

# Passive treatment of mine seepage with high arsenic concentrations

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## Abstract

In the tailings dump of the closed gold mine “Le Châtelet” (France), a containment cell created to store highly contaminated As wastes is slowly filling up due to water infiltration. Two passive solutions were investigated to treat this acidic water containing 2 to 4 g/L As, i.e. evaporation and adsorption. The evaporation rate studied in the laboratory and on site was in the range 415-523 L/m<sup>2</sup>/4 months (treatment only in summer). Adsorption tests carried out with iron waste (shavings) or iron-based commercial material ASP<sup>®</sup> (Ovive) showed that these two materials used in series allowed both an efficient As removal and acid consumption without releasing dissolved Fe.

**Keywords:** Seepage, arsenic, evaporation, adsorption

## Introduction

In the tailings dump of the closed gold mine “Le Châtelet” (north of Massif Central, France), a containment cell was created for the storage of 12,000 m<sup>3</sup> of arsenic (As) contaminated wastes. This cell is slowly (42 m<sup>3</sup>/y) filling with a seepage which then becomes acidic (pH 3.0) and must be emptied every 5 to 6 years to maintain its structural integrity. Due to the high As concentration (2 to 4 g/L), the pumped water is currently disposed of within an incinerator. Two passive alternative solutions were investigated: evaporation and adsorption.

Adsorption of As on iron (Fe) oxides is one of the most common processes used to remove As from water (Mohan and Pittman, 2007). Arsenate As(V) is more efficiently adsorbed than As (III) on goethite and ferrihydrite type-oxides under moderately acidic conditions (Dixit and Hering, 2003). It should thus be possible to use an inexpensive material rich in metallic Fe as the adsorbent, after iron oxidation induces the formation of Fe(III) oxides which adsorb As. As zerovalent Fe powder can be quite expensive, in this study it is proposed to replace it with industrial Fe waste. Neumann *et al.* (2013) used industrial granular waste rinsed with water then treated with acetic or citric acid to form Fe (III) on the surface. Their system consists of tanks in series, with multilayer filling (sand, Fe, layer

of activated carbon). Bretzel *et al.* (2020) also used tanks filled with nails, sand and gravel to remove As from drinking water in Burkina Faso; in this case the initial As concentration was around 1 mg/L. Sekula *et al.* (2018) used industrial Fe scrap to treat As in neutral mine drainage containing on average 0.5 mg/L of As. The residence time in this reactor was 2.2 h. The reactor operated for 2 years, treating 360 L/h. It contained 150 kg of Fe, and made it possible to eliminate approximately 3.15 kg of As in total, which represents 21 mg of As eliminated per g of Fe, a value close to that mentioned by Leupin *et al.* (2005). However, in both cases, the treated water was much less contaminated than this seepage water. In more comparable conditions, Makris *et al.* (2006) used Fe-based wastes from water treatment plant to adsorb As. The As concentrations tested ranged from 300 to 3000 mg/L (therefore the order of magnitude of the seepage water from Le Châtelet). Their experiments were carried out at pH 6 with As (III) or As (V). Adsorption kinetics was a little higher with As (V) but efficient adsorption was also observed with As (III). About 50% of the As (with an initial concentration of 3 g/L) was adsorbed in 1 hour, with adsorption increasing to as much as 80-90% after 50 hours.

Evaporation is not a traditional technique for treating mine drainage, probably

because large areas in an arid climate are necessary for the treatment of AMD and these areas generate naturally low flow rate AMD. However, work by Hanahan 2000, Mapanda *et al.* 2007 and Ravengai *et al.* 2004 demonstrate its potential to reduce the volume of water requiring treatment. This is especially true where water flow is low. Le Châtelet site makes it possible to consider this solution. The objective of the present study was to compare adsorption and evaporation in small scale systems to treat acidic seepage containing a high concentration of As.

