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Review of arsenic metallurgy: Treatment of arsenical minerals and the immobilization of arsenic

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ABSTRACT

The attention of mining industry has directed towards the processing of complex arsenic-bearing minerals due to a decrease in the traditional base metal reserves. Arsenic present in the minerals is usually mobilized through hydrometallurgical and pyrometallurgical processes. Arsenic has become a worldwide environmental challenge in the metals and mining industry. Hence, arsenic in the process streams must be immobilized properly prior to the discard of waste. The initial step for arsenic fixation is the oxidation of trivalent arsenic in order to improve both arsenic removal and stability of the final arsenical residues. Arsenic immobilization step could be accomplished using hydrometallurgical and pyrometallurgical techniques. Whereas, pentavalent arsenic is commonly precipitated using hydrometallurgical processes consisting of lime neutralization, sulfide precipitation, co-precipitation of arsenic with ferric ions and scorodite precipitation. In the pyrometallurgical methods arsenic and sulfur are captured using a fixing agent such as calcium and ferrous salts to produce a stable residue. This paper aims to provide a comprehensive review on past, current and future arsenic immobilization techniques related to the mining industry with a large focus on the practised processes and new developments.

1. Arsenic

1.1. Introduction

Arsenic is the 33rd element on the periodic table and is denoted by the chemical symbol ‘As’. It is located in group 15 on the periodic table. Arsenic, which has a long history of uses, is one of the world's prevalent contamination issues (Fujita et al., 2009). Elemental arsenic is a metalloid which primarily occurs in three allotropic forms: metallic arsenic, yellow arsenic and black arsenic. Metallic arsenic is the most stable allotrope and exists as a bright silver-gray trigonal crystal. It is brittle due to a weak bonding between its layers and it readily tarnishes in air. Yellow arsenic, which is characterized as soft and waxy, is the most toxic and unstable arsenic allotrope. Yellow arsenic rapidly changes into metallic arsenic via exposure to light or gentle heating. Solid yellow arsenic is formed by the fast cooling of arsenic vapor (As_4). Black arsenic, which is glassy and brittle, exhibits low electrical conductivity. The physical properties of elemental arsenic are depicted in Table 1.

Arsenic is an abundant element in the earth's crust and is found in >300 minerals (Drahota and Filippi, 2009). The average concentration of arsenic on earth is approximately 5 mg/L (Riveros et al., 2001). Geogenic and anthropogenic activities can liberate arsenical compounds that range in toxicity, mobility and bioavailability from arsenic-bearing minerals (Cheng et al., 2009). In the past, arsenic trioxide (As_2O_3) was used for wood preservation; however, as of 2003 its use in this industry has stopped due to the public health concerns (Long et al., 2012). Global industrial arsenic consumption has declined as a result of agricultural industries no longer using arsenic-based pesticides, herbicides and fungicides (Fujita et al., 2009). Arsenic is currently used in additives for lead car batteries, in anti-friction agents for bearings and for gallium-arsenide semiconductors (Long et al., 2012).

1.2. Chemistry of arsenic

The electron configuration of neutral arsenic is [Ar] $3d^{10}4s^24p^3$ which leads to an excess of electrons and unfilled orbitals (O'Day, 2006). The valency of arsenic allows for different formal oxidation states consisting of −3 (arsine), 0 (arsenic), +3 (arsenite) and +5 (arsenate). The structural form of As^{3+} contains three pyramidal bonds and a lone electron pair as the fourth arm of a tetrahedron. In an aqueous solution arsenite maintains the pyramidal structure including three oxygen ligands and the lone electron pair (Fig. 1). Pentavalent arsenic creates a regular tetrahedron bonded to oxygen ligands resulting in the stable arsenate anion $(AsO_4)^{3-}$. The behavior of arsenic in solution is not typical of other cations as it exists in the form of oxyanions rather than cation in hydrometallurgical processes.

Arsenic is typically found as inorganic oxyanions of arsenite (As^{3+}) or arsenate (As^{5+}) (Gallegos-Garcia et al., 2012). Arsenic compounds

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Table 1
Physical properties of elemental arsenic.

Property	Value
Atomic number	33
Atomic weight	74.92 g
Density (metallic arsenic)	5.72 g/cm3
Density (yellow arsenic)	2.03 g/cmic
Melting point at 3.7 MPa	817 °C
Boiling point at 0.1 MPa	613 °C
Heat of fusion	370.3 kJ/kg
Heat of vaporization	426.77 kJ/kg
Linear coefficient of thermal expansion	5.6×10^{-6} 1/K
Specific heat at 25 °C	328 J/kg.K
Electrical resistivity at 0 °C	26×10^{-6} Ω.cm

can exist as organic or inorganic species and typically the inorganic soluble arsenic species are more toxic than soluble organic arsenic compounds (Mandal and Suzuki, 2002). Fig. 2 illustrates the dominant species within the water line boundaries for As-H_2O at 25 °C and 1 bar total pressure. In an oxidizing environment arsenate is generally the dominant form of arsenic. Pentavalent arsenic is in the form of H_3AsO_4 at pH value below 2. H_3AsO_4 dissociates to $H_2AsO_4^-$ and $HAsO_4^{2-}$ and AsO_4^{3-} at a pH value above 2. Arsenite appears as H_3AsO_3 up to pH 9. H_3AsO_3 dissociates to $H_2AsO_3^-$, $HAsO_3^{2-}$ and AsO_3^{3-} at pH value above 9.

Both arsenite and arsenate are soluble in water; however, arsenite is more toxic and soluble than arsenate (Yang et al., 2013). Arsenate has more tendency than arsenite to precipitate out of solution with the addition of metal cations (Ritcey, 2005). The metal-arsenate precipitates generally follow the form $M_n(AsO_4)_m \cdot H_2O$ (Ritcey, 2005). The stability of the precipitate is dependent on the cation used to form the precipitate and the conditions at which the precipitate is maintained (temperature, pH and redox potential (Eh)) (Riveros et al., 2001).

The mobility of arsenic is dependent on the concentration of arsenic and other species present (such as metal cations, clay, etc.), the pH and Eh of the environment (Bissen and Frimmel, 2003a). Arsenic contamination is of great concern due to its high mobility under a large range of pH and Eh (Smedley and Kinniburgh, 2002).

The toxicity of arsenic species varies between the arsenic oxidation states: arsine (As^{3-}) is more toxic than arsenite, which is more toxic than arsenate (Vaughan, 2006). Arsenite and arsenate, though both toxic, have different biological effects. Ingestion is the main route of exposure but inhalation can also cause toxic effects (Gallegos-Garcia et al., 2012).

1.3. Arsenic minerals and reserves

Arsenic scarcely exists as a native element in the nature because it exhibits a high affinity to form chemical bonds with other elements and species. Arsenic, arsenide and arsenosulfides are typically found in anoxic hydrothermal ore deposits and metamorphic and intrusive igneous rocks. Arsenite and arsenate are formed when these minerals are subjected to oxygen and water under or near surface conditions.

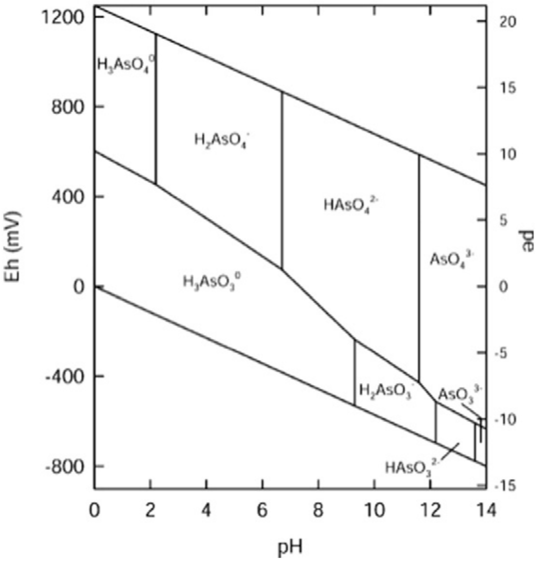

Fig. 2. Eh-pH diagram for the system As-H_2O at 25 °C and 1 bar total pressure (Smedley and Kinniburgh, 2002) (reproduced with permission).

Examples of arsenic-bearing minerals are listed in Table 2. The breakdown of the known arsenic compounds is approximately: 60% arsenates, 20% sulfides/sulfosalts, 10% oxides, and the remainder are arsenite, arsenides, native arsenic and/or metal alloys (Drahota and Filippi, 2009). The most abundant arsenic mineral is arsenopyrite (Smedley and Kinniburgh, 2002). High concentrations of arsenic-bearing minerals are often located with transition metals and cadmium, lead, silver, gold, antimony, phosphorus, tungsten and molybdenum (Smedley and Kinniburgh, 2002).

2. Arsenic mobilization

This section focuses on arsenic mobilization resulting from mining, mineral processing and metallurgical operations. Arsenic contamination of groundwater and soils due to the mining processes occurs globally in places such as: Ghana, Zimbabwe, South Africa, Mexico, Canada and the United States of America (Bissen and Frimmel, 2003a).

Arsenic-containing minerals that occur in base metal ores and concentrates enter metallurgical processing circuits accordingly. This causes a noticeable increase in the production costs, the deterioration of the product purity, and environmental hazards coupled with disposal issues. The mining of sulfidic ores can potentially lead to acid mine drainage (AMD) issues and elevated dissolved arsenic in water (Lengke et al., 2009). AMD can occur as a result of old mine drainage tunnels and tailings, which poses issues to aquatic life, ground water and connected bodies of water (Cheng et al., 2009). Mineral processing of arsenic-bearing ores can mobilize stable arsenic. As an example, due to the flotation of tennantite and enargite having similar floating

Arsenious acid or Arsenite

Arsenic acid or Arsenate

Fig. 1. Structural configuration of arsenite and arsenate.

Table 2
The list of the most 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	$FeAsO_4 \cdot 2H_2O$

characteristics as other copper sulfide ores, the concentrate from the float goes to the smelter where arsenic is then volatilized (Long et al., 2012). Regulations regarding operations of smelters are increasingly stricter about the composition of concentrate they process, as they prefer to have a lower concentration of arsenic so that disposal of the arsenic-bearing by-product is not as large of an issue (Long et al., 2012).

2.1. Pyrometallurgical activities

Pyrometallurgical operations of non-ferrous metals, including roasting, converting and smelting, yield by-product residues in the form of smelted slags, flue gases and flue dusts (Filippou and Demopoulos, 1997). The by-product residues can contain desirable metals (Cu, Ni, Pb, Zn and Ca) as well as unfavorable toxic materials (As, Sb and Hg). In many pyrometallurgical activities arsenic is in the form of either As_2O_3 or As_2S_3 dusts which are captured using electrostatic precipitator (ESP) or wet gas scrubbers. Stockpiling As_2O_3 flue dusts leads to serious problems due to its high degree of solubility in water and the toxicity of arsenic trioxide (Filippou and Demopoulos, 1997).

2.1.1. Arsenic in copper smelting

Arsenic is an unfavorable element which is mostly identified in the copper sulfide concentrates. The level of arsenic must be controlled during the smelting of copper concentrates. Since environmental regulations strictly limit the inlet and outlet arsenic levels of smelters for environmental and economic purposes (Coquerel, 1983). Smelters can only treat copper concentrates in which the arsenic level is <0.5 wt% and a penalty of $3 USD/kg arsenic is charged for an arsenic concentration over 0.2 wt%. In addition, arsenic is capable of forming compounds along the grain boundaries after copper solidification which negatively affect the mechanical and electrical properties of the resulting copper (Safarzadeh et al., 2014b).

Most of the arsenic is volatilized and oxidized to As_2O_3 and As_4O_6 when smelting the arsenic-bearing copper concentrates and only a small fraction of arsenic remains in the final slag (Weisenberg et al., 1979; Dalewski, 1999; Piret, 1999). The arsenic compounds must be eliminated from the SO_2 gas prior to the sulfuric acid production, as the arsenic level adversely influences the quality of the produced sulfuric acid. Hence, the arsenic in the process gases is treated through either dry or wet methods.

Dry method is based on the arsenic condensation between 200 °C–40 °C and the arsenic is consequently removed in the form of solid crystals from the process gases (Dalewski, 1999; Vircikova and Havlik, 1999). In the gas-cooling stage, the evaporative cooler is initially capable of decreasing the temperature of the gas to 400 °C. The dust present in the process gas is then eliminated using a hot ESP (Fig. 3A). Thereafter, the gas is further cooled to 120 °C using indirect or direct cooling with air, direct cooling with water, or two-stage direct cooling (Dalewski, 1999). As illustrated in Fig. 3A the arsenic trioxide is collected in the bag house and the volatilized arsenic trioxide is subsequently condensed and eliminated in the wet-gas cleaning system.

In the wet method, the arsenic-bearing process gas at 400 °C is initially pre-cleaned by a hot ESP. The arsenic-containing gas is then passed through the washing tower in order to cool down the process gas using water injection and consequently solubilize arsenic particles in the circulating sulfuric acid (Fig. 3B) (Dalewski, 1999). The residual arsenic is further eliminated at the wet cleaning plant.

It is worth mentioning that most of the dusts in ESP are sent back to the smelter for metal recovery. A fraction of the dust is leached to form an arsenic-bearing solution which is combined with an arsenic-bearing weak acid solution obtained from a wet gas scrubber - this is done to decrease the concentration of impurities in the dust (Opio, 2013). Arsenic-containing streams are then pumped to the smelter effluent treatment plant (ETP) to produce stable residues for disposal (Piret and Melin, 1989; Piret, 1999; Riveros et al., 2001).

2.1.2. Roasting of arsenic-containing concentrates

Over the past few decades the roasting of arsenic-bearing sulfide ore has been employed as a pretreatment method to oxidize the sulfide for further processing and extraction in arsenic-bearing gold and copper concentrates. Most of the gold-bearing deposits discovered and exploited for the metal exhibit refractoriness and consequently have low gold recoveries (<80%) when using the conventional cyanide leaching techniques. This is due to the gold being either chemically bound or encapsulated in sulfide minerals such as pyrite, pyrrhotite and arsenopyrite, and/or the presence of carbonaceous matter (Robins and Jayaweera, 1992; Celep et al., 2009). Hence, a series of pretreatment processes consisting of roasting, pressure oxidation and bio-oxidation are required to liberate the gold for subsequent leaching in cyanide solution (Arriagada and Osseo-Asare, 1984; Berezowsky and Weir, 1989; Marsden and House, 2009). Arsenic is present in the refractory arsenic-containing gold concentrates in the form of arsenopyrite. The gold deportment, the mineralogy of the gold-bearing minerals, the process economics and the ability of the process to fix arsenic into an environmentally stable residue are the main parameters which notably influence on selection of the most suitable pretreatment option (Filippou et al., 2007; Celep et al., 2009). Fig. 4 displays a typical roasting procedure to treat gold-bearing ore or concentrate before the cyanidation process. Roasting of refractory arsenic-bearing gold concentrates (400 °C–700 °C) leads to the volatilization of most of the arsenic in form of As_4O_6, which is cooled and captured as arsenic trioxide dust (As_2O_3) in the bag-house filters (Fraser et al., 1991).

A fluidized bed roaster is commonly used to oxidize sulfide minerals and remove arsenic from gold concentrates through a two-stage roasting (McMullen and Thomas, 2002; Van Der Meer et al., 2014). The main reactions taking place in stage 1 and stage 2 for arsenopyrite roasting are given in Eqs. (1)–(3). First step of roasting, where the temperature is adjusted between 400 °C–575 °C, is conducted via controlling the access of air to the concentrate to produce trivalent arsenic in the form of sulfide or oxide (McMullen and Thomas, 2002). Ferric

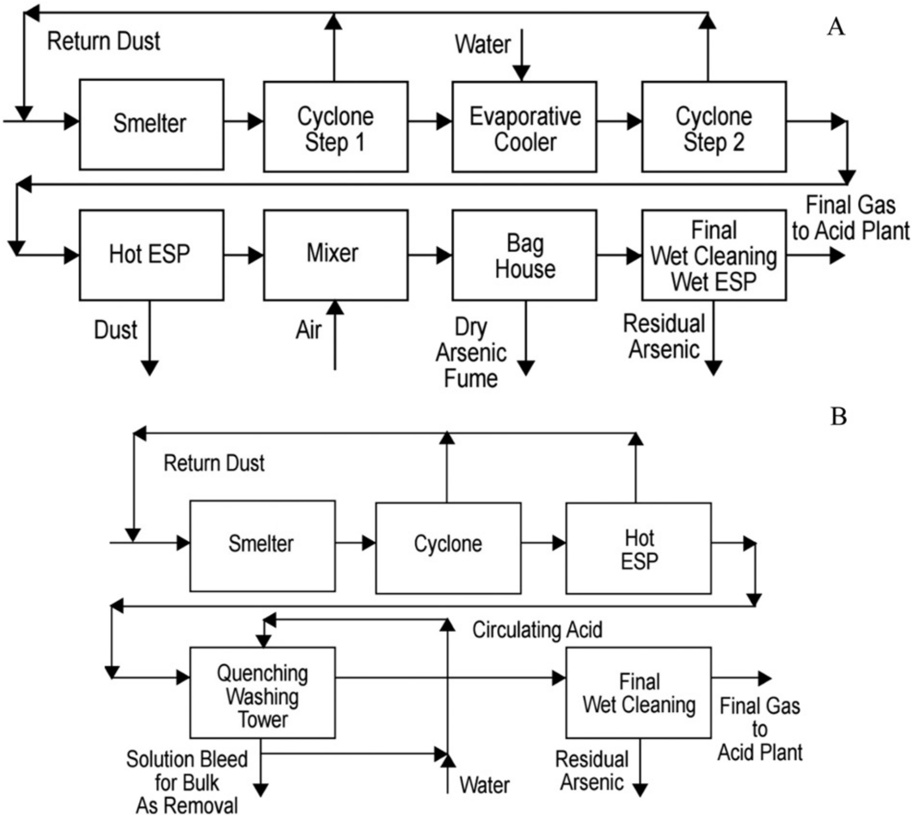

Fig. 3. Flow diagram of (A) dry gas cleaning and (B) wet gas cleaning employed for the arsenic removal from the process gas (Dalewski, 1999) (reproduced with permission).

arsenate ($FeAsO_4$ or $As_2O_5 \cdot Fe_2O_3$) will be otherwise generated through greatly oxidizing condition and high temperature resulting in the blockage of the pores of calcine and consequently lower gold recovery (Lebel et al., 2014). In the second stage, a remaining amount of sulfur is eliminated and a fraction of the magnetite is oxidized to hematite at temperatures up to 604 °C (McMullen and Thomas, 2002).

$$4FeAsS_{(s)} + 3O_{2(g)} \rightarrow 4FeS_{(s)} + As_4O_{6(g)} \qquad (1)$$

$$3FeS_{(s)} + 5O_{2(g)} \rightarrow Fe_3O_{4(s)} + 3SO_{2(g)} \qquad (2)$$

$$2Fe_3O_{4(s)} + 1/2O_{2(g)} \rightarrow 3Fe_2O_{3(s)} \qquad (3)$$

Chalcopyrite ($CuFeS_2$) is a significant source of copper that comes from sulfide minerals. It is frequently associated with arsenic-containing sulfidic minerals such as enargite (Cu_3AsS_4) and tennantite ($Cu_{12}As_4S_{13}$) (Fornasiero et al., 2001; Filippou et al., 2007; Sasaki et al., 2010b; Parada et al., 2014). El Indio in Chile, Lepanto in Philippines, and Chelopech in Bulgaria are examples of enargite deposits (Filippou et al., 2007). The processing of copper ores that contain arsenic is challenging due to the possible environmental and plant safety concerns.

