Removing and Stabilizing As in Acid Mine Water

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Arsenic is often present in a variety of forms in sulfide mineral deposits and can become a soluble constituent of mine drainage due to oxidation reactions taking place in mine workings and waste deposits. Its removal from solution must be carried out to meet water-quality discharge criteria, and it must be fixed in a solid form that is environmentally stable. The preferred form of arsenic for disposal is as a basic ferric arsenate, $FeAsO_4{\cdot}xFe(OH)_3$*, which can be readily produced by coprecipitation with iron in a high-density sludge process. High-density sludge plants are simple to operate and can be designed to meet stringent water-quality specifications and produce stable sludges over long periods of continuous operation.*

INTRODUCTION

Mine water and the drainage from waste rock piles and tailings impoundments at mines exploiting sulfide ore deposits are often contaminated with metals due to the oxidation of residual sulfides. The minerals pyrite, FeS_2, and pyrrhotite, $Fe_{1-x}S$, are the sulfides most commonly present in waste rock, tailings, and the mine workings due to their common association with base-metal sulfides and their relative abundance. The oxidation of these minerals produces acidity as well as ferrous and ferric ions, which can promote the oxidation and dissolution of other sulfide minerals. Mine water and drainages that contain the products of oxidation are usually referred to as acid rock drainage (ARD). The environmental impacts caused by ARD are the most significant environmental concern at many mine sites.

Arsenic is frequently found in many types of mineral deposits. It can occur in a large number of sulfides, sulfosalts, oxides, arsenites, and arsenates and is most commonly associated with sulfidic base metal and gold ores. Arsenic is, therefore, often present in small or large concentrations in the waste rock and tailings produced by mining and milling operations and is a common constituent of ARD. Removing arsenic and other contaminants to low residual dissolved concentrations is often necessary to meet water-quality discharge criteria.

One of the most critical aspects of arsenic removal from ARD is its fixation in an environmentally stable form to allow safe, long-term disposal. Precipitation of metals from ARD using lime is widely used, but in the absence of competing cations, the formation of calcium arsenate, $Ca_3(AsO_4)_2$, is favored. This compound, however, has a minimum stability at a high pH (>12), and its long-term stability has been shown to be unsatisfactory due to its interaction with carbon dioxide in air.[1,2] It is now generally accepted that precipitation of arsenic as a basic ferric arsenate, $FeAsO_4{\cdot}xFe(OH)_3$, formed by coprecipitation with ferric ion is preferred. While simple ferric arsenate, $FeAsO_4$, formed with a 1:1 Fe/As molar ratio, is relatively soluble at neutral pH, basic ferric arsenates with Fe/As ratios of three or more are stable in a wide pH range.[3–5]

Many processes have been proposed to remove arsenic and other metals from contaminated mine waters, although coprecipitation with iron combined with lime neutralization remains the process of choice for most operations to produce satisfactory effluent and to form stable sludges for disposal. While theoretical considerations of arsenic removal and the stability of the precipitates produced are an important aspect of process design, treatment plants need to be designed to provide simple yet reliable, low-cost performance. Operational experience at a large number of plants has shown that the high-density sludge (HDS) process is the best available technology to meet these design objectives and satisfy environmental criteria.

REMOVING ARSENIC FROM ARD

Removing arsenic from ARD and other process streams in the mining and metallurgical industries has been investigated using a wide range of processes.[7] Processes that have been used and proposed include precipitation with lime; coprecipitation using ferric ion, copper, zinc, lead, and other metals; precipitation at high temperature and pressure; adsorption with ferric hydroxide, aluminum hydroxide, carbon, and other absorbents; electrolysis; hydrogen reduction; ion exchange; solvent extraction; membrane separations; precipitate flotation; ion flotation; and various passive and active biological processes. Of all the processes evaluated, coprecipitation with ferric ion using ferric sulfate or ferric chloride as a reagent is the process of choice for most applications based on cost, relatively simple engineering and control, reliable performance, and production of environmentally satisfactory effluent and solid residue (sludge).

