



# Bioscorodite crystallization for arsenic removal

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## Abstract

In the bio-scorodite process, arsenic is precipitated as crystalline iron arsenate, i.e. scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ). This is a more economic and more environmentally friendly method for arsenic immobilization than the chemical production of iron- or calcium arsenate, as fewer chemicals are needed. Moreover, scorodite is an attractive medium for arsenic control and immobilization because it is stable, compact and has a very low solubility. Therefore it is regarded as the most ideal form for long-term arsenic storage.

We have demonstrated that bio-crystallization of arsenic into scorodite crystals is possible with the aid of microorganisms. The operational conditions of the bio-scorodite process allow for a fast growth of the microorganisms and facilitate the crystallization of scorodite, avoiding the precipitation of other iron oxides or amorphous iron arsenates. The bio-scorodite process brings several advantages compared to chemical crystallization such as the lower required temperature ( $70^\circ\text{C}$ ), the control of supersaturation by biological oxidation and no need for crystal parents or seeds to begin the crystallization. Arsenic concentrations are removed to ppm level with starting concentrations ranging from 1000 to 2000  $\text{mg L}^{-1}$ . The produced bioscorodite crystals are very similar to the scorodite mineral found in nature. By control of the iron feed and the pH, the production of other iron precipitates is avoided. The latter facilitates easy separation of the solid product. Based on their highly crystalline nature, the biogenic scorodite crystals seem very suitable for safe disposal.

At present the research has started with the continuous production of scorodite in bioreactors. The follow-up challenges are focused on the selection of a suitable reactor configuration.



# 1 Introduction

Arsenic can be found in natural materials, groundwater, mining wastes, commercial products and at contaminated sites [1]. The lack of waste management has resulted in sites that are seriously polluted with arsenic, posing a threat to human health [1]. New and low-cost technologies are desperately needed to effectively immobilize and safely dispose of arsenic.

Mining and metallurgical activities result in the generation of large volumes of arsenic containing solid wastes, mainly amorphous calcium and ferric arsenates [2]. Current methods for arsenic removal from such streams are mainly based on sorption onto iron oxides or on precipitation as amorphous calcium arsenate and arsenical ferrihydrite. The disposal and storage of these compounds is not entirely safe as they easily undergo physical and chemical changes with time [2, 3], resulting in arsenic release into the environment. Solid-liquid separation of arsenical ferrihydrite is extremely inefficient. This gelatinous material contains no more than 6 wt % arsenic, with a maximum solid content of 20-25 wt % [2]. Arsenical ferrihydrite requires a high iron consumption with respect to arsenic, i.e.  $Fe/As > 3$  [2].

Crystalline ferric arsenate, known as scorodite, is a naturally occurring secondary supergene arsenic mineral with the chemical formula  $FeAsO_4 \cdot 2H_2O$ . Scorodite formation and dissolution may be very important in controlling the mobility of arsenic in acid mine drainage, hot springs, and other surface and near-surface waters [1, 2, 4]. Because its low solubility, high arsenic content (25-30 wt.%), high stability and compactness, scorodite presently is considered an attractive medium for arsenic stabilization and the safest known storage material [4-8].

Arsenic immobilization from metallurgical streams has been accomplished by the use of hydrothermal scorodite crystallization. This process employs temperatures above 150°C, low pH (~0.7) and oxygen overpressures of up to 2,000 kPa [2, 9-11]. Because hydrothermal scorodite crystallization requires autoclave systems, the technology is not widely applied.

Atmospheric scorodite precipitation at lower temperatures ( $T < 95$  °C) rose as an alternative to hydrothermal crystallization. The feasibility of atmospheric scorodite precipitation was demonstrated by Demopoulos and co-workers at McGill University in Canada. They developed the ambient-pressure crystallization of scorodite from arsenic concentrated solutions ( $> 10$  g  $As^{5+}$   $L^{-1}$ ) by stepwise neutralization [12-14]. The maintenance of a low saturation level in combination with the addition of seed material effectively results in lowering the crystallization temperature [12-14]. With saturation control, scorodite was crystallized at 80-95 °C with a starting pH of 0.9 to 1.5 from ferric arsenate solutions. As a seed for scorodite crystallization, hydrothermally produced parent seeds were used, or external seeds such as gypsum crystals. Instead of ferric iron ( $Fe^{3+}$ ) and arsenate ( $As^{5+}$ ), also ferrous iron ( $Fe^{2+}$ ) and arsenite ( $As^{3+}$ ) can be used as the source for scorodite after chemical oxidation with peroxide or pure oxygen to the scorodite reactants [15, 16].



