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A REVIEW OF ARSENIC DISPOSAL PRACTICES FOR THE GIANT MINE, YELLOWKNIFE, NORTHWEST TERRITORIES

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MINING AND MINERAL SCIENCES LABORATORIES
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EXECUTIVE SUMMARY

A systematic literature review was carried out to obtain information about arsenic disposal practices in the mining-metals industry and about the long-term stability of the disposed arsenic compounds. This review was complemented with visits to operating metallurgical sites, currently precipitating arsenic from aqueous solution, in order to obtain information on their specific disposal practices and the behaviour of their impounded residues. This information was analyzed and evaluated to determine the applicability of current arsenic disposal technologies to the Giant Mine in Yellowknife, Northwest Territories. Lime precipitation, which was widely used in the past, is being abandoned as a result of strong evidence showing that calcium arsenate compounds decompose slowly in contact with atmospheric CO_2 to form calcium carbonate and soluble arsenic acid. The arsenic disposal procedure currently favoured by the mining industry involves the formation of an insoluble amorphous or poorly crystalline ferric arsenate compound, which is allowed to sediment at the bottom of tailings or residue ponds. It has been shown recently that this amorphous compound is similar to "arsenical ferrihydrite"; i.e., ferrihydrite containing adsorbed arsenate anions. Despite concerns about its long-term stability on thermodynamic grounds, arsenical ferrihydrite appears to be stable for many years in the proper environment, which includes a slightly acidic pH and oxidizing conditions. A high Fe/As ratio and the presence of heavy metals appear to increase the stability of arsenical ferrihydrite. High temperature operations, such as those encountered in the autoclave treatment of refractory gold ores, are conducive to the formation of scorodite, $FeAsO_4{\cdot}2H_2O$, and/or a series of ferric arseno-sulphate compounds, depending on the concentration of sulphate ions. Scorodite has several advantages over arsenical ferrihydrite as a

disposal compound, including a lower iron demand, a higher density and a greater thermodynamic stability. New procedures have been developed to generate scorodite at ambient pressure, which would offer a significant reduction in capital cost because of the elimination of the need for autoclaves. In all cases, the long-term stability of disposed arsenic compounds depends on a number of factors, including the disposal site characteristics, the particle crystallinity and size distribution, the presence of complexing agents, and the effect of bacterial activity.

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BACKGROUND

For several years, the Giant Mine, Yellowknife, Northwest Territories, operated a gold recovery circuit consisting of flotation, concentrate roasting and cyanide leaching. During the roasting operation, arsenic oxide and other compounds were volatilized and recovered in electrostatic precipitator and baghouse systems. During some 50 years of operation, this dust has been stored underground in a number of chambers formed in the rock, and the current inventory amounts to about 260,000 tonnes of dust, containing an average of 76% As_2O_3. The Department of Indian Affairs and Northern Development (DIAND) is currently considering options to reduce or eliminate the potential environmental impact of the As_2O_3-rich dust. Although a fraction of the dust might be re-processed to recover a purified arsenic oxide product for the wood preservative industry, it is likely that most of the As_2O_3-rich dust will have to be stabilized and impounded. Accordingly, a systematic review of current arsenic precipitation practices and of the data on the stability of the residues obtained by various mining operations and researchers was undertaken on behalf of DIAND. This report summarizes the findings of the investigation.

METHODOLOGY

The scientific literature was systematically searched from its beginning to the present time for information on arsenic disposal practices. The key words were: arsenic disposal, ferric arsenate, scorodite, and stability. The search was carried out using DialogWeb, which provides access to more than 500 different information collections, including Metadex (Metals Abstracts), Compendex (Engineering Abstracts), and the Chemical Abstracts On-line Catalogue. The NRC's CISTI Source (a collection of 14,000 scientific journals) was also searched electronically. In addition, various conference proceedings volumes dealing with arsenic disposal and gold leaching/arsenic disposal were surveyed, and personal contacts were made (via telephone or e-mail) with key authors. On the basis of the titles and abstracts, the original papers were obtained and reviewed. Any relevant references cited in these papers were also obtained for review. Copies of the reviewed papers are appended to this report.

In addition, three Canadian metallurgical sites currently precipitating arsenic from aqueous solution were visited to obtain information on disposal practices and the long-term stability of the ferric arsenate residues (Dutrizac and Spencer, 2000).

THE ARSENIC PROBLEM IN THE METALLURGICAL INDUSTRY

Arsenic is relatively abundant in the earth's crust, having an average terrestrial concentration of about 5 ppm. Escobar-Gonzalez and Monhemius (1988) published an extensive review of arsenic mineralogy, which lists more than 300 arsenate and associated minerals. Some common arsenic minerals that are frequently found in base metal ores and concentrates are presented in Table 1.

Table 1 - Common Arsenic-bearing Minerals (Valenzuela, 2000)

Type	Mineral	Formula
Arsenides	Nickeline	$NiAs_2$
	Safflorite	$(Co,Fe,Ni)As_2$
	Skutterudite	$CoAs_3$
Sulphides	Arsenopyrite	$FeAsS$
	Arsenical pyrite	$Fe(As,S)_2$
	Cobaltite	$CoAsS$
	Enargite	Cu_3AsS_4
	Orpiment	As_2S_3
	Realgar	As_4S_4
	Tennantite	$(Cu,Fe)_{12}As_4S_{13}$
Oxides	Arsenolite	As_2O_3
	Claudite	As_2O_3
Arsenates	Olivenite	$Cu_2(AsO_4)OH$
	Scorodite	$FeAsO_4 \cdot H_2O$

The presence of arsenic in metallurgical circuits increases the production costs, interferes with metal extractions, deteriorates the product purity, presents environmental hazards and creates disposal problems (Piret and Melin, 1989). Hydrometallurgical processes produce mostly soluble arsenic compounds, which are usually eliminated by precipitation and impoundment. In those cases where autoclaves are used, as in the processing of refractory gold by pressure oxidation, arsenic is fixed by the formation of crystalline scorodite-like compounds. In copper electrorefineries, arsenic is a major impurity, and bleed streams are usually operated to keep the arsenic in the electrolyte at a concentration less than about 20 g/l As. The usual method of dealing with refinery bleed streams is either to treat the copper electrolyte with excess lime to convert the acid into gypsum and to precipitate the remaining copper and other elements (including arsenic) from solution, or to electrolyze the solution in so-called liberator cells to remove copper and other impurities as an arsenide sludge, with the acid being recycled back to the main refinery circuit (Monhemius and Swash, 1999A).

Pyrometallurgical operations ultimately produce solid As_2O_3 as a result of roasting or smelting operations. During the sulphide converting/smelting process, most of the arsenic is volatilized and reports in the smelter flue dusts as either As_2S_3 or As_2O_3 (Weeks and Wan, 2000). Because of the limited solubility of arsenic compounds in conventional silica-based smelting and converting slags, the opportunity to dispose of arsenic in the insoluble glassy matrix of a silicate slag is limited (Hoffmann, 1993). Most of the arsenic is volatilized during copper smelting operations and, depending on its abundance, it is collected in the electrostatic precipitator or the wet gas cleaning section (Piret, 1999). Recycle of the arsenic-rich dust to the copper smelting operation causes an increase of arsenic in the recycle loop, ultimately increasing the concentration of arsenic in the anode copper destined for electrorefining (Hoffmann, 1993). Depending on its purity, the As_2O_3 dust may be sold to the wood preservative industry (Smith and Paredes, 1988; Stewart et al., 1994; Leach, 1999), the herbicide industry or stockpiled in protected areas.

In most cases, arsenic must be precipitated from solution in a storable form that is insoluble and stable, and this is most frequently done by precipitating ferric arsenate-type compounds. The problems associated with the present practices of arsenic disposal are the generation of large volumes of ferric oxyhydroxide and gypsum sludges upon neutralization of arsenic-rich acidic solutions and the long-term stability of those sludges (Hoffmann, 1993). The application of the so-called High Density Sludge (HDS) system, in which part of the sludge produced by precipitation is recycled to the process to increase the sludge density, appears to be effective in reducing the volume of the sludge produced (Lawrence and Higgs, 1999). Long-term stockpiling of As_2O_3 flue dusts is of even greater concern because of their high water solubility and the toxicity of the resulting soluble compounds (Filippou and Demopoulos, 1997).

Increasing environmental awareness is leading to more stringent regulations for the use and the disposal of arsenic compounds. Arsenic is toxic to both plants and animals, and its trivalent form is considered to be much more toxic than its pentavalent form. Both forms readily accumulate in living tissues because of their affinity for proteins, lipids and other cellular components (Harrington et al., 1998). A wide variety of adverse health effects, including skin and several internal cancers as well as cardiovascular and neurological effects, have been attributed to chronic exposure to high levels of arsenic, primarily from drinking water. The United States EPA's interim maximum contaminant level (MCL) for arsenic in drinking water is 50 μg/L. The Canadian MCL is 25 μg/L (Le, 1999). In Canada, there are proposed regulations which would classify As in the primary group of 21 persistent, toxic pollutants to be banned or phased out (Harris and Krause, 1993). Arsenic is included in the ARET (Accelerated Reduction and Elimination of Toxics) program. This is a Canadian industry/government voluntary emission reduction program the goal of which is to achieve a 50-90% reduction in the emission of persistent, bio-accumulative and toxic substances by the year 2000 (Valenzuela, 2000).

THE AQUEOUS CHEMISTRY OF ARSENIC

Arsenic, atomic number 33, is a member of the Group VB elements together with nitrogen, phosphorus, antimony and bismuth. In solution, arsenic can exist in the –3, +3 and +5 oxidation states, but the predominant aquatic forms are trivalent arsenite (+3) and pentavalent arsenate (+5). Arsenate is more common in aerobic surface waters, whereas arsenite is more common in anaerobic, or oxygen-deficient ground waters. Arsenic acid, H_3AsO_4, exists only in extremely acidic conditions. The species $H_2AsO_4^-$ is the predominant arsenate form in slightly acidic conditions, whilst $HAsO_2^{2-}$ predominates above neutrality. The deprotonated AsO_4^{3-} ion becomes the main arsenate form at extremely high pH conditions (Cadena and Kirk, 1995). Figure 1 shows an Eh-pH diagram for the As-H_2O system.

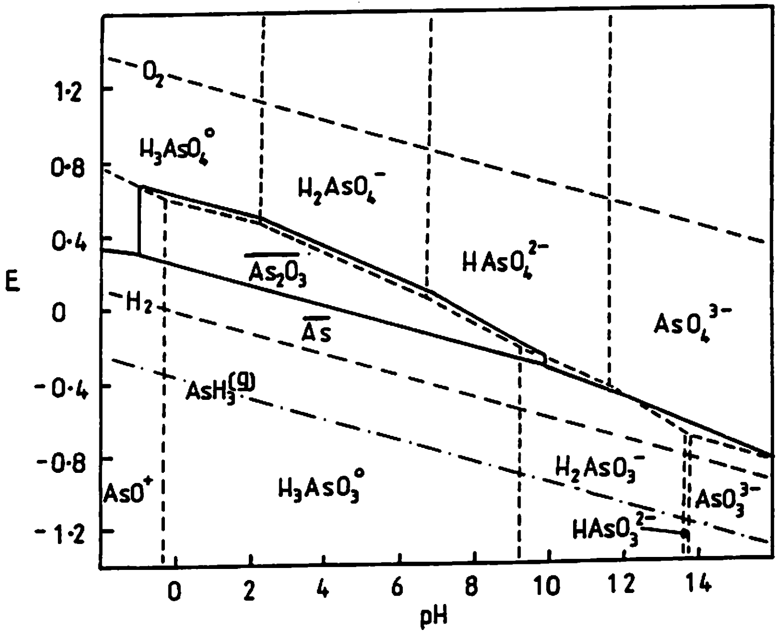

Figure 1 - Eh-pH Equilibrium Diagram for the System Arsenic-Water at 25°C and at Unit Activity of all Arsenic Species (Robins, 1988)

The thermodynamic properties of environmental arsenic species have been compiled by Nordstrom (2000). Arsenic acid, in its various forms, is significantly more soluble in water than arsenious acid. By contrast, most metal arsenates are less soluble than their corresponding arsenites. As a consequence, precipitation methods generally are most effective when arsenic is present in the As(V) form (Nishimura and Umetsu, 2000). However, As(III) is frequently found in ambient temperature metallurgical operations and it is quite stable. In fact, the oxidation of As(III) to As(V) is relatively difficult to effect, especially at room temperature. Oxygen and hydrogen peroxide are relatively inefficient oxidants for As(III) under most conditions (Harris and Monette, 1985; Molnar et al., 1994). According to Tozawa and Nishimura (1984), oxygen is ineffective in oxidizing As(III) species, except at higher pH and only then in the presence of a catalyst, such as cupric ions. Hydrogen peroxide can oxidize As(III) in alkaline media, but not in acid solutions unless high temperature are applied (Tozawa and Nishimura, 1984). Chlorine gas, potassium permanganate and ammonium persulphate completely oxidized 5 g/L of As(III) in 30-120 minutes at 60-90°C (Harris and Monette, 1985). Sodium hypochlorite, NaClO, can also be used to oxidize As(III) to As(V) effectively, as demonstrated by McClintok (1994). Ozone has been found to be a very effective oxidant for As(III), and it can achieve complete oxidation even in acidic media at ambient temperature; the oxidation rate is very fast and the effect of acidity and temperature on the oxidation rate is minimal (Tozawa and Nishimura, 1984; Nishimura and Umetsu, 1994). Unfortunately, the solubility of ozone in aqueous media is relatively low (Roca et al., 2000).

An important development in this field is the discovery that SO_2/O_2 mixtures can oxidize As(III) effectively (Nishimura et al., 1996). These researchers studied the oxidation of As(III) to As(V) using both SO_2/O_2 mixtures and a combination of gaseous O_2 and solid Na_2SO_3. The presence of Fe(II) as a catalyst and as a precipitant for arsenic was also evaluated. It was concluded that, in general, the oxidation reactions of S(IV), As(III) and Fe(II) induce each other. The oxidation of As(III) with oxygen was promoted by the oxidation of S(IV) to S(VI) over the pH range 5.0 to 11.0 at 50°C. The oxidation of S(IV) was appreciably enhanced by the presence of Fe(III) from either ferric sulphate or as a product of the oxidation of Fe(II) in a lower pH range. The induced oxidation of As(III) and its subsequent precipitation with Fe(III) as amorphous ferric arsenate was observed at an As(III) concentration as high as 0.1 M. The oxidation reaction was appreciably enhanced by a rise in temperature. Arsenic was removed to a concentration lower than the limit of industrial waste regulation (0.1 mg/L) at around pH 4 by oxidative precipitation.

