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ARSENIC DISPOSAL PRACTICES IN THE METALLURGICAL INDUSTRY

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INVITED REVIEW

Abstract — The literature on the arsenic disposal practices of the metallurgical industry and the long term stability of the disposed arsenic compounds were reviewed from a Canadian perspective. The review was complemented with visits to selected operating metallurgical sites to obtain information on their specific arsenic disposal practices and the behaviour of their impounded residues. The arsenic disposal procedure currently favoured by the industry involves the formation of an insoluble ferric arsenate compound which is allowed to sediment at the bottom of tailings or residue ponds. It has been shown recently that this poorly formed crystalline compound is similar to "arsenical ferrihydrite" which is ferrihydrite containing strongly 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-hydroxy-sulphate compounds depending on the solution composition. 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. These procedures would offer significant reductions in capital cost because of the elimination of the need for autoclaves. 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. In all cases, the long term stability of the disposed arsenic compounds depends on a number of factors including disposal site characteristics, particle crystallinity and size distribution, the presence of complexing agents and the effect of bacterial activity.

INTRODUCTION TO THE ARSENIC PROBLEM IN THE METALLURGICAL INDUSTRY

Arsenic is relatively abundant in the earth's crust with an average terrestrial concentration of about 5 ppm. More than 300 arsenate and associated minerals have been identified (Escobar-Gonzalez and Monhemius, 1988). Some common arsenic minerals frequently found in base metal ores and concentrates are presented in Table I. Inevitably, some of the arsenic contained in these minerals enters any metallurgical processing circuit and this increases the production costs, interferes with metal extractions, deteriorates the product purity, presents environmental hazards and creates disposal problems (Piret and Melin, 1989).

During pyrometallurgical operations, such as roasting, smelting and converting, most of the arsenic is volatilized as As_2O_3 or As_2S_3 (Weeks and Wan, 2000; Valenzuela *et al.*, 2000) and in modern plants these compounds are collected in an electrostatic precipitator or wet gas scrubbers (Piret, 1999). Stockpiling the As_2O_3-rich dusts may pose long term problems because of the relatively high water solubility and toxicity of arsenic trioxide (Filippou and Demopoulos, 1997). Concerns have arisen about the fate of approximately 260,000 tonnes of arsenic-rich dust containing an average of 76% As_2O_3 which were stored underground at the Giant Mine (Yellowknife, Northwest Territories) during 50 years of operation. If relatively pure, a limited amount of As_2O_3 may be sold to the wood preservative industry (Smith and Paredes, 1988; Stewart *et al.*, 1994; Leach, 1999). It is common practice to recycle arsenic-rich dusts within the pyrometallurgical operations to force the dissolution of arsenic into the slag. However, arsenic compounds have a relatively low solubility in conventional silica based

Table I – Common arsenic bearing minerals (Valenzuela, 2000)

Type	Mineral	Formula
Arsenides	Nickeline	$NiAs$
	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
	Claudetite	As_2O_3
Arsenates	Olivenite	$Cu_2(AsO_4)OH$
	Scorodite	$FeAsO_4 \cdot 2H_2O$

smelting and converting slags. This practice tends to increase the concentration of dissolved arsenic in subsequent parts of the processing circuit (Hoffmann, 1993).

In copper electrorefineries arsenic is a major impurity and bleed streams are commonly operated to keep the arsenic in the electrolyte at < 20 g/L As. The usual methods of dealing with refinery bleed streams are to recycle the solution to an adjacent solvent extraction operation, to electrolyze the solution in so-called liberator cells to remove copper and other impurities as an arsenide sludge or to treat the copper electrolyte with excess lime to form a gypsum/metal hydroxide precipitate (Monhemius and Swash, 1999A).

High temperature high pressure oxidation, as in the processing of refractory gold ores at Campbell Red Lake (Red Lake, Ontario) and the Con Mine (Yellowknife, Northwest Territories), promotes the formation of scorodite ($FeAsO_4 \cdot 2H_2O$) and/or other solid compounds but other leaching processes including biological oxidation, produce soluble arsenic species (Swash *et al.*, 2000).

Flotation tailings usually contain residual arsenic bearing sulphides and these compounds may become soluble as a result of pH changes brought about by acid mine drainage (Kwong *et al.*, 2000; Soprovich, 2000) or algal activity (Taschereau and Fytas, 2000). Kwong *et al.* (2000) observed elevated As concentrations in the pore water of the Ketza River (Yukon) beached and submerged tailings indicating the release of As from the solids. The enhanced As solubility was attributed to the high calcium content of the tailings arising from both naturally occurring limestone and the significant addition of lime (7.5 kg/tonne ore) during the milling process. The Ketza River tailings have been characterized as nearly amorphous to cryptocrystalline ferric oxyhydroxides which make up more than two-thirds of the solid phases; the other abundant phases are silicates and carbonates. The common As containing compounds in the tailings are arsenopyrite, scorodite, an Fe-Ca arsenate hydrate, arsenical ferrihydrite and AsO_4-bearing jarosite (Paktunc *et al.*, 1998).

Increasing environmental awareness is leading to more stringent regulations for the disposal of arsenic compounds. Arsenic is toxic to both plants and animals because of its affinity for proteins, lipids and other cellular components (Harrington *et al.*, 1998). Many 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 in drinking water. The United States Environmental Protection Agency's (EPA) interim maximum contaminant level (MCL) for arsenic in drinking water is 50 μg/L and 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, which is a Canadian industry/government voluntary emission reduction program whose goal is to achieve a significant reduction in the emission of persistent, bio-accumulative and toxic substances (Valenzuela, 2000).

PROCEDURE

The scientific literature was systematically searched from its beginning to the present for information on arsenic disposal practices. 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 were surveyed and personal contacts were made 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. In addition, several Canadian metallurgical sites currently precipitating arsenic from aqueous solution were visited to obtain information on specific disposal practices and the long term stability of arsenic bearing residues.

THE REMOVAL OF DISSOLVED ARSENIC

An extensive review of methods to remove soluble arsenic from effluents was recently compiled (Montana Tech and

MSE, 1994). A summary of this review, covering more than 160 papers on arsenate precipitation and more than 380 papers on arsenic adsorption, has been published by Twidwell *et al.* (1999). Table II summarizes the various processes that have been developed, proposed or studied for the removal of arsenic from solution. Most methods can effectively remove arsenic from solution but only a few generate an arsenic bearing material that can be directly impounded. The United States EPA has designated co-precipitation with ferric ions as "The Best Demonstrated Available Technology" (BDAT) for the removal of dissolved arsenic (Rosengrant and Fargo, 1990) and it is widely used in water purification plants (Hering *et al.*, 1996; McNeill and Edwards, 1995; Cadena and Kirk, 1995; Kartinen and Martin, 1995). In this context, co-precipitation with ferric ions is very cost-effective. Merrill *et al.* (1986, 1987) estimated that the total cost of applying ferric ion precipitation for selenium and arsenic removal from a power station scrubbing circuit would be \$0.093 (U.S.) (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 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 consumption accounts for 22% of the total process cost and sedimentation and sludge dewatering account for 18 and 21%, respectively. In the Canadian metallurgical industry, co-precipitation with ferric salts with subsequent storage of the resulting sludge under water is the preferred method for removing soluble arsenic. This technique has largely replaced lime neutralization which was the accepted technology until the early 1980s.

