 to 100 ppm arsenic and calibration was performed using 0, 5, 10, 25, 50 and 100 ppm arsenic standard solutions prepared from a certified 1000 ppm arsenic standard. For very low arsenic concentrations (<1mg/L) an AA machine equipped with a mercury-hydride system was used.

Iron analysis was also performed with the same Perkin Elmer AA instrument but the EDL system proved to be unnecessarry. The linear range for iron was between 0 to 20 ppm and calibration was performed using 0, 1.25, 2.5, 5, 10 and 20 ppm standards prepared from a 1000 ppm certified iron standard.

The identification of crystalline versus amorphous precipitates was achieved by X-Ray Diffraction (XRD) analysis, using a Phillips PW1710 machine. X-ray diffraction gives a qualitative analysis of the crystalline phases present in the sample. In case of pure crystalline material the diffractogram will have distinct peaks with a limited width. If the sample is not completely crystalline the width of the peaks increases. When enough amorphous material is present the diffractogram will not give distinct readings of the material. The diffractometer will detect

crystalline phases if the sample contains 5% or more of this crystalline phase. In cases where less than 5% of the precipitate was amorphous, leach tests had to determine wether the sample was purely crystalline. Another, less objective method of determining sample crystallinity was by observing the colour. Crystalline scorodite is light green and amorphous scorodite is beige-brown. It was determined that 1% of amorphous material in a crystalline matrix could cause a visual colour change.

The particle size distribution of the powders was measured with a sedigraph particle size analyzer (Micromeretics 5000D). The surface area was measured by means of a BET analyzer (Quantachrome-Quantasorb). The morphology of the produced scorodite powders was determined visually by a Scanning Electron Microscope (SEM, type: JEOL 840A). The samples were gold coated prior to examination. The SEM was also equipped with an Energy Dispersive Spectroscope (NORAN I-2 system), which could determine the quantitative composition of the individual particles.

4.3 CHEMICALS AND MATERIALS USED

The chemicals used in all experiments are listed in Table 2.

 Table 2.
 Chemicals used in experimental testwork.

<u>Name</u>	<u>Formula</u>	<u>Supplier</u>	<u>Grade</u>
Ferric sulphate pentahydrate	Fe ₂ (SO ₄) ₃ .5H ₂ O	Aldrich chemicals	Reagent
Magnesium Hydroxide	Mg(OH) ₂	Aldrich chemicals	Reagent
Sulfuric Acid (98%)	H₂SO₄	BDH	Reagent
Potassium Arsenic Acid	KH₂AsO₄	Sigma	Analytical
Sodium Hydroxide	NaOH	Sigma	Reagent
Calcium Hydroxide	Ca(OH) ₂	Sigma	Reagent
Ammonium Hydroxide	NH₄OH	Caledon	Reagent

All experiments were caried out with de-lonized water. The water was passed through two ion exchangers: first a Cole Parmer ion exchanger type 1506-25 "universal", the second ion exchanger type 1506-35 "Research".

The only other material used in the testwork was crystalline scorodite seed. Very fine powdery material was produced using a nitrate solution based autoclave method which was developed by Van Weert and Droppert⁽⁴¹⁾.

In this method to produce scorodite, 0.25M arsenic trioxide is dissolved in a 2.5M nitric acid solution by heating it to 160°C. 0.5M ferric nitrate is added to satisfy the iron demand during scorodite formation. During the heating phase, which takes approximately 30 minutes, all As_2O_3 dissolves around 100°C. At that temperature dissolved As(III) is oxidized by nitric acid to form As(V) species and NO-gas according to the overall reaction below.

$3As(III) + 2NO_3 + 8H^+ = = > 3As(V) 2NO(g) + 4H_2O$ (15)

When the temperature reaches \approx 140°C, As(V) rapidly reacts with the ferric ions in solution to form scorodite according to reaction 16. The progress of reactions 15 and 16 is illustrated in figure 26 (total [As] means [As(III)] + [As(V)]).

$Fe^{3+} + H_3AsO_4 + 2H_2O = = > FeAsO_4.2H_2O(s) + 3H^+$ (16)

The scorodite that is produced can then be filtered from the solution, resulting in a very clean powder which is excellent as reference and seed material. Solubility testing on this material has shown similar results as was indicated in the literature for pure synthetic and natural scorodite.



Figure 26. Dissolution, oxidation and transformation of arsenic trioxide to crystalline scorodite using nitric acid chemistry^[42].

CHAPTER 5 RESULTS AND DISCUSSION

5.1 PRELIMINARY WORK

In order to be able to control the supersaturation level in solution the "equilibrium" solubility line of scorodite had to be determined as a function of pH. Therefore, a number of leach tests were conducted where an excess of scorodite reference material was leached in sulphuric acid solutions of different acidity at 95°C. Each test was performed in duplicate and the average of the two results was used. The solutions were left to equilibrate for 24h and were continuously stirred throughout the duration of the test. After 24h the solutions were filtered to remove the excess scorodite and the pH of the filtrate was recorded. AA analysis was performed on the filtrate for both As and Fe, which resulted in the solubility line shown in figure 27. The solubility data were similar to what was reported for the chloride system at 95°C, although the point of incongruent dissolution lies at slightly higher pH in the sulphate system ($pH \approx 2.5$ versus $pH \approx 1.2$).