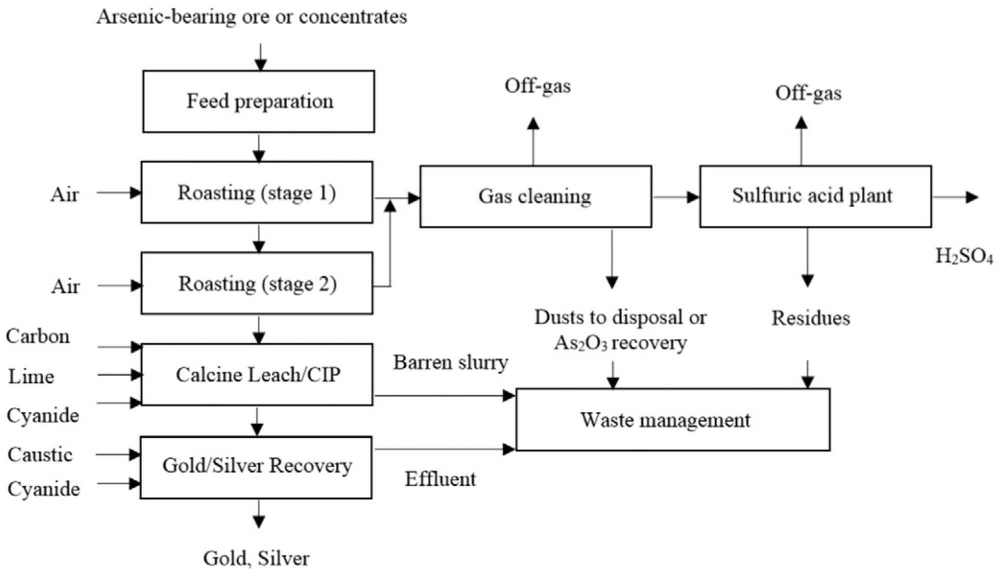

Fig. 4. Flow diagram for a two-stage roasting for arsenic-containing gold ores or concentrates (Robins and Jayaweera, 1992) (reproduced with permission).

The Cu-As-S phase has a relatively low melting point (640–690 °C) and is easily volatilized. This allows for arsenic removal as arsenic sulfide via heating in a reducing or inert atmosphere. The volatile arsenic sulfide is converted to arsenic trioxide via an oxidation reaction shown in Fig. 5. The presence of arsenic in the final copper product heavily influences its quality. Therefore, copper concentrates which have arsenic levels above 0.5% (enargite and tennantite) are pretreated by roasting to minimize the associated processing and environmental risks. Partial roasting of concentrates is carried out using multi-hearth furnace (550 °C–750 °C) in order to reach the required conditions for concentrates to be accepted by smelters. This results in the volatilization of arsenic sulfide and sulfur, as well as the formation of arsenic trioxide and sulfur dioxide in the presence of excess air at 750 °C. The resulting gases are cooled and the arsenic trioxide dust is captured in the bag-house filters. Table 3 illustrates arsenical mobilization reactions through various pyrometallurgical processes.

2.2. Hydrometallurgical activities

Pyrometallurgical processing of arsenic-bearing copper concentrates is associated with obstacles such as strict environmental regulations on arsenic release, the complexity of gas/dust capture, separation facilities and the stability of the arsenic compounds. Various hydrometallurgical techniques concerned with the arsenic in aqueous solution have been proposed to reduce the complicated nature of pyrometallurgical process involving arsenic (Safarzadeh et al., 2014b). Table 4 illustrates hydrometallurgical processing of enargite which dissolves either only arsenic to generate a clean copper concentrate or both copper and arsenic into a solution. This arsenical solution must then be treated according to the regulations set by the respective governing body.

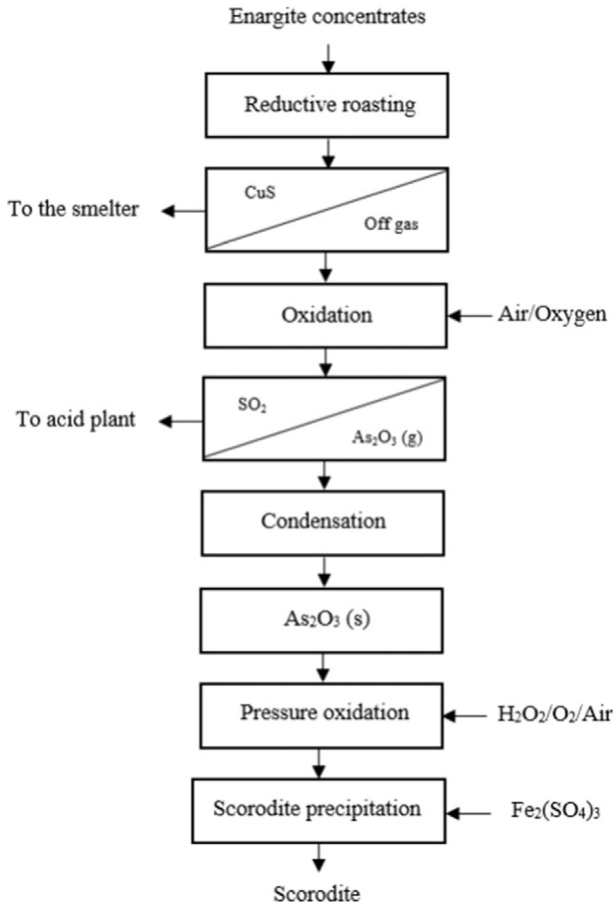

Fig. 5. Flowsheet of roasting of enargite concentrates in a reducing environment (Safarzadeh et al., 2014b) (reproduced with permission).

3. Arsenic immobilization

Arsenic must be removed from aqueous systems, particularly streams resulting from metallurgical operations. The concentration of arsenic in effluent streams and the stability of arsenic-bearing residues and waste are both governed by regulatory agencies. The toxicity characteristic leaching procedure (TCLP) for metallurgical industries has been developed by Environmental Protection Agency (EPA) in order to determine the stability of arsenic-bearing residues. In TCLP test the residue is mixed with a known volume of a pH 5 buffered acetic solution and after 20 h the concentration of dissolved elements is measured. This method only determines the stability of arsenic-containing residues in a short time period and not the long-term stability of the stabilized arsenic residues. Crystallinity, the presence or absence of oxygen, sulfides, complexing agents and disposal site characteristics significantly influence the long term stability of arsenic compounds.

The process used to remove arsenic depends on the amount of arsenic in solution and the arsenic species present. Regardless of the method used to remove arsenic from solution the majority of arsenic must be in its pentavalent oxidation state. For a process to be effective at removing arsenic in solution the dominant arsenic species must be arsenate; the immobilization process can simultaneously oxidize arsenic and precipitate the solid arsenic species or can require two or more steps (Molnár et al., 1994; Kim and Nriagu, 2000; Lièvremont et al., 2009). Most of the techniques used in the metallurgical industry are hydrometallurgical in nature; however, there are currently studies underway which use pyrometallurgical processes to oxidize arsenic for its immobilization.

3.1. As (III) oxidation

In most operations arsenic precipitation and stabilization are designed assuming pentavalent arsenic as the dominant species due to its characteristics of being less toxic, more stable and the ability for a higher degree of removal from the solution compared to those of trivalent arsenic. Only some operations, such as Codelco-Chile operations (e.g. Chuquicamata) and Noranda's Altonorte plant in Chile, dispose As (III) compounds (Harris, 2003). Chilean plants are situated in an arid area where the contamination of groundwater is unlikely. Therefore, trivalent arsenic fixation is acceptable. The first step to arsenic removal in the mining and metallurgy industry is arsenic oxidation. The weak acid bleed streams obtained from acid plants, smelters and copper tankhouses, as well as the re-treatment streams of smelter and roaster dusts contain a significant amount of trivalent arsenic. The oxidation of As (III) is therefore required in order to maximize arsenic removal and the stability of arsenical precipitates. The oxidation of trivalent arsenic to pentavalent arsenic can occur under ambient conditions with oxygen; however, without catalysts the kinetics of the oxidation reaction is slow (Molnár et al., 1994). It was shown that air and oxygen can act as an oxidant to arsenic for basic solutions (Demopoulos, 2014). A strong oxidant such as hydrogen peroxide, ozone, a mixture of SO_2/O_2 gas, chlorine and hypochlorite are required to achieve acceptable reaction kinetics.

The application of air and oxygen in As (III) oxidation is limited due to a very low oxidation rate (Frank and Clifford, 1986; Bissen and Frimmel, 2003b). It was shown that bubbling air through the solution containing 200 μg/L As (III) resulted in oxidizing 25% of As (III) after 5 days (Clifford et al., 1983).

Ultraviolet (UV) irradiation of a solution containing As (III) in the presence of an oxidant such as oxygen and ferric ions favours the oxidation rate of trivalent arsenic. 90% of As (III) oxidation was obtained in the presence of oxygen within 30–90 s by irradiating the water containing 40 μg/L As (III) using high pressure mercury UV lamps (Bissen and Frimmel, 2003b). The rate of As (III) oxidation in the presence of oxygen and dissolved ferric ions was elevated by several orders of magnitude via UV light illumination (Khoe et al., 1997; Emett and Khoe, 2001). This is due to the formation of highly oxidizing radicals such as hydroxyl

Table 3
Arsenic mobilization through pyrometallurgical processes.

Process	Reaction	Reference
Roasting of arsenopyrite under oxidizing atmosphere	(i) $4FeAsS_{(s)} + 3O_{2(g)} \rightarrow 4FeS_{(s)} + As_4O_{6(g)}$ (ii) $4FeS_{(s)} + 7O_{2(g)} \rightarrow 2Fe_2O_{3(s)} + 4SO_{2(g)}$	(Fraser et al., 1991)
Roasting of tennantite in the presence of pyrite	(i) $2Cu_{12}As_4S_{13(s)} \rightarrow 12Cu_2S_{(s)} + 2As_4S_{4(g)} + 3S_{2(g)}$ (ii) $2FeS_{2(s)} \rightarrow 2FeS_{(s)} + S_{2(g)}$ (iii) $4FeS_{(s)} + 10Cu_2S_{(s)} + S_{2(g)} \rightarrow 4Cu_5FeS_{4(s)}$ (iv) $As_2S_{3(g)} + 9/2O_{2(g)} \rightarrow As_2O_{3(g)} + 3SO_{2(g)}$ (v) $S_{2(g)} + 2O_{2(g)} \rightarrow 2SO_{2(g)}$	(Opio, 2013)
Roasting of enargite in the presence of pyrite	(i) $2Cu_3AsS_{4(s)} + 6FeS_{2(s)} \rightarrow 6CuFeS_{2(s)} + As_2S_{3(g)} + 5/2S_{2(g)}$ (ii) $As_2S_{3(g)} + 9/2O_{2(g)} \rightarrow As_2O_{3(g)} + 3SO_{2(g)}$ (iii) $S_{2(g)} + 2O_{2(g)} \rightarrow 2SO_{2(g)}$	(Smith, 1986)
Roasting of enargite in the presence of pyrrhotite	$2.857Cu_3AsS_{4(s)} + 1.714FeS_{(s)} \rightarrow 1.714Cu_5FeS_{4(s)} + 1.429As_2S_{3(g)} + S_{2(g)}$	(Wilkomirsky et al., 2014)
Roasting of enargite in the presence of pyrrhotite	$4Cu_3AsS_{4(s)} + 12FeS_{(s)} + S_{2(g)} \rightarrow 12CuFeS_{2(s)} + 2As_2S_{3(g)}$	(Wilkomirsky et al., 2014)
Roasting of enargite under neutral atmosphere	$2Cu_3AsS_{4(s)} \rightarrow Cu_2S_{(s)} + 4CuS_{(s)} + As_2S_{3(g)}$	(Smith and Paredes, 1988; Padilla et al., 2012)
	$2Cu_3AsS_{4(s)} \rightarrow 3Cu_2S_{(s)} + S_{2(g)} + As_2S_{3(g)}$	(Yoshimura, 1962; Padilla et al., 2001)
	$4Cu_3AsS_{4(s)} \rightarrow 6Cu_2S_{(s)} + 3S_{2(g)} + As_4S_{4(g)}$	(Padilla et al., 2001)
Outokumpu sulfidization roasting and arsenic halogenation (Cl_2, F_2, S_2Cl_2, SF_6, $FeCl_3$ and $CaCl_2$)	(i) $2Cu_3AsS_{4(s)} \rightarrow 3Cu_2S_{(s)} + S_{2(g)} + As_2S_{3(g)}$ (ii) $As_2S_{3(g)} + 3Cl_{2(g)} \rightarrow 2AsCl_{3(g)} + 3/2S_{2(g)}$ $As_2S_{3(g)} + SF_{6(g)} \rightarrow 2AsF_{3(g)} + 2S_{2(g)}$	(Mäkipirtti and Polvi, 1979; Mäkipirtti, 1980; Mäkipirtti et al., 1984; Hølmstrom, 1988a, 1988b, 1989)
Roasting of enargite under nitrogen atmosphere in two steps: (i) Formation of tennantite (ii) Decomposition of tennantite	(i) $4Cu_3AsS_{4(s)} \rightarrow Cu_{12}As_4S_{13(s)} + 3/2S_{2(g)}$ (ii) $Cu_{12}As_4S_{13(s)} \rightarrow 6Cu_2S_{(1+x)(s)} + As_4S_{4(g)} + (1.5\text{-}3x)S_{2(g)}$	(Padilla et al., 2001; Bruckard et al., 2010)
Roasting of enargite under oxidizing atmosphere	$4Cu_3AsS_{4(s)} + 13O_{2(g)} \rightarrow 6Cu_2S_{(s)} + 10SO_{2(g)} + As_4O_{6(g)}$ $2Cu_3AsS_{4(s)} + 2O_{2(g)} \rightarrow 3Cu_2S_{(s)} + 2SO_{2(g)} + As_2S_{3(g)}$ $4Cu_3AsS_{4(s)} + 13O_{2(g)} \rightarrow 6Cu_2S_{(s)} + 10SO_{2(g)} + 2As_2O_{3(g)}$ $4Cu_3AsS_{4(s)} + 22O_{2(g)} \rightarrow 6Cu_2O_{(s)} + 16SO_{2(g)} + As_4O_{6(g)}$ $4Cu_3AsS_{4(s)} + 7O_{2(g)} \rightarrow 12CuS_{(s)} + 4SO_{2(g)} + As_4O_{6(g)}$	(Padilla et al., 2012; Safarzadeh et al., 2014b)
The carbothermic reduction of enargite	$2Cu_3AsS_{4(s)} + 3CaO_{(s)} \rightarrow 3Cu_2S_{(s)} + 3CaS_{(s)} + As_2O_{3(g)} + S_{2(g)}$ $Cu_3AsS_{4(s)} + 4CaO_{(s)} + 4C_{(s)} \rightarrow Cu_3As_{(s)} + 4CaS_{(s)} + 4CO_{(g)}$	(Igiehon et al., 1994b; Filippou et al., 2007)

and dichloro radicals, thus facilitating As (III) oxidation. The UV-assisted sulfite-oxygen process was successfully practised to treat water containing 0.47 mg/L As (III) in Bangladesh (Zaw and Emett, 2002). TiO_2-assisted photocatalysis process was also employed to oxidize As (III) in the presence of oxygen (Yang et al., 1999; Lee and Choi, 2002; Ryu and Choi, 2004; Xu et al., 2005; Nguyen et al., 2008).