Soluble arsenic has been removed to less than 1 mg As/L by precipitation as As_2S_3 (Young and Robins, 2000). In general, As_2S_3 is considered unsuitable for long term storage because it has a relatively high water solubility (Robins, 1988) and it is susceptible to atmospheric and bacterial oxidation (Montana Tech and MSE, 1994). However, a Japanese smelter removes arsenic from its circuit as As_2S_3 and this is subsequently polymerized and stored *in situ* (Valenzuela, 2000; Valenzuela *et al.*, 2000A). Emerging 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) are promising, but they require additional investigation. In cyanide solutions, Fe(II) ions may be used to precipitate arsenic (Nishimura and Robins, 2000).

Table II – 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

THE STABILITY OF DISPOSED ARSENIC COMPOUNDS

There is no definitive test to determine the behaviour of hazardous compounds over long periods of time. It has become customary to determine the stability of compounds by subjecting them to leachate tests, usually the United States EPA Toxicity Characteristic Leaching Procedure (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 after 20 hours of reaction. The limit for the leached arsenic is 100 times the World Health Organization's primary drinking water standard of 50 μg/L As (5 mg/L As) (Hopkin, 1989). Common arsenical disposal compounds such as scorodite and arsenical ferrihydrite tend to pass the standard EPA TCLP test limit of 5 mg/L As (Table III). This is partly attributable to the fact that the lowest solubility for both scorodite and arsenical ferrihydrite lies in the weakly acidic pH range of 3-5 (Figure 1).

The TCLP test is not a comprehensive measure 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. Long term tests which attempt to simulate the conditions experienced by arsenical materials

Table III – 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

*Test limit is 5 mg/L As

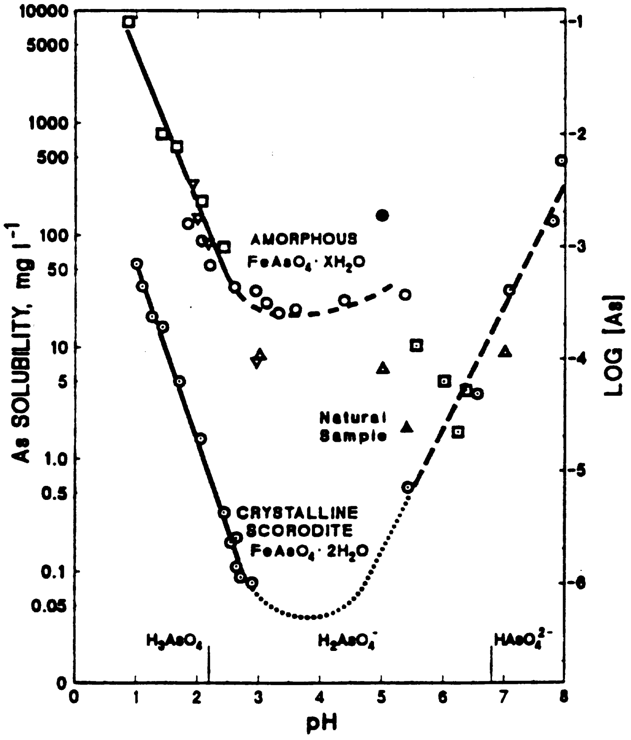

Fig. 1. Comparison of the arsenic solubility of scorodite and of "amorphous ferric arsenate" (arsenical ferrihydrite) (Krause and Ettel, 1989)

exposed to natural weathering have been developed and applied to a number of arsenical compounds (Monhemius and Swash, 1999A; Swash *et al.*, 2000).

The long term stability of arsenic compounds depends on a number of factors including disposal site characteristics, particle crystallinity and size distribution and the presence of oxygen, sulphides and complexing agents such as chloride or organic acids. As shown in Figure 2, arsenic can exist in the -3, +3 and +5 oxidation states but the predominant aquatic forms are trivalent arsenite (+3) and pentavalent arsenate (+5). Arsenic acid, H_3AsO_4, exists only in extremely acidic conditions. The species $H_2AsO_4^-$ is the predominant arsenate form in slightly acidic solutions, whereas $HAsO_2^{2-}$ predominates above neutrality. The deprotonated AsO_4^{3-} ion becomes the main arsenate species only at extremely high pH conditions (Cadena and Kirk, 1995).

In the environment, arsenates are stable in oxygenated systems such as shallow waters and they are very strongly adsorbed and efficiently immobilized by weakly acidic ferric oxyhydroxides (ferrihydrite or goethite) and by other hydroxides such as those of manganese and aluminum which are common constituents of soils and clays. However, the adsorption of arsenites which dominate in mildly reducing conditions is much weaker. In more strongly reducing conditions where sulphate reducing bacteria are active, nearly insoluble arsenical sulphides are formed (Hopkin, 1989; Norstrom, 2000). Changes in redox potential may cause the interconversion of arsenic species resulting in the liberation or fixation of arsenic. Bacterial activity can have an important effect on the speciation of arsenic (Newman *et al.*, 1998; Stichbury *et al.*, 2000). Sulphate reducing bacteria can indirectly reduce both arsenate and iron oxyhydroxides (Harrington *et al.*, 1998).

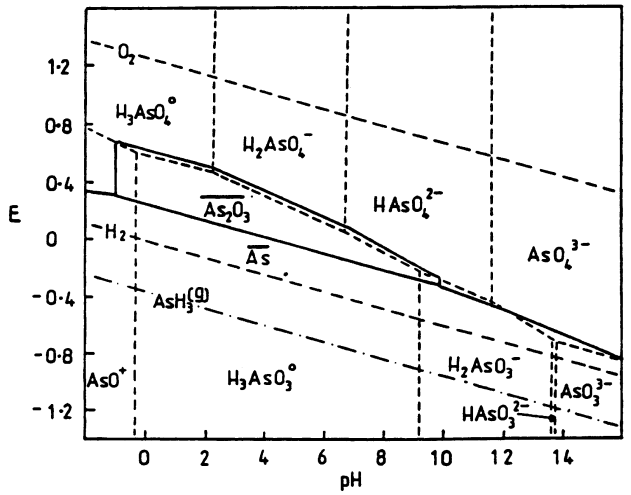

Fig. 2. Eh-pH equilibrium diagram for the system arsenic-water at 25 °C and at unit activity of all arsenic species (Robins, 1988)

ARSENIC REMOVAL BY CO-PRECIPITATION WITH FERRIC IONS

When a solution containing Fe(III) ions is rapidly neutralized, a ferric oxyhydroxide phase, modernly known as ferrihydrite, forms and precipitates (Jambor and Dutrizac, 1998):

$$Fe^{3+} + (3+x)\ H_2O = FeO(OH)(H_2O)_{1+x} + 3H^+ \qquad (1)$$

Ferrihydrite is known to have adsorption properties for many cations and anions including AsO_3^{3-} and AsO_4^{3-}.

$$\begin{aligned} &FeO(OH)(H_2O)_{1+x} + AsO_4^{3-} \\ &\quad = AsO_4^{3-} \cdot FeO(OH)(H_2O)_{1+x} \end{aligned} \qquad (2)$$

The co-precipitation of soluble arsenic with Fe(III) ions has been extensively studied and an excellent review of the past and current research in this field has been published (Harris, 2000). The optimum pH range for effective arsenical ferrihydrite precipitation is 4-7 but the presence of foreign cations such as Zn(II), Cd(II), Pb(II), Ca(II) and Mg(II) increases the pH range to 4-9 (Emett and Khoe, 1994; Khoe *et al.*, 1994).