Once the solubility line was established, the next step was to conduct controlled neutralization tests with 1g/L As(V) solutions. A 0.5L solution containing 0.4M H₂SO₄, 1g/L As(V) and Fe(III) in a 1:1 molar ratio to As (\approx 0.75g/L), was neutralized from an initial pH \approx 0.5 to a final pH = 2.5 by continuous addition of NaOH at 95°C. At pH = 0.75, 2 grams of seed material was added (4g/L). The NaOH solution (1M) was added at a constant rate to the stirred solution through a metering pump. The rate of NaOH addition was decreased in different tests in order to find the optimum residence time to reach the final pH. It was found that a residence time of 4h produced precipitate which was completely crystalline scorodite. At lower residence times, i.e. with faster addition of NaOH, the precipitated product always contained some amorphous ferric arsenate or was completely amorphous (the seed material remained crystalline).



Figure 27. The solubility of scorodite as a function of pH at 95°C. H₂SO₄ was used for pH control, equilibration time was 24h.



Figure 28. Scorodite neutralization path and solubility line. Conditions: $T=95^{\circ}C$, 0.4M [SO₄²⁻], Fe:As = 1, 4g/L seed, NaOH as base, t=4h.

Figure 28 shows the neutralization path of the test that resulted in crystalline scorodite production. It can be observed that despite the high pH and high S values, no more than 65% of the initial As precipitated (between 200-300 ppm As always remained in solution). In fact, solution analysis showed that precipitation, yielding amorphous and/or crystalline products, started only after the solution was neutralized to $pH \approx 1.3$ where the supersaturation was >70. This feature was totally in contradiction to what was observed in the chloride system where the maximum S values were < 10. Another discrepancy between the sulphate and the chloride work was that no scaling of scorodite (by means of heterogeneous nucleation), was observed in any of the sulphate tests.

The different behaviour of the sulphate system can probably only be explained by the complexation of ferric ions in solution that inhibit the precipitation reaction. It is well known from the literature that As(V) species do not form complexes in sulphate solutions, but it is also known that Fe(III) species do form complexes with sulphate as was described in section 3.2.1. From figures 20 to 22 it can be observed that at low pH ferric sulphate complexes are predominant, but at high pH values (>2) ferric hydroxyl complexes become increasingly important. It is around this pH that a change in precipitation behaviour is observed. Figure 29 shows a schematic speciation diagram for ferric sulphate and ferric hydroxyl complexes, which was obtained from a computer speciation program developed at McGill University by Fillipou et al.^[39]. It shows that ferric sulphate complexes are slowly replaced by ferric hydroxyl complexes between pH = 1.5 and pH = 2.5. It is thought that the ferric sulphate complexes are relatively inert to As(V) species in solution, resulting in inhibition of scorodite precipitation. However, as the solution is neutralized the iron precursor for precipitation slowly changes to ferric hydroxide, and it is in this so-called precursor change area that scorodite precipitation becomes possible. Obviously the rate at which ferric hydroxyl complexes react with As(V) species in solution is much faster.

Ferric sulphate (aq) + As(V) = = RATE1 = = > Scorodite

Ferric hydroxyl (aq) + As(V) = = RATE2 = = > Scorodite



Figure 29. Schematic speciation diagram of the Fe(III)-SO₄²⁻-H₂O system¹³⁸⁾.

5.2 PRECIPITATION OF SCORODITE USING NaOH AS BASE

Particle size growth: Despite the fact that the yield of precipitation was limited, $\approx 65\%$ of the initial As(V) could be precipitated as scorodite under the test conditions described above. Nevertheless the results were very encouraging and further work was conducted. First, the growth characteristics of the produced scorodite were studied by repeating the same test 7 times, using the product of each test as seed material for the next one. In this fashion growth of the seed particles was achieved which was monitored by performing a particle size distribution analysis on the different precipitation products. Figure 30 shows the results of this analysis, and it is clear that by recycling of seed material the particles grow. The D₅₀ increases from 3μ m (reference seed) to 18μ m after 7 recycles. The particle size distribution also becomes more narrow which is shown by the increasing tangent of the curves. The apparent growth of the particles also resulted in faster settling rates and better filtration with each consecutive test. In general filtration was very good for all tests.

SEM pictures of the starting and final material are shown in figures 31 A and B. The starting material produced from a nitrate solution at 140°C showed nice sharp angled crystals and twin crystals, while the final material showed a much more aggregated and well-rounded morphology. BET analysis on both samples showed a specific surface area of ≈0.5 m²/g despite the apparent difference in size. This suggests that the particles produced in the final test were partly porous. This was confirmed by Thermal Analysis data shown in Appendix A. The mass loss during thermal analysis was experienced over a greater temperature range than with high temperature, coarse, scorodite material.

