Assessment of Scorodite Precipitation from Mine Waters

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Abstract

Arsenic release from mine waters is often predicted to be limited by precipitation of scorodite ($FeAsO_4.2H_2O$). Although scorodite is often cited as the most stable form of arsenic in supergene environments its actual stability field in terms of redox potential and pH is highly limited and is sensitive to variations in trace element chemistry, redox potential, temperature and pH.

Several schemes have been developed to precipitate scorodite with the key features being oxidizing solution of ferrous iron reacting with high concentrations of arsenic (V). Limitations on the reaction in producing scorodite have been identified and include the presence of competing elements such as copper, zinc, barium, sodium, sulfate and chloride, all of which are common in mine waters. In this study, the precipitation of scorodite was assessed on a natural mildly acidic to neutral pH mine water with a high concentration of arsenic (20 mg/L). The reactions were carried out over a pH range of pH values from pH 2.5 to the natural pH of the mine water at pH 6. The mine water was acidified by ferrous sulfate, sulfuric acid and CO_2 injection to mimic components typical of the mine water environment.

The results were that in all tests below a temperature of 80ºC and in all tests where pH was greater than 3, no scorodite phase was produced as determined by X-Ray Diffraction (XRD). In all these tests a ferric hydroxide, ferric arsenate and/or ferric arsenate-sulfate was precipitated that showed variable solubility in a leach test. Where agitation and oxygen were introduced, at low pH (<3) then scorodite crystals up to 50 μm.

In tests at the natural pH of the mine water where natural air was used to agitate, the addition of ferrous sulfate produced Ferrihydrite ($Fe^{3+}_{10}O_{14}(OH)_2$), amorphous ferric arsenate-sulfate, Olivenite ($Cu_2(AsO_4)(OH)$) and Dussertite ($BaFe_3^{+3}(AsO_4)(AsO_3OH)$ $(OH)_6$) scavenging barium from the mine water although scorodite was formed at low pH. Where oxygen/air was used at pH above 6, arseniosiderite ($Ca_2Fe_3^{+3}(AsO_4)3O_2 \cdot 3H_2O$) was precipitated along with kolfanite ($Ca_2Fe_3^{3+}O_2(AsO_4)_3 \cdot 2H_2O$), goethite and hydrous ferric oxide. These phases demonstrated low solubility in leach tests although by mineralogical assessment some arsenic was associated with the hydrous ferric oxide phase indicating a strong degree of adsorption in addition to precipitation as arseniosiderite. Without the addition of an oxidant, arsenic removal efficiency was generally less than 30%.

This study clearly demonstrates that under the correct conditions scorodite can be formed from mine waters, however the range of conditions is extremely narrow and formation restricted to highly oxidized highly acidic environments. Critical issues are to ensure all arsenic is oxidized to arsenate, high iron:arsenic ratio in the mixing vessel and a low pH, high oxygen content is maintained in the reactor tanks.

Keywords: Arsenic treatment, precipitation

Introduction

Arsenic contamination of mine and metallurgical waters has long been recognized as a global problem (Matschullat 2000, 2011; Craw and Bowell, 2014). More stringent guidelines based on demonstration of potential toxicity to humans and ecological receptors have motivated regulators and operators to address arsenic levels in discharges from operating mines as well as legacy sites (Craw and Bowell, 2014). An important aspect in the evaluation of arsenic removal from waters is the characterization of the oxidation state of arsenic and its mineral speciation (Bowell et al 2014).

Arsenic can occur in several oxidation states in natural waters although the trivalent arsenite (As(III)) or pentavalent arsenate (As(V)) are the most common (Campbell and Nordstrom, 2014). The most thermodynamically stable species over the natural range of groundwater redox conditions (150-500 mV, Bass-Becking et al. 1960) and pH (4-7, Baas Becking et al. 1960) are H_2AsO^{4-}, $HAsO^{4-}$ and in acid rock drainage waters (pH below 5) H_2AsO^{4-} in more reduced waters, $As(OH)_3$ is the most common species, in highly reducing environments. The kinetics of arsenic reduction-oxidation (redox) reactions is not rapid, so the predicted proportions of arsenic species based on thermodynamic calculations do not always correspond to analytical results. An Eh-pH diagram showing the thermodynamically stable regions for arsenic species is shown in Figure 1.

