Biotechnology-based processes for arsenic removal

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ABSTRACT

The regulations for arsenic control have become strict. Therefore, better technologies to remove arsenic from bleeds and effluents are desired. In addition, no single solution is suitable for all cases. The properties of the process streams and the storage facilities are major factors determining the selection of a certain technology. In this paper, two technologies are described. What these technologies have in common is that they are based on high-rate engineered bioreactors that allow optimal control, efficient resource use, and predictable and reliable process performance. One technology (Arsenoteq) converts arsenic to corodite, which is most suitable for storage under oxidising conditions. The other technology (Thioteq) operates under reducing conditions and produces arsenic sulphide (As_2S_3, orpiment) with 61 mass% arsenic. The first technology is suitable for medium to high (> 1000 mg/L) concentrations of arsenic in acidic process streams, whereas the latter is ideal for effluent treatment up to < 5000 mg/L of arsenic. The residual arsenic concentration that can be obtained with the latter method is < 0.1 mg/L.

INTRODUCTION

Arsenic is widely distributed throughout the earth's crust. The various arsenic-containing minerals that enter mineral processing operations can have more than 200 different forms that include elemental arsenic, arsenides, sulphides, sulphosalts, oxides, arsenates, and silicates [1]. This crustal element occurs at relatively high levels in sulphide minerals of copper, lead, zinc, and gold-bearing minerals. Arsenic is mainly introduced into the process solutions through the treatment of such sulphide minerals [1].

The chemical characteristics of arsenic are dominated by the fact that it readily changes oxidation states or chemical form through chemical or biological reactions that are common in the environment. Therefore, the availability and mobility of arsenic is usually controlled by reduction-oxidation (redox) conditions, pH, biological activity, and adsorption/desorption reactions, rather than solubility equilibrium [2]. After hydrometallurgical processing, arsenic appears in solution mainly as arsenite (AsO_3^{3-}) for arsenic (III) and arsenate (AsO_4^{3-}) for arsenic (V) [1].

Arsenic is becoming more and more problematic because the utilisation of arsenic and its com-pounds has decreased drastically and will be phased out in the near future. Furthermore, rules and regulations for effluent discharge and storage are becoming stricter all the time. A portfolio of technologies is therefore required in other to select the proper technology for a specific case.

REMOVAL OF ARSENIC

Removal of arsenic from streams resulting from mining or metallurgical operations has received a lot of attention. Various methods considered to deal with arsenic in hydrometallurgical processes include: oxidation-reduction, precipitation and thermal precipitation (lower temperature precipitation used in the semi-conductor industry), co-precipitation, adsorption, electrolysis and cementation, solvent extraction, ion exchange, membrane separations including reverse osmosis, precipitation and ion flotation, and biological processing.

Precipitation as a basic ferric arsenate with Fe(III) is currently the most widely used method. For a removal of arsenic to < 0.05 mg/l, the Fe:As mole ratio should be at least 3 [3, 4]. The main drawback of this technology is that ferric iron must be added if the solution to be treated is not high in iron. Furthermore, the presence of associated ions such as phosphate, sulphate, carbonate, and dissolved organic species can greatly influence the removal of arsenic and the relative long-term stability of ferrihydrite [2]. Other methods such as encapsulation with lime-cement or high temperature fixation in ceramic-type materials are equally considered expensive and questionable from a long-term stability point of view [5].

In this paper two technologies for arsenic removal are described. These technologies have in common that they are based on high-rate engineered bioreactors that allow optimal control, efficient resource use, and predictable and reliable process performance. The selection of a certain technology depends on the properties of the process stream to be treated, on the arsenic concentration and on the projected storage facilities for the recovered arsenic product, *i.e.* whether the arsenic product will be stored under oxidising or reducing conditions.