Lime, CaO, which is usually converted to slaked lime $Ca(OH)_2$ as part of the treatment process, is the most widely used neutralizing agent due to its rapid kinetics and ability to raise the pH to high values. Other reagents can be used and might be preferred in specific cases, including sodium hydroxide, which has the advantage of not forming gypsum, $CaSO_4{\cdot}2H_2O$, as is the case with lime. Gypsum formation can, in some cases, cause scaling problems in treatment-plant equipment. Avoidance of gypsum formation also reduces the volume of sludge for disposal. However, sodium hydroxide is much more costly than lime. Limestone is usually available at a low cost, but has relatively low reactivity and can not be used to increase pH above 5.0 without excessive reagent consumption and subsequent sludge disposal problems. Its use might be applicable where the feed

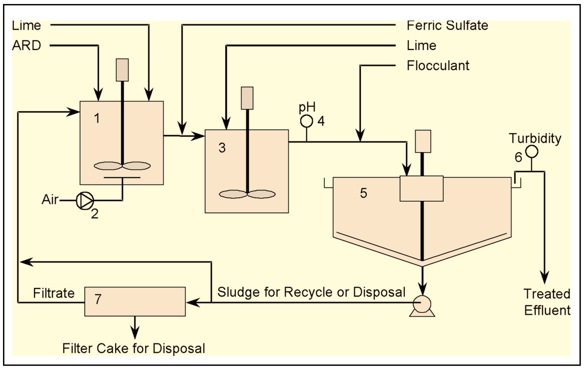

Figure 1. A treatment system for ARD containing arsenic. 1—reactor for partial neutralization; 2—air blower; 3—reactor to complete precipitation; 4—pH measurement and control; 5—clarifier; 6—turbidity measurement; 7—filter press.

streams are very acidic and where sludge disposal is available at a low cost, but it can only function in combination with another reagent, such as lime or caustic soda, to achieve the final pH needed to precipitate all metals to achieve regulatory compliance.

The addition of slaked lime and ferric ion to ARD precipitates the contained arsenic as ferric arsenate (Equation 1). The ferric ion is precipitated as ferric hydroxide (Equation 2).

$$2H_3AsO_4 + Fe_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2FeAsO_4{\cdot}2H_2O + 3CaSO_4{\cdot}2H_2O \quad (1)$$

$$Fe_2(SO_4)_3 + 3Ca(OH)_2 + 6H_2O \rightarrow 2Fe(OH)_3 + 3CaSO_4{\cdot}2H_2O \quad (2)$$

It has been shown[10] that with Fe/As molar ratios greater than one, the coprecipitation of As(V) and Fe(III) does not produce a mixture of ferric arsenate and ferric hydroxide, but forms chemical compounds termed basic ferric arsenates, $FeAsO_4{\cdot}xFe(OH)_3$. The binding of arsenic by absorption on amorphous ferric hydroxide has also been reported to be an effective mechanism of arsenic removal.[11] It should be noted that the presence of other cations, such as copper, zinc, or aluminum, in ARD can assist in the fixation of arsenic in the precipitates due to the formation of corresponding basic-metal arsenates.[11]

Arsenic can also precipitate with lime to form calcium arsenate (Equation 3), but this reaction should be avoided due to the instability of the precipitate.[1]

$$2\,H_3AsO_4 + 3\,Ca(OH)_2 \rightarrow Ca_3(AsO_4)_2 + 6\,H_2O \quad (3)$$

THE HDS PROCESS

Conventional practice for the removal of arsenic from ARD involves ferric-arsenate precipitation followed by flocculation and solids removal. This is carried out in a lime treatment plant in which part of the sludge produced by precipitation is recycled to the process to increase sludge density, which, in turn, increases the efficiency of metal removal and reduces the volume of the sludge produced; this configuration is called a HDS process. Apart from the importance of efficiently removing metals to meet water-quality discharge criteria, the reduction of sludge volumes can have significant economic implications as the cost of sludge storage and maintenance can often exceed the initial capital cost of the treatment plant in the long term.

