BIOLOGICAL TREATMENT OF MINING WATER CONTAINING ARSENIC: FROM LABORATORY TO PILOT SCALE

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ABSTRACT

In 1987, a mining prospecting campaign detected a gold-arsenopyrite mineralization in the Loperec site (Finistere department, Brittany, France). In 1992, the digging of an exploration gallery induced the outflow of 10 m^3 h^{-1} drainage water containing 5 to 12 mg L^{-1} of iron and 0.2 to 2.0 mg L^{-1} of arsenic (mainly in the form of AsIII) at the gallery outlet. These contents are higher than the quality standards and thus, require a treatment to remove As from the effluent before being discharged in the environment. Laboratory experiments showed that the indigenous bacterial population promoted As(III) and Fe(II) oxidation in temperature, water composition and oxygen availability conditions close to those of the site. Immobilizing the bacteria on pozzolana increased oxidation rates compared to on-site natural conditions. Thus, a study was launched in order to develop a passive on-site treatment process with low economical and environmental costs. This process was based on the biological oxidation of As and Fe by indigenous bacteria, followed by the co-precipitation of both elements. This paper presents the different stages of the process development, from laboratory investigations and on-site experiments, to pilot setting-up.

1. INTRODUCTION

Arsenic is a common trace-level constituent of gold-quartz vein deposits in mining regions. This toxic metalloid is often present in waste material, water and soil near gold mining areas. The discharge of mining drainage water containing arsenic contributes to its dispersion in the environment. The resulting contamination of surface waters, groundwater and sediments is a matter of great public concern due to the deleterious effects of arsenic on human health.

In 1987, a mining prospecting campaign detected a gold-arsenopyrite mineralization (cherts and quartz veins) in the Loperec site (Finistere department, Brittany, France). In 1992, the digging of an exploration gallery induced the formation of drainage water which was then discharged into the environment after partial refining in a settling pond. Drainage flow-rate varies between 10 and 30 m^3 h^{-1} and the arsenic concentration between 10 and 500 µg L^{-1} for a pH close to 6.5. These concentrations are higher than the French quality standards (which are set to 100 µg L^{-1} for arsenic in this kind of context), and thus, a treatment is required to remove the As from the effluent before discharging it in the environment.

In water, arsenic exists mostly as trivalent arsenite (As (III)) and pentavalent arsenate (As(V)), both forms being toxic to living organisms. Most of the existing treatment processes are effective only on As(V) which forms anionic complexes and is therefore more easily converted into solid waste, unlike As(III) which forms mobile neutral complexes. As a consequence, the removal of arsenic from water requires a preliminary oxidation step. The chemical oxidation of As(III) by O_2 is very slow (Jekel, 1994), and the use of oxidant chemicals entails high operation costs (US-EPA, 1998). In Loperec, a biological As(III)-oxidizing activity was detected in diverse micro-environments along the water stream, from the source to the discharge point (Battaglia-Brunet et al., 2006). In this context, the present study sought to investigate the possibilities of developping a passive on-site treatment process based on two steps:

(i) biological oxidation of As(III) by indigenous bacteria,

(ii) co-precipitation of As(V) with iron and/or its adsorption onto iron hydroxides contained in the drainage (2 to 10 mg L^{-1} Fe).

Several types of experiments were set up:

- laboratory experiments in columns with a synthetic effluent in order to determine the residence time needed to completely oxidize As(III) with Loperec bacteria;
- on-site experiments with the same column apparatus fed by the mining drainage water;
- long-term pilot experiments to confirm the results obtained in short-term column experiments and to determine critical operation parameters which will have to be taken into account when designing the entire treatment process.

This paper presents the first results of this study which is still under way.