## Methods

The seepage water presents the following range in chemistry: pH 2.7-4.5, total As 500 – 4 000 mg/L, SO<sub>4</sub> 2500 mg/L, Cl 400 mg/L, Fe 100–250 mg/L, Si 60 mg/L, PO<sub>4</sub> 8–140 mg/L, Mn 10 mg/L, Ni 0.7 mg/L, Zn 0.5 mg/L, Al 0.5 mg/L, Sb 0.4 mg/L.

Evaporation tests at laboratory scale (5.4 L in 257 cm<sup>2</sup>) were carried out for 37 days in an environmental chamber at a temperature of 16.7°C and a relative humidity of 70%, representative of the average conditions during the 4 summer months over the past 20 years on the site. Wind speed was uncontrolled and not measured. Evaporation was monitored via mass measurement. At pilot scale, tests were carried out for 122 days from May 7 to September 19 2022, on site, in a 64 L container (1660 cm<sup>2</sup>) located under a 2.3 m roof cover to prevent rain from refilling the pilot. Evaporation was monitored via water level measurement. Temperature and relative humidity were monitored nearby at Montluçon aerodrome (19 km from the mine) by the French national meteorological service. Evaporation rates were compared to a simulation based on Penman equation (1948) and taking into account the effect of salinity with the formula proposed by Bonython (1966): Salinity Factor = 1-salinity (‰) x 0.00086 and assuming no precipitation. The mineral precipitation produced during evaporation was analyzed by x-ray diffraction (XRD) (BRUKER™ D8 ADVANCE).

Adsorption tests were carried out in two 300 mL glass columns (32 X 3.5 cm), equipped with sampling ports, spaced 6 cm apart, used to take samples (syringes and needles) for

profiles. One column was filled with 145 g Fe waste (IW), (5 mm long shavings) and a second column was filled with 381 g Fe-based commercial adsorption material ASP® (2-4 mm, Ovive). Both columns were continuously fed with the seepage water (SW) for 60 days. The residence time measured by weighting the filling water and controlling the flow rate, was 80 h in the ASP column and 189 h in the IW column. After 30 days, the IW column was aerated by air bubbling to increase Fe oxidation and adsorption potential. Dissolved As was analysed by inductively coupled plasma mass spectrometry (ICP-MS), and total dissolved Fe was quantified by colorimetric method (phenanthroline complex), after reducing dissolved Fe (III) to Fe (II) using hydroquinone (Duke and Parchen, 1955).

## Results

### Evaporation

The evaporation rate measured in the laboratory was 0.11 L/d (Fig. 1) which corresponds to 523 L/m<sup>2</sup> evaporation over 4 months, a value that is 19% greater than the theoretical value calculated with Penman's formula. This is probably due to the unknown "wind" speed in the environmental chamber. Due to a technical issue, the experiment was interrupted before complete evaporation was achieved. Therefore, the effect of salinity on evaporation rate, which should be significant at higher salinity was not properly assessed. However, this does not undermine the conclusions, as during the evaporation of at least 85% of the water, the effect of salinity is negligible. Furthermore, dewatering should not be carried excessively for safety reasons (flying dust) and for practical reasons (sludge pumping).

During summer 2022, average onsite temperature and humidity was 20.7°C and 65.5% rH respectively. The evaporation rate was 0.56 L/d (Fig. 2), which is 415 L/m<sup>2</sup> for four months or 22% less than the theoretical value, shown in orange. This could be due to the unknown wind speed on site or because of the effect of the roof (limitation of air renewal above the evaporator). Based on these results and considering the average temperature and relative humidity during the four summer months over the past 20

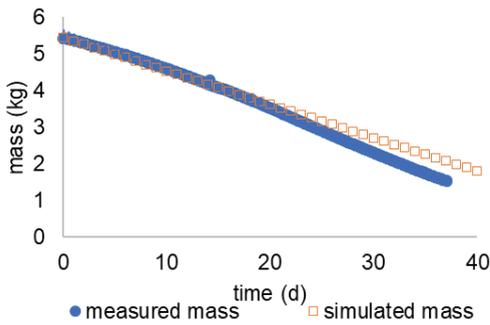


Figure 1 Measured and simulated water mass evolution during lab scale test in the environmental chamber

