Spring 4-2023

Treatment of Arsenic-Bearing Minerals and Fixation of Recovered Arsenic Products: An Updated Review

Larry G. Twidwell

Treatment of Arsenic-Bearing Minerals and Fixation of Recovered Arsenic Products: An Updated Review

L.G. Twidwell

(Emeritus Professor Montana Technological University
Metallurgical and Material Engineering Department)
LTwidwell@MTECH.edu; enviromet1@gmail.com

INTENT OF THIS PRESENTATION (The following presentation is an expanded and updated version of the previous SME Mineral Processing and Extractive Metallurgy Handbook Chapter 9.22 (*"Arsenic Production, Commodities, and Fixation"* Editors: R.C. Dunne, S.K. Kawatra, and C.A. Young). The update covers the period February 2019 to August 2021). The **TABLE OF CONTENT** is presented at the end of this review.

Mineral processing and extractive metallurgical operations have created and are creating appreciable arsenic bearing wastewater and waste solid products that have to be handled, treated for recycle, or treated for environmentally safe disposal. At present there are intense research and operational activities being conducted to provide the best viable processing procedures to ensure that the mineral processing and extractive metallurgical industries are profitable and environmentally secure. The focus of this presentation is on the element arsenic, even though many other deleterious elements may also be present in ores and concentrates. Numerous base metal resources contain arsenic bearing minerals, especially resources containing mineral sulfides. Information on presently treated metal-bearing resources and potential new resources is voluminous, especially for those containing arsenic mineralization. The influence of elevated arsenic concentrations in the treatment of copper-arsenic sulfides and to a lesser extent the treatment of copper-gold-arsenic sulfides are considered in this presentation. Because of chapter page limitations not all treatment processes are discussed, however, examples are provided to illustrate arsenic problems and industrial solutions. **The major emphasis of this presentation has been placed on the present state-of-the-art for arsenic immobilization/fixation and long-term storage considerations.**

BACKGROUND

Arsenic is the 20th most abundant element in the earth's crust. It rarely is found in its elementary form but is often associated with oxygen and sulfur. It is widely found in commonly processed base metal ores such as copper, lead, zinc and is often associated with gold and silver bearing ores. Arsenic minerals may be found as arsenides, sulfides, sulfosalts, oxides and arsenates (Valenzuela, 2000). Arsenic release has occurred originating from human activities, including metal smelting, chemical production, coal combustion, waste disposal practices, and widespread application of pesticides and fungicides (SME 2015).

"Atmospheric arsenic emissions from smelting represent the largest contribution of arsenic from the mining and metals industry by far and have been the focus of pollution control technologies and increasingly stringent regulations. Like other industries, the mining, mineral processing and extractive metallurgical industries are strictly regulated and monitored by multiple government departments, agencies, and bureaus at the local, state and federal levels. Regulations, including EPA's Resource Conservation and Recovery Act (RCRA) and Land Disposal Restrictions (LDR), have both narrative and numerical criteria and standards for protection of human health, aquatic life, air quality, endangered and threatened species, disposal of solid wastes and the environment" (SME 2015).

ARSENIC CONSUMPTION AND PRODUCTION IN THE UNITED STATES

Statistical information for arsenic production and commodities is provided yearly by the United States Geological Survey (USGS) in their publication, Mineral Commodity Summaries (USGS 2021). *"Arsenic trioxide and primary arsenic metal have not been produced in the United States since 1985. The principal use for arsenic trioxide was for the production of arsenic acid used in the formulation of chromated copper arsenide (CCA) preservatives for the pressure treating of lumber used primarily in nonresidential applications. Three companies produced CCA preservatives in the United States in 2020. The grids in lead-acid storage batteries were strengthened by the addition of arsenic metal. Arsenic metal was also used as an antifriction additive for bearings, to harden lead shot, and in clip-on wheel weights. Arsenic compounds were used in herbicides and insecticides. High-purity arsenic (99.9999%) metal was used to produce gallium-arsenide (GaAs) semiconductors for solar cells, space research, and telecommunications. Arsenic also was used for germanium-arsenide-selenide specialty optical materials. Indium-gallium-arsenide (InGaAs) was used for short-wave infrared technology"* (USGS 2021).

The USGS has summarized the relative distribution of arsenic into its major products (agricultural chemicals, pressure treated wood, glass, nonferrous alloys and electronic); their results are presented in Figure 1 illustrating the tonnages (metric tons/year) produced as a function of time. Note that the presented distributions only cover the period 1975-2002. Except for the graph of consumption which covers the period to 2020 (Figure 2), Most of the U.S. consumption has been based on imported arsenic trioxide. **There has been a major industrial shift (beginning in approximately 2000) away from recovery of arsenic and arsenic compounds that can be marketed to controlling its removal/immobilization, fixation, and environmentally safe long-term storage.**

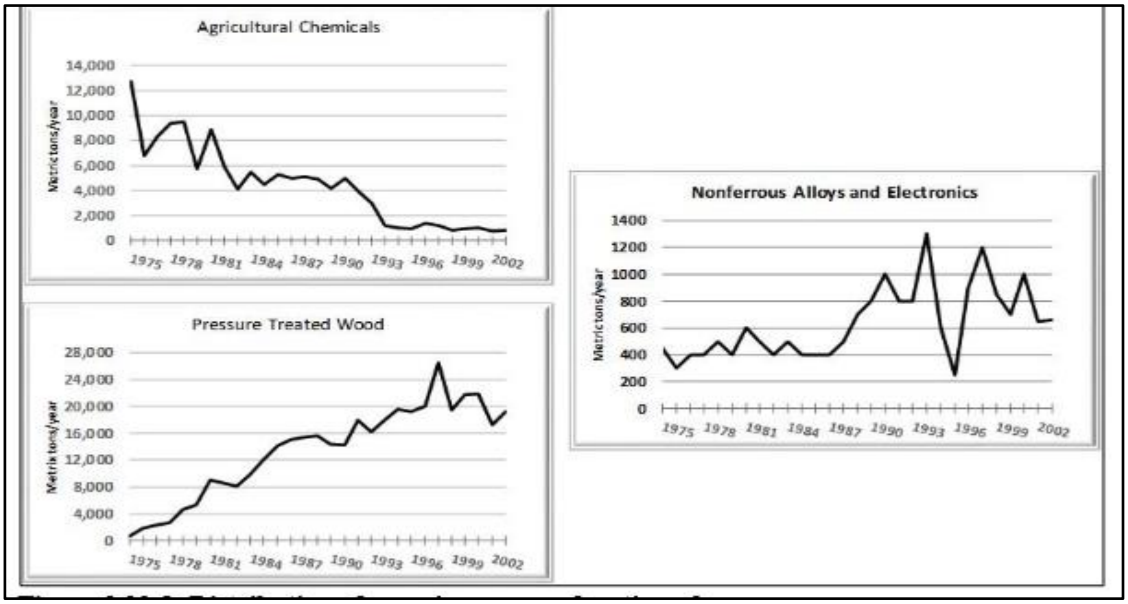


Figure 1. Distribution of arsenic uses as a function of year
Source: USGS 2021

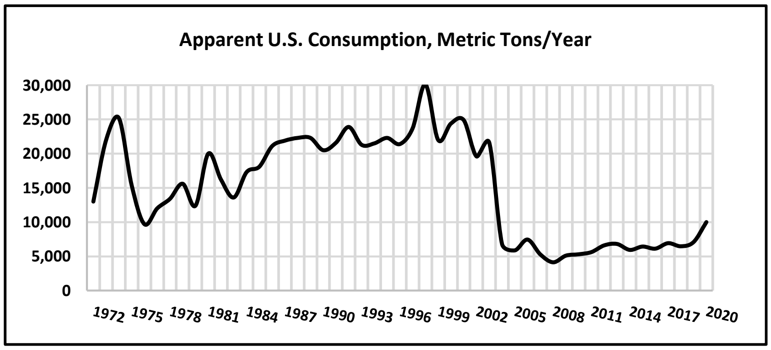


Figure 2. Apparent consumption of arsenic
Source of data used in constructing this figure: USGS 2021

Recycling

“*Arsenic metal was contained in new scrap recycled during GaAs semiconductor, manufacturing. Arsenic-containing process water was internally recycled at wood treatment plants where CCA was used. Although scrap electronic circuit boards, relays, and switches may contain arsenic, no arsenic was known to have been recovered during the recycling process to recover other contained metals. No arsenic was recovered domestically from arsenic-containing residues and dusts generated during nonferrous smelters in the United States”.* (USGS 2021)

Would Resources

“Arsenic may be obtained from copper, gold, and lead smelter flue dust as well as from roasting arsenopyrite, the most abundant ore mineral of arsenic. Arsenic has been recovered from realgar and orpiment in China, Peru, and the Philippines and from copper-gold ores in Chile; and arsenic was associated with gold occurrences in Canada. Orpiment and realgar from gold mines in Sichuan Province, China, were stockpiled for later recovery of arsenic. Arsenic also may be recovered from enargite, a copper mineral. Arsenic was produced at the hydrometallurgical complex of Guermassa, near Marrakech. Morocco, from cobalt-arsenide ore from the Bou-Azzer Mine”. (USGS 2021)

“Table 1. World production and reserves (gross weights): Source USGS 2021

	Production (arsenic trioxide)	
	2019	***2020***
United States	*-*	*-*
Belgium	***1,000***	***1,000***
Bolivia	***120***	***100***
China	***24,000***	***24,000***
Iran	***110***	*-*
Japan	***45***	***40***
Morocco	***5,500***	***5,500***
Russia	***1,500***	***1,500***
World Total (rounded)	***32,300***	***32,000”***

“World reserves data are unavailable but are thought to be more than 20 times world production”

Events, Trends, and Issues

“China and Morocco continued to be the leading global producers of arsenic trioxide, accounting for about 90% of estimated world production and supplying almost all of United States imports of arsenic trioxide in 2020. China was the leading world producer of arsenic metal and, with Hong Kong, supplied about 94% of United States arsenic metal imports in 2020. High-purity (99.9999%) arsenic metal was used to produce GaAs, indium-arsenide, and InGaAs semiconductors that were used in biomedical, communications, computer, electronics, and photovoltaic applications” (USGS 2021).

ENVIRONMENTAL REGULATIONS

The reader should be aware that a companion chapter in the referenced SME Mineral Processing and Extractive Metallurgy Handbook (*Environmental Considerations for Treatment of Effluent Waste Solutions and Solid Waste Products, Chapter 10.9*, Twidwell 2019) is focused on treatment technologies and environmental regulations that are important to mineral and extractive metallurgical processing, including the Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA). These regulations directed EPA to aggressively manage some hazardous waste and the Act restricted (banned) some hazardous waste from disposal without further stabilization, i.e., The Land Ban Restrictions (LBR) were initiated. Other environmental regulations have been formulated through the Clean Water Act and its amendments, the CERCLA (superfund) Act, and the Clean Air Act and its amendments that have significant consequences to the mineral processing and extractive metallurgical industries. Reference to the SME Mineral Processing and Extractive Metallurgy Handbook Chapter 10.9 is recommended.

TREATMENT OF ARSENIC CONTAINING RESOURCES

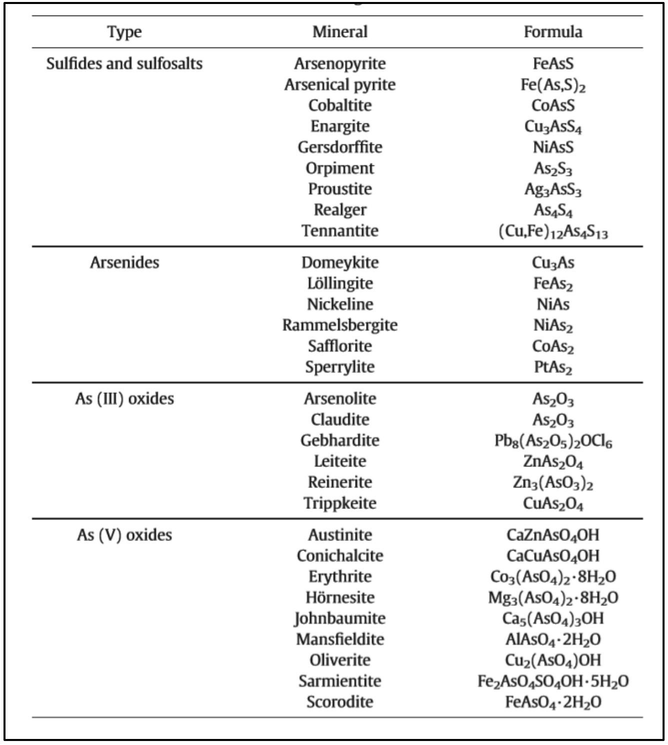
The growing demand for copper, depletion of high-grade ores, and a more robust regulatory environment has required and is requiring the metallurgical industry to treat more complex ores. In general, the complex ores that must be treated in the copper and gold industries contain arsenic bearing minerals. The presence of these minerals in mined copper sulfide deposits has, for decades, been processed by roasting and smelting processes. The arsenic presence was not considered a detriment in the past because arsenic trioxide was recovered as a marketable product which, of course, is not true today. Today the presence of arsenic in concentrates is considered a detriment and copper smelters, generally, require that their concentrates contain less than 0.5% arsenic.

Complex ores containing higher levels of arsenic sulfidic minerals, such as enargite, luzonite, tennantite, arsenical pyrite, and arsenopyrite must be considered for processing. *Under near-surface oxidizing conditions, sulfide minerals become unstable and their oxidative dissolution releases As. The alteration of arsenic sulfides can cause formation of secondary As-minerals such as scorodite* ($FeAsO_4{:}2H_2O$)*, yukonite* ($Ca_3Fe(AsO_4)_2(OH)_3.5H_2O$)*, arsenolite* ($As_4O_6$)*, and pharmacosiderite* ($KFe_4(AsO_4)_3(OH)_4{:}(6\text{-}7)H_2O$) *if saturation is reached with respect to these phases. Arsenic released from arsenic sulfide alteration can also be sorbed onto secondary minerals including schwertmannite* ($Fe_{16}O_{16}(OH)_{12}(SO_4)_2$) *and jarosite* ($KFe_3(OH)_6(SO_4)_2$) *mainly encountered in gold mine tailings (*Coudert et al. 2020). Safazadeh and Miller (2016) have summarized the need and problem facing the mineral processing and extractive metallurgical copper and gold industries*: “the downstream processing of high-arsenic copper concentrates represents a significant metallurgical challenge in terms of both arsenic separation and also its stabilization in an environmentally benign form that fulfills the current and future environmental policies”*. Therefore, there has been a current flurry of publications that address and discuss current processing capabilities and the areas where additional emphases should be placed. Recent literature **reviews** are especially important to evaluate the present state-of-the-art, define future processing treatment technologies and to ensure the handling, immobilization, and disposal practices are appropriate and are conducted in an environmentally safe manner. The following review publications are recommended: Filippou et al. 2007; Drahota and Filippi 2009; Long et al. 2012; Safazadeh et al. 2014a and 2014b; Safazadeh and Miller 2016; Lane et al. 2016; Nazari et al. 2017; Schlesinger 2019; Twidwell 2018, 2019, 2019b; and Coudert et al 2020.

Arsenic Mineral Sulfide Associations

Arsenic sulfide minerals are often associated with other sulfide minerals, especially in copper, gold and silver deposits. A list of arsenic bearing sulfide minerals is presented in Table 2 (Nazari et al. 2017). Others have suggested that the breakdown of known arsenic compounds is: 60% arsenates, 20% sulfides/sulfosalts, 10% oxides, and the remainder are arsenite, arsenides, and native arsenic (Bowell and Parshley 2001; Drahota and Filippi 2009). Gonzalez and Monhemius (1988) state that there are over 180 known arsenic-bearing minerals identified. Others suggest there are over 300 arsenic containing minerals (Zhang et al. 2019).

Table 2. List of common arsenic-containing minerals



Type	Mineral	Formula
Sulfides and sulfosalts	Arsenopyrite	$FeAsS$
	Arsenical pyrite	$Fe(As,S)_2$
	Cobaltite	$CoAsS$
	Enargite	Cu_3AsS_4
	Gersdorffite	$NiAsS$
	Orpiment	As_2S_3
	Proustite	Ag_3AsS_3
	Realger	As_4S_4
	Tennantite	$(Cu,Fe)_{12}As_4S_{13}$
Arsenides	Domeykite	Cu_3As
	Löllingite	$FeAs_2$
	Nickeline	$NiAs$
	Rammelsbergite	$NiAs_2$
	Safflorite	$CoAs_2$
	Sperrylite	$PtAs_2$
As (III) oxides	Arsenolite	As_2O_3
	Claudite	As_2O_3
	Gebhardite	$Pb_8(As_2O_5)_2OCl_6$
	Leiteite	$ZnAs_2O_4$
	Reinerite	$Zn_3(AsO_3)_2$
	Trippkeite	$CuAs_2O_4$
As (V) oxides	Austinite	$CaZnAsO_4OH$
	Conichalcite	$CaCuAsO_4OH$
	Erythrite	$Co_3(AsO_4)_2 \cdot 8H_2O$
	Hörnesite	$Mg_3(AsO_4)_2 \cdot 8H_2O$
	Johnbaumite	$Ca_5(AsO_4)_3OH$
	Mansfieldite	$AlAsO_4 \cdot 2H_2O$
	Oliverite	$Cu_2(AsO_4)OH$
	Sarmientite	$Fe_2AsO_4SO_4OH \cdot 5H_2O$
	Scorodite	$FeAsO_4 \cdot 2H_2O$

Source: Nazari et al. 2017 p 260

Occurrence of Arsenic Bearing Minerals

Enargite, tennantite, (copper/arsenic/sulfur) and arsenopyrite (iron/arsenic/sulfur) are common copper/arsenic and iron/arsenic minerals present in many of the world's base metal sulfide ores, especially copper, gold, and lead bearing ores. The USGS notes that *"85 porphyry copper deposits containing copper/arsenic minerals exist throughout the world "*(USGS 2021). Gold/silver ores are often associated with pyrite, auriferous arsenopyrite, tetrahedrite, tennantite, and in some cases enargite and tennantite (Gonzalez and Monhemius 1988).

Safarzadeh et al. (2014b) have listed several enargite and/or tennantite containing properties, e.g., enargite was first identified as an abundant mineral at Butte Montana. The Anaconda Smelter in Anaconda Montana (closed in 1985) processed concentrates from the Berkeley Pit ores in Butte, Montana containing arsenic contents of over ten percent for many years because the company produced arsenic trioxide as a saleable product. Over 400,000 tons of stockpiled arsenic bearing waste were stabilized by cement/lime encapsulation with subsequent storage in a membrane lined class "C" repository. Other smelters have treated high arsenic-bearing concentrates back when there was a market for arsenic trioxide, e.g., the El Indio plant (now closed) treated concentrates containing up to ten percent arsenic until it closed in 2002. U.S. arsenic-bearing deposits are not uncommon, e.g., such deposits exist at Goldfield and Pyramid, Nevada and Summitville, Colorado. Other important world deposits include Cheolpec, Bulgaria; Recsk, Hungary; Sardinia, Italy; Lepanto, Philippines; Frieda River, Papua New Guinea; La Coipa, Chile; and Bor, Serbia (Safazadeh et al. 2014b).

Filippou et al. (2007 Review) conducted a literature review for treatment of copper/arsenic minerals. The authors have listed enargite containing copper ore deposits that exist but which had not come into production (as of 2007): e.g., Tampakan and Southern Mindanao, Philippines; Colquijirca mining district, Central Guinea; and Furtei mine in Sardinia.

Long et al. (2012 Review) also reviewed the literature for copper/arsenic mineral removal from copper concentrates and have identified other enargite, tennantite (along with other arsenic minerals) containing deposits, e.g., Andean Porphyry copper deposits in Chile contain enargite and tennantite. Cananea chalcopyrite and enargite-copper deposits in Mexico; Chelopech mine copper-enargite sulphosalts in Bulgaria; NorthParkes chalcopyrite, bornite and tennantite in Australia; Gortdrum deposits in Ireland contain tetrahedrite and tennantite; the Iberian Pyrite Belt through Southern Portugal and Spain contain copper, lead, zinc and tin and arsenopyrite, tennantite and tetrahedrite.

Pyrometallurgical/Hydrometallurgical Processing

Copper and Gold/Silver Production

Present day conventional copper production technologies are described in the referenced SME Handbook: Chapters 9.1 (*Hydrometallurgy*; Anderson 2019) and 9.2 (*Pyrometallurgy*; Schlesinger 2019). For the reader who is interested in the details of conventional copper production and gold processing technologies, two texts are recommended, i.e., the *Extractive Metallurgy of Copper* (Fifth Edition) (Schlesinger et al. 2011) and the *Gold Ore Processing Handbook*, (Adams et al., 2016).

Most conventional treatment to recover copper from sulfide concentrates is via pyrometallurgical processing, i.e., approximately 75-80 percent of primary copper is/has been produced by this method for decades. The other 20-25 percent of the world's copper is recovered by hydrometallurgical processing of copper oxide ores and concentrates.

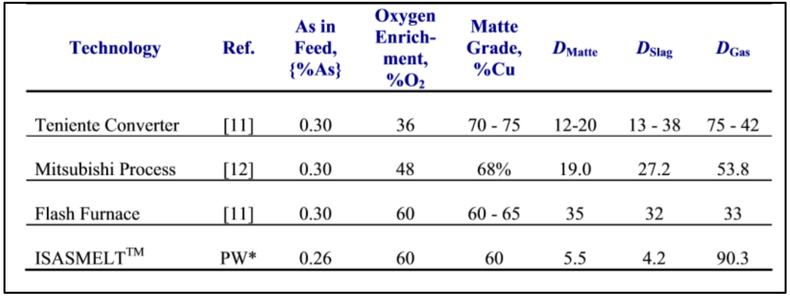
Present day pyrometallurgical processing of copper sulfides include the use of various ambient and elevated temperature unit operations, e.g., flotation concentration of sulfide minerals, roasting, smelting, converting, sulfuric acid production, casting and electrorefining. Arsenic (and other undesirable elements) and its compounds may be present in the concentrates, dusts, unreacted minerals, and condensed fumes from baghouses, dry and wet electrostatic precipitators, wet gas scrubbers, and sulfuric acid production. The majority of arsenic is volatized during the elevated temperature processing as arsenic trioxide (As_2O_3) and/or compounds of arsenic sulfide (As_2S_3) in the flue dust and gas cleaning products.

During the mineral processing operations arsenic sulfide minerals distribute to concentrates along with other non-arsenic sulfide bearing minerals and if the arsenic presence is >0.2% (Tayebi-Khorami et al. 2017) there are smelter penalty charges; and if >0.5% the concentrate is likely to be rejected from treatment via smelting. Collection of arsenic from the various unit operations, and the associated environmental regulations and health issues resulting from the handling, transportation, and impoundment/immobilization requirements have caused most currently operating smelters to shy away from treating resources with appreciable arsenic content.

Conventional Industrial Treatment of low-arsenic bearing copper concentrates

For treatment of concentrates with acceptable arsenic concentration, the collected arsenic and other impurity bearing dusts and smelting residues are normally recycled and blended with the incoming feed concentrate. Therefore, the arsenic bleed from the smelting system is primarily dissolved arsenic in the slag phase and there is no need to form disposable arsenic-bearing waste products. An example of the distribution of arsenic to the slag phase for four current technologies treating low arsenic-copper concentrates is presented in Table 3. Normally the arsenic content of smelting slags vary but, in general, they are <0.1% and, therefore can be safely disposed of in the smelter non-hazardous storage site.

Table 3. Arsenic distribution for four copper smelting technologies



Technology	Ref.	As in Feed, {%As}	Oxygen Enrich-ment, $\%O_2$	Matte Grade, %Cu	D_{Matte}	D_{Slag}	D_{Gas}
Teniente Converter	[11]	0.30	36	70 - 75	12-20	13 - 38	75 - 42
Mitsubishi Process	[12]	0.30	48	68%	19.0	27.2	53.8
Flash Furnace	[11]	0.30	60	60 - 65	35	32	33
ISASMELT^{TM}	PW*	0.26	60	60	5.5	4.2	90.3

D values are the percent copper distributed to the noted product.
Source: Alvear et al. 2006 p 683.

Example treatment of high-arsenic flue dust to form a disposable arsenic product

A joint Japanese-Chilean cooperative project for the development of a process to treat smelter dust from a Teniente furnace containing ~11% arsenic has been reported by Ichimura et al. (2007) A pilot scale demonstration (sized at 1/10 of expected operation scale) is described. The goal of the project was to recover copper for recycle to a smelting operation and to stabilize arsenic as scorodite ($FeAsO_4{:}2H_2O$). The project demonstrated that copper could be recovered and treated in an electrorefining circuit and arsenic could be immobilized by the formation of scorodite. The dust composition is presented in Table 4. The authors proposed dust treatment flowsheet is presented in Figure 3. The following conditions were reported for successfully removing arsenic from the final sulfuric acid leach solution: ambient pressure, temperature 95ºC, initial pH 1.25, time 12 hours, and Fe/As molar ratio 1.3. These conditions favor the formation of scorodite rather than amorphous ferrihydrite (described later). The scorodite, as a function of Fe/As molar ratio (1.2-3.6) and leachability (using the U.S. EPA Toxicity Characterization Leach Procedure (TCLP) Method 1311 regulatory test (EPA 1992) is presented in Table 5. The results showed an arsenic extraction of 0.6-12.6 mg/L; most results were <5 mg/L. The TCLP test results, in order for the waste to be considered non-hazardous, must be <5 mg/L arsenic.