Abstracts of the International Mine Water Conference
Proceedings ISBN Number: 978-0-9802623-5-3
Produced by: Document Transformation Technologies cc

19th – 23rd October 2009
Pretoria, South Africa
Conference organised by: Cilla Taylor Conferences

2. MATERIALS AND METHODS

Characteristics of Loperec Mine Drainage Water

Loperec mine drainage water is characterized by the high level of variability of its flow-rate and its As and Fe contents. The flow-rate varies between 10 and 30 m^3 h^{-1} depending on rainfall. As concentration varies between 10 and 500 µg L^{-1} whereas Fe contents is comprised between 2 and 10 mg L^{-1}. As can be seen in figure 1, As and Fe follow the same variations. The proportions of As(III) and As(V) also vary considerably (see figure 2).

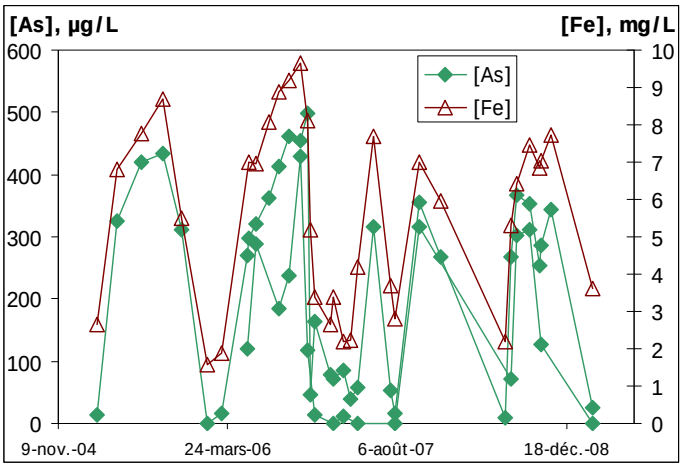


Figure 1. Evolution of arsenic and iron contents in Loperec mine drainage water from the beginning of 2005 until now

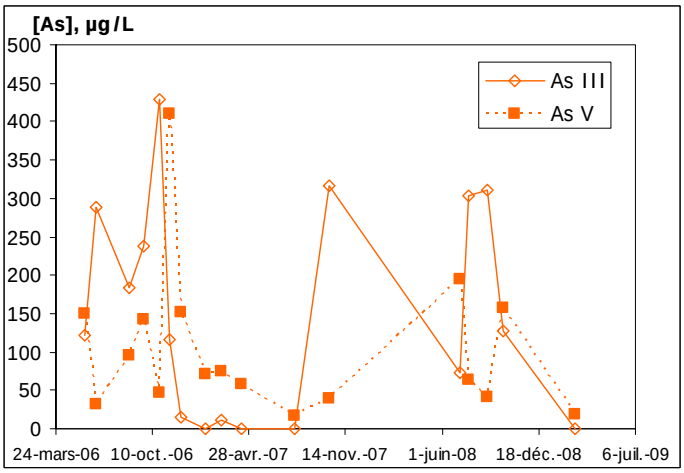


Figure 2. Evolution of As(III) and As(V) contents in Loperec mine drainage water from the beginning of 2005 until now

The other parameters measured are much more stable: pH 6.0 to 7.0; redox potential, -50 to -30 mV (ref. Ag/AgCl); temperature 11°C. The concentrations of other chemical components present in the water are as follows:

Ca 37.2 mg L^{-1}; Mg 11.5 mg L^{-1}; Na 16.7 mg L^{-1}; K 2.1 mg L^{-1}; HCO_3^- 102 mg L^{-1}; Cl 19 mg L^{-1}; NO_3^- 1.3 mg L^{-1}; NO_2^- 0.12 mg L^{-1}; SO_4^{2-} 53 mg L^{-1}; H_3PO_4 0.1 mg L^{-1}; F 0.1 mg L^{-1}; SiO_2 17.1 mg L^{-1}; Sr 0.12 mg L^{-1}; Ni 23 µg L^{-1}; Zn 18 µg L^{-1}; Ba 17 µg L^{-1}; Co 6 µg L^{-1}.