Hydrogen peroxide has been a significant oxidant in hydrometallurgical processes. Hydrogen peroxide in 100% stoichiometric excess can act as an effective arsenic oxidizing agent over a wide pH range particularly under alkaline environment at room temperature (Ritcey, 2005). A study on the oxidation of arsenite in a solution with 15 g/L As (III) illustrated that a time period of 5 min reduced the concentration of arsenite by 15 times in the presence of 100% stoichiometric excess hydrogen peroxide (Molnár et al., 1994). Whereas a further increase in the oxidation time did not exhibit a significant impact on the oxidation reaction. Debekaussen et al. (2001) reported that the oxidation kinetics of As (III) with an initial concentration of 38.5 g/L was noticeably facilitated through both slow addition of 10% stoichiometric excess H_2O_2 and increase of the temperature to 95 °C at pH 3 (Debekaussen et al., 2001). Caetano et al. (2009) observed the complete oxidation of trivalent arsenic at a concentration of 0.1–1.1 g/L using 20% stoichiometric excess H_2O_2 (Caetano et al., 2009). It is worth mentioning that the initial concentration of the trivalent arsenic in a solution noticeably influences the final concentration of arsenite which is of great significance for arsenic immobilization (Molnár et al., 1994). Pettine et al. (1998) suggested that the presence of Cu^{2+}, Fe^{2+} and Pb^{2+} at ppm levels accelerates the As (III) oxidation rate by H_2O_2 (Pettine et al., 1998). The reactions given in Table 5 demonstrate the oxidation of arsenic trioxide under acidic and basic conditions, where As_2O_3 is dissolved to form H_3AsO_3 (Molnár et al., 1994). Hydrogen peroxide is used as an oxidant in industry; for example, the Ecometales scorodite plant in Chile uses hydrogen peroxide to oxidize arsenic before the scorodite process can commence (Demopoulos, 2014). Hydrogen peroxide is expensive and decomposes in contact with solids; however, the Ecometales plant in Chile experiences arsenite concentrations of <15% of the total arsenic (Demopoulos, 2014).

Ferrate (iron in +6 oxidation state) has been considered as a powerful oxidant and coagulant for water and waste water treatment over the wide pH range. Several studies reported oxidation of As (III) by ferrate and subsequently elimination of As (V) from the solution (Schreyer et al., 1950; Fan et al., 2002; Jiang, 2007; Mohan, 2007; Prucek et al., 2013). Lee et al. (2003) stated that 90% of As (III) with an initial concentration of 517 μg/L was removed using 2 mg/L of Fe (VI) (Lee et al., 2003). However, this method is not economical because Fe (VI) is a relatively expensive material. Lee et al. (2003) recommended the use of a mixture of ferrate as an oxidant and ferric as a coagulant to lower the cost of the process.

Ozone is another oxidant which can effectively oxidize As (III) to As (V) (Bissen and Frimmel, 2003b). Ozone has a high oxidizing capability and it is therefore becoming a more commonly used oxidant for treating water and wastewater (Khuntia et al., 2014). The oxidation of As (III) with ozone is a pH dependent reaction. In order to improve the efficiency of the ozonation technique for As (III) oxidation, the gas must be dissolved in the aqueous arsenic-containing solution using microbubbles (Khuntia et al., 2012, 2014). Hydroxyl radicals produced by ozone microbubbles significantly increase the arsenic oxidation kinetics. According to the authors' knowledge, only few studies have been published which demonstrate the use of ozone for oxidizing arsenite to arsenate (Böckelen and Niessner, 1992; Kim and Nriagu, 2000; Dodd et al., 2006). Böckelen and Niessner (1992) and Kim and Nriagu (2000) illustrated that the As (III) was completely oxidized to As (V) within 20 min in the presence of ozone where the initial concentration of arsenic (III) was 40–200 μg/L. The study reported by Khuntia et al. (2014) used an arsenic concentration of 995 ± 5 mg/L (Khuntia et al., 2014). The study showed that arsenite is quickly oxidized at low arsenic concentrations and a neutral pH of 7. It can be advantageous to treat arsenic solutions at a pH of 1–2 with ozone in order to precipitate arsenic with manganese because ferric arsenate and ferric hydroxide do not precipitate under highly acidic conditions (Nishimura and Umetsu, 2001).

Oxygen mixed with sulfur dioxide (SO_2/O_2) is used as an oxidant to oxidize trivalent arsenic (Table 5) (Zhang et al., 2000). Hydroxyl

Table 4
Arsenic mobilization through hydrometallurgical processes.

Acid leaching of enargite Process	Reaction	Oxidation state of produced arsenic	Copper dissolution	Reference
Leaching of enargite in chlorine-chloride medium	$2Cu_3AsS_{4(s)} + 23Cl_{2(aq)} + 24H_2O_{(l)} \rightarrow 4CuSO_{4(aq)} + 2CuCl_{2(aq)} + 2H_3AsO_{4(aq)} + 42HCl_{(aq)} + 4S^{\circ}_{(s)}$	As(V)	Yes	(Herreros et al., 2002)
Leaching of enargite in H_2SO_4-NaCl-O_2 solution	$2Cu_3AsS_{4(s)} + 6H_2SO_{4(aq)} + 11/2O_{2(aq)} \rightarrow 6CuSO_{4(aq)} + 2H_3AsO_{4(aq)} + 8S^{\circ}_{(s)} + 3H_2O$	As(V)	Yes	(Padilla et al., 2005)
Atmospheric chloride leaching	$2Cu_3AsS_{4(s)} + 35Cl_{2(aq)} + 40H_2O_{(l)} \rightarrow 6CuSO_{4(aq)} + 2H_3AsO_{4(aq)} + 2H_2SO_{4(aq)} + 70HCl_{(aq)}$	As(V)	Yes	(Lei and Carnahan, 1984)
Atmospheric leaching in ferric sulfate solution	$Cu_3AsS_{4(s)} + 11Fe^{3+}{}_{(aq)} + 4H_2O_{(l)} \rightarrow 3Cu^{2+}{}_{(aq)} + 4S^{\circ}_{(s)} + AsO_4{}^{3-}{}_{(aq)} + 8H^+ + 11Fe^{2+}$	As(V)	Yes	(Dutrizac and MacDonald, 1972)
Albion process (in sulfuric acid solution)	$2Cu_3AsS_{4(s)} + 10O_{2(aq)} + 3H_2SO_{4(aq)} \rightarrow 6CuSO_{4(aq)} + 5S^{\circ}_{(s)} + 2H_3AsO_{4(aq)}$	As(V)	Yes	(Hourn et al., 1999; Hourn et al., 2006)
Galvanox^{TM} process	$2Cu_3AsS_{4(s)} + 9Fe_2(SO_4)_{3(aq)} + 6H_2O_{(l)} \rightarrow 6CuSO_{4(aq)} + 2H_3AsO_{3(aq)} + 18FeSO_{4(aq)} + 3H_2SO_{4(aq)} + 8S^{\circ}_{(s)}$ $2Cu_3AsS_{4(s)} + 11Fe_2(SO_4)_{3(aq)} + 8H_2O_{(l)} \rightarrow 6CuSO_{4(aq)} + 2H_3AsO_{4(aq)} + 22FeSO_{4(aq)} + 5H_2SO_{4(aq)} + 8S^{\circ}_{(s)}$	As(III) As(V)	Yes Yes	(Koch and Grasselly, 1952; Rivera-Vasquez and Dixon, 2009; Dixon and Rivera-Vasquez, 2012; Rivera-Vasquez and Dixon, 2015)
Atmospheric ferric sulfate leaching of enargite in the presence of carbon catalyst	$4Cu_3AsS_{4(s)} + 12H_2SO_{4(aq)} + 9O_{2(aq)} \rightarrow 12CuSO_{4(aq)} + 4H_3AsO_{3(aq)} + 6H_2O_{(l)} + 16S^{\circ}_{(s)}$	As(III)	Yes	(Chen, 1976; Safarzadeh et al., 2014c; Dixon and Rivera-Vasquez, 2015)
Leaching of enargite in ferric fluoroborate	$Cu_3AsS_{4(s)} + 9Fe(BF_4)_{3(aq)} \rightarrow 3Cu(BF_4)_{2(aq)} + 9Fe(BF_4)_{2(aq)} + As(BF_4)_{3(aq)\ (aq)} + 4S^{\circ}_{(s)}$	As(III)	Yes	(Safarzadeh et al., 2014b)
Pressure leaching of enargite	$2Cu_3AsS_{4(s)} + 11/2O_{2(aq)} + 6H_2SO_{4(aq)} \rightarrow 6CuSO_{4(aq)} + 8S^{\circ}_{(s)} + 2H_3AsO_{4(aq)} + 3H_2O_{(l)}$	As(V)	Yes	(Dreisinger, 2006; Padilla et al., 2008; Leppinen et al., 2009)
	$2Cu_3AsS_{4(s)} + 35/2O_{2(aq)} + 5H_2O_{(l)} + 4H^+{}_{(aq)} \rightarrow 6Cu^{2+}{}_{(aq)} + 2H_3AsO_{4(aq)} + 8HSO_4{}^-{}_{(aq)}$	As(V)	Yes	(Padilla et al., 2008)
	$4Cu_3AsS_{4(s)} + 35O_{2(aq)} + 10H_2O_{(l)} \rightarrow 12CuSO_{4(aq)} + 4H_3AsO_{4(aq)} + 4H_2SO_{4(aq)}$	As(V)	Yes	(Nadkarni and Kusik, 1988; Padilla et al., 2005)
	$Cu_3AsS_{4(s)} + 35Fe^{3+}{}_{(aq)} + 20H_2O_{(l)} \rightarrow 3Cu^{2+}{}_{(aq)} + AsO_4{}^{3-}{}_{(aq)} + 4SO_4{}^{2-}{}_{(aq)} + 40H^+{}_{(aq)} + 35Fe^{2+}{}_{(aq)}$	As(V)	Yes	(Padilla et al., 2005)
	$Cu_3AsS_{4(s)} + 11Fe^{3+}{}_{(aq)} + 4H_2O_{(l)} \rightarrow 3Cu^{2+}{}_{(aq)} + H_3AsO_{4(aq)} + 4S^{\circ}_{(s)} + 5H^+{}_{(aq)} + 11Fe^{2+}{}_{(aq)}$	As(V)	Yes	(Padilla et al., 2005)
	$Cu_3AsS_{4(s)} + 35Fe^{3+}{}_{(aq)} + 20H_2O_{(l)} \rightarrow 3Cu^{2+}{}_{(aq)} + H_3AsO_{4(aq)} + 4HSO_4{}^-{}_{(aq)} + 33H^+{}_{(aq)} + 35Fe^{2+}{}_{(aq)}$	As(V)	Yes	(Nadkarni and Kusik, 1988; Ruiz et al., 2011)
Acid bake-leach process	$4Cu_3AsS_{4(s)} + 28H_2SO_{4(aq)} \rightarrow 3CuO.CuSO_{4(s)} + 6CuSO_{4(s)} + 31/2S^{\circ}_{(s)} + 2As_2O_{3(s)} + 28H_2O_{(l)} + 39/2SO_{2(g)}$	As(III)	No	(Safarzadeh et al., 2012a, 2012b; Safarzadeh and Miller, 2014a, 2014b, 2014c; Safarzadeh et al., 2014a)
Metathesis process	$16Cu_3AsS_{4(s)} + 51CuSO_{4(aq)} + 84H_2O_{(l)} \rightarrow 11Cu_9S_{5(s)} + 16H_3AsO_{3(aq)} + 60H_2SO_{4(aq)}$	As(III)	No	(Dunn and Bartsch, 2008; Safarzadeh et al., 2014c)
	$58Cu_3AsS_{4(s)} + 189CuSO_{4(aq)} + 310H_2O_{(l)} \rightarrow 33Cu_9S_{5(s)} + 33Cu_2S + 58H_3AsO_{3(aq)} + 223H_2SO_{4(aq)}$	As(III)	No	
Extended milling in pure oxygen atmosphere at 25 °C	$4Cu_3AsS_{4(s)} + 27O_{2(g)} \rightarrow 12CuSO_{4(aq)} + 2As_2O_{3(s)} + 4S^{\circ}_{(s)}$	As(III)	No	(Welham, 2001)
Extended milling in pure oxygen atmosphere at 100 °C	$4Cu_3AsS_{4(s)} + 7O_{2(g)} \rightarrow 12CuS_{(s)} + 2As_2O_{3(s)} + 4SO_{2(g)}$	As(III)	Yes	
Extended milling in SO_2 atmosphere at 25 °C	$4Cu_3AsS_{4(s)} + 27SO_{2(g)} \rightarrow 12CuSO_{4(aq)} + 2As_2O_{3(s)} + 31S^{\circ}_{(s)}$	As(III)	Yes	
CESL process	$4Cu_3AsS_{4(s)} + 11O_{2(aq)} + 2Fe_2(SO_4)_{3(aq)} + 6H_2SO_{4(aq)} + 2H_2O_{(l)} \rightarrow 12CuSO_{4(aq)} + 4FeAsO_4 2H_2O_{(s)} + 16S^{\circ}_{(s)}$	As(V)	Yes	(Mayhew et al., 2010; Bruce et al., 2011; Mayhew et al., 2011)
Nitrogen species catalyzed (NSC) acid pressure leach	$3MeS_{(s)} + 2HNO_{3(aq)} + 3H_2SO_{4(aq)} \rightarrow 3MeSO_{4(aq)} + 2NO_{(g)} + 3S^{\circ}_{(s)} + 4H_2O_{(l)}$ (Me: metal)	As(V)	Yes	(Anderson, 2003b, 2003a; Anderson and Twidwell, 2008)
Atmospheric leaching in ferric sulfate and sulfuric acid solution (Ag_2SO_4 and $HgSO_4$ as the catalysts)	–	As (III)	Yes	(Flynn and Carnahan, 1989)
Atmospheric leaching in ferric sulfate and sulfuric acid solution (potassium iodide as a catalysts	–	As(V)	Yes	(Manabe, 2012)
Dynatec process	–	As(V)	Yes	(Kalanchey et al., 2007; Safarzadeh et al., 2014b)
Intec process	–	As(V)	Yes	(Moyes et al., 2000; Safarzadeh et al., 2014b)
HydroCopper^{TM} process	–	As(V)	Yes	(Hyvärinen and Hämäläinen, 1999; Hyvärinen et al., 2004; Hyvärinen and Hämäläinen, 2005; Baxter et al., 2010)
Platsol® process	–	As(V)	Yes	(Ferron et al., 2002; Ferron and Wang, 2003; Ford et al., 2009)

Table 4 (*continued*)

Acid leaching of enargite Process	Reaction	Oxidation state of produced arsenic	Copper dissolution	Reference
Leaching of enargite in sodium sulfide solution (Sunshine process and Equity Silver process)	$2Cu_3AsS_{4(s)} + 3Na_2S_{(aq)} \rightarrow 3Cu_2S_{(s)} + 2Na_3AsS_{4(aq)}$	As (V)	No	(Coltrinari and Holmes, 1973; Kusik et al., 1975; Nadkarni et al., 1975; Baláž et al., 2000; Delfini et al., 2003; Baláž and Achimovičová, 2006a; Baláž and Achimovičová, 2006b; Curreli et al., 2009; Awe and Sandström, 2010; Celep et al., 2011; Nakon and Way, 2014; Ruiz et al., 2015)
Leaching of enargite in sodium hydrosulfide solution	$2Cu_3AsS_{4(s)} + 3NaHS_{(aq)} + 3NaOH_{(aq)} \rightarrow 3Cu_2S_{(s)} + 2Na_3AsS_{4(aq)} + 3H_2O_{(l)}$	As (V)	No	(Tongamp et al., 2009; 2010)
Leaching of enargite in sodium hypochlorite solution	$2Cu_3AsS_{4(s)} + 35NaClO_{(aq)} + 22NaOH_{(aq)} \rightarrow 6CuO_{(s)} + 2Na_3AsO_{4(aq)} + 8Na_2SO_{4(aq)} + 35NaCl_{(aq)} + 11H_2O_{(l)}$	As (V)	No	(Roca et al., 2003; Viñals et al., 2003; Curreli et al., 2005; Mihajlovic et al., 2007; Musu et al., 2009; Ruiz et al., 2014)
Pressure leaching of enargite in sodium hydroxide solution (Sill process)	–	As (V) As (III)	No	(Nadkarni and Kusik, 1988)
Leaching of enargite in ammonia solution (Sherritt Gordon's process and Arbiter process)	$2Cu_3AsS_{4(s)} + 26NH_{3(aq)} + 35/2O_{2(aq)} + 5H_2O \rightarrow 6Cu(NH_3)_4SO_{4(aq)} + 2NH_4H_2AsO_{4(aq)} + 2H_2SO_{4(aq)}$	As (V)	Yes	(Kuhn et al., 1974; Arbiter and Kuhn, 1982; Gajam and Raghavan, 1983; Arbiter and McNulty, 1999; Kantar, 2002)
Cyanidation	–	As (III)	Yes	(Hedley and Tabachnik, 1958; Marsden and House, 2009; Safarzadeh et al., 2014b)