For this study the removal of arsenic by precipitation methods was assessed as this approach is generally the most common and potentially the most cost effective method of arsenic removal (Bowell, 2003; Nazari et al 2017).
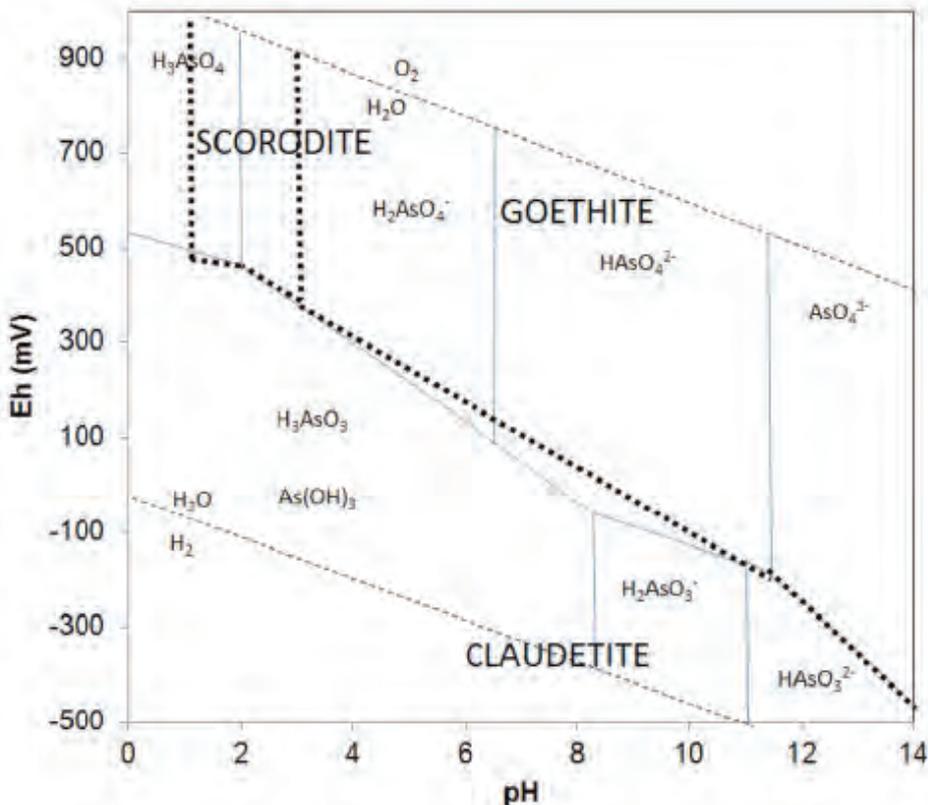
Figure 1: Eh-pH diagram for system Fe-As-H2O at 298 K

Methods

The methodologies applied to precipitate arsenic that were assessed in this paper and references are summarized in Table 1.

All testwork was completed as bench scale tests on site in Tanzania. The feed solution water for this work was a mine water collected in Tanzania from a gold mine. The analysis of the water is shown in Table 2. The water reflects typical mine water from a low sulphide mesothermal gold deposit. Analysis was through Analabs, Tanzania using IC-PAES for cations, kone analyser for chloride and sulfate and titration for bicarbonate. The pH was measured using a HACH meter.

The solids produced in this study were subject to a 2:1 dissolved water to solid leach test using a similar methodology to the EPA1312 test. Essentially the precipitate samples were agitated with deionised water for 24 hours. The solution was then filtered and analysed.

Mineralogy

The mineralogical examination was undertaken using p scanning electron microscopy (SEM) and fine powder X-Ray Diffraction (XRD). Samples were prepared from the testwork material as dry powders (for SEM). XRD analysis was carried out on pulverised samples of the precipitates.

Bulk analyses were carried out on the samples. Scans were run using the Philips PW1710 Automated Powder Diffractometer using Cu Kα radiation at 35kV and 40mA, between 2 and 70° 2θ at a scan speed of 0.04 °2θ/s. From the scans, phases were identified using Philips PC-Identify software and from the peak areas, semi quantitative analysis was performed and a percentage of each phase present calculated. Weighting factors were applied where necessary.