A hypothetical process flow sheet for a treatment plant for ARD containing arsenic is presented in Figure 1. In this case, two reactors are provided, as it is assumed that the concentration of arsenic in the feed is high (>50 mg/l), but the required concentrations of other metals necessary to precipitate arsenic, particularly iron, are low. If arsenic concentrations are low, a single reactor is usually adequate.

In the flow sheet, ARD is fed to the first reactor, where partial neutralization with lime is carried out to enhance the formation of ferric arsenate. Aeration is provided to oxidize any ferrous iron present. The pH of the first reactor is controlled between 4.5 and 6.5, depending on the feed characteristics. If the feed is deficient in iron (or other metals, such as copper), it might be necessary to add ferric sulfate to the first reactor. Additional ferric sulfate can be added to the overflow launder of the first reactor and lime can be added to the second reactor to adjust the pH to 7–8 to complete the coprecipitation of ferric arsenate with ferric hydroxide. Selection of the final pH will be dependent on the requirements to remove other metals.

Polyelectrolyte (flocculant) is added as a very dilute solution to promote improved settling of the precipitates. It can be added directly to the discharge launder from the second reactor or to a flocculating feed-well of the clarifier. Figure 1 shows the use of a conventional clarifier, in which flocculated precipitates and other suspended solids settle to produce a sludge and the treated effluent overflows for discharge. An arsenic effluent concentration of <0.05 mg/l can be achieved in most well designed plants. If the feed concentration of arsenic is high, however, particulate carryover with the treated effluent can result in exceedance of discharge criteria with respect to total (soluble + dissolved) arsenic. In this case, a final filtration step could be required. Alternatively, a high-efficiency clarification device, such as a lamella clarifier, can produce the required effluent quality, but at a higher capital cost than the cost of a conventional clarifier.

The thickened sludge from the clarifier is recycled back to the first reactor. Sludge recycle promotes and maintains a high sludge density and creates a higher surface area to assist in the removal of colloidal metal. A portion of the recycled sludge is removed periodically for disposal to maintain a constant sludge inventory. A filtration stage allows the removal of sludge from the system as a filter cake. This is an optional step, and its inclusion will depend on factors such as the disposal site characteristics and local regulatory requirements. The density of sludges discharged without filtering will typically be in the range of 20% to 45% solids. Final settled sludge densities in the sludge impoundment can reach 55% solids.

Factors that affect arsenic removal and

SOURCES AND CHEMISTRY OF ARSENIC

Arsenic is widely distributed in nature and occurs in a large number of minerals either as a primary constituent of the crystal structure or in small amounts in arsenic-carrier minerals. More than 300 arsenic and arsenic-carrier minerals are known.[6] Arsenopyrite, FeAsS, is the most abundant arsenic mineral associated with sulfidic mineral deposits. Other prominent arsenic minerals include enargite, Cu_3AsS_4; realgar, AsS; orpiment, As_2S_3; tennantite, $(Cu,Fe)_{12}As_4S_{13}$; niccolite, NiAs; and cobaltite, CoAsS.

Natural background concentrations of arsenic in groundwater and surface water are generally very low. Acidic drainage from mines, waste rock, and tailings, however, can contain significant concentrations of arsenic if the sulfides and other minerals that contain arsenic are present. The oxidation of these minerals can release arsenic into solution. Arsenic may also be present in mine waste as an oxide mineral such as scorodite, $FeAsO_4{\cdot}2H_2O$, or olivenite, $Cu_2(AsO_4)OH$. Since waste rock may contain mixtures of oxides and sulfides, arsenic mobilization may also occur when acid generated by sulfide oxidation contacts the oxide minerals.

