Arsenic and Antimony Removal from ARD and Sludge Stability

by

T.W. Higgs
T.W. Higgs Associates Ltd.

Arsenic and Antimony Removal from ARD and Sludge Stability

T.W. Higgs
T.W. Higgs Associates Ltd.
9145 Shaughnessy Street
Vancouver, B.C.
V6P 6R9

1. Chemistry of Arsenic and Antimony

Arsenic and antimony, which may be present as soluble or colloidal anions in ARD, require separate attention in design of ARD treatment processes. Chemical behaviour of these metals is considerably different than heavy metals such as zinc and copper. The stability and disposal of sludges from ARD treatment systems where arsenic is present, also needs to be addressed separately.

Arsenic and antimony are metalloids, which chemically resemble phosphorous and in fact compete with phosphorous for chemical binding sites. These metals commonly exist in two oxidation states in minerals - trivalent (+3) and pentavalent (+5) forms which are common in complex arsenate, arsenite, antimonates and antimonites. The chemistry of arsenic and antimony is quite similar and the same treatment processes are used for their removal. Arsenic forms a number of oxide and sulphide minerals such as scorodite and arsenopyrite. The common carrier for arsenic in gold ore is arsenopyrite where arsenic substitutes for sulphur in pyrite. Natural weathering of arsenopyrite bearing minerals releases arsenites and arsenates into solution which can migrate under acidic conditions. However, in nature the presence of iron immobilizes arsenic by co-precipitation of the metal arsenates with iron oxides. Natural background concentrations of arsenic in groundwater and surface water are generally very low.

1.1 Oxidation Mechanism for Arsenopyrite

The oxidation mechanism for arsenopyrite can be described by Equation (1). Arsenopyrite reacts with oxygen in the presence of water to generate ferric hydroxide, arsenate ion, sulfate ion and acidity. Complete oxidation generates 5 moles of acidity per mole of arsenopyrite oxidized. If iron precipitates, the arsenate ion released according to Equation (1) would be relatively mobile.

$$FeAsS + 3\ O_2 + 4H_2O \longrightarrow Fe(OH)_3 + AsO_4^{-3} + SO_4^{-2} + 5H^+ \hspace{2cm} (1)$$
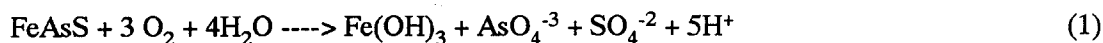
2. Sources of Arsenic

Acidic drainage from waste rock and tailings can contain soluble arsenic if the sulphide minerals that contain arsenic are present. These minerals are listed in Table 1. The weathering of these minerals can release arsenic into solution. The reactivity of the individual arsenic sulphide minerals can be expected to vary. The degree of mobilization of arsenic will also be dependent on the composition of the individual sulphide mineral and the resultant secondary mineral.
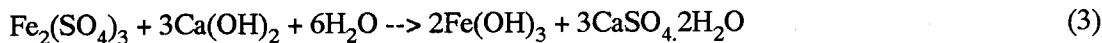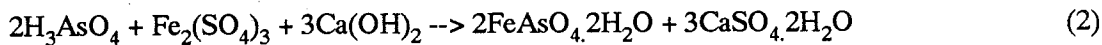
Table 1   Arsenic Sulphide Minerals

Arsenopyrite $FeAsS$
Realgar AsS
Orpiment As_2S_2
Tetrahedrite $Cu_{12}(Sb,As)_4S_{13}$
Cobaltite $CoAsS$
Niccolite $NiAs$

Arsenic may also be present in waste rock as an oxide mineral such as scorodite or olivenite. Since waste rock may contain mixtures of oxides and sulphide, arsenic mobilization may also occur when acid generated by sulphide oxidation contacts oxide minerals containing arsenate or arsenite.

3.   Arsenic Treatment Process Description

Conventional practice for arsenic removal involves ferric sulphate precipitation followed by flocculation and solids removal in a high sludge density recycle system.