OXIDISING CONDITIONS: ARSENIC REMOVAL AS SCORODITE

Scorodite, $FeAsO_4.2H_2O$, is a naturally occurring, pale green mineral formed in oxidised zones of arsenic-bearing ore deposits with a Fe:As stoichiometric ratio of 1. Its wide occurrence in comparison to other secondary arsenate minerals has led many to advocate it as an acceptable carrier for the immobilisation of the arsenic that is released during pyrometallurgical or hydrometallurgical processing of arsenic-containing ores such as gold, copper [3], and uranium [4]. Hence, considerable research has been carried out looking into the experimental determination of either its solubility or its thermodynamic stability [6].

There are a number of operational advantages associated with the production of scorodite when the treatment of arsenic-rich and iron-deficient sources is considered. Among those are the high arsenic content of scorodite, the stoichiometric (1:1) low requirement for iron, and its excellent settling and dewatering characteristics. Crystalline scorodite ($FeAsO_4.2H_2O$) is two orders of magnitude less soluble than amorphous iron (III) arsenate precipitate that is normally formed in low temperature systems [3]. In this context, the standard method of Fe(III)-As(V) coprecipitation is not attractive due to the large volume of sludge generated and the prohibitive cost of the purchase of large quantities of ferric sulphate. Furthermore, it is known that the generally large excess of iron (III) in the feed solution leads to the precipitation of basic ferric sulphate that interferes with the formation of scorodite ($FeAsO_4.2H_2O$). This is best illustrated by the failure of a hybrid Biox-POX process [7]. This shows that control of the super saturation is essential.

Scorodite was previously thought only to form at temperatures above 120 ^{o}C, which implies that the process has to take place under high pressure. The consequent autoclave technology comes with a price tag that tends to be too high for environmental applications.

Recent research showed that scorodite can also be formed at ambient pressures and temperatures below the boiling point of water as reported by Dymov *et al.* [7]. The key to the success of this technology is seeding and super-saturation/neutralisation control. At present, the process flow sheet consists of three precipitation reactors in series followed by a thickener with solids recycling for the seeding of the precipitation reactors. If some of the arsenic is present as As(III), an arsenic oxidation step will have to be added in front of the flow sheet. Commonly, oxidation of As(III) to As(V) is obtained by adding chlorine, hypochlorite, permanganate, hydrogen peroxide or SO_2/O_2 [8]. A simpler process with lower operational costs would be attractive.

Biologically induced oxidation & precipitation

Bacteria are well known for their ability to perform redox reactions, such as in bioleaching. The right type of naturally-occurring arsenic oxidising bacteria can biologically oxidise As(III) to As(V) using air as oxidant. This also enables super-saturation control because the ferric iron is made *in situ* from ferrous iron. Besides the savings on reagents, biological oxidation is also advantageous because it occurs under milder conditions and at lower costs because air is the cheapest oxidant available. This is due to the superior catalytical properties of selected bacteria that can perform the oxidation more efficiently in comparison to a pure physical chemical process.

The patented knowhow of Paques B.V. for the production of scorodite is a combination of specific biotechnological processes and a proven airlift bioreactor with solids retention (Paques' CIRCOX® reactor). The retained solids will act as seed and core material for the crystallisation process. Super-saturation control can be achieved through the controlled production of ferric iron through biological ferrous iron oxidation as described above.

For the simultaneous iron and arsenic oxidation and scorodite precipitation, the precipitation reactions should occur at 60 °C to 90 °C using organisms similar to those used in bioleaching. The use of moderate thermophiles is preferred as higher temperatures aid the scorodite precipitation process. The details of the biologically-induced scorodite precipitation are described in the next paragraph.

How does bio-induced scorodite precipitation work?

The reaction for oxidative arsenic trioxide dissolution can be summarised by:

$$H_3AsO_3 + 0.5\ O_2 \xrightarrow{\text{bacteria/iron}} H_3AsO_4 \qquad (1)$$

Both pyrite and scrap iron can be used to provide iron for ferric arsenate precipitation. Bacterial pyrite oxidation can be summarised as:

$$2\ FeS_2 + 7.5\ O_2 + H_2O \xrightarrow{\text{bacteria}} Fe_2(SO_4)_3 + H_2SO_4 \qquad (2)$$