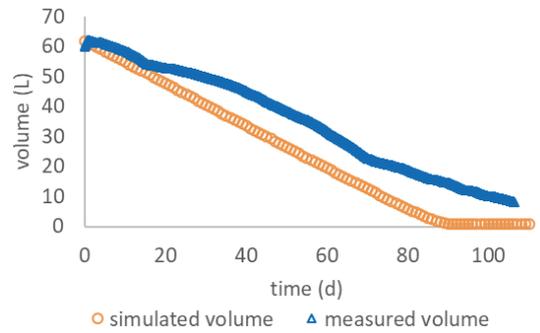


Figure 2 Measured and simulated water volume evolution during pilot scale test on site

years on the site, the surface area required to treat one year's accumulation of seepage was estimated at 122 m<sup>2</sup>. In September, the decrease in temperatures and the increase in humidity caused a slowdown of evaporation and the experiment was therefore stopped. Once again, this experiment cannot inform the effect of salinity. However, the sample was fully evaporate in the laboratory oven, which produced 1.3 kg of sludge (at 50% humidity). Complete evaporation induces a decrease of waste volume by at least 98%.

The partial chemical composition of the solid produced during the on-site evaporation test is: SO<sub>4</sub> 24.7%, Fe as Fe<sub>2</sub>O<sub>3</sub> 3.1% and As 27.1%. Iron was analysed by XRF, sulfate by gravimetric determination and arsenic by ICP-MS after tri-acid

digestion. The XRD results (Fig. 3) shows that the main As bearing mineral is Juansilvaite (Na<sub>5</sub>Al<sub>3</sub>[AsO<sub>3</sub>(OH)]<sub>4</sub>[AsO<sub>2</sub>(OH)<sub>2</sub>](SO<sub>4</sub>)<sub>2</sub>), and that it co-precipitated with gypsum and other phases listed in Figure 3.

### Adsorption

During the first experimental step, the two adsorption columns worked independently, with each directly fed with the seepage water. The ASP column effectively removed dissolved As, with As concentration decreasing from 1800 mg/L in the inlet to less than 100 µg/L in the outlet. The IW column did not remove As prior to aeration, but following aeration, the dissolved As concentration was decreased from 1800 mg/L in the feed to values close to 10 mg/L in the effluent.