The majority of the metallurgical streams have diluted arsenic concentrations, commonly ranging from 1 to 3 g As L<sup>-1</sup>. As opposed to the relatively dilute concentrations found in metallurgical streams, most studies conducted on atmospheric scorodite precipitation in sulphate media used arsenic concentrations ranging from 10 to 50 g As L<sup>-1</sup> [12, 13, 15]. One study demonstrates continuous scorodite precipitation using dilute arsenic streams of less of 2 g L<sup>-1</sup> at 95 °C [17]. They used hydrothermal scorodite seeds to stimulate scorodite precipitation in a continuous CSTR type of reactor. The applied system needs sufficient surface area for crystal growth, i.e. a solids recycle of 35 to 40 g L<sup>-1</sup> scorodite, to achieve a steady state of 0.2 g As L<sup>-1</sup>. Besides a continuous solids recycle, this system also needs a pre-oxidation step of arsenic and ferrous iron.

Scorodite is considered to have several advantages over other materials for arsenic immobilization such as good thickening and filtration properties, compact volume, low water retention and a high arsenic content. These advantages make scorodite the most suitable and stable material to store arsenic safely.

## 2 Bioscorodite precipitation

The “Bioscorodite Process” is a new biological concept that proposes the use of microorganisms to control the saturation level in crystallization reactors [18]. The main challenge of the bioscorodite process is to simultaneously carry out the biological oxidation reactions and scorodite crystallization in one process step. In the following sections we show a summary of the first experimental results on this process and we discuss some applications.

Previously, we demonstrated that bio-crystallization of arsenic into scorodite crystals is possible with the aid of microorganisms [19]. In the bioscorodite process, the biological oxidation and crystallization reaction take place simultaneously. The biological process has two main advantages:

- 1) low cost of the oxidizing chemical (oxygen in air) and
- 2) the supersaturation level is controlled on a microscale level by controlling the rate of biological oxidation, resulting in higher crystallinity of the scorodite. As opposed to the bioscorodite process, in chemical scorodite formation high supersaturation zones can occur due to poor control of the saturation level.

Currently the bioscorodite process is carried out in bioreactors at 70-75 °C and a pH between 1-1.2. Parent seeds or other seeds are not needed to start the crystallization. The operational conditions of the process allow us to obtain a rapid growth of the microorganisms and facilitate the crystallization of scorodite, avoiding the precipitation of other iron oxides or amorphous iron arsenates.

### 2.1 Balancing oxidation and crystallization rates

To achieve a stable scorodite formation process, the oxidation and crystallization rates need to be balanced. The iron oxidation rate is influenced by the type of bacteria used, the retention of biomass in the reactor, dissolved oxygen concentration and environmental conditions (pH, temperature,



salinity, metal concentration). The crystallization rate is mainly influenced by the temperature, crystal concentration in the reactor, and the supersaturation level. Below, the parameters that affect oxidation and crystallization rates are further described.

### 2.1.1 Temperature

The atmospheric scorodite chemical precipitation in sulphate media is carried out at temperatures between 85-95 °C with the aid of seeds (gypsum crystals), thus secondary precipitation is stimulated. In the bioscorodite process, thermophilic Archaea of the order Sulfolobales are used to induce bioscorodite crystallization. Sulfolobales archaea mediate the oxidation of mineral sulphides through simultaneous sulphur and iron oxidation at temperatures between 70 to 95 °C [20-24]. Thus, it is possible to use microorganisms for the bioscorodite process at 70 °C for iron and arsenic oxidation. We did not find any bioscorodite crystallization at temperatures below 70 °C.

### 2.1.2 pH

The induction pH of amorphous ferric arsenate is above 1.5 when relatively low arsenic concentrations are used (1 to 3 g As L<sup>-1</sup>). We found that the optimum pH for the bioscorodite process is in the range of 1-1.2. At these pH values, scorodite precipitation is favoured and the growth of Sulfolobales by iron oxidation. Although the optimum pH for growth of Sulfolobales is between pH 1.5 to 2.5 [25], we observed that these microorganisms keep their oxidizing capabilities at pH values as low as pH 0.8 in the presence of 3 g As L<sup>-1</sup> [19].