Several factors can influence arsenic co-precipitation (Tahija and Huang, 2000). Cadena and Kirk (1995) reported that the presence of elevated concentrations of NaCl has little effect on arsenic precipitation but 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. As shown in Table IV, sulphate was extensively incorporated into the precipitates which had Fe/As ratios >4.0. The solids contained up to 2.4% Na when the Fe/As ratio was <4.0.

The co-precipitation is more effective if 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 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 values and only then in the presence of a catalyst such as cupric ions. Hydrogen peroxide can readily oxidize As(III) in alkaline media but not in acid solutions unless high temperatures are applied (Tozawa and Nishimura, 1984). Chlorine gas, potassium permanganate, ammonium persulphate (Harris and Monette, 1985) and sodium hypochlorite (McClintok, 1994) can oxidize As(III) to As(V) under specific conditions. Ozone has been found to be a very effective oxidant for As(III) even in acidic media and at ambient temperatures (Tozawa and Nishimura, 1984; Nishimura and Umetsu, 1994) but the solubility of ozone in aqueous media is low (Roca *et al*., 2000). Mixtures of SO_2/O_2 can oxidize As(III) effectively (Nishimura *et al*.,1996). Zhang *et al*. (2000) studied the oxidation of As(III) by SO_2/O_2 mixtures (catalyzed by iron) and by O_2 (catalyzed by UV light and iron), and reported that the rate of oxidation with the SO_2/O_2/Fe system is fast and complete oxidation of 7.5 g/L As(III) is achieved in about 2 hours between 25 °C and 60 °C. With the O_2/UV/Fe system, the rate of oxidation of As(III) was similar at low initial concentrations of As(III) (7.5 mg/L) but was much slower at higher initial concentrations (487 mg/L). Fundamentally, the SO_2/O_2/Fe system is preferred for oxidizing the more concentrated As(III) solutions likely to be found in hydrometallurgical processes. The oxidation of As(III) using UV radiation has also been discussed by Khoe *et al*. (2000) who give 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 wells that have arsenic concentrations ranging from 0.2 to 1 mg/L.

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 postulated but in recent years it has been demonstrated that at temperatures below 100 °C, the precipitate formed from Fe(III) and As(V) solutions is ferrihydrite containing strongly adsorbed arsenate ions (Robins *et al*., 1991; Robins and Jayaweera, 1992). According to this new evidence, As(V) is tenaciously chemisorbed on ferrihydrite and this results in a stable inner-sphere complex. There are no water molecules between the arsenate and the ferrihydrite surface (Waychunas *et al*., 1993, 1996; Rancourt *et al*., 2001). However, some authors have noted that, when high concentrations of Fe(III) and As(V) are present and the pH is gradually raised, ferric arsenate precipitates before ferrihydrite can attain saturation and precipitate (Langmuir *et al, 1999).*

For economical reasons, lime is commonly used as the neutralizing agent and in this case, the final product is a mixture of compounds depending on the relative concentrations of Fe(III) and As(V) initially present. 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 2-3, arsenical

Table IV – Fe(III)/As(V) precipitates showing incorporation of sulphate and sodium from Na_2HAsO_4-$Fe_2(SO_4)_3$ solutions (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.

ferrihydrite begins to form and this removes most of the arsenic from solution, if sufficient iron is present. Only if the Fe:As ratio in the liquor is low will arsenic be left in solution to combine with the lime to form calcium arsenates which begin to precipitate at pH 3-4 (Swash and Monhemius (1995).

Arsenical ferrihydrite forms a voluminous sludge which is difficult to filter because of its poorly crystalline nature. 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 sludge produced (Lawrence and Higgs, 1999). Ferrihydrite precipitation is also associated with a high consumption of iron and neutralizing agent (Hoffmann, 1993). Despite these characteristics, precipitation and impoundment of arsenical ferrihydrite are widely utilized by the metallurgical industry. Canadian examples include the Inco CRED plant (Sudbury, Ontario), the Noranda Horne Smelter (Rouyn-Noranda, Quebec), the Giant Mine (Yellowknife, Northwest Territories), the Con Mine (Yellowknife, Northwest Territories) and Teck-Corona (Hemlo, Ontario).

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 products 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 2-3 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 40 psi. Lime is added to the autoclaves to control the pH to ~3.3 in the first autoclave and to ~4.0 in the second. The Fe/As molar ratio of the solution is usually >8 and accordingly, the Fe/As molar ratio of the precipitate is also >8 because 99.5% of the Fe and 99.9% of the As are precipitated in the autoclave circuit. The precipitate contains 6-15% Fe and 0.5-2.0% As together with 13-23% Ca as gypsum. After filtration, washing and repulping in water, the slurry at pH 3-4 is pumped to the residue pond. About 30-40 t/day of residue is produced and this contains about 300-500 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 deposited into an area that contains pyrrhotite-rich flotation tailings underlying the iron arsenate-precipitate. The final effluent from the arsenic precipitate-tailings impoundment area is at pH 5.5 and it contains only 0.02 mg/L As (Krause, 1992).

The Horne Smelter, which is located in Rouyn-Noranda, Quebec, is a custom facility 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 from 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 remove 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 As, Bi, Sb and Pb. This dust fraction, which contains 3-10% arsenic in the form of various soluble and insoluble As(III) and As(V) species, is slurried in water and is treated in a gravimetric separator to recover copper and precious metals with the reject fraction sent to the weak acid treatment plant. Another feed to the weak acid treatment plant is the weak acid solution generated in the wet scrubbers prior to the passage of the SO_2-bearing gas 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. An interesting characteristic of the arsenic precipitation process 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 40 mg/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. Hydrogen peroxide was initially used for iron oxidation but has been replaced by a proprietary oxidation process. 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 in order 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 the slag flotation tailings/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 flotation tailings/ arsenic precipitate pond has been monitored since 1993; the overflow liquor is at pH 8.5-

9.5 and analyzes 0.1 - 0.2 mg/L Pb and <0.5 mg/L As which is the stipulated environmental limit.

The Giant Mine (Yellowknife, Northwest Territories) has used ferric co-precipitation since 1980 to treat various process and effluent streams. According to Harris and Krause (1993), ferric sulphate is 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.

THE DISPOSAL 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 eventually decompose releasing soluble arsenic. Furthermore, the thermodynamic calculations indicate that over a sufficiently long period of time, arsenical ferrihydrite will decompose to goethite (α-FeOOH) or hematite (α-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" (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 pH 12. Figure 3 shows the transformation kinetics at various pH values and Figure 4 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 precipitate 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).

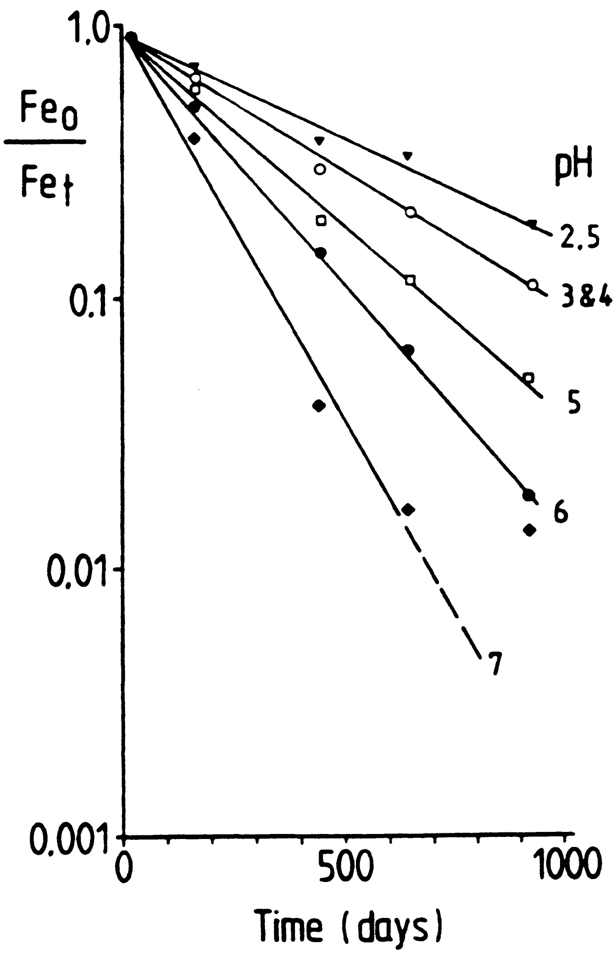

Fig. 3. First order reaction plot for the transformation of ferrihydrite at various pH values (Schwertmann and Murad, 1983)