Semi-quantitative energy dispersive analysis of precipitates was carried out using a Zeiss Sigma HD Analytical Field Emission Gun SEM with INCA wave-and energy-dispersive X-Ray spectroscopy at the Department of Earth Sciences, Cardiff, UK. This method allows micro-chemical data to be collected that reports the chemical composition of the surface of the mineral phase. The electron beam utilised to gather the information required is approximately 1 to 5 µm in diameter, so even very small phases can be quantified. An accelerating voltage of 20 kV was used with a probe current of 5.0 nA.

Table 1. Summary of Arsenic Precipitation Approaches

Method	Reference	Approach	Proposed precipitate	Arsenic
Scorodite process	Fujita et al 2008;Caetano et al 2009	Peroxide addition, Temp 30-95oC, excess ferrous, sulfuric acid	Scorodite	
HDS process	Dey et al 2009; Salokannel et al 2013	Ambient temperature, pH buffer with lime, hydrogen peroxide, ferric sulfate	Ferric Arsenate	

Table 2. Geochemical analysis of Mine Water feed

Parameter	Concentration, mg/L	Parameter	Concentration, mg/L
pH	5.8	Arsenic, arsenite	10.8
Sulfate	220	Arsenic, arsenate	8.6
Chloride	65	Iron, ferrous	0.05
Sodium	56	Iron, ferric	0.97
Magnesium	15	Aluminium	1.58
Calcium	52	Manganese	0.33
Potassium	10	Barium	2.12
Bicarbonate	65	Copper	1.13

Results

Scorodite Process

Using the methodology of Caetano et al (2009) that was similar that applied by Fujita et al (2008a) the reaction of hydrogen peroxide, sulfuric acid, ferrous sulfate and mine water was followed over temperatures ranging from ambient to 95°C and variable levels of Fe/As ratio (Table 3).

Results shown in Table 3 demonstrate that at high acid concentration (low pH) and high Fe/As ratio (3/1 and 5/1) scorodite was produced after 4 hours of reaction. At lower Fe/As ratios, ferric hydroxide and a hydrated ferric arsenate, possibly similar to the Type I salt ($Fe_2(HAsO_4)_3.xH_2O$ where X<4 or HFA) reported by Swash and Monhemius (1995) was produced along with Dussertite ($BaFe_3+3(AsO_4)(AsO_3OH)(OH)_6$) and a ferric-arsenate-sulfate salt (HFAS) with similar chemistry to that reported by Swash and Monhemius (1995) as a type II precipitate ($Fe_4(AsO_4)_3(OH)x(SO_4)y$ where x+2y=3).

In addition, where longer time period was applied dussertite and olivenite was observed at low pH, high temperature along with scorodite and a copper bearing HFAS phase. The complexity of treating mine waters with arsenic and cation metals has been reported as potentially interfere with scorodite formation and intermediate copper (and zinc)

bearing HFA phases have been reported in testwork by other studies (Fujita et al., 2008; Gomez et al., 2011).

The agitated tank shows improvement in arsenic removed when compared to static tanks (Bowell, 2003) or when reactions are executed in a chloride-dominated system (Demopoulos et al. 1995). This is most likely reflecting a stronger oxidant in the testwork, more efficient mixing and arsenic oxidation and possibly also reflect lower sodium impurity in the acid medium. Sodium has been shown to inhibit scorodite formation (Gomez et al 2011). The formation of dussertite was only seen in one test and is possibly an anomaly of high Ba in the mine water but does open the possibility that $BaCO_3$ addition to mine waters could also represent a possible removal mechanism.

HDS approach

Following the methodology of Dey et al (2009) a small batch reactor comprising of three reactor vessels allowing for flocculation, thickening and precipitation. The low iron/arsenic ratio in the mine water meant that ferric sulfate was required along with lime to form a high-density sludge. The testwork was completed at ambient temperature (approximately 20-25°C in the on-site laboratory)