Zhang et al. (2000) studied the As(III) oxidation by SO_2/O_2 mixtures (catalyzed by iron) and by O_2 (catalyzed by UV light and iron). It was found that the rate of oxidation with the $Fe/SO_2/O_2$ system is fast, and complete oxidation of 100 mM (7.5 g/L) As(III) is achieved in about 2 hours between 25°C and 60°C. With the $UV/Fe/O_2$ system, the rate of oxidation of As(III) was similar at low initial concentrations of As(III) (~0.1 mM or 7.5 mg/L), but was much slower at higher initial concentrations (~6.5 mM or 487 mg/L). Fundamentally, the $Fe/SO_2/O_2$ system is preferred for oxidizing the more concentrated As(III) solutions found in hydrometallurgical processes.

The oxidation of As(III) using UV radiation has also been discussed by Khoe et al. (2000). These researchers gave examples of large scale applications: 1) the treatment of acid mine waters using ferric salts and either sunlight or UV lamps, and 2) a sunlight-enhanced process to treat water samples from tubewells with As concentrations ranging from 0.2 to 1 mg/L.

METHODS FOR REMOVING SOLUBLE ARSENIC

Arsenic can be found in the waste streams from a variety of industrial processes. For example, arsenic waste can be generated from petroleum refining, glass melting, and the smelting of ores that are mined for their lead, copper, zinc, gold and silver contents. Arsenic is also released into the environment by the dispersion of arsenic-containing fertilizers, pesticides and wood preservatives (Bothe and Brown, 1999). Numerous methods to remove arsenic from various industrial effluents have been studied and proposed. An extensive review of these methods has been compiled by the Montana Tech and the MSE (1994) under the auspices of the United States EPA and the United States Department of Energy. A summary of this review has been published by Twidwell et al. (1999). These researchers cite over 160 papers covering arsenate precipitation and over 380 papers discussing arsenic adsorption. Table 2 summarizes the various processes that have been developed, proposed or studied for the removal of arsenic from solution.

Table 2 - Summary of Arsenic Removal Processes (Twidwell et al., 1999)

Precipitation	Calcium arsenate ←
	Mineral-like arsenates
	Ferrous arsenates
Adsorption	Ferrihydrite
	Aluminum hydroxide
	Alumina
	Activated carbon
	Other sorbents
Ion Exchange/Reverse Osmosis	Ion exchange
	Liquid ion exchange
	Reverse osmosis
Cementation processes	Iron cementation

Although many of these methods can effectively remove arsenic from solutions to very low levels, only a few have ever been applied on a large scale. For practical and economical reasons, those processes that generate an arsenic-bearing material that can be directly impounded are the most attractive. However, some the materials may not be suitable or stable for long-term disposal. Precipitation techniques dominate the field of As removal from solution.

Efforts to stabilize arsenic wastes by mixing them with cement, slaked lime, blast furnace slag, ceramics and other products have been partly successful (Kyle and Lundt, 1991; Twidwell et al., 1994; Khoe et al., 1994; Broadbent et al., 1994; Dutré and Vandecasteele, 1995; White and Toor, 1996; Dutré and Vandecasteele, 1998; Monhemius and Swash, 1999), but they are outside the scope of this review. Other methods, such as the formation of lanthanum arsenate (Nanor et al., 1999; Misra et al., 2000), barium arsenate (Weir and Masters, 1982) or phospho-arsenates (Twidwell et al., 1994) and hydroxyapatites (Twidwell et al., 1999) may hold promise, but they are still in a developmental stage.

Arsenic can be precipitated from solution by sulphide precipitation to less than one mg/L, but the precipitated arsenic sulphide is not stable or suitable for storage (Montana Tech and MSE, 1994). The reported solubility of As_2S_3 (orpiment) is 28.5 mg/L in the pH range 1-4 (Robins, 1988), and this value is too high for storage under water. According to Valenzuela (2000), at least one Japanese smelter removes arsenic from its circuit as arsenic sulphide, which is then polymerized and stored in-situ. In general, however, arsenic sulphide is not favoured for disposal because of the possibility of atmospheric and bacterial oxidation.

In water treatment operations, soluble arsenic is most commonly removed by co-precipitation with ferric salts, and this method has been designated as "The Best Demonstrated Available Technology" (BDAT) for the removal of dissolved arsenic by the United States EPA (Rosengrant and Fargo, 1990). The current practice involves oxidizing the As(III) to As(V), usually with Cl_2, to achieve better removal rates (Hering et al., 1996; McNeill and Edwards, 1995). The best arsenic removal rates are obtained at a pH of less 8.5 (Cadena and Kirk, 1995; Kartinen and Martin, 1995). This is one of the most cost-effective methods for purifying water. Merrill et al. (1986, 1987) estimated that the total cost of applying Fe(III) precipitation for selenium and arsenic removal from a power station scrubbing circuit would be US\$0.093 (1987) per m^3 of wastewater treated. The treatment facility was assumed to process an average flow of 1.1 m^3/s and to use an to what concentration of arsenic

iron dosage of 14 mg/L. The process flowsheet included influent pumping, chemical storage and feeding, rapid mixing, clarification, sludge thickening and dewatering, and disposal of the dewatered sludge in a municipal landfill. Ferric chloride additions, sedimentation and sludge dewatering were the major treatment costs. Ferric chloride consumption accounts for 22% of the total process cost; sedimentation and sludge dewatering account for 18 and 21%, respectively.

The mining industry must deal with soluble arsenic because of the presence of arsenic in many ores and concentrates. There are several sources of soluble arsenic in the mining and metallurgical processing of ores. Tailings may contain residual arsenic sulphides, and these compounds may become soluble as a result of pH changes brought about by acid mine drainage (Kwong et al., 2000) or algal activity (Taschereau and Fytas, 2000). Biological oxidation is being increasingly used to treat refractory gold ores, and during the biological oxidation of arsenical gold ores, the majority of the arsenic in the ore dissolves and leaves the process in the bioleach liquor after solid/liquid separation (Swash et al., 2000). Soluble arsenic present in mining effluents is sometimes removed by precipitation as As_2S_3 (Young and Robins, 2000), but more commonly, lime neutralization or precipitation with Fe(III) salts is used (Tahija and Huang, 2000). In cyanide solutions, Fe(II) ions may be used to precipitate arsenic, as discussed by Nishimura and Robins (2000). In most cases, a combination of lime and ferric salts is used. For example, in the case of acid mine drainage, Fe(III) ions are usually present in solution, when lime is added to neutralize the free acid and to promote the precipitation of metals. The work carried out by Swash and Monhemius (1995) provides some understanding of the likely precipitation behavior during the neutralization of iron-arsenic effluents with lime. During the low-temperature neutralization of arsenical liquors by the addition of excess lime, any sulphate present will preferentially combine with the calcium to form gypsum, thereby removing most of the sulphate from solution. At pH 1-3, arsenical ferrihydrite begins to form, and this removes most of arsenic from solution, if sufficient iron is present. Only if the Fe:As ratio in the liquor is low will arsenic be left in solution to combine with the lime to form calcium arsenates, which begin to precipitate at pH 3-4.

Lime Precipitation

Precipitation of As with lime is still widely practiced, despite concerns about the long-term stability of the resulting precipitate (Valenzuela, 2000). Neutralization of an As(V) solution with lime leads to the formation of a series of calcium arsenate compounds, whose compositions have not been completely established. Bothe and Brown (1999) identified several insoluble compounds, including $Ca_4(OH)_2(AsO_4)_2{\cdot}4H_2O$, $Ca_5(AsO_4)_3OH$ and $Ca_3(AsO_4)_2{\cdot}3^2/_3H_2O$. Nishimura and Tozawa (1985) used the formulas $Ca(AsO_2)_2{\cdot}Ca(OH)_2$ and $Ca_3(AsO_4)_2{\cdot}Ca(OH)_2$ to represent the precipitates obtained from solutions containing As(III) and As(V) ions, respectively. According to Swash and Monhemius (1995), the compounds most likely to precipitate at ambient temperature are $CaHAsO_4{\cdot}xH_2O$, $Ca_5H_2(AsO_4)_4$ or $Ca_3(AsO_4)_2$-type compounds. A Ca-Fe-As compound does exist (Type 4), but this is produced under rather specific conditions, and hence, it is unlikely that this compound will form during ambient temperature neutralization. At higher temperatures, Swash and Monhemius synthesized a series of calcium arsenate compounds, whose structure also depended on the pH and the Ca:As ratio. At low temperatures (<100°C) and pH (< 7), the precipitated solids comprised partially hydrated $CaHAsO_4$-type compounds. These compounds were crystalline, but did not have known XRD patterns; however, their IR spectra matched those of natural arsenate minerals, in particular haidingerite and pharmacolite (see Table 3). At pH 8 and in the temperature range 20-75°C, the precipitated compounds had a different Ca:As ratio and were comparable to the mineral guerinite, $Ca_5H_2(AsO_4)_4{\cdot}9H_2O$. At temperatures above 100°C, the solids had little water of hydration and the predominant compound was similar to the mineral weilite, $CaHAsO_4$. At 225°C, the synthesized solids had distinct IR patterns and their DTA-TG patterns showed negligible levels of constitutional water, suggesting the composition $Ca_3(AsO_4)_2$. Solids precipitated at higher pH's at temperatures above 100°C contained a similar compound, although this is more likely to be the basic calcium arsenate.

Table 3 - Characteristics of Synthetic Calcium Arsenate Compounds (Swash and Monhemius, 1995)

Mineral	Composition	Ca:As	Synthesis conditions
Haidingerite	$CaHAsO_4{\cdot}H_2O$	1:1	Ca:As 1:1, pH 6, 50°C
Pharmacolite	$CaHAsO_4{\cdot}2H_2O$	1:1	Ca:As 1:1, pH 6, 20°C
Gueinite	$Ca_5H_2(AsO_4)_4{\cdot}9H_2O$	5:4	Ca:As 1:1, pH 8, 50°C
Weilite	$CaHAsO_4$	1:1	Ca:As 1:1, pH 7, 200°C
Ca arsenate	$Ca_3(AsO_4)_2{\cdot}xH_2O$	3:2	Ca:As 1:1, pH 5, 225°C
Basic Ca arsenate	$Ca_3(AsO_4)_2{\cdot}Ca(OH)_2$	>2:1	Ca:As 1:1, pH 11, 100°C

Swash and Monhemius (1995) also found that all calcium arsenate compounds gave relatively high arsenic solubilities when subjected to the United States EPA TCLP tests. In fact, the arsenic solution concentrations for the calcium arsenate compounds were in the range 900-4,400 mg/L As, which is at least two orders of magnitude higher than the values produced by iron arsenate compounds. EPA TCLP testing of the calcium arsenate phases precipitated under a wide range of conditions showed that they are considerably more soluble than the precipitated iron arsenate phases. The calcium arsenate solids synthesized at higher temperatures, although being more crystalline and of different compositions, have similar solubilities to those formed at lower temperatures.

There is also strong evidence that calcium arsenate compounds decompose slowly in contact with atmospheric CO_2 to form calcium carbonate and soluble arsenic acid (Robins, 1981, 1983 and 1988; Robins and Tozawa, 1982; Nishimura et al., 1985), as shown in Equation 1.

$$Ca_3(AsO_4)_2 + 3CO_2 + 3H_2O = 3CaCO_3 + 2H_3AsO_4 \qquad (1)$$

An illustrative example of an industrial facility that had a major problem with the conversion outlined by Equation 1 is provided by the Pasminco lead smelter at Port Pirie, Australia. At this plant, lime precipitation was used to remove arsenic from wastewaters. Subsequently the redissolution of arsenic in the pond waters occurred to give very high levels (grams/liter) of dissolved arsenic (Montana Tech and MSE report, 1994).

Nishimura and Tozawa (1985) proposed calcining calcium arsenite and arsenate precipitates in order to increase their stability. The procedure involves heating above 700°C at Ca/As ratios of >4.6 for calcium arsenite and >2.1 for calcium arsenate. The end result of the calcination process is the transformation of the amorphous arsenical precipitates into a crystalline form, as illustrated by the following equation:

$$Ca_3(AsO_4)_2\cdot Ca(OH)_2 \xrightarrow{700°C} Ca_3(AsO_4)_2 \text{ (crystalline)} + CaO + H_2O \quad (2)$$

Apparently, the calcination is not accompanied by arsenic oxide vapourization because the chemical analyses showed that the Ca/As molar ratio in the precipitates calcined at temperatures from 110 to 1,000°C was constant. Leaching tests, carried out at pH 12.0, showed that the product obtained at 700°C was very insoluble, giving an arsenic solubility of only 0.02 mg/L. For the calcination of calcium arsenite, Nishimura and Tozawa propose the following equation:

$$Ca(AsO_2)_2\cdot Ca(OH)_2 + nCa(OH)_2 + O_2 \xrightarrow{700°C} Ca_3(AsO_4)_2 + (n-1)CaO + (n+1)H_2O \quad (3)$$

The leaching tests, also carried out at pH 12, of the product calcined at 600°C, showed that the concentration of arsenic in the leachate was >5 mg/L even in the presence of a large amount of calcium hydroxide. In contrast, for the product obtained at 700°C and a Ca/As molar ratio >4.6, the leachate contained only 0.02 mg/L As. From these results, the authors conclude that their procedure can effectively remove both As(III) and As(V) from solutions to less than the 0.5 mg/L regulation limit without the need for oxidizing As(III) to As(V) in solution. Any As(III) is oxidized during calcination and the calcined product is suitable for stockpiling.

The calcination of calcium arsenite and arsenate was further studied by Stefanakis and Kontopoulos (1987). These researchers confirmed that calcination significantly reduces the dissolution of As from calcium arsenate and calcium arsenite precipitates, as determined by alkaline leach tests (Table 4). For example, calcination at 800°C reduced the As dissolution to levels below the EPA guideline of 0.5 mg/L. However, calcination of calcium arsenite precipitates was less effective because the transformation to arsenate was not complete even at 800°C. A higher calcination temperature is probably required as some residual calcium arsenite was still identified in the X-ray diffraction pattern of the calcined precipitate.

Table 4 - Stability of Calcined Ca Arsenite and Ca Arsenate Precipitates as a Function of the Calcination Temperature (Adapted from Stefanakis and Kontopoulos, 1988)

Oxidation State	Feed Ca/As Molar ratio	Arsenic Solubility, mg/L (pH = 11.5, 72 h)				
		None	500°C	600°C	700°C	800°C
As(III)	7	20	30	1.5	1.5	0.6
As(III)	5	20	1.0	2.0	2.0	1.0
As(III)	3	50	4.0	2.5	2.0	1.2
As(III)	1.5	60	8.0	40.0	10.0	10.0
As(V)	14	0.3	—	—	2.5	1.5
As(V)	10	0.4	—	—	2.5	0.6
As(V)	6	1.5	—	—	2.5	0.5
As(V)	3	10	—	—	2.5	0.5

As pointed out by Swash and Monhemius (1995), calcium arsenites and arsenates appear to have low solubilities in the presence of excess lime. However, over a long period of time, when the high pH (>10) buffering effect of the excess lime is reduced through lime dissolution and carbonation, arsenic will be mobilized. Such mixtures have only relatively short term stability and are unsuitable as a long-term disposal option. According to these authors, it is likely that calcium arsenates and arsenites, which were originally considered as stable industrial wastes, will need to be reprocessed and the arsenic converted into a more stable ferric arsenate form.