Arsenic is a Group VA element and has a chemical behavior considerably different than the heavy metals, such as zinc and copper, with which it is commonly associated in ARD. It chemically resembles phosphorous and, in fact, competes with phosphorous for chemical-binding sites. The chemistry of arsenic is also quite similar to that of antimony, and the same treatment processes are used for removing both metals. Arsenic can be present as a soluble anion or a colloidal particle in ARD and requires separate attention in the design of ARD treatment processes.

The aqueous chemistry of arsenic related to hydrometallurgical processes has been well reviewed.[7,8] In ARD, both arsenic (III) and arsenic (V) can exist, with the relative proportions of each dependent on the source of the dissolved arsenic and on the characteristics of the ARD, particularly with respect to the iron concentration and its valency state [i.e., Fe(II) of Fe(III)].

Equations A–E illustrate reactions that can occur. Iron is usually the principal cation present in ARD due to the oxidation of pyrite, FeS_2, and/or pyrrhotite, $Fe_{1-x}S$. The initial oxidation products of these iron sulfides are acidity (H^+) and Fe(II) (Equation A), which can be oxidized to Fe(III) (Equation B) in the neutral pH range, if solutions are well aerated, or under acidic conditions by chemoautotrophic bacteria that use Fe(II) as an energy source. The ferric ions produced will promote the further oxidation of pyrite (Equation C), pyrrhotite, and other sulfide minerals producing additional acidity, causing the dissolution of the contained metals and Fe(II), which can then be re-oxidized as shown in Equation B.

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (A)$$

$$Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O \quad (B)$$

$$FeS_2 + Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (C)$$

Using arsenopyrite, FeAsS, as an example, the oxidation of arsenic minerals can initially result in the appearance of As (III) in solution (Equation D). In acidic conditions, As (III) is not oxidized to As (V) by air (oxygen) except under pressure and elevated temperatures.[9] Fe (III), if present in ARD, can, however, oxidize As (III) (Equation E).

$$FeAsS + 2.75O_2 + 0.5H_2O \rightarrow HAsO_2 + Fe^{2+} + SO_4^{2-} \quad (D)$$

$$HAsO_2 + 2Fe^{3+} + 2H_2O \rightarrow H_3AsO_4 + 2Fe^{2+} + 2H^+ \quad (E)$$

sludge stability include the oxidation state of iron and arsenic, the Fe/As ratios, pH, polyelectrolytes, sludge recycle and solids inventory, and process and plant considerations.

Oxidation State of Iron and Arsenic

Iron is usually present in mine drainage or other effluents as both Fe(II) and Fe(III). The oxidation of Fe(II) is essential to maximize the Fe(III) content for As(III) oxidation and ferric-arsenate precipitation and to prevent the formation of ferrous arsenate, which is more soluble than basic ferric arsenate. In addition, the precipitation of ferrous hydroxide should be avoided as lime consumption is much higher and the resulting sludge is less stable and more difficult to handle and de-water than ferric hydroxide. The use of air in the arsenic precipitation reactor will ensure that all ferrous iron is oxidized to ferric iron. It should be noted that commercial-grade ferric sulfate added to the process often contains a significant percentage of iron as Fe(II).

As discussed, arsenic should be present as As(V), since the precipitated arsenate compounds generally have a lower solubility than the equivalent As(III) form. If As(III) is high, oxidation using oxidizing agents, such as hydrogen peroxide, might be necessary.

Fe/As Ratios

Operating experience in a large number of plants has shown that the ferric-sulfate addition rate should be set to maintain the Fe/As molar ratio greater than 5:1. This ratio maximizes removal efficiency and ensures that the resultant sludge will be stable. This minimum ratio might be higher than actually required to produce a stable sludge, but the incremental cost of over-addition of the reagent is more than offset by operational simplicity and the elimination of the monitoring costs that would be incurred to demonstrate that the lower ratio is meeting objectives for sludge stability.

pH

The flow sheet in Figure 1 illustrates the neutralization of the arsenic-containing feed in two reactors. Performing neutralization in steps can benefit the precipitation of arsenic by ensuring that ferric arsenate, and not calcium arsenate, is formed. Since calcium-arsenate formation is favored under alkaline conditions, maintaining the pH of the first reactor between 4.5 and 6.5 will favor ferric-arsenate formation. In the second step, neutralization to pH 7–8 takes place over a range where ferric hydroxide has a minimum solubility, and the coprecipitation of ferric arsenate is optimal.