The transformation mechanisms of "pure" ferrihyrite into stable ferric oxyhydroxides or oxides were further studied by Manceau and Drits (1999) by means of EXAFS spectroscopy. These researchers concluded that the structure of 6-line ferrihydrite consists of structural anionic ABA and ACA fragments in which Fe(III) 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 internal dehydration-rearrangement, because the latter would necessitate 1) the breaking of face linkages and 2) deeply altering the anionic packing 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 temperatures

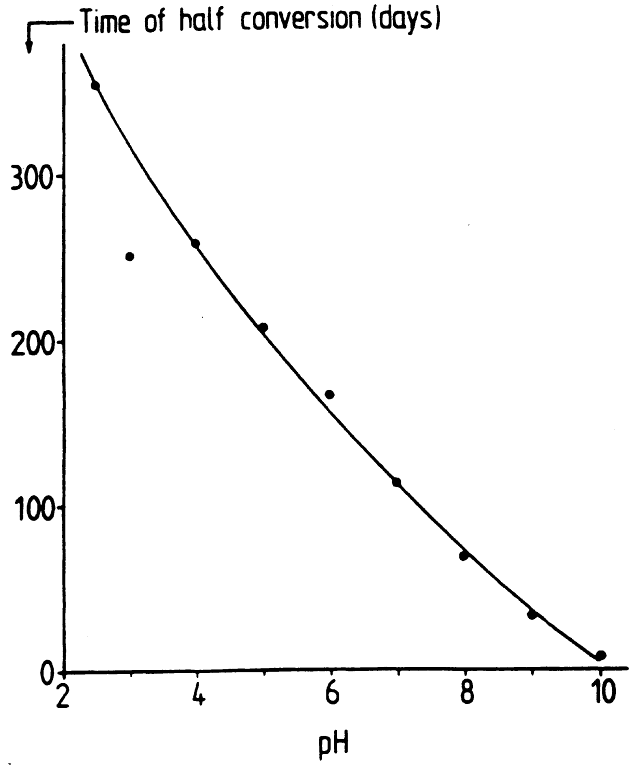

Fig. 4. Length of time for the half conversion of ferrihydrite to goethite and hematite versus pH (Schwertmann and Murad, 1983).

and pressures without dissolving the material. 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 properly maintained disposal sites. 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 independently in the late 1980s by Inco and Noranda researchers (Krause and Ettel, 1985, 1987, 1989; Harris and Monette, 1988, 1989). In these tests, the stability of various arsenical ferrihydrite precipitates 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. As shown in Table V, the experimental results indicate that the stability of arsenical ferrihydrite is higher (the As dissolution is less) when the Fe/As ratio is high and the pH is slightly acidic. The precipitates obtained with CaO as the neutralizing agent are more stable than those made using NaOH. In general, high-iron (Fe/As molar ratio >3) arsenical ferrihydrites are stable in the pH range 4-7. The data also indicate that by increasing the Fe/As molar ratio, some degree of stability is conferred in the alkaline region. On the other hand, it is clear that stoichiometric or low-iron (Fe/As molar ratio <3) precipitates are not sufficiently stable for long term storage. It is also evident that at neutral and alkaline pH most compounds tend to dissolve incongruently and release arsenic. Even a compound having a Fe/As molar ratio of 17.1/1 exhibited some arsenic dissolution at pH 8.2.

Harris and Monette (1989) have shown that a minimum Fe/As molar ratio of 3:1 is necessary to confer stability to an arsenical ferrihydrite precipitate over the pH range 4-7 (Figure 5). However, as pointed out by Harris and Krause (1993), this ratio applies specifically to precipitates formed continuously from Fe(III)/As(V) feed solutions and may not apply to all Fe- and As-containing waste materials. Krause (1992) indicated that the mode of precipitation has an important influence on the stability of arsenical ferrihydrite. Continuous precipitation from a solution containing Fe(III) and As(V) at steady state, as practiced in industry, will produce only one product with a constant Fe/As molar ratio. In contrast, batchwise precipitation from the same solution will generate a range of precipitates with changing Fe/As molar ratios. According to this researcher, similar differences apply for precipitation processes involving the simultaneous oxidation of Fe(II)/As(III) because the oxidation of Fe(II) can be expected to proceed before that of As(III) and this will lead to precipitates having different Fe/As ratios.

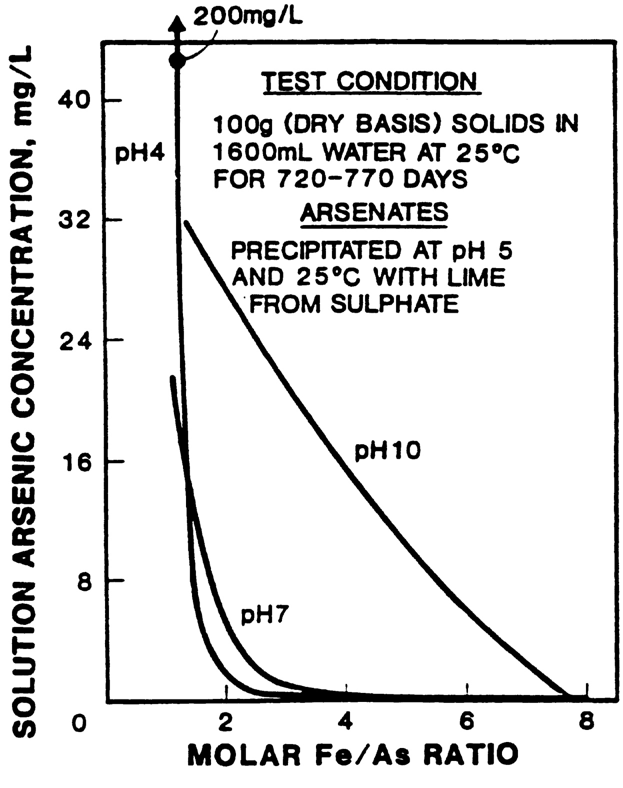

Fig. 5. Effect of the molar Fe/As ratio on the solubility of arsenic from high ferric arsenates (arsenical ferrihydrite) as a function of the test pH (Harris and Monette, 1989).

Table V – 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	843	97	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)

Leaching operations, involving the dissolution of different Fe and As minerals, can also be expected to produce a wide range of Fe/As precipitates particularly in batch leaching processes.

The fact that the solubility of arsenic from arsenical ferrihydrite increases as the pH increases above neutrality must 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 rationalized by the limited amount of Fe(III) available in solution after ferric oxyhydroxide precipitation. In fact, the total Fe(III) 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. Since 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 note that as the pH is increased, more iron is required for the same amount of arsenic removal; this is consistent, not with a ferric arsenate precipitation mechanism, but with the adsorption of arsenic on the ferric oxyhydroxide solid phase.