According to Valenzuela (2000), variations of the lime precipitation/calcination process are currently used by Chilean copper smelters with subsequent storage in chemical ponds without any apparent problem. This is probably acceptable because the dry climate of northern Chile will delay indefinitely the dissolution of excess lime by rain.

Precipitation of Iron/Arsenic Compounds

The composition, structure and stability of compounds containing iron and arsenic have been extensively studied. Harris (2000) provides an excellent review of past and current research in this field. The compounds that have received more attention are: 1) the amorphous or poorly crystalline compound obtained by reacting Fe(III) and As(V) at low temperature, and 2) a series of crystalline compounds produced by reacting Fe(III) and As(V) at high temperatures.

Low-temperature Fe/As compounds The structure of the Fe(III)/As(V) precipitate obtained at room temperature has been the subject of much controversy. Originally, the formation of an "amorphous ferric arsenate" was assumed:

$$Fe^{3+} + AsO_4^{3-} + xH_2O = FeAsO_4 \cdot xH_2O \qquad (4)$$

However, in recent years it has been demonstrated that at temperatures below 100°C, the precipitate formed from Fe(III) and As(V) solutions is likely a poorly crystalline ferric oxyhydroxide phase, known as 2-line or 6-line ferrihydrite, containing adsorbed arsenate ions (Robins et al., 1991; Robins and Jayaweera, 1992). According to this new evidence, As(V) is tenaciously adsorbed on ferrihydrite by complexation (chemisorption), and this results in a stable inner-sphere complex; i.e., there are no water molecules between the arsenic and the ferrihydrite surface (Waychunas et al., 1993, 1996; Rancourt et al., 2000). Species that are adsorbed as inner-sphere complexes are not desorbed by an increase in the electrolyte concentration and their stability constants are several orders of magnitude greater than those species forming outer-sphere complexes (Khoe et al., 1994).

Ferrihydrite is a poorly crystallized ferric oxyhydroxide, which forms as a result of the hydrolysis of ferric ions (Jambor and Dutrizac, 1998):

$$Fe^{3+} + (2+x)H_2O = FeO(OH)(H_2O)_x + 3H^+ \qquad (5)$$

Ferrihydrite has strong adsorption properties for several anions and cations, including arsenates:

$$FeO(OH)(H_2O)_x + AsO_4^{3-} = AsO_4^{3-} \cdot FeO(OH)(H_2O)_x \qquad (6)$$

Arsenical ferrihydrite forms a voluminous sludge which is difficult to filter because of its poorly crystalline nature. It is also associated with a high consumption of iron and neutralizing agent. Despite these characteristics, precipitation and impoundment of arsenical ferrihydrite is widely utilized by the mining industry. Canadian examples include the Inco CRED plant (Sudbury), the Noranda Horne smelter (Rouyn Noranda), Giant Mine (YK), Con Mine (YK) and Teck-Corona (Hemlo).

The Inco CRED plant has been removing and impounding arsenical ferrihydrite since 1973 (Harris and Krause, 1993). Inco uses the pressure carbonyl process (IPC) to produce high purity nickel powders and to concentrate the precious metals collected in the Ni-Cu smelter. The residue from the IPC process contains Cu, Ni, Co, Fe, As and S, in addition to the precious metal values. This residue is subjected to metathesis leaching in a $CuSO_4$-H_2SO_4 solution to form a copper sulphide-precious metals residue, and to generate a leach solution containing Ni, Co, Fe and As in a sulphate medium. This solution is the feed to the arsenic precipitation circuit, which removes the contained Fe and As and generates a Ni-Co solution for further treatment. The solution feed to the arsenic precipitation circuit contains 15-25 g/L Fe and 2-5 g/L As. The actual precipitation is effected in two vertical autoclaves connected in series. The autoclaves operate at 80°C and use an O_2 overpressure of 50 psi. Lime is added to the autoclaves to control the pH to ~3.2 in the first autoclave and 3.6-4.1 in the second. The Fe/As ratio of the solution is always >4, and accordingly, the Fe/As ratio of the precipitate is also >4, because 99.5% of the Fe and 99.9% of the As are precipitated in the autoclave circuit. The precipitate contains 5-20% Fe and 0.8-2.5% As, together with ~25% gypsum. After filtration, washing and repulping in water, the slurry, at pH 3-4, is pumped to the residue pond. About 40 t/day of residue is produced, and this contains 500-600 kg/day of As. The iron-arsenate precipitate is pumped to Inco's extensive tailings impoundment area which covers ~38 km^2. Originally, the iron-arsenate precipitate was stored in a separate area of the pond, but for the past several years, it has been mixed with the flotation tailings. The final effluent from the present arsenic precipitate-tailings impoundment area is at pH 5.5, and it contains only 0.02 mg/L As (Dutrizac and Spencer, 2000).

The Horne smelter, which is located in Rouyn-Noranda, is a custom smelter producing 190,000 t/y of copper anodes and 550,000 t/y H_2SO_4. About 50% of the feed originates from numerous small mines in the area, while other concentrates are purchased abroad or from British Columbia. As mentioned above, arsenic is commonly present in copper concentrates and during pyrometallurgical processing this arsenic is volatilized as gaseous As_4O_6. At the Horne smelter, the gases from the smelting operation are treated to generate sulphuric acid after being cooled and passed through electrostatic precipitators to removed the entrained dust. Most of the dust is recycled within the smelting operation, but 15-25% is bled from the circuit to control the build-up of impurities, such as Bi, Sb and Pb. This dust fraction, which contains 3-10% of arsenic in the form of various soluble and insoluble As(V) species, is slurried in water and is sent to the arsenic precipitation plant. Another feed to the arsenic precipitation plant is the weak acid solution used to clean the cooled gases prior to their passage to the acid plant. This weak acid solution has a pH ~1.0 and typically contains 1.3 - 4.0 g/L As (mostly as As(III)), 0.004 g/L Fe, 0.3 g/L Zn and ~ 20 g/L SO_4 (Dutrizac and Spencer, 2000). An interesting characteristic of the arsenic precipitation plant is the use of acid mine drainage, which originates from the nearby Gallen open pit mine, as a cheap source of iron for arsenic precipitation. The acid mine drainage analyzes 7-8 g/L Fe(III), 3-4 g/l Fe(II), 10 g/L Zn and 4 g/l Cd. The development of the process using acid mine drainage was described by Godbehere et al. (1995). The actual precipitation of arsenic takes place in a series of three tanks, operating at atmospheric pressure. In the first tank, all of the weak acid scrubber solution (60-100 m^3/h) is added together with reactor dust slurry and the iron-rich Gallen acid mine drainage. Lime is added to control the pH at 5.2, and technical grade O_2 is diffused beneath the single agitator. Most of the O_2 is consumed in the first tank where the majority of the iron oxidation occurs. The elevated pH promotes iron oxidation, and the ferric ion hydrolyzes and precipitates spontaneously. The precipitate removes ~90% of the total As and yields a first tank discharge typically containing ~40 mg/L As. The precipitation process is operated such that the ratio of (Fe+Zn)/As is >3 in the first tank. In the second reactor, 10 m^3/h of acid mine drainage is added to the overflow slurry from the first tank to lower the pH to 4.5. This circuit operates with a ratio of (Fe+Zn)/As>>4, and the result is that the As concentration is lowered to <0.5 mg/L. Lime is added to the third tank to control the pH at 9.5 to precipitate any residual dissolved metals as hydroxides or basic sulphates. The tailings pond is 4.5 km from the plant site and has a 15 year capacity remaining for slag-arsenic precipitates. Sulphide tailings are not stored in this pond to prevent any possible reduction of the Fe(III) and/or As(V). The overflow from the slag tailings-arsenic precipitate pond has been monitored since 1993; the overflow liquor is at pH 8.5 - 9.0 and analyzes 0.1 - 0.2 mg/L Pb and <0.5 mg/L As, the stipulated environmental limit (Dutrizac and Spencer, 2000).

The Giant Mine has used the ferric precipitation method since 1980 to treat various processing streams, and the conditions are pH 8.5 and an Fe/As ratio of ~ 10. Data published in 1985 and 1987, although not comprehensive, demonstrated the practical effectiveness of arsenic precipitation at the Giant Mine. Alkaline chlorination of the gold barren solution was practiced for cyanide destruction, a process which ensured that all the arsenic (10-100 mg/L) would be in the pentavalent state. Ferric sulphate was added at a pH of ~8.5, at a ratio of 7-8 Fe/As by weight (molar ratio of ~10), to precipitate >98% of the arsenic in solution. The resulting ferric arsenate sludge is sent to a tailings pond, where the run off averages 0.8 mg/L As, with maximum concentrations up to 1.6 mg/L As (Harris and Krause, 1993).

2008 used 5:1 Fe:As ratio

High-temperature Fe/As compounds High temperature operations, such as those involving the use of autoclaves, produce a different type of Fe(III)/As(V) compound. Unlike arsenical ferrihydrite, the compounds produced in autoclaves are crystalline and compact. Pressure oxidation is an established technology for treating gold ores, which are refractory as a result of the presence of sulphides, including arsenopyrite (AsFeS), realgar (AsS) and orpiment (As_2S_3). Acid pressure oxidation employs temperatures above the melting point of sulphur (119°C), preferably above 170°C, and high oxygen overpressures up to 2,000 kPa (Papangelakis and Demopoulos, 1990). Frostiak et al. (1990) have listed the following advantages of pressure oxidation over roasting for treating refractory gold ores:

- The elimination of the discharge of arsenic trioxide and sulphur dioxide to the atmosphere
- The elimination of worker exposure to sulphur dioxide gas, arsenic gas and arsenic trioxide particulates
- The elimination of the need for arsenic trioxide storage underground
- The reduction in the levels of arsenic and heavy metals in the aqueous effluents
- The increased recovery of gold.

Because of these reasons, pressure oxidation and, to a lesser extent, bio-oxidation are replacing roasting as the preferred method for treating refractory gold ores. An important Canadian example is the introduction of pressure oxidation at the Campbell mine in Red Lake, Ontario, in June 1991. Prior to that, the roasting operation was discharging 18 tonnes of sulphur dioxide daily into the atmosphere. Autoclaving eliminates the formation of sulphur dioxide entirely, fixes the arsenic in an insoluble form and immobilizes the associated heavy metals (Anon., 1991).

The Campbell mine commenced operations in 1951. Initially, roasting was used to treat the refractory ore, and as a result, both SO_2 and As_2O_3 were vented to the atmosphere. In 1974, an electrostatic precipitator and baghouse were installed to collect the As_2O_3-rich dust while continuing to vent the associated SO_2 to the atmosphere. Gold was recovered from the roaster calcine using a carbon in pulp circuit. A small amount of the As_2O_3-rich dust was sold in the period 1981-1987, but most of the As_2O_3-rich dust was pneumatically conveyed to two abandoned stopes in the mine. The Sherritt-designed pressure oxidation circuit began operations in 1991, and roasting was discontinued at that time. A flowsheet of the new process at Campbell Red lake is shown in Figure 2. Gold ore, containing ~13 g/t Au, consists of some free milling ore coupled with refractory gold associated with pyrite, arsenopyrite and pyrrhotite. The crushed ore is milled and is first treated in a Knelson gravity concentrator which recuperates 45-50% of the total gold in the ore. Next the ore is floated to produce a concentrate containing 15% Fe, 1-3% As, 10-16% S and 250 g/t Au. Because of the presence of some carbonate in the concentrate, the feed is pre-leached at atmospheric pressure in recycled autoclave discharged before injection into the autoclave. The gold flotation concentrate is oxidized in a single five-compartment autoclave, having a capacity of 160 t/day of concentrate, which operates at 190-200°C and under a pressure of 300 psi. The autoclave is made of steel, lined with lead, a fiberglass layer and 2½ inch acid-proof bricks. The autoclave oxidation circuit results in complete sulphur oxidation and a final acid concentration of 10-30 g/L H_2SO_4. The autoclave feed has a Fe/As ratio > 5 and, as a result, the autoclave discharge contains mostly Fe_2O_3 and $Fe_3(AsO_4)_2(OH)(SO_4)\cdot nH_2O$-type compounds. The slurry is neutralized with lime, combined with the flotation tailings, and passed to a conventional CIP circuit for gold recovery. The Inco SO_2-air process is employed for cyanide destruction in the barren solution. The neutralized slurry is sent to a residue pond, which overflows into two settling ponds and then to an established wetlands prior to discharge. The As concentration in the ponds is typically 0.15 mg/L As and the final discharge always contains <0.1 mg/L As. The pond has operated since 1991 with admixed flotation tailings and As-bearing autoclave residue, and low As discharge concentrations have consistently been recorded (Dutrizac and Spencer, 2000). The operating cost per tonne of concentrate treated is \$132 (1991) versus \$46 (1991) for roasting and gas-handling plants. On the credit side, the enhanced recovery of gold is equivalent to \$156 (1991) per tonne (Anon., 1991).

