

# Treatment Of A Mine Water Containing Arsenic And Thiocyanates: Four Years Results On A Pilot Plant Scale

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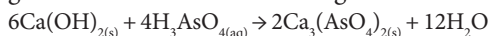
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## Abstract

About 8 million metric tons storage of cyanidation tailings from a former French gold mine produces a 6.5 m<sup>3</sup>/h mine drainage that contains between 11 mg/L and 15 mg/L of As and around 1 g/L of SCN<sup>-</sup> and is currently treated with a lime process. The existing treatment plant produces large amounts of sludge reflecting the large amounts of sulfate present in water and calcium from the lime. The aim of the present study is to validate at pilot scale a semi-passive mine water treatment process that would produce a lower amount of sludge and improve treatment efficiency with target discharge level below 100 µg/L of arsenic. After a review and lab-scale experiments (Vaxelaire 2019) for arsenic and thiocyanates removal, the process tested in the pilot is the adsorption of arsenic on ferrihydrite precipitate combined with the biodegradation of SCN<sup>-</sup>.

## Introduction

The lime treatment of arsenic waters is a precipitation process and has commonly been used in metallurgical production units (Riveros 2001). Arsenic (V) co-precipitates to give calcium arsenate according to:



This process generates large amounts of contaminated sludge, potentially able to release arsenic with time, thus it is not efficient at long term.

In the lime process, arsenic is trapped as calcium arsenate. Process efficiency reaches 90% on average, the outlet concentration being between 0.5 and 1 mg/L of arsenic when objective is generally 0.1 mg/L in discharge waters. However, calcium arsenate is an unstable product that reacts with atmospheric CO<sub>2</sub> to form soluble arsenic and calcite (Riveros 2001). In addition, the current process does not remove thiocyanate from the effluent. Instability of calcium arsenate, the large quantities of sludge produced and high operating cost of lime process led the post-mining department (DPSM) of BRGM (the French geological survey, in charge of the site since 2009) to look for a more efficient process.

In order to develop a new treatment process after a bibliographic review, lab experiments were first performed (Vaxelaire 2019) in batch conditions for assessing

different treatments options that gave the following preliminary findings:

- sulfate reduction is difficult to implement due to water pH between 7.5 and 8, and its buffering capacity, because arsenic sulfide solubility is elevated at high pH;
- adsorption on iron hydroxide sludge is effective and allows sufficient removal of arsenic to meet a discharge threshold of about 50 or 100 µg/L, but it requires large quantities of iron hydroxide sludge that will be converted in As-polluted waste;
- treatment by adding an iron sulfate solution seems to be the most promising.

Subsequently, continuous lab experiment were implemented in columns filled with pozzolana for both thiocyanate bio-oxidation and arsenic adsorption on freshly precipitated iron oxides onto pozzolana, and finally this column was replaced by a settling tank for Fe II oxidation, arsenic adsorption and co-precipitation with iron.

Main results obtained in lab experiments are:

- for thiocyanate biodegradation: a degradation rate of  $4.5 \pm 1$  mg/L/h was observed repeatedly in batch experiments and a 2.5 mg/L/h degradation rate was observed in continuous experiments in columns filled with pozzolana. Higher rate (81 mg/L/h) was obtained by Dictor (1997) over the course of a 6-months

optimization experiment with the same type of mine effluent. The short duration of our experiments could explain the observed low degradation rate. The lack of biofilm development is suspected to be the major factor limiting the degradation rate.

- For arsenic adsorption on iron hydroxide, batch experiments have shown that iron (II) was more efficient than iron (III). Continuous lab experiments in column filled with pozzolana shown that 98% of arsenic removal can be achieved, reaching a discharge concentration below 100 µg/L. This result was obtained by adding a concentrated ferrous sulfate solution to the contaminated water flow in order to have an iron concentration of 20 mg/L corresponding to a molar ratio iron-arsenic of 4.4. In order to improve the process and to optimize operational cost, a simpler process was tested. It consists of mixing iron and contaminated water in a tube before injecting it in a longitudinal settling tank. An arsenic removal rate of 70% has been obtained in settler tank with a discharged concentration of 300 µg/L dissolved arsenic.