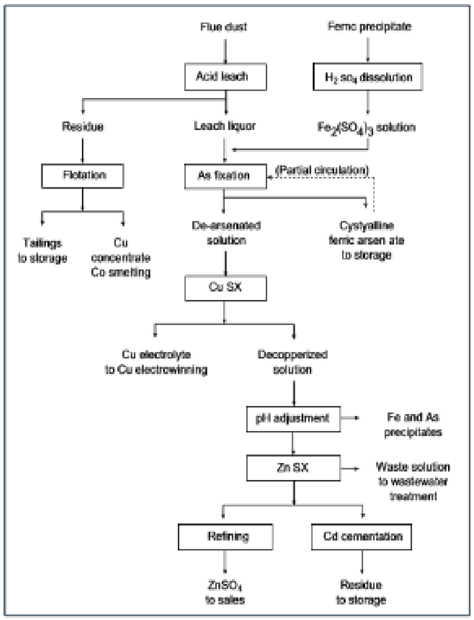
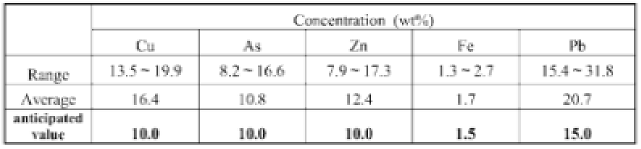


Figure 3. Process flowsheet for treatment of Teniente furnace dust *Source*: Ichimura et al. 2007 p 278.

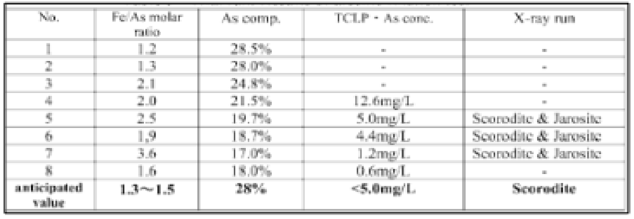
Table 4. Composition of Teniente furnace dust



	Concentration (wt%)				
	Cu	As	Zn	Fe	Pb
Range	13.5 ~ 19.9	8.2 ~ 16.6	7.9 ~ 17.3	1.3 ~ 2.7	15.4 ~ 31.8
Average	16.4	10.8	12.4	1.7	20.7
anticipated value	**10.0**	**10.0**	**10.0**	**1.5**	**15.0**

Source: Ichimura et al. 2007 p 277.

Table 5. TCLP test results for leaching



No.	Fe/As molar ratio	As comp.	TCLP - As conc.	X-ray run
1	1.2	28.5%	-	-
2	1.3	28.0%	-	-
3	2.1	24.8%	-	-
4	2.0	21.5%	12.6mg/L	-
5	2.5	19.7%	5.0mg/L	Scorodite & Jarosite
6	1.9	18.7%	4.4mg/L	Scorodite & Jarosite
7	3.6	17.0%	1.2mg/L	Scorodite & Jarosite
8	1.6	18.0%	0.6mg/L	-
anticipated value	**1.3～1.5**	**28%**	**<5.0mg/L**	**Scorodite**

Source: Ichimura et al. 2007 p 286.

According to the International Mining newsletter (IM, 2017) there are only four copper smelters in the world that can presently treat high arsenic concentrates: "*Tsumeb, Namibia; Altonorte, Chile; Guixi, China; and Horne, Canada. Tsumeb is the only option for treating large volumes of very high-As concentrates with >1% As".* It is also stated in the newsletter that the arsenic content in mines that are producing complex concentrates include: Marcapunta Peru, 8% As; Chelopech Bulgaria, 6% As; and Chuquicamata Chile, 1.2% As.

Mineral Processing Flotation for arsenic removal from copper sulfide concentrates

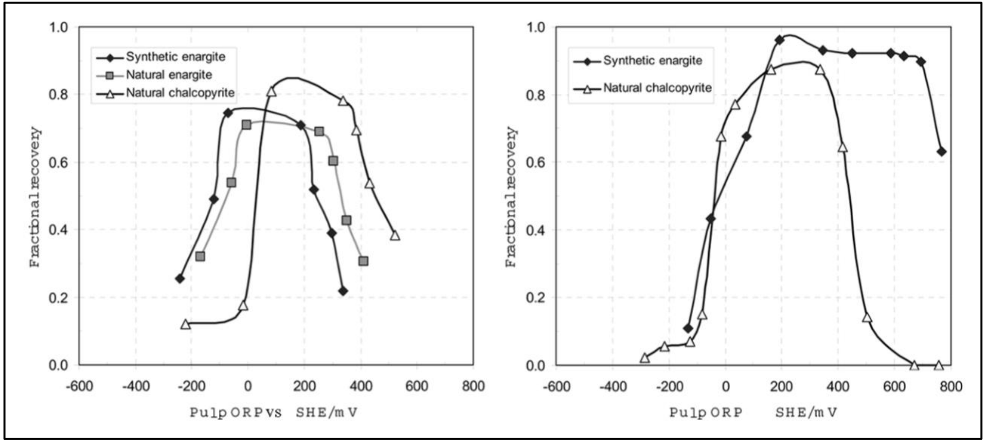
In most cases it is desirable to remove or partially remove arsenic-bearing minerals from a sulfide concentrate before the concentrate enters the pyrometallurgical processing sequence. Long et al. (2012) and Filippou et al. (2007) describe possible approaches for separating enargite and tennantite from non-arsenic containing copper sulfides. A few generalities are presented here: "*the separation of copper/arsenic minerals from non-copper gangue minerals (pyrite, pyrrhotite, sphalerite and galena) is easy because enargite does not exhibit natural floatability. However, what is more difficult is the separation of enargite and tennantite from other copper sulphides, such as chalcocite, covellite, and chalcopyrite*" (Filippou et al. (2007*)*, i.e., the arsenic minerals end up in the processed concentrate which then enters the smelting unit operations. In the past this result was desirable for those smelters that produced marketable arsenic trioxide.

Numerous study results have been reported that have demonstrated that successful flotation separation of enargite and tennantite (and other arsenic-sulfide minerals) from copper sulfides such as chalcocite, covellite, chalcopyrite. What is apparent from the literature is that the arsenic mineral separations are dependent on several factors, including mineralogical make-up of the concentrate, particle size distribution, pre-oxidation of the flotation pulp (or not), type of collector, selection and use of depressants, gas sparging, controlled dissolved oxygen content, and pH. However, the flotation separations are, for some arsenic mineral make-ups especially dependent on proper E_H (solution potential) to control the surface oxidation characteristics of the arsenic mineral sulfide or associated metal sulfides and metal oxides (Filippou et al. 2007; Ma et al. 2009; Long et al. 2012; Plackowski et al. 2014; and Chimonyo et al. 2017). Brief descriptions of the separations are presented by the authors listed above. Details of the separations are presented in the individual study publications. A few recommended publications are listed here:

- enargite, tennantite separation from covellite, chalcocite, and chalcopyrite (Fornasiero et al. 2000, 2001)
- enargite, tennantite from chalcocite (Huch 1993)
- enargite separation from chalcopyrite (Menacho et al. 1993; Yen et al. 2000; and Guo and Yen 2005)
- NorthParkes copper-gold concentrate used for separation of tennantite from chalcopyrite and bornite (Smith and Bruckard 2007).

Filoppou et al. (2007) present Figures 4 and 5 as examples to illustrate the possible separation of enargite from chalcopyrite to show the effect of E_H and pH (pH 9 and 10). The authors note that enargite can be floated from chalcopyrite at an E_H potential of zero mV (pH 9) or the reverse can be achieved at a potential of +350 mV.

Two additional example studies are reported here to illustrate the importance of pulp potential control. Senior et al. (2006) investigated single mineral flotation using pH and E_H control to form a basis for the possible beneficiation of Tampakan deposits in the Philippines. Their investigation was conducted using single mineral pulps (enargite, chalcocite, cuprite, and chalcopyrite) over the E_H range -500 to + 500 mV and pH values of 8 and 11. Their results for possible separation using E_H and pH control are presented in Figures 6, 7, 8. The authors conclusions were that pH and E_H conditions could be set for effective separations of two component copper sulfides. This flotation work was followed by studies on an actual Tampakan porphyry copper-gold ore (not on single minerals) primarily containing enargite, chalcopyrite and bornite (Tayebi-Khorami et al. 2017). The mineralogical make-up of the studied samples is presented in Table 6. Two arsenic bearing ore samples (0.64% and 0.57%) were studied. Particle size, pulp E_H control, -200 to +400 mV and pH 11 were investigated. The results of the study demonstrated that significant differences in flotation separations can be observed for sample that show little difference in arsenic content and that the presence of gangue mineral content may be very important. The authors proposed flowsheet is presented in Figure 8.



Figures 4 and 5. Enargite-chalcopyrite flotation recoveries against pulp ORP (On left: pH 9.0, 20 mg/L potassium amyl xanthate, Na_2S and $KMnO_4$ used for ORP adjustment (Yen and Tajadod 2000). On right: pH 10.0, 14 mg/L potassium amyl xanthate, Na_2S and NaOCl used for ORP Adjustment (Guo and Yen 2005). *Source*: Filippou et al. 2007 p 259.

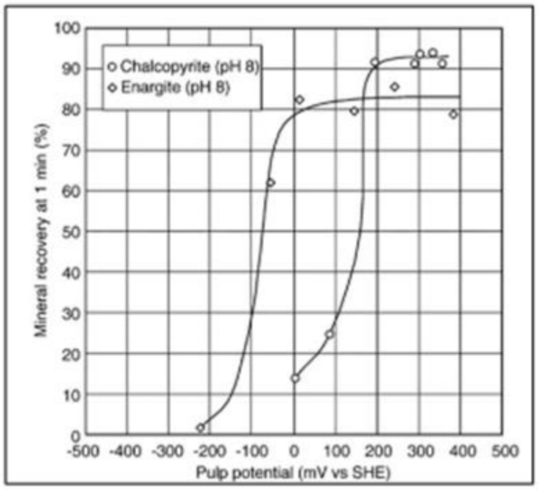


Figure 6. Enargite and Chalcopyrite recovery at 1 minute and pH 8 as a function of pulp potential (enargite 20 g/t KEX, stainless steel mill, chalcopyrite; 40 g/t KEX, glass mill)
Source: Senior et al., 2006 p 22.

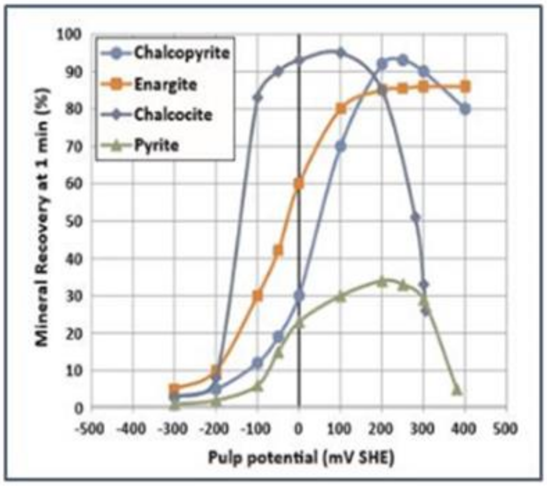


Figure 7. Chalcopyrite, Enargite, Chalcopyrite, and Pyrite recovery at 1 minute and pH 11 as a function of pulp potential

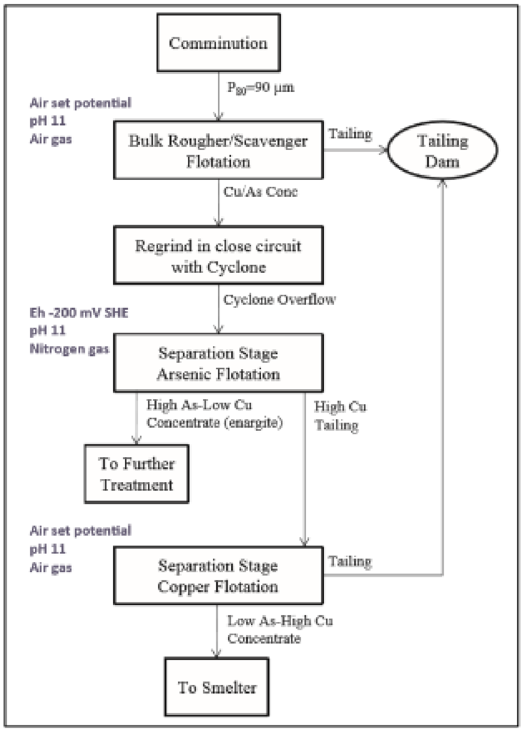
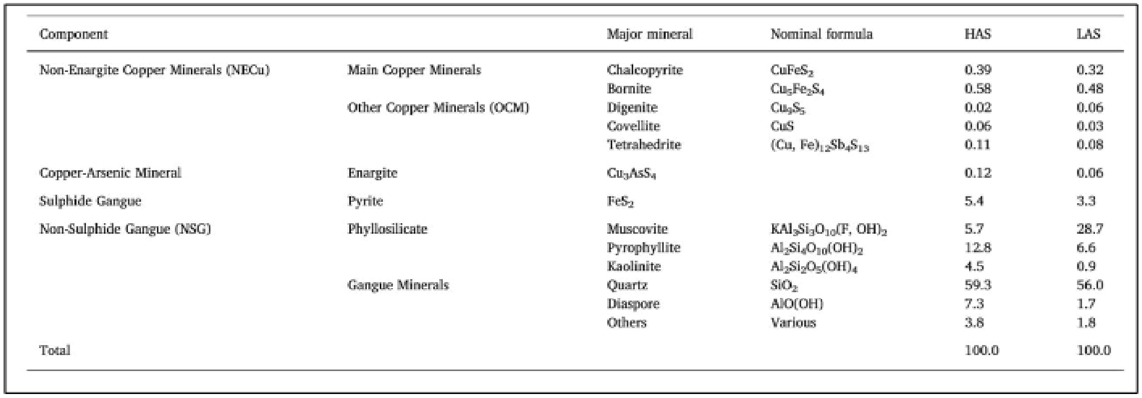


Figure 8. Proposed flowsheet for separating enargite from other minerals
Source: Tayebi-Khorami et al. 2017 p 9.

Table 6. Overall modal mineralogy of the HAS and the LAS ore samples (%)



Component		Major mineral	Nominal formula	HAS	LAS
Non-Enargite Copper Minerals (NECu)	Main Copper Minerals	Chalcopyrite	$CuFeS_2$	0.39	0.32
		Bornite	$Cu_5Fe_2S_4$	0.58	0.48
	Other Copper Minerals (OCM)	Digenite	Cu_9S_5	0.02	0.06
		Covellite	CuS	0.06	0.03
		Tetrahedrite	$(Cu, Fe)_{12}Sb_4S_{13}$	0.11	0.08
Copper-Arsenic Mineral	Enargite	Cu_3AsS_4		0.12	0.06
Sulphide Gangue	Pyrite	FeS_2		5.4	3.3
Non-Sulphide Gangue (NSG)	Phyllosilicate	Muscovite	$KAl_3Si_3O_{10}(F, OH)_2$	5.7	28.7
		Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	12.8	6.6
		Kaolinite	$Al_2Si_2O_5(OH)_4$	4.5	0.9
	Gangue Minerals	Quartz	SiO_2	59.3	56.0
		Diaspore	$AlO(OH)$	7.3	1.7
		Others	Various	3.8	1.8
Total				100.0	100.0

Source: Tayebi-Khorami et al. 2017 p 4.

Studies for separation of enargite, tennantite by flotation from other common sulfide constituents is a currently active research area. Successful flotation separations may produce a "clean" concentrate that can be recycled to the conventional smelting circuit and a "dirty" concentrate. The dirty concentrate may be bled with incoming concentrate or it may be treated to recover additional copper and to produce an arsenic product that can be disposed of in an environmental acceptable manner.

Mineral Processing Flotation for treatment of refractory gold ores-Arsenic minerals that occur in gold ores and concentrates include: arsenopyrite ($FeAsS$), cobaltite ($CoAsS$), enargite (Cu_2AsS_4), gersdorffite ($NiAsS$), proustitse (Ag_3AsS_3), realgar (As_4S_4), orpiment (As_2S_3), tennantite ($Cu_{12}(As_4 S_{13}$), and others. The mineral flotation concentration of pyrite and arsenical sulfide minerals is well established and widely practiced. Some gold ores show refractoriness when subjected to conventional cyanide leaching, e.g., they may have less than 80 percent gold recovery. The refractoriness is because the gold is encapsulated in sulfide minerals such as pyrite (FeS_2), pyrrhotite (FeS) and arsenopyrite ($FeAsS$) and, in some cases, contain carbonaceous material. Treatment is necessary because arsenopyrite is not susceptible to cyanide leaching (Robins and Jayaweera 1992, Marsden and House 2006). In addition to the arsenic-bearing minerals listed above the ores commonly contain pyrite, marcasite (FeS_2) and pyrrhotite (Swash 1988). Dunne (2005) presents an excellent overview for flotation of refractory gold ores, including detailed discussions of collectors, frothers, activators, depressants, and flotation practices for refractory gold ores; arsenopyrite, pyrrhotite and pyrite ores; and copper-gold ores. The author states that there are three Brazilian refractory gold flotation plants, four in North America, six in the Australasian region, and three on the African continent. The gold-sulfide concentrates are treated in a variety of ways: bacterial leaching, pressure leaching, roasting, or supplied to a smelter. Deportment of arsenic to final disposal is discussed in the upcoming sections, especially in the section Fixation of Arsenic.

Mineral Processing pretreatment of concentrates-Selective separation of a high arsenic concentrate is not always possible by flotation treatment and other approaches may be necessary. Pretreatment options in copper and gold processing include roasting, atmospheric pressure leaching, and autoclave leaching.

Roasting-Enargite is considered a refractory copper mineral, and its concentrates are not amenable to conventional extraction technologies, hence, ores and concentrates containing enargite often need pre-oxidation before further treatment (Safarzadeh and Miller 2016). Roasting is a viable option for the removal of arsenic from enargite concentrates. The authors point out that there are *"at least two smelters that process high-arsenic concentrates without pretreatment: Xstrata Horne smelter in Canada and the NCS smelter in Tsumeb, Namibia, both product blister copper and arsenic trioxide".:*

Historically enargite and tennantite bearing concentrates have been treated by roasting in a neutral or low oxygen environment. The classic examples are the El Indio treatment process in Chile and the Anaconda smelter in Anaconda Montana. Both of these facilities used multi-hearth roasters (500-700^oC) to treat copper concentrates containing ~8-10% arsenic. The roaster product calcine arsenic content was <0.3% and was, therefore, appropriate for use in the conventional copper smelting process. Arsenic oxide was condensed and collected from the roaster and smelting unit operations. The final arsenic trioxide product contained >90-97.5 As_2O_3. The Anaconda smelter was closed in 1985 and the El Indio was shut down in 2002 because the markets for arsenic trioxide disappeared (Valenzuela 2000). Also, treatment of arsenical ores and concentrates to process *"refractory"* gold bearing resources has been practiced for decades using multi-hearth roasters.

An example of a present day concentrate pretreatment roasting process is the Outotec's Partial Roaster using a two-stage fluidized bed reactor. The arsenic is volitized in the first bed under a controlled low oxygen condition (partial roasting) at 400-575^oC to produce arsenic oxide, then the bed is subsequently treated in the second stage at a higher temperature (dead roasting >600^oC) to convert the the iron to hematite and to remove sulfur. The arsenic oxide is then stripped from the roaster gas through a series of cleaning operations (Van der Meer et al. 2014) and is further treated for arsenic immobilization as scorodite (ambient pressure, elevated temperature process described later) and long-term storage in a permitted site. The Outotec's process is applicable to copper-arsenic ores and concentrates, and also to copper-iron-gold ores (containing copper-arsenic minerals and arsenopyrite) and concentrates. The process flowsheet is illustrated in Figure 9. Codelco uses the Outotec Partial Roaster at its

Ministro Hales mine in the Calama region, Chile to produce a high-arsenic copper concentrate and a low arsenic calcine. Process water is treated in an integrated effluent plant to produce calcium arsenite. The low-arsenic calcine can be utilized in a conventional smelting circuit. The high-arsenic concentrate may be blended with third party low-arsenic concentrates at the Ocean Partners' concentrate blending facility in Taiwan. The blended product can be marketed to Chinese smelters (IM 2017).

The oxidative roasting-smelting of enargite-bearing concentrates is performed at the Bor copper operations in Serbia and Codelco and has been selected for roasting treatment of the Ministro Hales deposit (Safarzadeh et al. 2014b).

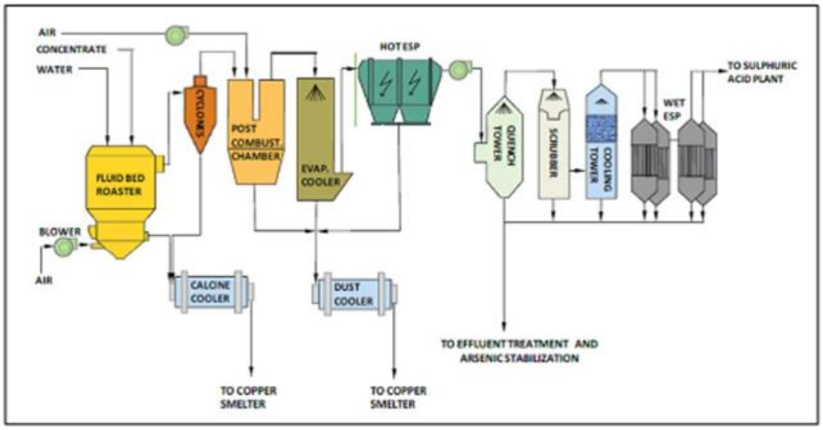


Figure 9. Outotec's partial roasting process for arsenic removal using a fluidized bed reactor (Van der Meer et al. 2014) *Source:* Safazadeh and Miller 2016 p106

The two-stage roaster treatment shown in Figure 10 is appropriate for treating arsenopyrite/pyrite/gold concentrates. Examples of where conventional roasting operations are used include Fairview (South Africa), La Belliere (France, Getchell (Nevada US), Mount Morgan (Australia) and Campbell Red Lake and giant Yellowknife (Canada) (Marsden and Sass 2014).

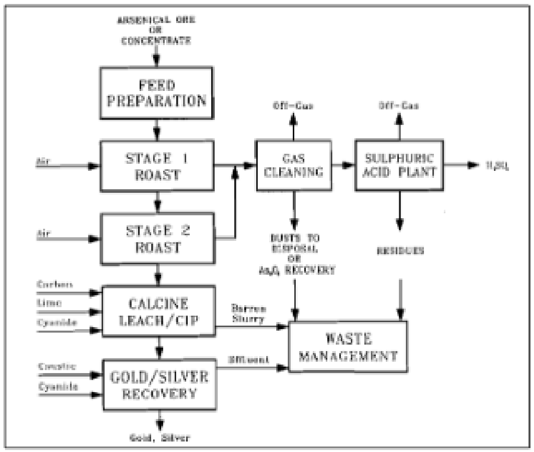


Figure 10. Conceptual flow diagram for a 2-stage pretreatment roast process for arsenical gold ores or concentrates.

Source: Robins and Jaiyaweera 1992 p 259.

Hydrometallurgical Processing of arsenic bearing sulfide concentrates

Hydrometallurgical processes account for about twenty percent of the world primary production of copper; *Chile produces about five times more that the United States* (Hiskey 2014). This illustrates the importance of a hydrometallurgical approach. Safarzadeh et al. (2014a, 2014b) and Lane et al. (2016) suggest that hydrometallurgical processes can be grouped into two categories as shown in Figure 11, i.e., "*selective arsenic leaching or collective leaching of both copper and arsenic*". The listed treatments are labeled according to whether they are commercial or laboratory/pilot processes, e.g., commercial processes that dissolve both copper and arsenic include the Albion, Total Pressure Oxidation, HydroCopper, and Galvanox technologies. Only the Sunshine process is listed as commercial (but is not operating today). Each of the listed treatments are discussed in the review publications. Two of the hydrometallurgical treatments have been selected for further comments in this chapter because they show *"copper extraction and arsenic fixation"*. The selections include the Alkaline Sulfide Leach (ASL) to illustrate a selective leach; and the High Temperature Pressure Oxidation (HTPOX) for processes dissolving copper and arsenic.