Arsenic co-precipitates with ferric hydroxide to form a basic ferric arsenate.

$$2H_3AsO_4 + Fe_2(SO_4)_3 + 3Ca(OH)_2 \longrightarrow 2FeAsO_4.2H_2O + 3CaSO_4.2H_2O \qquad (2)$$

$$Fe_2(SO_4)_3 + 3Ca(OH)_2 + 6H_2O \longrightarrow 2Fe(OH)_3 + 3CaSO_4.2H_2O \qquad (3)$$

Arsenic can also precipitates with lime to form a basic calcium arsenate.

$$2 H_3AsO_4 + 3 Ca(OH)_2 \longrightarrow Ca_3(AsO_4)_2 + 6 H_2O \qquad (4)$$
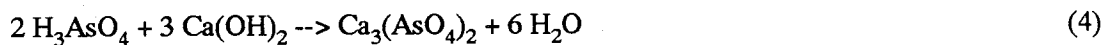
A hypothetical process flow diagram for a treatment plant for ARD containing a high concentration of arsenic is presented in Figure 1 to demonstrate the arsenic removal process. In this case it is assumed that the concentration of arsenic in the feed is high but the required concentrations of other metals necessary to precipitate arsenic are low. The process flow diagram can be described as follows:

1) ARD would be fed to the first reactor where partial neutralization with lime would be carried out to enhance formation of ferric arsenate. Aeration would be provided to oxidize any ferrous iron present. The pH of the first reactor would be controlled at between 5 and 6 depending on the feed characteristics. If the feed was deficient in iron (or other metals such as copper) it may also be necessary to add ferric sulphate to the first reactor.

2) Additional ferric sulphate and lime would be added to the second reactor and the pH would be adjusted to neutral to complete the co-precipitation of ferric arsenate with ferric hydroxide.

3) A dilute polyelectrolyte solution would then added to the neutralized slurry in a flash mixer followed by flocculation in a separate slow mix chamber and discharge to a clarifier.

4) The clarifier would separate out the suspended solids and generate a thickened sludge that would be recycled back to the first reactor. Sludge recycle maintains sludge density and creates a high surface area to remove colloidal metal.

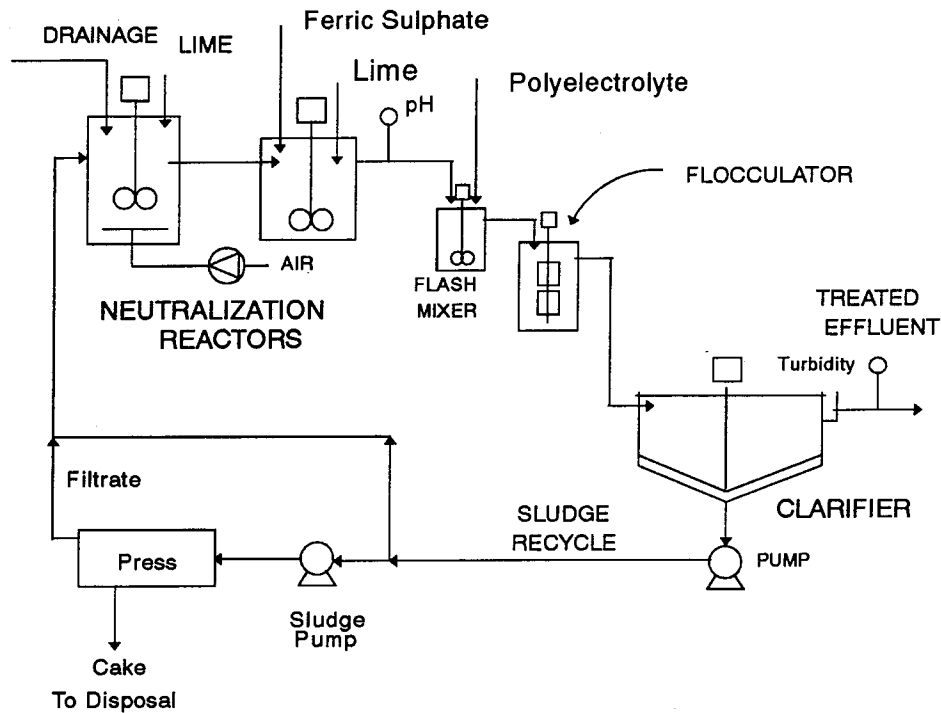5) A portion of the recycled sludge would be wasted to maintain a constant sludge inventory.