Finally, these experiments led to the definition and scaling of the treatment process retained for the pilot experiments. This process consists of a first stage of biodegradation of thiocyanates in aerated pozzolana filter and a second step of treatment of arsenic by addition of ferrous sulfate, composed of a

mixer/settling tank followed by a pozzolana filter to remove the particles remaining in suspension at the outlet of the settling tank.

### Pilot plant description

Figure 1 shows the process diagram of the on-site pilot plant. The pilot is fed with a representative mixture of water collected from tailings storage, 70% water from the “penstocks” bottom drain and 30% water from “top drains”. These waters are pumped and mixed in a tank which allows to feed the pilot by gravity. The treatment of the water in the pilot plant is then carried out in four steps. The first step is the degradation of the thiocyanates by bio-oxidation using three aerated pozzolana filters in series of one cubic meter each, i.e. a total filter volume of about 3 m<sup>3</sup> with a working volume of 1.9 m<sup>3</sup> evaluated by measuring residence times. A second treatment step allows the arsenic to be removed by adding iron and adsorbing the arsenic on the formed iron oxi-hydroxide precipitate. This second treatment step is made up of a settling tank with a volume of 3 m<sup>3</sup>, i.e. an initial theoretical residence time of 30 h. This volume should also allow the produced sludge to be stored for the duration of experiments with the pilot. A concentrated solution of FeSO<sub>4</sub> is injected at the entrance to the settling tank. At the outlet of the settling tank, a third step is achieved by a 1 m<sup>3</sup> pozzolana filter which should stop fine particles that have not settled. A 6 m<sup>2</sup> pond

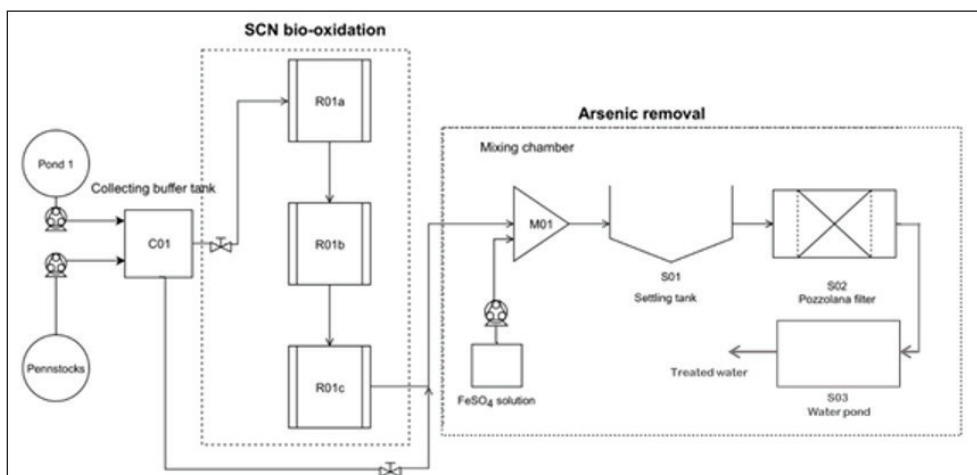


Figure 1 Process flow diagram of on-site pilot experiment.

for a "finishing" treatment as final step (figure 2b) has been added in 2021.

### Operating conditions and monitoring program of on-site pilot

The pilot was operated and monitored on site during four years, between 2019 and 2022. Table 1 shows average operating conditions during the years of monitoring. The pilot plant has treated a  $0.08 \pm 0.03$  m<sup>3</sup>/h flow of contaminated drainage water. The pilot plant was scaled for treating a contaminated water inflow of 0.1 m<sup>3</sup>/h, but due to the clogging of the pumps by iron precipitates, it was difficult to maintain flow at 0.1 m<sup>3</sup>/h. Table 2 shows average composition of inflow-contaminated water. Inflow arsenic concentrations were between 11 and 15 mg/L and thiocyanates concentrations were between 0.87 and 1.1 g/L. Arsenic concentrations were also under estimated at the pilot design step due to an increase of arsenic concentrations in mine drainage. In order to reach an arsenic discharge concentration below 100 µg/L, the flow of concentrated FeSO<sub>4</sub> solution have thus been adapted to obtain a molar rate iron-arsenic around 4.4 as determined in lab experiments.