Bioleaching of enargite Process	Reaction	Oxidation state of produced arsenic	Copper dissolution	Reference
Dissolution of enargite using *Acidithiobacillus ferrooxidans*	$Cu_3AsS_{4(s)} + 27Fe^{3+}{}_{(aq)} + 2O_{2(aq)} + 16H_2O_{(l)} \rightarrow 3Cu^{2+}{}_{(aq)} + H_3AsO_{4(aq)} + 4SO_4{}^{2-}{}_{(aq)} + 29H^+{}_{(aq)} + 27Fe^{2+}{}_{(aq)}$	As (V)	Yes	(Sasaki et al., 2010c)
Dissolution of enargite in the presence of *Leptospirillum ferrooxidans*	$Cu_3AsS_{4(s)} + 9/2Fe_2(SO_4)_{3(aq)} + 2H_2O_{(l)} \rightarrow 3CuSO_{4(aq)} + HAsO_{2(aq)} + 9FeSO_{4(aq)} + 4S^{\circ}{}_{(s)} + 3/2H_2SO_{4(aq)}$	As (III)	Yes	(Watling, 2006)
Ferric leaching of enargite in the presence of *Sulfolobus BC*	$Cu_3AsS_{4(s)} + 9Fe^{3+}{}_{(aq)} + 2H_2O_{(l)} \rightarrow 3Cu^{2+}{}_{(aq)} + AsO_2{}^-{}_{(aq)} + 4S^{\circ}{}_{(s)} + 4H^+{}_{(aq)} + 9Fe^{2+}{}_{(aq)}$	As (III)	Yes	(Jian et al., 2008)
Direct bioleaching of enargite by *Sulfolobus BC*	$2Cu_3AsS_{4(s)} + 10H^+{}_{(aq)} + 9/2O_{2(aq)} \rightarrow 6Cu^{2+}{}_{(aq)} + 2AsO_2{}^-{}_{(aq)} + 8S^{\circ}{}_{(s)} + 5H_2O_{(l)}$ $AsO_2{}^-{}_{(aq)} + 2Fe^{3+}{}_{(aq)} + 2H_2O_{(l)} \rightarrow AsO_4{}^{3-}{}_{(aq)} + 2Fe^{2+}{}_{(aq)} + 4H^+{}_{(aq)}$ $AsO_4{}^{3-}{}_{(aq)} + Fe^{3+}{}_{(aq)} \rightarrow FeAsO_{4(s)}$	As (V)	Yes	
Dissolution of enargite in the presence of *Thiobacillus ferrooxidans*	$Cu_3AsS_{4(s)} + 11/2Fe_2(SO_4)_{3(aq)} + 4H_2O_{(l)} \rightarrow 3CuSO_{4(aq)} + H_3AsO_{4(aq)} + 11FeSO_{4(aq)} + 4S^{\circ}{}_{(s)} + 5/2H_2SO_{4(aq)}$ $Cu_3AsS_{4(s)} + 9/2Fe_2(SO_4)_{3(aq)} + 2H_2O_{(l)} \rightarrow 3CuSO_{4(aq)} + HAsO_{2(aq)} + 9FeSO_{4(aq)} + 4S^{\circ}{}_{(s)} + 3/2H_2SO_{4(aq)}$	As (V) As (III)	Yes	(Escobar et al., 1997)
Galvanic bacterial leaching of enargite in the presence of pyrite	$4Cu_3AsS_{4(s)} + 33O_{2(aq)} + 10H_2O_{(l)} \rightarrow 12Cu^{2+}{}_{(aq)} + 4H_3AsO_{3(aq)} + 16SO_4{}^{2-}{}_{(aq)} + 8H^+{}_{(aq)}$	As (III)	Yes	(Sasaki et al., 2010a)

radicals, which are generated through the oxidation of S (IV) by oxygen, account for the oxidation of arsenite. SO_2/O_2 is relatively less costly than other oxidants used to oxidize arsenic (Demopoulos, 2014). Table 6 shows the versatility of SO_2/O_2 as an oxidant. Sodium sulfite or metabisulfite can be used instead of sulfur dioxide as they are easier to handle due to the sulfur dioxide hazardous nature (Demopoulos, 2014). Various parameters such as solution pH, temperature, the mole ratio of SO_2/O_2 in the gas mixture, supply rate of SO_2 and stirring rate can significantly control the oxidation kinetics of trivalent arsenic (Wang et al., 1998). The SO_2/O_2 gas mixture can also oxidize ferrous to ferric (Table 6) and therefore it can be used to co-precipitate arsenic and iron from solution as a ferric arsenate (Wang et al., 1998; Zhang et al., 2000). Wang et al. (1998) carried out a series of experiments at a pH ranging from 0.3 to 2 in order to probe the oxidation behavior of As (III) using SO_2-assisted oxygen at different temperatures (25 °C–90 °C) (Wang et al., 1998). It was illustrated that the oxidation rate of trivalent arsenic at a low temperature was slow. However, increasing temperature to 90 °C led to the complete oxidation of 10 g/L As (III) within approximately 120 min in the presence of 7.46 g/L ferric ions at pH 0.75. Wang et al. (1998) also indicated that the addition of iron source prior or during oxidation process significantly increased the kinetics of As (III) oxidation due to an increase in the oxidation rate of S (IV) which results in the formation of a higher number of hydroxyl radicals (Wang and Demopoulos, 1998; Wang et al., 1998). They also observed that goethite with an initial dosage of 17.6 g/L at pH 0.75 not only expedited As (III) oxidation rate at 90 °C, but also played a significant role in the formation of scorodite precipitates (Wang et al., 1998). Furthermore, acid neutralizing ability of goethite resulted in a lower amount of neutralizing agent required for pH adjustment.

Permanganate has been considered as a suitable oxidant in order to treat both drinking water and groundwater (Lee et al., 2011). The reaction of As (III) oxidation using permanganate given in Table 5 exhibits rapid kinetics and a small pH dependency (USEPA, 2001, 2003; Na et al., 2007). Na et al. (2007) reported that the trivalent arsenic, whose dosage was in the range of 200 μg/L–600 μg/L, was completely eliminated at a Mn (VII):As (III) mole ratio of 0.53:1 (Na et al., 2007). However, as shown in Table 5, 1 mol of Mn (VII) can theoretically oxidize 2.5 mol of As (III) over a wide range of pH. It was demonstrated that the solid MnO_2-based media produced accounts for the secondary heterogeneous oxidation of As (III) to As (V) (Stumm and Morgan, 1981; Nesbitt et al., 1998; Manning et al., 2002; Lafferty et al., 2011). In addition, Lee et al. (2011) stated that secondary oxidation occurs in three consecutive steps: (i) sorption of As (III) to the solid product; (ii) oxidation to As (V); (iii) desorption of As (V) into the solution (Lee et al.,

Table 5
Arsenite oxidizing reagents.

Arsenic oxidizing agent	Reaction	Reference
Hydrogen peroxide	$H_3AsO_{3(aq)} + H_2O_{2(aq)} \rightarrow H_3AsO_{4(aq)} + H_2O_{(l)}$ $pH < 2$ $H_3AsO_{3(aq)} + H_2O_{2(aq)} \rightarrow H_2AsO_4{}^{-}{}_{(aq)}\ H^{+}{}_{(aq)} + H_2O_{(l)}$ $2 < pH < 6$ $H_3AsO_{3(aq)} + H_2O_{2(aq)} \rightarrow HAsO_4{}^{2-}{}_{(aq)}\ 2H^{+}{}_{(aq)} + H_2O_{(l)}$ $6 < pH < 9$ $H_2AsO_3{}^{-}{}_{(aq)} + H_2O_{2(aq)} \rightarrow HAsO_4{}^{2-}{}_{(aq)}\ H^{+}{}_{(aq)} + H_2O_{(l)}$ $9 < pH < 11.5$ $HAsO_3{}^{2-}{}_{(aq)} + H_2O_{2(aq)} \rightarrow AsO_4{}^{3-}{}_{(aq)}\ H^{+}{}_{(aq)} + H_2O_{(l)}$ $11.5 < pH < 13.5$	(Molnár et al., 1994)
Ozone	$H_3AsO_{3(aq)} + O_{3(g)} \rightarrow H_2AsO_4{}^{-}{}_{(aq)} + O_{2(aq)} + H^{+}{}_{(aq)}$ $2 < pH < 6$ $H_3AsO_{3(aq)} + O_{3(g)} \rightarrow HAsO_4{}^{2-}{}_{(aq)} + O_{2(aq)} + 2H^{+}{}_{(aq)}$ $6 < pH < 9$	(Ghurye and Clifford, 2001; Khuntia et al., 2014)
SO_2/O_2 system	$HAsO_{2(aq)} + SO_{2(g)} + O_{2(g)} + 2H_2O_{(l)} \rightarrow HSO_4{}^{-}{}_{(aq)} + H_3AsO_{4(aq)} + H^{+}{}_{(aq)}$	(Wang et al., 1998)
Biooxidation process	$Cu_3AsS_{4(s)} + 27Fe^{3+}{}_{(aq)} + 2O_{2(aq)} + 16H_2O_{(l)} \xrightarrow{\text{Acidithiobacillus ferrooxidans}} 3Cu^{2+}{}_{(aq)} + H_3AsO_{4(aq)} + 4SO_4{}^{2-}{}_{(aq)} + 29H^{+}{}_{(aq)} + 27Fe^{2+}{}_{(aq)}$	(Battaglia-Brunet et al., 2002; Rhine et al., 2006; Ito et al., 2012)
Permanganate	$3H_3AsO_{3(aq)} + 2MnO_4{}^{-}{}_{(aq)} \rightarrow 3H_2AsO_4{}^{-}{}_{(aq)} + 2MnO_{2(s)} + H^{+}{}_{(aq)} + H_2O_{(l)}$	(Ghurye and Clifford, 2001; Sorlini and Gialdini, 2010)
Solid MnO_2-based media	$MnO_{2(s)} + H_3AsO_{3(aq)} + 2H^{+}{}_{(aq)} \rightarrow Mn^{2+} + H_3AsO_{4(aq)} + H_2O_{(l)}$	(Alker and Hayes, 1990; Driehaus et al., 1995; Nesbitt et al., 1998; Manning et al., 2002)
Sodium hypochlorite	$H_3AsO_{3(aq)} + NaOCl_{(aq)} \rightarrow H_2AsO_4{}^{-}{}_{(aq)} + NaCl_{(aq)} + H^{+}{}_{(aq)}$ $6.5 < pH < 9$	(USEPA, 2001)
Chlorine dioxide	$H_3AsO_{3(aq)} + 2ClO_{2(aq)} + H_2O_{(l)} \rightarrow H_2AsO_4{}^{-}{}_{(aq)} + 2ClO_2{}^{-}{}_{(aq)} + 3H^{+}{}_{(aq)}$	
Monochloramine	$5H_3AsO_{3(aq)} + 2ClO_{2(aq)} + H_2O_{(l)} \rightarrow 5H_2AsO_4{}^{-}{}_{(aq)} + 2Cl^{-}{}_{(aq)} + 7H^{+}{}_{(aq)}$	
	$H_3AsO_{3(aq)} + NH_2Cl_{(aq)} + H_2O_{(l)} \rightarrow HAsO_4{}^{2-}{}_{(aq)} + NH_4^{+} + Cl^{-}{}_{(aq)} + 2H^{+}{}_{(aq)}$	
Potassium ferrate	$3H_2AsO_3{}^{-}{}_{(aq)} + 2FeO_4{}^{2-}{}_{(aq)} + 5H_2O_{(l)} \rightarrow 3H_2AsO_4{}^{-}{}_{(aq)} + 2Fe(OH)_{3(s)} + 4OH^{-}{}_{(aq)}$ $3HAsO_3{}^{2-}{}_{(aq} + 2FeO_4{}^{2-}{}_{(aq)} + 5H_2O_{(l)} \rightarrow 3HAsO_4{}^{2-}{}_{(aq)} + 2Fe(OH)_{3(s)} + 4OH^{-}{}_{(aq)}$	(Fan et al., 2002)
Ultraviolet (UV)-assisted oxidation process	$2FeOOH_{(s)} + HAsO_{2(aq)} + 3H^{+}{}_{(aq)} \xrightarrow{h\nu} 2Fe^{2+}{}_{(aq)} + H_2AsO_4{}^{-}{}_{(aq)} + 2H_2O_{(l)}$ $H_2O_{(l)} \xrightarrow{h\nu} OH^{\cdot} + H^{\cdot}$ $As\ (III) + OH^{\cdot} \rightarrow As\ (IV) + OH^{-}$ $As\ (IV) + O_{2(aq)} \rightarrow As\ (V) + O_2^{-}$ $2\ OH^{\cdot} \rightarrow H_2O_{2(aq)}$ $2O_2^{-\cdot} + 2H_2O_{(l)} \rightarrow O_{2(aq)} + H_2O_{2(aq)} + 2OH^{-}{}_{(aq)}$ $HO_2^{\cdot} + HO_2^{\cdot} \rightarrow O_{2(aq)} + H_2O_{2(aq)}$ $H_2AsO_3{}^{-}{}_{(aq)} + H_2O_{2(aq)} \rightarrow HAsO_4{}^{2-}{}_{(aq)} + H^{+}{}_{(aq)} + H_2O_{(l)}$ $S_2O_8{}^{2-}{}_{(aq)} \xrightarrow{h\nu} 2SO_4^{-}$ $As(III) + 2SO_4^{-\cdot} \rightarrow As\ (V) + 2SO_4{}^{2-}{}_{(aq)}$	(Yang et al., 1999; Bissen et al., 2001; Emett and Khoe, 2001; Hug et al., 2001; Neppolian et al., 2008; Yoon et al., 2008; Bhandari et al., 2012)
O_2/activated carbon process	$H_2O_{(l)} + 1/2O_{2(aq)} \xrightarrow{\text{carbon surface}} H_2O_{2(aq)}$ $H_3AsO_{3(aq)} + H_2O_{2(aq)} \rightarrow H_3AsO_{4(aq)} + H_2O_{(l)}$ $pH < 2$	(Choi et al., 2014b; Choi et al., 2014a)

2011). In other words, oxidation of As (III) leads to the reductive dissolution of the MnO_2 and consequently the formation of As (V) and Mn (II) at a low pH (Manning et al., 2002).

Sodium hypochlorite is a strong oxidant to oxidize As (III) (Vasudevan et al., 2006). Trivalent arsenic with an initial dosage of 50 and 300 μg/L present in the demineralised water was completely oxidized in the presence of hypochlorite ions (oxidant:As (III) concentration ratio of 3:1) in 5 min at the pH range of 5.7–8 (Sorlini and Gialdini, 2010). Ghurye and Clifford (2001) reported that chlorine dioxide and monochloramine were inefficient for As (III) oxidation (Ghurye and Clifford, 2001). 100-times stoichiometric loading of chlorine dioxide resulted in the oxidation of 76% of As (III) (initial dosage of 50 μg/L) within 5 min at pH 8.3. Sorlini and Gialdini (2010) claimed that 60% of 50 μg/L As (III) in demineralised water was converted to As (V) by chlorine dioxide (oxidant:As (III) concentration ratio of 3:1) after two days (Sorlini and Gialdini, 2010). However, the oxidation yield of 50 μg/L As (III) in the real groundwater increased to 80% using chlorine dioxide at an oxidant:As (III) concentration ratio of 3:1 after 30 min due to the presence of various species such as metal ions which improve the oxidation kinetics of arsenite. Furthermore, 100% As (III) oxidation was achieved for both demineralised and real water after two days contact time at pH 6 when the monochloramine:As (III) concentration ratio was set at 3:1 (Sorlini and Gialdini, 2010). The oxidation of arsenite by monochloramine and chlorine dioxide is highly pH dependent. The dissociation of monochloramine is expedited in water with a decrease in the pH and therefore a higher number of chlorine ions are available to oxidize As (III) (Sorlini and Gialdini, 2010).

Table 6
Usage of SO_2/O_2 in hydrometallurgical applications (Zhang et al., 2000) (reproduced with permission).

Systems	pH range	Oxidation products	Potential application
$Fe\text{-}SO_2/O_2$	0–3	$Fe^{2+} \rightarrow Fe^{3+}$ $S(IV) \rightarrow SO_4^{2-}/S_2O_6^{2-}$	Leaching of metal oxide Oxidation of As (III)
$Mn\text{-}SO_2/O_2$	3–6	$Mn^{2+} \rightarrow Mn(III)/Mn(IV)$ $S(IV) \rightarrow SO_4^{2-}/S_2O_6^{2-}$	Oxidative precipitation of Mn
$Ni\text{-}SO_2/O_2$	7–8.5	$Ni(II) \rightarrow Ni(III)$ $S(IV) \rightarrow SO_4^{2-}$	Production of $Ni(OH)_3$
$Cu\text{-}SO_2/O_2$	9–10	$Cu^{+} \rightarrow Cu^{2+}$ $S(IV) \rightarrow SO_4^{2-}$ $CN^{-} \rightarrow CNO^{-}$	Oxidation of CN^{-}

Activated carbon catalyzes the oxidation reaction of arsenite and oxygen to arsenate (Bissen and Frimmel, 2003b). It was shown that 90% of As (III) was oxidized using 5–10 g/L of activated carbon in 20 to 30 min when the initial concentration of As (III) in the water was 40 μ/L (Bissen and Frimmel, 2003b). A novel and robust arsenic oxidation process was created which uses activated carbon to catalyze the arsenic oxidation reaction and only has one consumable reagent which is oxygen (Choi et al., 2014b). The new process patented by Choi et al. (2014a) is carried out in acidic conditions at ambient temperature and pressure in <24 h and has an oxidation efficiency of up to 99% (Choi et al., 2014a). Choi et al. (2014b) used activated carbon to catalyze the arsenic oxidation reaction to have arsenic in its pentavalent state (Choi et al., 2014b). Though the process is proven to work effectively to oxidize arsenite it is still unclear as to what oxidation mechanism occurs. One hypothesis to describe the novel process that is proposed by the authors is that water and oxygen react on the activated carbon surface to produce a strong oxidant, such as hydrogen peroxide, which consequently reacts with arsenite to form arsenate (Lamb and Elder, 1931; Kolthoff, 1932; Ahumada et al., 2002; Navarro and Alguacil, 2002; Choi et al., 2014b). Two pieces of evidence that the authors of the study state which show that reactions illustrated in Table 5 are plausible are: (i) using pure oxygen has faster oxidation kinetics than that of air; (ii) both continuous and batch experiments show negligible changes in the system's pH and this is expected from the reactions shown in Table 5. The authors are currently investigating the mechanism of this novel process, i.e. arsenic oxidation with carbon catalyst.