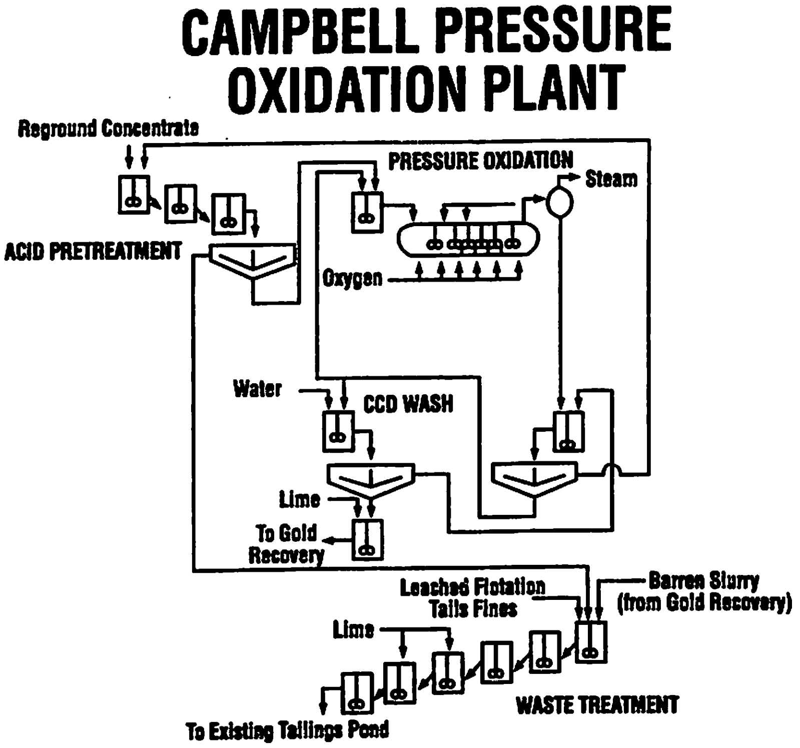

Figure 2 - Campbell Pressure Oxidation Plant (Anon., 1991)

Several laboratory studies have been carried out in order to synthesize and characterize the iron-arsenate compounds that form under high temperature and pressure conditions. Dutrizac and Jambor (1988) synthesized crystalline scorodite from a ferric nitrate medium at pH ~0.7, and found that temperatures greater than 125°C (ideally 160°C) were needed to ensure good crystallinity. pH values in the 0.2 to 1.8 range were found to have little effect on either the structure or composition of the scorodite, but an As(V) concentration higher than 15 g/L was required to ensure a pure product for an initial Fe(III) concentration of 0.3 M. The presence of dissolved sulphate resulted in the incorporation of up to 1% SO_4^{2-} in the scorodite structure, but the SO_4^{2-} content decreased with increasing solution pH. Once removed from the aqueous synthesis environment, scorodite decomposed on heating at 100-200°C with the simultaneous release of its two H_2O molecules to form anhydrous $FeAsO_4$. The formation of scorodite during the pressure chloride leaching (O_2-H_2SO_4-NaCl) of arsenopyritic gold concentrates was reported by Demopoulos et al. (1989). Typical leach conditions were 170 to 200°C, 0.5 to 1.5 N H^+ (free), 1.5 to 3.5 N NaCl, 1 to 6 hours, 5 to 10% slurry density and 20 atm O_2 pressure. Papangelakis and Demopoulos (1990) produced euhedral scorodite crystals (~20 µm) during the pressure oxidation of arsenopyrite for 2 hours in a 0.5 M H_2SO_4 solutions at temperatures > 150C. According to these researchers, arsenopyrite reacts with O_2 to yield elemental sulphur and sulphate, the latter being the dominant product. The formation of elemental sulphur is favored with increasing acidity. The elemental sulphur persists at temperatures as high as 180°C. On the other hand, H_3AsO_4 (aq) was found to be the principal arsenic oxidation product. The latter appears to be the direct result of the heterogeneous oxidation process and not the result of a consecutive homogeneous reaction (i.e., initially formed As(III) being oxidized to As(V)). Iron reports in solution as Fe(II), which is further oxidized to Fe(III). The oxidation of Fe(II) to Fe(III) is also favored by high slurry densities and low acidities, in addition to higher temperatures. The ferric ion produced combines with arsenic acid to form ferric arsenate which precipitates as euhedral scorodite crystals. The precipitation of scorodite is endothermic whereas the oxidation of arsenopyrite is extremely exothermic; thus, the overall process is exothermic.

Ugarte and Monhemius (1992) used X-ray diffraction analysis coupled with infrared spectroscopy to identify the products arising from the high-temperature processes, and found that, in the presence of SO_4^{2-}, a series of hydrated ferric arseno-hydroxy-sulphate compounds are formed. Some of these compounds have been found in medieval ore dumps as secondary minerals produced by weathering of the original arsenopyrite ore, suggesting that they are stable under normal environmental conditions. This work was extended by Swash and Monhemius (1994) and Carageorgos and Monhemius (1994), who reported that the precipitation of arsenic carried out at pH<1, with a Fe/As ratio ≥1 and temperatures >150°C, leads to the formation of crystalline and well-defined compounds. These included scorodite and two ferric arseno-hydroxy-sulphate compounds, which were designated as Type I and Type II. More in-depth research by Monhemius and Swash (1999) found that the predominant phase is a function of temperature and the Fe:As molar ratio in the initial mother liquor. At 150-200°C and for Fe/As ratios of 1.5 or higher, a crystalline, hydrated iron arsenate is formed, which is identical to the mineral scorodite. At temperatures above 200°C, a phase designated by these researchers as Type II becomes predominant. Type II is an unhydrated ferric arseno-hydroxy-sulphate compound, which has no natural mineral analogue. It shows a range of stoichiometries, particularly with respect to the arsenate/sulphate ratio, but its formula can be generalized as $Fe_3(AsO_4)_2SO_4OH$. In solutions, where there is an excess of iron over that required to form the Type II compound, the extra iron tends to coprecipitate with the Type II phase as basic iron sulphate, $FeSO_4OH$. Where the initial Fe/As molar ratio in solution is near unity, a third phase (designated as Type I) predominates at all temperatures above ~150°C. Type I has been assigned the approximate composition $Fe_2(HAsO_4)_3{\cdot}H_2O$ (Monhemius and Swash, 1999). Table 5 summarizes these recently characterized compounds.

Table 5 - Compounds Formed in Iron-Arsenate Hydrothermal System (Adapted from Swash and Monhemius, 1994, 1995)

Compound	Fe (%)	AsO_4 (%)	SO_4[(a)] (%)	Average Fe:As	H_2O[(b)] (%)	Size (µm)
Scorodite $FeAsO_4 \cdot 2H_2O$	20.7-24.7	50.0-70.1	< 4.0	1.0	11-16	< 30
Type I $Fe_2(HAsO_4)_3 \cdot xH_2O$ $x<4$	21.4-23.0	56.3-75.6	< 1.0	0.9	<5	< 5
Type II $Fe_4(AsO_4)_3(OH)_x(SO_4)_y$ where $x+2y = 3$[(c)]	27.4-38.0	32.6-52.0	< 13.0	1.3	<4	< 50
Type III $Fe_2(AsO_4)_x(HAsO_4)_y$	---	---	---	---	---	---
Type IV $CaFe_2(AsO_4)_x(HAsO_4)_y$ where $x>2$ and $y<1$	---	---	---	---	---	---

Notes: (a) dependant on solution composition, (b) mass loss determined by DTA-TG, (c) for charge balance

Although the formation of scorodite is usually associated with autoclave operations, there is evidence that scorodite may form also at temperature <100°C. Dutrizac and Jambor (1987), while studying the behaviour of arsenic during jarosite precipitation at 97°C, observed the formation of well crystallized scorodite in chloride media. However, in sulphate media an amorphous phase, chemically similar to scorodite, was observed. The production of scorodite without the need for autoclaves would be very attractive from an economic viewpoint, and important advances have been made in this regard. For example, a method to produce scorodite at ambient pressure and at temperatures below the boiling point has been developed (Demopoulos et al., 1994,1995; Wang et al., 2000). The method is based on the concept of supersaturation control. According to these authors, supersaturation (defined as $S = C/C_{eq}$, where C is the concentration of As(V) in the supersaturated solution and C_{eq} the equilibrium concentration of As(V)) is the primary crystallization parameter which controls the nucleation-growth process. For the attainment of crystallinity, it is imperative that homogeneous nucleation be prevented, and this is achieved by maintaining S below $S_{cr,homo}$, the critical supersaturation level associated with the onset of homogenous nucleation. By maintaining $S<S_{cr,homo}$ and using seed at the same time, suspension crystal formation is favoured. The methodology involves establishing the solubility line of scorodite ([As] versus pH) in the process solution, at a constant temperature, and then performing controlled precipitation following a step-wise neutralization path. Thus, for example, crystalline scorodite was produced at 95°C from a 3 M Cl^- solution, containing initially 2,000 mg/L As(V) and a Fe/As molar ratio 1, by adding 2 g/L seed and by following a four-step neutralization path from pH=0.3 to pH=1.5. Subsequent work has shown that scorodite can also be precipitated from sulphate media at ambient pressure by following a supersaturation-controlled precipitation procedure (Droppert et al., 1996). These authors reported that solutions containing up to 10 g/L As were precipitated at 95°C, as scorodite, at an As yield of >93% within two hours. It was noted that in sulphate media, the precipitation of amorphous ferric arsenate is inhibited at lower pH, a feature which can be used to benefit the production of scorodite. An application of ambient pressure scorodite precipitation has been described by Filippou and Demopoulos (1997). In this application, the soluble arsenic found in the effluent of the acid plant of a gold/copper smelter was fixed as scorodite. The laboratory procedure consisted of aerating the effluent, containing 10 g/L As(III) and 25 g/L H_2SO_4, to remove any dissolved SO_2. Oxidation of As(III) to As(V) at 90°C was achieved with 50% weight by volume H_2O_2 and a total retention time of 30 minutes. The fully oxidized solution was then pumped to a two-stage scorodite precipitation circuit. In this circuit, ferric sulphate was added at a stoichiometric ratio to arsenic, together with recycled scorodite/gypsum seed. A retention time of four to six hours was deemed necessary for the removal of 95% of the arsenic in the form of crystalline scorodite by the stepwise neutralization with slaked lime at 90°C.

THE LONG-TERM STABILITY OF ARSENIC RESIDUES

It is important to note that the long-term chemical stability of arsenic compounds depends on a number of factors, including the disposal site characteristics, the particle crystallinity and size distribution, and the presence of oxygen, sulphides and complexing agents, such as cyanide, chloride or naturally occurring organic ions. Hopkin (1989) has summarized the chemical behavior of arsenic in the environment: the major inorganic arsenic species are the arsenates, arsenites and the arsenical sulphides, such as arsenopyrite and orpiment. Arsenates are stable in oxygenated systems such as surface and shallow waters, soil and rocks. Within limits, arsenate is very strongly adsorbed and efficiently immobilized by weakly acidic or alkaline ferric oxyhydroxides (e.g., ferrihydrite) and to a lesser extent by other high surface area hydroxides such as those of manganese and aluminum, thus soils and clays. Arsenites dominate in mildly reducing anaerobic conditions where ferrous and manganous ions are also stable. Adsorption is weaker in such shallow soils and ground waters, and in the porewaters of, for example, marine or lacustrine sediments. In more strongly reducing conditions where sulphate reducing bacteria are active as in deep sediments, the arsenical sulphides form essentially insoluble species, the origins of minerals of the future. Changes in the redox potential cause interconversion of these species, mainly catalyzed by biochemical processes, and thus potentially can result in the liberation or fixation of arsenic (Hopkin, 1989). Bacterial activity can have an important effect on the speciation of arsenic (Newman et al., 1998). Besides microorganisms, which are capable of direct As(III) oxidation and direct As(V) reduction, the iron-reducing and the sulphate-reducing bacteria can have an important effect on the arsenic solubility. In an iron-rich environment, iron oxyhydroxides bind arsenic; however, iron-reducing bacteria can utilize iron hydroxides as terminal electron acceptors, releasing bound trace elements. Production of aqueous sulphide by sulphate-reducing bacteria can directly reduce both arsenate and iron oxyhydroxides (Harrington et al., 1998).

There is no definitive test to determine the behaviour of hazardous compounds over long periods of time, and the development of such a protocol would be useful. It has become customary to determine the stability of compounds by subjecting them to leachate tests, usually the United States EPA TCLP test, which involves mixing the solid with a measured volume of buffered acetic acid solution (pH 5) and determining the dissolution of elements into the aqueous solution. The limit for the leached arsenic is 100 times the World Health Organization primary drinking water standard of 50 µg/L As (i.e., 5 mg/L As) (Hopkin, 1989). The TCLP test cannot objectively be a comprehensive and legal test of a hazardous waste; it can be of value only as a preliminary screening test, applicable to the very short term and to the particular test conditions. Several alternative tests have been proposed to circumvent the limitations of the United States EPA TCLP test and have been applied to a number of compounds (Monhemius and Swash, 1999A; Swash et al., 2000). Long-term tests, which can be carried out for months or years, use either static or dynamic methods. The solutions are sampled periodically for analysis and the solution compositions are adjusted if necessary. Dynamic leach tests are usually carried out in columns packed with the arsenical solids. Leach solutions are percolated through the columns on a regular basis, often with a drying period between applications of the solution. The wet-dry sequencing is an attempt to simulate the conditions experienced by materials exposed to natural weathering (Monhemius and Swash, 1999A).

Figure 3 shows that the lowest solubility for both scorodite and arsenical ferrihydrite lies in the weakly acidic pH range of 3-5. For this reason, these compounds pass the TCPL test, as shown in Table 6. It is evident, however, that if these compounds were stored under neutral or alkaline conditions, the dissolution of arsenic would be higher.

Table 6 - EPA TCLP Test Results of Precipitated Iron Arsenates
(Swash and Monhemius, 1995)

Precipitated Phase	TCLP Solubility (mg As/L in filtrate)
Scorodite	<5
Type I	5-85
Type II	<5
Ferrihydrite	
Fe:As = 9.1	<0.5
Fe:As = 2.3:1	1-2

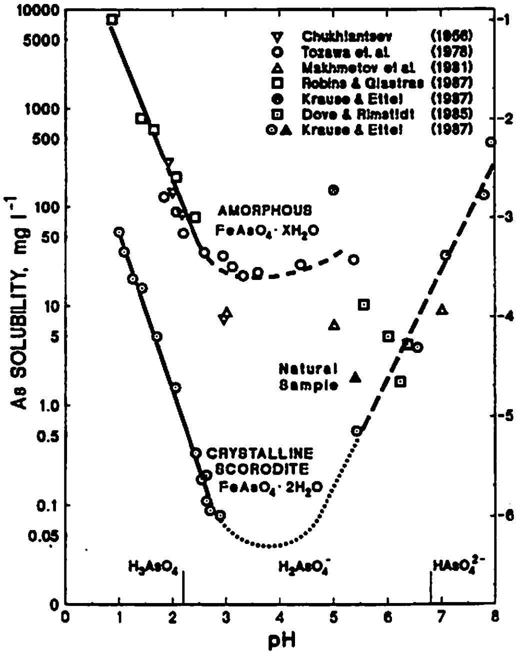

Figure 3 - Comparison of Arsenic Solubility for Scorodite and "Amorphous Ferric Arsenate" (Arsenical Ferrihydrite) (Krause and Ettel, 1989)

The fact that the solubility of arsenic from amorphous ferric arsenate increases as the pH increases above neutrality should be an important consideration for the long-term storage of these materials. As pointed out by Cadena and Kirk (1995), the increased As solubility at higher pH values may be explained by the limited amount of Fe(III) available in solution after ferric oxyhydroxide precipitation. In fact, the total ferric iron solubility reaches a minimum at a pH of approximately 8.3, and this condition coincides with the location of the point of zero charge for ferric oxyhydroxide. Thus, positively charged iron species dominate at pH values below the point of zero charge. Negatively charged iron compounds are predominant above 8.3. Because the arsenate species exist in anionic form, the solubility of arsenic should increase with increasing pH above 8.3 because of the repulsion of like charges. It is also important to observe that as the pH is increased, more iron is required for the same amount of arsenic removal, and this is consistent, not with a ferric arsenate precipitation mechanism, but with the co-precipitation of arsenic with the ferric oxyhydroxide solid phase. Cadena and Kirk (1995) also studied the effect of sodium chloride and sodium sulphate on the solubility of amorphous ferric arsenate. The presence of elevated concentrations of NaCl has little effect on arsenic removal. However, the presence of elevated sulphate levels decreases the arsenic removal efficiency at pH 3-4. This was attributed to the fact that sulphate and bisulphate ions compete with arsenate for sites in the network of the ferric oxyhydroxide precipitate.