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Figure 30. Particle size distribution of scorodite precipitates before and after recycling.

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Figure 31A. SEM picture of the starting material produced from a nitrate solution at 160°C.





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Effect of sulphate: Because sulphate ions in solution seem to be the cause of the observed inhibitive behaviour of the sulphate system in comparison to the chloride system, it was decided to investigate the direct influence of $[SO_4^{2}]$. The same test was conducted as before, except that the pH was first rapidly raised to the point where amorphous precipitation was observed. When under continuous agitation this amorphous precipitate appeared to be stable, the pH was decreased slightly so that a clear solution was obtained again. This pH was called the induction pH; at this pH seed was added and the solution was slowly neutralized to pH = 2.5. the test was repeated for each sulphate concentration until the optimum residence time was determined, which produced pure crystalline scorodite. The residence time and induction pH were monitored as a function of $[SO_4^{2}]$ and are plotted in figure 32.

The induction pH increases from 1.05 to 1.50 when the $[SO_4^{2^2}]$ is increased from 0.1M to 0.4M. This is in accordance with the hypothesis that sulphate ions inhibit scorodite production, because at lower $[SO_4^{2^2}]$ where the ferric sulphate complexes are weaker the inhibition of the reaction diminishes, resulting in a lower inhibition pH. The residence time also decreases when the $[SO_4^{2^2}]$ is decreased. The residence time decreased from 4h to \approx 2h and in all cases resulted in \approx 65% precipitation yield. This feature directly relates to faster precipitation kinetics, which supports the hypothesis made earlier.

<u>Jarosite formation</u>: During several tests the formation of a beige/brown precipitate was observed, which was thought to be amorphous ferric arsenate. However, in tests with slightly higher concentrations of As(V) this precipitate could not be avoided. Even tests with residence times of >6h resulted in a mixture of this beige/brown precipitate and scorodite. Solubility tests revealed that no amorphous ferric arsenate was present (the solubility was 0.1ppm at pH=4, which corresponds to pure scorodite).

XRD analysis could not reveal the identity of this compound because it was present in concentrations below the detection limit of the apparatus (<5%). However, it was assumed that the beige/brown precipitate was sodium jarosite. It

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is known from industrial plant practice¹⁴³¹ that sodium jarosite precipitates in the same pH area as scorodite and that its solubility is similar to that of scorodite.



Figure 32. The effect of $[SO_4^{2-}]$ on scorodite precipitation kinetics and induction pH. Conditions: T=95°C, $[As]_{init}$ =1g/L, Fe:As =1, 4g/L seed, NaOH as base, controlled neutralization from pH_{ind} to pH=2.5.

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5.3 EFFECT OF TYPE OF BASE

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<u>Magnesium hydroxide:</u> The co-precipitation of jarosite assumed above made the identification of crystalline scorodite (light green) more difficult as it resulted in discoloration of the precipitates. It was decided to continue the testwork with $Mg(OH)_2$ because of the inert nature of Mg^{2+} in sulphate solutions. The same tests as outlined earlier were conducted with the difference that $Mg(OH)_2$ slurry instead of NaOH was continuously added. The optimum neutralization path was established and is compared in figure 33 to the same test using NaOH. Although the induction pH of the precipitation reaction remained the same, the reaction kinetics were totally different. The 1g/L As(V) solution could be neutralized within 2h from the induction pH=1.6 to the final pH=2.5 resulting in pure crystalline scorodite precipitation. Under the same conditions using NaOH, 4h were needed to obtain the same result.

During the tests with Mg(OH)₂ no other precipitates were observed except crystalline and amorphous scorodite (the latter was formed when neutralization was completed too quickly). This implies that the formation of small quantities of sodium jarosite had a negative effect on the kinetics of scorodite formation and is the reason for the difference in results as seen in figure 33. It is thought that the ferric ions in solution undergo a precursor formation for jarosite which is in competition with ferric ions required for scorodite precipitation. This behaviour subsequently slows down the kinetics of scorodite formation.

From a practical point of view, $Mg(OH)_2$ is not a preferred base because it was found that the slurry could not be pumped into the solution by a metering pump because of the rapid settling of the $Mg(OH)_2$ solids. Therefore, $Mg(OH)_2$ slurry had to be added manually through a pipet. In order to avoid this labour intensive work, ammonium hydroxide solution (NH₄OH) was tested as a substitute for Mg(OH)₂.



Figure 33. Comparison between Mg(OH)₂ and NaOH as base. Conditions: T=95 °C, [As]_{ink}=1g/L, Fe:As =1, pH_{ind}=1.6, pH_{final}=2.5, 0.4M [SO₅²⁻], 4g/L seed.