Table 3. *Results of Batch Method with Sulfuric acid*

Test #	Test pH	Fe/As ratio	Temp, oC	Length reaction (mins)	Arsenic removed, %	Arsenic minerals
SP1	1.5	3/1	95	60	98	Scorodite
SP3	2.5	3/1	95	60	96	Scorodite, HFA
SP4	2.5	2/1	95	60	71	Scorodite, HFA
SP5	2.5	1/1	95	60	50	HFA
SP6	2.5	1/1	30	60	14	HFO, HFA
SP7	2.5	3/1	95	120	86	Cu-HFAS, olivenite, dussertite, scorodite, HFA
SP11	4	3/1	30	60	67	HFO, HFA
SP13	4	1/1	95	60	84	HFO, HFA, HFAS
SP15	4	3/1	95	60	83	HFO, HFA
SP18	4	5/1	80	60	90	HFO, HFA
SP19	4	5/1	95	60	96	Scorodite, HFO, HFA
SP22	5.8	3/1	95	60	46	HFO, HFA
SP31	6.5	3/1	95	60	40	HFO, HFA
SP42	7	3/1	95	60	28	HFO, HFA

and hydrogen peroxide was added to oxidize arsenite to arsenate in the first tank. This approach is similar to conventional plants currently in operation, such as the Boliden Harjavalta plant (Salokannel et al. 2013).

Throughout all testwork scorodite was not formed and the main phase observed was HFA phase comprised of As-bearing HFO phase (Table 4).

Environmental Testwork

To compare the suitability of the different methods applied here a 2:1 distilled water to precipitate 24-hour leach was undertaken on all the samples and selected results are shown below in Table 5. The required concentration was discharge of the mine water was an arsenic concentration less than 0.05 mg/L. In the testwork this was met in some of the tests, particularly where scorodite was formed but also where the HFAS phase was observed (Table 5). The leach concentration reflects the portion of arsenic initially precipitated as well solubility of the precipitate.

Table 4. Results of HDS treatment

Test #	Test pH	Fe/As ratio	Arsenic removed, %	Arsenic minerals
HDS2	2.5	3/1	69	HFA,Jarosite
HDS5	4	3/1	58	HFO, HFA
HDS6	4	2/1	37	HFO, HFA
HDS9	5.8	1/1	9	HFO, HFA
HDS10	5.8	1/1	8	HFO
HDS12	5.8	3/1	28	HFO
HDS15	6.5	1/1	13	HFO
HDS18	6.5	3/1	53	HFO, HFA
HDS23	7	5/1	54	HFO, HFA
HDS24	7	5/1	53	HFO, Arseniosiderite, Kolfanite
HDS30	8	3/1	26	HFO, HFA Kolfanite
HDS32	8 (NO H2O2)	3/1	6	HFO

Table 5. Results of Bleach Tests on Arsenic Solids

Test #	Test pH	Arsenic in leach, mg/L	Arsenic minerals
SP1	1.5	<0.002	Scorodite
SP3	2.5	<0.002	Scorodite, HFA
SP4	2.5	<0.002	Scorodite, HFA
SP5	2.5	0.17	HFA
SP6	2.5	0.12	HFO, HFA
SP7	2.5	0.014	Cu-HFAS, olivenite, dussertite, scorodite, HFA
SP11	4	0.22	HFO, HFA
SP13	4	0.013	HFO, HFA, HFAS
SP19	4	0.007	Scorodite, HFO, HFA
SP22	5.8	0.19	HFO, HFA
SP42	7	0.38	HFO, HFA
HDS2	2.5	21.8	HFA,Jarosite
HDS5	4	19.7	HFO, HFA
HDS6	4	20.2	HFO, HFA
HDS10	5.8	39.6	HFO
HDS18	6.5	33.6	HFO, HFA
HDS24	7	42.1	HFO, Arseniosiderite, Kolfanite
HDS30	8	44.3	HFO, HFA Kolfanite
HDS32	8 (NO H_2O_2)	12.3	HFO

Conclusions

This study clearly demonstrates that under the correct conditions scorodite can be formed from mine waters, however the range of conditions is extremely narrow and formation restricted to highly oxidized highly acidic environments. Critical issues are to ensure all arsenic is oxidized to arsenate, high iron:arsenic ratio in the mixing vessel and a low pH, high oxygen content is maintained in the reactor tanks.

Complexity occurs with other competing cations that can lead to the formation of other arsenates such as those of barium or copper in low temperature or calcium-bearing arsenates at high pH. This leads potentially to more leachable phases in environmental tests. The formation of hydrous ferric arsenate sulfate phases present potentially another stable solid for arsenic disposal and they appear also to form suitable materials for arsenic mitigation.

Acknowledgements

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