Laboratory Experiments in Fixed Bed Column Reactors

Column experiments were performed in 2 L PVC columns equipped with water jackets, with an inner diameter of 7.2 cm. They were filled with 1400 g of 2-5 mm pozzolana pieces. Both the column and the feed reactor were maintained at 12°C using a cryothermostat. The columns were inoculated with 2L of mine water from the site and then continuously down-flow fed with a synthetic mine water basal solution at pH 6. Air was injected at the bottom of the columns. Dissolved oxygen (O_2 4100 transmitter with a Inpro® 6400 sensor, Mettler-Toledo, Colombus, OH, USA), pH and redox potential (pH 197-S, WTW, Weilheim, Germany) were measured at the top and bottom of the columns.

In the first column, C1, the residence time was lowered from 24 to 4h whereas, in the second column, C2, the residence time was lowered from 10 to 0.5h.

On-Site Experiments in Fixed Bed Column Reactors

After 40 days of laboratory experiment, column C2 was carried on-site and continuously fed with mine water from the site with a residence time of 1h-. A blank column filled with fresh pozzolana was fed in the same conditions. These two on-site columns were aerated by injecting 5 L h^{-1} air.

On-Site Pilot Experiments

Using the results from the column experiments, a pilot bio-reactor was designed and built on-site (see figure 3). It was composed of two ponds: the first one (5.4 m^3) was dedicated to iron hydroxide settling whereas the second one (1.75 m^3) which was filled with 20-40 mm pozzolana pieces was dedicated to biological oxidation of As(III) and As(V) co-precipitation with Fe. The pilot was continuously fed with mine water at a flow-rate corresponding to a residence time of 1h in the second pond. The settling pond was added to the bio-reactor in order to prevent a premature plugging of the pozzolana by iron hydroxides which formed in the feeding water due to the high Fe concentration of the drainage mine water. Both ponds were connected with a pipe which fed the second one by up-flow. This type of feeding was chosen to prevent the appearance of short-circuits due to pozzolana plugging by iron hydroxides.

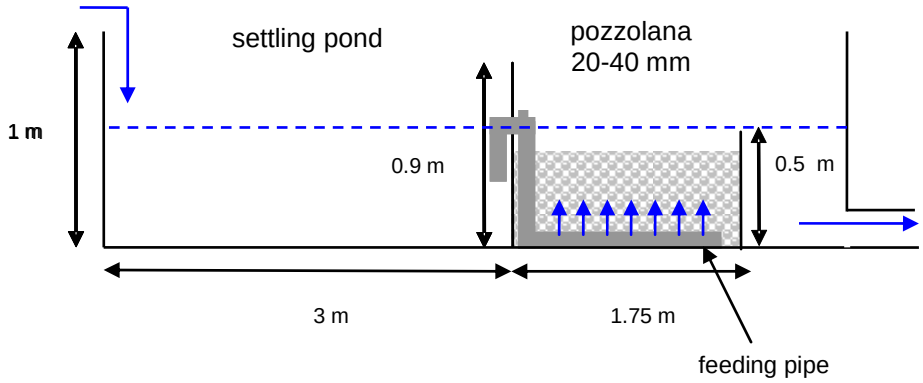


Figure 3. Drawing of the pilot bio-reactor of Loperec

3. RESULTS AND INTERPRETATION

Laboratory Experiments

Figure 4 shows the evolution of As(III) and As(V) concentrations at the inlet and outlet of columns C1 and C2. A few days after inoculation, the As(III) oxidation was nearly complete whatever the experimental conditions (residence time, As(III) content at the inlet, O_2 concentration).