### 2.1.3 Biological ferrous iron oxidation

At the pH of 1, the contribution of chemical iron oxidation can be neglected [26]. Sulfolobales use oxygen and carbon dioxide (carbon source) from the air to oxidize ferrous iron. Ferrous iron oxidation is used as energy source for growth and maintenance. At high iron concentrations, the biological oxidation rate may be controlled by the air supply rate. Once ferric iron precipitates with the arsenic from solution, the toxic effect of arsenic to the microorganisms is likely to be reduced. This mechanism also avoids inhibition by ferric iron, which may occur when ferric iron accumulates to concentrations above 10 g Fe<sup>3+</sup> L<sup>-1</sup>. In our research, we supplied ferrous sulphate to the reactors.

### 2.1.4 Arsenic resistance and oxidation

Sulfolobales are resistant to high concentrations of arsenate (As<sup>5+</sup>) and arsenite (As<sup>3+</sup>), without losing their capability to oxidize ferrous iron. These microorganisms can also oxidize arsenite to arsenate in the presence of ferrous iron, i.e. they may use both substrates as an energy source. The microorganisms are tolerant up to 3 g As L<sup>-1</sup>, which is in the range of concentrations often found in metallurgical streams.



### 2.1.5 Fe/As molar ratio requirements

Scorodite mineral has a Fe/As molar ratio of 1 based on its composition. Therefore, ferric iron and arsenate must be supplied with the a similar molar ratio to produce scorodite. When the Fe/As molar ratio is less than 1, no scorodite is produced. When the Fe/As molar ratio is above 3, jarosite precipitation is induced.

### 2.1.6 Crystallization seeding

Chemical scorodite crystallization at 85 °C requires seed addition to initiate the process. In contrast, bioscorodite crystallization starts with the aid of microorganisms and does not require the addition of seeds or crystal parents [19, 27]. As a result, the final product of the process is pure bioscorodite without any other solid phase or seeds such as gypsum. Therefore obtaining the final product does not require a solid phase separation step.

In continuous reactor experiments we have observed that parent crystals are not needed to start the crystallization. Nonetheless, in CSTR type reactors a small fraction of bioscorodite seeds can be added to avoid excessive crystals growth on the walls.

## 2.2. Bioscorodite compared to scorodite crystals

### 2.2.1 Bioscorodite structure

Bioscorodite has the same structural composition as scorodite mineral found in nature. Several analytical methods confirmed that bioscorodite has the same properties as mineral scorodite and no other precipitates were found in the structure of the crystals. A complete characterization of bioscorodite crystals may be found in Gonzalez et al 2010 [19]. XRD analysis confirmed that bioscorodite is highly crystalline as scorodite mineral. The Fe/As molar ratio measured with ICP-OES and SEM-EDX in bioscorodite crystals is always bordering 1 (0.98-1.0). Thermo-gravimetric analysis of bioscorodite (TGA curve) revealed the presence of 15 % structural water (theoretical value for mineral scorodite is  $2 \cdot \text{H}_2\text{O} = 15.6 \%$ ). TGA also revealed that there are no other solid phases present. Additional analysis with FT-IR also confirmed that the bioscorodite structure is exactly the same as that of scorodite mineral.

The bioscorodite crystals initially develop in suspension (batch experiments) but they also adhere to the bottom of the batch bottles. Figure 1 shows the habit of the bioscorodite crystals, which is the same as described for scorodite mineral: orthorhombic with a dipyramidal habit [28]. Other studies on the chemical crystallization of scorodite do not report the dipyramidal habit of scorodite, but an agglomeration of small undefined particles [13, 14]. The crystal size observed in bioscorodite crystals is between 1 to 2  $\mu\text{m}$ . Fully grown crystals developed in bioreactors may however reach a size of several centimetres (Figure 2).



The bioscorodite resembles scorodite found in nature but it shows differences with scorodite produced by chemical crystallization. The similarity of biogenic scorodite crystal with natural scorodite suggests that microorganisms could mediate the occurrence of scorodite in nature.

