

Striving for a Sustainable Mining Industry: Arsenic Control through an Integrated Approach

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Abstract

The sustainable development of the mining industry has become more dependent on a proper and responsible management of all streams resulting from the treatment of impure and relatively poor mineral resources. This is even more vital when dealing with extremely hazardous materials containing arsenic. Arsenic control in the mining industry needs an integrated approach involving each stage of the process, i.e. exploration, process development, mine operation and mine closure. Possible strategies and methods for arsenic control at each step are briefly reviewed. The emphasis is placed upon the removal and the fixation of arsenic through the hydrometallurgical processing of arsenic-containing ores or materials. Present commercial operations and processes developed to stabilise arsenic, more particularly scorodite formation and the co-precipitation of As(V) with Fe(III), are discussed in details.

INTRODUCTION

Arsenic is one of the main contaminants of concern for the mining industry. In addition to the increasing amount of arsenic contained as impurity element in most gold, uranium and base metal ores, some metal arsenide minerals have already been or could well be processed as primary sources of metals. Those arsenic minerals include the gold-bearing iron arsenide minerals (eg. arsenopyrite), copper arsenides (1) (enargite), and cobalt and nickel arsenides (2) (skutterudite, niccolite, cobaltite, •••). On the other hand, the regulations for the release of arsenic to the environment are becoming more stringent with increasing public awareness of the toxicity of arsenic and better understanding of its impact on the environment. The development of an integrated approach to effectively control the arsenic is the key to a profitable and sustainable operation, in full regulatory compliance.

INTEGRATED APPROACH FOR ARSENIC CONTROL

The improvement of the environmental performance of the mining industry with regards to arsenic is based on an integrated approach involving every phase of a mining project i.e. exploration, process development, mine operation, and mine closure.

Rejection of arsenic minerals during the early stages of exploration, mining and beneficiation

During the exploration stage, focus is usually placed on the mineralogy and ore texture of the pay metals, for obvious reasons. For arsenic containing ores, it has now become imperative to appreciate from the early start of a project the environmental implications of the process and incorporate the cost of arsenic control into the economic model to decide the profitability of a deposit or part of a deposit.

Wherever possible, the separation of arsenic minerals in their original forms during mineral beneficiation presents an attractive solution to the arsenic control issue. There are two possible routes that could be followed:

- Separate the arsenic minerals from the rest of the ore (by any suitable methods such as flotation, gravity, ...) and reject them to the tailing streams, if the arsenic minerals are barren. In that case, whenever possible, the arsenic minerals should be put back into the mine where they came from.
- Separate the arsenic minerals from the rest of the ore and treat them using the process guaranteeing the best arsenic control, while the rest can be processed using other technologies.

Arsenic control during metallurgical treatment of concentrates

High temperature processing

During the roasting of arsenopyrite concentrates for their gold recovery, flue dust containing 60-70% arsenic trioxide is collected through the gas handling system. This flue dust is mostly consumed in the production of chromated copper arsenate (CCA) as wood preservative. The future market of CCA is uncertain in the long term, and therefore alternative methods of controlling the arsenic must be developed. A typical example is the work conducted by DIAND (3) to handle the ~230,000 tonnes of dust generated by the Giant Yellowknife mine in the NWT. The approaches which have been or are presently evaluated involve encapsulation of the dust into a stable matrix (4) (bitumen, cement, vitrification) or ground freezing.

Hydrometallurgical processing

The chemical approach to control arsenic is mainly based on the formation of stable arsenic compounds or arsenical sludge through the hydrometallurgical processing of arsenic-containing materials. The commercially practiced processes for chemical fixation of arsenic includes the precipitation of calcium arsenite or arsenate, arsenic sulfide (As_2S_3), arsenical ferrihydrite and crystalline scorodite. Among them, the scorodite process has been widely accepted as currently the most suitable method for stabilization of arsenic in terms of its high arsenic content, low TCLP arsenic solubility and environmental stability, if disposed appropriately (5).