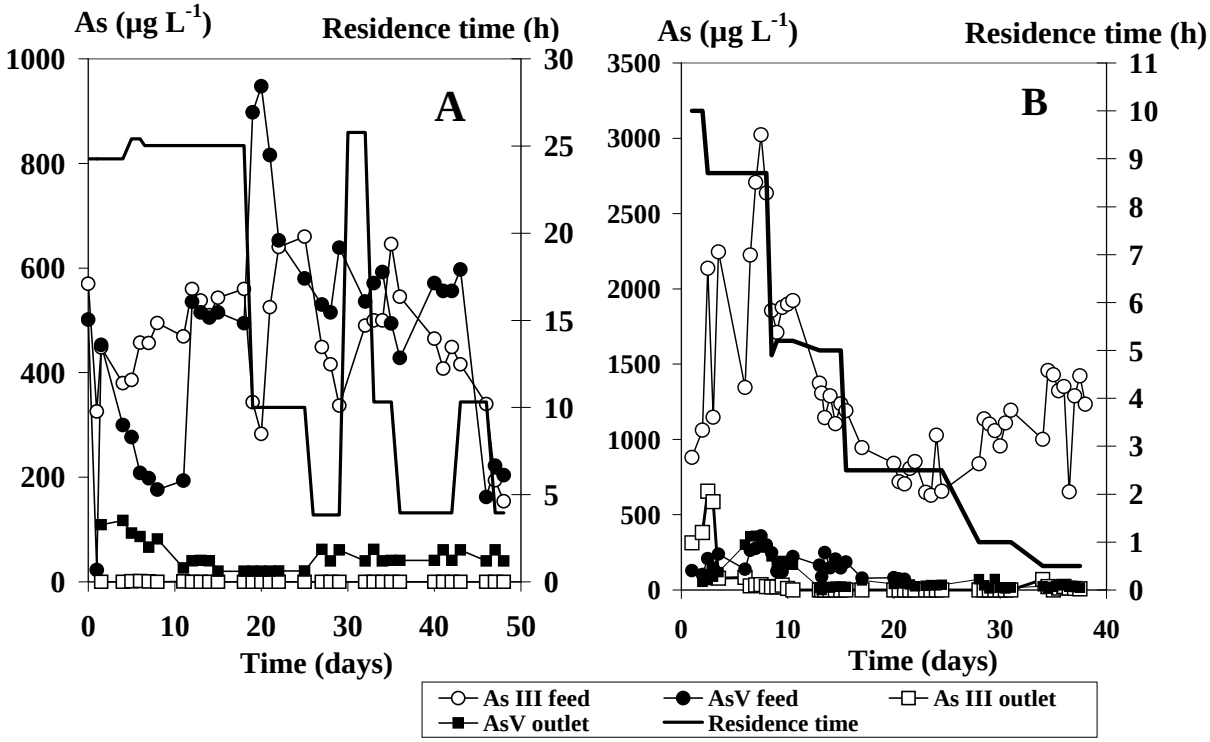


Figure 4. Evolution of As(III) and As(V) contents at the inlet and outlet of columns C1 (figure A) and C2 (figure B)

As(V) concentration at the outlet was higher than As(III) concentration but much lower than the total As concentration at the inlet of the columns. This indicates that a significant part of As(V) was adsorbed by iron hydroxides which precipitated in the column as shown by the development of a red sludge starting from the top of the column and slowly progressing down towards the bottom. Moreover, in the experimental conditions tested, nearly all the Fe(II) contained in the feeding water was oxidised.

When bacterial activity was well established (after 20 days of experiment), the concentration in dissolved O_2 (varying between 2 and 8 mg L^{-1} depending on air flow-rate injection) didn't influence the oxidation rates of Fe(II) and As(III). Fe(II) was totally oxidised, and the oxidation rate of As(III) was higher than 90%.

On-Site Column Experiments

Figure 5 shows the evolution of Fe(II), As(III) and As(V) in the laboratory inoculated column and in the non-inoculated column both fed with mine water on site. In the bio-reactor inoculated in the laboratory, As(III) and Fe(II) oxidation was almost complete from the beginning of the on-site experiment. The removal of As(V) was also efficient since its concentration at the outlet of the column was lower than 20 µg l^{-1}.

In the non-inoculated blank column, the same efficiency as in the laboratory inoculated column was obtained after 15 days of operation, which is thus the time needed to form an efficient biofilm with the bacteria contained in the mine water.

We noticed that the air injection in the column gives O_2 concentrations between 2 and 3 mg L^{-1}, which seems to be enough to allow biological oxidation.