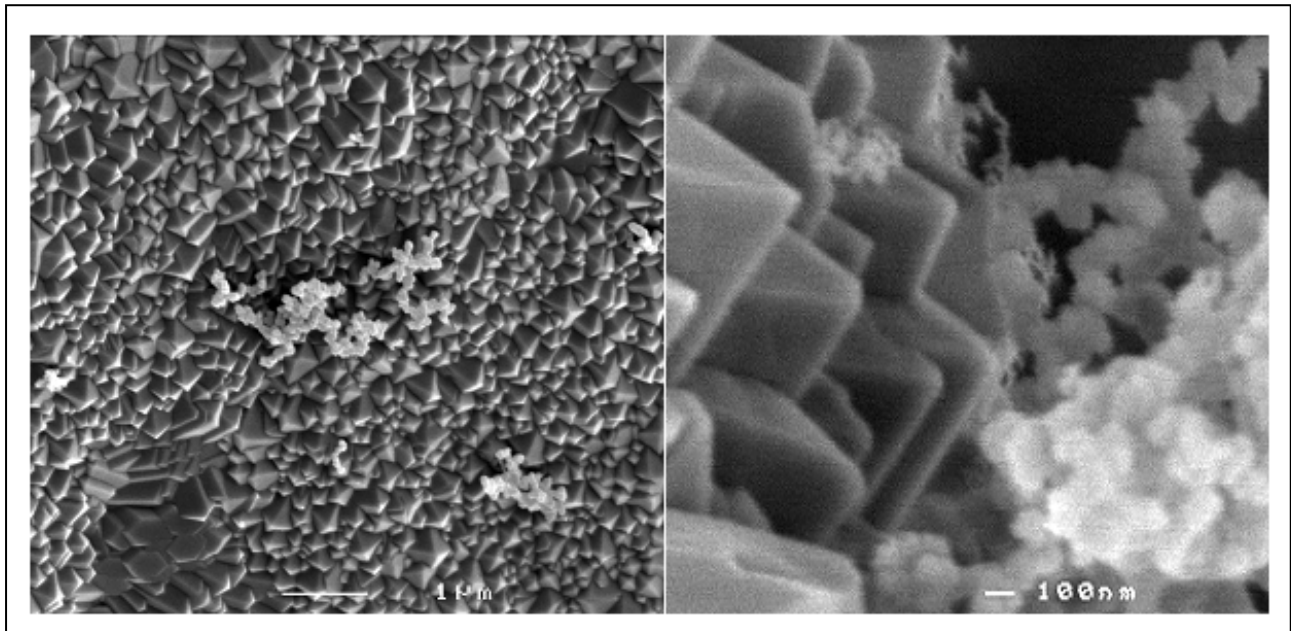


Figure 1: SEM photographs of bioscorodite crystals. The right photograph shows a detail from the typical octahedron habit.