In cases where the arsenic content of the feed is very high, a two-stage arsenic removal system incorporating two separate reactors and clarifiers with interstage solids separation might be considered. Operating experience indicates that treatment efficiency is not overly sensitive to pH fluctuations if the Fe/As molar ratio is above 5:1.

Polyelectrolyte

Proper polyelectrolyte feed is essential in meeting stringent effluent specifications. A number of factors influence the selection and effectiveness of polyelectrolyte addition, including type, charge, charge densities, feed-solution concentration, dosage, air entrainment, and floc shear and dosage.

Solids Inventory

Maintaining a high-solids inventory using recycle and controlled sludge removal can produce low dissolved arsenic and suspended-solids concentrations if coupled with an effective flocculant. Recycled sludge yields maximum settling rates and sludge densities. These factors, in turn, improve overall process stability and result in lower total arsenic concentrations in the effluent. Although ferric-hydroxide floc has a low density, the recycle of ferric hydroxide builds density by incorporating inert components, such as gypsum, into the sludge. In addition, ferric-arsenate precipitates can be colloidal and sludge recycle will provide a high surface area to aid in the removal of these colloids from suspension.

Process and Plant Design

Process and plant design are site specific and depend on a number of factors, including feed volume and composition, effluent discharge criteria, selected neutralizing reagent, storage capacity for the ARD feed, and the sludge disposal method. In all cases, the process fundamentals, with respect to oxidation, precipitation, and sludge stability, must be considered in design, but the plant must also have low capital and operating costs, be simple to operate, and mechanically reliable. Designs should be practical and take into account the selection of construction materials and plant equipment, and the need to supply system back-ups in the event of mechanical and control system failures. Back-up equipment is especially important if the feed-storage capacity is limited.

Although the plant is designed to carry out chemical reactions, it is the physical set-up of the plant that will determine its reliability over long periods of continuous operation and provide assurance that the effluents and sludges will meet the required chemical specifications. The operating conditions of the plant, particularly with respect to reagent dosage, should be selected to allow the plant to produce effluent with significant lower concentrations than the discharge standard. This will reduce the need for costly monitoring and analyses required to check that the plant discharge is in compliance.

SLUDGE STABILITY AND DISPOSAL

In addition to the ferric and other metal arsenates formed in an ARD treatment plant, treatment sludges will contain mixtures of gypsum, heavy-metal hydroxides, heavy-metal carbonates, antimonates, and heavy-metal basic sulfates. The impact of exposure to water and air on the chemical nature of the sludge components and how this might affect their stability must be considered.

The evaluation of ARD sludge stability requires a comprehensive understanding of the physical and chemical behavior of these compounds. The physical characteristics are influenced by the unit processes involved in the treatment—specifically, neutralization, oxidation, and precipitation. The long-term chemical stability of these sludges also depends on a number of factors, including process design and control in the water-treatment process; disposal-site physical characteristics; in-place permeability; particle-size distribution; and the presence of oxygen, sulfides, and complexing agents, such as cyanide, chloride, or naturally occurring organic ions.

Sludge-disposal options include deposition in tailings ponds, separate sludge ponds, marine and lake disposal, and landfills. Although careful selection of the disposal site is essential, HDS sludges are typically stable under neutral leaching conditions and usually contain significant excess residual alkalinity to prevent acidification and resolubilization under most site conditions. As previously discussed, basic ferric arsenates are stable over a wide pH range.

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