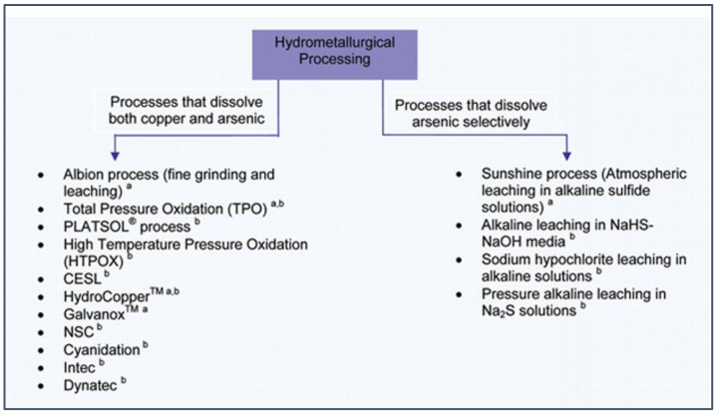
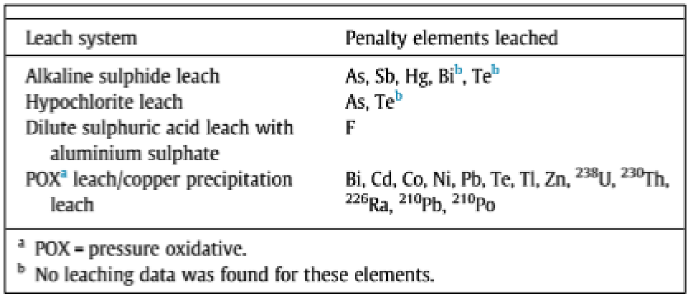


Figure 11. Summary of the processes that have been demonstrated for the treatment of enargite concentrates (*^{a}commercial and ^{b}laboratory or pilot scale*). *Source:* Safarzadeh et al. 2014a p 296

Lane et al. (2016) have also published a review that covers hydrometallurgical processes that have been considered for the selective removal of *"penalty"* elements from copper concentrates. The Lane selection of treatments are summarized in Table 7 and include the ASL, Hypochlorite leach, Sulfuric Acid leach, and POX leach. The authors of both literature reviews suggest that the ASL and elevated pressure oxidation processes may provide an appropriate approach for treating arsenic bearing concentrates. The two treatments are discussed below.

Table 7. Leach systems for the selective extraction of penalty elements



Leach system	Penalty elements leached
Alkaline sulphide leach	As, Sb, Hg, Bi[b], Te[b]
Hypochlorite leach	As, Te[b]
Dilute sulphuric acid leach with aluminium sulphate	F
POX[a] leach/copper precipitation leach	Bi, Cd, Co, Ni, Pb, Te, Tl, Zn, ^{238}U, ^{230}Th, ^{226}Ra, ^{210}Pb, ^{210}Po

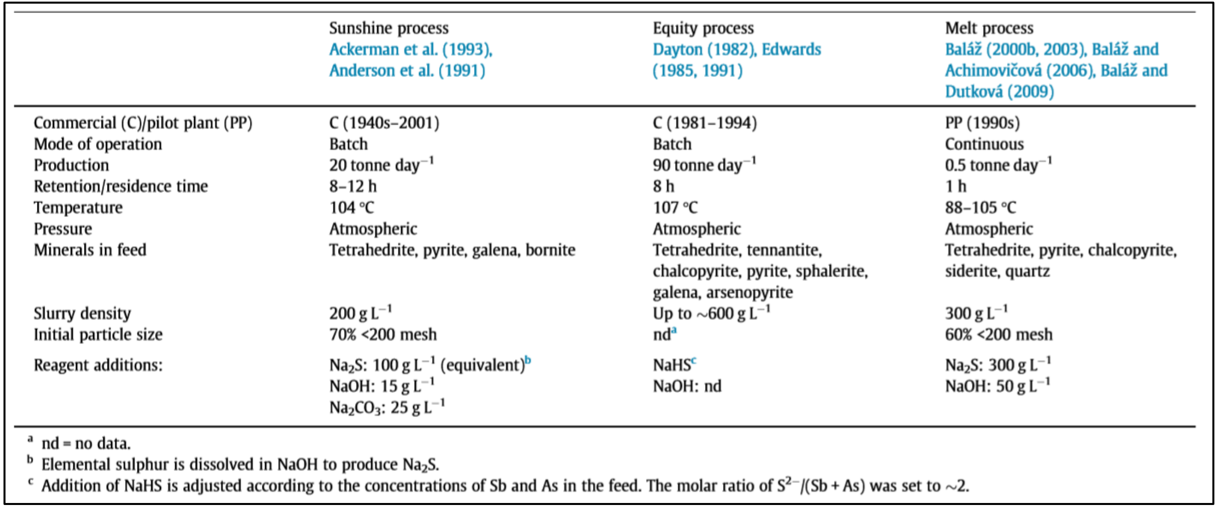
[a] POX = pressure oxidative.
[b] No leaching data was found for these elements.

Source: Lane et al. 2016 p 112.

Alkaline Sulfide Leach (ASL)-The alkaline sulfide leaching of enargite and other arsenic bearing minerals result in selectively dissolving arsenic and leaving a copper residue, and under some treatment conditions a gold-bearing residue. The reagents, sodium sulfide (Na_2S) or sodium bisulfide (NaHS), dissolve arsenic from enargite, tennantite, realgar (As_2S_2), orpiment (As_2S_3) and arsenic trioxide but not from arsenopyrite (Anderson et al. 2016).

The general process conditions for the ASL treatment are illustrated in Table-8 (Lane et al. 2016). The treatment is conducted at ambient pressure, elevated temperature near boiling, Na_2S, NaOH reagents, high slurry density, and in most cases long contact times. Most studies show that copper is almost completely retained in the leach residue. Leaching enargite, tennantite, and tetrahedrite produces predominately covellite (CuS) and chalcocite (Cu_2S). Safarzadeh et al. (2014b) suggest the process flowsheet presented in Figure 12. Note that the stabilization of As(V) is via ambient pressure scorodite precipitation (discussed later). The flowsheet is based on the results from the previously operated Sunshine Mining and Refining Company's antimony plant in Idaho (Anderson et al. 1991, 1995, 2016); the Equity Silver Plant in British Columbia, Canada (Lane et al. 2016); the MELT pilot process in Krompachy, Slovakia (Balaz and Dutkova 2009); and multiple research papers. As noted in Table 8 none of these processes are currently operating.

Table 8 Summary of operating parameters used in ASL technologies



	Sunshine process Ackerman et al. (1993), Anderson et al. (1991)	Equity process Dayton (1982), Edwards (1985, 1991)	Melt process Baláž (2000b, 2003), Baláž and Achimovičová (2006), Baláž and Dutková (2009)
Commercial (C)/pilot plant (PP)	C (1940s–2001)	C (1981–1994)	PP (1990s)
Mode of operation	Batch	Batch	Continuous
Production	20 tonne day^{-1}	90 tonne day^{-1}	0.5 tonne day^{-1}
Retention/residence time	8–12 h	8 h	1 h
Temperature	104 °C	107 °C	88–105 °C
Pressure	Atmospheric	Atmospheric	Atmospheric
Minerals in feed	Tetrahedrite, pyrite, galena, bornite	Tetrahedrite, tennantite, chalcopyrite, pyrite, sphalerite, galena, arsenopyrite	Tetrahedrite, pyrite, chalcopyrite, siderite, quartz
Slurry density	200 g L^{-1}	Up to ~600 g L^{-1}	300 g L^{-1}
Initial particle size	70% <200 mesh	nd[a]	60% <200 mesh
Reagent additions:	Na_2S: 100 g L^{-1} (equivalent)[b] NaOH: 15 g L^{-1} Na_2CO_3: 25 g L^{-1}	NaHS[c] NaOH: nd	Na_2S: 300 g L^{-1} NaOH: 50 g L^{-1}

[a] nd = no data.
[b] Elemental sulphur is dissolved in NaOH to produce Na_2S.
[c] Addition of NaHS is adjusted according to the concentrations of Sb and As in the feed. The molar ratio of $S^{2-}/(Sb + As)$ was set to ~2.

Source: Lane et al. 2016 p 113

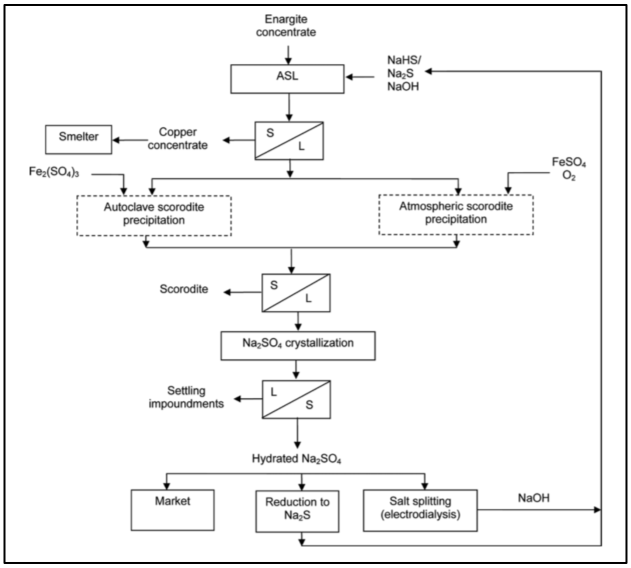
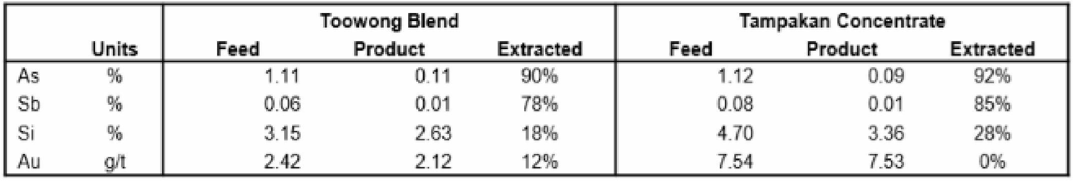


Figure 12 ASL flowsheet proposed for enargite concentrates
Source: Safarzadeh et al. 2014a p 342.

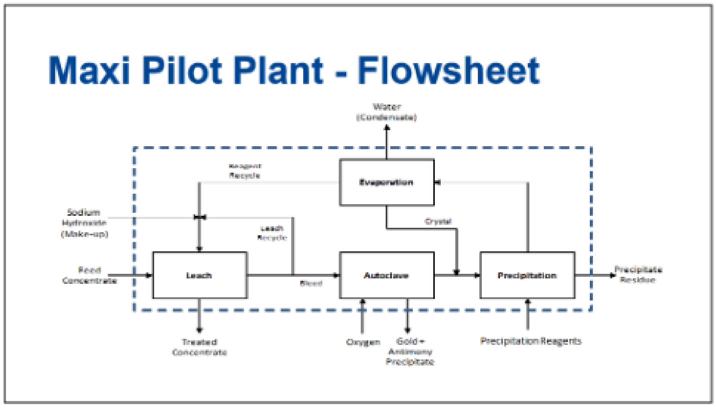
Recent pilot scale demonstrations for the application of an ASL process (designated the Toowong Process) to flotation concentrates (Tampakan copper-gold project in the Philippines) has been reported by Rohner et al. (2016). The process has been demonstrated to be applicable to the dissolution of enargite, tennantite, and other arsenic sulfide minerals. The authors suggest that the Toowong process has several advantages over other ASL applications, e.g., more rapid leaching kinetics, selective arsenic dissolution, and lower reagent additions are required; compare NaOH 11-13 kg/t and $Na_2S.xH_2O$ 0-15 kg/t feeds to the values presented in Table 8. The authors state that the leach does not dissolve gold or arsenopyrite. The other ASL processes leach a portion of the gold but the Toowong process does not leach the gold. Example results from recent Toowong pilot demonstration studies are presented in Table 9; the pilot scale plant flowsheet is presented in Figure 13. The dissolved arsenic resulting from the leach can be precipitated/stabilized by ferrihydrite precipitation or by the ambient pressure, elevated temperature precipitation of scorodite. In 2018 the Toowong process had not been commercialized.

Table 9. Arsenic extracted from Toowong blends and Tampakan concentrates



		Toowong Blend			Tampakan Concentrate		
	Units	Feed	Product	Extracted	Feed	Product	Extracted
As	%	1.11	0.11	90%	1.12	0.09	92%
Sb	%	0.06	0.01	78%	0.08	0.01	85%
Si	%	3.15	2.63	18%	4.70	3.36	28%
Au	g/t	2.42	2.12	12%	7.54	7.53	0%

Source: Rohner et al. 2016



Maxi Pilot Plant - Flowsheet

Figure 13. Toowong Process flowsheet for treating gold-arsenic concentrates. *Source*: Rohner et al. 2016 p 10.

Although most of the ASL processes listed above note that gold is only partially solubilized (or not at all), two investigations report that gold can be solubilized in an alkaline sulfide solution by changing the conditions so that polysulfides are formed (Anderson 2016; Wassink et al. 2005). Polysulfides are formed by the addition of elemental sulfur. The polysulfides perform as an oxidizer to the gold with subsequent formation of aqueous gold sulfide complexes. If arsenic is present it dissolves in the alkaline solution as sodium arsenite which is oxidized by the polysulfides to sodium arsenate. Anderson et al. (2016) state that the recovery of arsenic can be accomplished by ferrihydrite adsorption or formation of scorodite.

Alkaline Hypochlorite Leach-There are many studies demonstrating that arsenic can be effectively removed from copper-arsenic sulfide concentrates by sodium hypochlorite leaching. The general conditions include ambient to 60ºC temperatures at alkaline pHs 12-12.5 (Lane et al. 2016; Nazari et al. 2017) note that *"hypochlorite leaches have been largely limited to laboratory-scale studies and unlike ASL has not been employed on an industrial scale"*. The major reasons for this are that hypochlorite is not very selective for non-arsenic copper sulfides and exceedingly high additions of hypochlorite are required for effective removal of arsenic, e.g. 17.5 moles of sodium hypochlorite are required per mole of enargite. Most of the hypochlorite leach studies do not discuss the final deportment of arsenic.

Pressure Oxidation (POX)-Examples follow:
Outotec provides autoclave technology for treating copper-arsenic and gold-arsenic-pyrite concentrates (Ruonala et al. 2011). The process is based on the atmospheric oxidation/precipitation of amorphous ferric arsenate. The precipitation conditions include: oxidation of As(III) and Fe(II) at atmospheric pressure; an Fe/As mole ratio of 1-3.5, and a pH of 1.5-4.5. The amorphous ferric arsenate is then converted to crystalline scorodite by autoclave treatment using the operating conditions: 160-200ºC, pH 1.5-4.5, and an Fe/As mole ratio 1-1.5. The stated advantage of this treatment is that only the ferric arsenate residue need be treated in an autoclave and not the entire solution.

CESL (Cominco Engineering Services Limited) have patented and demonstrated their POX process (Figure 14) to treat copper-gold-arsenic sulfide concentrates (Salomon-de-Friedberg et al. 2017). The CESL process is an intermediate temperature, pilot scale autoclave treatment which has been applied to over 18 high arsenic copper-gold concentrates (up to 18% As). Autoclave conditions include: ~150ºC, ~14 bar pressure, 60-90-minute reaction time to oxidize copper sulfides and As(III) to As(V). The oxidized arsenic, As(V), reacts with Fe(III) and precipitates as Type II scorodite (described later). The product residue contains scorodite and appreciable copper. The residue is subjected to atmospheric acidic leaching to recover copper. The copper-free arsenic-bearing leach residue is washed through multiple contact stages and disposed of as scorodite. The "*TCLP test was applied to many residue samples during the pilot studies and the results were always <0.15 mg/L As(V)"*. Stability of the scorodite has been evaluated by contacting the residue with twenty times its weight in water using the U.S. EPA SPLP (Method 1312) and observing the dissolution of arsenic as a function of time. The results have shown leachability of less than the British Columbia limit of <2.5 mg/L when aged over a three-year period. The process had not progressed to industrial use in 2018.

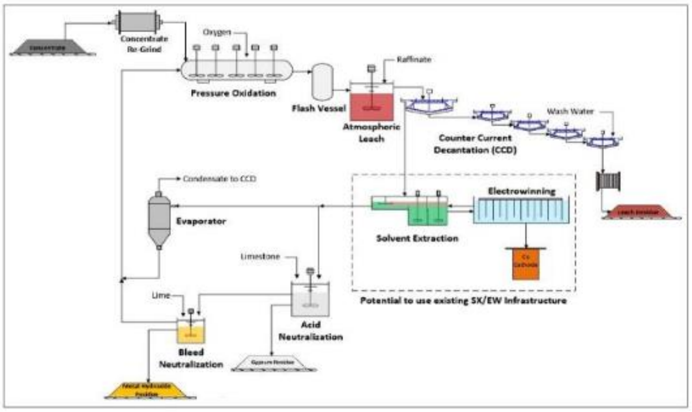


Figure 14. CESL copper process flowsheet
Source: Salomon-de-Friedbert et al. 2017 p 3.

Hydrometallurgical Processing of arsenic bearing gold concentrates

Similar hydrometallurgical processes discussed above for pretreatment of *"refractory"* arsenic-copper concentrates exist for arsenic-bearing gold concentrates and include: High Pressure Acid Oxidation, Low Pressure Acid Oxidation, Alkaline Oxidation Processes and Bacterial Leaching Processes (Swash and Monhemius 1999; Robins and Jayaweera 1992; Marsden and House 2006; Nazari et al. 2017; and Strauss et al. 2017; Strauss et al. 2021).

High Pressure Acid Oxidation-There are many elevated pressure acid oxidation facilities presently in operation; in general, the reaction conditions include oxygen pressures of 1800-2000 kPa and temperatures of 180-210^{o}C. The product residue after pressure oxidation is a mixture of scorodite, hematite, basic ferric sulfates, jarosites and arsenical ferrihydrite, as well as sulfur and gangue residues (Robins and Jayaweera 1992). Arsenic in the leach solution may be several hundred mg/L and these solutions are usually treated by neutralization where calcium arsenate and a variety of calcium products form. Robins and Jayaweera (1992) have examined products from several elevated pressure autoclaving operations and the authors state that very fine amorphous ferrihydrite particles exist (100-500 nm) that were formed along with calcium products. The autoclave residues are made up relatively stable mineral forms that are considered safe for disposal (scorodite, ferric arsenate); however, because of the presence of ferrihydrite and the presence of calcium arsenates and arsenites formed during the neutralization stage, the authors have concerns in regard to long-term stability in storage *"the long term stability of these ferric materials is poor, but could lead to the acceptance of a slow release option rather than complete containment of residues"*.

In the mid-1980s several autoclave reactors to treat gold ores or concentrates were commissioned and operated. *"This established pressure oxidation as a viable method for treating a range of refractory ores and concentrates, with high gold recovery"* (Marsden and Sass 2014). Plants were installed *"between 1988 and 2000 at Goldstrike, Getchell, Lone Tree, and Twin Creeks (all in Nevada), Campbell Red lake and Con (Canada), Lihir and Porgera (Papua New Guinea), and Macraes (New Zealand)"* (Marsden and Sass, 2014). An advantage of autoclave oxidation is that the arsenic is fixed as scorodite.

The Placer Dome Campbell Mine autoclave process for the treatment of high arsenic (10%) auriferous sulfide (18% sulfur) concentrates is another example of Acidic Pressure Oxidation. The operating parameters included: 190-195C, 2200 kPa pressure. Arsenopyrite is oxidized producing sulfuric acid and ferric arsenate. The reaction sequence that occurs is presented to be as follows: oxidation of FeAsS to $HAsO_2$ (arsenite) and $FeSO_4$ (ferrous sulfate) to $Fe_2(S0_4)_3$ (ferric sulfate); oxidation of arsenite to H_3AsO_4 (arsenate); reaction of the arsenate with ferric sulfate to form ferric arsenate solid. The disposable ferric arsenate is considered stable in a tailings impoundment to a pH of eight (Thomas 2005). Thomas states that *"there were fifteen gold pressure oxidation plants in the world in 2005"*.

Bacterial Oxidation "*Bacterial oxidation is now considered to be a proven commercial technique for the treatment of refractory sulfide gold concentrates….testimony for the continuing emergence and acceptance of bacterial oxidation is provided by evidence that the number of bacterial-oxidation plants for gold concentrate treatment now rivals that for pressure leaching"* (Miller and Brown 2005).

BIOX is an industrial example of bacteria biohydrometallurgy (Gonzalez-Contreras et al. 2012; Gonzalez-Contreras 2014) applied to oxidize refractory gold ores containing pyrites, arsenopyrite and copper sulfides. The process is currently being used at twelve sites. *The bacteria are mesophilic (40-45^{o}C) and acidophile (pH 1.2-1.8) microorganisms that can function in arsenic concentrations up to 20 g/L of As(V) and 6 g/L As(III)* (Gonzalez-Contreras, 2012). Scorodite (designated Bioscorodite by the author) is formed as the arsenic bearing disposable product. Additional examples of bacterial biohydrometallurgy are presented in the following section "FIXATION OF ARSENIC".

FIXATION OF ARSENIC (Additional information on this subject is presented by Twidwell 2018)

Past Practice

For decades, the major practice for the disposal of arsenic bearing solutions was lime addition to form calcium arsenate/calcium arsenite with placement in containment ponds or tailings impoundments (Velenzuela 2000). R.G. Robins (University of New South Wales) and Tozawa (University of Tohoku) were the first to alert industry that "*calcium arsenate is unstable when exposed to carbon dioxide in air*" (Figure 15) and is, therefore, *not suitable for storage of calcium As(III) or As(V) compounds* (Robins and Tozawa 1982). Note in Figure 15 that there is a range of pH values where calcium arsenate is stable in the absence of carbon dioxide, i.e., at a TCLP value of 5 mg As/L, and that in the presence of carbon dioxide calcium arsenate is not thermodynamically stable at 5 mg/L. Riveros et al. (2001) have demonstrated that calcium arsenate sludge can leach up to 4400 mg As/L using the TCLP leach test. Nishimura and Umetsu (1985) have shown that crystalline calcium arsenate can be formed by calcination and that its solubility is greatly decreased. Regardless of this, dissolution of arsenic will occur with time. However, Nazaro et al. (2017) state that two smelters in Chile (Codelco's Chuquicamata and Noranda's Altonorte plant) still (2017) employ lime neutralization to form calcium arsenite/gypsum and calcium arsenate/gypsum products. The resulting residues are stored and monitored in permitted hazardous waste landfills. Zhang et al. (2019) evaluated the stability of calcium arsenate solids as a function of pH and aging time, e.g., slurries were formed from arsenate bearing solutions (1000 and 2000 mg As(V); Ca/As molar ratios of 1, 2, and 4) at various pH levels (8, 10, 12) and were aged in the presence of atmospheric carbon dioxide for up to 1120 days. The results showed appreciable arsenic leached for all combinations of the studied variables, e.g., approximately 10 to 300 mg/L at 1120 days. Coudert et al. (2020) in an extensive literature review concluded: *"Despite the satisfactory efficiency of lime neutralization in As removal from mine waters (>95%), it is now acknowledged that this process is a unsuitable option for As-rich effluents".*

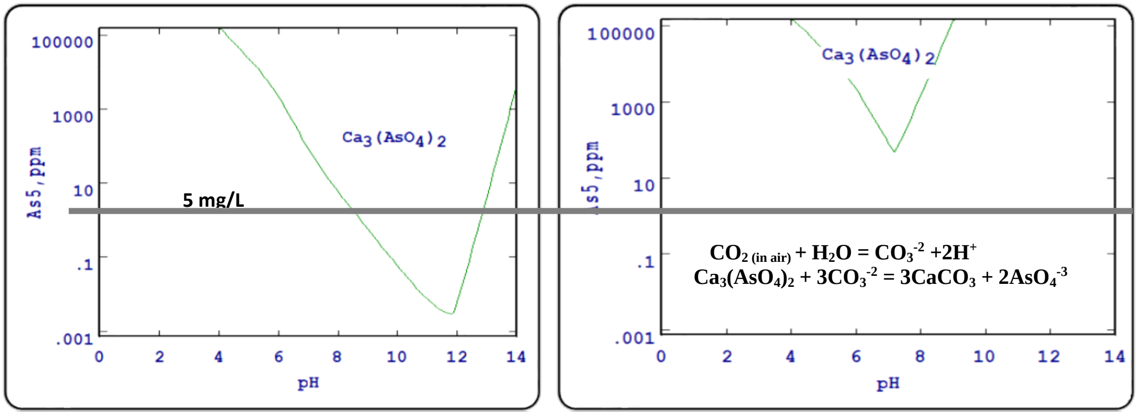


Figure 15. The conversion of calcium arsenate to calcium carbonate by carbon dioxide in air
(line drawn at the U.S. EPA TCLP required level of <5 mg/L to designate the solid as non-hazardous)
Source: Diagram generated by STABCAL, Huang 2021.