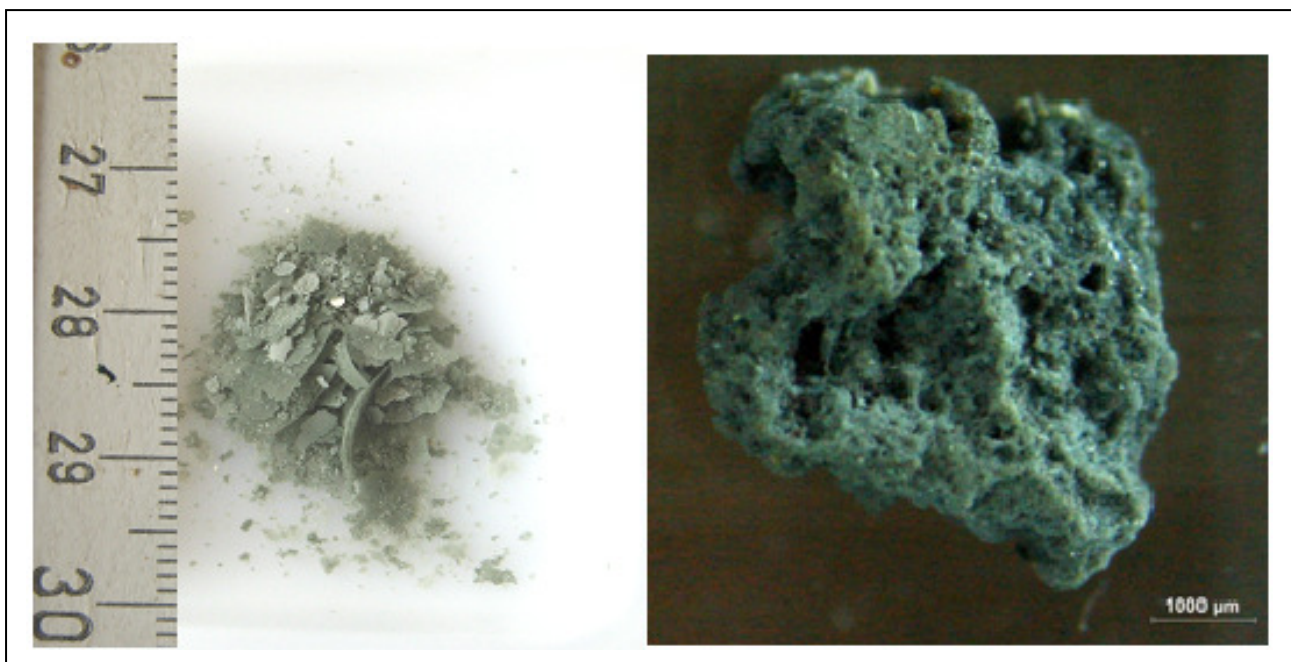


Figure 2: Photographs from bioscorodite crystals produced in batch tests (left) and continuous bioreactors (right) at 70 °C.



### 2.2.2 Bioscorodite stability

The stability of solid toxic waste is assessed by the TCLP (Toxicity Characteristic Leaching Procedure) test, which assesses the leaching a waste will undergo under landfill conditions (pH 5). The threshold concentration for arsenic after 20 h of agitation is  $5 \text{ mg As L}^{-1}$ . This is 500 times higher than WHO maximum contaminant level drinking water of  $10 \mu\text{g L}^{-1}$  [1].

We have used the TCLP test to compare our data to scorodite produced by chemical crystallization. Besides the short term TCLP test (20 h), we have conducted long term stability tests (one year). Reported data on the stability of hydrothermal and atmospheric scorodite is compared in Figure 3 with the long-term stability of bioscorodite crystals. Bioscorodite crystals produced in batch tests result to be highly stable even for long time, equalling the stability of hydrothermal scorodite. The results show a lower stability of bioscorodite produced at the higher Fe/As molar ratio of 3. Bioscorodite crystals are highly stable and highly suitable for arsenic disposal if they are produced with a Fe/As molar ratio of 1. The high stability values of scorodite are due to the slow crystal growth and due to the ageing process favoured in the reactors