<u>Ammonium hydroxide:</u> Dilute ammonium hydroxide was used as base for the same tests as before, i.e. neutralizing a 1g/L As(V) solution from $pH_{ind} = 1.6$ to $pH_{ind} = 2.5$. A trend similar to Mg(OH)₂ was observed, as shown in figure 34. By using NH₄OH 2.5h were needed to reach pH = 2.5 (2h for Mg(OH)₂ and 4h for NaOH). This result supports the mechanism that was suggested above for jarosite precursor formation. Another supporting argument for this mechanism comes from the observations that were made during the tests with the three different bases. The addition of NaOH resulted in the formation of brown clouds, caused by local pockets of high oversaturation. These clouds disappeared as long as the pH was $< pH_{ind}$. However, when Mg(OH)₂ and NH₄OH were added, the formation of white clouds was observed. This is also similar to what was observed during the work with the chloride system. The brown clouds are assumed to be colloidal sodium jarosite.

Tests with ammonium hydroxide using higher As(V) concentrations showed a different behaviour. In solutions with 5g/L As(V) (and Fe(III) in a 1:1 ratio) brown clouds were seen to form upon base addition, and the final precipitate was always beige/brown coloured. The kinetics of scorodite precipitation decreased as well. This is thought to be caused by ammonium jarosite precipitation. For this reason no further tests were conducted with ammonium hydroxide. The limited success with NH₄OH as opposed to NaOH is attributed to the higher solubility of ammonium jarosite in comparison to the solubility of sodium jarosite.

Lithium hydroxide: Lithium hydroxide (LiOH) was tested as a substitute base because it can be pumped in as a liquid and because of its inability to form a jarosite phase. It was considered to be useful only for the investigation of several parameters of the synthetic ferric arsenate precipitation system, as LiOH has no use as an industrial base because it is expensive. Several tests were conducted using LiOH, all resulting in the formation of a reddish coloured precipitate. Even residence times of >6h did not result in the production of crystalline scorodite. Obviously lithium was not as inert to the test solution as was expected, so no
further tests were conducted using this base. No attempt was made to identify the precipitates.

Despite the practical problems imposed by using $Mg(OH)_2$ as base, it was decided to do all further testwork with $Mg(OH)_2$. Ca(OH)₂ was not tested as a substitute because of the simultaneous formation of gypsum. The use of Ca(OH)₂ is described in a separate section (section 5.8).



Figure 34. Comparison between NH₄OH and NaOH as base. Conditions: T=95°C, [As]_{init}=1g/L, Fe:As =1, pH_{ind} =1.6, pH_{final} =2.5, 0.4M [SO₄²⁻], 4g/L seed.

5.4 EFFECT OF SLOW Fe(III) ADDITION

In many industrial cases, solutions containing arsenic are generated with little or no dissolved iron, resulting in Fe:As ratios <<1. In such cases iron must be added in some form, usually as ferric sulphate salts. This can be very costly, especially when a Fe:As ratio of 4 must be maintained for stable amorphous ferric arsenate precipitation. Scorodite requires a Fe:As ratio of 1, which appreciably decreases iron requirements.

For situations where iron must be added to precipitate arsenic, it was thought that by slowly adding ferric sulphate to the As(V)-containing solution (in the presence of seed) it might be possible to control supersaturation and thus favour the precipitation of scorodite. The first tests conducted with slow Feaddition were at pH = 2.5 because it was expected that the ferric sulphate complexes at that pH would be replaced by ferric hydroxyl complexes, which would lead to faster precipitation kinetics. To test this hypothesis, a 1g/L As(V) solution containing 0.4M H_2SO_4 was first neutralized to pH = 2.5 using Mg(OH), at 95°C. 4g/L seed was added to the solution and then ferric sulphate solution was slowly added with a metering pump. This test was repeated at different pump rates in order to determine the optimum conditions. The fastest iron addition rate which produced scorodite was ~0.035 mmolFe/min.L. This rate required a residence time of \approx 5h (see figure 35). When the iron addition rate was increased, it was found that amorphous ferric arsenate was precipitated. The final [As] was 35 mg/L, corresponding to a total As precipitation yield of 96%. In each test Fe(III) was added as a 10% excess to As(V) to ensure that sufficient Fe(III) was always present during the test.

A similar series of tests was performed at pH=2.0. At this pH, the maximum scorodite-producing iron addition rate increased to ≈ 0.06 mmolFe/min.L, requiring a residence time of $\approx 3h$. The As precipitation yield in this case was 83%. Tests were also conducted at pH=1.5, where the solution was found to behave very differently. There was no limitation to the iron addition rate as there was total

suppression of the ferric arsenate precipitation reaction. The addition of ferric sulphate in a single large dose resulted in a clear and chemically stable solution despite the high S (S>70). However, when seed was added at that point the precipitation of arsenic as scorodite was induced, resulting in 60% of the initial arsenic being precipitated as scorodite after 2h. Figure 36 shows the relationship between pH, Fe-addition rate and arsenic precipitation yield. This figure Indicates that the Fe-addition rate increased when the addition pH was closer to the induction pH. The As precipitation yield increased with increasing pH because of the lower scorodite solubility at higher pH values. It is more difficult to precipitate scorodite at higher pH because of the corresponding high S values which result from the lower solubility of scorodite. The driving force for precipitation (both amorphous and crystalline) increases at higher pH, which makes it more difficult to avoid homogeneous nucleation and thus the formation of an amorphous precipitate.