Figure 1
Process Flow Diagram for a Treatment System for ARD Containing a High Concentration of
Arsenic

3.1   Operating Characteristics

Factors that affect arsenic removal and sludge stability in a treatment plant for arsenic using the ferric
sulphate HDS process, can be summarized as follows;

3.1.1   Oxidation State of Arsenic

Arsenic should be present as arsenate As(V) since some arsenite compounds have higher solubilities than
the equivalent arsenate. Oxidation using chemicals such as hydrogen peroxide may be necessary if the
concentration of As(III) is high. Oxidation with air may not be adequate.

3.1.2   Fe to As Ratios

Iron dosage, i.e ferric sulfate, should be set to maintain an Fe/As molar ratio greater than 5:1. This ratio
maximizes removal efficiency and ensures that the resultant sludge will be stable.

3.1.3   Oxidation State of Iron

Some commercial grade ferric sulfate can contain an appreciable percentage of ferrous iron. Since
ferrous arsenates are more soluble than the equivalent ferric arsenate it may be necessary to oxidize

ferrous to ferric in order to achieve low residual arsenic concentrations. The oxidation of ferrous to ferric is rapid under neutral pH conditions. The use of air mixing in the arsenic precipitation reactor will ensure that all ferrous iron is oxidized to ferric iron.

3.1.3   pH

Operating pH should be maintained in the 7-8 range to optimize arsenic removal. Removal under acidic pH conditions relies on ferric arsenate solubility which is a minimum at pH 2. However, low effluent concentrations at neutral pH are due to co-precipitation mechanisms that are in turn influenced by the solubility of ferric hydroxide which has a minimum solubility at pH 8.5 to 9.0. Operating experience indicates that treatment efficiency is not overly sensitive to pH fluctuations, if the Fe/As molar ratio is above 5:1.

3.1.4   Sludge Recycle and Solids Inventory

Maintaining a high solids inventory using recycle and controlled sludge wastage can produce low dissolved arsenic and suspended solids concentrations if coupled with proper flocculation with a polyelectrolyte. Recycled sludge yields maximum settling rates and sludge densities. These factors in turn improve overall process stability and lower effluent total arsenic concentrations. Ferric hydroxide floc has a low density, however recycle of ferric hydroxide builds density by incorporating inerts such as gypsum into the sludge. In addition ferric arsenate precipitates can be colloidal and sludge recycle will provide a high surface area to sweep these colloids from suspension.

3.1.5   Polyelectrolyte

Proper polyelectrolyte feed is essential in meeting tight effluent specifications. A number of factors influence the effectiveness of polyelectrolyte addition; namely, type, charge, charge densities, feed solution concentration, air entrainment, floc shear and dosage. These factors need to be considered in selection of the polyelectrolyte.

3.2   Step Neutralization and Multiple Stage Systems

In some cases step neutralization can benefit precipitation of arsenic. Arsenate can be precipitated as either ferric or calcium arsenate. Precipitation as calcium arsenate is not desirable since subsequent release of arsenate can take place when calcium arsenate hydrolyzes to calcium hydroxide in an alkaline environment. The formation of calcium arsenate is favoured under alkaline conditions. A two step neutralization process can improve soluble arsenic removal by maximizing the formation of ferric arsenate. The pH of the first step is controlled between 4.5 and 6 which maintains a reasonable concentration of ferric iron in solution and enhances ferric arsenate formation. In the second step neutralization to pH 7.5 to 8 takes place which favors precipitation of ferric hydroxide and subsequent co-precipitation of ferric arsenate.