The incorporation of sulphate in arsenical ferrihydrite has been investigated by Krause and Ettel (1989) who analyzed a series of Fe(III)/As(V) precipitates formed at pH 5.0 and 80°C from a ferric sulphate solution. The precipitates were filtered and the Fe/As cake was repulped twice in distilled water, filtered and washed. Based on the XRD evidence, none of the precipitates were crystalline. Table 7 presents the results. The solids contained significant quantities of Na (up to 2.4%), when the Fe/As ratio was <4.0. Sulphate was mainly incorporated into the precipitates which had Fe/As ratios >4.0. A sample of ferric oxyhydroxide (ferrihydrite), precipitated in the absence of arsenic, contained 6.5% sulphate.

Table 7 - Fe(III)/As(V) Precipitates Showing Incorporation of Sulphate
(Adapted from Krause and Ettel, 1989)

Feed Fe/As Molar Ratio	Washed Precipitate Assay (%)			
	Fe	As	SO_4^{2-}	Na
1	27.4	26.0	<0.08	2.40
2	32.6	21.0	0.08	1.40
4	40.6	14.0	0.19	0.19
8	47.2	8.0	1.89	0.009
16	49.2	4.2	3.67	0.004
Very high[1]	54.8	<0.09	6.50	0.003

[1] No arsenic was present.

The Long-term Stability of Arsenical Ferrihydrite

There is controversy about the long-term stability of arsenical ferrihydrite, because of strong discrepancies between theoretical considerations and practical observations. Robins (1981, 1983, 1985, 1987, 1990), on the basis of a comprehensive thermodynamic study of the stability of metal arsenates, concluded that most arsenates are metastable under atmospheric conditions and that they will eventually decompose, releasing soluble arsenic. Furthermore, the thermodynamic calculations indicate that, over a relatively long period of time, arsenical ferrihydrite will decompose to goethite (α-FeOOH) or hematite ($\alpha-Fe_2O_3$) and release arsenic acid into the solution (Robins 1983, 1990; Robins and Jayaweera, 1992; Robins et al., 1988). On the other hand, a number of experimental studies have shown that, under proper storage conditions, high-iron arsenical ferrihydrite is stable for at least several years (Harris and Monette, 1988,1989; Krause and Ettel,1985, 1987,1988,1989; Harris and Krause,1993; Kontopoulos et al., 1988; Dove and Rimstidt, 1985; Nordstrom and Parks, 1987; Robins, 1987; Rimstidt and Dove, 1987; Vircikova et al., 1994, 1995, 1998).

The transformation of "pure" (i.e. arsenic free) ferrihydrite into goethite and hematite has been observed in laboratory experiments by Schwertmann and Murad (1983). These researchers monitored aqueous suspensions of ferrihydrite at 24°C and pH values between 2.5 and 12 for up to three years, and found that most of the ferrihydrite transformed into goethite and hematite. The transformation into hematite was favoured at pH 7-8, whereas goethite was the main product at pH 4 and 12. Figure 4 shows the transformation kinetics at various pH values, and Figure 5 presents the estimated time for half-conversion as a function of pH. It was postulated by these researchers that goethite and hematite develop from ferrihydrite by two different and competitive mechanisms: goethite crystals form in solution from dissolved Fe(III) ions produced by the dissolution of ferrihydrite, whereas hematite forms through an internal dehydration and rearrangement within the ferrihydrite aggregates. Therefore, goethite should be favoured as the concentration of Fe(III) ions in equilibrium with ferrihydrite increases, and hematite should be favoured as the concentration decreases (Schwertmann and Murad, 1983.

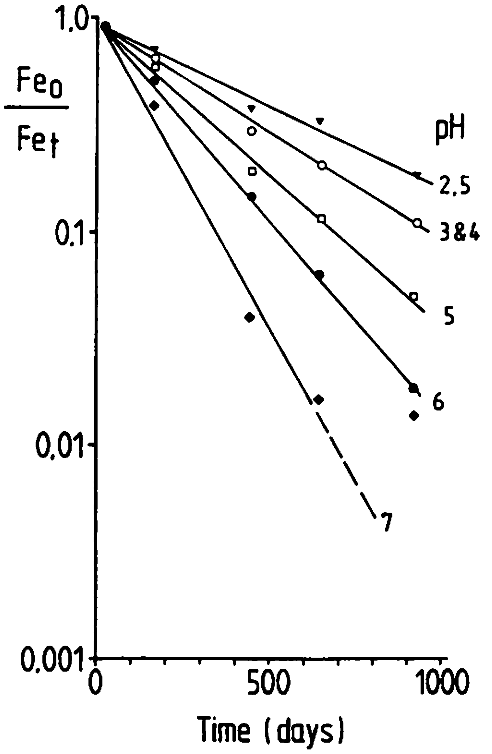

Figure 4 - First-order Reaction Plot for the Transformation of Ferrihydrite at Various pH Values (Schwertmann and Murad, 1983)

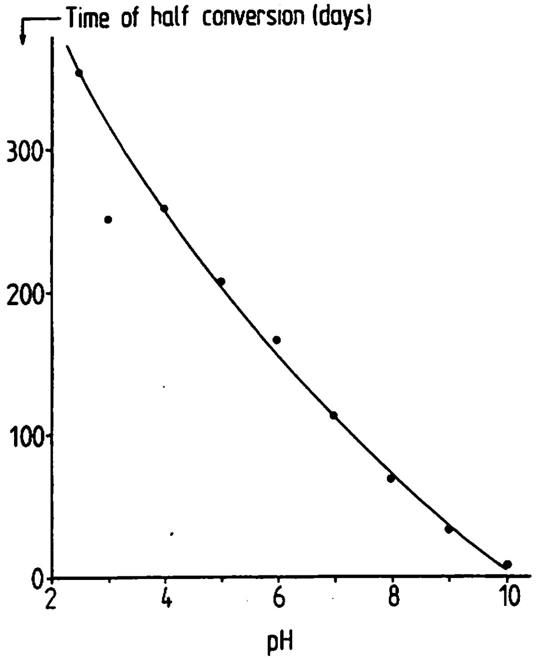

Figure 5 - Length of Time for Half-Conversion of Ferrihydrite to Goethite and Hematite versus pH (Schwertmann and Murad, 1983)

The transformation mechanisms of ferrihyrite into stable ferric oxyhydroxides or oxides have been studied by Manceau and Drits (1999) by means EXAFS spectroscopy. These researchers concluded that the structure of 6-line ferrihydrite consists of structural anionic ABA and ACA fragments in which Fe cations occupy only octahedral sites. In most particles, these fragments regularly alternate according to the pattern ABACAB... forming a three dimensional periodic structure. This structural model implies that the ferrihydrite-goethite transformation takes place through dissolution and reprecipitation and not by an internal dehydration- rearrangement because the latter would necessitate (i) the breaking (i.e. hydrolysis) of face linkages and (ii) deeply altering the anionic packings in going from ABACAB... to ABABAB... stackings. According to these researchers, the displacement of O atoms from a C-type to a B-type position seems hardly feasible at low temperature and pressure without dissolving the structure. The ferrihydrite-hematite transformation is more complex, but it appears to involve both dissolution and solid state transformation.

In contrast, the decomposition of arsenical ferrihydrite obtained from process solutions has not been observed in actual disposal sites. Furthermore, laboratory studies have shown that arsenical ferrihydrite having Fe/As molar ratios >3 are stable for years, provided that the pH is kept moderately acidic. The most complete tests on the long-term stability of arsenical ferrihydrite were carried out in the late 1980's independently by Inco and Noranda researchers (Krause and Ettel, 1985, 1987,1989; Harris and Monette, 1988, 1989). In these tests, a series of Fe(III)/As(V) compounds was precipitated under various experimental conditions. The stability of these compounds was studied by mixing them with water, periodically adjusting the pH to pre-set values, and measuring the concentration of As in the aqueous phase. Some of these tests were continued for more than 3 years. Table 8 summarizes the results of three sets of these tests.

The experimental results of the Inco and Noranda tests indicate that the stability of the arsenical ferrihydrite is higher (i.e., the As dissolution is less) when the Fe/As ratio is high and the pH is slightly acidic. In general, high-iron (Fe/As molar ratio >3) arsenical ferrihydrites are stable in the pH range 4-7. The data were extrapolated by Harris and Monette (1989) to show that a minimum Fe/As molar ratio of 3:1 is necessary to confer stability over the pH range 4-7 (Figure 6).

The data also indicate that by increasing the Fe/As molar ratio, some degree of stability is also conferred in the alkaline region. On the other hand, it became clear that stoichiometric or low-iron (Fe/As molar ratio <3) precipitates are not sufficiently stable for long-term storage. It was also evident that at neutral and alkaline pH, most compounds tend to dissolve. Even a compound having a Fe/As molar ratio of 17.1/1 exhibited an arsenic dissolution of 1 mg/L at pH 8.2.

Table 8 - Effect of the Fe/As Molar Ratio, the pH and Formation Conditions on the Stability of Precipitates Made at 25°C

Fe/As Molar Ratio	Preparation, Reagents and Experimental Conditions	Time (days)	Test pH	Arsenic Dissolution mg/L As	Ref.
5.4	NaOH, 80°C, pH 5	911	10	394	c
1.1	CaO, 25°C, pH 8	439	4	158	a
10.3	NaOH, 80°C, pH 5	911	10	34	c
2.6	CaO, 25°C, pH 5	722	10	31	c
1.1	CaO, 25°C, pH 8	439	10	31	a
3.9	NaOH, 80°C, pH 5	648	6.8	23	b
1.1	CaO, 25°C, pH 8	439	7	18	a
3.3	CaO, 90°C, pH 5	767	10	6	c
17.1	NaOH, 80°C, pH 5	562	8.2	1	b
5.4	NaOH, 80°C, pH 5	911	7	0.85	c
2.6	CaO, 25°C, pH 5	722	7	0.6	c
2.6	CaO, 25°C, pH 5	730	4	0.3	c
8.0	NaOH, 80°C, pH 5	431	5	0.01	b
3.9	NaOH, 80°C, pH 5	636	4.9	<0.2	b
7.9	NaOH, 80°C, pH 5	538	5.2	<0.2	b
15.9	NaOH, 80°C, pH 5	636	4.8	<0.2	b
7.6	CaO, 25°C, pH 5	767	4	0.03	c
17.1	NaOH, 80°C, pH 5	562	4	<0.2	b
17.1	NaOH, 80°C, pH 5	562	7.4	<0.2	b

a - Harris and Monette (1988),
b - Krause and Ettel (1987),
c - Harris and Monette (1989).

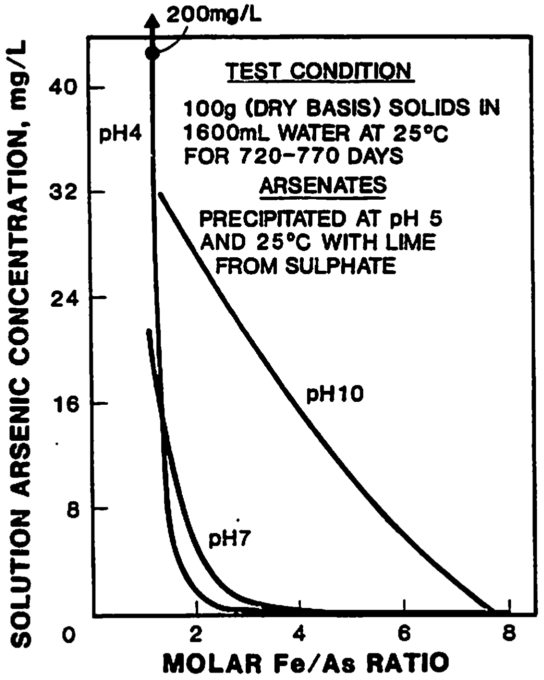

Figure 6 - Effect of the Molar Fe/As Ratio on the Solubility of Arsenic from High Ferric Arsenates as a Function of Test pH (Harris and Monette, 1989)

Additional research carried out by Inco and Noranda showed that atmospheric CO_2 has no discernable effect on ferric arsenates, although CO_2 was found to have a considerable destabilizing effect on a number of arsenates, notably those of Ca, Mg and Cd. It was also found that precipitates formed from chloride media, or formed using caustic soda as the precipitant from sulphate media, appeared to be less stable (i.e., to have a higher arsenic solubility) than similar precipitates formed using lime.

The reasons why the arsenical ferrihydrite precipitates generated by the mining industry apparently do not transform into goethite or hematite and soluble arsenic are not clear. Jambor and Dutrizac (1998), reviewing the work of other researchers, concluded that the adsorption of arsenate while ferrihydrite is polymerizing interferes with the chain-building process, thereby retarding further polymerization and the transformation to hematite. Rancourt et al. (2000) have recently carried out an extensive characterization of arsenic-rich hydrous ferric oxide samples, using powder

X-ray diffraction (pXRD), transmission electron microscopy (TEM), Mössbauer spectroscopy and other modern techniques. They concluded that arsenical ferrihydrite has a fundamentally different structure from natural and synthetic As-free hydrous ferric oxide or As-free ferrihydridite. For example, the pXRD pattern of arsenical ferrihydrite shows systematic differences with the pattern of 2-line ferrihydrite, and this is interpreted as evidence for significant populations of oxygen-coordinated Fe-As pairs. Mössbauer spectroscopy shows octahedrally coordinated ferric iron, with a large fraction (~20%) of the octahedral Fe environments significantly distorted by the presence of As, compared to the Fe local environments in As-free ferrihydrite and hydrous ferric oxide samples. It was also observed that arsenic seems to prevent particle growth and to cause smaller hydrous ferric oxide primary particles to be formed. Based on the increased thermal stability of the synthetic As-bearing hydrous ferric oxide materials, the researchers suggest that the adsorbed arsenic stabilizes the structure of ferrihydrite and retards the transformation to As and Fe oxides.

Harris and Monette (1988, 1989) observed that the presence of co-adsorbed base metal ions on ferrihydrite appears to increase its stability. As shown in Table 9, "pure" arsenic-bearing ferrihydrite is stable only at pH ≤7, but the presence of Cu, Zn and Cd confers stability over the whole pH range of 4-10. The data also illustrate the beneficial effect of gypsum, because the precipitate obtained in a chloride medium, where gypsum is not produced, exhibited a relatively high As solubility.