Biological oxidation, "biooxidation", utilizes microbial mechanisms to oxidize chemical species. The oxidation mechanism is typically characterized as an indirect oxidation mechanism as the microorganisms oxidize ions, such as ferrous to ferric, which then oxidize other species. The copper industry has used heap leaching and dump leaching since the 1900s to treat low-grade copper ores and these techniques for copper extraction work on the basis of bioleaching (Marsden and House, 2009). Biooxidation improves the kinetics of otherwise slower oxidation processes when bacteria such as *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* are present (Okereke and Stevens, 1991; Marsden and House, 2009). In the late 1970s Glencor Process Research in South Africa developed the BIOX™ Process which has the capability to oxidize arsenite to arsenate, and the arsenate can then be removed as a ferric arsenate in subsequent plant processes (Van Aswegen et al., 2007).

Few of the studies in this section focused on water and wastewater treatment where the concentration of As (III) is very low (<10 mg/L). However, As (III)-bearing streams obtained from the 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 SO_2/O_2 gas mixture process could be more interesting if SO_2 is available in the plant area from either a sulfide roasting process or burning the elemental sulfur source. Activated carbon assisted oxidation of arsenical solutions also appears to be of interest in the metals and minerals industry.

3.2. Hydrometallurgical immobilization processes

Precipitation is a widely used process to remove arsenic from waste streams. The most common arsenic precipitates from hydrometallurgical processes are: arsenic sulfides, calcium arsenite, calcium arsenate and ferric arsenate. Each of these precipitates exhibits relatively low solubility in their respective pH range.

3.2.1. Lime neutralization

Lime (CaO) neutralization is a simple technique to precipitate arsenite and arsenate as calcium arsenite and/or calcium arsenate at pH 11–12. Calcium arsenate compounds that have been proposed by researchers are listed in Table 7. It was shown that the type of precipitate formed and its solubility are dependent on the solution pH, temperature, ageing time and initial molar ratio of Ca:As (Moon et al., 2004; Zhu et al., 2006). The precipitates are formed through lime addition to the arsenic-containing solution. Lime neutralization is a relatively economic process for arsenic immobilization; however, the precipitates show poor long-term stability and therefore must be deposited in hazardous landfills.

Pentavalent arsenic-containing precipitates exhibit more stability compared to those with trivalent arsenic. It is therefore necessary to oxidize As (III) present in the solution to As (V) and this is typically accomplished by means of neutralization and aeration to produce gypsum and calcium arsenate (Eqs. (4)–(6)).

$$Ca(OH)_{2(s)} + H_2SO_{4(aq)} \rightarrow CaSO_4 \cdot 2H_2O_{(s)} \tag{4}$$

$$HAsO_{2(aq)} + 1/2O_{2(aq)} + H_2O_{(l)} \rightarrow H_3AsO_{4(aq)} \tag{5}$$

$$6Ca(OH)_{2(s)} + 4H_3AsO_{4(aq)} \rightarrow 2Ca_3(AsO_4)_{2(s)} + 12H_2O_{(l)} \tag{6}$$

Swash and Monhemius (1995) used the USEPA TCLP method to illustrate the high degree of calcium arsenite and calcium arsenate residue solubility (1650–3600 mg/L) (Swash and Monhemius, 1995). Various types of calcium arsenate were synthesized under different conditions; however, none of the resulting precipitates passed the EPA TCLP (Nishimura and Tozawa, 1985). Other researchers reported that calcium arsenite and calcium arsenate slowly decomposed in the presence of atmospheric carbon dioxide and moisture which resulted in the calcium carbonate formation and arsenic discharge into the solution (Eq. (7)) (Robins and Tozawa, 1982; Nishimura and Tozawa, 1985; Robins and Jayaweera, 1992). It was also shown that calcium arsenite and calcium arsenate had a low degree of solubility when they were in contact with an excess of lime for a short period of time but arsenic dissolution increased with time due to the dissolution and carbonation of lime (Swash and Monhemius, 1995). Nishimura and Tozawa (1985) proved that calcination with an excess of lime elevated the stability of calcium arsenite and calcium arsenate due to the formation of a more crystalline calcium arsenate which were less soluble than their amorphous analogs (Eqs. (8)–(9)) (Nishimura and Tozawa, 1985).

$$Ca_3(AsO_4)_{2(s)} + 3CO_{2(g)} + 3H_2O_{(l)} \rightarrow 3CaCO_{3(s)} + 2H_3AsO_{4(aq)} \tag{7}$$

$$Ca_3(AsO_4)_2 \cdot Ca(OH)_{2(s)} \rightarrow Ca_3(AsO_4)_{2(s)}(\text{Crystalline}) + CaO_{(s)} + H_2O_{(l)} \tag{8}$$

$$Ca(AsO_2)_2 \cdot Ca(OH)_{2(s)} + (n+1)\ Ca(OH)_{2(s)} + O_{2(g)} \rightarrow Ca_3(AsO_4)_{2(s)}(\text{Crystalline}) + nCaO_{(s)} + (n+2)\ H_2O_{(l)} \tag{9}$$

Twidwell et al. (2005) synthesized an arsenate phosphate hydroxy apatite (APHAP) compound ($Ca_{10}(As_xP_yO_4)_6(OH)_2$) which was extremely resistant to transformation to calcium carbonate (Twidwell et al., 2005; Lee et al., 2009; Zhang et al., 2011). It was demonstrated that APHAP with a P:As molar ratio above 7 released <1 mg/L arsenic back into the solution after a long period of time at a pH range of 11–12 (McCloskey et al., 2006). The arsenate analogue of fluorapatite (FAP) and svabite ($Ca_5(AsO_4)_3F$) have recently gained attention because FAP compounds exhibit more stability than hydroxyapatite (HAP) (White and Toor, 1996; Zhu et al., 2011; Noël and Demopoulos, 2014). Svabite was synthesized via aqueous precipitation and thermal methods (Kucharski et al., 2002; Zhu et al., 2011; Noël and Demopoulos, 2014). Kucharski et al. (2002) reported that 5.5 mg/L of arsenic was leached by thermally-formed svabite at pH 9.8 (Kucharski et al., 2002). However, the amount of arsenic released was 50 mg/L in the case of aqueous precipitated svabite at pH 10 which was approximately 10 times greater than that of thermally-synthesized svabite (Zhu et al., 2011).

The copper smelters located in northern Chile employ lime neutralization to treat smelter weak acid and dust effluent due to its dry climate (Opio, 2013). At the Codelco's Chuquicamata smelter in Chile the arsenite-bearing stream is neutralized using lime to generate calcium arsenite and gypsum. The calcium arsenite filter cake (5–10 wt% As) is then trucked to the disposal site and subsequently discharged into ponds that are lined with high density polyethylene (HDPE). At the Caletones smelter in Chile the arsenite compound is oxidized to As (V) either before precipitation using hydrogen peroxide or after precipitation by calcining filter cakes in a rotary kiln to form calcium arsenate and gypsum. Both cases require the resulting calcium arsenate residues to be disposed of in a hazardous landfill (Smith, 1986).

Table 7
Synthetic calcium arsenate compounds (Swash and Monhemius, 1995) (reproduced with permission).

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

A novel process to treat arsenic-bearing weak acid was developed at Atlantic Copper's smelter in Huelva, Spain to reduce the volume of waste to be disposed and its associated costs (Ante et al., 2005). This technique includes three steps: (i) lime addition at 50–80 °C to precipitate pure gypsum at $pH < 1$; (ii) increasing the pH to 12 in order to precipitate gypsum, calcium arsenite and heavy metal hydroxides; (iii) the residual arsenite is precipitated as ferric arsenite at pH 7 with an Fe:As molar ratio >3:1. The calcium arsenite and ferric arsenite produced are then discharged to a tailings pond and the gypsum from step (i) is sold as a by-product to cement plants (Ackerman et al., 1993).

3.2.2. Sulfide precipitation

The alkaline sodium sulfide leach process was first employed to remove antimony from tetrahedrite in order to upgrade silver concentrates (Raudsepp, 1981; Edwards, 1985; Ackerman et al., 1993; Filippou et al., 2007). The two major operations which used this technique were the Sunshine antimony refinery in Idaho, USA (Ackerman et al., 1993) and the Equity silver mine in British Columbia, Canada (Edwards, 1985); however, both operations are now ceased. The alkaline sodium sulfide method was later adopted to eliminate arsenic from enargite concentrates at the Lepanto mining company in the Philippines; however, the Lepanto Mining Company has changed its operation from copper to gold production. Fig. 6 shows a flowsheet of sulfide precipitation: the feed is leached using Na_2S in the presence of NaOH at 80–105 °C; this temperature is below the boiling point of a sodium hydroxide-sodium sulfide solution (Eq. (10)). The arsenic-free concentrate and leach solution are then separated from sodium thioarsenate which is crystalized through evaporation, cooling and filtration. The crystals are then treated with sulfuric acid to form As_2S_5 as presented in Eq. (11).

$$2Cu_3AsS_{4(s)} + 3Na_2S_{(aq)} \rightarrow 3Cu_2S_{(s)} + 2Na_3AsS_{4(aq)} \tag{10}$$

$$2Na_3AsS_{4(aq)} + 3H_2SO_{4(aq)} \rightarrow 3H_2S_{(g)} + As_2S_{5(s)} + 3Na_2SO_{4(aq)} \tag{11}$$

At the Saganoseki copper smelter in Japan As (III)-bearing weak acid bleed and converter dust effluents are neutralized with sodium hydrosulfide (NaSH) to fix trivalent arsenic as arsenic sulfide (As_2S_3) containing 60 wt% of As (Eq. (12)) (Peacey et al., 2010; Opio, 2013). Eq. (12) clearly shows that the sulfidization process is not associated with additional acid generation and therefore neutralizing reagents are not required prior to arsenic precipitation. This renders to absence of gypsum, and consequently produces a smaller volume of sludge compared to the amount produced using the conventional lime treatment method. Another advantage of sulfide precipitation is that there is a much higher water recovery due to the high specific gravity of the sulfide, ease of filtration and settling of sulfide solids. A higher water recovery allows for the treatment of arsenic-free acidic effluents to recover other valuable metals. As_2S_3 is stable under acidic and reducing conditions ($pH < 4$) but is prone to atmospheric and bacterial oxidation. The solubility of arsenic sulfide is 1 mg/L at $pH < 4$. Arsenic sulfide residue is treated in an autoclave with sulfur additions (60 wt%) at 200 °C and 20 atm in order to dry, polymerize and densify the arsenic sulfide compounds. This will increase the long-term stability of arsenic sulfide for storage. The resulting arsenic sulfide cake is stored in concrete and has approximately 1 wt% moisture and a low bulk density of 1.3 t/m^3 (Hino et al., 1995; Valenzuela, 2000).

$$2HAsO_{2(aq)} + 3NaHS_{(aq)} + 1.5H_2SO_{4(aq)} \rightarrow As_2S_{3(s)} + 1.5Na_2SO_{4(aq)} + 4H_2O_{(l)} \tag{12}$$

BioteQ Environment Technologies used the sulfidization process in conjunction with ion exchange at the batch scale for immobilizing As (III) and recovering precious metals present in the flue-gas scrubber effluent with high acidity (Fig. 7) (Mohammadi et al., 2014). The resulting effluent contained a high concentration of copper and rhenium and the recovery of these elements was conducted to reduce the cost of arsenic fixation. Hydrogen sulfide gas was used as a source of sulfur as shown in Eq. (13). The sulfidization process produced a smaller volume of high grade arsenic solid residues with a lower arsenic concentration.

$$2HAsO_{2(aq)} + 3H_2S_{(g)} \rightarrow As_2S_{3(s)} + 4H_2O_{(aq)} \tag{13}$$

At the Kennecott Utah copper smelter in Magna, Utah, arsenite-containing weak acid and dust treatment plant streams are sent to a hydrometallurgical plant to eliminate arsenic from the circuit in a two-stage continuous process (Gabb and Davies, 1999). First copper and a portion of arsenic are precipitated out of solution and the arsenic-copper filter cake is recycled to the smelter. Next, the remaining arsenic is precipitated with cadmium as a sulfide residue and consequently discharged in the hazardous waste facility.

This process is much more expensive compared to lime neutralization due to the high cost of reagents required, particularly NaSH (Hino et al., 1995). Additionally, pH control during the arsenic precipitation with NaSH is difficult due to the formation of caustic. Chemical and

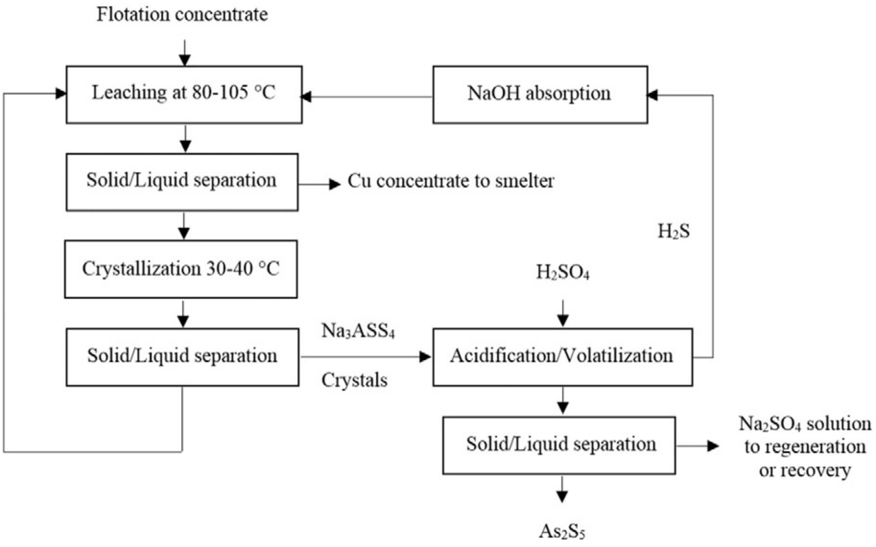

Fig. 6. Flow diagram of Na_2S-leaching process used in Lepanto Mining Company (Nadkarni and Kusik, 1988) (reproduced with permission).

biological generation of H_2S not only improves pH control of the process, but also significantly decreases operating cost. However, safety when using this compound can be of concern and therefore the proper safety precautions must be in effect.

3.2.3. Co-precipitation of arsenic using ferric ions

Neutralization of solutions containing Fe (III) ions leads to the formation of a ferric oxyhydroxide phase known as ferrihydrite (FH). FH as an adsorbent exhibits favourable sorption properties to uptake cations and anions such as AsO_4^{3-} via Eq. (14) (Riveros et al., 2001). This method is the Best Demonstrated Available Technology (BDAT) by the USEPA to treat acidic arsenic-bearing effluent solutions (De Klerk et al., 2012; Demopoulos, 2014).

$$Fe_2(SO_4)_{3(aq)} + 3Ca(OH)_{2(s)} + 2AsO_4{}^{3-}{}_{(aq)} + 4H_2O_{(l)} \rightarrow 2FeOOH \cdot AsO_4{}^{3-}{}_{(s)} + 3CaSO_4 \cdot 2H_2O_{(s)} \tag{14}$$

Robins et al. (1988) proposed that arsenic removal from dilute arsenate-bearing solution, where the concentration of arsenic was <100 mg/L, occurred by the adsorption of pentavalent arsenic through the formation of a bidentate inner sphere complex on extremely fine FH particles (Robins et al., 1988). Furthermore, it was shown that arsenates prevented the FH crystallization and subsequently formed hematite which was a more stable species (Jambor and Dutrizac, 1998). Langmuir et al. (1999) demonstrated that ferric arsenate precipitates began to form at pH 1 during neutralization of arsenate and ferric-bearing solution, where Fe:As molar ratio was between 3–5:1, and ferric arsenate was the dominant arsenic-iron compound at the higher pH (Langmuir et al., 1999, 2006). Several researchers reported that ferric arsenate, a poorly crystalline material, was formed in an acidic solution with high concentration of arsenic. Promising As (V) removal was implemented up to mildly alkaline conditions, while the Fe:As ratio was equal to or >3:1. Lime was typically used as a neutralizing agent for this process.

Aqueous streams obtained from hydrometallurgical and mineral processing facilities can contain sulfate ions which critically influence the stability of the co-precipitation process and the aqueous chemistry including complexation and ion speciation before and after precipitation. It was illustrated that co-existing divalent ions such as calcium, nickel and aluminum ions promoted arsenic stability (Jia and Demopoulos, 2008; De Klerk et al., 2012; Demopoulos, 2014; De Klerk et al., 2015). The presence of aluminum ions noticeably decreases the residual arsenic concentration and they can act as a suitable substitute for ferric ions (Robins et al., 2005; De Klerk et al., 2012). Furthermore, aluminum significantly hinders the recrystallization of amorphous FH ((Fe + Al):As molar ratio > 10:1) through the larger surface area adsorption leading to the stability of arsenic species in the solution (Violante et al., 2009). Aluminum and magnesium form double hydroxide species at a high pH, around 11, providing suitable hosts for arsenic adsorption (Gomez et al., 2013). Sulfate ions in the solution react with calcium ions in the presence of excess lime to generate gypsum which results in the elimination of most of the sulfate from the solution, whereas at low Fe:As molar ratios lime combines with the arsenic remaining in the solution to generate calcium arsenate at a pH of 3–4 instead of an arsenate-FH (Swash and Monhemius, 1995). Formation of arsenical FH precipitates is favoured at a pH ranging from 4 to 7; however, the range is extended to pH 10 in the presence of cations such as Zn (II), Cd (II), Pb (II), Ca (II) and Mg (II). Furthermore, arsenic precipitation is influenced by high concentrations of both sodium chloride and sulfate as presented in Table 8 (Krause and Ettel, 1989). Sulfate ions significantly decrease the effectiveness of arsenic removal because sulfate and bisulfate ions compete with arsenate for active binding sites present in structure of ferrihydrite.