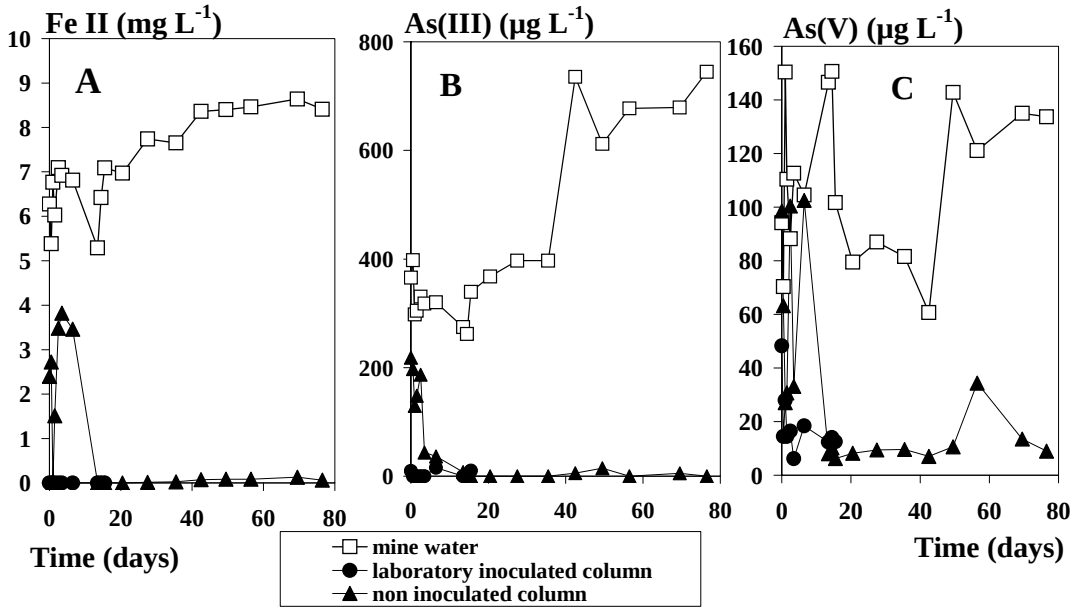


Figure 5. Evolution of Fe(II), As(III) and As(V) concentrations in the mine water and at the outlet of the columns

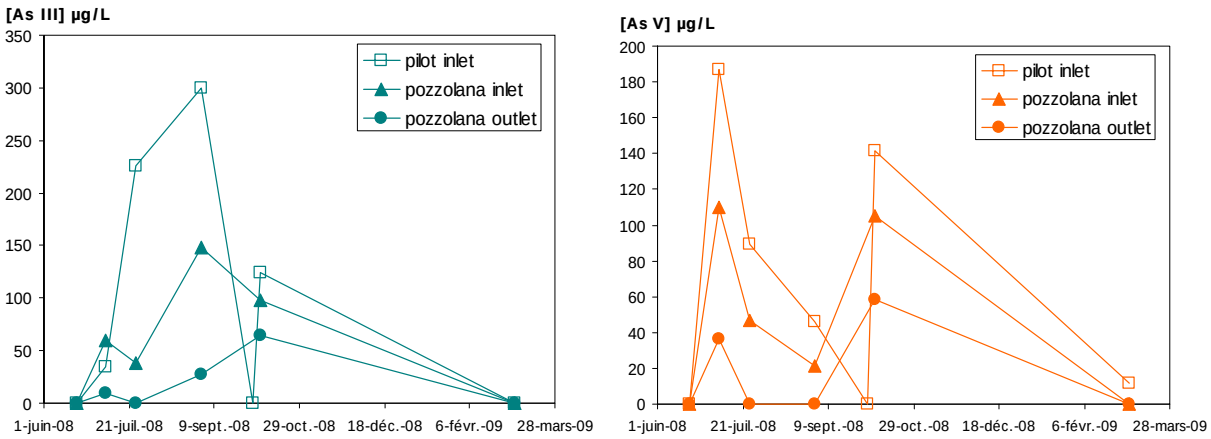
On-Site Pilot Experiments

Figure 6 shows the evolution of As(III), As(V), As, and Fe concentrations at the pilot inlet and at the pozzolana pond inlet and outlet. As was already mentioned, the chemical characteristics of the mine water that feeds the pilot vary significantly with time.