It is known that scorodite compounds are favorably formed in acidic solution of Fe(III) and As(V) at high temperature (eg. 160°C), i.e under autoclave conditions. This allows it possible for the scorodite process to be conveniently integrated with sulfide oxidation and metal extraction processing in a single autoclave to treat arsenic-bearing ores. The most successful application of the scorodite process is the autoclave processing of arsenopyrite gold ore. Under autoclave conditions, the iron sulfide (FeS , FeS_2) and arsenopyrite (FeAsS) minerals are oxidized to liberate gold which can be efficiently recovered in the subsequent cyanidation stage. Simultaneously,

the Fe(III) and As(V) ions formed from the oxidative dissolution of sulfide minerals react to precipitate stable crystalline scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) for safe disposal in the cyanidation tailing ponds. The same type of process has been briefly used commercially for cobalt arsenide minerals (2) and is being considered for the treatment of arsenic-bearing copper ore (1).

It has been reported (6), in a laboratory investigation on the formation of scorodite in an acidic solution of Fe(III) and As(V) under autoclave conditions, that several arsenic compounds can be formed, depending on the temperature and the initial iron to arsenic molar ratio in solution. The various arsenic compounds obtained have different TCLP arsenic solubility values, and crystalline scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) and the so-called type-2 arsenic compound ($\text{Fe}_4(\text{AsO}_4)_3(\text{OH})_x(\text{SO}_4)_y$) appear the least soluble. In addition, it was also observed that increasing Fe(III) to As(V) molar ratios (>1) in the initial solution appear to result in slower kinetics for the precipitation of arsenic compounds. In actual autoclaving operation, the Fe(III)/As(V) ratio in solution depends not only on the total contents of Fe and As in the autoclave feed, but also on their oxidation and dissolution kinetics, which are in turn affected by their mineralogy and the autoclave conditions applied, such as oxygen pressure, temperature and acidity. Hence, in the preparation of the autoclave feed, both the iron to arsenic ratio and their mineral types should be considered. The iron to arsenic ratio in the autoclave feed and the operating conditions favorable for the production of stable arsenic-bearing solid phases may differ with ore types and need to be determined by experiment.

Recently, it was demonstrated that crystalline scorodite can also be formed at ambient pressure in acidic solutions of both chloride and sulfate ions (7,8). The precipitation kinetics are industrially viable at enhanced temperature ($>90^\circ\text{C}$) and at a reasonable concentration of seed which can be provided by recycling the scorodite product (9). A multi-stage precipitation process at gradually increased pH can remove arsenic as scorodite to low concentration (eg. 50 mg/L at pH around 2). Lime or limestone can be used to adjust

pH and to neutralize the acid generated from the formation of scorodite. The base metals, if any present in solution, remain in the aqueous phase during scorodite precipitation. The scorodite product produced at ambient pressure is as stable as the scorodite solids produced at high temperature (ie in autoclaving process) in terms of their TCLP results.

Potential application of the ambient pressure scorodite process includes the treatment of arsenic-rich metallurgical hazardous materials, such as arsenic-rich process liquor, effluent from acid plant in copper smelter or historically produced unstable arsenical sludge. For the treatment of those materials alone, autoclave processing is impractical in terms of its capital cost. For an arsenic-rich solution or solids with deficient iron for the formation of scorodite, iron-containing metallurgical sludge, such as arsenic ferrihydrite from historic operation, either ferrous or ferric sulfate salts or other iron-rich industrial streams (eg. acidic effluent from sulfide tailing ponds), are the potential sources of iron.

Oxidation of As(III) and Fe(II), if present in solution, is required, prior to the formation of crystalline scorodite at ambient pressure. Hydrogen peroxide is a suitable agent, but the use of gas mixture of SO₂ and O₂ is more cost-effective for the oxidation of both As(III) and Fe(II) in acidic solution (9).

The ambient pressure scorodite process can also be used to treat autoclave discharge to maximize the stabilization of arsenic as scorodite. In some autoclave operations to treat arsenic-bearing ores, the aqueous discharge contains high concentration of arsenic. That is primarily the result of high final acid concentration caused by the acid generated by the oxidation of sulfide minerals, or the need to maintain high acidity for a more efficient extraction of the metals in the ore. The ineffective control of the iron to arsenic ratio in the autoclave feed and the need to prioritize the metal extraction in the selection of operating conditions may also add to the high arsenic concentration in the aqueous discharge. In industrial practice, the high arsenic aqueous discharge is usually treated by the conventional arsenic ferrihydrite precipitation method. This practice usually needs the