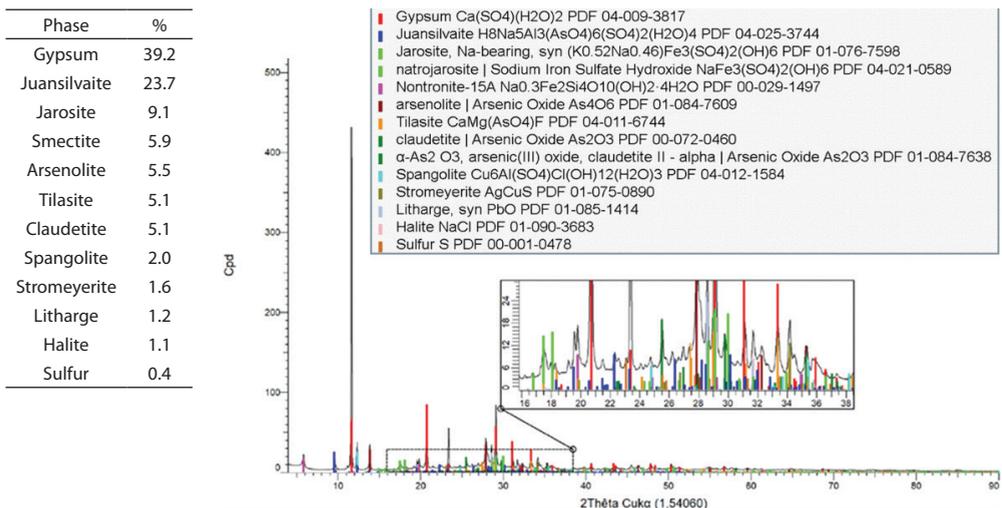


Figure 3 Results of XRD analysis of the final waste resulting from evaporation

The profile of dissolved As, dissolved Fe and pH were measured on day 50 as shown in Figure 4. The dissolved As concentration decreased along the ASP profile down to 22 µg/L, but remained higher than 1 mg/L in the IW column (Fig. 4A). The ASP column did not release dissolved Fe, whereas Fe was dissolved in the IW column (Fig. 4B). Dissolved Fe peaked at 500 mg/L in the IW column, probably due to Fe corrosion (Bretzel *et al.*, 2020, Srin *et al.*, 2004). Soluble Fe was probably oxidized and precipitated downstream of L4 with final dissolved Fe concentration remaining elevated (100 mg/L) in the effluent. An increase in pH was initially observed in both columns (Fig. 4C), neutral pH was observed in the ASP column effluent whereas the IW maintained a pH of 5, reflecting equilibrium with iron until it dropped due to acid production following iron oxidation. These results are likely explained by the presence of carbonate minerals in the ASP adsorbant, and by the corrosion of Fe by H<sup>+</sup> in the IW column. Corrosion of Fe in the IW column was followed by oxidation of dissolved Fe (II) and precipitation of Fe (III) hydroxides, this last reaction producing H<sup>+</sup> ions.

The amount of As adsorbed during this experimental phase was calculated for the ASP material from the total volume of seepage water treated during this experimental phase. This calculation indicated that ASP had adsorbed 18.25 mg As/ g Fe and retained capacity for further sorption. Leupin *et al.* (2005) found an

adsorption capacity of 18 mg As / g Fe using granular elemental Fe mixed with sand to treat a groundwater containing 500 µg/L As. Here, we showed that the adsorption capacity of ASP material was at least as efficient as other Fe-based adsorbants, in spite of the high concentration of As and other dissolved minerals present in the seepage. Columns with ASP and IW materials had different capacity for As sorption from the seepage water. The commercial ASP adsorbant was more efficient for As removal and acid consumption, but it is more expensive than IW which was able to reduce the initial As concentration by 99%. These results suggest that a combination of these materials in a two-step adsorption process could optimize both treatment efficiency and cost. To this end, we tested the two columns in series, where the IW column was fed with seepage and the ASP column was fed with effluent from the IW column.

Samples were collected after 3 weeks of continuous experimentation under these operating conditions. Dissolved As concentrations decreased from 2044 mg/L (seepage feed) to an effluent concentration of 350 µg/L (Fig. 5A). Dissolved Fe concentration peaked at 58 mg/L in the IW column, then decreased to less than 50 µg/L in the outlet (Fig. 5B). The pH in the IW column increased from 2.36 (seepage feed) to 6.67 in the outlet (Fig. 5C). These results confirmed the efficiency of combining the two materials