The reasons for the apparent high stability of the arsenical ferrihydrite generated by the metallurgical industry are not completely clear. Jambor and Dutrizac (1998) concluded that the adsorption of arsenate while ferrihydrite is polymerizing interferes with the chain building process, thereby retarding further polymerization and the subsequent transformation to hematite. Rancourt *et al.* (2001) 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 ferrihydrite. 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 co-ordinated Fe-As pairs. Mössbauer spectroscopy shows octahedrally co-ordinated Fe(III), 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.

Table VI – Stability tests 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] Significant amounts 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.

Harris and Monette (1988, 1989) observed that the presence of co-adsorbed base metal ions on ferrihydrite increases its stability. As shown in Table VI, “pure” arsenic-bearing ferrihydrite is not stable at pH >7, but the presence of Cu(II), Zn(II) and Cd(II) confers stability up to pH 10. The data also indicate that the precipitates formed from sulphate media are more stable than those formed in chloride media. This may be explained by the preferential formation of gypsum which effectively removes sulphate and bisulphate ions from the solution. These anions have been shown to compete with arsenate for sites in the ferrihydrate network (Cadena and Kirk, 1995).

In the absence of sulphate, Ca-Fe-AsO_4 ternary compounds can form and these are significantly more soluble than the corresponding calcium-free Fe-AsO_4 compounds. Swash and Monhemius (1995) prepared a range of Ca-Fe-AsO_4 solid compositions by precipitation at 20 °C using calcium hydroxide to adjust the pH over the range from 3 to 12. These solids were subjected to the EPA TCLP test. 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 (Figure 6). 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 this leads to lower apparent solubilities of the precipitates formed.

It has been found that atmospheric CO_2 has no discernable effect on ferric arsenates, although CO_2 is known to have a considerable destabilizing effect on a number of arsenates, notably those of Ca, Mg and Cd (Krause and Ettel, 1985; Harris and Monette, 1988).

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 pyrrhotite and pyrite and found that under the conditions tested the solubility of arsenic from arsenical ferrihydrite did not increase in the presence of these sulphides. Table VII 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 subsequently mixed

Table VII – Effect of sulphide tailings on the arsenic solubility from arsenical 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.

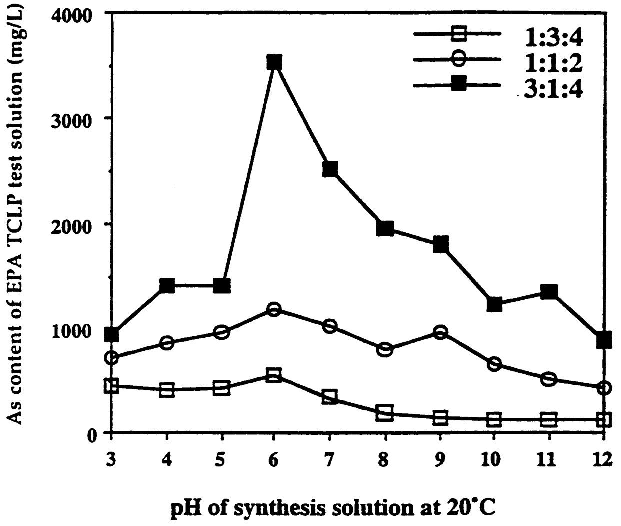

Fig. 6. EPA TCLP solubility plots of the Ca-Fe-As solids stabilized at various pH values with calcium hydroxide at 20 °C (Swash and Monhemius, 1995).

with mill tailings containing 40% pyrrhotite. Another experiment was carried out at pH 9 using pyrite concentrate mixed with 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 eight complete solution exchanges, the mean As solubility was determined to be 5.3 mg/L. This result was only slightly lower than the 5.8 mg/L As dissolution observed at pH 9 in the absence of pyrite. The data from Inco's CRED plant in which sulphide tailings were mixed with arsenical ferrihydrite appear to confirm the above observations.

It has 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 having a Fe/As molar ratio ~ 1 were equilibrated for up to three months in arsenic acid solutions at 25 °C.

ARSENIC REMOVAL BY LIME PRECIPITATION

Precipitation of arsenic with lime is still widely practiced despite concerns about the long term stability of the resulting precipitates (Valenzuela, 2000; Castro and Muñoz, 2000). The neutralization of an As(V) solution with lime at room temperature leads to the formation of several calcium arsenate compounds including $Ca_4(OH)_2(AsO_4)_2{\cdot}4H_2O$, $Ca_5(AsO_4)_3OH$ and $Ca_3(AsO_4)_2{\cdot}3^2/_3H_2O$ (Bothe and Brown, 1999) as well as $CaHAsO_4{\cdot}xH_2O$ and $Ca_5H_2(AsO_4)_4$ (Swash and Monhemius, 1995). At higher temperatures, Swash and Monhemius synthesized a series of calcium arsenate compounds the structure of which depended on the pH and the Ca:As ratio. At temperatures <100 °C and pH values < 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 (Table VIII). At pH 8 and in the temperature range of 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 which suggested the composition $Ca_3(AsO_4)_2$. Solids precipitated at higher pH values and at temperatures above 100 °C contained a compound believed to be basic calcium arsenate.

Swash and Monhemius (1995) reported that all calcium arsenate compounds give relatively high arsenic solubilities when subjected to the United States EPA TCLP tests. In fact, the arsenic concentrations of the solutions in contact with the calcium arsenate compounds were in the range of 900-4,400 mg/L As which is at least two orders of magnitude higher than the values produced by the iron arsenate compounds. The 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 having different compositions, exhibited solubilities similar to the compounds 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) (Equation 3).

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

The Pasminco lead smelter at Port Pirie, Australia provides an illustrative example of an industrial facility that had a major problem with the conversion outlined by Equation 3. 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 (g/L) of dissolved arsenic (Montana Tech and MSE report, 1994).

Calcination at ~700 °C in the presence of excess lime has been proposed as a method of increasing the stability of calcium arsenate and calcium arsenite precipitates

Table VIII – 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
Guerinite	$Ca_5H_2(AsO_4)_4{\cdot}9H_2O$	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

(Nishimura and Tozawa (1985). The end result of the calcination process is the transformation of the amorphous calcium arsenate and calcium arsenite into a crystalline compound as illustrated by the following equations which are applicable at 700 °C:

$$Ca_3(AsO_4)_2{\cdot}Ca(OH)_2 = Ca_3(AsO_4)_2\ \text{(crystalline)} + CaO + H_2O \qquad (4)$$

$$Ca(AsO_2)_2{\cdot}Ca(OH)_2 + (n+1)Ca(OH)_2 + O_2 = Ca_3(AsO_4)_2 + nCaO + (n+2)H_2O \qquad (5)$$

The procedure involves heating the precipitates with Ca/As ratios of >4.6 for calcium arsenite and >2.1 for calcium arsenate above 700 °C. Apparently, the calcination is not accompanied by arsenic oxide vaporization because the chemical analyses showed that the Ca/As molar ratio of 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. Since calcium arsenite is oxidized during calcination, this procedure can be applied to the precipitates formed from solutions containing both As(III) and As(V) without the need for oxidizing As(III) prior to lime precipitation. However, Stefanakis and Kontopoulos (1987) found that calcination is less effective for calcium arsenite because the transformation to arsenate is incomplete below 800 °C, as evidenced by their X-ray diffraction studies of the calcine. Table IX shows the aqueous arsenic solubilities in alkaline media of calcium arsenites and calcium arsenates calcined at various temperatures.