Figure 35. Scorodite precipitation by slow Fe(III)-addition at pH=2.5. Conditions: T=95°C, [As]_{int}=1g/L, 0.4M [SO₄²⁻], 4g/L seed, Mg(OH)₂ as base.



Figure 36. The effect of pH on Fe(III)-addition rate and As precipitation yield. Conditions: $T = 95 \,^{\circ}$ C, $[As]_{init} = 1g/L$, 0.4M $[SO_4^2]$, 4g/L seed, Mg(OH)₂ as base.

5.5 EFFECT OF SEED CONCENTRATION

The results from the previous section indicated that scorodite could be precipitated at a constant pH from a clear As(V)/Fe(III) solution, provided that the solution pH was $< pH_{ind}$ and seed was added. By adding only 4g/L seed material a yield of $\approx 60\%$ was obtained in 2h. In order to improve these results the same test was repeated at pH = 1.5, varying the seed concentrations from 4g/L to 50g/L. A 1g/L As(V) solution containing 0.4M H₂SO₄ was neutralized to pH = 1.5 using Mg(OH)₂. At this pH a 1:1 molar ratio of Fe(III) was added as ferric sulphate together with the seed material. The pH was kept constant throughout the whole test by manual addition of Mg(OH)₂. Samples were taken as a function of time and the results are shown in figure 37. Increasing the concentration of seed material was shown to have a dramatic effect on the precipitation rate and final yield. In all tests pure crystalline scorodite was precipitated because the pH was maintained below pH_{ind}.

By using 50g/L seed instead of 4g/L, the yield after 3h increased from 60% to 83%. Even more importantly, the rate at which the scorodite precipitated increased dramatically. Figure 38 shows this observation by plotting the initial rate of each neutralization path of figure 37 against seed concentration. The initial rate of precipitation increases from 0.03 mole As/min.L at 4g/L seed to 0.47 mole As/min.L at 50g/L seed. The relationship at 50g/L is still linear which means that the optimum seed concentration is higher than that. No further tests were performed to find this optimum point. Clearly, the increased surface area provided for more readily accessible precipitation sites on which As(V) and Fe(III) can react.



Figure 37. The effect of seed concentration on scorodite precipitation. Conditions: $T=95^{\circ}C$, $[As]_{init}=1g/L$, 0.4M $[SO_4^2]$, Mg(OH)₂ as base, $pH_{init}=1.5$, Fe:As=1.



Figure 38. The initial scorodite precipitation rate versus seed concentration. Conditions: T = 95 °C, $[As]_{init} = 1g/L$, 0.4M $[SO_4^{2}]$, Mg(OH)₂ as base, $pH_{ind} = 1.5$, Fe:As = 1.

5.6 THE EFFECT OF INITIAL [As(V)]

All results reported in the previous section were obtained with 1g/L As(V) solutions. In industry it is possible to encounter solutions containing much higher As(V) levels. Especially solutions resulting from arsenical flue dust treatment can contain arsenic concentrations in excess of 1g/L. Therefore, a number of tests were conducted with concentrations of 5 and 10g/L As(V).

The induction pH, which is a unique property of each system, was first determined by neutralizing the solution in the absence of seed material; the induction pH decreasing with increasing [As(V)] and [Fe(III)]. Then the same starting solution was neutralized using Mg(OH)₂ to this induction pH, after which 50g/L seed was added. Because of the substantial amount of arsenic that precipitated, more Mg(OH)₂ had to be added during these tests to maintain a constant pH. The results of these precipitation tests are shown in figure 39. A solution with an initial As(V) concentration of 5g/L required 1h to precipitate >95% of all As as crystalline scorodite; the final [As] after 3h was ~180 mg/L. An initial [As(V)] of 10g/L required 2h to precipitate >93% of all As; the final [As] after 3h was ~400 mg/L.

It was shown with these tests that the inhibition of the precipitation reaction will decrease with increasing [As(V)], i.e. the induction pH will decrease with [As(V)]. At the same time it was determined that around 80 to 90% of arsenic precipitates in a single step as long as the pH was maintained just below the corresponding induction pH. This has significant practical implementations for an industrial application, as fewer tanks would be needed to precipitate arsenic as scorodite than was thought previously (see figure 19). In other words, the inhibition of the precipitation reaction can be used advantageously in this manner.



Figure 39. The effect of initial [As(V)]. Conditions: $T=95^{\circ}C$, 0.4M [SO₄²⁻], Mg(OH)₂ as base, pH_{ind} indicated in graph, Fe:As = 1, 50g/L seed.

5.7 EFFECT OF Fe/As RATIO IN SOLUTION

In many industrial solutions more iron is present than arsenic. A high Fe:As ratio was shown to have an effect on the precipitation kinetics during the previous work in the chloride system^[6]. This effect was investigated in sulphate solutions, using a 5g/L As(V) solution at pH = 1.1 (similar conditions as in the previous section). Fe(III) was added in excess as ferric sulphate salt at the beginning of the test, after which the solution was neutralized using Mg(OH)₂ to pH = 1.1 (the induction pH). Fe:As ratios of 1, 2 and 5 were tested and the results are shown in figure 40.