Reaction 2 is acid producing, whereas the overall scrap-iron dissolution reaction is acid consuming:

$$2\ Fe^0 + 1.5\ O_2 + 3\ H_2SO_4 \xrightarrow{\text{bacteria}} Fe_2(SO_4)_3 + 3\ H_2O \qquad (3)$$

Crystalline scorodite precipitation is acid generating:

$$2\ H_3AsO_4 + Fe_2(SO_4)_3 + 4\ H_2O \longrightarrow 2\ FeAsO_4.2H_2O + 3\ H_2SO_4 \qquad (4)$$

The overall reaction is acid-producing unless an acid-consuming iron source is used. The use of scrap iron would make the overall reaction acid-neutral:

$$2\ H_3AsO_3 + 2\ Fe^0 + 2.5\ O_2 + H_2O \xrightarrow{\text{bacteria}} 2\ FeAsO_4.2H_2O \qquad (5)$$

The process for overall reaction is schematically represented in Figure 1.

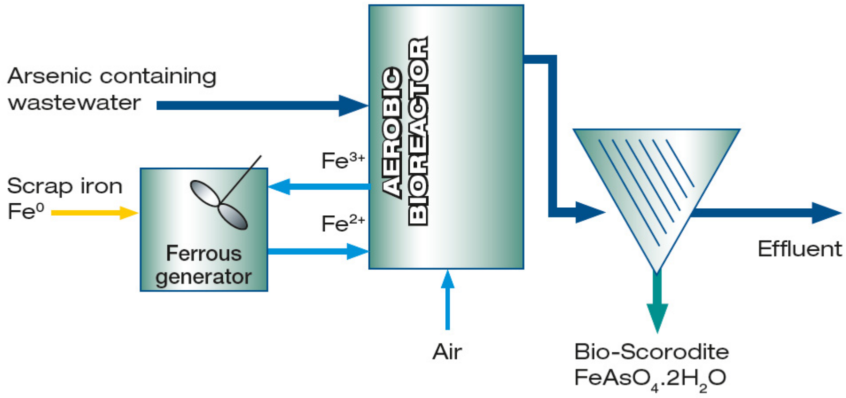

Figure 1 Block diagram of the Arsenoteq process for scorodite formation

The Arsenoteq™ process operates at a pH of 1 ~2 and a temperature of 60 °C ~ 90 °C. This technology has been proven on bench scale and is currently in the scale-up phase. Further scale-up is expected to go smoothly as it makes use of standardised CIRCOX® bioreactors that have an installed base of over 30 units.

The stability of the scorodite proved to be very good and better than chemically-produced scorodite. In a leaching test, only 0.1 mg/L of dissolved As was found after 40 days whereas chemically produced scorodite had 5.8 mg/L after 56 days. The composition of the pale green product as being scorodite was confirmed by various methods like ICP-AES & SEM-EDX (ratio Fe:As = 1:0.98~1.0), XRD (material is highly crystalline), FR-IR (no contaminants) and TGA (2 molecules of crystal water). Figure 2 shows several SEM photographs [9].