In order to maximize arsenic removal through co-precipitation with ferric ions, arsenic must be in the form of arsenate (Riveros et al., 2001). In addition, pentavalent arsenic shows a higher affinity to ferrihydrite compared to trivalent arsenic; however, arsenite is the arsenic species that is most commonly found in metallurgical operations at ambient temperature. It is therefore advantageous and often required to oxidize As (III) to form As (V).

Iron-arsenic containing minerals present in nature such as tooeleite ($Fe_6(AsO_3)_4SO_4(OH)_4 \cdot 4H_2O$), schwertmannite ($Fe_8O_8(OH)_x(SO_4)_y \cdot nH_2O$ where $8\text{-}x = y$ and $1 \le y \le 1.75$), karibibite ($Fe_2As_4(O,OH)_9$), symplesite ($Fe_3(AsO_4)_2 \cdot 8H_2O$) and schneiderhohnite ($FeFe_3As_5O_{13}$) play a significant role in the immobilization of toxic oxyanions such as As (III) and As (V) (Welham et al., 2000; Sadiq et al., 2002). Tooeleite, a ferric arsenite sulfate hydrate phase, was initially found at the U.S. Mine Gold Hill, in Tooele County, Utah in 1984 (Opio, 2013). The metabolic activity of bacteria such as *Acidithiobacillus ferrooxidans* present in AMD deposits led to the Fe (III) and As (III) removal from the solution and consequently the formation of nanocrystalline tooeleite (Casiot et al., 2003; Duquesne et al., 2003; Morin et al., 2003). Tooeleite has similar characteristics to scorodite and is thus known as the trivalent arsenic form of scorodite. Tooeleite was selected by Nishimura and Robins (2008) as a suitable As(III)-carrier since tooeleite precipitates present in the waste at US Mine Gold Hill have maintained their stability under severe weathering conditions (Nishimura and Robins, 2008). Moreover, tooeleite possesses a high arsenic removal efficiency, a high arsenic content (~25 wt%), and a low Fe:As weight ratio (1.2:1) (Nishimura and Robins, 2008; Opio, 2013). It is also stable in a pH between 2–3.5 and will transform to arsenical-FH above pH 3.5 (Nishimura and Robins, 2008). Tooeleite was synthesized by Opio (2013) using sodium hydroxide and lime as the neutralizing agents at different initial Fe:As molar ratios (1:1, 1.5:1 and 2:1) at 25 °C (Opio, 2013). It was shown that the tooeleite particles were formed at pH ranging from 2 to 4 and were quickly converted to a poorly crystalline ferric arsenite phase at a pH above 4. A series of TCLP stability analysis experiments on tooeleite precipitates, which were synthesized at different conditions, showed a high arsenic release at pH 5. A more crystalline phase with a higher Fe:As molar ratio was formed through a high temperature precipitation of tooeleite at 95 °C (Opio, 2013). Whereas, no obvious improvement was observed in the arsenic removal percentage and stability of tooeleite synthesized at 95 °C. In addition, calcination of the tooeleite at 600 °C resulted in the formation of a highly stable mixture of hematite and ferric arsenate with a TCLP arsenic solubility of 0.5 mg/L (Opio, 2013). The tooeleite precipitates containing gypsum

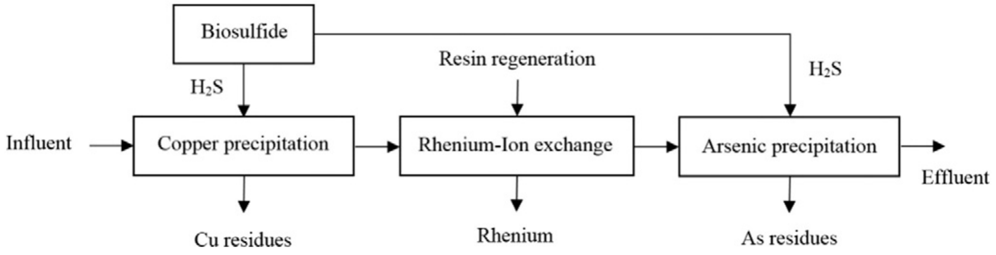

Fig. 7. Flowsheet of arsenic immobilization and copper/rhenium recovery process proposed by BioteQ Environment Technologies (Mohammadi et al., 2014) (reproduced with permission).

Table 8
Impact of SO_4^{2-} and Na^+ ions on Fe (III)/As (V) precipitates at 80 °C and pH 5 (Riveros et al., 2001) (reproduced with permission).

Feed Fe/As molar ratio	Washed precipitate assay (%)			
	Fe	As	SO_4^{2-}	Na^+
1	27.4	26.0	<0.08	2.4
2	32.6	21.0	0.08	1.4
4	40.6	14.0	0.19	0.19
8	47.2	8.0	1.89	0.009
16	49.2	4.2	3.67	0.004
Very high	54.8	<0.09	6.5	0.003

exhibited a higher TCLP arsenic leachability of 13.1 mg/L resulting from the formation of calcium arsenite/arsenate compounds after calcination at 600 °C.

Schwertmannite is a poorly crystalline trivalent iron-oxyhydroxysulfate mineral which is commonly generated in AMD via the oxidation of iron-bearing sulfide minerals in a pH ranging from 2.5 to 4.5 (Bigham et al., 1990, 1994; Yu et al., 1999; Paikaray et al., 2014). Arsenite and arsenate could be adsorbed on the surface of schwertmannite as a result of an anion exchange mechanism for sulfate ions (Carlson et al., 2002; Fukushi et al., 2003; Regenspurg and Peiffer, 2005; Burton et al., 2010). No significant structural disruption is observed after arsenic uptake because arsenic stabilizes schwertmannite and inhibits its transformation to a crystalline goethite phase (Burton et al., 2009, 2010). However, alkaline conditions facilitate the transformation of schwertmannite to goethite (Regenspurg et al., 2004; Schwertmann and Carlson, 2005; Knorr and Blodau, 2007). Raghav et al. (2013) studied the stability of arsenic-containing solids consisting of scorodite, arsenate hydroxyapatites, ferrous arsenates (symplesite-type minerals), tooeleite and schwertmannite (Raghav et al., 2013). Tooeleite precipitates showed a high TCLP arsenic solubility (100 mg/L). In contrast, As-loaded schwertmannite showed the lowest arsenic leachability among the other candidates under both TCLP and a simulated landfill leachate (SLL). However, the magnitude of arsenic dissolution of schwertmannite in SLL (10 mg/L) was dramatically greater than that in TCLP. HoungAloune et al. (2015) reported no change in the mineralogical phase of As-loaded schwertmannite precipitates which were aged for 120 days at a pH range of 3–11 (HoungAloune et al., 2015). The pH of the solution noticeably influenced the arsenic release for As-containing schwertmannite. Despite a negligible amount of arsenic solubility over a pH range of 2–7, arsenic dissolution was observed under highly acidic and alkaline conditions (approximately 90 mg/L As at pH 1 and 12 after a day).

Arsenate-FH residues exhibit a high degree of stability which improves with an increase in the Fe:As molar ratio (Krause and Ettel, 1989; Riveros et al., 2001). The solubility of ferric arsenate is <0.2 mg/L at 25 °C and a pH range of 3–5. In many copper smelter ETPs the arsenite-bearing weak acid stream is treated in two steps: (i) lime neutralization is implemented at a pH of 11–12 in order to generate calcium arsenite precipitates, where the concentration of the residual solution is approximately 100 mg/L; (ii) ferric solution is added at an Fe:As molar ratio > 3:1 and pH 8 to precipitate arsenite-FH; this reduces the arsenic level to <1 mg/L. The combined residues are discharged to a hazardous waste disposal site.

The precipitation of arsenite-FH has been employed by Xstrata's Horne smelter as depicted in Fig. 8 (Godbehere et al., 1995). The Horne smelter can treat higher volumes of arsenic-bearing effluents compared to the other smelters due to the availability of low cost of iron-containing effluents (10–20 g/L Fe) obtained from discontinued nearby mines and the presence of a large tailings facility. Iron-containing waste is oxidized using hydrogen peroxide to produce ferric ions. The ferric ions are added to the weak acid (2–5 g/L of As (III)) and dust leach slurry at an Fe:As molar ratio of approximately 3:1 and pH 4.5 to form a mixture of ferric arsenite and As (III)-FH. The pH of the residual arsenite-bearing solution (<50 mg/L of As (III)) is then increased to pH 9.5 using lime in the presence of Fe (III) to precipitate arsenite compounds with the other base metal hydroxides (Peacey et al., 2010). The precipitates acquired from the arsenic immobilization process are then co-deposited with smelter slag tailings in a tailings facility. The arsenic-containing material that is discharged to the waste disposal site in this case study meets the governing regulations (by the province of Quebec, Canada) as the arsenic level is below 1 mg/L. Opio (2013) carried out synchrotron-based analysis to characterize the arsenic-containing precipitates. The residues primarily contained a mixture of gypsum and amorphous ferric arsenate which were responsible for 49–84% of total arsenic. The high level of arsenate was due to the oxidation of As (III) to As (V) by means of Fe (III) and consequently formation of a ferrous arsenate phase which was stable at pH 9 (Opio, 2013). Ferrous arsenate in the form of symplesite has a very low arsenic solubility (Raghav et al., 2013).

A uranium mill located in northern Saskatchewan, Canada uses a similar method to fix arsenic in its waste solution (Demopoulos, 2014). The respective concentration of arsenite and arsenate in the solution is dependent on the amount and type of oxidant used. The arsenic-containing solution is neutralized using lime to pH 4 at an Fe:As molar ratio of 2.3 to precipitate 99% of arsenic species. The pH of the residual solution is then increased to 7.5 in order to precipitate the remaining iron and base metals as hydroxides before discharging the stream to a tailings facility. Saskatchewan regulations require frequent sampling of the tailings pond water to ensure that the arsenic level is maintained below 2 mg/L. A recent study illustrated that the precipitate was mostly transformed to arsenate over four years of storage under anoxic conditions at pH 7–8, which was in compliance with the findings reported by Opio (2013).

Boliden metal company in western Finland uses the ferric arsenate precipitation process to immobilize arsenic-bearing effluents (Salokannel et al., 2013). Arsenic mobilization for this company is a result of smelting arsenic-containing concentrates (Copper and nickel) at the Boliden Harjavalta plant. Copper cathodes, gold and silver are produced as the main products and sulfuric acid is made as a by-product. In the process of sulfuric acid production there are two condensate streams which contain arsenic with a concentration of 600 mg/L and 1.5 w/w% of sulfuric acid. The two condensate effluents are collected in a condensate pump tank to homogenize the feed. Thereafter, the effluent is pumped into the precipitation reactors in which precipitation and neutralization occur (Fig. 9). The solution pH in the first two reactors is adjusted at 4–4.5 using an automatically controlled lime slurry feed. Ferrous sulfate at an Fe:As molar ratio of 4:1 is added to the first two reactors while compressed air is bubbled through the solution to oxidize Fe (II) and As (III). In the third reactor the pH is increased to 8 in order to stabilize ferric arsenate and precipitate other impurities as metal hydroxides. The neutralized stream is sent to the gypsum slurry tank and a portion of the slurry is pumped back to the first reactor for the purpose of seeding the reaction. The seeding process highly improves the settling properties of the solids. The liquid obtained from the gypsum tank, where the arsenic level is <1 mg/L, is pumped to an effluent treatment plant before being released into the environment.

Immense quantities of sludge are generated through the formation of arsenical ferrihydrite which is difficult to filter due to its poorly crystalline structure. However, a fraction of the sludge is recycled to a process using a high density sludge (HDS) system to reduce the volume of sludge. Ferrihydrite requires a high consumption of iron and neutralizing agents. The ferrihydrite phase will undergo chemical and physical changes over time and transform to alpha-goethite (α-FeOOH), consequently releasing arsenic to the environment (Filippou and Demopoulos, 1997). In addition, there is a potential for arsenate to reduce to arsenite, and ferric iron to reduce to ferrous iron due to the biochemical activities (Smedley and Kinniburgh, 2002; Twidwell and McCloskey, 2011).

3.2.4. Scorodite precipitation

Scorodite, a crystalline ferric arsenate, is a naturally occurring secondary supergene mineral with the chemical formula of $FeAsO_4 \cdot 2H_2O$.

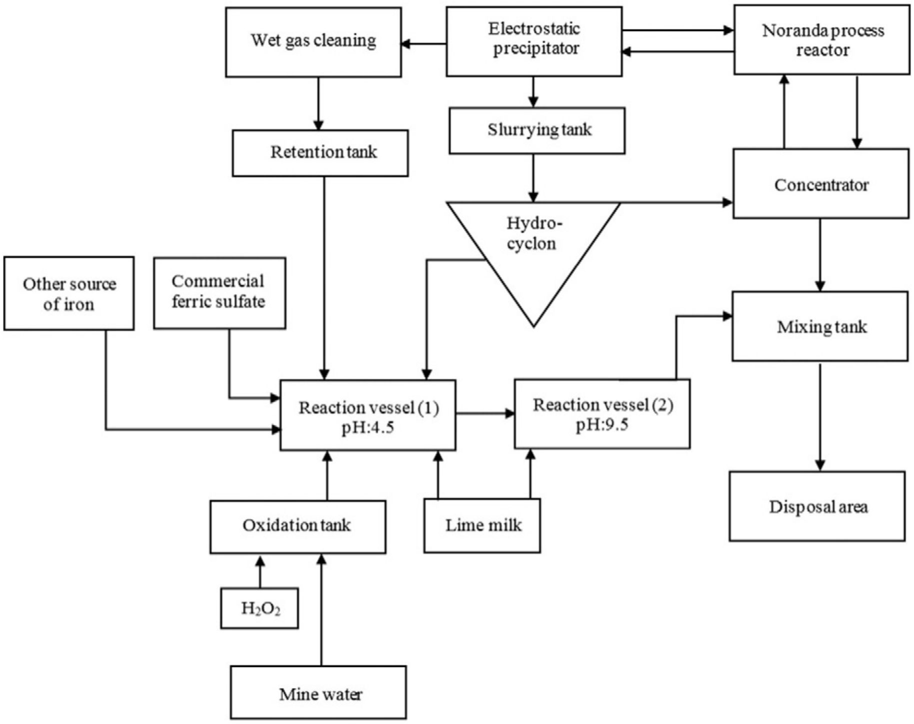

Fig. 8. Flow diagram for arsenic fixation implemented by Xstrata's Horne smelter (Godbehere et al., 1995) (reproduced with permission).

It is frequently associated with arsenic-bearing primary minerals such as arsenopyrite (Flemming et al., 2005; Salzsauler et al., 2005; Corkhill and Vaughan, 2009) and enargite (Lattanzi et al., 2008). The weathering of primary minerals, including chemical and biological oxidation mechanisms, aids in incongruent dissolution of arsenate and ferric ions and consequently scorodite formation (Dove and Rimstidt, 1985). Naturally occurring scorodite contains 30 wt% As and has an Fe:As molar ratio of 1:1. There is currently a large focus on the scorodite as a means of immobilization and disposal of arsenic due to the mineral's low arsenic solubility, high arsenic removal efficiency, high arsenic content (25–30 wt%), low iron requirements (Fe:As molar ratio = 1–1.5:1) and a relatively high stability and compactness in acidic to neutral conditions (Riveros et al., 2001; Paktunc and Bruggeman, 2010). Furthermore, scorodite demonstrates suitable settling and filtration properties in the light of its crystalline structure (Filippou and Demopoulos, 1997).

Scorodite is stable under oxidizing conditions in the pH range of 2.8–5.3 (Riveros et al., 2001). It was shown that scorodite has a very low USEPA TCLP solubility (<5 mg/L As) (Swash and Monhemius, 1995; Filippou and Demopoulos, 1997). The long term stability of scorodite is of major concern as arsenic dissolves at pH > 5 to form 2-line ferrihydrite which results in arsenic discharge to the environment (Krause and Ettel, 1989; Welham et al., 2000; Bluteau and Demopoulos, 2007). Scorodite decomposes under either anoxic conditions or in the presence of reducing bacteria (Papassiopi et al., 2003; Verdugo et al., 2012). Fe (III) and As (V) are reduced in the presence of sulfides. Storing ferric arsenic residue under water is a high risk design because environments

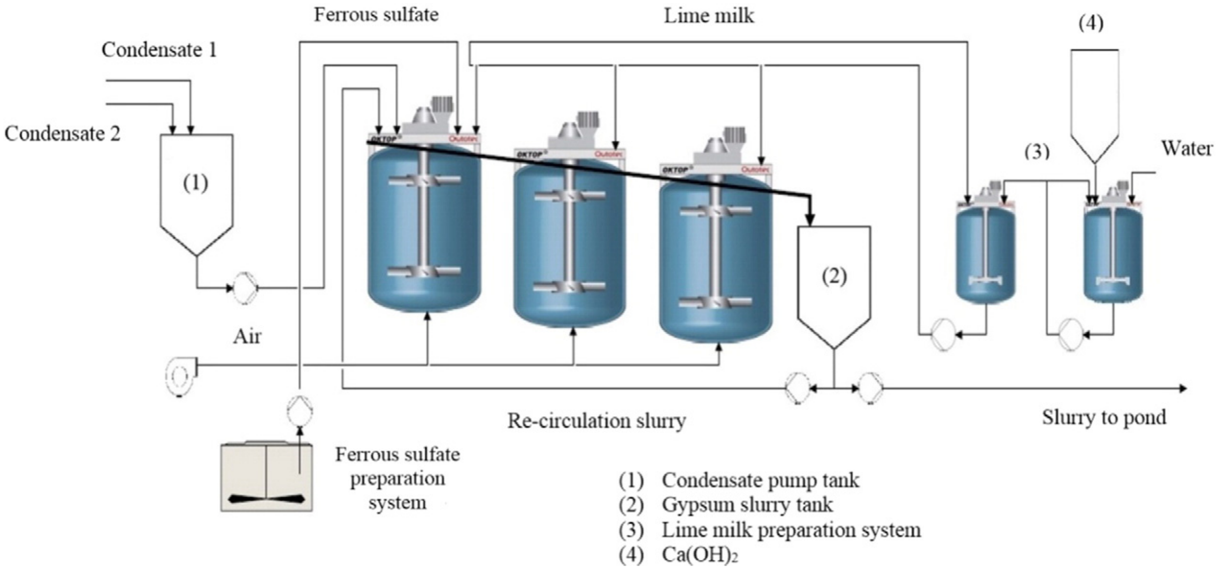

Fig. 9. Flow sheet of ferric arsenate process to remove arsenic conducted at Boliden Harjavalta plant (Salokannel et al., 2013) (reproduced with permission).

become anaerobic after a depth of two meters, thereby increasing the activity of sulfides (Rochette et al., 1998; Welham et al., 2000). Two other phases of ferric arsenate, in addition to scorodite, were identified as Type I ($Fe_2(HAsO_4)_3 \cdot xH_2O$, $x < 4$) and Type II ($Fe_4(AsO_4)_3(OH)_x(SO_4)_y$, $x + 2y = 3$) (Table 9). Type I does not pass the TCLP test (Monhemius and Swash, 1999). Several parameters such as the source of arsenic, the amount of arsenic in solution, the medium characterization (sulfate, nitrate and chloride) and initial iron concentration significantly impact the nature of ferric arsenate precipitates.