Figure 40. The effect of Fe:As ratio in solution. Conditions: T = 95 °C, Mg(OH)₂ as base, pH_{ind} = 1.1, 50g/L seed, [As]_{ink} = 5g/L.

The test with an Fe:As ratio of 2 showed slower kinetics and a smaller final precipitation yield than the 1:1 ratio solution. When the Fe:As ratio was increased to 5, hardly any As precipitated as scorodite after 3h. Some precipitation was observed during the first 30 minutes of the test, but throughout the remainder of the test the [As] stayed at \approx 4g/L. The negative effect the increased Fe:As ratio had on precipitation kinetics and yield at pH = 1.1 could be attributed to the further stabilization of ferric ions as ferric sulphate complexes. The more Fe(III) and sulphate are added to the solution, the more the solution becomes inhibited, resulting in decreased precipitation kinetics and yield. It is also possible that the solubility of scorodite changed in the different tests because of the differing sulphate concentrations. However, the induction pH was similar for all three tests, indicating that a possible change in solubility would have been minimal.

5.8 EFFECT OF Ca(OH)₂ AS BASE

In all previous experiments the use of lime or $Ca(OH)_2$ was avoided. The reason for this was the complication introduced to the system by the coprecipitation of gypsum. The addition of calcium ions into the sulphate solution induces the immediate precipitation of calcium sulphate (reaction 18).

$Ca(OH)_{2} + H_{2}SO_{4} = -> CaSO_{4}.2H_{2}O$ (gypsum) (18)

It was therefore, necessary to first study and demonstrate the successful production of scorodite (at ambient pressure) in simple systems and to then introduce complicating features such as the gypsum formation reaction. The effect gypsum co-precipitation had on the production of scorodite was studied by performing tests similar to the tests described in previous sections, but replacing Mg(OH)₂ with Ca(OH)₂.

First, the induction pH was determined for a 5g/L As(V) solution containing

0.4M H_2SO_4 and Fe(III) as a 1:1 ratio to As(V). Ca(OH)₂ addition at the initial pH = 0.5 resulted in the immediate formation of (white) gypsum. Only when pH = 1.1 the solution colour started to turn brownish, indicating that the induction pH for amorphous ferric arsenate was reached. This induction pH was similar to the induction pH determined by using Mg(OH)₂. A number of precipitation tests were conducted at a constant pH of 1.1 by adding 50g/l seed to the solution. All of the tests resulted in precipitation of ~90% of the initial As(V) as a mixture of gypsum, amorphous ferric arsenate and scorodite. Figure 41 shows the typical results obtained from one of the tests in comparison with a similar test using Mg(OH)₂ as base. When the solution was neutralized to pH = 1.1, almost half of the As(V) in solution had "co-precipitated" with the gypsum. Seed was added at this point, giving the solution a greenish colour (scorodite), which was visible for approximately 30 minutes, after which the samples showed signs of amorphous ferric arsenate, i.e. a brownish colour. However, after 2h the solution turned green again, resulting in more than 90% conversion of As as scorodite after 3h.



Figure 41. The effect of using Ca(OH)₂ versus Mg(OH)₂ as base. Conditions: T=95°C, pH_{ind} =1.1, 50g/L seed, [As]_{ink}=5g/L, 0.4M [SO₄²⁻].

The initial fast removal of arsenic from solution was attributed to a combination of As(V) adsorption on gypsum and amorphous ferric arsenate precipitation. The amorphous material slowly redissolved during the test, but its presence severely slowed down the rate of scorodite formation. It is possible that this amorphous material covered the surface of the seed material, thereby disabling the scorodite precipitation reaction. Alternatively, gypsum had covered part of the seed surface. Figure 42 shows the results of a similar test, conducted at a slightly lower pH (pH=0.9) to avoid the formation of amorphous material. Pure crystalline scorodite was produced throughout the test, and adsorption of As(V) on gypsum was still observed. However, this adsorption was far less profound than in the previous tests (see figure 41) because the initial neutralization to pH=0.9 was performed slowly, resulting in more controlled conditions for gypsum formation. The scorodite precipitation kinetics were slightly slower than the kinetics observed when Mg(OH)₂ was used. The final yield was lower as well, but this must be attributed to the lower pH used in this test.



Figure 42. The effect of using Ca(OH)₂ at pH=0.9. Conditions: T=95°C, 50g/L seed, [As]_{int}=5g/L, 0.4M [SO₄²⁻].

The adsorption of As(V) on gypsum was tested by repeating the same test as in figure 42, in the absence of Fe(III) and seed material. It was observed from sample analysis that during the initial neutralization to pH=0.9 the As(V) levels dropped slightly from 5g/L to 4.2g/L. By keeping the solution stirred at 95°C the adsorbed As was slowly released and after 2h the solution concentration was back to 5g/L.