The monitoring of the pilot was carried out at a weekly frequency during the first 3 years of monitoring and a bi-monthly frequency in 2022, at four points and then 5 points (after the addition of the pond) at the inlet and outlet of the different treatment steps. The physicochemical parameters (pH, ORP, conductivity, temperature and dissolved

oxygen) and the substances presented in Table 2 were monitored. The monitoring of thiocyanates, ammonia and NTK allows to make a balance on nitrogen. Determination of arsenic species (Arsenic III and Arsenic V) was also carried out at the different sampling points in 2019 by separation on ion exchange resin (Ficklin 1983, Montiel 1996, Edwards 1998). These results are partially exploitable because of the uncertainties of the results, mainly because it was not possible to make balance on arsenic: [total arsenic]  $\neq$  [arsenic III] + [arsenic V]. However, from these analyses, it was possible to determine that 70% of the arsenic in the pilot inlet water was in the form of arsenic (III).

### On-site pilot plant results and discussion

Table 3 shows the average results obtained for each year of experiment and figures 3 and 4 show the results of the monitoring obtained in the year 2021. The hatched areas in figure 4 represent the periods during which the pilot was not supplied with iron sulfate.

#### *Thiocyanate bio oxidation:*

The average results (table 3 and figure 3) show a thiocyanate biodegradation rate between 13 and 20%. Thiocyanate degradation kinetics observed from the pilot plant are increasing from year to year between 7 to 12 mg/h/L, over 2020 to 2022. These kinetics are also higher than those observed during the laboratory experiments, ranging from 2.5 to 4.5 mg/h/L.



Figure 2 Pictures of on-site pilot (a: pozzolana bio-filter and iron oxi-hydroxide settling tank, b: finishing pond).

*Table 1 Operating conditions.*

Parameter	Unit	2019	2020	2021	2022
Water flow	L/h	86	86.9 ± 13.9	82.4 ± 20	86 ± 35
SCN flow	g/h	–	78 ± 25	94 ± 34	98 ± 55
Dissolved As flow	g/h	0.93 ± 0.07	1.1 ± 0.2	0.95 ± 0.31	1.3 ± 0.6
Fe <sup>2+</sup> flow	g/h	2.6	3.6 ± 0.4	3.2 ± 0.3	4.2 ± 1
Molar ratio Fe/As	–	3.32 ± 0.46	4.31 ± 0.83	4.9 ± 1.8	5.4 ± 2.6

These results confirm the assumptions made during the design of the pilot (Jally 2019) invoking the slow development of the biofilm. However, the degradation kinetics observed in the biofilters remain lower than the one observed by Dictor (1997) of 81 mg/L/h. It could be explored to stimulate the biological activity that allows the degradation of thiocyanates either:

- by providing nutrients in particular phosphates, however the latter are competitors of arsenic and adsorb on iron hydroxides and can cause a release of arsenic (Senn 2018).
- or by using another support than pozzolana such as activated carbon favoring the development of a more important biofilm (Dictor 1997).

#### *Arsenic adsorption on iron oxi-hydroxide:*

The average results show a dissolved arsenic removal rate of 99.5% from 2020 to 2022. The rate is only 96% in 2019 but in this experiment the iron / arsenic molar ratio was only 3.32 and oxidation of the iron sulfate solution was observed during the experiment. The dissolved arsenic concentration in the discharge is less than 100 µg/L. A concentration of 20 µg/L has been reached in 2022 with an iron/arsenic molar ratio of 5.4. These yields for dissolved arsenic are comparable with the highest obtained in the laboratory experiments which was 98%. The iron / arsenic molar ratios and yields obtained are comparable to that obtained by Halder (2018) who showed that it was possible to remove 99.9% of As V in the form of arsenical ferrihydrite with an iron / arsenic molar ratio between 3 and 6.

The total arsenic removal rate is about 70% over the 4 years of testing. In addition, Figure 4 shows peaks in total arsenic concentration, which correspond to the release of iron

oxi-hydroxide particles in suspension. The addition of a pond (end of 2021) to the pilot plant has improved the total arsenic removal, the efficiency at the outlet of the pond being 83 ± 11% with a discharge concentration of 2.6 ± 2.0 mg/L during the year 2022.