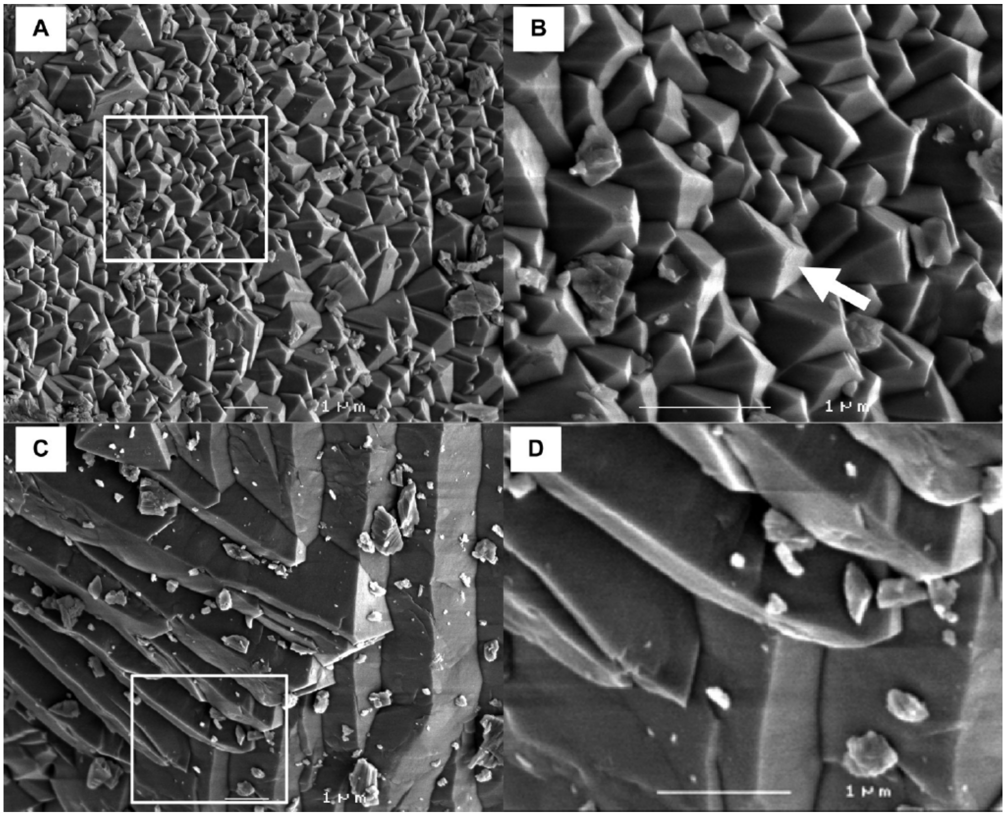

Figure 2 SEM photographs of biogenic scorodite crystals obtained at 80 °C and 1 g L-1 As5+. Crystal habit I (a) with 1000 magnification and (b) with 30 000 magnification. Crystal habit II (c) with 1000 magnification and (d) with 30 000 magnification. The arrow in b) shows the typical octahedron habit of the crystal, and the squares show the selected area for high magnification

The only drawback of the Arsenoteq process is that the lowest arsenic level that has been achieved is 80 mg/L As in the presence of 200 mg/L Fe^{2+}. This means that a final stage whereby amorphous ferric arsenate is precipitated is required. We are investigating whether this ferric arsenate can be recycled to the Arsenoteq reactor conversion to scorodite.

Typical arsenic-rich waste solutions or solids that can be treated for the productions of crystalline scorodite are: acid plant effluents, Cu-ER electrolyte bleed streams, As_2O_3 flue dusts, and arsenic-contaminated soils [7]. The long-term stability will be determined by the local storage conditions. Even though the stability of scorodite appears to be superior over orpiment, it must be kept in mind that scorodite is not completely stable under anaerobic conditions. Degradation of scorodite under the release of As(III) at a redox potential < 100 mV and 5.5 < pH < 7 has been reported [8]. In contrast, orpiment is stable under these conditions. Therefore, in the solution of the arsenic problem the storage facility should also be included in the evaluation. Orpiment as an alternative is discussed in the following sections.

REDUCING CONDITIONS: ORPIMENT PRECIPITATION

Arsenic oxide can react with sulphide to form stable orpiment that has a low solubility under anoxic conditions. Arsenic present in the form of arsenite can precipitate directly:

$$2\,H_2AsO_3^- + 3\,HS^- + 5\,H^+ \rightarrow As_2S_3 + 6\,H_2O \tag{6}$$

Arsenate is first converted to arsenite by sulphide:

$$H_2AsO_4^- + HS^- + H^+ \rightarrow H_2AsO_3^- + H_2O + S^0 \tag{7}$$

and subsequently precipitates as shown in Eq. 6.

The most interesting aspect of this precipitation reaction is that it occurs best under acidic to very acidic conditions. The pH should be < 3 to reach a residual arsenic concentration of < 0.2 mg/l. A lower pH results in a lower residual arsenic concentration. Only under very acidic conditions (> 200 g/L H_2SO_4) does the solubility increase slightly again. An advantage of the orpiment is that it is a compact substance with 61 mass% arsenic and no crystal water.