Several research groups have extensively focussed on scorodite formation using various approaches and mechanisms; however, each technique has advantages and disadvantages. In this section various methods proposed by researchers to form scorodite are elucidated and industrial practises employing scorodite to stabilize arsenic will be discussed.

High temperature pressure oxidation (HTPO) is a technique in which the temperature and oxygen pressure are 150–230 °C and 2000 kPa, respectively. Ferric sulfate is added to the solution containing As (III) in an autoclave to form crystalline ferric arsenate precipitates (Dutrizac and Jambor, 1988; Demopoulos et al., 1995; Monhemius and Swash, 1999). HTPO is most often conducted to pretreat gold refractory ore. This liberates gold which is initially locked in the ore structure and immobilizes pentavalent arsenic as scorodite precipitates which stay stable even after cyanidation at pH > 10. The reactions involved in HTPO are depicted in Eqs. (15)–(18) (Papangelakis and Demopoulos, 1990; Robins and Jayaweera, 1992; Swash and Monhemius, 1994). It is evident that arsenic acid and ferrous sulfate are produced during arsenopyrite oxidation (Eq. (15)). However, Eq. (16) which frequently takes place at a temperature between 110 °C–150 °C, results in the formation of elemental sulfur. Arsenic is fixed as scorodite via Eq. (18) and is then deposited in a lined tailings pond.

$$4FeAsS_{(s)} + 13O_{2(aq)} + 6H_2O_{(l)} \rightarrow 4H_3AsO_{4(aq)} + 4FeSO_{4(aq)} \tag{15}$$

$$4FeAsS_{(s)} + 7O_{2(aq)} + 4H_2SO_{4(aq)} + 2H_2O_{(l)} \rightarrow 4H_3AsO_{4(aq)} + 4FeSO_{4(aq)} + 4S^{\circ}_{(s)} \tag{16}$$

$$4FeSO_{4(aq)} + O_{2(aq)} + 2H_2SO_{4(aq)} \rightarrow 2Fe_2(SO_4)_{3(aq)} + 2H_2O_{(l)} \tag{17}$$

$$Fe_2(SO_4)_{3(aq)} + 2H_3AsO_{4(aq)} + 4H_2O_{(l)} \rightarrow 2FeAsO_4 \cdot 2H_2O_{(s)} + 3H_2SO_{4(aq)} \tag{18}$$

Capital cost is the main drawback associated with this method due to the use of autoclaves to produce synthetic scorodite. The process becomes economically viable if arsenic stabilization is performed in tandem with the processing of valuable concentrates such as gold and silver-bearing pyrite (Filippou and Demopoulos, 1997; Singhania et al., 2005). Codelco process has implemented HTPO at pilot scale to immobilize As (III)-bearing weak acid at an Fe:As molar ratio between 1.6–3.6:1 and at a temperature of 220 °C. Pyrite and low-grade chalcopyrite concentrates supply the iron requirements.

Table 9
Various iron and calcium arsenate species and TCLP solubility (Swash and Monhemius, 1995; Monhemius and Swash, 1999) (reproduced with permission).

Compound	TCLP solubility (As in mg/L)
Scorodite	<5
Type I	5–85
Type II	<5
FH (Fe:As = 9:1)	<0.5
FH (Fe:As = 2.3:1)	1–2
Haidingerite	>3000
Pharmacolite	>3000
Guerinite	>1000
Weilite	>2000

Outotec has recently patented a process to immobilize As (V) as scorodite in two steps (Ruonala et al., 2010, 2014): (i) atmospheric precipitation of amorphous ferric arsenate via simultaneous oxidation of the solution (Fig. 10); (ii) autoclave treatment (160 °C–180 °C) of the precipitates after solid/liquid separation to produce scorodite. The pH of solution is set in the range of 1.5–4. Amorphous ferric arsenate is highly filterable once the Fe-As mole ratio is fixed between 1–1.5:1. A small autoclave is required for this process and only the precipitates are treated rather than the entire solution.

An alternative technique to form scorodite from arsenic-rich solutions at ambient-pressure was developed by researchers at McGill University, Canada (Filippou and Demopoulos, 1997). Scorodite was produced at 90 °C from a solution where the concentration of arsenate and ferric ions were 19 g/L and 7.2 g/L, respectively. The pH was adjusted to below 0.9 in order to initiate amorphous ferric arsenate. Chemical crystallization was carried out through a slow stepwise neutralization and the addition of either scorodite seed (hydrothermally produced parent seed) or foreign seeds (gypsum crystal). Prior to this work, most of studies were focused on the rapid neutralization of the As-bearing solution to pH above 4 (Filippou and Demopoulos, 1997). This leads to a sharp rise in the arsenic and iron supersaturation in the solution and an increase of generation of small solid-phase nuclei resulting in the formation of amorphous ferric arsenic precipitates. It was shown that scorodite could be formed in the presence of arsenite and ferrous ions when they are oxidized with hydrogen peroxide or pure oxygen to produce arsenate and ferric ions (Fig. 11). This process incurs a relatively lower capital cost and high degree of versatility compared to HTPO. The efficiency and effectiveness is independent from the size of the process and can therefore be employed to treat both small and large amounts of arsenic-containing effluents.

Becze and Demopoulos (2007) were the first to suggest the formation of less soluble hydrated basic calcium ferric arsenate phase such as yukonite ($Ca_2Fe_3(AsO_4)(OH) \cdot 12H_2O$) as a result of a partial transformation of the scorodite and As (V)-Fe (III) co-precipitate in the presence of gypsum at pH > 7 (Becze and Demopoulos, 2007; Gomez et al., 2010). Yukonite was first identified in Tagish Lake, Yukon, Canada in 1913 (Tyrrell and Graham, 1913; Gomez et al., 2010). Poorly crystalline ferric arsenate co-precipitates with an Fe:As molar ratio of 2:1 were synthesized by Jia and Demopoulos (2008) via lime neutralization at pH 8 and 22 °C. It was illustrated that the ferric arsenate residues transformed to yukonite at 75 °C after seven weeks. Bluteau et al. (2009) reported that scorodite produced by a hydrothermal method partially converted to yukonite in a gypsum-saturated solution at 75 °C and pH of 7 and 9. Yukonite was synthesized by the neutralization of a solution with a Ca:Fe:As molar ratio of 0.5:0.75:1 followed by ageing at 95 °C for 24 h (Becze et al., 2010; Bohan, 2014). Data obtained from chemical composition analysis and X-ray powder diffraction (XRD) of synthetic yukonite were in accordance with those of natural yukonite (Gomez et al., 2010; Bohan, 2014). A series of stability experiments on a synthetic yukonite showed a low arsenic solubility (3.1–11.9 mg/L As at pH 7), particularly in the case of a gypsum-saturated solution (0.6–0.9 mg/L As at pH 7) under oxidizing conditions over pH range of 5–8 (Bohan, 2014; Bohan et al., 2014). Yukonite, however, was noticeably unstable in the presence of CO_2 and under strongly reducing conditions which consequently led to arsenic release into the environment.

Ecometales, a subsidiary of Codelco, launched a commercial operation of scorodite plant in northern Chile in 2012 which stabilizes 10,000 t of arsenic annually and recovers over 25,000 t of copper annum (Lagno et al., 2009; Demopoulos, 2014). This plant was built in order to treat approximately 70,000 t/year flu dust produced by Codelco's Chuquicamata, Potrerillos and Ventanas copper smelters. Smelter dust consists of a variety of chemical elements depending on the operating conditions, the stage of the process, the equipment used and the characteristics of raw materials. The elements which can be found in this operation includes: copper, iron, zinc, bismuth, antimony, arsenic and lead. Two processes are now being conducted at the

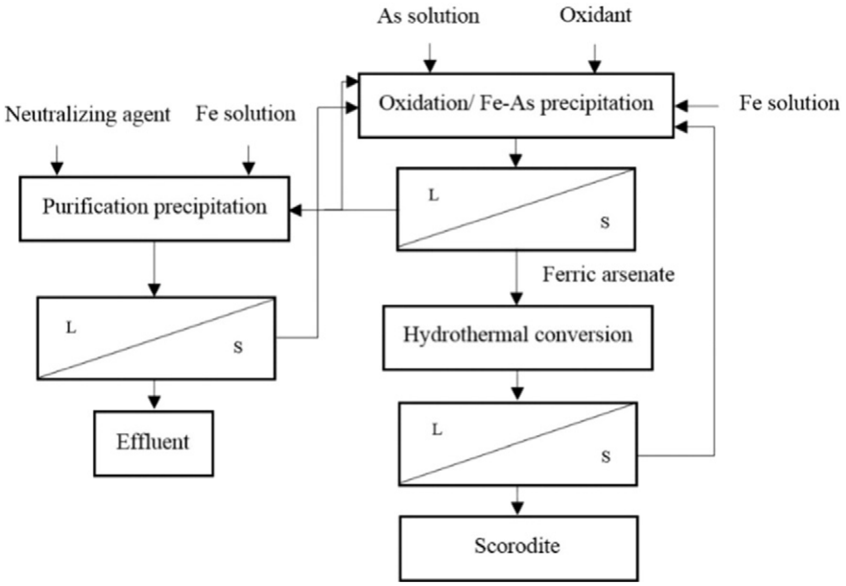

Fig. 10. The Outotec scorodite process flowsheet (Ruonala et al., 2014) (reproduced with permission).

Ecometales plant: (i) leaching and recovery of copper; (ii) arsenic and antimony abatement (AAA) (Fig. 12). The arsenic-containing dust is leached with sulfuric acid and water to generate a copper-rich pregnant leach solution (PLS). The PLS is then oxidized using hydrogen peroxide to form pentavalent arsenic in the solution. The pH is adjusted by lime addition to the required pH value and then ferric sulfate is added to the solution at a temperature of 80–85 °C to form scorodite. This scorodite process is based on the supersaturation control. Ferric sulfate is produced by the plant from magnetite and sulfuric acid which reduce the operating costs. The resulting precipitates which contain scorodite and gypsum are sent to the authorized Ecometales disposal site. The arsenic-free leach solution is directed to the solvent extraction-electrowinning operation at the Chuquicamata operations for copper recovery.

The other industrial atmospheric scorodite plant is the Dowa scorodite plant in the copper smelter site located in Kosaka, Japan (Abumiya et al., 2012). This plant fixes 30 t/month of arsenic as scorodite. Trivalent arsenic is initially oxidized to arsenate using hydrogen peroxide. Scorodite precipitation is then carried out through oxidation of a $FeSO_4$/As (V) solution at 95 °C. The process diagram is illustrated in Fig. 13.

Scorodite can be synthetically produced via microorganism activity. Naturally occurring microorganisms account for arsenic speciation and mobility via biogeochemical arsenic reactions (Duquesne et al., 2003; Inskeep et al., 2004; Stolz et al., 2006; Wang and Mulligan, 2006). The activity of Fe (II) oxidizing microbes results in the biomineralization of Fe (III) minerals such as Fe (III) oxyhydroxide, schwertmannite, jarosite and goethite. Biomineralization plays a significant role in natural arsenic immobilization processes (Acero et al., 2006; Hohmann et al., 2009). Thermophilic microorganisms use oxygen from the air as the electron acceptor to oxidize ferrous ions to ferric ions at a temperature between 70–80 °C (Segerer et al., 1986; Plumb et al., 2007). Several research groups have systematically performed a series of experiments to fix arsenic with a concentration of <3 g/L as bioscorodite using microbial species illustrated in Table 10. The bioscorodite precipitation process proposed by González Contreras et al. (2009) is similar to Dowa's process in terms of the oxidation of ferrous iron in the presence of pentavalent arsenic; although, they are unique in terms of the oxidation mechanisms involved in their respective process (González Contreras et al., 2009, 2010). The bioscorodite crystallization process is based on the saturation of a solution which is controlled by the biological oxidation rate (Gonzalez Contreras, 2014). The biological oxidation rate which is dependent on the type of microorganism, metal concentration, oxygen supply and operational conditions such as solution pH and

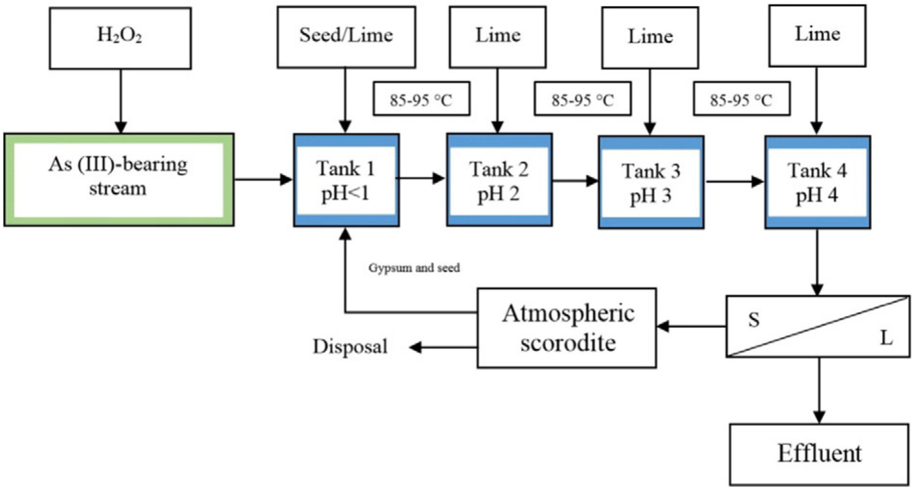

Fig. 11. Atmospheric scorodite precipitation system.

temperature (Gonzalez Contreras, 2014). It was found that the dosage of ferrous ions must be controlled because an Fe (II):As (V) molar ratio of 5:1 led to the prolongation of the bioscorodite precipitation time which resulted from the formation of a high concentration of ferric ions via the biological oxidation (González Contreras et al., 2009). In addition, Gonzalez-Contreras et al. (2012a, b) reported that arsenic removal by scorodite particles decreased from 99% to 40% at an Fe (II):As(V) molar ratio between 2–5:1. The presence of foreign seed, such as gypsum, did not expedite the kinetics of bioscorodite crystallization; however, a greater degree of arsenic removal was observed due to the formation of amorphous scorodite precipitates (González Contreras et al., 2009). Bioscorodite precipitates were synthesized in a continuously stirred reactor (CSTR) where the initial concentration of arsenate and ferrous ions were 2.8 g/L and 2.4 g/L, respectively (González-Contreras et al., 2012a). 3.2 g of the bioscorodite precipitate contained 1 g arsenic. TCLP experiments on the produced scorodite precipitates led to an arsenic release of 0.4 mg/L after 100 days. It was also shown that the ageing time and bioscorodite crystallization rate had a significant effect on the TCLP results (González-Contreras, 2012). An airlift reactor was employed by Gonzalez-Contreras et al. (2012a, b) to improve a continuous bioscorodite process; airlift reactors have several advantages such as a mixing via aeration, a lower shear rate and the presence of oxygen and carbon dioxide for biological oxidation and growth (González-Contreras et al., 2012b; Gonzalez Contreras, 2014). It was reported that biologically induced-crystallization demonstrated promising results in comparison with chemical crystallization processes (González-Contreras et al., 2010; Gonzalez Contreras, 2014). The chemical composition, colour and structural characterization of bioscorodite are similar to those of the naturally-occurring mineral. Furthermore, seed material and a strong chemical oxidant are not required to scorodite precipitation. The agglomeration of scorodite precipitates and the formation of flakey precipitates facilitate efficient solid-liquid separation (González-Contreras et al., 2012a). In addition, only a limited amount of neutralizing reagent, such as lime, is required which minimizes the formation of gypsum. Okibe et al. (2015) showed that the presence of cupric ions significantly hindered the biooxidation of trivalent arsenic and ferrous ions, and consequently the formation of biogenic scorodite (Okibe et al., 2015). Whereas, the addition of crystalline scorodite particles reduced the negative effect of cupric ions.

ARSENOTEQ™ is a process to fix arsenic via the biological formation of very stable, crystalline and compact scorodite using airlift reactor (González-Contreras, 2012). As shown in Fig. 14, trivalent arsenic is initially oxidized by H_2O_2 prior to be pumped to the reactor. Ferrous ions are biologically oxidized in the presence of air at ambient pressure at pH 1.2 and 70 °C. The Fe:As mole ratio is set at 1.5.