Swash and Monhemius (1995) pointed out that calcium arsenites and calcium arsenates appear to have low water 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 can be mobilized. According to Valenzuela (2000), however, the lime precipitation and calcination process is currently used by several Chilean copper smelters without any apparent problems. The implication is that this process may be acceptable in a dry climate where the dissolution of excess lime by rain is negligible.

THE FORMATION OF SCORODITE AND RELATED COMPOUNDS

High temperature operations such as those involving the use of autoclaves produce crystalline and compact Fe(III)/As(V) compounds. Pressure oxidation is an established technology for treating gold ores which are refractory as a result of the presence of gold-bearing 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 the treatment of refractory gold ores: 1) the elimination of the discharge of arsenic trioxide and sulphur dioxide to the atmosphere, 2) the elimination of worker exposure to sulphur dioxide gas, arsenic gas and arsenic trioxide particulates, 3) the elimination of the need for arsenic trioxide storage underground, 4) the reduction in the levels of arsenic and heavy metals in the aqueous effluents, and 5) the increased recovery of gold. For these reasons, pressure oxidation may replace 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 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 at the rate of 18 tonnes/day. Gold was recovered from the roaster calcine

Table IX – 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

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 operation in 1991 and roasting was discontinued at that time. A flowsheet of the new process at Campbell Red Lake is shown in Figure 7. The 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. Since there is some carbonate in the concentrate, the feed is preleached at atmospheric pressure in recycled autoclave discharge 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 and lined with lead, a fiberglass layer and 21/2 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 CIP circuit 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. Clearly, autoclaving eliminates the formation of sulphur dioxide entirely, fixes the arsenic in an insoluble form and immobilizes the associated heavy metals. The operating cost

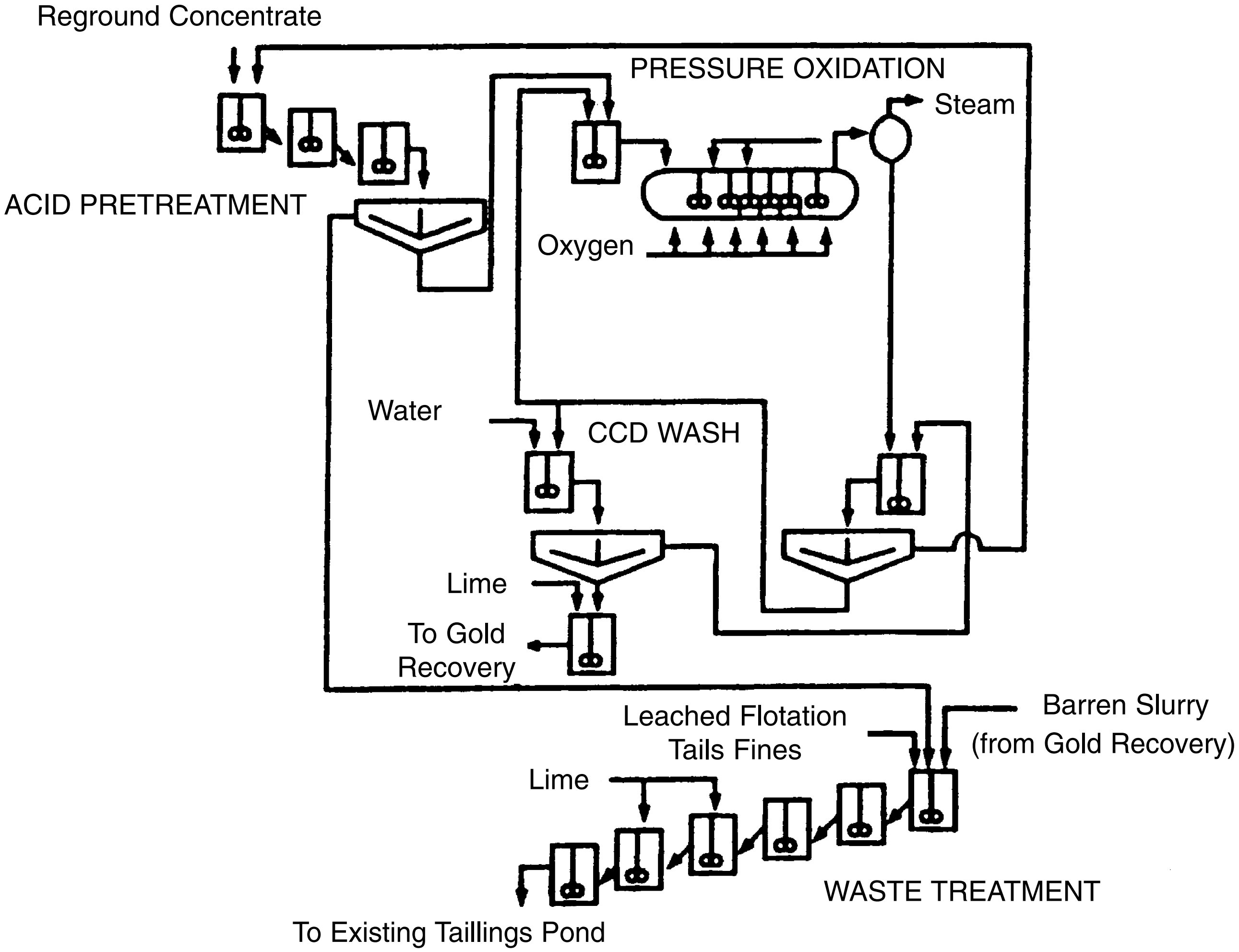

Fig. 7. Campbell Red Lake pressure oxidation plant (Anon., 1991)

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 for an overall benefit of \$70 per tonne for the pressure oxidation process (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. Initial solution 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, the 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% pulp 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 0.5 M H_2SO_4 solutions at temperatures > 150 °C. According to these researchers, arsenopyrite reacts with O_2 to yield elemental sulphur and sulphate with the latter being the dominant product. The formation of elemental sulphur is favoured 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 such as the oxidization of the initially formed As(III) 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 favoured by high slurry densities and low acidities in addition to higher temperatures. The ferric ion reaction product 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. They found that in the presence of SO_4^{2-} a series of hydrated ferric arseno-hydroxy-sulphate compounds formed. It was subsequently found that the precipitation of arsenic at pH<1, with a Fe/As ratio ≥1 and temperatures >150 °C, leads to the formation of crystalline and well-defined compounds (Swash and Monhemius, 1994; Carageorgos and Monhemius, 1994). At 150-200 °C and for Fe/As ratios of 1.5 or higher, crystalline scorodite is formed. Above 200 °C, the predominant phase is an unhydrated ferric arsenate-hydroxy-sulphate compound with the generic formula $Fe_3(AsO_4)_2SO_4OH$. If there is an excess of iron, basic iron sulphate, $FeSO_4OH$, is precipitated. Where the initial Fe/As molar ratio of the solution is near unity, the predominant phase at temperatures above ~150 °C has the approximate composition of $Fe_2(HAsO_4)_3 \cdot H_2O$. Table X summarizes the most important compounds identified so far which have been designated as Types I, II, III and IV (Monhemius and Swash, 1999).

Although the formation of scorodite is usually associated with autoclave operations, there is evidence that scorodite also may form at temperatures <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. 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 extensive homogeneous nucleation be prevented and this is achieved by maintaining S below $S_{cr,homo}$, which is the critical supersaturation level associated with the onset of homogenous nucleation. By maintaining $S<S_{cr,homo}$ and using seed at the same time, precipitation

Table X – Compounds formed in iron-arsenate hydrothermal systems (adapted from Swash and Monhemius, 1994, 1995).