Brief Summary of Current Industrial Practice

Three ferric/arsenic precipitation removal technologies are presently practiced by industry throughout the world: (1) ambient temperature arsenic adsorption/co-precipitation to form arsenical **ferrihydrite (FH)**; (2) elevated temperature and elevated pressure autoclave precipitation of **scorodite** ($FeAsO_4.2H_2O$); and (3) more recently an ambient pressure, elevated temperature precipitation of **scorodite**.

The ambient temperature/pressure FH technology (1) is relatively simple and the presence of commonly associated metals (aluminum, copper, lead, zinc) and gypsum have a stabilizing effect on the long-term stability of the outdoor storage of the product. The disadvantages of the adsorption technology is that: a relatively large amount of waste material is created (Fe/As mole ratio varies but is usually approximately three to four but can be as high as ten); the product is difficult to filter (20-25 wt.% solids); the requirement that the arsenic be present in the fully oxidized state (arsenate); the presence of competitive associated anionic species may negatively influence the adsorption of arsenate; and the question as to long-term stability of the product in the presence of reducing substances in anoxic and/or bacterial environments. However, according to the U.S. EPA the FH/arsenate technology is the Best Demonstrated Available Technology (BDAT) available for removing arsenic from wastewater and storage of the precipitated arsenical FH (Rosengrant and Fargo 1990). It is the most utilized treatment procedure throughout the world (greater detail is presented later).

The second technology (2) practiced at several copper smelting facilities is arsenic removal by precipitation of **scorodite**. The advantages of the scorodite process over the FH technology is that less waste is formed (Fe/As molar ratio of one); greater density (better filterability); and better thermodynamic stability (under some conditions). The disadvantages of autoclave scorodite precipitation are that the treatment process is more capital and energy intensive; the compound may dissolve incongruently to form arsenical FH if the pH is >3-4; and its long-term storage may not be stable under reducing and/or anaerobic bacterial conditions. The third technology (3) is the elevated temperature, ambient pressure scorodite process which is likely to be widely adopted in the future (Fujita et al. 2010, 2012; Demopoulos 2008). In general, the FH adsorption process is favored for treating relatively low-level arsenic (<1 g/L) bearing waste solutions, whereas the scorodite precipitation process is more suitable for elevated arsenic bearing solutions.

Ferrihydrite/Arsenic Treatment

The U.S. EPA promulgated regulations for the Best Demonstrated Available Technology (BDAT) to be use for the following Listed and Characteristic waste containing Arsenic or Selenium: K031, K084, K101, K102, Arsenic wastes (D004). Selenium wastes (D010), and Phosphorus and Uranium wastes (Rosengrant and Fargo 1990). The specified BDAT technology for treatment of effluent solutions is adsorption on FH. This technology has also been selected by EPA as one of the Best Available Technologies (BAT) for removing arsenic from drinking waters and its application is widespread.

What is Ferrihydrite (FH)

FH is a ferric oxyhydroxide. The accepted formulae is $5Fe_2O_3{:}9H_2O$ (Paktunc et al. 2008). It is a large surface area solid phase often referred to as an amorphous material but it is actually a metastable nano-crystalline material. Important reviews detailing conditions for formation and the stability of FH are presented by Jambor and Dutrizac (1998), Schwertmann and Cornell (2000), and Cornell and Schwertmann (1996, 2003), Paktunc (2008). The reviews by Jambor and Dutrizac (314 references) and Cornell and Schwertmann (approximately 1500 references) are, indeed, excellent sources of information on FH occurrence, structure, chemical composition, adsorptive capacity for cations and anion, its transformation rate, and a summary of factors that influence its transformation to hematite (Fe_2O_3) or goethite ($FeOOH$).

FH is characterized by x-ray diffraction as having a two-line structure, which relates to the number of broad peaks present. Two-line FH is formed by rapid hydrolysis to pH 4-7 at ambient temperature and is the form usually precipitated in industrial treatment systems. Crystallite sizes have been reported to be 2–4 nm. The surface area of freshly precipitated two-line FH is 150-340 m^2/g (Paktunc et al. 2008). Hohn (2005) has demonstrated arsenic-loaded (7% As(V)) FH prepared at pH 4 and 7 self-flocculate to a mean agglomerate size of 5-10 micrometers.

Ferrihydrite Transformation

FH is considered a metastable phase that transforms to hematite or goethite with time. The rate of transformation has been investigated in detail and the rate of transformation is a function of time, temperature, pH, and the presence of adsorbed anions and cations, e.g., conversion of 2-line FH to hematite at 25ºC is half complete in 280 days at pH 4 but is completely converted at 100ºC in four hours. Transformation results in a relatively large change in surface area, e.g., freshly prepared 2-line FH showed a surface area of ~150 m^2/g that, when converted to goethite at 25ºC, was reduced to 92 m^2/g; when converted to goethite at 90ºC the particulate surface area was reduced to 9 m^2/g (Schwertmann and Cornell 2000). The fact that conversion occurs reasonably rapidly and that the conversion results in a significant decrease in surface area may hold important negative consequences for long-term outdoor storage stability for adsorbed arsenic. However, in real industrial systems, the FH conversion rate may be mitigated (changed from days to years or decades) by the presence of other species and solution conditions during precipitation and subsequent storage. General factors that have been shown to decrease the rate of conversion to more crystalline forms include lower pH; lower temperature; presence of adsorbed arsenate, silicate, aluminum, manganese, heavy metals, and organics.

Ferrihydrite/Arsenic (arsenical FH)

The structural relationships for FH adsorption of arsenate are via the formation of inner-sphere complexes rather than simple surface adsorption. The exact nature of the adsorption is controversial, but the use of EXAFS spectroscopy has shown that the adsorption is by bidentate corner-sharing surface complexes without the formation of mondentate corner sharing (Sherman and Randall 2003).

The terms scorodite, ferric arsenate, and arsenical FH are often used throughout the arsenic literature; sometimes incorrectly. Paktunc et al. (2010) and Paktunc (2015) experimentally investigated the structure of scorodite, ferric arsenate, and arsenical FH and they have clarified the distinction between the three forms, e.g., scorodite is a fully crystallized phase containing a Fe/As molar ratio of one ($FeAsO_4{:}2H_2O$); ferric arsenate is an amorphous product ($FeAsO_4{:}4\text{-}7H_2O$); and arsenical FH is arsenate absorbed within the FH ($5Fe_2O_3{:}9H_2O$) structure. Ferric arsenate forms at low pH and is transformed rapidly to scorodite at pH levels below ~1.7. Above that pH ferric arsenate and arsenical ferrihydrite form up to approximately a pH of 4.5 for Fe/As ratios from one to ten. See also Paktunc (2015) for further information on the formation and stability of scorodite and arsenical FH.

Removal of Arsenic from Aqueous Solutions

A relatively wide range of arsenic removal results, by FH precipitation/adsorption, are reported in the literature; this is to be expected because there are several experimental factors that influence the removal process. The influencing factors include:

the method of FH/arsenic contact, the iron/arsenic molar ratio, pH, time, initial concentration of arsenic, arsenic valence, and the presence of other anionic species (Twidwell 2011, 2015, 2019b).

Arsenic Speciation-Figure 16 illustrates the thermodynamic stability regions for arsenic species at ambient temperature as a function of solution potential and pH. Arsenate As(V) species are stable under the more oxidizing potentials whereas, arsenite As(III) species exist under more reducing potentials. The effectiveness of FH removal of arsenic depends on the arsenic being present as As(V) species.

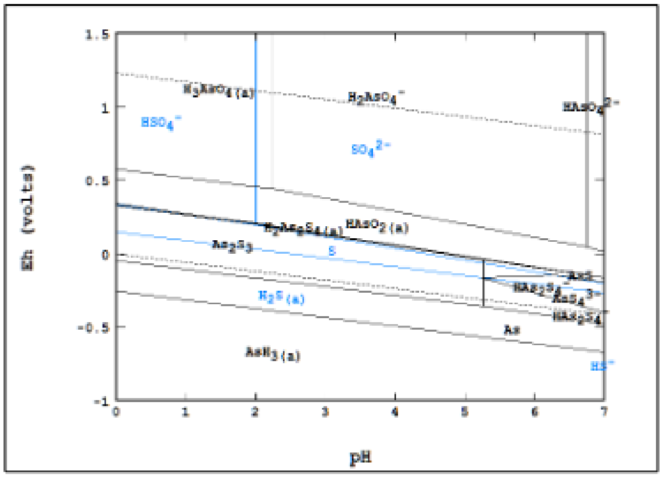


Figure 16. Potential/pH diagram for the As-S-water system
(arsenic concentration 10 mg/L) Source: Diagram generated by STABCAL, Huang 2016.

Method of Contact-Two approaches are currently used in industry: Co-precipitation or Adsorption**.**

Co-precipitation occurs when iron and arsenic are present as dissolved species in the solution phase. When the solution pH is raised FH precipitates insitu throughout the solution with intimate contact between the solid and the arsenic in the solution phase. The second approach is termed **Adsorption.** Adsorption is promoted when a ferric containing solution is added to an arsenic solution at the desired pH upon addition of the dissolved ferric, FH forms and supplies surfaces for arsenic adsorption. The arsenic loading densities achieved by the two approaches are very different, e.g., co-precipitation results in a greater loading density (mole As/mole Fe is 0.7-1.0); whereas, adsorption results in a loading density of 0.3-0.5.

Fe/As molar ratio, pH, initial arsenic concentration-The influence of Fe/As molar ratio as a function of pH is illustrated in Figures 17, 18, 19. However, it is important to restate that the actual Fe/As molar ratio requirement for effective arsenic removal depends on the several experimental factors stated above.

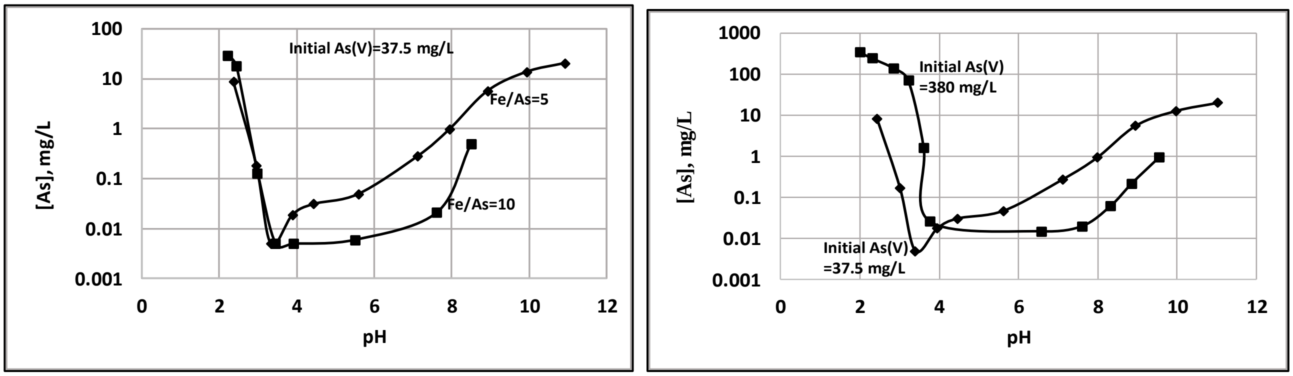


Figure 17. The influence of Fe/As molar ratio and pH on the removal of arsenic, As(V), by FH co-precipitation (left figure) and **Figure 18 The influence of initial arsenic concentration and pH on the removal of arsenic by FH co-precipitation** (right figure). *Source:* Adapted from Wang, Nishimura and Umetsu 2000.

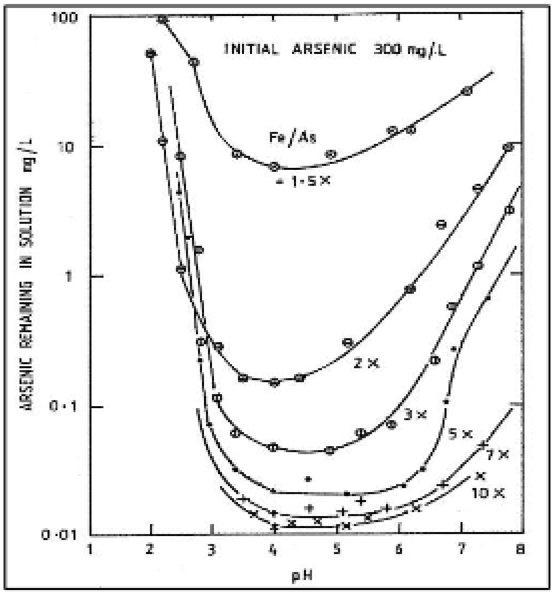


Figure 19. The influence of Fe/As molar ratio, and pH on the removal of arsenic by FH co-precipitation. (The Fe/As molar ratio is indicated by 1.5x, 2x, 3, etc). *Source:* Robins et al. 1988 p 104

Valence state-The presence of arsenite, As(III), and other dissolved aqueous species are important aspects that need to be considered when selecting an appropriate FH technology. The normal approach when considering FH removal of arsenic is to consider ways to oxidize the As(III) to As(V). It is often stated that As(V) is much more effectively removed by FH than As(III). However, the relative removal of As(V) and As(III) depends upon the Fe/As ratio, pH, and whether the arsenic species are present individually or as mixtures. As(III) is often found in appreciable concentration in ambient temperature metallurgical operation flue dust leaching solutions, acid blowdown solutions, wastewater, groundwater, and surface waters. In fact, Borho et al. (1996) state that *approximately thirty percent of the arsenic present is often As(III).*The influence of Fe/As molar ratio, arsenic valence state, and pH is illustrated in Figure 20.

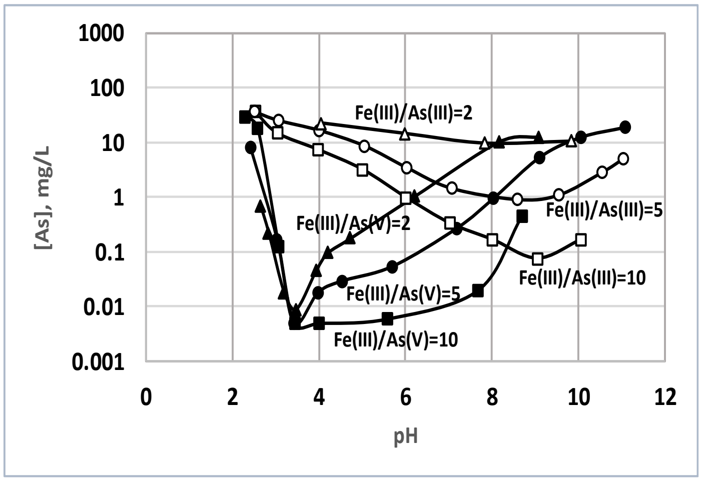


Figure 20. The influence of Fe/As molar ratio, arsenic valence, and pH on the removal of arsenic by FH co-precipitation. (Initial As(V) or As(III)=37.5 mg/L, 25ºC, 30 minutes). *Source:* Adapted from Wang, Nishimura, Umetsu 2000

Oxidation of As(III)-The oxidation of As(III) has been the focus of many studies. Nazari et al. (2017) present detailed discussions concerning what oxidants have been studied and a summary of the application conditions. The reader is referred to that publication. With respect to industrial applications the authors state that: *"As(III) bearing streams obtained from* *hydrometallurgical and pyrometallurgical processing frequently consist of a high concentration of As(III). Hydrogen peroxide, permanganate, ozone and SO_2/O_2 gas mixture have been typically employed in industrial scale to oxidize As(III) to As(V)".* The oxidation of As(III) is an important consideration because successful removal of arsenic by FH adsorption or scorodite precipitation requires that the arsenic be present as arsenate. This is especially true when forming scorodite.

Presence of Associated Ions-The presence of associated ions such as phosphate, sulfate, carbonate, and dissolved organic species can **greatly** influence the removal of arsenic and the relatively long-term stability of FH. A review of the effect of associated ions is beyond the scope of the present chapter and the reader is referred to the following publications of Jain and Loeppert (2000); Appellos et al. (2002); Grafe et al. (2002); Viloante et al. (2003); and Frau et al. (2008). The presence of cations, such as Al(III), has been shown to enhance the removal arsenic and to increase the long- term stability of FH (De Klerk et al. 2012; Twidwell and McCloskey 2015). Krause and Ettel (1989) have shown that the presence of divalent cations; Zn, Cd, Pb, Ca, and Mg, extend the FH formation and stability range from pHs of 4-7 to ~4-10.

Stability of Ferrihydrite and example industrial applications

Many investigations have focused on the formation and stability of FH (Ford 2002; Riveros et al. 2001; Harris 2000, 2002, 2003; Hohn 2005; Twidwell et al. 2007 and many more). A few examples are presented here:

Ford (2002) investigated the storage stability of 2-line FH and arsenate-loaded FH for periods up to 112 days at 40 °C and pH 6. He found that the stability with respect to rate of conversion to hematite (Fe_2O_3) was a function of arsenate loading and that for some lower-level arsenate loadings the arsenic release from the solid phase did not occur even though appreciable FH was converted to Fe_2O_3 as a function of time. Ford also demonstrated, for arsenate loadings less than the maximum loading capacity of FH, that a significant fraction of the retained arsenate was lost from the originally co-precipitated FH but was not released to the solution phase. That is, the arsenate transferred to the crystalline Fe_2O_3 phase that was created during the aging process.

Twidwell et al. (1996-2008) investigated the stability of FH and aluminum modified FH (AMF, Al/Fe molar ratio of one) under a variety of conditions, including the [Al+Fe]/As molar ratio, temperature (25 and 70°C), initial As(V) concentration (0.1 to 10 mg/L), and aging time (30 minutes to 500 days). The partitioning of arsenate after 500 days at 70°C to the AMF formed hematite was significantly greater than for the FH solid, whereas the extent of conversion for the As-loaded AMF solids was much lower (17%) than for the As-loaded FH (73%) solids, showing that greater arsenic loading to the hematite conversion product occurred. Partitioning of arsenate from the amorphous solids to hematite or to the solution phase at ambient temperature did not occur over 500 days for either AMF or FH, i.e., the initial amorphous solids did not convert to crystalline ferric oxide. The influence of pH on arsenic solubility by formation of AMF and FH initially and at 367 days is presented in Figure 21. For additional information on this topic refer to the EPA Mine Waste Technology Program (MWTP) studies (MWTP-1996, 2007, 2008a, b, c).

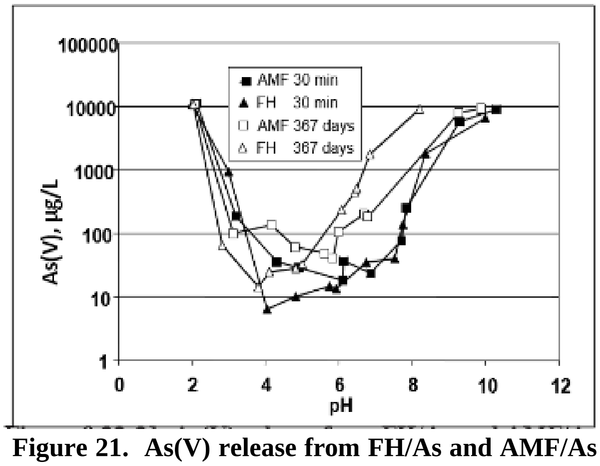


Figure 21. As(V) release from FH/As and AMF/As at 30 minutes and 367 days. (Conditions: initial As(V) = 10,000 µg/L; Fe/As or [Al+Fe]/As molar ratio = 5, ambient temperature). *Source:* Twidwell et al. 2007.

Removal of arsenic from solution by ferric precipitation has been or is practiced at numerous extractive metallurgical facilities, e.g., the Xstrata's Horne smelter; the Giant Mine, the Con Mine, and the Teck-Corona mine; the Kennecott Utah Smelter; Placer Dome Lonetree and Getchell mines (on a periodic basis); Barrick's gold mining operations in Nevada; and the Saganoseki and Kosaka copper smelters in Japan (Valenzuela, 2000). Harris (2000) has tabulated worldwide industrial operating practice (as of 2000/2001) for removal and stabilization of arsenic by the FH, autoclave, lime neutralization processes or by production of copper arsenate. Harris (2003) states that: "*by far the most popular approach is arsenical ferrihydrite, although possibly not always with the requisite level of understanding INCO's CRED plant in Sudbury has been operating for close to thirty years, with no sign of ferrihydrite breakdown, or of arsenic release. As noted earlier, it is however, well known that the incorporation of small amounts of cations and anions into the ferrihydrite matrix appreciably slows down any crystallization process to the formation of goethite/and or hematite, and hence the consequent release of adsorbed ions. To all intents and purposes, it appears that recrystallization in these ferrihydrite materials in these situations is virtually non-existent. Certainly, the EPA regards the arsenical ferrihydrite process as the BDAT, and operations applying it correctly (molar Fe(III)/As(V) ratio >4 have not reported any contamination of local groundwater"*.

Nazari, et al. (2017) noted several industrial facilities that control their arsenic removal by arsenical FH adsorption and/or ferric arsenate formation. Examples presented include: the Xstrata Horne smelter (data from reference Godhehere et al. (1995) and Peacey et al. (2010); a uranium mill in northern Saskatchewan, Canada (Demopoulos 2014), and the Boliden Harjavalta plant in western Finland (Salokannel et al. 2013). The arsenic disposal practices are summarized: Xstrata's product includes ferric arsenate, arsenical FH, and ferric arsenite. The products are mixed with smelter slag and are placed in their smelter slag tailings impoundment. Arsenic release is < 1 mg/L as required by the province of Quebec. The uranium mill product is ferric arsenate which is placed in their tailings facility. Arsenic release is below Saskatchewan regulations of 2 mg/L. The Boliden products are ferric arsenate and metal hydroxides; placement was not specified.

A comprehensive survey of *"Arsenic Management in the Metallurgical Industry"* (Valenzuela, 2000) is a recommended reference. This review includes identification of industrial applications throughout the world for both copper and gold processing and their arsenic removal and storage practices, at least up to the year 2000.

Additional data are presented in several publications. Please refer to SME Mineral Processing and Extractive Metallurgy Handbook; Chapter 10.9. For further information concerning the long-term stability of arsenical FH refer to publications presented by Welham et al. (2000 Review); Paktunc et al. (2008); Riveros and Dutrizac (2001); and Drahota and Fillppi (2009 Review); and Paktunc (2015). Several conclusions taken from these publications follow.

A detailed review of the stability of scorodite, ferrihydrite, and ferrihydrite arsenate adsorption is presented by Welham et al. (2000 Review). The authors state that: *"there are significant problems with the use of jarosite and scorodite as phases for the disposal of iron and/or arsenic from metallurgical systems. Neither phase is stable under typical atmospheric weathering conditions with transformation to goethite predicted to occur. The currently permitted discharge level of arsenic is only achieved due to the slow kinetics of the transformation releasing arsenic over time. Crystalline scorodite is two orders of magnitude less soluble than amorphous iron (III) arsenate precipitates often formed in low temperature systems."*

Paktunc et al. (2008) concluded from their extensive study of phase transformations of arsenic bearing solids that: *Industrial practice to stabilize arsenic in metallurgical circuits is to form precipitates having Fe/As molar ratios greater than 3 or 4. Despite its important implication, the meaning of this ratio in terms of controlling arsenic releases has remained unknown. As described above, the precipitates with different Fe/As ratios, invariably referred to as ferric arsenate or arsenical ferrihydrite, are not composed of a single phase. Instead, they are mixtures of ferric arsenate and ferrihydrite. Following the precipitation of ferric arsenate from arsenic-rich solutions, ferrihydrite forms at pH 2 and above. Its formation drives the solution composition to undersaturation with respect to ferric arsenate and promotes dissolution of ferric arsenate. With this, the ferrihydrite would impose control on the ferric arsenate. The increasing relative abundance of ferrihydrite would impose control on the As concentration in solution by providing additional sites for arsenate adsorption. Accordingly, formation of ferrihydrite coupled with ferric arsenate dissolution would be considered as an efficient process in terms of maximizing As release".*

Riveros and Dutrizac (2001 Review) concluded from their review of the literature that *"for practical purposes, arsenical ferrihydrite can be considered stable provided the Fe/As molar ratio is greater 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".*

Conceptual Flowsheet for forming arsenical Ferrihydrite

A conceptual Flowsheet for Forming Arsenical Ferrihydrite is presented in Figure 22.