In cases where the arsenic content of the feed is very high a two stage arsenic removal system may be required. This system would involve two separate reactors and clarifiers with inter stage solids separation.

4. Sludge Stability

The question of sludge stability in arsenate control has had a significant impact on treatment process design. Robins and Tozawa (1982) reviewed the stability of calcium arsenate as a product of waste treatment for gold processing waters. Theoretical and experimental results were cited to show that calcium arsenate can break down releasing arsenate ion when in contact with carbon dioxide, bicarbonate, or carbonate. They concluded that a number of other metal arsenates would exhibit improved stability in equilibrium with atmospheric carbon dioxide.

Additions of ferric iron have been used to reduce arsenic in solution to low levels while achieving stable sludges. Krause and Ettel (1985) conducted experiments to show that while the simple ferric arsenate, FeAsO4 is unacceptably soluble for the safe disposal of arsenic, "basic ferric arsenates" with Fe/As molar ratios greater than 4 give acceptable solubilities over the pH range of 3-7 and are therefore environmentally safe for disposal. The presence of CO_2 was found not to increase the As solubility. The Krause and Ettel (1985) paper provides the basis for the ferric sulphate precipitation high density sludge process for arsenic removal. This process hinges on careful neutralization to ensure precipitation of ferric arsenate rather than calcium arsenate, and provision of sufficient ferric iron in the feed to ensure that the molar ratio is high enough to limit solubility.

4.1 Mobilization of Arsenic

Mobilization of arsenic can be examined by examining the chemistry of the two species of arsenate which dominate in many systems, calcium arsenate and ferric arsenate.

4.1.1 Chemistry of Calcium Arsenate

Calcium hydroxide can be used to precipitate arsenates and arsenites to form basic calcium arsenates and arsenites. Basic calcium arsenates exhibit minimum solubilities at high pH i.e. >12, with solubility increasing dramatically as pH drops. The solubility of these compounds is enhanced by contact with carbon dioxide in air. Carbon dioxide depresses the pH of calcium arsenite or calcium arsenates slurry to 8.3.

In the calcium-arsenate-water-air system $Ca_3(AsO_4)_2$ and $CaCO_3$ coexist as stable solid phases at pH 8.3 according to the following reaction.

$$Ca_3(AsO_4)_2(s) + 3HCO_3^- \longleftrightarrow 3\ CaCO_3(s) + 2\ HAsO_4^{-2} + H^+ \qquad (5)$$
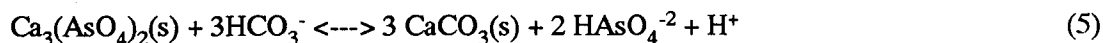
Experimental tests conducted by Nishimura, Tozawa and Robbins (1985) indicated that the pH of a basic calcium arsenite or arsenate slurry was depressed to 8.3 from 12.5 by bubbling air due to the following reaction;

$$Ca^{+2} + CO_2(g) + H_2O \longrightarrow CaCO_3 + 2H^+ \tag{6}$$
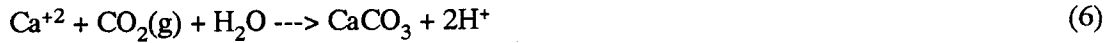
Calcium carbonate is the stable solid phase in a calcium-arsenic-water-air system.

Therefore as a slurry containing insoluble calcium arsenate contacts carbon dioxide soluble arsenate ion will be released in order to maintain the equilibrium between calcium arsenate and calcium carbonate.

A plot illustrating basic calcium arsenate solubility versus pH is provided in Figure 2.