Source of sulphide

There are various possibilities to obtain sulphide for metal sulphide precipitation. Na_2S and NaSH are commonly used. Also gaseous H_2S is possible. However, transport, traditional production and handling of this compound can be complicated and expensive.

A real disadvantage in the process operation is that the introduction of concentrated sulphide solution leads to a high supersaturation of the sulphide mineral. It is generally known that this leads to small particles that are difficult to separate and to dewater.

Thioteq™ process as alternative: off-line biogenic sulphide generation

Sulphide precipitation of arsenic would be an attractive method if the high cost of transporting, storing or producing sulphide on site (as Na_2S, NaSH or H_2S) would not have hampered its widespread application in the metal and mining industry. In present applications for heavy metal removal with sulphide, the sulphide needed for precipitation is mostly obtained from chemical sources such as Na_2S, NaHS, CaS, FeS and H_2S. However, Thioteq technology enables the production of sulphide on-site and on-demand using biotechnology. This eliminates the hazards and costs that accompany the transport, handling and storage of chemical sulphides.

The Thioteq™ process, which is patented by Paques B.V., has two stages: one chemical and the other biological. A schematic flowsheet for the recovery of one metal as its metal sulphide is shown in Figure 3. The water to be treated only passes through the chemical stage. Sulphide is produced in the biological stage and transported to the chemical (precipitation) stage with a recycled carrier gas.

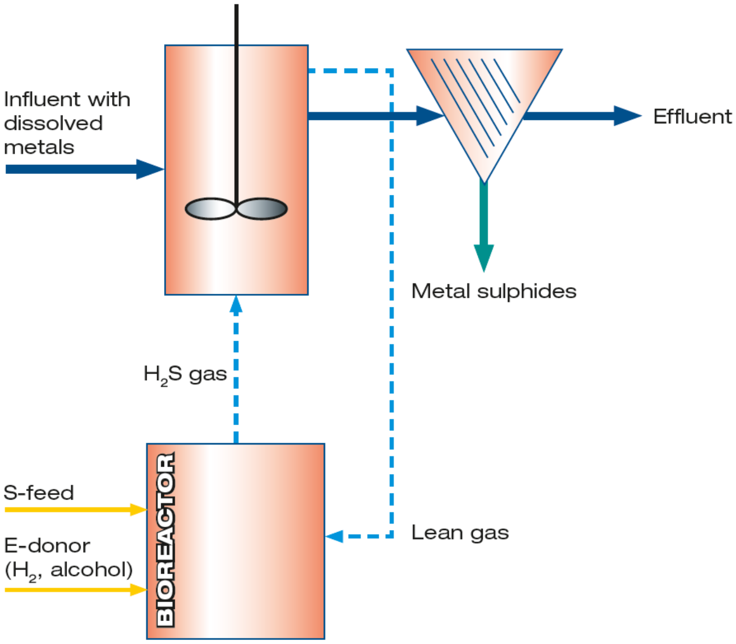

Figure 3 Basic principle of the Thioteq™ bleed treatment. The contactor (stirred tank reactor in this case) is fed with H_2S gas from the bioreactor through a gas recycle. The As_2S is separated from the effluent in the separator. More contactors can be fed from one bioreactor.

Biological stage

The process is the so-called "off-line process"; in other words, the bioreactor is not in direct contact with the process stream to be treated. This makes the process versatile and widely applicable. Selected, naturally-occurring biomass converts elemental sulphur (or waste sulphuric acid) to sulphide in an engineered, high-rate bioreactor. With ethanol used as an example of a reductant, the conversion can be written as:

$$6\ S^0 + \text{ethanol} + 3\ H_2O \rightarrow 6\ HS^- + 6\ H^+ + 2\ CO_2 \qquad (8)$$

The bioreactor is fed with powdered sulphur. The biological conversion to sulphide occurs via poly-sulphides, which are formed when sulphide reacts with the S8-ring of elemental sulphur. In addition to ethanol, acetic acid, hydrogen or other waste sources of organics (*e.g.* distillery waste) are typical electron donors (reductants).