consumption of a large amount of iron source and neutralization agent, and also leads to the production of a voluminous sludge with low arsenic content and poor solids/liquid separation property. An attractive alternative to this is the use of the ambient pressure scorodite process for the stabilization of the arsenic in the aqueous autoclave discharge. Since the autoclave discharge is hot and contains scorodite formed during autoclaving, the application of ambient pressure scorodite processing directly on autoclave discharge can reduce or eliminate the need to heat and to add scorodite seed. Lime can be used for pH adjustment. Obviously, the ambient pressure scorodite precipitation can be conveniently and reasonably fitted between the autoclaving and down stream processing in terms of its operating condition requirements (eg. pH range 1~3, and temperature >90°C).

Effluent treatment for arsenic removal and fixation

Low arsenic streams are generated from mining activities throughout the world. Those effluents widely differ in pH, arsenic concentration and speciation, the type and content level of other components, such as iron and other metals, and can be primarily classified into the following types, in terms of their sources.

- Underground and surface water from historical landfill, sediment or contaminated soil in mine sites closed or under current operation
- Liquor discharges from metallurgical processing of a variety of arsenic-containing ores
- Acid mine drainage from a range of mines
- Effluent from tailing ponds in closed or currently operated mines

The technologies that have been practiced or studied for the treatment of arsenic-containing effluent include:

- Neutralization with lime
- Co-precipitation with ferric ion or other chemicals
- Absorption
- Biotechnical approach

Lime neutralization to a high pH (~12) was widely practiced for the treatment of effluent to remove arsenic, due to the convenience in its operation. But it is no longer considered acceptable in terms of the high As solubility and the environmental instability of the produced calcium arsenite or arsenate sludge.

The co-precipitation of As(V) with Fe(III) is considered an environmentally more acceptable method for the treatment of arsenic effluent. Arsenic(V) can be readily removed to low level (e.g. <0.1 mg/L) at Fe(III)/As(V) ratio of >3 and pH around 4, and the produced arsenical ferrihydrite sludge can be disposed in an environmentally safe way. Over the past decade, this method has gradually replaced the lime neutralization method and become the primary treatment method for low arsenic stream. Recently, a new method called mineral-like precipitation has been investigated. This method is based on the formation of a solid solution compound ($\text{Ca}_{10}(\text{As}_x\text{P}_y\text{O}_4)_6(\text{OH})_2$) at high pH of 12 with the addition to the effluent of phosphoric acid (H_3PO_4) and lime (CaO); it can achieve low residual arsenic level (<50 ppb), and produce a stable sludge (10).

Adsorption is a widely recognized technology for the removal of arsenic from water, e.g. the naturally occurring low arsenic-containing underground and surface water. The adsorbents available include alumina, natural or artificial minerals, and ion exchange resin. This method needs desorption or elution of arsenic to reactivate the adsorbent and the stabilization of desorbed or eluted arsenic in an environmentally stable form. For the effluent from mine site and metallurgical processing, the adsorption technology is less likely to be an efficient and cost-effective solution due to the relatively high level of arsenic and other species which may compete with arsenic for adsorption sites or contaminate the surface of the adsorbent particles.

Biological treatment of arsenic-containing effluents is based on the biological formation of arsenic sulfide, i.e. reduction of arsenic(V) to As(III) by bacteria and formation of insoluble arsenic sulfide complex under anaerobic conditions. It could be practiced in a bioreactor or

anaerobic/wetlands cell, and appears to have the capability to remove arsenic in the effluent to low levels that exceed or meet the site discharge criteria (11). The biological treatment appears to be an attractive approach for naturally occurring low arsenic-containing underground and surface water or as a polishing step in arsenic effluent treatment. As compared with arsenical ferrihydrite precipitation method, the biotechnological method does not need oxidation of arsenic(III), but it has other disadvantages. Firstly, it is more sensitive to the chemical composition and temperature of the effluent to be treated and usually expensive biotreatability and optimization testing is needed for a given effluent to determine its suitability and efficiency. Secondly, the arsenic removal kinetics in the bioprocess is much slower than that in a chemical process. Thirdly, the environmental stability of the formed insoluble arsenic sulfide sludge and the possible effect of the bacteria in effluent discharged to the environment are still uncertain. These disadvantages might make the bioprocess less competitive for the treatment of large volume effluent from mining industry with relatively high levels of arsenic and other contaminant species.