Compound	Formula
Scorodite	$FeAsO_4 \cdot 2H_2O$
Type I	$Fe_2(HAsO_4)_3 \cdot xH_2O$ x<4
Type II	$Fe_4(AsO_4)_3(OH)_x(SO_4)_y$ x+2y = 3
Type III	$Fe_2(AsO_4)_x(HAsO_4)_y$
Type IV	$CaFe_2(AsO_4)_x(HAsO_4)_y$ x>2 and y<1

of scorodite on the seed crystals 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 stepwise neutralization path. Thus, crystalline scorodite was produced at 95 °C from a 3 M Cl^- solution, initially containing 2,000 mg/L As(V) and a Fe/As molar ratio of 1, by adding 2 g/L of 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 arsenic was precipitated as scorodite in 2 hours at 95 °C from solutions containing up to 10 g/L As at an As yield of >93%. It was noted that in sulphate media the precipitation of amorphous ferric arsenate (arsenical ferrihydrite) is inhibited at lower pH values which is a feature that 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 present in the effluent of the acid plant of a copper/gold 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 in a stoichiometric ratio to arsenic together with recycled scorodite/gypsum seed. A retention time of 4 to 6 hours was 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.

STABILITY OF SCORODITE AND RELATED 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)

$$\begin{aligned} &FeAsS + 14Fe^{3+} + 10H_2O \\ &\quad = 14Fe^{2+} + SO_4^{2-} + FeAsO_4{\cdot}2H_2O + 16H^+ \qquad (6) \end{aligned}$$

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. 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 long term laboratory tests on the stability of scorodite and related compounds in metallurgical 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 of 0.4 - 3.6 mg As/L was reported. Recently, Swash *et al.* (2000) carried out long term column leaching 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 high columns and once a 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 having a Fe:As ratio > 3:1 and is 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 out, however, that Swash and Monhemius (1995) 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 end member Fe(III) arsenates. These researchers recommend that in order to minimize the calcium content of iron arsenate compounds precipitated 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) 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 permitted discharge levels of arsenic are met only because of the slow kinetics of the transformation reaction which releases arsenic gradually 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 oxidation of the arsenopyrite is complete, arsenate activities decline and the pH increases causing scorodite to dissolve incongruently to iron oxyhydroxide and soluble arsenic acid.

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

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

There are also indications that crystalline arsenic(V) bearing 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 deposited in a sub-aqueous environment. Originally, a lined impoundment was created for the storage of autoclave residues 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. Consequently, combined oxidation residues/tailings were used to fill the impoundment. The geochemical behaviour of this material was extensively studied by McCreadie (1996) and McCreadie *et al.* (1998). These researchers found through mineralogical studies of the material in 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 ferric sulpho-arsenate phases, 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 phase, but some As 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 the ferric sulpho-arsenate phase and jarosite is occurring. There is evidence that the arsenate minerals are slowly decomposing to release soluble As(III) into the environment 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) environments can become anaerobic below ~2 metres of water. 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(V)-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(V)-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 the elevated concentrations of As found near the base of the impoundment are released by reductive dissolution. 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.

ARSENIC RESIDUES FROM PYROMETALLURGICAL OPERATIONS

Arsenic trioxide is a byproduct 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. Disposal of the collected arsenic is a problem because of the high water solubility and toxicity of As_2O_3. Several processes have been proposed to convert the As_2O_3-rich dusts into a marketable product or stable arsenic compounds (Riveros *et al.*, 2000; Valenzuela, 2000; Valenzuela *et al.*, 2000A). 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).

Kyle and Lunt (1991) conducted an investigation of disposal options for the arsenic trioxide produced in the roasting operations at the Western Mining Corporation Windarra nickel/gold facility in Australia. In this work, the As_2O_3-bearing dust was dissolved in water, and the dissolved arsenic was 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-bearing dust into cement was also evaluated. Their conclusions were that 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 indicated that this route is not economically viable unless cheap sources of the chemicals are available. Ferric arsenite, although insoluble, suffers from the same problem 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-bearing dust itself (arsenic content 11.9-17.8% As) or of precipitated 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. However, the long term stability of these solidified products 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, the 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 strong 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) in 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-rich dust and slurry which are stockpiled at the Con Mine, Yellowknife, Northwest Territories has been described by Geldart *et al.* (1992). These arsenical 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-rich dust is mixed with gold/arsenopyrite concentrate produced by the current flotation plant and is fed to the 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 produced high gold recoveries and liberated sufficient iron to react with the arsenic. A pilot plant campaign, based on the flowsheet shown in Figure 8, was carried out at Lakefield Research, Ontario. A patent application has been submitted on this process (Maltby, 1991).

In the pilot plant circuit, the autoclave feed was preconditioned to pH 2 with recycled acid to decompose carbonates, before being pumped into a 4 compartment horizontal autoclave. Lignosol was added at a concentration of 1 kg/t to disperse elemental sulphur. The autoclave was an externally heated 4 compartment titanium vessel 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 these conditions, the Fe(III) and the As(V) precipitate as insoluble crystalline ferric arsenate. During the process, the gold locked in the feed materials is liberated

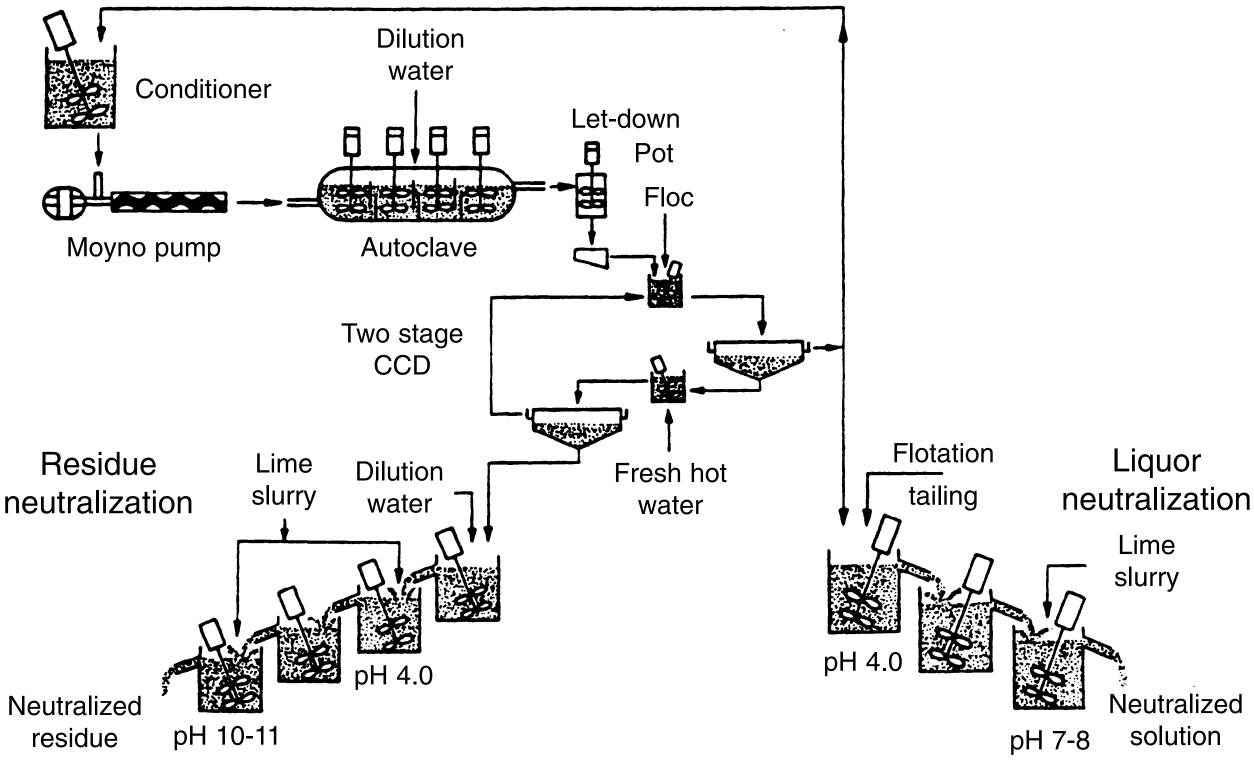

Fig. 8. Nerco pilot plant flowsheet (Geldart *et al.*, 1992)