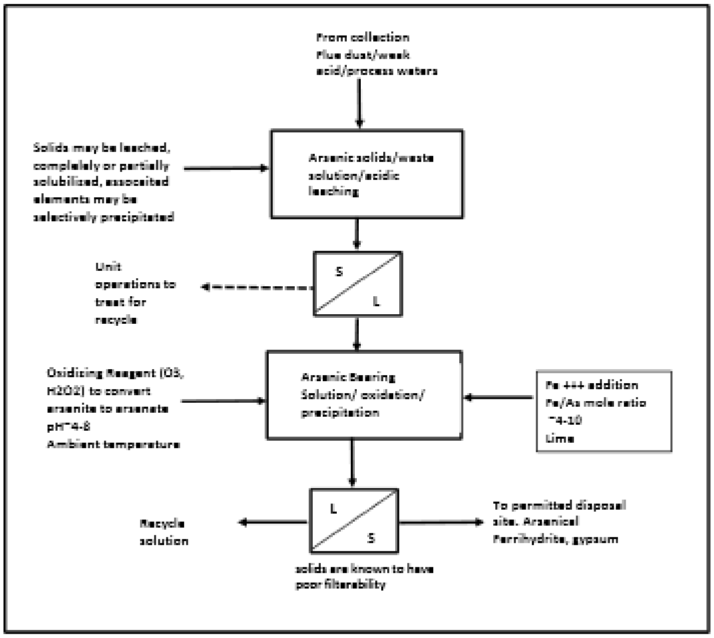


Figure 22. Conceptual flowsheet for forming arsenical FH

Ferrihydrite Stability Concerns

In general, arsenical FH passes the U.S. EPA TCLP (Method 1311) toxicity test and the waste products do not have to be subjected to further stabilization as required by the U.S. LBR (Land Ban Restrictions). However, an important unknown at this time is whether the product from FH adsorption of arsenic will be stable if storage conditions are anaerobic or may become anaerobic or contain microbial agents. Many investigations have considered FH stability under oxic conditions. However, is FH stable when mixed with sulfide tailings and the mixture becomes reducing and are buried where the local environment may be anoxic?

Anoxic Conditions-Doerfelt et al. (2016) have considered the stability of FH and aluminum containing ferrihydrite (AMF) in the presence of sulfide as a reducing agent at anoxic conditions at relatively high pH levels. Their investigation focused on molar ratios of Fe(III)/As(V)=4 and Fe(III)/Al(II)/As(V)=2/2/1 co-precipitated products. The products were subjected to *"excess"* sulfide (molar ratio of sulfide/Fe(III)=1) at *"extremely reducing"* conditions in a nitrogen protected environment. The results of the study were very encouraging and demonstrated that FH and aluminum FH were stable under these severe treatments. Their results were: *"It was found that the ferric-arsenate co-precipitates could retain up to 99% of its arsenic content despite the high pH (10.5) and extremely reducing (E_H<-200 mV) environment. There was no significant reduction of arsenate and only 45% of ferric iron was reduced by 50% (down to 15 mg/L) hence mixed Fe(III)/Al(III)-arsenate co-precipitates may offer better resistance to reductive destabilization over the long term than all iron co-precipitates".*

Additional example study results follow: Ebs et al. (2010) demonstrated that induced reduction conditions using hydroquinone resulted in arsenic and iron reduction and that coprecipitated FH/As(V) showed less arsenic release than adsorbed arsenic on previously precipitated FH. Brannon et al. (1987) have demonstrated that anaerobic lake sediments convert As(V) to As(III) (pH 5-8). However, when the anaerobic conditions were shifted by aerobic leaching the previously reduced As(III) was reconverted to more immobile As(V) which was associated with aluminum and iron oxyhydroxides. Chatain et al. (2005a) investigated the effect of controlling the solution redox potential (E_H) and pH using sodium ascorbate (–7 to 345 mV) and sodium borohydride (–500 to 140 mV) to treat an arsenic bearing gold mining soil (2.8 % As, 1.8% on FH). The release of arsenic from the soil under oxidizing conditions (410 mV) showed the normal FH release of arsenic (V) (i.e., ~0.3 mg/L); whereas the treatment with 0.046 mole/L sodium ascorbate at an E_H = –7 mV (pH ~6) released ~80 mg/L As(III).

Also, it is known that the effect of bacterial reduction of FH and arsenate can be extensive. Kocar et al. (2010) found that the effect of sulfate reducing bacteria (that produces dissolved sulfide species) was to reduce FH to other iron solids along with the reduction of arsenate to arsenite. Chatain et al. (2005b) investigated the influence of anaerobic conditions (at pH ~ 7) with indigenous bacterial activity on the release of arsenic (and other metals) from a contaminated mining soil (3% As, 0.3% on FH). The results showed <4 mg/L arsenic release from baseline soil/ water leaches (80 days) and ~100 mg/L As(III) for nutrient fed indigenous bacteria. Langner and Inskeep (2000) have investigated the possible reduction of As(V) to As(III) on FH. They adsorbed arsenate onto previously precipitated 2-line FH solids, added a reducing fulcose fermenting microorganism to a suspended slurry containing the precipitated arsenate and arsenate species in solution at pH 6.8 and aged for 24 days. The solution arsenate was reduced to arsenite in less than one day but precipitated As(V) and FH were not reduced.

Scorodite Formation

The second technology practiced at several copper and gold facilities is arsenic removal by precipitation of **scorodite.**

What is Scorodite?

Scorodite is a naturally occurring iron-arsenic mineral, $FeAsO_4.2H_2O$. It has a low solubility in a water environment and has one mole of arsenic/mole of iron, i.e., it contains 25-30% arsenic, whereas the maximum arsenic that FH can contain is 0.5 to 7%, depending on the required Fe/As molar ratio (usually 3-10). *"Scorodite is found in hydrothermal deposits and as a secondary mineral in gossans worldwide. Scorodite was discovered in the Schwarzenbert Saxony district, Erzgebirge, Sacony, Germany. Named from the Greek Scorodion, garlicky. When heated it smells of garlic, which gives it the name."* (Wikipedia 2017). Scorodite thermodynamic standard free energy of formation ($\Delta G^o{}_f$) has been determined to be -1,284.8 kj/mole (Majzlan et al. 2012): orthoarsenate ($FeAsO_4 \cdot 0.75{}_2O$) standard free energy of formation $\Delta G^o{}_f = -993.15 \pm 2.57$ kJ/mol and $\Delta H^o{}_f = -1140.38 \pm 2.59$ kJ/mol (however, synthesis of this compound requires an elevated temperature >200C). the solubility of orthoarsenate is lower than the solubility of scorodite (at pH 3), 29 and 92 µg/L, respectively (Maizlan et al. 2016). Natural scorodite is often associated with arsenopyrite and enargite and is found in copper and gold bearing deposits. It is relatively stable at pHs of 2.8-5.3 (Riveros et al. 2001) and passes the EPA TCLP Method 1311 solubility test of <5 mg As/L.

There are several technologies that can be used to form scorodite:

- Autoclave hydrothermal precipitation of scorodite from acidic solutions (pH ~1, ~150ºC) containing Fe(III) and As(V) (Gomez et al. 2011a; 2011b, and many others)
- Elevated temperature, ambient pressure precipitation from acidic solutions (pH ~1, 90-95ºC) containing Fe(III) and As(V) or As(III) (Demopoulos 2005, 2008, and many others)
- Intermediate temperature, ambient pressure precipitation by insitu oxidation of Fe(II) in the presence of As(V) from acidic solutions (pH ~1, ~70ºC, 95ºC) (Fujita et al. 2008a, 2008b, 2009a, 2012, and others)
- Intermediate temperature, ambient pressure precipitation by biogenic insitu oxidation of Fe(II) in the presence of As(V) from acidic solutions (pH ~1, ~70ºC) (Okibe et al. 2013; Gonzalez-Contreras et al. 2012, 2014)
- Intermediate temperature, ambient pressure precipitation by biogenic insitu oxidation of Fe(II) and As(III) from acidic solutions (pH ~1, ~70ºC) (Okibe et al. 2013, 2014).

Autoclave Applications

There have been many autoclave studies demonstrating the successful formation of scorodite and scorodite-like phases. Gomez et al. (2011a) present a brief comparison of the phases formed and identified by past research efforts. Detailed laboratory studies indicated that several Fe(III)-arsenate type compounds may be formed under typical conditions of autoclave treatment of refractory gold ores (Swash & Monhemius 1994; Dutrizac & Jambor 2007; Gomez et al. 2010a, 2011a*).* The basic ferric arsenate (BFAS) phase (Gomez et al. 2008), also known as Type II ferric arsenate (Swash and Monhemius 1994) or Phase 3 (Dutrizac and Jambor 2007) is one of the most common arsenic bearing products (Harris 2003; Dutrizac & Jambor 2007). BFAS precipitation is viewed as one of the best routes for arsenic stabilization and performed equally well to scorodite during environmental stability test (Harris 2003; Swash & Monhemius 1994; Dutrizac & Jambor 2007; Gomez et al. 2011).

Swash and Monhemius (1994) have shown that scorodite-like phases may form during autoclave ferric precipitation (especially in a sulfate bearing solution). They have designated the products Type I and Type II: e.g., Type 1 $[(Fe_2HAsO_4)_3{:}xH_2O]$) and **BFAS** (also referred to by Swash and Monhemius (1994) as Type II $[Fe_4(AsO_4)_3(OH)_x.(SO_4)_y]$. Type I does not pass the U.S. EPA TCLP test for arsenic (5-85 mg/L) and Type II does (<5 mg/L). Information is not available concerning the long-term stability of these compounds.

The results of an extensive study of the formation and characteristics of three phases formed during the hydrothermal precipitation of Fe(III) and As(V) are presented by Gomez et al. (2011a). The phases formed included: Sulfate substituted **Scorodite** $[(FeAsO_4)_{1-0.67x(}(SO_4)_x{:}2H_2O]$ $x \leq 0.16$; **FASH** (also referred to by Swash and Monhemius as Type I $[FeAsO_4)_{0.988}(SO_4)_{0.01}0.72H_20]$; and **BFAS** (also referred to by Swash and Monhemius (1994) as Type II) $[FeAsO_4)_{1-x}wH_20$ x=0.3to 0.7]. The conditions for temperature and initial molar ratio of Fe(III)/As(V)) to form the various products are summarized by the authors in a table designated the GBD Precipitation Diagram (Gomez-Becze-Demopoulos) shown here as Table 10. The authors also report that TCLP stability tests were conducted on the products during short and long-term aging. The results follow: Short term (multiple TCLP solution contacts for 24 hours at pH ~5) results were: **FASH** was slightly more soluble than scorodite and **BFAS;** all gave <1 mg/L after 7 contacts. Long-term (>**8 months** at pH 3, 5, and 7.5) test results were: **BFAS** and scorodite about equivalent; **FASH** had a higher release. At pH 3 all were < 1 mg/L; at pH 5 **FASH** was 2.5 mg/L; **BFAS** was ~0.1 mg/L; sulfate substituted scorodite was 0.6 mg/L. At pH 7 all were relatively high, >>1 mg/L. The authors recommend that the **BFAS** may be the best form for storage at pH<7.

Table 10. GBD diagram for the conditions required to form various autoclave products. *Source*: Gomez et al. 2911a.

225	FAsH 10 hrs	FAsH 10 hrs	FAsH 10 hrs	BFAS 10 hrs	BFAS 10 hrs	BFAS 10 hrs
200	FAsH 10 hrs	FAsH 24hrs FAsH+Scorodite 10 hrs	FAsH 10 hrs	BFAS 10 hrs	BFAS 10 hrs	BFAS 10 hrs

A recent autoclave scorodite formation (205ºC, 5 bar O_2, 50 minutes) study has been reported by Strauss, Yahorava, and Gomez (2017) and Strauss et al. (2021). The study investigated the stability of the BFAS product before and after cyanidation. *"BFAS precipitates, as well as their cyanidation residues were found to pass the respective environmental tests in terms of arsenic release".* The stability tests were short term studies using exposure to the U.S. TCLP (EPA Method 1311) and SPLP (EPA Method 1312, a water leach test at a pH of ~4.8) test procedures. The results were: before cyanidation 0.55 mg/L (SPLP) and 0.56 mg/L (TCLP); after cyanidation 0.16 mg/L (SPLP) and 0.16 mg/L (TCLP). Long-term test work was not reported.

Autoclave production of scorodite has been investigated by Nazari et al. (2017). This treatment is referred to as HTPO (High Temperature Pressure Oxidation) and has been applied to gold refractory ores containing arsenopyrite. The specific treatment conditions were: 150-230ºC, 2000 kPa, Fe/As molar ratio ~1. Ferric sulfate was added as an iron source and arsenopyrite was reacted to form As(III) which was then oxidized to As(V) and scorodite was precipitated. The residue containing scorodite and gold was leached in cyanide: scorodite was not solubilized in the cyanide solution. The scorodite residue can be stored in a permitted disposal site.

Autoclave /POX production of ferric arsenate compounds and other products have been reported on by Strauss et al. (2021). The group produced autoclave products by solution precipitation from controlled Fe/As mole rates experienced in pyrite/arsenopyrites treatment in the gold industry; and they investigated autoclave/POX treatment of gold industry concentrates containing similar Fe/As ratios as present in the synthetic solutions. The products formed from the synthetic solutions included "*basic ferric sulphate (As-BFS), basic ferric arsenate sulfate (BFAS) and ferric arsenate sub—hydrate (FAsH)"*. However, the *"major Fe-As's generated in the POX residues form the concentrates were As-BHS and BFAS".* This work points out that great care must be taken when evaluating and comparing actual treatment parameters.

Atmospheric Pressure Formation of Scorodite-

Atmospheric scorodite formation has been investigated for more than twenty years and has now advanced to industrial application. Filippou and Demopoulos (1997) and Demopoulos (2009) have described the process: ferric ions are fed to a reactor at ~80-95º, at ambient pressure, containing arsenate at a pH of ~0.9 to form amorphous ferric arsenate; crystallization is accomplished by slow addition stepwise neutralization over a pH range of 0.9-4 in the presence of scorodite seed crystals with the result being that the ferric arsenate formed crystalline scorodite. The ambient pressure process also requires relatively high initial arsenic bearing solutions, e.g., 1 to 10 g/L. Fujita et al. (2012, 2010, 2009, 2008a, 2008b) have shown that scorodite can be formed at ambient pressure at lower temperatures, e.g., 50-70ºC, by insitu oxidation of ferrous ions in arsenate solutions. Su and Ma et al. (2021) have recently reported on their studies using ferrous carbonate (siderite) to treat concentrated waste sulfuric acid with the formation of scorodite. Their conditions were similar to that quoted by Fujita et al., i.e., pH 1.1, Fe/As molar ratio 2, 95ºC, 10 hours. Their products were scorodite with >99.6% arsenic containment for solutions containing 5.7-32 g/L As. The studied process was pH adjustment with lime to ~1 (gypsum formation), H_2O_2 oxidation of As(III) and Fe(II) with subsequent precipitation of scorodite. The product passed the U.S. EPA TCLP test 0.19 mg/L but longer stability test work was not reported.

It is often stated in the literature that scorodite can only be formed at ambient pressure from elevated arsenic containing solutions (>10 g/L; however, Caetano et al. (2009) have demonstrated that scorodite can be formed from dilute arsenic bearing solutions, e.g., 0.1 to 1.1 g/L under ambient pressure, elevated temperature treatment. The advantage of non-autoclave processing is that it is less costly, more energy efficient than the autoclave process and produces less waste material to be disposed of when compared to the FH process.

Rong et al. (2020) have investigated the conditions to transform arsenical ferrihydrite to scorodite. "*A series of experiments were carried out to investigate the optimal reaction conditions and applicable scope of initial arsenic concentration for this process. The results indicated that 99.9% of arsenic was removed from aqueous solution and immobilized as stable scorodite* *at reaction time of 6 h, pH 1.5, Fe/As molar ratio of 1.1 and reaction temperature of 90◦C. This process is applicable to the solution with initial arsenic concentration ranging from 1 to 10 g/L, which shows great potential for practical applications".* All the scorodite products were subjected to the TCLP conditions and less than 0.1 mg As/L was leached. Long-term aging tests were not preformed. Rong et al. (2020b) also discuss the ferrihydrite to scorodite pathway and they note that the transformation is dependent on the initial arsenic concentration, e.g., crystalline scorodite is formed (six hours required) for solutions initially containing 20-30 g/L arsenic but not at concentrations below 10 g/L or above 30 g/L. "*At 10 and 20 g/L initial arsenic concentration, the oxidation of ferrous ions produces ferrihydrite. The transformation of ferrihydrite into scorodite goes circularly through four stages: (i) surface complex of arsenate and ferrihydrite, (ii) release of ferric ion by the dissolution of ferrihydrite, (iii) the adsorption of ferric ion on adsorbed arsenate, and (iv) re-adsorption of arsenate on adsorbed ferric ion [29,30]. This cycle ensures the transformation of ferrihydrite into scorodite".*

Stability of Scorodite

Scorodite formed by all the processes listed above pass the short-term EPA TCLP test. Example longer-term test results are summarized in Table 11.

Please note that the EPA TCLP test is not considered a reasonable measure of stability by many investigators. The test is an acetate pH buffered environment (pH~5) designed to simulate co-disposal conditions in a municipal landfill. It is a test used to determine if a solid waste should be considered hazardous (for arsenic the measured concentration must be <5 mg/L to be considered non-hazardous). It is a test conducted under oxidizing conditions at only one pH, one solid/liquid ratio, one temperature, and one reaction time. However, an industrial waste may be stored under reducing conditions, under microbiological conditions, changing pH conditions, changing oxidation/reduction potentials and temperature. The TCLP results are biased by not considering reaction kinetics, particulate size, time and susceptibility to reagent complexation and valence state.

Ma et al. (2021) demonstrated that hydrous ferric arsenate HFA (Fe(III)/As(V) molar ratio of ~1) transforms to symplesite and parasymplesite in anaerobic and circumneutral leaching conditions in the presence of added Fe(II). Significant transformation occurred within a fifteen-day period (aging was evaluated to 72 days) at pH 6-8. The authors summarized their results: *"HFA is stable at pH 2 in the presence of Fe(II). At pH 4, HFA can react with Fe(II) and form a Fe(II)-bearing semi-crystalline phase. At pH 6, crystalline symplesite and parasymplesite were formed and constituted the major As-bearing phases in the host solids, regardless of the amount of Fe(II) added. At pH 8, parasymplesite became the dominant crystalline phase in the host solids with the input of Fe(II)".* Symplesite and Parasymplesite are both Fe(II) and As(V) compounds.

Zidan et al. (2020) in a follow up paper (Ma et al. 2021) investigated the stability of scorodite under reducing conditions. Their study demonstrated significant transformation of the scorodite to parasymplesite. The reduction of scorodite after 134 days at pH 6 to7 released approximately thirty percent of the arsenic. The test environment was maintained reducing by enolic hydroxyl groups (AH_2) common to natural organic matter. The authors presented summation was: *"scorodite, therefore, was unstable during its long-term storage in an Fe-reducing environment at (slightly) circum-neutral pH".*

Coudert et al. (2020) reported on their extensive review of the literature for the treatment of As-rich mine effluents and produced residues stability: *"An extensive literature review showed that Fe(III)-As(V) precipitates, especially bioscorodite and (nano)scorodite, appear to be the most appropriate forms to immobilize As due to their low solubility and high stability, especially when encapsulated within an inert barrier such as hydroxyl gels".*

Zhu et al. (2019) have recently reported on their re-evaluation of the thermodynamics and kinetics of scorodite dissolution. Their evaluation is not good news for using scorodite as a stable secure waste disposal procedure. A few of their conclusions follow: *"Assuming scorodite (grain size > 5microm) is the main storage of As in a porous geological medium (e.g., aquifer) that has an average water content of 15% (w/w) and a background As concentration of 15 ppm (Smith et al., 1998), dissolution at this rate (log rn = 11.3 mol/m2/s at* 25oC*) would render initially As-free water to one with arsenic concentration surpassing the 10 ppb threshold value within 17 h".* Also *"On the other hand, calculated ambient condition scorodite dissolution rate is one to two orders of magnitude higher than that of common rock-forming minerals, indicating that previously assumed low solubility may not be a solid rationale for treating scorodite as a safe storage for As in natural environments or industrial settings".*

Table 11. Examples of long-term stability test work for scorodite

Reference	Study Period	Results, mg As/L	Comments
Demopoulos 2005; Bluteau 2004 (Thesis); Bluteau and Demopoulos 2007	**20-weeks** at 75ºC **66-weeks** at 22ºC	For the 22ºC 66-week water solubility tests, the results were: pH 5, 0.35 mg/L; pH 6, 0.97 mg/L; pH 7, 5.89 mg/L. The 66-week tests showed that scorodite "*undergo slow incongruent dissolution yielding a highly metastable nano-sized 2-line ferrihydrite phase*" *(2004, 2005*). "the *growth and re-crystallization of ferrihydrite was apparently retarded by arsenate adsorption"* (2007).	At pH levels above ~4 incongruent dissolution of scorodite will slowly form nano-size FH. After 20-weeks at 75ºC or 66- weeks at 22ºC the authors did not observe any signs of growth or transformation of the amorphous arsenical FH.

Reference	Study Period	Results, mg As/L	Comments
Gomez et al. 2011a	>**8-months** at pH 3, 5, and 7	Short term (multiple TCLP solution contacts for 24 hours at pH ~5), FASH slightly more soluble than scorodite (SR) and BFAS-all gave <1 mg/L after 7 contacts. Long-term (>8months) pH 3 all were <0.1 mg/L pH 5 SR 0.6 mg/L; FASH 2.5 mg/L; BFAS ~0.1 mg/L pH 7 all high >>1	Tested the short and long- term stability of Scorodite (SR), FASH (Type I); BFAS (Type II), autoclave products in TCLP.
Lagno et al. 2010 (See also Katsarock 2011)	**10-days, 6-weeks**	Results: Oxic-the coating was protective (reduced As release from 1.5 mg/L to ~0.15 mg/L at pH 4; 45 mg/L to 1.5 mg/L at pH 8). Anoxic-pH 7, 100mV, not as protective, Fe(III) and As(V) partially reduced to Fe(II) and As(III). Uncoated scorodite showed ~200 mg/L As at six-weeks (pH 8); coated showed <10 mg/L (values not given by authors, data from their Figure 13).	Scorodite was encapsulated with aluminum phosphate and then subjected to oxic and anoxic water aging. Oxic aging was conducted for 10-days; anoxic aging for 6-weeks. Four materials were evaluated: scorodite; one, two, and three layers of aluminum phosphate on scorodite.
Bluteau et al. 2009	Up to **57-weeks**	The gypsum saturated equilibrium arsenic concentration was 3.6 mg/L at pH 7; without gypsum the value (as reported by Bluteau and Demopoulos, 2007) was 5.9 mg/L	Scorodite dissolution tests were conducted in deion water saturated with gypsum (4-8 g/200 mL) at 22ºC, pHs 5, 7, 9 for up to 57 weeks.
Gonzalez-Contreras 2012 Gonzalez-Contreras et al. 2012	Up to **1-year**	Aging time after formation was 10 or 22-days. The TCLP exposure was for 1-year: the 10-day aged product leached 1.5-2 mg/L; the 22-day aged product leached 1 mg/L to 0.16 µg/L. The most stable crystals were formed at pH 1.2, aged 22-days and when exposed to synthetic landfill conditions for 1-year leached 16 µg/L	Bioscorodite stability tests were conducted in EPA TCLP Method 1311 test conditions.
Salomon-de-Friedberg et al. 2017 (CESL)	**3-years**	Water leachability was less than the British Columbia limit of <2.5 mg/liter for 3-year aging. TCLP was applied to "many residue samples during the pilot studies; results were always <0.15 mg/L	Stability of scorodite was evaluated by contacting the residue with twenty times its weight in water and observing the dissolution of arsenic as a function of time.
Leetman et al. 2016	**169-days 900-days**	A sulfate gel/scorodite system (at a low Al(III)/As(V) molar ratio of 0.1 and 0.2) was aged in a water environment at a pH of ~7 for up to 900 days. The reported results were that arsenic dissolution was <2 mg/L for unwashed gel/scorodite and <0.5 mg/L for washed (TCLP solution). Also, the authors state "There was only 0.2 mg/L of As released from the sulfate gel sample/scorodite system (Al/As=1 equilibrated at pH 7.3 for 169-days; that is 50 times lower than the solubility of the control scorodite".	Aluminum hydroxide gel encapsulated scorodite was evaluated by long-term aging in a water leach environment.

Example Industrial Applications that Produce Scorodite

Blanchard et al. (2017) investigated arsenic speciation in the JEB Tailings Management Facility (TMF) at McClean Lake, Saskatchewan to verify that atmospheric precipitated scorodite is stored in their repository. The facility uses an oxidizing sulfuric acid leach of uranium ore that contains appreciable arsenic (as nickel arsenide), e.g., ~300 to 50,000 µg/g. The arsenic is leached as As(V) and As(III) in concentrations of ~100 mg/L to ~10,000 mg/L. The arsenic removal process is performed on their process raffinate solution: ferric sulfate is added to provide a Fe(III)/As molar ratio of at least 3; conditions are E_H +680 mV, pH ~1; pH is adjusted with lime to pH 4 then to 7.5. The precipitated product is thickened along with other residues and pumped to their tailings disposal site. Laboratory studies showed that poorly crystalline scorodite formed up to a pH of 3.2. Excess iron then precipitates as amorphous arsenical FH during the near neutral pH adjustment. Prior to this study scorodite had not been identified in the TMF. However, using XANES spectroscopy showed the following: the tailings samples consisted of *"scorodite and poorly crystalline iron-containing arsenates"*. The iron-containing arsenates were assumed to be FH, *"arsenate adsorbed on ferrihydrite is likely present given the abundance of ferrihydrite in the TMF"*.