Contrary to the column experiments, As(III) and Fe removal was not complete in the pilot. For As(III) the removal rate varied between 48% and 100%, whereas for Fe, it varied between 36% and 100%. Fe precipitated under the form of amorphous iron hydroxides, probably ferrihydrites. Eh, pH, and temperature didn't change between the inlet and the outlet of the pilot and remained stable in time; O_2 concentration varied from 4 to 5 mg L^{-1} at the pilot inlet, which is much higher than the minimum of 2 mg L^{-1} used in on-site column experiments. These results suggest that an active population of As(III)-oxidizing indigenous bacteria present in the mine water settled in the pilot, but its activity was not enough to completely remove As(III). We noticed that part of the oxidation process occurred in the settling pond and not only in the pozzolana bed. In some cases even, As(III) removal was far from being negligible in the settling pond.

As(V) concentration in the pilot outlet varied from 0 to 60 µg L^{-1}, which remained much lower than the total As concentration at the pilot inlet (from 0 to 350 µg L^{-1}). Most of the As(V) present in the feeding water or resulting from As(III) oxidation was thus removed by co-precipitation and/or adsorbtion onto iron hydroxides. Two As(V) peaks were observed at the pilot outlet in July and October 2008, both corresponding to Fe peaks. This suggests that Fe oxidation and precipitation were not enough to allow a sufficient As(V) removal.

Most of the time, total arsenic concentrations at the pilot outlet were lower than 100 µg L^{-1} which is the threshold concentration for discharge in the environment. Moreover, both As peaks higher than 100µg L^{-1} correspond to bad iron removal.



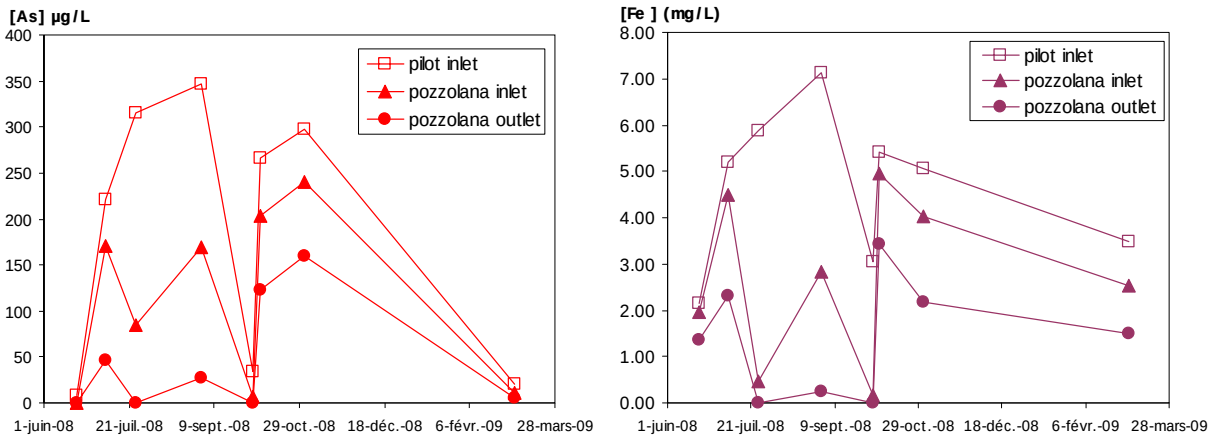


Figure 6. Evolution of As(III), As(V), As, Fe concentrations in the pilot

4. CONCLUSION

The present study showed that the bacterial community naturally present in Loperec mine water is able to promote As(III) oxidation and thus arsenic removal from the liquid phase. Pilot-scale experiments showed that this phenomenon can be used to develop an on-site passive treatment process. Pilot experiments will be continued in order to explain the difference of As(III) and As(V) removal between columns and pilots scale experiments and to optimize the process. In particular, further investigations will be carried out in order to study the influence of As concentration variations in the feeding water on bacterial activities, to understand the differences and similarities between the settling pond and the pozzolana bed, and finally to determine the optimal residence time.

5. REFERENCING

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