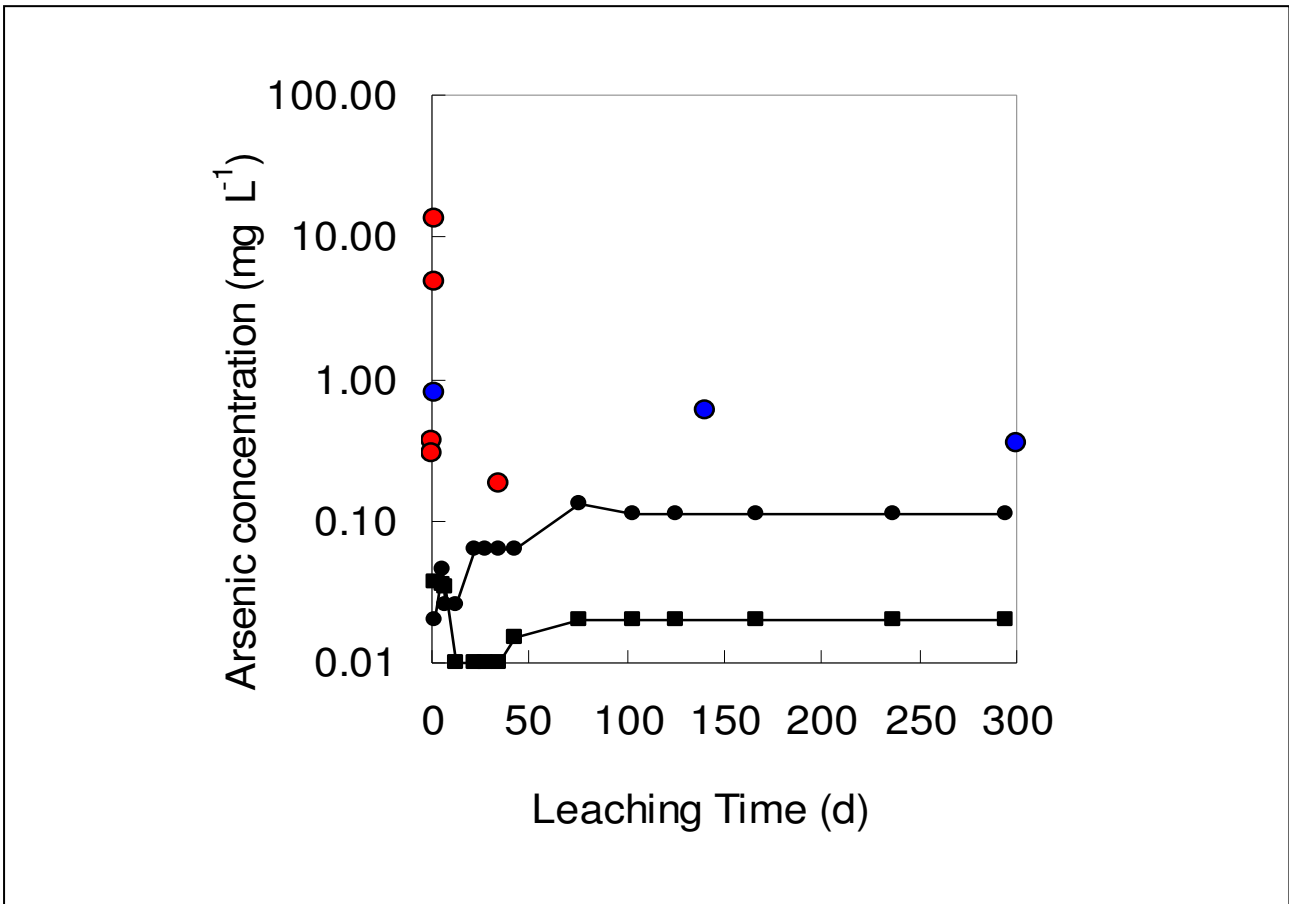


Figure 3: Arsenic leaching concentration from bioscorodite crystals produced in batch tests at 70 °C and pH 1. The values are compared to data reported in literature for hydrothermal crystallized scorodite (blue dots) and atmospheric crystallized scorodite (red dots) Legend: ■ Fe/As=1, ● Fe/As=3.



### 3 Bioscorodite reactors

CSTR type bioreactors are currently applied for continuous bioscorodite crystallization. The supply of ferrous iron and arsenic in these tests is adjusted to a Fe/As molar ratio of 1 to avoid jarosite precipitation. In the CSTR system, high arsenic precipitation rates are obtained, leading to effluent concentrations of  $10 \text{ mg As L}^{-1}$  at steady state conditions. Operating with a hydraulic retention time of 40 h, the scorodite production rate was  $4 \text{ g L}^{-1} \text{ d}^{-1}$  corresponding to  $1.3 \text{ g As removed L}^{-1} \text{ d}^{-1}$ . The biological ferrous oxidation was never affected even though we operated with arsenic concentrations up to  $3 \text{ g L}^{-1}$ . Characterization of the precipitates showed the same bioscorodite composition as found previously in batch tests: highly crystalline bioscorodite without any other solid phase. Bioscorodite crystals grew in the continuous reactor up to a size of 1 cm. The crystals produced in continuous scorodite precipitation experiments were larger than  $0.2 \mu\text{m}$ .

The morphology of bioscorodite produced in continuous bioreactor experiments was different to the flakes obtained previously in batch tests (Figure 4). The layered morphology observed in the continuous reactor was attributed to the lack of seed at the beginning of the operation, which could have promoted the growth of crystals on the walls of the reactor. To avoid excessive crystal growth on the walls, the addition of parent seeds is suggested in CSTR type reactors.

Currently, our studies focus on decreasing the HRT to less than 20 h and to run the process with simultaneous arsenite ( $\text{As}^{3+}$ ) oxidation, ferrous oxidation and scorodite crystallization.