CESL (Cominco Engineering Services Limited), have patented and pilot plant demonstrated their POX process to treat copper-gold-arsenic sulfide concentrates (Salomon-de-Friedbert et al. 2017). Their flowsheet was presented previously in Figure 14. The CESL process is an intermediate temperature autoclave treatment applied to over 18 high arsenic-copper concentrates (up to 18% As). Autoclave conditions included: ~150ºC, ~14 bar pressure, 60-90 minute reaction time to oxidize copper sulfides and As(III) with the precipitation of scorodite. The process consists of autoclave formation of Type II scorodite; atmospheric leaching the residue to recover copper; multiple washing stages; and disposal of scorodite by impoundment. The TCLP test was applied to many residue samples during the pilot studies and the results were always <0.15 mg/L. Stability of the scorodite has been evaluated by contacting the residue with twenty times its weight in water and observing the dissolution of arsenic as a function of time. The results have shown leachability of less than the British Columbia limit of <2.5 mg/L over a three-year period.

Outotec (process described previously) provides POX technology for treating copper-arsenic and gold-arsenic-pyrite concentrates (Ruonala et al. 2010; Haavanlammi 2017). The process is based on atmospheric oxidation/precipitation of amorphous ferric arsenate with subsequent recovery of the ferric-arsenate residue and treatment to convert the ferric arsenate to crystalline scorodite in an autoclave using the following operating conditions: 160-200ºC, pH 1.5-4.5, and an Fe/As molar ratio 1-1.5. The stated advantage of this treatment is that only the ferric arsenate residue need be treated in an autoclave and not the entire solution. A smaller autoclave operating at a lower temperature than conventional HTPO processes should give it an economic advantage.

EcoMetales Copper Flue Dust Treatment Plant (PTPA) and the Arsenic and Antimony Abatement Process (PAAA) near Calama, Chile treat smelter flue dust, refinery effluent and other solid hazardous waste from Codelco's Chuquicamata, Potrerillos and Ventanas smelter and refinery complexes (MI 2017). Dusts are acid leached and leach residues are recycled to the smelters. The As(III) bearing leach solutions are oxidized, ferric reagent (Fe/As mole ratio ~1) is added pH (1-1.2) at ambient pressure and elevated temperature (80-85ºC) to form scorodite (Demopolous et al. 2014). The product is disposed of in an authorized/permitted nearby site.

Monhemius and Swash (1999) have applied an autoclave process that allows bleed streams from copper electrorefining to be treated to produce scorodite. The electrolyte solution builds up the arsenic content to 20 g/L which must be treated to prevent contamination in the smelters copper product. The operating conditions used in their study were: bled solution containing 13 g/L as, ~21 g/L F, ~150-190ºC, 2500 kPa O_2, free acid <60 g/L, Fe/As molar ratio of 1/1 to 2/1, residence time 2 hrs. Arsenic removal was >90-95% as scorodite.

Nazari et al. (2017) state that atmospheric scorodite plant is operated at the DOWA plant in Osaka, Japan. The Dowa plant uses the conditions: 95ºC and the iron source is ferrous which is oxidized insitu to react with As(V) (Abumiva et al. 2012).

Plaque's (Huismann et al. 2011) ASENOTEQ process illustrate that scorodite can be formed using a biological oxidation process. As(III) solutions are oxidized to As(V) by H_2O_2 prior to being fed into a reactor at ~70ºC, pH 1.2 and an Fe/As molar ratio of 1.5. Ferrous ions are oxidized biologically to ferric ions insitu and scorodite forms (Gonzalez-Contreras 2012). The preferred application is to solutions containing arsenic concentrations >1000 mg/L.

BIOX (described previously) is a well commercialized example of bacteria biohydrometallurgy applied to oxidize refractory gold ores containing pyrites, arsenopyrite and arsenical pyrites, and copper sulfides. The process is currently being used at twelve sites. The bacteria are mesophilic (40-45ºC) and acidophile (pH 1.2-1.8) microorganisms that can function in arsenic concentrations up to 20 g/L As(V) and 6 g/L As(III). Scorodite is formed as the disposable product (Gonzalez-Contreras 2012; van Aswegen et al. 2006).

Biogenic scorodite or bioscorodite formation has also been described by Gonzalez-Contreras (2012) in her doctorate thesis and in related publications (Gonzalez-Contreras et al. 2012, 2014). The process is based on the biological oxidation of ferrous ions in the presence of arsenate and the formation of scorodite was demonstrated in a continuous stirred two tank reactor system (CSTR). The conditions were: 72ºC, 2.8g/L As(V), and 2.4 g/L ferrous were fed to the reactor system at a pH 1.2. A 10% by volume biomass (thermoacidophilic microorganisms) oxidized the ferrous to ferric insitu with the As(V). The reported rate of As(V) removal was 1 g/L/day and the formation of scorodite was 3.2 g scorodite/L/day. The study conclusion was that the effluent contained ~30 mg/L arsenic, and that 99% of the incoming arsenic was removed and that bioscorodite formed. Testing in TCLP solutions showed good stability, e.g., only 0.4 mg/L As(V) was leached in one hundred days of exposure. When jarosite was present the stability test resulted in a solution As(V) concentration of 0.8 mg/L. Gonzalez-Contreras et al. (2012) note that the relative stability of the bioscorodite is dependent on several factors including the rate of precipitation and aging time. They present aging stability data, e.g., in a leaching test (conditions not given) showed 0.1 mg/L of dissolved arsenic after 40 days. The authors suggest that the process could be utilized "*for treating acid plant effluents, copper electrorefining electrolyte bleed streams, leach solutions from treatment of arsenic oxide dusts and contaminated soils*". Paques has commercialized the process as Arsenoteq (Huisman et al. 2011).

Conceptual Flowsheets for formation of arsenical FH and scorodite

Conceptual flowsheets for forming arsenical FH and scorodite are presented in Figure 23.

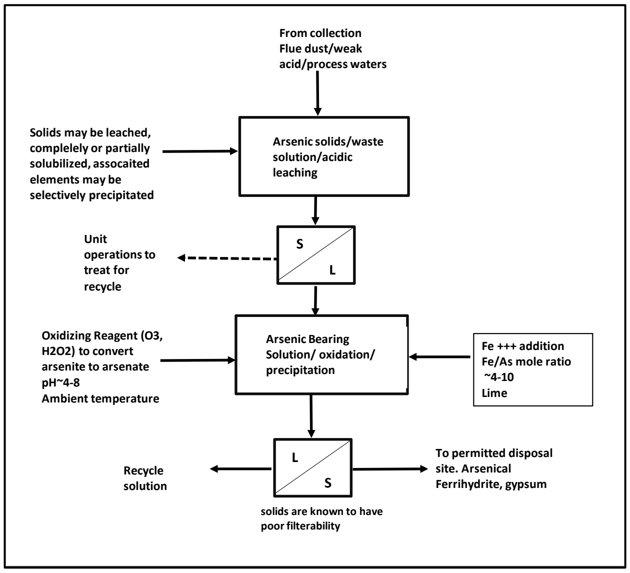
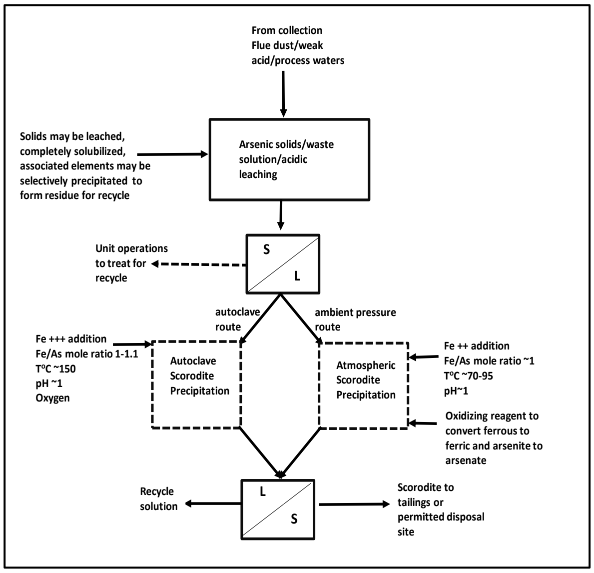


Figure 23. Conceptual flowsheet for forming arsenical FH



Conceptual flowsheet for forming scorodite by autoclave or ambient pressure, elevated temperature treatment

Other Fixation Possibilities

Encapsulation Possibilities

Scorodite is unstable in a variety of conditions including alkaline solutions. There have been several studies designed to increase scorodite stability at high pH levels, e.g., the use of surface coatings to encapsulate and provide a protective barrier. Encapsulation of scorodite particles with hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) and hydroxyfluoapatite (FAP) showed arsenic leachability of <1 mg/L for HAP and ~8 mg/L for FAP when exposed to an anoxic environment at pH 9 for 40 days (Katsarou 2012). Uncoated scorodite released 22 mg/L in the same environment. However, chemical, and mechanical stability was not sufficient to protect the scorodite (Demopoulos 2014; Lagno et al. 2010).

Leetmaa et al. (2016) have investigated the use of an aluminum hydroxyl gel made from aluminum sulfate salts (chloride salts were also investigated) that appear to have protective properties. The gel procedure was applied to ambient pressure formed precipitated scorodite. Several variables were investigated, e.g., type of gel, Al(III)/As(V) molar ratio, liquid/solid ratio, prewashing technique, etc. The sulfate gel/scorodite system (at low Al(III)/As(V) molar ratios of 0.1 and 0.2) was aged in a water environment (initially at a pH of 8 and allowed to drift to 7) for up to 900 days. The reported results were that arsenic dissolution was <2 mg/L for unwashed gel/scorodite and <0.5 mg/L for washed (TCLP solution). Additional data are presented and discussed in the investigator's publication.

Ke et al. (2019) have reported on their studies using polyferric sulfate as an agent to facilitate the formation of a ferrihydrite particle coatings on scorodite to enhance its stability. The coating procedure utilized the conditions: pH 1.5, 90°C, PFS mass ratio was controlled at 0-30%. The coating technique resulted in decreasing the TCLP leach result from 10-30 mg/L to below 0.01 mg/L. No long-term aging test-work was performed.

Wang et al. (2019) coated scorodite to form a core-shell structure of first ferrihydrite particles on the surface of the scorodite which then grew with time to shield the scorodite core with goethite (FeOOH) and thereby protecting underlying arsenide material. *"Through analysis of the synthesized core-shell materials using XRD, SEM, XPS and EDS techniques, it was confirmed the core was* $FeAsO_4{:}2H_2O$*, and the shell was FeOOH, TCLP tests at pH 4.93 and leaching time tests were carried out in alkaline solutions with pH of 9.30 and 10.0. The results indicated that S@F(pH 1, 6 h) had significant stability on both weak acid and alkaline solution, the concentrations of As extraction liquid were all below 0.01 mg/L".*

Orgon et al. (2019) also investigated the stabilization of scorodite by precipitating ferrihydrite onto scorodite surfaces. Their procedure was to form scorodite first then to precipitate ferrihydrite to form a complex mixture of scorodite and ferrihydrite. They treated 5 g/L As(III) with ozone, pH 3, for 3 hours. Then ferrous sulfate was added and reacted at 90°C for 2 hours. The pH was then raised and ferrihydrite was precipitated. "*The effects of Fe/As molar ratio and pH were evaluated. The TCLP tests demonstrate that the solids generated under these conditions (Fe/As ratio 4, final pH 3 and 4) are stable and no arsenic can be detected in leaching tests for 72 hours".*

Coudert et al. (2020 Review) conducted a review of treatment processes that emphasized product stability. Their conclusion was *"An extensive literature review showed that Fe(III)-As(V) precipitates, especially bioscorodite and (nano)scorodite, appear to be the most appropriate forms to immobilize As due to their low solubility and high stability, especially when encapsulated within an inert material such as hydroxyl gels. Research is still required to assess the long-term stability of these As-bearing residues under mine-site conditions for the sustainable exploitation of refractory gold deposits".*

An extensive review of acid mine drainage literature by Park et al. (2019) is highly recommended for its microencapsulation information. The paper deals with stabilization of pyrites and other sulfide minerals to limit their dissolution to form acid mine drainage waste solutions. However, their review includes encapsulating techniques and successes that may lead the reader of this review to capture appropriate techniques for stabilizing arsenic bearing processing products. The authors present references for studies that lead to passivation by organic coatings *(formation of hydrophobic coatings on sulfide mineral surfaces to inhibit mineral-water interactions*), microencapsulation (ferrihydrite*, apatite, iron phosphate, silica coatings*) and silane-based coatings (for forming *coatings composed of both and inorganic components).*

Arsenic Trisulfide

Arsenic (III) trisulfide, As_2S_3, has a very limited solubility in water, e.g., <1 mg/L at pH <4 and is relatively stable under anoxic and reducing conditions. It contains a very high arsenic content, ~60% which makes it a desirable storage product. However, it is susceptible to atmospheric and bacterial oxidation. Therefore, it cannot be stored in landfill disposal sites. An example of the production of arsenic trisulfide is sulfidation of As(III) solutions practiced at the Saganosseki copper smelter; the arsenic bearing solution is treated by lime neutralization and NaHS to form arsenic trisulfide. The arsenic trisulfide is then stabilized by treating it in a non-oxidative autoclave at 200ºC, 20-atm to polymerize and densify the product. The product is compact, contains ~60% arsenic, 1% water and is stored in concrete (Nazari et al. 2017; Valenzuela et al. 2006). Another example for a treatment that produces arsenic trisulfide is described by Gabb and Davies (1999) at the Kennecott Utah smelter. Leach solutions are treated to control the distribution of copper, arsenic, and cadmium. Copper is first selectively precipitated by pH and E_H control (at 40-60ºC) into a residue solid that is recycled to the smelter. Arsenic and cadmium are then precipitated as sulfides by addition of either H_2S gas or NaHS. The solids are recovered and are routed to their EPA permitted hazardous waste disposal facility.

Plaques (Huismann et al. 2011) has developed and patented the THIOTEQ process for forming arsenic trisulfide. The process has two stages, one chemical and the other biological. Bisulfide (HS-) is produced in a biological reactor external to the chemical reactor. Elemental sulfur and ethanol are fed to the biological reactor to form bisulfide. The reaction is: $6S^o$ + ethanol (electron donor) + $3H_2O = 6HS^- + 2CO_2$ (reaction in presence of bacteria). The HS- solution is fed to the chemical reactor at pH 1-2, 60-90ºC, to precipitate As(III) as orpiment (As_2S_3). Very acidic solutions in the biological reactor are desirable, e.g., pH <3 is required to attain a final arsenic concentration of <0.2 mg/L. Orpiment must be stored in suitable permitted repositories. The authors state that the THIOTEQ technology is used at more than ten industrial plants for the reduction of sulfur compounds. The preferred application is to solutions containing high arsenic concentrations but <5 g/L.

Hu et al. (2019) proposed *"a safe treatment of arsenic-containing acid wastewater, a new process was proposed, including arsenic removal via sulfide precipitation and hydrothermal mineralization stabilization*". Arsenic trisulfide was precipitated using sodium sulfide, the conditions were: pH 4, S^{-2}/As molar ratio 3, 25ºC, 60 minutes; mineralization conditions were: 240ºC, filling rate 70%, glucose mass fraction 5%, hydrothermal duration 12 hours. The resulting TCLP test result was 4.8 mg/ L (for untreated arsenic sulfide the TCLP leached 212.97 mg/L). Long-term aging was not reported.

Mirazimi, M., J. Fan, and W. Liu (2021) have recently published the results of their studies to delineate the characteristics of the effect of pH, dissolved oxygen, and temperature on the release of arsenic and sulfur from arsenic trisulfide. This paper is a valuable contribution to understanding the leachability of arsenic trisulfide. The authors present their rate equation and have identified that the leaching results are controlled by surface chemical reaction rather than by diffusional transport. The authors present the TCLP leach test results for arsenic trisulfide reported by Lehimura (2007) e.g., 25 mgAs/L.

Shakya and Ghosh (2019) evaluated the stability of biogenic arsenosulphides (mainly orpiment and realgar) generated under reducing conditions. Biosolids were formed in a sulphidogenic growth reactor using a mixed bacterial culture containing sulphate, nitrate, and arsenic. Recovered biosolids were subjected to the TCLP tests (for 24 and 84-hours), including samples containing (or not containing) various amounts of dissolved oxygen (to study the effect of an oxic environment) on the TCLP result. The TCLP results for the 24-hour tests were 21µg/L (anoxic) and 14µg/L (oxic). Kinetic evaluations were also performed in column exposure tests (with aerated DI water at pH 7 for 90 days). "*For all protocols tested, leachate arsenic concentrations were always below 300µg/L, which was far below than the current maximum Australian TCLP leachate limits for arsenic of 700µg/L"*. The authors concluded: *"that the biogenic arsenosulphides formed under reduced environment is stable and do falls under the category of hazardous waste".*

Wang et al. (2019) coated scorodite to form a core-shell structure of first ferrihydrite particles on the surface of the scorodite which then grew with time to shield the scorodite core with goethite (FeOOH) and thereby protecting underlying arsenide material. *"Through analysis of the synthesized core-shell materials using XRD, SEM, XPS and EDS techniques, it was confirmed the core was $FeAsO_4{:}2H_2O$, and the shell was FeOOH, TCLP tests at pH 4.93 and leaching time tests were carried out in alkaline solutions with pH of 9.30 and 10.0. The results indicated that S@F(pH 1, 6 h) had significant stability on both weak acid and alkaline solution, the concentrations of As extraction liquid were all below 0.01 mg/L".*

Arsenate Phosphate HydroxyApatite (APHAP)

Formation and long-term stability of aluminum/arsenate/phosphate hydroxyapatites [APHAP; $Ca10(As_xP_yO_4)_6(OH)_2$] have been investigated by Twidwell, et al. (1998-2015) and his research graduate students. These compounds were investigated because they are produced by utilizing a lime-based precipitation process; and it is known that apatite compounds are very stable in the presence of carbon dioxide in air (which is not true for the various calcium arsenate compounds). The studies (Figures 24 and 25) demonstrated excellent stability for arsenate-apatite containing a PO_4/AsO_4 molar ratio greater than seven, e.g., the APHAP compounds showed an arsenic release of less than five micrograms/liter using the water-based EPA SPLP Method 1312 and the EPA TCLP Method 1311. The aging solubility results in the SPLP tests were <1.4 µg/L and <0.8µg/L (at pH 12.3) after 4 years and 8 years of exposure to air, respectively.

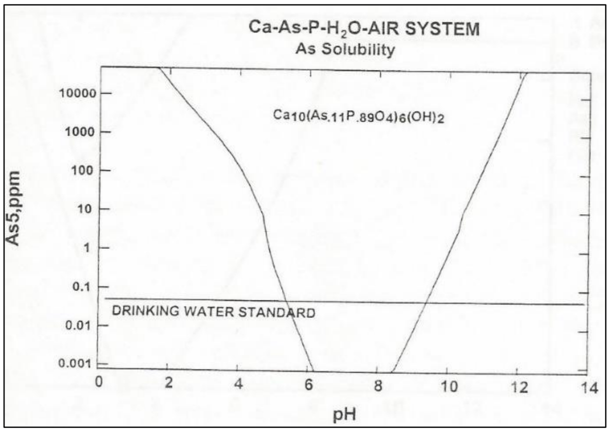


Figure 24. Stability of APHAP (PO_4/AsO_4 mole ratio=7) mineral-like precipitated product exposed to air. *Source:* Generated by Huang STABCAL 2015.

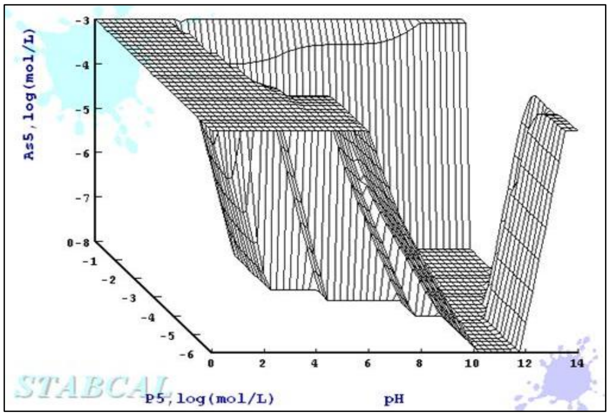


Figure 25. 3-D illustration of the solubility of APHAP (PO_4/AsO_4 mole ratio=7) as a function of pH (Initial arsenic 0.01 mole/L) *Source:* Generated by Huang STABCAL 2015.

Symplesite

McCloskey and Twidwell (2008b) and McCloskey (2010) designed and conducted a full-scale operation using a two-stage treatment system at an industrial site in Emeryville, California to lower As(V) concentrations from 100 mg/L to <25 µg/L. The plant was operated for a four-year period to clean contaminated water to less than the drinking water standard. The first stage of treatment was precipitation of symplesite [$Fe_3(AsO_4)_2{:}8H_2O$] by the addition of lime and ferrous sulfate (at pH at 7). The arsenic was lowered to <6 mg/L. The resulting water was then treated by FH precipitation using hydrogen peroxide as the oxidant for Fe(II) conversion to Fe(III) at an Fe/As molar ratio of 4. The residues from the two stages were mixed, dried, and sent to a permitted disposal facility. Symplesite does not pass the TCLP test requirement and must, therefore, be subjected to stabilization as required by the RCRA-LDR regulations.

Ma et al. (2021) demonstrated that hydrous ferric arsenate HFA (Fe(III)/As(V) molar ratio of ~1) transforms to symplesite and parasymplesite in anaerobic and circumneutral leaching conditions in the presence of added Fe(II). Significant transformation occurred within a fifteen-day period (aging was evaluated to 72 days) at pH 6-8. The authors summarized their results: *"HFA is stable at pH 2 in the presence of Fe(II). At pH 4, HFA can react with Fe(II) and form a Fe(II)-bearing semi-crystalline phase. At pH 6, crystalline symplesite and parasymplesite were formed and constituted the major As-bearing phases in the host solids, regardless of the amount of Fe(II) added. At pH 8, parasymplesite became the dominant crystalline phase in the host solids with the input of Fe(II)".* Symplesite ($Fe_2^{+3}(AsO_4)_2.8H_2O$)and Parasymplesite are both Fe(II) and As(V) compounds.

Zidan et al. (2020) in a follow up paper (Ma et al. 2021) investigated the stability of scorodite under reducing conditions. Their study demonstrated significant transformation of the scorodite to parasymplesite. The reduction of scorodite after 134 days at pH 6 to7 released approximately thirty percent of the arsenic. The test environment was maintained reducing by enolic hydroxyl groups (AH_2) common to natural organic matter. The authors presented summation was: *"scorodite, therefore, was unstable during its long-term storage in an Fe-reducing environment at (slightly) circum-neutral pH".*

Yukonite

Bluteau et al. (2009) and Gomez et al. (2010) have proposed that the mineral Yukonite [$Ca_2Fe_3(AsO_4)_3(OH)_{4-10}$:$xH_2O$ where x=2-11] likely forms from poorly crystalline scorodite with aging time, especially at pH levels of seven and above. Yukonite has been identified in mine waste and cyanidation tailings, and near neutral pH in natural environments (Drahota and Filippi 2009; Drahota et al. 2018 Review). Stability studies have shown positive results such as an arsenic solubility of <5 mg/L at pH 5-10 in an oxidizing, gypsum containing environment for 66 days, e.g., values were pH 5, 3.1 mg/L; pH 7, 8, 10 were 0.4, 0.45, 1.12 mg/L, respectively (Bohan et al. 2014). Jia and Demopoulos (2008) demonstrated that a poorly crystalline ferric arsenate (Fe(III)/As(V) molar ratio of 2), formed by lime neutralization at 22°C, pH 8, does, indeed, transform to Yukonite [$Ca_2Fe_3(AsO_4)_4(OH).12H_2O$] when aged at 75°C for seven weeks. Coudert et al. (2020 Review) present the formula for Yukonite to be [$Ca_3Fe(AsO_4)_2(OH)_3.5H_2O$].