4.2   Chemistry of Ferric Arsenate

Ferric arsenate ($FeAsO_4$) at a molar ratio of 1:1, has a minimum solubility at pH 2.2. Above this pH ferric arsenate decomposes to release ferric hydroxide ($Fe(OH)_3$);

$$FeAsO_4 + 3OH^- \longrightarrow Fe(OH)_3 + AsO_4^- \tag{7}$$

However basic ferric arsenates at Fe/As molar ratios above 4 which are generated by co-precipitation of ferric arsenate and ferric hydroxide have low solubility under neutral pH conditions. The solubility of basic ferric arsenates at 4:1 Fe/As molar ratios increases substantially above pH 5.0. Basic ferric arsenates at higher Fe/As ratios exhibit increased stability at higher pH. However as demonstrated in Figure 3 from Krause and Ettel (1985), basic ferric arsenates even at 8:1 ratios are increasingly soluble at pH values above 8.0.

4.3   Sludge stability and Disposal

4.3.1   Evaluation of Sludge Chemical Characteristics

The evaluation of ARD sludge stability requires a comprehensive understanding of the physical and chemical behavior of metals, hydroxides, carbonates and sulphate. The physical characteristics of ARD sludge are influenced by the unit processes involved in the treatment; namely neutralization, oxidation and precipitation. Sludge stability is also influenced by a number of other facets; namely crystallization, consolidation, dewatering, oxidation, carbonate reactions, neutralization capacity and permeability.

The sludges resulting from the treatment of ARD can contain gypsum, heavy metal hydroxides, heavy metal arsenates, calcium arsenate, and heavy metal sulfides. For disposal, it is desirable that the various components of the sludge remain fixed, rather than re-enter the environment. The impact of exposure to water and air on the chemical nature of the sludge and how this might affect remobilization must be addressed.

At the chemical conditions of its production (pH, temperature, solution composition), the sludge components are immobile, and the sludge is stable, at least on a short term basis. Instability might result as the sludge is exposed to solutions of differing composition, or if slower chemical reactions result in chemical changes over time periods significantly longer than those used in the treatment process.

4.3.2 Gypsum

Gypsum has a significant solubility in water, and its presence makes the water "hard". Its solubility in pure water at 25 $^{\circ}$C is about 2.1 g/L (Seidel and Link, 1952), a significant contribution to dissolved solids loading. Nevertheless, lime treatment is an accepted method for neutralization of sulphate solutions, and these processes normally produce gypsum-saturated effluent, evidently without significant harm to the environment.

Water percolating through ARD treatment plant sludge would theoretically be able to dissolve significant quantities of gypsum over time. However, gypsum sludges, and particularly mixtures of gypsum and metal hydroxides, generally exhibit low permeability. Thus dissolution may not be a significant problem as long as the sludge is disposed of in a way that minimizes its exposed surface.

4.3.3 Heavy metal hydroxides

The solubility of the metal hydroxides in water generally increases as pH drops. The pH at which the treatment process operates may be above that which would result from long-term exposure of the sludge to atmosphere and groundwater. Thus, potential for resolubilization of the heavy metals exists, and this could dictate the need to treat the sludge as a special waste, requiring special containment to control water passage.

4.3.4 Complexing Agents

Presence of complexing ions (such as cyanide, chloride, or naturally occurring organic ions) can greatly enhance the solubilities of many heavy metals. Careful selection of the disposal site must be made to ensure that waters bearing such ions do not have opportunity to leach the heavy metals and carry them back into the environment.

The best assurance of stability of these precipitates will come from testwork which exposes the sludge to conditions expected to exist in the disposal area under circumstances that accelerate achievement of equilibrium between the solution and the sludge.