Table 9 - Stability Test of Synthetic Iron Arsenate Compounds (Harris and Monette, 1989)

Metal/Arsenic Molar Ratio[1]	Days	Arsenic Solubility[2] (mg/L)		
		pH 4	pH 7	pH 10
Fe/As 6.7:1	768	0.04	0.13	11.0
Fe/As 6.7:1 (chloride medium)	735	0.12	0.48	238.0
(Fe+Cu+Zn+Cd)/As 6.8:1[3]	649	0.06	<0.01	0.48

[1] Preparation conditions: lime, 25°C, pH 5 and sulphate medium, except otherwise indicated.

[2] A significant amount of the base metals also dissolved, especially at pH 4.

[3] The chemical analysis of the precipitate showed 15.6% Fe, 1.15% Cd, 1.62% Cu, 0.80% Zn and 3.58% As.

Emett and Khoe (1994) and Khoe et al. (1994) later confirmed that the presence of co-adsorbed Zn(II), Cd(II) or Pb(II) in ferrihydrite increases the pH range for effective arsenical ferrihydrite precipitation from pH 4-7 to pH 4-9. These researchers found a similar effect for Ca(II) and Mg(II), and they inferred that the presence of these cations in the ferrihydrite would increase its stability in the long term. However, Swash and Monhemius (1995), who studied systematically the precipitation of arsenical ferrihydrite from Ca-Fe-AsO_4 solutions and subjected the precipitates to the EPA TCLP test, reported that these ternary compounds are significantly more soluble than the corresponding calcium-free ferric arsenates. The presence of even small amounts of calcium in the crystal structure of arsenical ferrihydrite compounds exerts a destabilizing influence and makes the solids more soluble. In their work, Swash and Monhemius prepared a range of Ca-Fe-AsO_4 solid compositions by precipitation at 20°C using calcium hydroxide in the adjustment of the pH of precipitation (3 to 12). These solids were subjected to the EPA TCLP test and the results are given in Figure 7. The results show that the higher the calcium content of the synthesis solution (Ca:Fe:As = 3:1:4) and hence that of the precipitate, the more soluble is the compound. The more iron-rich solids, produced from the Ca:Fe:As = 1:3:4 solutions, are significantly less soluble. The intermediate solution compositions (Ca:Fe:As = 1:1:2) yield solids with intermediate solubilities. The solids are most soluble when synthesized from pH 6-7 solutions. As the synthesis pH is increased above 7, the excess of calcium in solution combines with any available arsenic and leads to lower apparent solubilities. The authors point out, however, that in sulphate solutions, calcium incorporation is unlikely, as it will usually precipitate preferentially as gypsum. Interestingly, gypsum has been found to increase the stability of arsenical ferrihydrite (Harris and Monette, 1989).

These is evidence suggesting that arsenic is being released from old tailings as a result of a high calcium content and mineralogical transformations. Kwong et al. (2000) observed that, although the Ketza River tailings are characterized by very high Fe/As ratios, there are elevated As concentrations in the pore water of both the beached and the submerged tailings, indicating the release of As from the tailings solids. The enhanced As mobility was attributed to the high calcium content of the tailings because, in addition to the naturally occurring limestone, there is a significant addition of reactive lime (7.5 kg/tonne ore) during the milling process. It is suspected that the presence of Ca destabilizes the As-bearing ferric oxyhydroxides, as discussed above. According to Paktunc et al. (1998), the Ketza River tailings are largely amorphous to cryptocrystalline ferric oxyhydroxides, making up more than two thirds of the solid phases; the other abundant phases are silicates and carbonates. The common As-containing minerals observed are: arsenopyrite, scorodite, an Fe-Ca arsenate hydrate, As-bearing ferric oxyhydroxides and AsO_4-bearing jarosite.

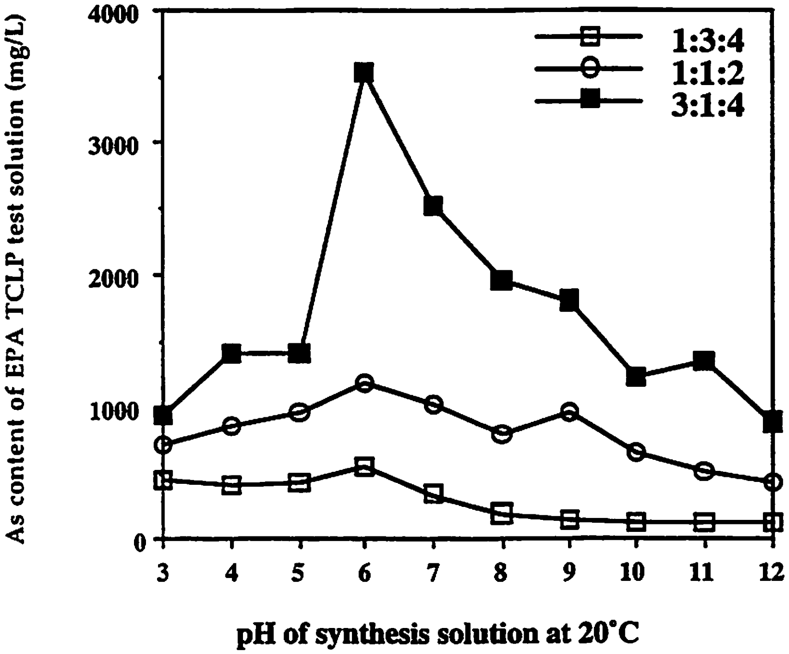

Figure 7 - EPA TCLP Solubility Plots of the Ca-Fe-As Solids Stabilized at Various pH Values with Calcium Hydroxide at 20°C (Swash and Monhemius, 1995)

There is no conclusive evidence that arsenical ferrihydrite undergoes reduction because of the presence of sulphides, although such reactions are thermodynamically possible. Krause and Ettel (1985) studied the effect of reactive solids, such as pyrrhotite and pyrite, and found that the solubility of arsenic from arsenical ferrihydrite did not increase in the presence of these sulphides. Table 10 summarizes the resulting arsenic solubility from arsenical ferrihydrite precipitates formed using lime, a Fe/As molar ratio of 4, 80°C and pH 5.0, and mixed with mill tailings containing 40% pyrrhotite

Table 10 - Effect of Sulphide Tailings on the Arsenic Solubility from Arsenic Ferrihydrite Precipitates (Adapted from Krause and Ettel, 1985)

Test pH	As solubility (mg/L)	
	No tailings	Mill tailings*
5.0	0.45	0.34
7.0	1.73	1.47
9.0	5.8	4.0

*Mill tailings containing 40% pyrrhotite and analyzing 27.5% Fe, 13.8% S and 30% SiO_2.

Another experiment was carried out at pH 9 using pyrite concentrate and a 4:1 Fe/As precipitate. The ground pyrite concentrate (40 g/L) was added to 10 g/L of lime-precipitated arsenical ferrihydrite. After 8 complete solution exchanges, the mean As solubility was determined to be 5.3 mg/L. This result was only slightly lower than the As dissolution observed at pH 9 in the absence of pyrite (5.8 mg/L). The data from Inco's CRED plant, in which sulphide tailings are mixed with the arsenical ferrihydrite, appear to confirm the above observations.

It has also been suggested that arsenical ferrihydrite could transform over time to scorodite and other crystalline ferric arsenates (Harris, 2000). In fact, Nishimura and Robins (1996) observed the formation of scorodite and two other crystalline products, when amorphous arsenical ferrihydrite compounds (Fe/As molar ratio ~ 1) were equilibrated for up to three months in arsenic acid solutions at 25°C.

The Long-term Stability of Scorodite and Related Crystalline Arsenate Compounds

Scorodite is found in nature, where it forms as a result of the oxidation of arsenopyrite and other arsenic-bearing minerals (Dove and Rimstidt, 1985):

$$FeAsS + 14Fe^{3+} + 10H_2O = 14Fe^{2+} + SO_4^{2-} + FeAsO_4 \cdot 2H_2O + 16H^+ \qquad (5)$$

This process is catalyzed by Ferrooxidans bacteria which oxidize Fe^{2+} to Fe^{3+}. Natural scorodite is a mineral of widespread occurrence in many climatic zones, and this suggests that it is highly stable in the environment (Monhemius and Swash, 1999A). Its persistence in nature suggests that its solubility may control the concentration of arsenate in natural waters (Dove and Rimstidt, 1985).

Although the thermodynamic solubility of pure scorodite has been extensively studied (Dove and Rimstidt, 1985, 1987; Rimstidt and Dove, 1987; Robins, 1987; Nordstrom and Parks, 1987; Krause and Ettel, 1988; Welham et al., 2000), there are only a few laboratory long-term tests on the stability of scorodite and related compounds under mining disposal environments. Krause and Ettel (1987) studied the stability of synthetic scorodite for 241 days in a test based on stirring a ground sample in water (2.5% solids) at 22-25°C and pH ~5. A relatively high As dissolution (0.4 - 3.6 mg As/L) was reported. Recently, Swash et al. (2000) carried out long-tern column tests of synthetic scorodite, Type II ferric arsenate and other arsenic-bearing compounds. In these tests, approximately 600 g of each solid was placed in 1.5 m columns and, once per week, 400 g of distilled water was added and allowed to percolate through the bed of test material. It is reported that these column tests have been underway for a period of 3 years at Imperial College, London. The results have shown that synthetic scorodite and the Type II compound generate very low concentrations of arsenic in the column leachates (<0.1 mg/L As). The researchers conclude that synthetic scorodite is as stable as arsenical ferrihydrite (Fe:As > 3:1) and more stable than other residues produced by the neutralization of iron(III) and arsenic(V) contained in bioleach liquors and effluents. It should be pointed our that Swash and Monhemius (1995) had previously found that the presence of even small amounts of Ca in the crystal structure of scorodite and the $Fe_2(HAsO_4)_3 \cdot xH_2O$ compounds exerts a destabilizing influence and makes the solids more soluble than the pure Fe(III) arsenates. These researchers recommend that, to minimize the calcium content of iron arsenate compounds from solutions containing soluble calcium, the hydrothermal processing should be carried out at low pH (<1) and at temperatures above 150°C.

However, other studies have shown that scorodite is metastable under most conditions. Welham et al. (2000) have concluded, on the basis of an extensive review of available thermodynamic data, that scorodite is stable towards transformation to goethite only below pH 4. These researchers also estimate that scorodite is not stable under typical atmospheric weathering conditions and that the current permitted discharge level of arsenic is achieved only because of the slow kinetics of the transformation releasing arsenic over time. According to Dove and Rimstidt (1985, 1987), scorodite is stable during the oxidation of arsenopyrite because the arsenate activities are high and the pH is low. After the arsenopyrite oxidation ceases, arsenate activities decline and the pH increases, causing scorodite to dissolve incongruently to iron oxyhydroxide and arsenate ion solutions.

$$FeAsO_4 \cdot 2H_2O \;=\; FeOOH \;+ H_3AsO_4 \qquad (7)$$

Thus, the final products of arsenopyrite weathering are goethite and soluble arsenate.

There are also indications that crystalline arsenical compounds can decompose under reducing conditions. One case that has received significant attention is the disposal of minerals from the pressure oxidation circuit at the Campbell mine (see above). According to current practice, the pressure leach residue from the autoclave is mixed with sulphide tailings and then is disposed of in a subaqueous environment. Originally a lined impoundment was created for the storage of autoclave wastes and the acid-pretreatment overflow, but subsequently it was decided that a dedicated containment of these wastes would be environmentally inappropriate in the long term, and combined wastes were used to fill the impoundment. The geochemical behaviour of these tailings has been extensively studied by McCreadie (1996) and McCreadie et al. (1998). These researchers found, through mineralogical studies of the lined impoundment, that the products from the autoclave are recognizable by the presence of abundant rhombs of hydronium-potassium jarosite, $(H_3O,K)Fe_3(SO_4)_2(OH)_6$, and coexisting crystalline iron sulpho-arsenate, whereas the flotation tailings consist of quartz, dolomite, chlorite, talc, and variable but minor to trace amounts of amphibole, siderite, calcite, muscovite, pyrrhotite, arsenopyrite, and several other minerals. Most of the As occurs as a crystalline ferric sulpho-arsenate, and some is associated with Fe oxides and with H_3O-K jarosite. Field pore-water geochemical data from 1994 and 1995 showed increases in the Fe(II) and As(III) concentrations. The differences in the pore-water concentrations of Fe(II), As(III), Ca and K suggest that the ferric sulpho-arsenate, jarosite and possibly the ferric oxyhydroxides are unstable in the anoxic zone and will potentially release As to the pore water. Stoichiometric analysis, equilibrium geochemical modeling, calculated Fe speciation and analytical

As speciation studies suggest that reductive dissolution of ferric sulpho-arsenate and jarosite is occurring. There is evidence that the arsenate minerals are slowly decomposing to release soluble As(III) into the environment, although in concentrations below the regulated discharge limits. Harris et al. (2000) attributed this behaviour to the reducing environment caused by the presence of sulphides in the tailings. According to Hopkin (1986), below ~ 2 meters of water, environments can become anaerobic. Under such conditions, the sulphides can potentially reduce both the iron and arsenic to their lower oxidation states. However, as suggested by McCreadie, the arsenic is most likely being released to the pore water through bacterially-mediated reductive dissolution of the As-bearing iron minerals in the tailings. Recent work by Stichbury et al. (2000) has largely confirmed that bacterial activity causes the reductive dissolution of As-bound ferric oxide minerals in anaerobic sediments. These researchers conducted a field study of one of the Campbell Red Lake tailings ponds to determine if elevated concentrations of As, found near the base of the impoundment, are released by reductive dissolution. The monitoring involved measuring the Eh and the pH, as well as determining the pore-water chemistry and the bacteria population as a function of the tailings depth. The results of this extensive study are summarized in Figure 8.