Tooeleite (an As(III) containing mineral)

Tooeleite ($Fe_6(AsO_3)_4SO_4(OH)_4$:$4H_2O$) is a ferric arsenite oxyhydroxysulfate hydrate nano-crystalline compound found in waste at the U.S. Mine Gold Hill in Tooele County Utah (Opio 2013). *It is the only known ferric arsenite sulfate mineral and has environmental significance for arsenic remediation* (Liu and Wang 2020). Tooeleite has been found in acid mine drainage (AMD) areas and is thought to be formed via bacterial oxidation of Fe(II) (Morin et al. 2007; Egal et al. 2009). Tooeleite is similar to scorodite and is known as the trivalent arsenic form of scorodite (Nazari et al. 2017). It has been proposed to be an As(III) storage compound (Nishimura and Robins 2008; Liu and Wang 2020). However, Raghav et al. (2013) showed appreciable leachability in the TCLP test (which is conducted at a nominal pH ~5) *"tooeleite and silica amended tooeleite often was as least an order of magnitude higher than the TC (toxicity concentration)".* Opio (2013) noted that preparation of tooeleite can be formed at ambient temperature at pHs in the range 2-3.5 but is rapidly converted to poorly crystalline ferric arsenite at pH>4. Calcination at 600°C produced a ferric arsenate calcine with a TCLP solubility of <5 mg/L. Synthesis at 95°C showed no improvement for arsenic extraction in TCLP solutions. Their conclusion was *"the resultant precipitation of tooeleite from an As(III)-bearing weak acid and calcination of the resultant precipitate may offer a new process for As(III) fixation from copper smelter weak acid effluents*". Long-term stability testing was not reported. Choi et al. (2017) suggests that Tooeleite forms from FH using conditions; pH 1.8-4.5, initial As(III) concentration >0.75 g/L, an Fe/As mole ratio of 0.8-2, and ambient temperature. The authors report that they tested the short-term stability of tooeleite in TCLP solutions as a function of pH (1.8-9). The authors present a figure but did not provide the numerical values for the leach results except in the graph. The arsenic concentration values for pHs 1.8 to 4.5 appear to be greater than 5 mg/L and at pHs of five and above show hundreds of mg/L arsenic.

Wang et al. (2020) studied the biotransformation of As(III) to tooeleite via the oxidation of Fe(II) using Acidithioibacillus ferrooxidans. Optimized conditions were pH 2, 30o, initial As(III) of 500 mg/L. 95.4% of the arsenic was removed as tooeleite. Stability testing was not reported.

Yuan et al. (2020) reported on the formation of a chloride tooeleite-like compound ($Fe_5(AsO_3)_3Cl_2(OH)_45H_2O$). Conditions for the effective removal of arsenite were established, e.g., Fe(III)/As(III) molar ration 1.7 in a chloride solution at pH 2.3. However, the leachability of the precipitated solids resulted in relatively high arsenic leach results in the EPA TCLP static test procedure, e.g., 32mg/L (about the same as compared to tooeleite, i.e., 30mg/L). Long-term aging stability was not evaluated.

Majzhan et al. (2016) determined the thermodynamic properties of tooeleite, e.g., the standard free energy of formation was determined to be -5,376.3 kj/mol. Their evaluation as to whether tooeleite is an appropriate compound for outdoor long-term storage follows: "*Tooeleite has stability field only at very high activities of aqueous sulfate and arsenate. As such, it does not appear to be a good candidate for arsenic immobilization at polluted sites. An inspection of speciation diagrams shows that the predominance field of* Fe^{3+} *and* As^{3+} *overlap only at strongly basic conditions. The formation of tooeleite, therefore, requires strictly selective oxidation of* Fe^{2+} *to* Fe^{3+} *and, at the same time, firm conservation of the trivalent oxidation state of arsenic. Such conditions can be realized only by biological systems (microorganisms) which can selectively oxidize one redox-active element but leave the other ones untouched. Hence, tooeleite is the first example of an "obligatory" biomineral under the conditions prevailing at or near the Earth's surface because its formation under these conditions necessitates the action of microorganisms.*

Chai et al. (2018) reported on their study of the hydrothermal formation of tooeleite at elevated temperatures (105-120°C). The *optimized tooeleite* was reported to be formed at 120°C, pH 1.6, Fe(III)/As(III) molar ratio 1.5. The short-term stability was evaluated in TCLP test solutions to be 9 mgAs/L. They also investigated the use of a silica coating (siloxane bonding) to enhance the stability of the compound: *"this decreased the arsenic leaching concentration to 4 mg/L".*

Other Possible Storage Compounds

Majzhan et al. (2018) suggest that *"If some of the less common arsenate minerals have been shown to be less soluble than the currently used options for arsenic disposal (especially scorodite and arsenical iron oxides), they should be further investigated as promising storage media".* The authors studied several possible storage compounds but suggested that Kamarizaite ($Fe_3(AsO_4)_2(OH)_3.3H_2O$) may be such a compound *"Kamarizaite is predicted to have aa very similar solubility* *to scorodite, making it a phase of potential interest for further study".* The mineralogical makeup is presented by Chukanov et al. (2010).

Wang et al. (2021) have investigated the removal and stabilization of As(III) by the formation of Layered Double Hydroxides (LDH, e.g., ZnFe-As LDHs). Under optimized conditions of pH (8), molar ratios of Zn/Fe (2), Fe/As 3) the following transformations occurred *"The non-crystalline ferric arsenate was firstly formed. And then the phase transferred to amorphous ferrihydrite, followed by incorporating of zinc ions and intercalating of arsenic oxyanions and SO4. Finally, the "stone-like" LDH was obtained"*. Arsenic in initial solution was lowered from 100 mg/L to 0.13 mg/L and the TCLP test results applied to the solid products were always < 5 mg/L (for the optimized conditions the result was 1.87 mg/L). The products contained a mixture of arsenite and arsenate compounds (55% of the arsenite was oxidized to arsenate).

Lu et al. (2020) have investigated the anoxic reduction of adsorbed AsO_4 using Layered Double Hydroxides of Mg(III), Al(III) and Fe(III). The reader is referred to this publication. *"A 2-stage release and re-adsorption mechanism of total As(aq) occurred following the order:* $MgAlFeCO_3SO_4$ *>MgAlSO4 >*$MgFeCO_3$ *>*$MgAlCO_3$ *>*$MgFeSO_4$*. A significant portion of the solid surfaces (30–90%) was found as As(III) for all reacted LDHs. This work provides a guideline for the environmental behavior of As(V) adsorbed LDHs where relevant underwater cover TMF abiotic reducing conditions may exist".*

Layered Double Hydroxide containment of arsenic is presently a very active research area. A review of this topic has not been considered in this paper. The reader may be interested in the publications Wang 2021, Lu 2020, Majzhan 2018, Gomez 2014, 2013

CONCLUDING REMARKS

Mineral processing and extractive metallurgical operations have created and are creating appreciable arsenic-bearing wastewater and waste solid products that must be handled, treated for recycle, or treated for environmentally safe disposal. This is particularly true as the base metals and precious metals processing industries are faced with the necessity of treating more complex arsenic-bearing mineral ore bodies. As a result of the need to treat complex ores, and the need to meet present and future environmental regulations, research and operational emphases are presently being placed on the ways to produce stable arsenic-bearing residual products that can be safely stored in appropriate impoundments. These efforts must be continued.

RECOMMENDED READING

Anderson, C.A., 2019. Hydrometallurgy of Copper. In *SME Mineral Processing and Extractive Metallurgy Handbook*. Chapter 9.1, Society for Mining, Metallurgy, and Exploration Inc. (SME). 12999 E. Adam Aircraft Circle Englewood, Colorado 80112 www.smenet.org.

Coudert, L., R. Bondu, T.V. Rakotonimaro, E. Rosa, M. Guitstonny, C.M. Neculita. 2020 (Review). Treatment of As-rich mine effluents and produced residues stability: Current knowledge and research priorities for gold mining, *J. Hazardous Materials*, 386:19p.

Drahota, P., M. Filippi. 2009. (Review). Secondary arsenic minerals in the environment: A review. *Environment International*. 35:1243-55.

Filippou, D., P. St-Germain, T. Grammatikopoulos. 2007 (Review). Recovery of metal values from copper-arsenic minerals and other related resources. *Mineral Processing and Extractive Metallurgy Review*. 28(4):247-298. DOI: 10.1080/08827500601013009.

Lane, D.J., N.J. Cook, S.R. Grano, K. Ehrig. 2016. (Review). Selective leaching of penalty elements from copper concentrates: A review. *Minerals Engineering*. 98:110-121.

Nazari, A.M., R. Radzinske, A. Gahrema. 2017. (Review). Review of arsenic metallurgy: Treatment of arsenical minerals and the immobilization of arsenic. *Hydrometallurgy* 174:258-281.

Riveros, P.A., J.E. Dutrizac, P. Spenser. 2001. (Review). Arsenic disposal practices in the metallurgical industry, *Canadian Metallurgical Quarterly*. 40(4):395-420.

Schlesinger, M.E. 2019. Pyrometallurgy of Copper. In *SME Mineral Processing and Extractive Metallurgy Handbook*. Chapter 9.2. Society for Mining, Metallurgy, and Exploration Inc. (SME). 12999 E. Adam Aircraft Circle Englewood, Colorado 80112 www.smenet.org.

Safarzadeh, M.S., M.S. Moats, J.D. Miller. 2014a. (Review). Recent trends in the processing of enargite concentrates. *Mineral Processing Extractive Metallurgy Review*. 35(5):283-367.

Safarzadeh, M.S., M.S. Moats, J.D. Miller. 2014b. (Review). An update: Recent trends in the processing of enargite concentrates. *Mineral Processing Extractive Metallurgy Review*. 35(6):390-422.

Safarzadeh, M.S., J.D. Miller. 2016. (Review). The Pyrometallurgy of Enargite: A literature guide. *International Journal of Mineral Processing*. 157:103-110.

Twidwell, L.G. 2018. (Review). Treatment of arsenic-bearing minerals and fixation of recovered arsenic products: A review. Contact-ltwidwell@mtech.edu or www.researchgate.net/profile/Larry_Twidwell/contributions/?ev=prf_act. DOI: 10.13140/RG.2.2.12890.44486.

Twidwell, L.G. 2019. Environmental Considerations for Treatment of Effluent Waste Solutions and Solid Waste Products. In *SME Mineral Processing and Extractive Metallurgy Handbook*. Chapter 10.9. Society for Mining, Metallurgy, and Exploration Inc. (SME). 12999 E. Adam Aircraft Circle Englewood, Colorado 80112 www.smenet.org. 38p.

Twidwell, L.G. 2019b. (Review). Arsenic Production, Commodities and Fixation. In *SME Mineral Processing and Extractive Metallurgy Handbook*. Chapter 9.22. Society for Mining, Metallurgy, and Exploration Inc. (SME). www.smenet.org.

REFERENCES

Adams, M.D., 2016. Gold Ore Processing: Project Development and Operations. Second Edition. Elsevier, N.Y. 1027p.

Alyear, G.R., S.P. Hunt, B. Zhang. 2006. Copper Isasmelt-dealing with impurities. Proceedings Sohn International Symposium Advanced Processing of Metals and Materials. Volume 8-International Symposium of Sulfide Smelting. Editors: F. Kongoli, R.G. Reddy. TMS.

Anderson, C. G., S.M. Nordwick. 1995. Pretreatment using alkaline sulfide leaching and nitrogen species catalyzed pressure oxidation on a refractory gold concentrate. In EPD Congress 1996. Editor: G. W. Warren. Warrendale, PA: The Minerals, Metals and Materials Society, (TMS). pp323–341.

Anderson, C. G., S.M. Nordwick, L.E. Krys. 1991. Processing of antimony at the Sunshine mine. In Residues and Effluents: Processing and Environmental Considerations. Editors: R. G. Reddy, W. P. Imrie, and P. B. Queneau, Warrendale, PA. TMS. Pp349-366.

Anderson, C.A. 2019. Hydrometallurgy of Copper. In *SME Mineral Processing and Extractive Metallurgy Handbook*. Chapter 9.1. Society for Mining, Metallurgy, and Exploration Inc. (SME). www.smenet.org.

Anderson, C.G. 2005. The treatment of arsenic bearing ores, concentrates, and materials with alkaline sulfide hydrometallurgy. In Arsenic Metallurgy. The Minerals, Metals, and Materials Society (TMS) Warrendale, Pennsylvania, pp. 255-263.

Anderson, C.G, 2016. Alkaline sulfide gold leaching kinetics. *Mineral Engineering*. 92:248-256.

Balaz, P., E. Dutkov. 2009. Fine milling in applied mechanochemistry. *Mineral Engineering*. 22(7):681-694.

Balbonik, E., K.F. Smith, L.M. Moreau, T.T. Li, M. Maloubie, C. H. Booth, A.B. Kersting, M. Zavarin. 2020. Transformation of Ferrihydrite to Goethite and the Fate of Plutonium. *American Chemical Society Earth space Chemistry*. 4:11p

Blanchard, P.E.R., L.L. Van Loon, J.W. Reid, J.N. Cutler, J. Rowson, K.A. Hughes, C.B. Brown, J.J. Mahoney, L. Xu, M.

Bohan, G.P. Demopoulos. 2017. Investigating arsenic speciation in the JEB Tailings Management facility at McClean Lake, Saskatchewan using X-ray absorption spectroscopy. *Chemical Geology*. 466:617-625.

Bluteau, M., L. Becze, G. P. Demopoulos. 2009. The dissolution of scorodite in gypsum-saturated waters: Evidence of Ca-Fe-AsO_4 mineral formation and its impact on Arsenic retention. *Hydrometallurgy*. 97:221-27.

Bluteau, M-C, G. P. Demopoulos. 2007. The incongruent dissolution of scorodite-Solubility, kinetics and mechanism. *Hydrometallurgy*. 87:163-177

Bluteau, M-C. 2004. The incongruent dissolution of scorodite-solubility, kinetics, and mechanisms. Master of Engineering Thesis, McGill University, QC, November 2004.

Bohan, M., J. Mahoney, G.P. Demopoulos. 2014. The synthesis, characterization, and stability of Yukonite: Implications in arsenic mobility. Corresponding author: george.demopoulos@mcgill.ca. McGill University, Montreal. Canada.

Boboev, I.R. and R.S. Tabarov. 2021. Removal of scorodite arsenic from gold ore in the form of As2S3 and As4S4. *Hydrometallurgy*, 199:7p.

Bowell RJ, Parshley J. 2001. Arsenic cycling in the mining environment. Characterization of waste, chemistry, and treatment and disposal, Proceedings and Summary report on U.S. EPA workshop on managing arsenic risks to the environment, May 1–3, Denver, Colorado, USA.

Brannon, J., W. Patrick. 1987. Fixation, transformation and mobilization of As in sediments. *Environmental Science and Technology*. 21:450-59.

Caetano, M.L., et al. 2009. Batch and continuous precipitation of scorodite from dilute industrial solutions. *Hydrometallurgy* 95(1-2):44-52.

Chai, L., M. Yue, Q. Li, G. Zang, M. Zhang, Q. Wang, H. Liu, Q. Liu. 2018. Enhanced stability of tooeleite by hydrothermal method for the fixation of arsenite. *Hydrometallurgy* 175:91-101.

Chatain, V., F. Sanchez. 2005a. Effect of experimentally induced reducing conditions on the mobility of arsenic from a mining soil. *J. Hazardous Materials* B122:119-28.

Chatain, V., R. Bayard. 2005b. Effect of indigenous bacterial activity on Arsenic mobilization under anaerobic conditions. *Environmental. International* pp221-26.

Chimonyo, W., K.C. Corin, J.G. Wise, C.T. O'Connor. 2017. Redox potential control during flotation of a sulphide mineral ore. *Minerals Engineering* 110:57-64.

Choi, Y., O. Olvera. 2017. Enhanced leaching of arsenopyrite concentrates as a pretreatment for gold recovery from refractory ores. ALTA, 2017. In Proceedings of the ALTA Gold-PM Conference, May 25-26, 2017. 8 pages. www.altamet.com.au.

Chukanova , N.V., I. V. Pekovb , S. Möckelc , A. A. Mukhanovad , D. I. Belakovskye , L. A. Levitskayaf , and G. K. Bekenova. 2010. Kamarizaite, (AsO4)2(OH)3 · 3H2O, a New Mineral Species, Arsenate Analogue of Tinticite. Geology of Ore Deposits. 52(7):599-605. Pleiades Publishing, Ltd.

Coudert, L., R. Bondu, T.V. Rakotonimaro, E. Rosa, M. Guitstonny, C.M. Neculita. 2020. (Review). Treatment of As-rich mine effluents and produced residues stability: Current knowledge and research priorities for gold mining. *J. Hazardous Materials*, 386:19p.

Cornell, R.M., U. Schwertmann. 1996 and 2003. *The Iron Oxides, Structure, Properties, Reactions, Occurrence and Uses*, VCH, NY, 1996, 573p; 2nd Edition, 2003. 663 p.

De Klerk, R.J., Y. Jia, R. Daenzer, M.A. Gomez, G.P. Demopoulos. 2012. Continuous circuit co-precipitation of arsenic (V) with ferric iron by lime neutralization: Process parameter effects on arsenic removal and precipitate quality. *Hydrometallurgy* 111:65-72.

Demopoulos, G.P. 2005. On the preparation and stability of scorodite. In Proceedings of Arsenic Metallurgy. Editors: R.G. Reddy, V. Ramachandran. The Minerals, Metals & Materials Society (TMS), Warrendale, PA. pp25–50.

Demopoulos, G.P. 2008. Advanced hydrometallurgical technology for the immobilization of arsenic, In Proceedings of Arsenic Stabilization Workshop, Santiago, Chile, May 2008.

Demopoulos, G.P, 2009. Aqueous precipitation and crystallization for the production of particulate solids with desired properties. *Hydrometallurgy* 96(3):199-214.

Demopoulos, G.P. 2014. Arsenic immobilization research advances: Past, present and future. In Proceedings Conference of Metallurgists (COM), Canadian Institute of Mining, Metallurgy and Petroleum, Vancouver, Canada

Doerfelt, C., T. Feldmann, R. Roy, G.P. Demopoulos. 2016. Stability of arsenate-bearing Fe(III)/Al(III) co-precipitates in the presence of sulfide as reducing agent under anoxic conditions. *Chemosphere* 151:318-323.

Drahota, P., M. Filippi. 2009 (Review). Secondary arsenic minerals in the environment: A review. *Environment International*. 35:1243-55.

Drahota, P., O. Kulakowski, A. Culka, M. Knappova, J. Rohovec, F. Veselovsky, M. Racek. 2018. Arsenic mineralogy of near-neutral soils and mining waste at the Smolotely-Lisnice historical gold district, Czech Republic. *Applied Geochemistry*. 89:241-254.

Dunne, R. 2005. Flotation of gold and gold-bearing ores. In: Proceedings Developments in Mineral Processing-Advances in Gold Ore Processing. Editor: M.D. Adams. Elsevier, pp 309-344.

Dutrizac, J.E., J.L. Jambor 2007. Characterization of the iron arsenate-sulphate compounds precipitated at elevated temperatures. *Hydrometallurgy* 86:147-63.

Erbs, J.J., T.S. Berquo, et al. 2010. Reductive dissolution of arsenic-bearing ferrihydrite. *Geochimica et Cosmochimica Acta* 74:3382-95.

EPA 1992. Toxicity Characteristic Leaching Procedure (TCLP). http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/1311.pdf. 35p.

Filippou, D., P. St-Germain, T. Grammatikopoulos. 2007. Recovery of metal values from copper-arsenic minerals and other related resources. *Mineral Processing and Extractive Metallurgy Review*. 28(4):247-298.

Filippou, D., G.P. Demopoulos. 1997. Arsenic immobilization by controlled scorodite precipitation. *Journal of Metals* (JOM). 49(12):52-55

Ford, R.G. 2002. Rates of hydrous ferric oxide crystallization and influence of co-precipitated arsenate, *Environmental Science and Technology* (ES&T) 36:2459-63.

Fornasiero, D., D. Fullston, C. Li, J. Ralston. 2001. Separation of enargite and tennantite from non-arsenic copper sulfide minerals by selective oxidation or dissolution. *International Journal of Mineral Processing*, 61:109–119.

Fujita, T., E. Shibata, T. Nakamura. 2010. Solubility of scorodite synthetized by oxidation of ferrous ions. In Proceedings Copper 2010, Hamburg, Germany, 7:2923–2934.

Fujita, T., S. Fujeda, K. Shinoda, S. Suzuki. 2012. Environmental leaching characteristics of scorodite synthesized with Fe(II) iron. *Hydrometallurgy* 111-112:87-102.

Fujita, T., R. Taguchi, M. Abumiya, M. Matsumoto, E. Shibata, T. Nakamura. 2009. Effect of pH on atmospheric scorodite synthesis by oxidation of ferrous ions: Physical properties and stability of the scorodite. *Hydrometallurgy* 96:189-198.

Fujita, T., R. Taguchi, M. Abumiya, M. Matsumoto, E. Shibata, T. Nakamur. 2008a. Novel atmospheric scorodite synthesis by oxidation of ferrous sulfate solution. Part 1. *Hydrometallurgy* 90:92-102.

Fujita, T., R. Taguchi, M. Abumiya, M. Matsumoto, E. Shibata, T. Nakamur. 2008b. Novel atmospheric scorodite synthesis by oxidation of ferrous sulfate solution. Part I1. Effect of temperature and air. *Hydrometallurgy* 90:85:91.

Gab, P.J., A.I. Davies. 1999. The industrial separation of copper and arsenic as sulfides. *Journal of Metals* (JOM). September. pp8-9.

Gomez, M.A., L. Becze, R.I.R Blyth, J.N. Cutler, G.P. Demopoulos. 2010. Molecular and structural investigation of yukonite (synthetic & natural) and its relation to arseniosiderite, *Geochimica et Cosmochimica Acta*, 74:5835-51.

Gomez, M.A., L. Becze, J.N. Cutler, G.P. Demopoulos. 2011a. Hydrothermal reaction chemistry and characterization of ferric arsenate phases precipitated from Fe2(SO4)3–As2O5–H2SO4 solutions. *Hydrometallurgy* 107:74-90.

Gomez, M.A., L. Becze, M. Celikin, G.P. Demopoulos. 2011b.The effect of copper on the precipitation of scorodite (FeAsO4_2H2O) under hydrothermal conditions: Evidence for a hydrated copper containing ferric arsenate sulfate-short lived intermediate, *Journal Colloid and Interface Science*., 360;508-18.

Gonzalez-Contreras, P.A. 2012. Bioscorodite: Biological crystallization of scorodite for arsenic removal. Wageningen University, Wageningen, Netherlands. Doctorate Thesis. 206 p.

Gonzalez-Contreras, P.A. 2014. The biological method to immobilize arsenic bearing waste as scorodite. Conference of Metallurgists (COM). In Proceedings Canadian Institute of Mining, Metallurgy and Petroleum. Vancouver, Canada.

Gonzalez-Contreras, P.A., J. Weijma, J.N. Buisman. 2012. Continuous bioscorodite crystallization in CSTRs for arsenic removal and disposal. *Water Research.* 46:5883-5892.

Harris, B. 2000. The removal and stabilization of arsenic from aqueous process solutions: Past, present, future. In Proceedings Minor Elements 2000, Processing and Environmental. Aspects of As, Sb, Se, Te, and Bi. Editors: C. Young et al., Littleton, CO. p3-21.

Harris, B. 2001. The removal and arsenic from process solutions: Theory and industrial practice. In Proceedings 5th International Symposium on Hydrometallurgy. Editors: C. Young, A. Alfantazi, C. Anderson, A. James, D. Dreisinger, B. Harris. TMS, Warrendale. pp1889-1902.

Harris, B. 2003. The removal of arsenic from process solutions: theory and industrial practice, In Proceedings Hydrometallurgy 2003-Fifth International Conference in Honor of Ian Ritchie, Volume 2: Electrometallurgy and Environmental Hydrometallurgy, Vancouver, Canada, TMS. pp 1717-1727,

Hiskey, J.B. 2014. Innovative strategies for copper hydrometallurgy. In Mineral Processing and Extractive Metallurgy-100 Years of Innovation. Edited by C.G. Anderson, R.C. Dunne, J.L. Uhrie. Society for Mining, Metallurgy and Exploration (SME). Englewood, Colorado. pp347-360. https://www.smenet.org/SME/media/Government/The-Role-of-Arsenic-in-the-Mining-Industry. 5p.

Hohn, J.W. 2005. Modified ferrihydrite for enhanced removal of arsenic from mine wastewater. M.Sc. Thesis, Department of Metallurgical/Materials Engineering, Montana Tech of the University of Montana, Butte, MT, May 2005, 182p.

Hu, B., T. Yang, W. Liu, D. Zhan, L. Chen. 2019. Removal of arsenic from acid wastewater via sulfide precipitation and its hydrothermal mineralization stabilization. *Transactions Nonferrous Metallurgical Society China*. 29:2411-2421.

Huch, R.O. 1993. Method for achieving enhanced copper-containing mineral concentrate grade by oxidation and flotation. PCT World Patent 93/22060. November and US Patent 5295585, 1994. Cyprus Minerals, USA.

Huang, H.H., 2010, 2016, 2018. Stability Calculations Software. Montana Technological University, Department of Metallurgy/ Materials, Butte, Montana.

Huisman, J., M.O. Weghuis, P. Gonzalez. 2011. Biotechnology-based processes for arsenic removal. In Proceedings Clean Mining 2011. 9th International Conference on Clean technologies for the Mining Industry, April 10-12, Santiago, Chile.

Ichimura, R., H. Tateiwa, C. Almendares, G. Sanchez. 2007. Arsenic immobilization of Teniente furnace dust. In Proceedings Cu 2007. Volume VI. Sustainable Development. HS&E, and Recycling. Editors: D. Rodier, W. Adams, CIMM. Toronto, Canada. Pp275-288.