4.3.5 Sulphides

If contaminants are precipitated as sulphides, careful consideration must be given to the possibility of acid mine drainage reoccurring in the deposited sludge. While the equilibrium solubilities would be low, the precipitates that would likely be formed in such a treatment process would be very fine, having a high specific surface area, and would thus be very amenable to chemical or biological oxidation, with remobilisation of the contaminants.
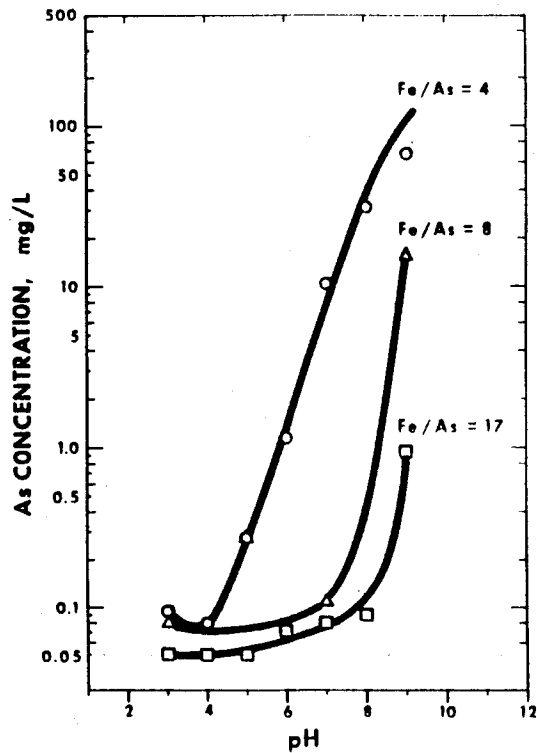
Figure 1
Effect of pH and Fe/As Ratio on As Solubility at 25 C
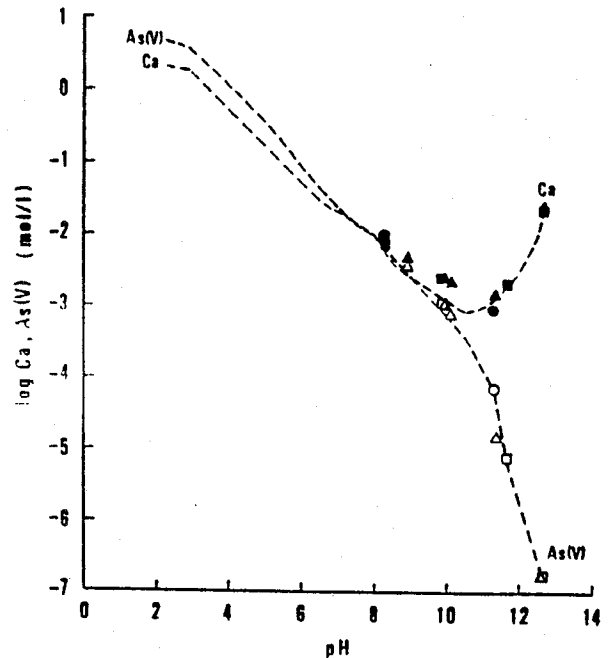(Krause and Ettel, 1985)

Figure 2
Relationship between Concentrations of
Calcium and Arsenic (V) in Solution during Air-
Bubbling (Nishimura et al., 1985)

References

Robins, R.G., 1985. "The Aqueous Chemistry of Arsenic in Relation to Hydrometallurgical Processes". Impurity Control and Disposal, proceedings of the 15th Annual Hydrometallurgical Meeting, Vancouver, August 18-22, 1985, pp. 1-1 to 1-26.

Robins, R.G., and Tozawa, K., 1982. "Arsenic Removal from Gold Processing Waste Waters: The Potential Ineffectiveness of Lime". CIM Bulletin, April, 1982, pp. 171-174.

Krause, E. and Ettel, V.A., 1985. "Ferric Arsenate Compounds: Are They Environmentally Safe? Solubilities of Basic Ferric Arsenates". Impurity Control and Disposal, proceedings of the 15th Annual Hydrometallurgical Meeting, Vancouver, August 18-22, 1985, pp. 5-1 to 5-20.

Nishimura, T., Tozawa, K. and Robins, R.G., 1985. "The Calcium - Arsenic - Water - Air - System". Impurity Control and Disposal, proceedings of the 15th Annual Hydrometallurgical Meeting, Vancouver, August 18-22, 1985, pp. 2-1 to 3-19.

Seidell, A. and Linke, W.F., 1952. Solubilities of Inorganic and Metal Organic Compounds, supplement to 3rd ed. Van Nostrand, New York, p. 341.