5.9 THE SOLUBILITY/STABILITY OF THE PRODUCED SCORODITE

The scorodite samples produced were tested for their solubility/stability by leaching them as a 10% slurry for 24 hours at pH 4-5. After each leach the solids were filtered, re-slurried and leached again for 24 hours. This procedure was repeated several times to allow for any entrained mother liquor inside the particles to escape. After a certain number of repeat leach tests all mother liquor had escaped and stable solubility data were obtained.

Solubility/stability tests were conducted for scorodite produced from tests using Mg(OH)₂ as base, as well as scorodite/gypsum samples produced from tests using Ca(OH)₂ as base. Both samples were produced from 5g/L As(V) solutions at 95°C, at pH = 1. The results are shown in Table 3. Surprisingly the solubility data of both samples were higher than expected for pure synthetic scorodite (see figure 7, page 14). The scorodite produced with Mg(OH)₂ has a solubility that levels out at approx. 0.7mg/L As(V), while the scorodite produced with Ca(OH)₂ has a slightly higher solubility of approx. 1.4mg/L As(V). More repeats of the leach test are required for the Ca(OH)₂ scorodite in order to deplete all entrained mother liquor than for the Mg(OH)₂ scorodite. This must be attributed to the presence of adsorbed As(V) species on the gypsum particles which takes longer to deplete than the physically entrained (not adsorbed) As(V). Nevertheless, it is expected that a stable and low As(V) release will be obtained from these samples when exposed to a non-steady state environment.

The reason why the solubility of the scorodite produced from sulphate media

is higher than pure crystalline scorodite samples prepared from nitrate or chloride media^(0,18,41) is probably due to the presence of small amounts of sulphate ions incorporated into the scorodite crystal lattice. Wet chemical analysis on the scorodite produced in this work showed the consistent presence of small amounts of sulphate (0.2-0.4%). This sulphate could not be removed, even after extensive washing with dilute HCI or water. An independent analytical investigation was conducted by Swash of the Royal School of Mines in London on the samples produced in this work^[43] (see appendix A). They subjected the samples to Infra Red Spectroscopy and Thermal Analysis (DTA-TG) and confirmed the presence of crystalline scorodite. They also found some indication of the presence of small amounts of sulphate but could not conclude whether this was present as a separate phase or included in the scorodite crystal lattice. The fact that scorodite samples without the presence of sulphate show typical (ideal) solubility data (see solubility data from chloride and nitrate scorodite⁽⁰⁾), indicates that the presence of small amounts of sulphate affect the solubility of the scorodite samples produced in this work. The actual mechanism causing this anomaly is, however, unknown.

Table 3.	Solubility data of produced scorodite samples. Conditions: $T=25$ °C,
	10% solids, 24 hours retention time at pH 4-5.

NO. of repeat leach tests	Mg(OH) ₂ scorodite	Ca(OH) ₂ scorodite
	solubility (mg/L)	solubility (mg/L)
1	1.41	6.88
2	0.85	4.76
3	0.65	3.27
4		
5	0.67	1.60
6	-	1.58
7	•	1.38
8	•	1.41

5.10 PRACTICAL IMPLICATIONS

The results described in this thesis show that the supersaturation controlled precipitation of scorodite from sulphate solutions works differently than that from chloride solutions. Because of the inhibition of amorphous ferric arsenate precipitation, very high supersaturation values (>70) can be maintained while still ensuring the precipitation of crystalline scorodite. Because of these high S values more than 90% of the initial arsenic in solution can be precipitated at a constant pH, i.e. in one reactor working at constant pH. This is different than the observations of the chloride system where S_{cr} values were low (<10), necessitating a large number of reactors in series to obtain high precipitation yields.

Because fewer reactors are needed to precipitate all arsenic as scorodite, a potential flowsheet will be more simple (easy to control, and economically more favourable). A general schematic flowsheet was conceived for the treatment of an effluent containing As(V), Fe(III) and sulphate and it is shown in figure 43. In this process, the process solution or effluent is heated to 95°C to enable scorodite precipitation. Mg(OH)₂ or Ca(OH)₂ is added in a controlled manner in the neutralization reactor(s). More than 90% of the initial As present in the effluent is precipitated in this circuit and separated from the effluent, for disposal (if so desired) or simply passed with the effluent to the next polishing step. If there is not sufficient Fe(III) present in the effluent initially, extra Fe(III) must be added as ferric sulphate. This will be added in such a way that the effluent exiting the controlled circuit has a Fe:As ratio >4. This effluent, having a pH of approximately 1.5-2.0, will subsequently be treated in a polishing step to remove the residual arsenic as a high Fe:As amorphous ferric arsenate sludge. This is achieved by neutralizing further to pH 7-9 using lime. The amorphous ferric arsenate sludge, which is stable due to its high Fe:As ratio, is discarded together with the bulk scorodite residue. The final effluent should contain arsenic at concentrations less than 0.5mg/L.



Treated effluent ([As]<0.5ppm)

Figure 43. Schematic flowsheet of treatment of Arsenic(V)-bearing effluents by scorodite precipitation.