The interpretation of these profiles by Stichbury et al. (2000) is as follows. In most of the profiles there are marked changes in the pore water chemistry at the tailings/peat contact. The pH is between 7 and 8 above the contact, but drops to pH 6-7 below the contact. Dramatic changes in Eh are also observed in the impoundment. At 3 m the Eh decreases from 348 mV to ~100 mV, and at 6 m the Eh increases from >100 mV to 200 mV. The sharp increase in Eh upon entry into the peat suggests that this is a region of redox change. Dissolved Fe concentrations are greatest (~40 mg/L) at a depth of 5.9 m to 6.1 m. There is a smaller peak of Fe at 3.1 m. Otherwise, the iron concentrations in the tailings profile are very low. Dissolved Fe occurs predominantly in the Fe(II) state which is expected given the relatively low redox potential of the pore water. Iron-reducing bacteria are abundant, and this suggests that Fe(II) occurs as a result of Fe(III) reduction. The highest concentration of dissolved Fe is found at the tailings/peat contact, and this suggests that peat-derived organic carbon is the electron donor for Fe(III) reduction. There is strong evidence

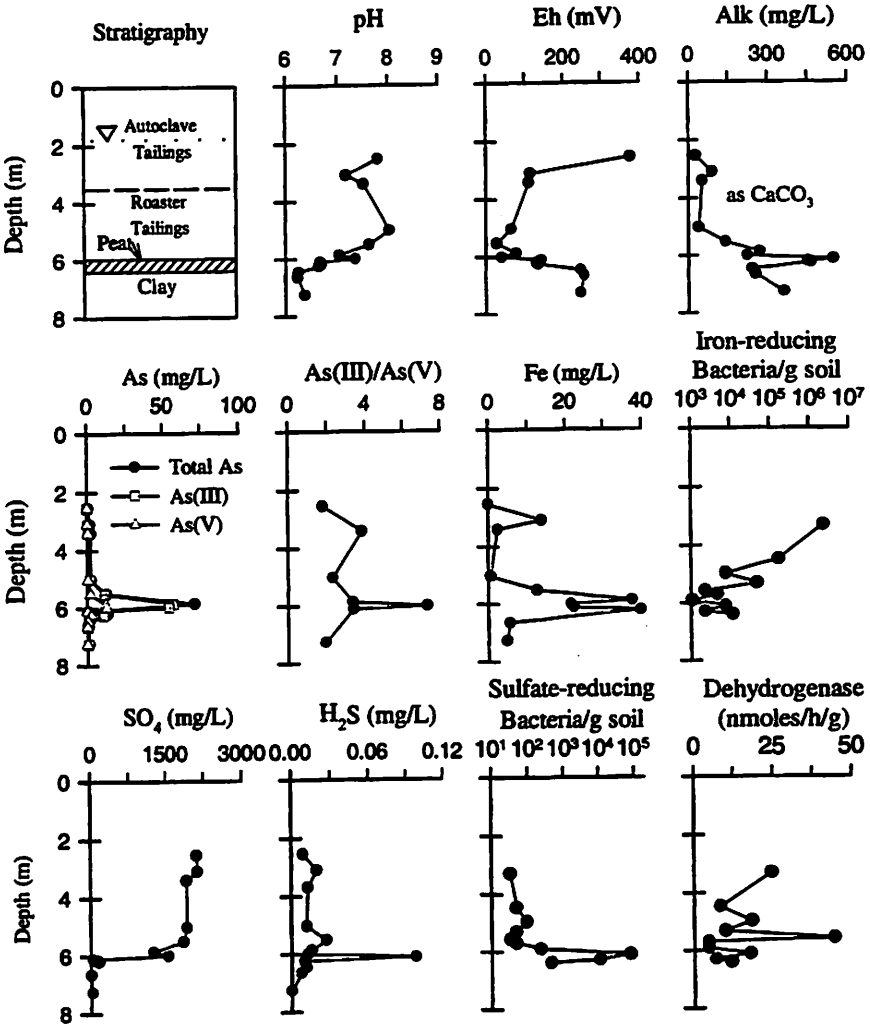

Figure 8 - Depth Profiles Illustrating the Pore-water Chemistry and Microbiology of a Tailings Impoundment at Campbell Red Lake (Stichbury et al., 2000)

for sulphate-reduction in the tailings, most evidently in the peat. Dissolved sulphate, a principal constituent of the process water, remains at a concentration of ~2,000 mg/L as it travels downward through the tailings with the flow of groundwater. At a depth of 5.9 m, there is a pronounced decrease in sulphate, and at 6.1 m, the concentration of sulphate approaches the detection limit (0.5 mg/L). Also at 6.1 m, the concentration of dissolved H_2S increases five-fold from 0.02 mg/L to 0.1 mg/L. There is a large peak of dissolved As (75 mg/L) at 5.9 m depth at the contact between the tailings and the peat. Arsenic concentrations decrease to those measured in the original tailings slurry (<1.5 mg/L) above and below this peak. The As peak corresponds to the upper Fe peak and suggests that As is being released in association with the release of Fe. The reduction of roaster-derived hematite or maghemite by reducing bacteria can be represented by the following reaction:

$$2Fe_2O_3 \cdot xH_3AsO_4 + CH_2O + 7H^+ \Longrightarrow 4Fe^{2+} + HCO_3^- + 4H_2O + 2xH_3AsO_3 \quad (8)$$

The speciation studies showed that As is predominantly in the trivalent form throughout the profile. The ratio of As(III) to As(V) ranges from 2 to 8; the highest ratio occurs where the As concentrations are the greatest. The elevated As(III) concentration in this region is consistent with more reducing water (Eh ~50 mV) and with microbial reduction of As(V) to As(III).

The general conclusion of this extensive study is that that microbially-mediated reactions release and reprecipitate As-containing minerals in the tailings/oxidation residue mixture. These tailings contain potentially high concentrations of sorbed and precipitated As which could be liberated through reductive dissolution.

PROCESSES TO CONVERT ARSENIC WASTES INTO STABLE ARSENIC COMPOUNDS

Arsenic trioxide is a by-product of many pyrometallurgical operations, such as the roasting of gold arsenopyrite ores/concentrates and the smelting of arsenical base-metal concentrates. The sulphide ores or concentrates are processed under conditions conducive to the formation of As_4O_6, which volatilizes and then condenses as solid As_2O_3 when the gas temperature drops. If the arsenic trioxide is not marketable, disposal of the collected arsenic becomes a problem because of the toxicity and instability of As_2O_3. Several processes have been developed to convert the As_2O_3-rich dusts and slurries into stable arsenic compounds, such as scorodite or arsenical ferrihydrite, which are more suitable for disposal.

Treatment of As_2O_3-rich Dust from Roasting Operations

Kyle and Lunt (1991) conducted an investigation of disposal options for the arsenic trioxide produced by the roasting operations at the Western Mining Corporation Windarra nickel/gold project in Australia. In this work, the As_2O_3 dust was dissolved in water and precipitated with lime and/or ferric sulphate, with or without oxidation to As(V) using H_2O_2. The incorporation of the As_2O_3 dust into cement was also evaluated. Their conclusions were as follows. The formation of so-called "ferric arsenate" precipitates produces a very low solubility product but requires large quantities of oxidant, lime and ferric sulphate. Initial cost estimates have indicated that this route is not economically viable unless cheap sources of the chemicals are available. Ferric arsenite, although insoluble, suffers from the same problems of chemical requirements. Calcium arsenate is also a low solubility precipitate that requires fewer chemicals for its formation than for the ferric arsenate route. However, the precipitate is known to be thermodynamically unstable in the long term in the presence of atmospheric carbon dioxide or carbonate ions. Calcium arsenite precipitates are too soluble and also suffer from long-term instability. Chemical solidification with cement, either of the arsenic trioxide itself (arsenic content 11.9-17.8% As) or after precipitation as calcium arsenate (arsenic content 4.4-7.5% As), appears to offer attractive prospects as a disposal option, both in terms of the low leachability of arsenic from the matrix, and in terms of preventing contact with atmospheric carbon dioxide or carbonate ions. The long-term stability of these solidified products, however, requires further investigation.

Hazen Research developed and patented a process for removing and stabilizing arsenic contained in materials such as sulphide ores, concentrates and metallurgical wastes (Downey et al., 1999; Downey and Mudgett, 1998). The process consists of roasting the arsenical material in a highly oxidizing atmosphere to convert the arsenic to the less volatile pentavalent oxide, As_2O_5; ideally iron is converted to hematite and/or ferric sulphate in the roaster. Both objectives can be accomplished by maintaining the temperature of the solid charge within the range of 500-650°C and the oxygen and sulphur dioxide partial pressures between 5 and 10% of 1 atmosphere total pressure. Depending on the composition of the material, conditions can be adjusted to retain 90 to 95% of the arsenic in the calcine. Leaching the As_2O_5 from the calcine using a strongly acidic solution of ferric sulphate is the next step. The leach is conducted under atmospheric pressure and at a temperature of approximately 60°C. Finally, the soluble As(V) from the pregnant leach solution is precipitated as amorphous ferric arsenate (arsenical ferrihydrite) by increasing the solution pH to ~2.5 using hydrated lime, $Ca(OH)_2$.

A novel process to treat the As_2O_3 dust and slurry which are stockpiled at the Con Mine, Yellowknife, NWT, Canada, has been described by Geldart et al. (1992). These arsenic waste materials were generated by the roasting operations, which are now closed. The new process aims to solve the environmental problems posed by the arsenic-bearing materials, and at the same time, to recover their gold contents. In the process, the As_2O_3 dust is mixed with gold/arsenopyrite concentrate, produced by the current flotation plant, and is fed to an autoclave, which was commissioned in 1992 to replace the roasting technology. Laboratory batch tests showed that a feed mixture of 40% flotation concentrate, 30% roaster calcine and 30% arsenic sludge would produce the desired results of high gold recoveries and sufficient liberated iron to react with the arsenic. A pilot plant campaign, based on the flowsheet shown in Figure 9, was carried out at Lakefield Research, Ontario. A patent application has been submitted on this process (Maltby, 1991).

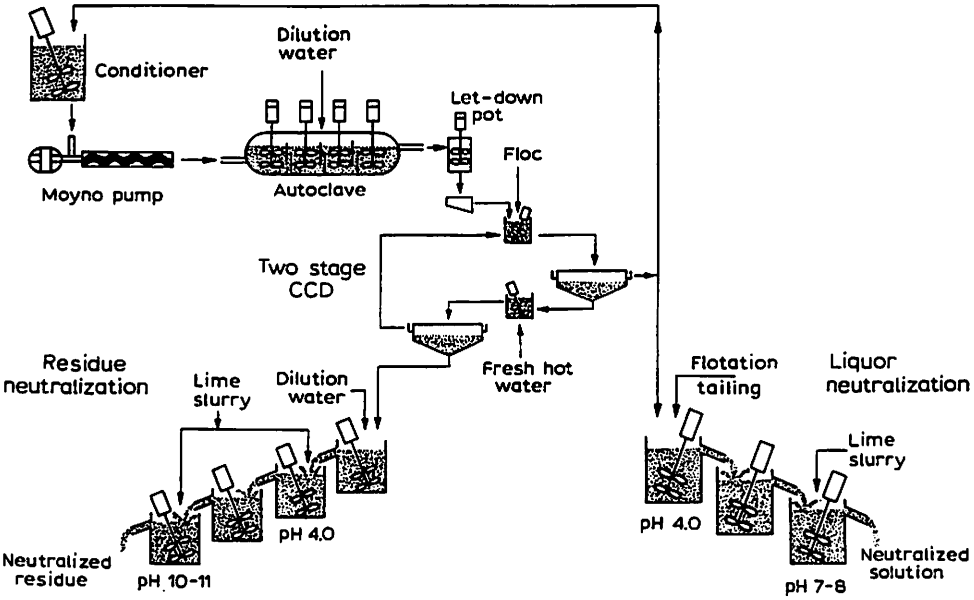

Figure 9 - Nerco Pilot Plant Flowsheet (Geldart et al., 1992)

In the pilot plant circuit, the autoclave feed was preconditioned to pH 2 with recycled acid to decompose carbonates, before being pumped into a four-compartment horizontal autoclave. Lignosol was added at a concentration of 1 kg/t to disperse elemental sulphur. The autoclave was an externally heated four-compartment titanium unit with a total slurry capacity of 331 L. Feed density was 24% solids. The circuit was operated for 24 hours at 210°C, 690 kPa oxygen overpressure and 2 hours autoclave retention time. Under the pressure oxidation conditions, the Fe(III) and the As(V) precipitate from solution as insoluble crystalline ferric arsenate. During the process, the gold locked in the feed materials is liberated and is subsequently extracted by cyanidation. The pregnant autoclave solution averaged 57 g/L H_2SO_4, 1.1 g/L As, 7.8 g/L Fe(total) and 6.8 g/L Fe(III). The autoclave discharge solids averaged 0.57% sulphide sulphur, and this was equivalent to 96% sulphide oxidation. The autoclave discharge (16.5% solids) was washed in a two-stage countercurrent decantation (CCD) circuit. The thickened solids were neutralized with lime slurry in two stages, to pH 4 and to pH 11, before batch cyanidation. Gold extraction from the neutralized thickener underflow was 84%, although it was demonstrated that the gold recovery could be improved by additional treatment designed to oxidize residual sulphides and sulphur. Mineralogical studies showed that the arsenic in the autoclave discharge residue occurred primarily as scorodite, but was also present as a ferric sulphate-arsenate compound, arsenical goethite (containing an average of 6 wt% As) and residual arsenopyrite. The scorodite formed rims of 1 to 30 μm thickness around goethite particles. Environmental tests indicated that the final solids were within the environmental guidelines for general waste disposal. This process has been successfully adopted by the Con Mine (Ferron and Stogran, 2000).

Demopoulos et al. (1994) described a method, originally developed at the Delft University of Technology, The Netherlands (Van Weert and Droppert, 1994), which involves the conversion of baghouse arsenic trioxide dust to scorodite by mixing the dust with HNO_3 and scrap iron in an autoclave at 130-160°C. The reactions are given as:

$$Fe + 4HNO_3 = Fe(NO_3)_3 + NO_{(g)} + 2H_2O \qquad (9)$$

$$3As_2O_{3(s)} + 4HNO_3 + 7H_2O = 6H_3AsO_{4\,(aq)} + 4NO_{\,(g)} \qquad (10)$$

$$Fe(NO_3)_3 + H_3AsO_{4\,(aq)} + 2H_2O = FeAsO_4{\cdot}2H_2O_{\,(s)} + 3\,HNO_3 \qquad (11)$$

According to these reactions, As_2O_3 is oxidized with HNO_3 (>1.5 N) to As(V), which in turn reacts with $Fe(NO_3)_3$ to produce scorodite. The As_2O_3 was found to dissolve first as trivalent arsenic and then to oxidize totally to As(V) between 115 and 145°C. Iron oxides were tried as a source of iron, but showed very slow to no dissolution in HNO_3 solutions, even at temperatures >100°C. Iron hydroxides, however, proved to have good dissolution rates in HNO_3 and thus they are another cheap source of iron, provided that they are added at a slow rate into the autoclave after the oxidization of As_2O_3 has taken place in order to control the supersaturation regime.

Stefanakis and Kontopoulos (1988) investigated the stability of calcium arsenite and calcium arsenate, and of ferrous arsenate and ferric arsenate produced from solid As_2O_3. The As_2O_3 was dissolved in water and the resulting As was precipitated as calcium arsenite or calcium arsenate with $Ca(OH)_2$. The effect of the Ca/As ratio in solution, precipitation pH, and thermal treatment of the resulting precipitate on its stability was studied. Further, As was precipitated as ferrous arsenate or ferric arsenate with lime and Fe^{2+} or Fe^{3+} additions. The effect of the Fe/As ratio in solution, pH, temperature of precipitation, and the Fe^{2+}/Fe^{3+} ratio on the stability of the resulting precipitate was reported. Their data showed a generally low solubility for high-iron ferric arsenates, but also indicated that the solids were more stable when precipitated at lower pH (3 as opposed to 5 or 7) and lower temperature (33°C as opposed to 80°C). These findings regarding precipitation temperature and pH are at variance with previously published data; according to Harris and Monette (1989), the differences may be the result of the incomplete washing of the solids and/or the formation of jarosites because of the presence of sodium in the leach solution.