The biological process is carried out under ambient conditions, which makes it safe to operate. In addition, the process is self-controlling; high sulphide concentrations become inhibitory to the bacteria that subsequently stop producing but are not killed. Therefore, a dangerous runaway situation is impossible. The bacteria become active again when the sulphide is withdrawn from the bioreactor by the precipitation process. Finally, the sulphide inventory in the bioreactor is mostly maintained as ionic –and therefore dissolved– HS^-. Little H_2S is therefore released in case of a leak. The sulphide is available on demand within the capabilities of the process as long as the sulphide demand is balanced by the addition of an electron donor.

Chemical stage: contactor

The block diagram in Figure 3 is a standalone plant with one metal precipitation circuit, although multiple contactor-clarifier units can be provided if more than one metal product is to be recovered as will be shown below.

The chemical stage consists of a gas-liquid contactor. The sulphide is transported to the contactor with the help of gas recycling with a carrier gas (a mixture of CO_2 and N_2), and metal-loaded water (*e.g.* acid mine drainage) is fed to the contactor. In the contactor, the sulphide reacts as S^{2-} with dissolved metals and precipitates as their sulphides, for example for copper:

$$Cu^{2+} + H_2S \rightarrow CuS + 2H^+ \qquad (9)$$

Arsenic can precipitate in a similar manner as already shown in Equations 6 and 7.

The properties of the sulphide gas from the bioreactor and the contactor design results in metal sulphides with good settleability and filterability. The contactor off-gas, containing primarily N_2, CO_2 and water vapour, is recycled to the bioreactor again.

A typical application for this technology is metal recovery from, for example, acid streams.

Overall process

Sulphide produced by the Thioteq™ process has a lower cost than typical chemical sulphide reagents such as NaHS, Na_2S or H_2S. Exact costs will depend on the local availability of reductant (*e.g.* waste alcohol). The technology has the advantage that the reagent is produced only on demand, which results in more efficient utilisation and eliminates any safety concerns related to transportation and on-site storage. Thioteq™ technology is a safe and economic alternative to common sources of hydrogen sulphide. There are more than 10 industrial plants utilising Paques technology for the reduction of sulphur compounds.

CONCLUSIONS

Arsenic fixation and disposal is expected to remain a hot issue in the mining and metals industry. High-rate biotechnological processes in engineered bioreactors are very effective in removing both arsenate and arsenite from both high and low concentrations of arsenic contamination. This contrasts with the low-rate technology that often has unreliable and unpredictable performance.

Paques B.V. has developed two robust technologies that are marketed to the metal and mining sector for arsenic removal based on modern, high-rate biotechnology. Each of these technologies has its own field of application (see
Table 1):

- Scorodite precipitation combined with biological arsenite oxidation for high arsenic/low iron bleeds and effluents
- Orpiment precipitation for high arsenite/arsenate concentration for electrolyte bleed purification allowing reuse

In both cases, the systems are effective in removing arsenic while producing a compact and stable sludge, ensuring minimal disposal costs. The efficiency of the biological system means that consumables are used effectively resulting in competitive economics.

Table 1 Overview of technologies supplied by Paques for arsenic removal

Technology	ARSENOTEQ **Bulk – Scorodite precipitation**	THIOTEQ **Bulk - Orpiment**
Preferred Arsenic feed concentration	> 1000 mg/L As(III) + As(V)	> 50 mg/L As(III) + As(V)
Obtainable discharge concentration	<100 mg/L, so a final treatment is required	<0.2 mg/L
Projected storage	Enclosed, oxidising conditions	Dry and/or under exclusion of oxygen (reducing conditions)
Typical application	Wash tower blow down, high-As bleed	Electrolyte bleed treatment; acid is recovered. Nickel recovery possible
Remarks	As(III) is biologically oxidised to As(V) with air and precipitated with Fe(III) on seeds	As(V) is a-biotically reduced to As(III) and precipitated as orpiment.

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