The experiments also show that it is more difficult to remove total arsenic, which is associated with iron hydroxide particles suspended in the water, than dissolved arsenic. Our results, with a yield of 70% removal of total arsenic, was comparable to the yield observed at the settling tank outlet during laboratory experiments. A pond treatment system allows the removal of these suspended particles with a surface removal rate (Ra) of 5.9 ± 3.0 g/m<sup>2</sup>/d.

Moreover, the treatment by addition of ferrous iron (II) appears to be efficient despite the presence of thiocyanates in solution. Finally, it was observed during the experiments that the oxidation of iron (II) into iron (III) of the concentrated iron sulfate solution could reduce the performance of the treatment. One of the possible explanations for the better efficiency of ferrous iron (II) can originate from the fact that the oxidation of iron (II) into iron (III) is coupled with an oxidation of arsenic (III) to arsenic (V) by Fenton effect (Ding 2018). The arsenic (V) then precipitates as arsenical ferrihydrite.

## **Conclusion**

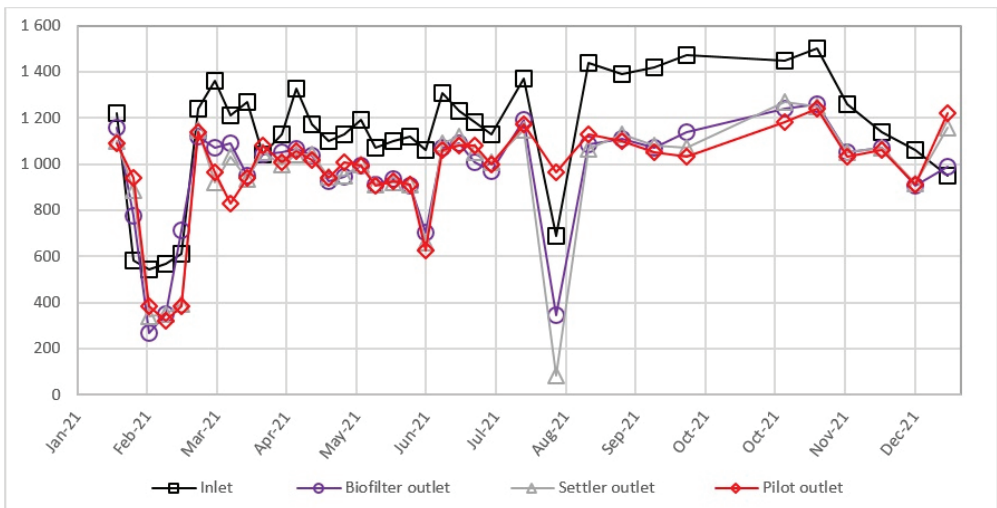
This study was conducted in order to develop and build an optimized mine water treatment plant that will replace the current lime treatment plant. The goal is to develop a more efficient (reduced amount of sludge) and cost effective process. In order to achieve this goal, after lab scale experiments, on-site pilot plant experiments were conducted and key data for the treatment of a mine water containing arsenic and thiocyanate were

**Table 2** Average composition of inflow contaminated water.

Substance	Unit	2019	2020	2021	2022
SO <sub>4</sub> <sup>2-</sup>	mg/L	5725 ± 171	5840 ± 230	5910 ± 630	6120 ± 1000
Na <sup>+</sup>	mg/L	2900 ± 476	2240 ± 420	2200 ± 510	2140 ± 370
SCN <sup>-</sup>	mg/L	1126 ± 67	868 ± 245	1120 ± 260	940 ± 310
HCO <sub>3</sub> <sup>-</sup>	mg/L	190 ± 8	221 ± 28	199 ± 20	190 ± 38
Cl <sup>-</sup>	mg/L	170 ± 8	764 ± 222	174 ± 25	260 ± 250
K <sup>+</sup>	mg/L	77.2 ± 1.5	120 ± 17	79 ± 10	87 ± 19
NH <sub>4</sub> <sup>+</sup>	mg/L	61 ± 57	0.10 ± 0.02	48 ± 20	60 ± 22
NTK	mg N/L	317 ± 21	252 ± 74	302 ± 55	250 ± 54
As <sub>tot</sub>	mg/L	11.4 ± 2.0	13.3 ± 1.8	14.0 ± 4.3	14,9 ± 3,7
As <sub>dis</sub>	mg/L	12.3 ± 1.9	12.9 ± 1.5	12.0 ± 1.4	13,5 ± 3,4
Mn <sub>tot</sub>	mg/L	0.91 ± 0.08	0.75 ± 0.13	0.93 ± 0.20	1,02 ± 0,23
Mn <sub>dis</sub>	mg/L	0.98 ± 0.16	0.52 ± 0.10	0.83 ± 0.20	0,96 ± 0,22
Fe <sub>tot</sub>	mg/L	0.44 ± 0.18	0.40 ± 0.14	1.0 ± 1.1	0,57 ± 0,39
Fe <sub>dis</sub>	mg/L	0.16 ± 0.03	0.08 ± 0.02	0.17 ± 0.21	0,14 ± 0,04