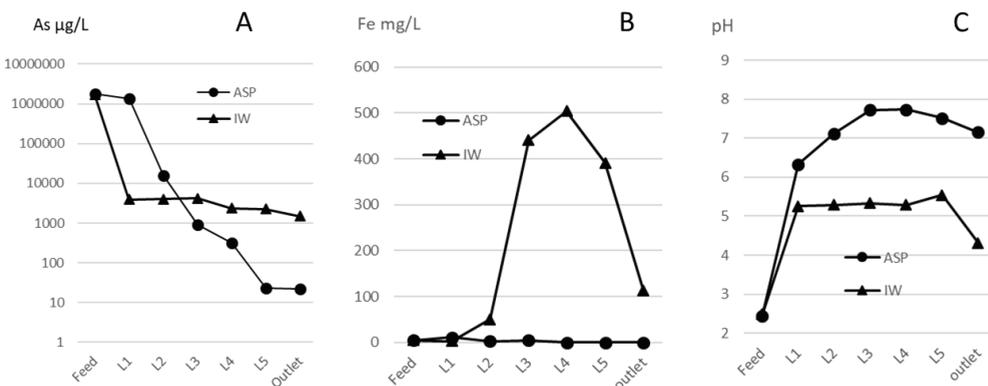


Figure 4 Profiles of dissolved As (A), dissolved Fe (B) and pH (C) in the two adsorption columns independently fed with the seepage water on day 50. Ovine ASP commercial adsorbent (ASP), iron waste (IW). L1 to L5: sampling levels in the columns spaced 6 cm apart.

to remove As from the seepage water and increase pH without increasing the dissolved Fe concentration in the treated water.

## Conclusions

The results of laboratory and on-site pilot evaporation tests showed that the theoretical and measured rates of evaporation were close. The overall measured rate of evaporation during the pilot test was only slightly lower than the theoretical value. Accounting for this difference and based on the average temperatures and humidity of the past 20 years, the required surface area was calculated (122 m<sup>2</sup>) and is compatible with the space available on site. The objective is to pump the water annually to an evaporation pond located at the top of the site, protected from rain by a roof, to enhance removal of As via mineral precipitation due to evaporation during the four summer months.

Passive filters filled with the tested Fe-based materials could be considered as a treatment step to remove As and consume acidity from the seepage water. The high concentration of potential competing chemical species (PO<sub>4</sub>, SO<sub>4</sub>, Cl...) present in the seepage did not limit the As-adsorption efficiency of the tested materials compared with data from other similar applications (Makris *et al.*, 2006; Bretzel *et al.*, 2020). Complementary experiments including adsorption isotherms to determine the sorbents maximum capacity

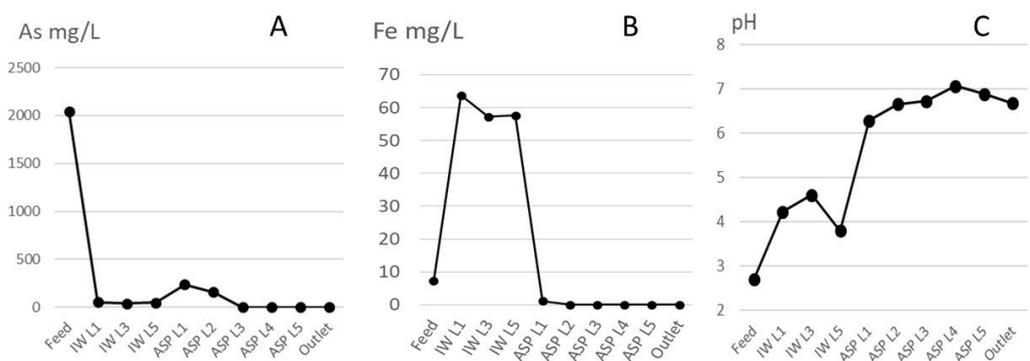
and complementary analysis are needed to up-scale the process and evaluate its capacity to remove other chemical species from the seepage, such as Ni, Zn, Sb, and PO<sub>4</sub>, which could also be adsorbed on Fe oxides. However, this process will probably not remove other solutes from the seepage water, such as Cl, Mn, and SO<sub>4</sub>. Other treatment steps might be needed to reduce the concentrations of these chemical species if their impact on the receiving water is estimated to be significant.

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**Figure 5** Profiles of dissolved As (A), dissolved Fe (B) and pH (C) in the adsorption system composed of the columns working in series. IW column was fed with the seepage water. Ovine ASP commercial adsorbent (ASP), iron waste (IW). L1 to L5: sampling levels in the columns spaced 6 cm apart.

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