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 only 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 circuit. The thickened solids were neutralized with lime slurry in two stages to pH 4 and then 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 satisfied 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 As_2O_3-rich 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:

$$Fe + 4HNO_3 = Fe(NO_3)_3 + NO_{(g)} + 2H_2O \qquad (8)$$

$$3As_2O_{3(s)} + 4HNO_3 + 7H_2O = 6H_3AsO_{4\,(aq)} + 4NO_{\,(g)} \qquad (9)$$

$$Fe(NO_3)_3 + H_3AsO_{4\,(aq)} + 2H_2O = FeAsO_4{\cdot}2H_2O_{\,(s)} + 3\,HNO_3 \qquad (10)$$

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) at temperatures between 115 and 145 °C. Iron oxides were evaluated 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 media. Thus, they are another potentially 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 effects of the Ca/As ratio of the solution, the precipitation pH and thermal treatment of the resulting precipitate on its stability were studied. Further, As was precipitated as ferrous arsenate or ferric arsenate with lime and Fe(II) or Fe(III) additions. The effects of the Fe/As ratio in solution, pH, temperature of precipitation and the Fe(II)/Fe(III) ratio on the stability of the resulting precipitate were reported. Their data showed a generally low solubility for high iron ferric arsenates (arsenical ferrihydrite), but also indicated that the solids were more stable when precipitated at lower pH (pH 3 as opposed to pH 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 solutions.

One of the major arsenic bearing waste byproducts from smelting is flue dust. Vast quantities of flue dust presently exist; some contain up to 20% As in addition to Bi, Sb and other metals. Several procedures have been developed to treat smelter 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 also describe a hydrometallurgical approach to treat copper smelter precipitator dusts produced at the Noranda Horne smelter. The process whose technical feasibility was demonstrated in a pilot plant comprises leaching the dust in zinc plant spent electrolyte, recovering a Pb/Ag residue by centrifugation, chlorinating the centrate to oxidize trivalent arsenic to the pentavalent state, evaporating the solution to 70% H_2SO_4 to recover zinc and cadmium as crystalline sulphates and to eliminate halogens and neutralizing 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 $16,000,000(Cdn) (1983) and the direct operating costs (including freight charges) to be $335(Cdn)/tonne of dust. In breaking down the costs, over 30% of the equipment costs were related to solid/liquid separation requirements and 25% were 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, 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. Oxygen (sometimes air) is used 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. The process was tested on a pilot plant scale at Hazen Research. The integrated circuit, including continuous recycle, operated from August to October 1989 when several tons of flue dust were processed. Based on this pilot program, the process was deemed technically feasible and produced commercially saleable 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 modest amounts of arsenic (Table XI). Sodium sulphide solution was used as the leaching agent in a reactor at 80 °C. The optimum conditions are leaching temperature, 80 °C; leaching time, three hours; sodium sulphide concentration, 130 g/L and the ratio of solids 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 concentration in solution depends on the initial As content of 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 any of the arsenic precipitates is not known.

Ke and Qin (2000) developed a hot sulphuric acid leaching process to treat the 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. By carefully controlling the leaching conditions (120-130 °C, 1 M H_2SO_4 and the absence of O_2), about 90% of the arsenic was leached, whereas most of the copper remained in the residue as cupric sulphide. The dissolved arsenic and iron were oxidized and precipitated as 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 using standard technologies.

Zhang *et al.* (1998) studied the treatment of flue dusts generated by Australian nickel smelters. These dusts often contain arsenic as As(III) oxide which must be recovered and disposed in addition to 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, H_2SO_4 at pH 1.5, a SO_2/O_2 gas mixture containing 2% SO_2 and pH 1.5, a caustic leach with 10% NaOH and a 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. The dilute H_2SO_4 solution at pH 1.5 selectively leached up to 25% of the arsenic with very little nickel extraction. Sufficient Fe(II) for the eventual coprecipitation 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.

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 most common arsenic disposal materials (Table XII).

In the metallurgical 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 tempera-

Table XI – 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

Table XII – 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 (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 $CaCO_3$ and soluble arsenic species • With time, the buffering effect of the excess lime is reduced by dissolution and carbonation and this leads to lower 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

tures. Lime precipitation has been widely used, but it has been extensively demonstrated that calcium arsenate compounds are not stable after the excess lime has been consumed. A crystalline calcium arsenate can be obtained by high temperature calcination. This phase is apparently significantly less soluble than the material before heating. However, not enough information is available on this option and the long term stability of the calcined products. Extensive research carried out by many workers has established that arsenical ferrihydrite is stable in tailings ponds over the pH range 4-7 provided 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 coprecipitated 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. Scorodite ($FeAsO_4 \cdot 2H_2O$), which commonly forms under pressure oxidation conditions is 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 arsenosulphate compounds which form at high temperatures and in the presence of sulphate (Type I) appear to be less stable than scorodite.

Each material has its own advantages and disadvantages. Arsenical ferrihydrite is easier to form since it requires no heating. However, the iron consumption is high (Fe/As ≥ 3) and the As must be oxidized to As(V) which can be a relatively inefficient process at ambient temperature and pressure. The long term stability of arsenical ferrihydrite is in question because ferrihydrite is thermodynamically unstable with respect to goethite. 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. For practical purposes, arsenical ferrihydrite can be considered stable provided that its Fe/As molar ratio is higher than 3, the pH is slightly acidic and that it does not come in contact with reducing substances such as reactive sulphides or reducing conditions such as deep water, bacteria or 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 the pH stability range of the ferrihydrite. Arsenical ferrihydrite is voluminous and relatively difficult to filter and dewater because it is poorly crystalline. By contrast, crystalline ferric arsenate or scorodite is more compact and easier to filter. The iron demand for scorodite is 1/3 or less than that for making arsenical ferrihydrite. Scorodite is also more thermodynamically stable than its amorphous counterpart, although it dissolves incongruently at pH >4 and it may decompose under reducing conditions or in the presence of reducing bacteria. The formation of scorodite is expensive because it has traditionally required high temperatures which are normally obtained by the use of 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 either approach would significantly lower the cost and would make scorodite an obvious option for arsenic disposal.

According to Swash *et al.* (2000), from the point of view of the safe disposal of arsenic, there is no clear experimental evidence yet 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 6 wt% arsenic and is a gelatinous material which is very difficult to densify beyond 20-25 wt% solids. These disadvantages of ferrihydrite precipitation, however, have to be weighed against the extra capital and operating costs of the pressurized equipment traditionally required for the formation of scorodite.

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