Of all the methods described above for the treatment of arsenic effluents from mining industry, the arsenical ferrihydrite precipitation is currently considered to be the most suitable method. In this method, all the arsenic in the effluent needs to be in pentavalent oxidation state, i.e. As(V), if low residual arsenic concentration (eg. 0.1 mg/L) and stable arsenic sludge are desired at economically reasonable Fe(III) to As ratio (eg. Fe/As=4) (12). However, under many situations, this is not the case. Arsenic(III) is more or less present in effluents, depending on their sources. Multi-stage precipitation and high Fe/As ratio have been used to improve arsenic removal and product stability in the treatment of As(III)-containing effluents with incomplete or without oxidation. However, those practices, which are considered still satisfactory under the current regulations, will no longer be acceptable in terms of the expected more stringent regulations for arsenic in effluent discharge (from 0.5 mg/L to 0.1 mg/L or below). There is a necessity to review and polish the current technology or to develop new methods for arsenic oxidation and removal.

Hydrogen peroxide is widely used for the oxidation of arsenic in the treatment of low As(III) effluent treatment. However, the effectiveness of this method largely depends on both the oxidation conditions (pH, temperature and H₂O₂ dosage) and the composition of the effluent treated. Complete conversion of As(III) to As(V) in a given effluent can be achieved only under certain conditions (12). The SO₂/O₂ gas mixture with appropriate composition is effective for arsenic oxidation in acidic solution in the presence of iron (12). It provides a cost-effective alternative for the oxidation of arsenic when present at considerable levels. Other oxidizing agents include ozone, permanganate, chlorine gas and hypochlorite. The choice of the oxidizing agent mainly depends on their oxidation efficiency and cost, and it may be site or effluent-specific.

Maintaining product stability after it has been disposed

Effective management of the disposal of arsenic-bearing materials requires both a full characterization of the arsenic-bearing materials to dispose of and the understanding of the environment for their disposal. Currently, there are different testing methods to evaluate the stability of arsenic-bearing materials, including the EPA Toxicity Characteristics Leaching Procedure (TCLP), but those testing methods do not give sufficient consideration to the interaction between the arsenic material and the environment in which it is disposed of. Therefore, they are usually helpful in making a preliminary judgement on whether an arsenic-bearing material can be considered for disposal in a given environment, but do not adequately assess its long-term stability. For those materials which can pass the preliminary stability testing, such as arsenic-bearing minerals, crystalline scorodite and arsenical ferrihydrite (Fe(III)/As(V)>4) formed from metallurgical processing, improved methods must be developed to assess the long-term stability. The methods should involve complete characterization of the materials (including chemical, mineralogical analysis and physical properties) and full consideration of the interaction between the arsenic materials and the environment so that favorable disposal conditions

can be identified and predictions of behavior can be made.

Given the range of arsenic-bearing materials and the diversity of the potential disposal environments at the mine and mill sites, the long-term stability of the arsenic-bearing materials for disposal and the environmental risks posed by the disposed materials are still likely to be evaluated on the case-by-case basis.

CONCLUSIONS

To improve the environmental performance and the sustainability of the mining industry, an integrated approach is necessary to insure the arsenic control at each phase of the mine life, in a proper and responsible way. Maximize arsenic rejection in its original minerals at the mine and mill, through careful evaluation of the arsenic minerals and optimization of mineral processing, is an attractive option whenever possible. The environmental and economic impact of this option is often not fully appreciated and needs more attention. Currently, the primary approach for arsenic control is to stabilize arsenic as a stable product through metallurgical processing. The most environmentally acceptable methods includes crystalline scorodite formation for the treatment of arsenic-rich materials and arsenical ferrihydrite precipitation with Fe(III)/As(V)>3 for the treatment of low-arsenic stream. However, the long-term stability of the both materials in a given environment, depends on the method and conditions applied for the disposal. A comprehensive protocol has to be designed for the full understanding of the interaction between the materials and environmental surroundings so that an effective and durable management of arsenic disposal can be achieved.

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