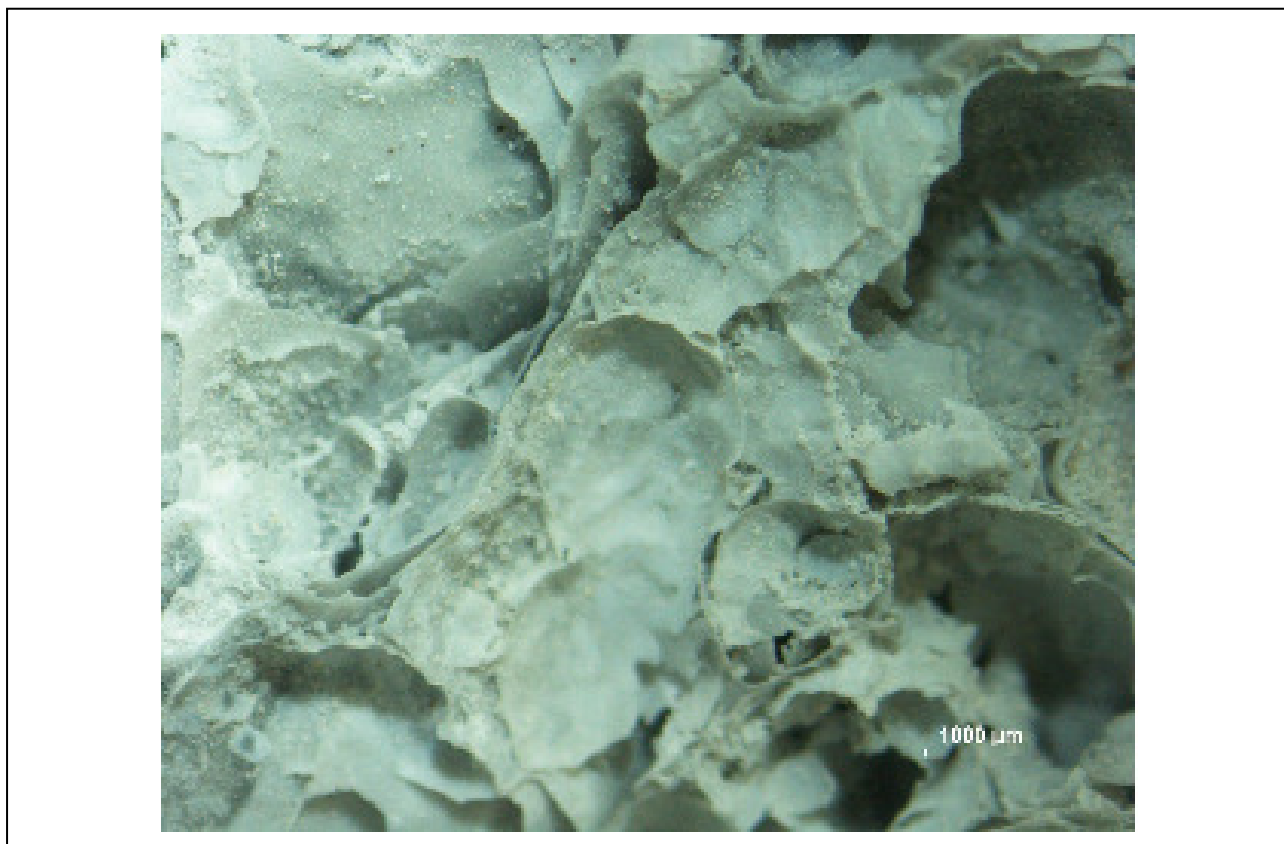


Figure 4: Bioscorodite produced in continuous CSTR type reactors at  $70 \text{ }^\circ\text{C}$  and pH 1.





## 4 Bioscorodite perspectives and applications

The use of the CIRCOX® air-lift loop reactor developed by Paques BV (The Netherlands) is currently studied for the bioscorodite process. The bioscorodite process by itself has several advantages over chemical precipitation. In the Circox reactor, the solids mixing is induced by aeration, which means that energy cost associated to mixing by an impeller are avoided. The later also brings the possibility to use large volume CIRCOX® reactors as mechanical problems due to mixing are avoided.

The bioscorodite process applied in a CIRCOX® bioreactor may have the follow advantages:

- Low investment costs in reactor construction and scale up.
- A low supply of Iron per Arsenic (Fe/As molar ratio = 1). Besides there are different sources of iron or arsenic that can be used for the process, depending on the streams to be treated (as shown in Figure 5).
- Low operational costs. Chemical oxidants like pure oxygen or hydrogen peroxide, pH neutralization and external seeds such as gypsum are not needed for the bioscorodite process. Mixing in the biocrystallization reactor is achieved by air supply. Air supply also provides oxygen for the biological oxidation of ferrous and carbon dioxide as a carbon source for growth.
- Low shear rates for thermophilic microorganism may be beneficial at high conversion rates.
- Solids retention leads to bioscorodite solid separation and purge. The latter is favoured by the high density and the big size of bioscorodite flakes, which make it possible to operate the process at high upflow velocities. While smaller, nascent crystals remain on the top of the bed, larger solids settle at the bottom of the reactor. The bioscorodite purge is selected from the older crystals deposited at the bottom of the reactor. Thus, selection of stable crystals is feasible and safe disposal can be achieved.