IM 2017. High-arsenic copper concentrates. International Mining Newsletter. https://imining.com/2016/02/23/high-arsenic-copper-concentrates. Site visited 12/7/2017.

Jambor, J., J.E. Dutrizac. 1998. Occurrence and constitution of natural and synthetic ferrihydrite, a widespread iron oxyhydroxide. *Chemical Review* 98:2549-85.

Jia, Y., G.P. Demopoulos. 2008. Co-precipitation of arsenate with iron(III) in aqueous sulfate media: Effect of time, lime as base and co-ions on arsenic retention. *Water Research* 42(93):661-68.

Katsarock, L. 2011. Synthesis and application of hydroapatite and fluorapatite to scorodite encapsulation, M.Sc. Thesis, McGill University, Open Access Theses and Dissertations.

Ke, P., K. Song, A. Ghahreman, Z. Liu. 2019. Improvement of scorodite stability by addition of crystalline polyferric sulfate. *Hydrometallurgy* 185:162-172.

Kocar, B., T. Borch, S. Fendorf. 2010. Arsenic repartitioning during biogenic sulfidization and transformation of ferrihydrite. *Geochimica et Cosmochimica Acta* 74: 980-94

Krause, E., V.A. Ettel. 1989. Solubility and stabilities of ferric arsenate compounds. *Hydrometallurgy*.89(22):311-337.

Lagno, F., S.D.F. Rochab, S. Chryssoulisc, G.P. Demopoulo., 2010. Scorodite encapsulation by controlled deposition of aluminum phosphate coatings, *Journal of Hazardous Materials* (JHM). 181:526–34.

Lane, D.J., N.J. Cook, S.R. Grano, K. Ehrig. 2016 (Review). Selective leaching of penalty elements from copper concentrates: A review. *Minerals Engineering*. 98:110-121.

Leetmaa, K., F. Guo, L. Becze, M.A. Gomez, G.P. Demopoulos. 2016. Stabilization of iron arsenate solids by encapsulation with aluminum hydroxyl gels. *Journal of Chemical Technology and Biotechnology* 91:408-415. Wileyonlinelibrary.com. DOI 10.1002/jctb.4590.

Lehimra, R. 2007. Arsenic immobilization of Teniente furnace dust. D.R. Adams (Ed.), Cu 2007-Vol VI Sustainable Development HS&E, and Recycling, *Canadian Institute of Mining, Metallurgy and Petroleum*.

Li, Q., M. Zhang, J. Yang, Q. Liu, G. Zhang, Q. Liao, H. Liu, Q. Wang. 2020. Formation and stability of biogenic tooeleite during Fe(II) oxidation by Acidithiobacillus ferrooxidans. *Materials Science and Engineering* C111:8 p.

Long, G., Y. Peng, D. Bradshaw. 2012 (Review). A review of copper-arsenic mineral removal from copper concentrates. *Minerals Engineering* 36-38, 127-138.

Ma, X.W., J. Bruckard. 2009 (Review). Rejection of arsenic minerals in sulfide flotation-A literature review. International *Journal of Mineral Processing* 93, pp. 89–94.

Ma, X.W., S. Li, Z. Yan, S. Yao, Y. Jia, S. Wang 2019. Stabilization of scorodite by aluminum silicate microencapsulation. Journal of Environmental Engineering. 145(4):11p

Ma, X.W., Z. Yuan, G. Zhang, J. Zhang, X. Wang, S. Wang, Y. Jia. 2020. Alternative method for the treatment of hydrometallurgical arsenic–calcium residues: The immobilization of arsenic as scorodite. American chemical Society Omega. 5(22):12979-12988.

Ma, X., R. Su, X. Zhao, S. Liu, X. Wu, S. Wang, Y. Jia. 2021. Phase transformation of hydrous ferric arsenate in the presence of Fe(II) under anaerobic conditions: Implications for arsenic mobility and fate in natural and anthropogenic environments. *Chemical Geology* 578:11p.

Majzlan, J., P. Drahota, M. Filippi, K.D. Grevel, W.A. Kahi, J. Plasil, J. Boerio-Goates, B.F. Woodfield, 2012. Thermodynamic properties of scorodite and parascorodite (FeAsO4·2H2O), kankite (FeAsO4·3.5H2O), and FeAsO4, *Hydrometallurgy*. 117-118:47-56

Majzlan, J., E. Dachs, A. Benisek, P. Drahota. 2016. Thermodynamic properties of $FeAsO_4.0.75H_2O$-a more favorable disposable product of low As solubility. Hydrometallurgy. 164:136-140.

Majzlan, J., E. Dachs, A. Benisek, et al. 2016. Thermodynamic properties of tooeleite, Fe6(AsO3)4(SO4)(OH)4:4H2O. *Journal Chemie Der erde-Geochemistry* 76(3):419-428.

Majzlan, J., U.G. Nielsen, E. Dachs, A. Benisek, P. Drahota, et al. 2018. Thermodynamic properties of mansfieldite (AlAsO (sub 4) .2H (sub 2) O), angelellite (Fe (sub 4) (AsO (sub 4)) (sub 2) O (sub 3)) and kamarizaite (Fe (sub 3) (AsO (sub 4)) (sub 2) (OH) (sub 3) .3H (sub 2) O). *Mineralogical Magazine* 82(6)1333-1354.

Marsden, J. O., C. I. House. 2006. *The Chemistry of Gold Extraction*, 2nd Edition. SME. Littleton, CO. pp. 258–260.

Marsden, J.O., S.A. Sass, 2014. Innovations in gold and silver extraction and recovery. *Mineral Processing and Extractive Metallurgy-100 Years of Innovation*. Edited by C.G. Anderson, R.C. Dunne, J.L. Uhrie. Society for Mining, Metallurgy, and Exploration (SME), Englewood, Colorado. pp361-388.

McCloskey, J., L.G. Twidwell, M. Lee. 2008a. Arsenic removal from mine and process waters by lime phosphate precipitation: pilot scale demonstration. Mine Waste Technology Program. MSE Butte, Montana. Report MWTP 305:60p.

McCloskey, J., L.G. Twidwell. 2008b. Removal of arsenic from Sherwin Williams ground water in Emeryville, CA. MSE, Butte, Montana. Internal Report.

McCloskey, J., L.G. Twidwell, H.H. Huang, L. Goldstien. 2010. Fundamental procedures to evaluate and design industrial wastewater metals treatment systems, case study discussions. In: Proceedings of the 7th Int. Symposium Hydrometallurgy. SME. Tucson, AZ.

Miller, P., A.R.G. Brown. 2005. Bacterial Oxidation of Refractory Gold Concentrates. In: Developments in Mineral Processing-Advances in Gold Ore Processing. Editor: M.D. Adams. Elsevier, pp 371-402.

Mirazimi, M., J. Fan, W. Liu. 2021. Kinetics of arsenic and sulfur release from amorphous arsenic trisulfide. *Hydrometallurgy*. 200: 8p.

MWTP (EPA Mine Waste Technology Program) Reports (related to arsenic ferrihydrite sequestration and aluminum modified ferrihydrite), Contact: https://cfpub.epa.gov/si/si_public_record_report.cfm?dirEntryId=61400&Lab=NRMRL

MWTP-90 Issues identification and prioritization for Arsenic, Activity I, Volume 5, 1996/60p.
MWTP-282 Modified Ferrihydrite for enhanced removal of Arsenic from mine wastewater, 2007/92p.
MWTP-293 Modified Ferrihydrite for enhanced removal of dissolved metals mine wastewater, 2008a/162p.
MWTP-305 Physical solutions for acid rock drainage at remote sites demonstration project-Arsenic: Activity III, Project 42, 2008b/60p.
MWTP-307 Influence of anions on the removal of Arsenic by co-precipitation and long-term stability of Ferrihydrite and Modified Ferrihydrite, 2008c/201p.

Nazari, A.M., R. Radzinske, A. Ghahreman. 2017 (Review). Review of arsenic metallurgy: Treatment of arsenical minerals and the immobilization of arsenic. *Hydrometallurgy* 174:258-281.

Nishimura, T., R.G. Robins. 2008. Confirmation that tooeleite is a ferric arsenite sulfate hydrate and is relevant to arsenic stabilization. *Mineral Engineering* 21(4):246-251.

Nishimura, T., Y. Umetsu. 1985. Removal of arsenic from wastewater by addition of calcium hydroxide and stabilization of arsenic-bearing precipitate by calcination. Canadian Institute Mining Metallurgy Petroleum. 78(878):75.

Okibe, N., Koga, M., K. Sasaki, T. Hirajima, S. Heguri, S. Asano. 2013. Simultaneous oxidation and immobilization of arsenite from refinery wastewater by thermoacidophillic iron-oxidizing archaeon, Acidianus brierleyi. *Mineral Engineering* 48:26–134.

Okibe, N., M. Koga, S. Morishita, M. Tanaka, S. Heguri, S. Asano. 2014. Microbial formation of crystalline scorodite for treatment of As(III)-bearing copper refinery process solution using acidianus brierleyi, *Hydrometallurgy* 143:34-41.

Opio, F.K. 2013. Investigation of Fe(III)-As(III) phases and their potential for arsenic disposal. Doctorate Thesis. Graduate Theses, Dissertations and Projects. Queen's University, Kingston, Ontario, Canada.

Orgon, N., G. Zhang, K. Zhang, C. Yang. 2019. Removal and fixation of arsenic by forming a complex precipitate containing scorodite and ferrihydrite. *Hydrometallurgy* 186:58-65.

Paktunc, D. 2015. Phase transformations in the system Fe-AsO4-SO4 and the structure of amorphous ferric arsenate: Implications for arsenic stabilization in mine drainage and industrial effluents, *Canadian Mineralogist* 53(5):921-936.

Paktunc, D., J.E. Dutrizac, V. Gertsmann. 2008. Synthetic and phase transformations involving scorodite, ferric arsenate and arsenical ferrihydrite: Implications for arsenic mobility, *Geochimica et Cosmochimica Acta* 72:249-72.

Paktunc, D., K. Bruggeman. 2010. Solubility of nano-crystalline scorodite and amorphous ferric arsenate: Implications for stabilization of arsenic in mine wastes. *Applied Geochemistry* 25:674–683.

Raghav, M. J. Shan, A.E. Saez, W.P. Ela. 2013. Scoping candidate minerals for stabilization of arsenic-bearing solid residues. *Journal of Hazardous Materials* 263:525-532.

Park, I, C.B. Tabelin, S. Jeon, X. Li, K. Seno, M. Ito, and N. Hiroyoshi. 2019 (Review). A review of recent strategies for acid mine drainage prevention and mine tailings recycling, *Chemosphere* 219:588-606.

Riveros, P.A., J.E. Dutrizac, P. Spenser. 2001 (Review). Arsenic disposal practices in the metallurgical industry, *Canadian Metallurgical Quarterly* 40(4):395-420.

Robins, R.G., K. Tozawa.1982. Arsenic removal from gold processing waste waters: The potential ineffectiveness of lime, *CIMM Bulletin* 75(4):171-74.

Robins, R.G., L.D. Jayaweera. 1992 (Review). Arsenic in gold processing. *Mineral Processing and Extractive Metallurgy Review* 9(1-4):255-271. https://doi.org/10.1080/08827509208952710.

Rohner, P., J. Loraine, L. MacDonald, M. Ross, P. Bangerter, J. Gaillie. 2016. The economics of removing arsenic from copper concentrates using the Toowong Process. In Proceedings ALTA 2016 Nickel-Cobalt-Copper. May 23-25. Perth, Australia. 14 p. www.altamet.com.au. CORE Mineral Technologies.

Rohner, P., D. Turner, D. Walker, L. MacDonald. 2016. The Toowong Process: Developing a viable solution for copper's dirty problem. In Proceedings of ALTA 2016 Nickel-Cobalt-Copper. May 23-25. Perth, Australia. 14 p. www.altamet.com.au. CORE Mineral Technologies.

Rong, Z., X. Tang, L. Wu, X. Chen, W. Dang, Y. Wang. 2020. A novel method to synthesize scorodite using ferrihydrite and its role in removal and immobilization of arsenic. *Journal Material Research and Technology* 9(3)/5818-5857.

Rong, Z., X. Tang, L. Wu, X. Chen, W. Dang, X. Li, L. Huang, Y. Wang. 2020. The effect of precursor speciation on the growth of scorodite in an atmospheric scorodite synthesis. *Royal Society Open science 7:14p*.

Rosengrant, L., L. Fargo 1990. Final best demonstrated available technology (BDAT) background document for K031, K084, K101, K102, As wastes (D004), Se wastes (D010), and P and U wastes containing As and Se listing constituents. EPA/530/SW-90/059A, Washington, DC. 124p.

Ruonala, M., J. Leppinen, V. Miettinen. 2011. Method for removing arsenic as scorodite, Outotec Patent EP 2398739A1, 6 p.

Safarzadeh, M.S., J.D. Miller 2016. The Pyrometallurgy of enargite: A literature guide. *International Journal of Mineral Processing* 157:103-110.

Safarzadeh, M.S., M.S. Moats, J.D. Miller. 2014a (Review). Recent trends in the processing of enargite concentrates. *Mineral Processing and Extractive Metallurgy Review*. 35:283-367, DOE: 10.1080/08827508/2012.723651, Link: http://dx.doi.org/10. 1080/08827508/2012.723651.

Safarzadeh, M.S., M.S. Moats, J.D. Miller. 2014b (Review). An update: Recent trends in the processing of enargite concentrates. *Mineral Processing Extractive Metallurgy Review* 35(6):390-422.

Salokannel, A., L.M. Nevatalo, M. Martikainen, T. Meer, J. McCulloch. 2013. Technology selection for removal of contaminants from an industrial wastewater. In Proceedings Metallurgical Plant Design and Operating Strategies. Perth, Australia.

Salomon-de-Friedberg , H., K. Mayhew, A. Lossin, V. Omaynikova. 2017. Hydrometallurgical considerations in processing arsenic-rich copper concentrates. In Proceedings ALTA Conference Perth, Australia, May 23-25, 2017. 13p, CESL Teck Resources.

Schlesinger, M.E. 2019. Pyrometallurgy of Copper. In *SME Mineral Processing and Extractive Metallurgy Handbook*. Chapter 9.2, Society for Mining, Metallurgy, and Exploration Inc. (SME). www.smenet.org.

Schlesinger, M.E., M.J. King, K.C. Sole, W.G. Davenport. 2011. *Extractive Metallurgy of Copper*. Fifth Edition. Elsevier, N.Y., 481p.

Senior, G.D., P.J. Guy, W.J. Bruckard. 2006. The selective flotation of enargite from other copper minerals-a single mineral study in relation to beneficiation of the Tampakan deposit in the Philippines. *International Journal Mineral Processing* 81:15-26.

Shakya, A.K., P.K. Ghosh. 2019. Stability against arsenic leaching from biogenic arsenosulphides generated under reducing conditions. *Journal of Cleaner Production* 208:1557-1562.

Sherman, D.M., S.R. Randall. 2003. Surface complexation of arsenic(V) to iron(III) (hydro)oxides: Structural mechanism from ab- initio molecular geometries and EXAFS spectroscopy. *Geochimica et Cosmochimica Acta* 67(22):4223-30

SME. 2015. The role of arsenic in the Mining Industry. Society for Mining, Metallurgy & Exploration, 12999 E. Adam Aircraft Circle, Englewood, CO, http://www.smenet.org/SME/media/Government/The-Role-of-Arsenic-in-the-Mining-Industry.pdf, 5p.

Smith L.K., W.J. Bruckard. 2007. The separation of arsenic from copper in a NorthParkes copper-gold ore using controlled-potential flotation. *International Journal Mineral Processing* 84:15-24.

Strauss, J.A., V. Bazhko, G. Ventruti, X. Liguo, M.A. Gomez. 2021. Arsenic behavior during the treatment of refractory gold ores via POX: Characterization of Fe-AsO4-SO4 precipitates. *Hydrometallurgy* 203:11p, paper 105616..

Strauss, J.A., V. Yahorava, M.A. Gomez. 2017. Pressure oxidation in gold circuits: Basic ferric arsenate sulphate and basic ferric sulphate behavior in downstream processing. In Proceedings World Gold and Nickel Cobalt, Conference of Metallurgist. Canadian Institute of Mining, Metallurgy and Petroleum. www.metsoc.org 13p.

Su, R., X. Ma, X. Yin, X. Zhao, Z. Yan, J. Lin, X. Zeng, D. Zhang, S. Wang, Y. Jia. 2021. Arsenic removal from hydrometallurgical waste sulfuric acid via scorodite formation using siderite. *Chemical Engineering Journal*. 424:10 p.

Swash, P.M., A.J. Monhemius. 1994. Hydrothermal precipitation from aqueous solutions containing iron (III), arsenate and sulphate. *Hydrometallurgy*. Chapman & Hall, Cambridge, England. pp177–90.

Tayebi-Khorami, M., E. Manlapig, E. Forbes, D. Bradshaw, M. Edraki. 2017. Selective flotation of enargite from copper sulphides in Tampakan deposit. *Minerals Engineering* 112:1-10.

Twidwell, L.G. 2010. Removing Arsenic from aqueous solutions and long-term product storage. *JOM* 63(8): 94-100.

Twidwell, L.G. 2018 (Review). Treatment of arsenic-bearing minerals and fixation of recovered arsenic products: a review. School of Mines, Metallurgy/Materials Engineering Department, Montana Tech of the University of Montana, Butte, MT. November2018.Contact-ltwidwell@mtech.edu DOI: 10.13140/RG.2.2.12890.44486. www.researchgate.net/profile/Larry_Twidwell/contributions/?ev=prf_act.

Twidwell, L.G. 2019. Environmental considerations for treatment of effluent waste solutions and solid waste products. In *SME Mineral Processing and Extractive Metallurgy Handbook*. Chapter 10.9. Society for Mining, Metallurgy, and Exploration Inc. (SME). www.smenet.org.

Twidwell, L.G. 2019b. Arsenic Production, Commodities and Fixation. In *SME Mineral Processing and Extractive Metallurgy Handbook*. Chapter 9.22. Society for Mining, Metallurgy, and Exploration Inc. (SME). www.smenet.org.

Twidwell, L.G., J.A. Hohn, R.G. Robins. 2007. Modified ferrihydrite for enhanced removal of arsenic from mine wastewater. Mine Waste Technology Program, Activity IV, Project 39, MSE-TA, Butte, MT. 92p.

Twidwell, L.G., J.W. McCloskey. 2011. Removing arsenic from aqueous solution long-term product storage. *Journal of Metals* 63(8):94-110.

Twidwell, L.G. et al. multiple years. Master of Science Theses for studies concerning research on arsenic fixation in environmentally stable arsenic/phosphate apatite structures. All listed theses are available (as PDFs) at Montana Technological University Library, Montana Tech Theses (1932 to present).

Wilson, S. *Removal of Arsenic from ASARCO Blow-Down Water and Long-Term Stability of the Product Solids*. January 1998.
Saran, J. *Removal of Arsenic from Berkeley Pit Wastewater and Long-Term Stability of the Product Solids*. May 1997.
Gale, M. *Removal of Arsenic from Wastewaters by Iron/Phosphate Precipitation*, May 1998.
Orser, T. *Removal of Arsenic from Wastewaters as Stable Calcium Mineral Compound*. Jan 2001.
Hohn, J., *Arsenic Removal by Modified Ferrihydrite Adsorption*. May 2005.
Leonhard, J., Heavy Metals *Removal by Modified Ferrihydrite Adsorption*, Dec 2006.
Glasgow, M., *Modified Ferrihydrite/Arsenic: Effect of Anions*, May 2007.

USGS. 2016. (Daniel M. Flanagan), Mineral Commodity Summaries 2017, Arsenic. United States Geological Survey, United States Department of the Interior. Jpubs.https://minerals.usgs.gov/minerals/pubs/mcs/2016/mcs2016.pdf; dflanagan@usgs.gov, pp 26-28.

USGS. 2017. Mineral Commodity Summaries 2016, Arsenic. United States Geological Survey, United States Department of the Interior. https://www.mrdaa.usgs.gov.

USGS. 2021. Mineral Commodity Summaries 2021, Arsenic. United States Geological Survey, United States Department of the Interior. https://pubs.usgs.gov/periodicals/mcs2021/mcs2021.pdf.

Valenzuela, A. 2000. Arsenic management in the metallurgical industry. Doctorate Thesis. National Library of Canada, Acquisitions and Bibliographic Services. 209p.

Valenzuela, A., E. Balladares, D. Cordero, M. Sanchez. 2006. Arsenic management in the metallurgical industry: The Chilean experience. In Proceedings of the Sohn International Symposium: Advanced Processing of Metals and Materials, Vol 9: Legal, Management and Environmental Issues, San Diego, CA. TMS, pp407–422.

Van Aswegen, P.C., J. van Niekerk, W. Olivier. 2006. The BIOX process for the treatment of refractory gold concentrates, In Proceedings Biomining, Editors: D.E. Ralings and B.D. Johnson. Springer. pp1-33.

Violante, A.M., M. Ricciardella, M. Pigna. 2003. Adsorption of heavy metals on mixed Fe-Al oxides in the absence or presence of organic ligands. *Water, Air, and Soil Pollution*, 45(1):289-306.

Wang, Q., T. Nishimura, Y. Umetsu. 2000. Oxidative precipitation of arsenic removal in effluent treatment. Minor Elements 2000. Editor: C. Young. Society of Mining, Metallurgy, and Exploration, Inc., SME. pp 39-52.

Wang, S., D. Zhang, X. Li, G. Zhang, Y. Wang, X. Wang, M.A. Gomez, Y. Jia. 2018. Arsenic associated with gypsum produced from Fe(III)-As(V) coprecipitation: Implications for the stability of industrial As-bearing waste. *J. Hazardous Materials* 360:311-318.

Wang, Q., Q. Lin, Q. Li, K. Li, L. Wu, S. Li, H. L. 2021. As(III) removal from wastewater and direct stabilization by in-situ formation of Zn-Fe layered double hydroxides. *J. Hazardous Materials* 403:11p. 123920.

Wang, Q., Q. Li, A. Liao, Y. Yan, J. Xia, Q. Lin, Q. Wang, Y. Liang. 2020. Arsenic(III) biotransformation to tooeleite associated with the oxidation of Fe(II) via Acidithiobacillus ferrooxidans. *Chemosphere*. 248:9p. 126080..

Wang, Y., Z. Rong, X. Tang, S. Cao, X. Chen, W. Dang, L. Wu, D. Zhang, X. Li, G. Zhang, Y. Wang, X. Wang. 2019. The design of scorodite@FeOOH core-shell materials and its stability treatment of arsenide. *Applied Surface Science* 496:8p.

Wassink, B., D. Dreisinger, P. West-Sells, N. Fisher. 2005. Leaching of a gold ore using the hydrogen sulfide-bisulfide-sulfur system. In Proceedings Treatment of Gold Ores. First International Symposium. 44th Annual Conference of Metallurgists of CIM, Calgary, Alberta, Canada. Editors: G. Deschenes, D. Hodouin, L. Lorenzen. p225.

Yuan, Z., X. Ma, X. Wu, G. Zhang, X. Wang, S. Wang, Y. Jia. 2020. Characterization of $Fe_5(AsO_3)_3Cl_2(OH)_45H_2O$, a new ferric arsenite hydroxychloride precipitated from FeCl3-As2O3-HCl solutions relevant to arsenic immobilization. *Journal of Environmental Sciences* 90:205-215.

Yuan, Z, X. Ma, J. Lin, X. Wang, S. Wang, Y. Jia. 2020. The effect of iron reduction on the long-term stability of scorodite in the presence of enolic hydroxyl groups and mineral transformation. *Applied Geochemistry* 122:8p.

Zhang, D., S. Wang, M.A. Gomez, Y. Wang, Y. Jia. 2019. Long-term stability of the Fe(III)-As(V) coprecipitates: Effects of neutralization mode and the addition of Fe(II) on arsenic retention. *Chemosphere* 237:10p.

Zhang, D., S. Wang, Y. Wang, M.A. Gomez, Y. Jia. 2019. The Long-term stability of calcium arsenates: Implications for phase transformation and arsenic mobilization. *Journal of Environmental Sciences* 84:29-41.

Zhang, D., S. Wang, Y. Wang, M.A. Gomez, Y. Wang, Y. Jia. 2019. The Long-term stability of FeIII-AsV coprecipitates at pH 4 and 7: Mechanisms controlling the arsenic behavior. *Journal of Hazardous Materials* 374:276-286.

Zidan, Y., X. Ma, J. Lin, X. Wang, Shaofen, et al. 2020. The effect of iron reduction on the long-term stability of scorodite in the presence of enolic hydroxyl groups and mineral transformation. *Applied Geochemistry* 122:8p.

Zhu, X., D.K. Nordstrom, R. B. McCleskey, R. Wang, X. Lu, S. Li, H. Henry Teng. 2019. On the thermodynamics and kinetics of scorodite dissolution. *Geochimica et Cosmochimica Acta* 265:8p.

TABLE OF CONTENTS