3.2.5. Encapsulation technology

Encapsulation is a method in which heavy metal/metalloid-bearing pollutants in the form of either small particles or large blocks are isolated within an inert compound with a high structural integrity. This minimizes the surface area of hazardous waste exposed to a leaching solution and subsequently the dissolution of toxic materials. The encapsulation technique is completed through chemical interaction (cement-based, lime-based and phosphate-based processes), physical interaction (non-chemical encapsulation) and thermal interaction (vitrification and thermoplastic polymer encapsulation) between the waste and solidifying reagents (Conner and Hoeffner, 1998).

In Dundee Sustainable Technology, As (III) is initially oxidized to As (V) using a natural oxidizer such as manganese dioxide at a temperature ranging from 50 °C to 100 °C (Fig. 15) (Lemieux et al., 2014; Lalancette et al., 2015). The source of manganese dioxide is pyrolusite, a low-cost mineral, which is composed of 40 to 80% of manganese dioxide. Calcium hydroxide is then added to the solution to generate the calcium arsenate which is not volatile at the melting temperature of glass (Eq. (19)). Recycled glass or glass-forming components such as silica, sodium carbonate, sodium oxide, calcium oxide, alumina and feldspar of potassium are then introduced to the calcium arsenate residues and the mixture is heated to a temperature between 1000 °C and 1200 °C. Vitrified arsenic oxide is in the form of a very stable and insoluble glass containing 1–20 wt% of arsenic. It is claimed that the arsenic concentration from vitrified arsenic oxide after the leaching test is well below the environmental regulations; however, unfortunately no data is available regarding the As-containing product stability in TCLP test.

$$As_2O_{3(s)} + 3CaOH_{2(s)} + 2MnO_{2(s)} \rightarrow Ca_3(AsO_4)_{2(s)} + 3H_2O_{(l)} + 2MnO_{(s)} \quad (19)$$

As previously stated in Section 3.2.4, crystalline scorodite is not stable under strongly reducing and alkaline conditions. A novel stabilization process for scorodite was recently developed which focuses on the controlled precipitation of aluminum and apatite coatings (Lagno et al., 2010; Rocha et al., 2012). Lagno et al. (2010) reported that a crystalline hydrated aluminum phosphate shell ($AlPO_4 \cdot 1.5H_2O$) formed a matrix around scorodite particles present in an acidic sulfate solution. It was also demonstrated that arsenic dissolution was significantly reduced by more than one order of magnitude in a wide range of disposal conditions with this technology. Encapsulation of the scorodite particles through deposition of HAP and FAP was investigated by Katsarou (2012). HAP- and FAP-coated systems resulted in 1 mg/L and 7.7 mg/L of arsenic release in an anoxic environment at pH 9 for 40 days, respectively; however, the amount of dissolved arsenic for uncoated scorodite was 22 mg/L. Aluminum phosphate and apatite coatings were not

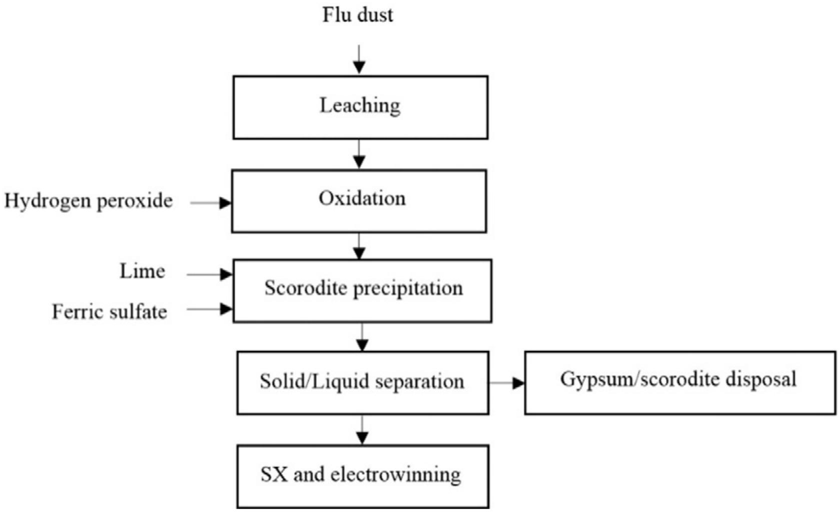

Fig. 12. Flow diagram for stabilization of pentavalent arsenic as scorodite used by Ecometales.

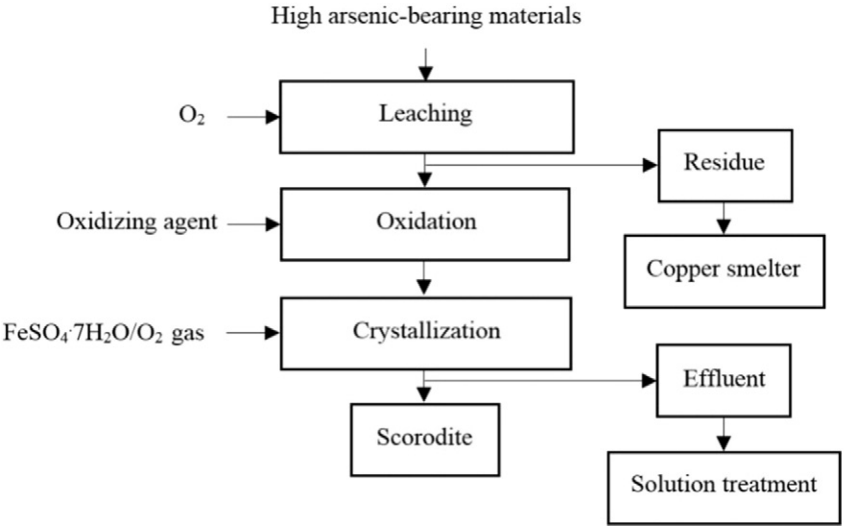

Fig. 13. The Dowa scorodite process flowsheet (Kubo et al., 2010; Abumiya et al., 2012) (reproduced with permission).

mechanically or chemically robust enough to keep arsenic from releasing into an anoxic environment (Katsarou, 2012; Demopoulos, 2014). Silica gel as an encapsulant was synthesized via a reverse titration technique to improve the stability of scorodite particles (Adelman et al., 2015). In spite of using various ageing methods, a high arsenic release was observed for a scorogel system resulting from an anion exchange mechanism (Si-O ↔ As-O) occurring near the surface of scorodite particles. However, a hydrothermally treated scorogel with an As:Si molar ratio of 100:1 discharged less arsenic back into the solution compared to that of scorodite particles due to the formation of a resistant iron-silicate layer around the scorodite particles. Encapsulation of the scorodite precipitates with an amorphous aluminum hydroxyl gel derived from chloride and sulfate salts was carried out by Leetmaa et al. (2016). It was shown that the $Al(SO_4)_{1.5}$-derived gel was a promising encapsulating material, as 0.2 mg/L of arsenic was released at pH 7.3 after 169 days. In addition, a three year-coating stability test demonstrated that the sulfate gel was very robust over a long period of time under an oxidizing environment.

3.3. Pyrometallurgical processes

Arsenic-fix roasting (AFR) is a pyrometallurgical technique in which arsenic and sulfur are captured by a fixing agent such as calcium, sodium and ferrous salts to form stable compounds (Agar, 1991; Hannaford, 1992; Taylor and Yin, 1993; Safarzadeh et al., 2014c; Taylor and Putra, 2014). Haver and Wong (1972) and Bartlett and Haung (1973) were the first to propose the AFR process in order to treat copper sulfide concentrates (Haver and Wong, 1972; Bartlett and Haung, 1973). AFR was applied to the refractory gold concentrates in the early 1990s by Taylor and co-workers to remove sulfur and arsenic as calcium sulfate and arsenate (Taylor et al., 1991; Taylor and Yin, 1993). Arsenic trisulfide gases are rapidly oxidized by calcium oxide (CaO) (Eq. (20)). Trivalent arsenic then reacts with CaO in absence of oxygen to form a calcium arsenite compound (Eq. (21)) (Igiehon et al., 1994a).

$$As_2S_{3(s)} + 3CaO_{(s)} \rightarrow 1/2As_4O_{6(g)} + 3CaS_{(s)} \tag{20}$$

$$1/2As_4O_{6(g)} + 3CaO_{(s)} \rightarrow Ca_3(AsO_3)_{2(s)} \tag{21}$$

Obstacles associated with the AFR process to pretreat the arsenic-containing refractory gold ores and concentrates with a high sulfur content are as follows: (i) a large amount of fixing agent (CaO) is required to immobilize sulfur which forms a substantial volume of calcium sulfate resulting in a decrease in the gold grade in the feed to cyanidation circuit; (ii) the amount of calcium sulfate increases on the surface of reactors and pipelines; (iii) the sulfur cannot be recovered as a by-product and consequently produces a secondary solid waste; (iv) it is very difficult to eliminate calcium arsenate present in the solid calcine (Liu et al., 2000). Liu et al. (2000) described a two-stage roast to selectively fix arsenic present in a refractory gold concentrate and generate sulfuric acid as a by-product from the sulfur dioxide fumes (Liu et al., 2000). As illustrated in Eq. (22), trivalent arsenic is immobilized in the form of calcium arsenate in the presence of hydrated CaO and oxygen.

$$As_2O_{3(g)} + 3CaO_{(s)} + O_{2(g)} \rightarrow Ca_3(AsO_4)_{2(s)} \tag{22}$$

Adham and Harris (2014) suggested a two-step roasting method to immobilize arsenic from roaster off-gas (Adham and Harris, 2014). In the first stage arsenic, predominantly in the form of sulfide species, is volatilized via a neutral roasting process (Fig. 16). Arsenic is then

Table 10
Synthesis of the crystalline bioscorodite precipitates in the different experimental conditions reported by researchers.

Bacteria	Forms of As/Fe	Fe/As mole ratio	pH	Pressure	T (°C)	Reference
Acidianus sulfidivorans	Fe(II) As(V)	1, 1.1	0.8,1	Ambient	80	(González Contreras et al., 2009; González-Contreras et al., 2010)
Acidianus sulfidivorans	Fe(II) As(V)	1, 1.3	1.2	Ambient	72	(González-Contreras et al., 2012a; González-Contreras et al., 2012b)
Acidianus brierleyi	Fe(II) As(III)	1.3–1.4	1.5	Ambient	70	(Okibe et al., 2013; Okibe et al., 2014; Okibe et al., 2015)

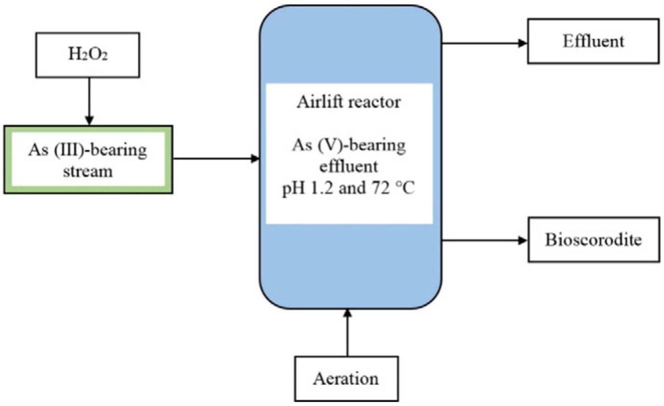

Fig. 14. Scheme for bioscorodite formation system.

immobilized as a ferric arsenate compound in the presence of air and hematite at 750 °C.

4. Conclusions

This paper has reviewed the recent developments and future research trends for arsenic immobilization and industrial processes employed for arsenic elimination. As-containing ore is increasingly becoming a key source of producing base metals. Hence, mining operations should inevitably build As immobilization plants in the near future due to the strict environmental regulations on arsenic release. As (III) oxidation is frequently in conjunction with the arsenic fixation processes. Currently hydrogen peroxide is a promising reagent for As (III) oxidation. However, it is expected that some novel methods such as activated carbon-assisted As oxidation process, which are less costly compared to the traditional oxidation technique, will be conducted in order to oxidize trivalent arsenic.

Lime neutralization is a low-cost technique for arsenic fixation and is mostly implemented in a dry area such as Codelco's Chuquicamata and Caletones smelters where the contamination of groundwater is implausible. Whereas, calcium arsenite and calcium arsenate precipitates exhibit a high solubility in the presence of carbon dioxide and moisture and convert to calcium carbonate which leads to the arsenic release into the environment. Different types of As-bearing FAP and HAP compounds were synthesized to improve the resistance of As-Ca residues to transformation to calcium carbonate. At Saganoseki copper smelter, arsenic (III) is immobilized as arsenic trisulfide containing 60% As. However, arsenic trisulfide precipitate is susceptible to atmospheric and bacterial oxidation. Sulfide precipitation process is more costly compared to lime neutralization technique due to the high cost of NaHS. Sulfidization process using hydrogen sulfide gas was developed by BioteQ Environment Technologies at the batch scale to improve pH control of the process and noticeably reduce operating cost. The co-precipitation of arsenic using ferric ions with an Fe:As molar ratio above 3:1 is the best practice known to date for arsenic immobilization. Large volumes of poorly crystalline As-FH with a low filterability are formed. In addition, As-FH precipitates transform to α-FeOOH over time which consequently release arsenic into the environment. This process has been practised by Xstrata's Horne smelter due to the availability of both low cost iron-bearing waste and a large tailing facility. It was illustrated that the trivalent arsenic present in residue was oxidized by Fe (III) and subsequently ferrous arsenate phase in the form of symplesite was produced. Scorodite precipitation process with a low Fe:As molar ratio (1.5:1) is selected, as iron source is either not readily available or costly for a plant. Arsenic present in the valuable concentrates such as gold-bearing pyrite is usually immobilized in the form of scorodite using HTPO process. Outotec developed a process in which the amorphous ferric arsenate precipitates convert to crystalline scorodite particles using an autoclave. Ecometales in Chile and Dowa scorodite plant in Japan use the atmospheric scorodite precipitation process to fix arsenic. The ARSENOTEQ™ process attempts to biologically synthesize crystalline scorodite precipitates which are similar to naturally-occurring scorodite in terms of chemical composition and structural properties.

Recent developments for As immobilization have focused on the encapsulation of As-bearing precipitates as a double-guarantee to increase the stability of As-bearing residues. Dundee Sustainable Technology proposed a technique to vitrify arsenic oxide in the form of a stable glass at high temperature. Moreover, the encapsulation of scorodite particles using deposition of aluminum phosphate and apatite coatings significantly diminishes arsenic dissolution. Different research groups synthesized novel As (III)-containing compounds to improve the TCLP results. Schwertmannite as an As (III) carrier demonstrates very low TCLP compared to those of scorodite, arsenate hydroxyapatites, ferrous arsenates (symplesite-type minerals and tooeleite). However, arsenic solubility of schwertmannite is greater in highly acidic and alkaline conditions.

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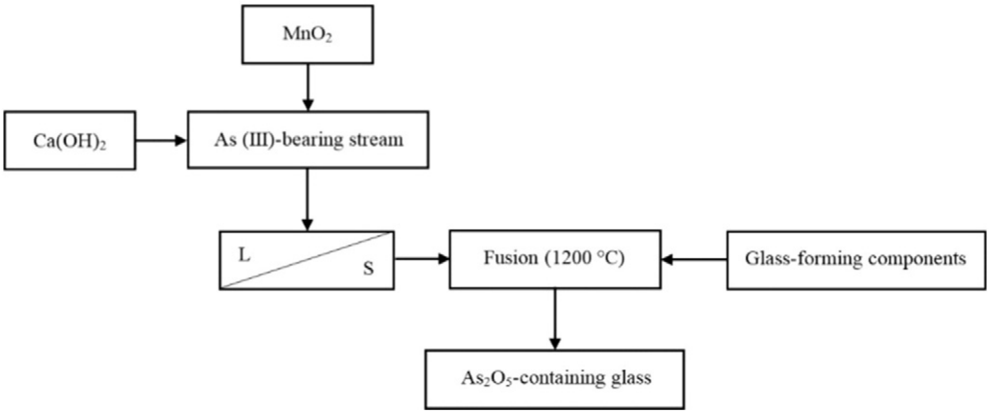

Fig. 15. Flowsheet of arsenic encapsulation technique proposed by Dundee Sustainable Technology.

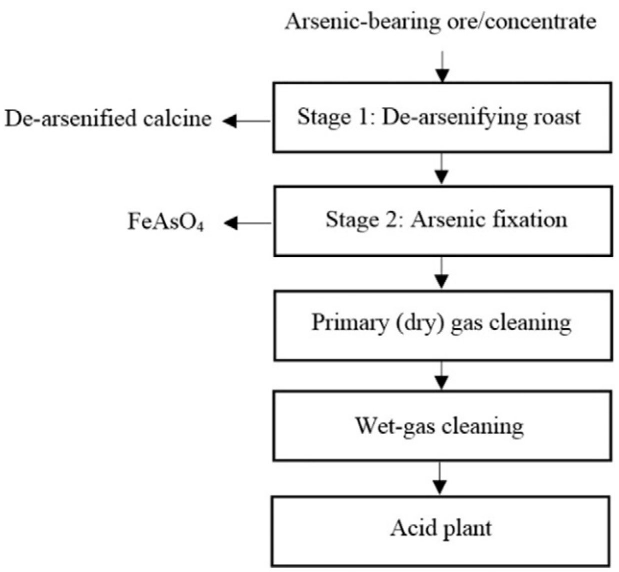

Fig. 16. Two-stage roasting process to immobilize trivalent arsenic (Adham and Harris, 2014) (reproduced with permission).

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