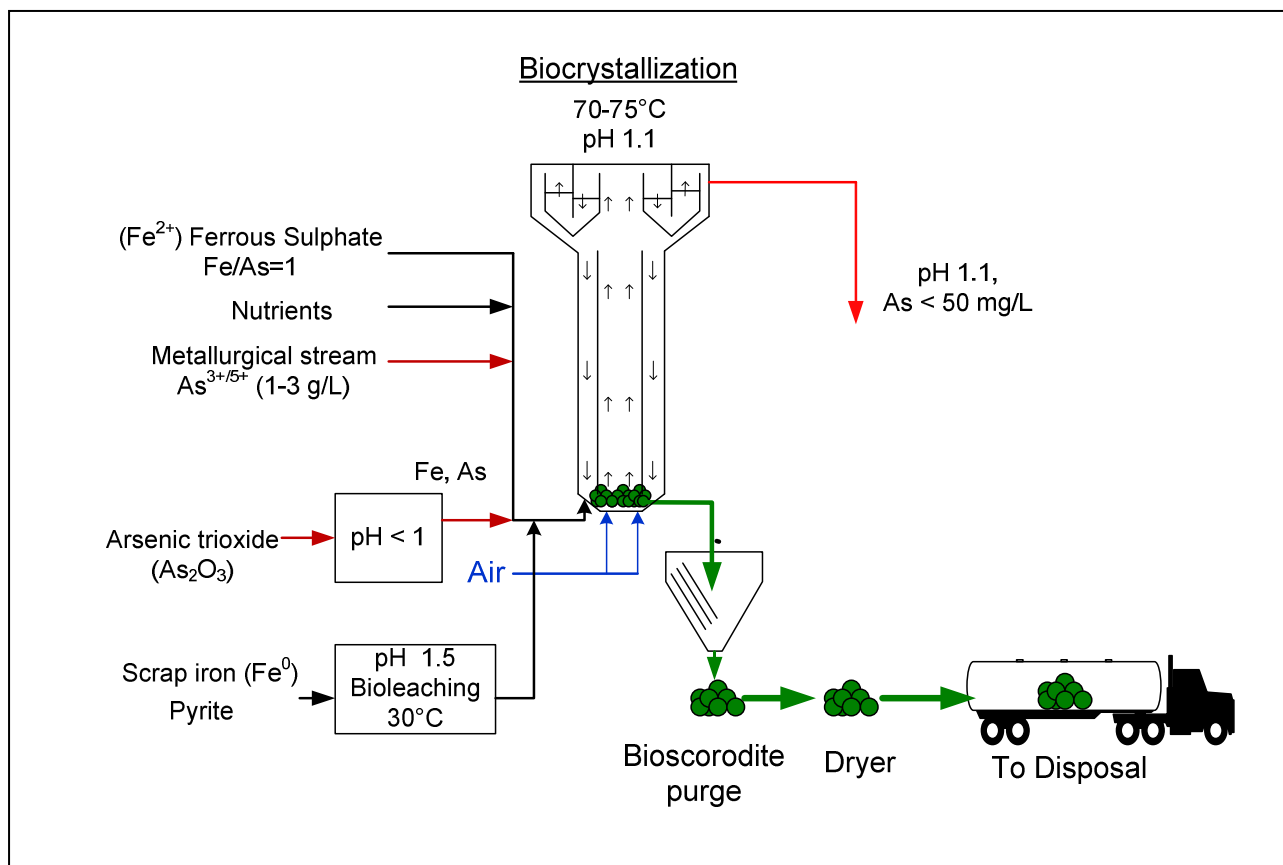


Figure 5: Lay-out of the bioscorodite process and its applications.

Suitable applications for the bioscorodite process can be found in various processes. The main applications for the bioscorodite process are in metallurgical processes. Arsenic trioxide from smelting or roasting of nonferrous metal ores can also be transformed into bioscorodite.

## 5 Environmental impact of Bioscorodite

Bioscorodite crystals resemble very much the mineral scorodite. Its long time stability properties suggests that bioscorodite is very safe material to dispose arsenic at landfill conditions.

The operational and economical advantages of the bioscorodite process make it a suitable process for safe arsenic immobilization.

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