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A more detailed look on the controlled neutralization circuit is given in figure 44. The effluent, which contains arsenic concentrations between 0.5 to 10g/L, enters the first precipitation tank which is operating at a constant pH between 0.8-1.5, depending on the [As]. If necessary, extra Fe(III) is added in the form of a ferric sulphate solution. Scorodite seed is added in a continuous fashion and Mg(OH)₂ or Ca(OH)₂ is added to maintain the pH at a constant level. The residence time in this first reactor will be somewhere between one and three hours, depending on the initial [As]. The solution exiting the reactor, contains 200-500 mg/L As, and is further neutralized to pH 1.5-2.0 in a second reactor. The solution exiting reactor 2 contains less than 100 mg/L As and is fed to a hydrocyclone. The bulk of the scorodite particles report to the underflow (the coarse fraction), after which they can be separated if desired or passed along with the effluent to the polishing step as described in figure 43. A small fraction, consisting of small particles, reports to the overflow of the cyclone and is send back to the first reactor as seed material. As there are no fresh scorodite particles generated during the precipitation, all particles will eventually grow to such an extend that no fine seeds will be recycled and thus the available surface area in the precipitation stages will decrease. This can be resolved by sending the recycle seed through a particle attrition step where the seed particles will undergo comminution prior to being added to the first reactor.



Figure 44. Supersaturation controlled neutralization circuit for sulphate-based effluents containing 0.5 to 10g/L As(V).

CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS:

- Pure crystalline scorodite was produced from synthetic sulphate solutions at 95°C by employing a supersaturated controlled precipitation technique. However, the sulphate system was shown to act very differently from the chloride system, as the scorodite precipitation reaction is partially inhibited by what is thought to be the formation of kinetically inert ferric sulphate complexes in solution.

- Very high supersaturation values (>70) could be attained while still avoiding amorphous ferric arsenate precipitation. The pH at which amorphous ferric arsenate formed was defined as induction pH (pH_{ind}). Surface nucleation could be induced by addition of scorodite seed material to a solution with pH slightly below pH_{ind} . No heterogeneous nucleation (scaling) was observed in sulphate solutions. The induction pH was found to decrease with increasing As(V) concentrations.

- NaOH was observed to have a negative effect on the precipitation kinetics of scorodite. Mg(OH)₂ was found to be the preferred base because of its lack of interference with the scorodite precipitation reaction.

- Supersaturation control by slow Fe(III) addition was shown to be a viable method. Scorodite precipitation kinetics were controlled by the Fe(III) addition rate; the latter increased with decreasing pH.

- The seed concentration was shown to have a dramatic effect on the precipitation kinetics and yield. By addition of sufficient seed, solutions containing up to 10 g/L

As(V) could be easily treated.

- High Fe:As ratios in solution were observed to have a negative effect on the scorodite formation kinetics and final precipitation yield.

- Because of the inhibition of the precipitation of amorphous ferric arsenate, more than 90% of all initial As(V) in solution could be precipitated as scorodite in one step at a constant pH, as long as this $pH < pH_{ind}$. Residence times for >90% precipitation yield varied from \approx 1h for a 1g/L As solution to \approx 2h for a 10g/L As solution.

- The use of $Ca(OH)_2$ as base was shown to decrease the scorodite precipitation kinetics slightly. This is caused by As(V) adsorption on the co-precipitating gypsum crystals. Nevertheless, $Ca(OH)_2$ or lime was found to be a viable option as neutralization agent during scorodite precipitation.

- The solubility of the produced scorodite precipitates is slightly higher (0.7-1.4 ppm at pH=5 versus 0.1-0.2 ppm) than that of scorodite produced from chloride or nitrate media. This is probably caused by the incorporation of small amounts of sulphate ($\approx 0.3\%$) in the scorodite mineral lattice.

RECOMMENDATIONS FOR FURTHER WORK:

- The scorodite precipitation technique developed in this work should be tested on industrial effluents, possibly on a continuous pilot plant scale.

- The effect of impurities on scorodite precipitation should be investigated.

- More work should be conducted with $Ca(OH)_2$ in order to minimize the adsorption of As(V) on gypsum.

- The use of other (less expensive) neutralizing agents such as limestone or dolomite should be tested.

- The exact mechanism of the inhibition of the scorodite precipitation reaction should be studied.

- Other than scorodite seed materials like iron oxides should be investigated.

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APPENDIX A

Comparison of two low temperature scorodite compounds produced using sulphate and chloride media

by

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1. Origin of samples

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 under ambient temperatures in the range 80 - 95°C, employing a supersaturation controlled procedure. Acidic chloride solutions contained 2g/L As(V), the procedure involved the step-wise neutralisation under low supersaturation environment in the presence of seed.

2. IR Spectra

The IR spectra of the two samples both show typical scorodite features. The distinct spike in the 3300cm^{-1} 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⁻¹). 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⁻¹ region possibly indicates the presence of an HAsO₄ functional group.

3. Thermal analysis data (DTA-TG)

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 FeAsO4.2H₂O) 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.











VERSION: VA. 90





VERSION: V4.30