Treatment of Smelter Flue Dusts

One of the major arsenic-bearing waste by-products from smelting is flue dust. Vast quantities of these flue dusts presently exist; some contain up to 20% As in addition to Bi, Sb and other metals. Several procedures have been developed to treat these flue dusts.

Harris and Monette (1985) provide references for early hydrometallurgical processes for dust treatment, which are mostly variants on sulphuric acid leaching. These authors describe a hydrometallurgical approach to treat copper smelter precipitator dusts produced at the Noranda Horne smelter. The process, the technical feasibility of which was demonstrated in a pilot plant, comprises leaching the dust in zinc plant spent electrolyte, recovery of the Pb/Ag residue by centrifugation, chlorination of the centrate to oxidize trivalent arsenic, evaporation of the solution to 70% H_2SO_4 to recover zinc and cadmium as crystalline sulphates and to eliminate halogens, and neutralization of an arsenic-containing acid bleed from the evaporator for arsenic disposal in the form of a ferric arsenate/gypsum sludge. A preliminary economic estimate for a plant treating 8,400 tonnes/year of dust was done. The capital cost for the leach plant was estimated to be Can$ 16,000,000 (1983), and direct operating costs (including freight charges) to be Can$ 335/tonne of dust. In breaking down the costs, over 30% of the equipment costs were related to solid/liquid separation requirements, and 25% was for the evaporation section. Similarly, over 30% of the operating costs were related to the operation and maintenance of the submerged combustion evaporator required for halogen removal.

Kunter and Bedal (1991 and 1992) describe a low-pressure, low-temperature chloride leach process, called the Cashman process, which can be used to extract metals from arsenical flue dusts and residues, and to fix the arsenic in an environmentally stable form as ferric arsenate (scorodite). The Cashman process utilizes a hydrochloric acid leach at somewhat elevated temperatures and pressures. It solubilizes metals of economic interest such as Cu, Zn, Pb, Ag, Au, Ni, Co, and Bi, and simultaneously leaves the toxic elements such as arsenic in an environmentally stable leach residue. To bring about the oxidation of arsenic(III) to arsenic(V) necessary for the precipitation reactions, as well as for the oxidation of any base-metal sulphides and arsenopyrite, oxygen (sometimes air) is used. The process was tested at a pilot plant scale at Hazen Research. The integrated circuit, including continuous recycle, operated from August to October 1989, during which period several tons of flue dust were processed. Based on this pilot program, the process was deemed technically feasible and produced commercially salable products. Residues from this pilot program were subjected to a long-term stability test jointly designed by PTI environmental services and the United States EPA.

A laboratory-scale process for the hydrometallurgical treatment of the dust from the copper converters at the Krompachy works, Slovakia, has been developed (Virkova and Havlik, 1999). The dusts collected from the converting operation contained significant amounts of arsenic (Table 11).

Table 11 - Average Composition of the Flue Dust from the Krompachy Converter (Vircikova and Havlik, 1999)

As Phases	Oxides	Metal	Zinc Arsenate	Lead Arsenate	Sulphides	Residue
Content (%)	0.32	0.07	0.33	1.19	0.18	0.06
Distribution (%)	14.9	3.2	15.3	55.3	8.4	2.9

Sodium sulphide solution was used as the leaching agent in a reactor at 80°C. The optimum conditions are: leaching temperature, 80C; leaching time, three hours; sodium sulphide concentration, 130 g/L; and the ratio of solid to liquid, 1:6. Under these conditions, 99.9% arsenic, 4.7% tin, and 6.6% antimony can be dissolved. The Bi, Zn, Pb, and Cu remained in the solid phase. The arsenic concentrations in solution depend on the initial As content in the copper converter dust. In these experiments, the arsenic concentration was 0.3-6.78 g/L. The solution was treated with H_2O_2 to oxidize As(III) to As(V) and then was neutralized. Arsenic was precipitated from solution either with a copper sulphate solution or a mixture of phosphoric acid and calcium oxide solution, and the addition of calcium oxide. In most cases, the efficiency of arsenic removal was more than 99%. The long-term stability of the arsenic precipitate is not known.

Ke and Qin (2000) describe a hydrometallurgical process to treat copper smelter flue dust from the Shenyang Smelter in China. The typical composition of the flue dust is: 1.45% Cu, 1.30% As, 2.10% Bi, 35.5% Pb, 10.2 % Zn, 0.86% Cd, 0.18% Sb, 2.46% Fe and 13.0% S. The best separation of copper and arsenic was obtained when leaching conditions were maintained at 120-130°C, 1 M H_2SO_4, 2 h leaching time, liquid/solid ratio of 5 and ambient pressure in the absence of oxygen (O_2 was found to decrease the extent of As leaching). About 90% of the arsenic and less than 10% of the Cu in the dusts were dissolved during leaching. Most of the copper remained in the residue as cupric sulphide. The dissolved arsenic and iron were oxidized and precipitated in a stable and disposable form as amorphous ferric arsenate (arsenical ferrihydrite). The Bi, Cu and Pb remaining in the residue were recovered as Bi sponge, and copper and lead concentrates, respectively. Soluble zinc and cadmium were recovered as zinc sulphate and Cd sponge products, according to standard technology.

Zhang et al. (1998) studied the treatment of flue dusts arising from Australian nickel smelters. These dusts often contain arsenic as As(III) oxide which must be recovered and disposed, as well as significant amounts of base metals and iron. One nickel smelter dust was found to contain low levels of arsenic associated with magnetite, forsterite and a nickel spinel (trevorite) present as glassy spheres. The following leaching conditions were examined: H_2SO_4 at 1 M and 5 M concentrations, H_2SO_4 at pH 1.5, SO_2/O_2 gas mixture containing 2% SO_2 and pH 1.5, caustic leach with 10% NaOH and NaOH solution at pH 12. Leaching was followed by oxidation and precipitation of iron(III) arsenate using SO_2/O_2. It was concluded that up to 25% of the arsenic can be selectively leached by NaOH; however, its subsequent removal as ferric arsenate requires uneconomic additions of acid and Fe. Attempts to completely extract the dust with 5 M H_2SO_4 resulted in only partial recovery of the arsenic and nickel. Dilute H_2SO_4 solution at pH 1.5 selectively leaches up to 25% of the arsenic with very little nickel extraction. Sufficient Fe(II) for the eventual co-precipitation of ferric arsenate, after oxidation of As(III) and Fe(II) with SO_2/O_2, was also leached. The latter method provides a potential way for the removal of arsenic from other smelter dusts which contain high levels of both arsenic and iron phases.

DISCUSSION AND CONCLUSIONS

Numerous arsenic-bearing compounds have been considered for the long-term disposal of arsenic. Monhemius and Swash (1999) have summarized the characteristics of the best known arsenic materials (Table 12).

Table 12 - Long-term Considerations for the Various Arsenic Disposal Options (Monhemius and Swash, 1999)

Arsenic Compound	Long-term Disposal Considerations
Arsenical ferrihydrite (Fe:As > 3:1)	• Dehydration can lead to instability • Recrystallization to goethite? • Possibility of biochemical reduction of As(V) to As(III) and Fe(III) to Fe(II) • Voluminous material containing only low concentrations of arsenic
Crystalline ferric arsenates (e.g., scorodite)	• Compact, high grade arsenic materials of low solubility • Scorodite is a widespread natural mineral, thus the synthetic analogue is unlikely to undergo further physical or chemical change
Calcium arsenates	• High intrinsic solubilities • Ca-arsenates can convert to $CaCO_3$ with the release of arsenic • High lime levels in the precipitated solids result in high pH's (11-12). With time, the lime is converted to $CaCO_3$. This leads to reduced pH and increased solubility of arsenic
Arsenical slags	• Long-term stability unknown; quenched slags have low solubilities • Require highly specific conditions for incorporation of arsenic into slag
Arsenical cements	• Carbonation of lime in the cements may reduce the buffering action and lead to reduced pH and arsenic mobilization • Long-term physical integrity of arsenical cements is unknown

In the mining industry, compounds containing Fe(III) and As(V) are currently considered to be the most suitable forms for arsenic disposal, either as poorly crystalline arsenical ferrihydrite that is obtained at relatively low temperatures or as crystalline ferric arsenates, such as scorodite, which are normally obtained at higher temperatures. Lime precipitation has been widely used, but it has been extensively demonstrated that calcium arsenate compounds will not be stable after the excess lime has been consumed. A crystalline calcium arsenate can be obtained by high temperature calcination, and this phase is apparently significantly less soluble than the initial material. However, not enough information is available on this option. Extensive research carried out by different workers has established that:

A) Arsenical ferrihydrite is stable in tailings ponds over the pH range 4-7, providing that the Fe/As molar ratio is 3>1. The pH range of stability can be increased to 4-10 with the presence of small amounts of co-precipitated base metals, notably Cd, Zn and Cu. The effect of Ca is controversial; although the presence of Ca(II) appears to destabilize arsenical ferrihydrite, gypsum has the opposite effect.

B) Scorodite ($FeAsO_4 \cdot 2H_2O$), which commonly forms under pressure oxidation conditions, is very insoluble and stable, provided that is stored under proper conditions. As in the case of ferrihydrite, the presence of Ca(II) ions appears to have a negative effect on the stability. Some crystalline arseno-sulphate compounds, which form at high temperatures and in the presence of sulphate (e.g., Type I) appear to be less stable than scorodite.

Each category has its own advantages and disadvantages. Arsenical ferrihydrite is easier to form, requiring no heating. However, the iron consumption is high (Fe/As $\geq$ 3) and the As must be oxidized to As(V), which can be a relatively inefficient process at ambient temperature. The long-term stability of arsenical ferrihydrite is in question because ferrihydrite is thermodynamically unstable with respect to goethite, and this implies that the adsorbed arsenic will eventually be released into the environment. However, the rate at which this conversion takes place appears to be extremely slow, and for practical purposes, arsenical ferrihydrite can be considered stable, provided that its Fe/As ratio is higher than 3, the pH is slightly acidic and that it does not come in contact with reducing substances (sulphides) or reducing conditions (deep water, bacteria, algae). The conversion of ferrihydrite into goethite involves dissolution and reprecipitation of Fe(III) ions, and this necessitates an aqueous phase at a relatively low pH or, alternatively, at a high pH. The presence of some foreign ions increases its pH stability range. Arsenical ferrihydrite is voluminous and relatively difficult to filter and dewater because of its poorly crystalline nature. By contrast, crystalline ferric arsenate or scorodite is more compact and easier to filter. The iron demand for scorodite would be 1/3 or less than that for making arsenical ferrihydrite. Scorodite is also more thermodynamically stable than its amorphous counterpart, although it may decompose slowly under the action of reducing conditions and reducing bacteria. The formation of scorodite is expensive because it requires high temperatures, which are normally obtained using an autoclave. However, there is experimental evidence that scorodite may be formed at ambient pressure, either by using supersaturation control as suggested by Droppert et al. (1996) or by having a high As/Fe ratio as described by Nishimura and Robins (1996). The success of this approach would significantly lower the cost and would make scorodite the obvious option for arsenic disposal.

According to Swash et al. (2000), from the point of view of safe disposal of arsenic, there is yet no clear experimental evidence favouring the low temperature precipitates over the high temperature precipitates or vice versa. It is clear that the storage requirements for high temperature scorodite will be lower compared with arsenical ferrihydrite, because the former compound contains 30 wt% arsenic as dense, compact, easily washed crystals, whereas the latter phase rarely contains more than about 6 wt% arsenic and is a gelatinous material, which is very difficult to densify beyond 20-25 wt% solids. These disadvantages of ferrihydrite, however, have to be weighed against the extra capital and operating costs of the pressurized equipment required for the formation of scorodite.

RECOMMENDATIONS

In order to choose the best option for treating and disposing of the 260,000 tonnes of As_2O_3-rich dust stored at the Giant Mine, several factors will have to be carefully considered. Because of its geographical location, it will be important to reduce reagent consumption and the associated transportation costs. This literature survey and analysis of arsenic disposal practices indicate that both arsenical ferrihydrite and scorodite would be acceptable products for long-term storage provided that the proper measures were taken to avoid the effect of reducing and alkaline agents. Transformation into scorodite is probably the best option for the Giant mine, despite the high capital cost of installing an autoclave. As a reference, Placer Dome reportedly spent $23.6 million (1991) on its autoclave and the creation of new tailings facilities (Anon., 1991). The main advantage of scorodite precipitation is that the iron demand will be much lower and this factor will be important in a remote area where the cost of obtaining an iron source might be quite high. Scorodite is produced using a Fe/As molar ratio of ~1/1, whereas the Fe/As molar ratio for arsenical ferrihydrite should be at least 4/1. Filippou and Demopoulos (1997) estimated that the cost of ferric sulphate would make up 60% of the total operating cost in an application to form scorodite. It follows that the iron demand for forming arsenical ferrihydrite would be four times higher at the same location. Kyle and Lund (1991) estimated that the production of arsenical ferrihydrite from roaster As_2O_3 dust would not be economically viable because of the large quantities of oxidant, lime and ferric sulphate needed. Their initial cost estimates indicated that this route is not economically viable unless cheap sources of chemicals are available. Therefore, the cost of arsenical ferrihydrite would be significantly higher at the Giant Mine site. Also the oxidation of As(III) to As(V) will be faster at high temperatures, and this again, may be an important economic consideration. For example, Filippou and Demopoulos (1997) estimated the cost of H_2O_2 as being 20% of the total operating cost for their process which operated at 90°C.

The use of an autoclave allows considerable flexibility because it can be employed to produce pure As_2O_3, if the market exits, or scorodite for long-term storage. It could also be used to treat refractory gold ores if these became available.

There is a question about the most suitable iron source for scorodite formation. Some operators favour the use of iron sulphides, such as pyrite or pyrrhotite, because the oxidation of these minerals generates both the Fe(III) ions and the H_2SO_4 which are needed for the formation of scorodite. If ferric oxides, such as hematite or goethite, are used as an iron source, then H_2SO_4 is not generated and must be purchased separately. However, the dissolution of ferrous sulphides needs significantly more oxygen, and therefore an economic evaluation of acid versus oxygen costs should be carried out. In the latter case, scorodite is the main product, and its characteristics are well known. The presence of excess sulphate, arising from the sulphide minerals, may promote the formation of ferric arseno-hydroxy-sulphates (Type I, II and III), whose stability may be lower than that of pure scorodite (see Table 6).

The possibility of forming scorodite at ambient pressure appears attractive, but this technique has been developed only recently and there be may be several unknowns which make this option too risky for immediate application at a high profile operation such as the Giant Mine.

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