**Table 3** Average results by year.

Parameter	Unit	2019	2020	2021	2022
SCN treatment ratio	%	–	20 ± 13	13,4 ± 6,0	17,8 ± 7,4
SCN degradation rate	mg/h/L	–	7.0 ± 4.0	9.6 ± 3.9	12 ± 11
Asdis treatment ratio	%	96 ± 6	99,5 ± 0,5	99,6 ± 0,8	99,9 ± 0,1
Asdis discharge concentration	µg/L	205 ± 400	62 ± 64	50 ± 97	20 ± 12
Astot treatment ratio	%	70 ± 12	76 ± 19	67 ± 34	71 ± 16
Astot discharge concentration	mg/L	3.45 ± 1.6	3.2 ± 2.5	4.3 ± 4.6	4.6 ± 2.9



**Figure 3** Evolution of thiocyanate concentration in the pilot during year 2021.



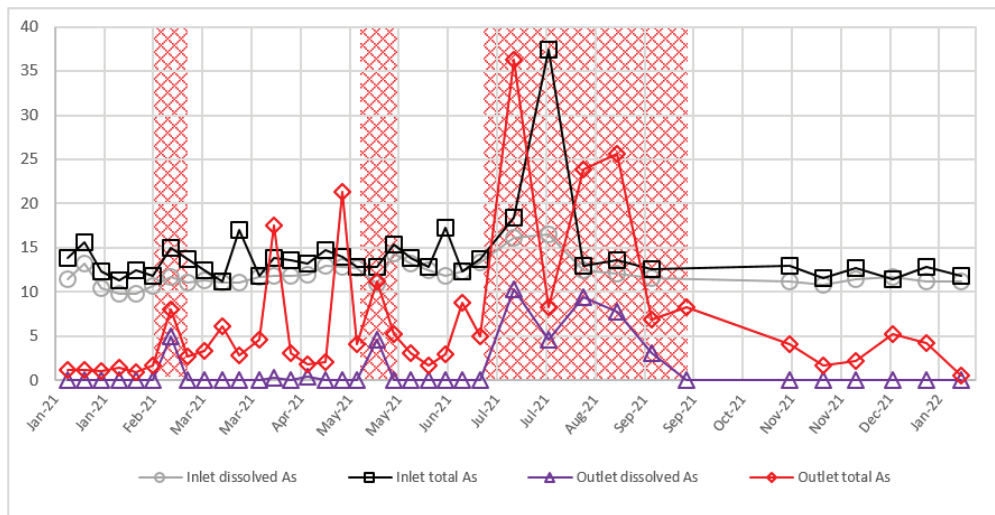


Figure 4 Evolution of arsenic concentration at the inlet and outlet of the pilot during the experiments in 2021.

validated. The experiments showed that it is possible to reduce dissolved arsenic to meet a discharge level lower than 100 µg/L without having to remove thiocyanate in a first step. If thiocyanate should be treated to meet a discharge level, the experiments carried out on the pilot plant have validated that it is possible to decrease thiocyanate concentration by biodegradation. In order to scale up to a treatment plant, these experiments must be completed with a technical and economic analysis to evaluate the benefits of implementing this treatment compared to the current lime treatment.

## References

- Riveros P, Dutrizac J and Spencer P (2001). Arsenic Disposal Practices in the Metallurgical Industry
- Dictor MC, Battaglia-Brunet F, Morin D, Bories A and Clarens M (1997) Biological treatment of gold ore cyanidation wastewater in fixed bed reactors. *Environmental Pollution* 97 (3) pp. 287–294. doi.org/10.1016/S0269-7491(97)00077-8
- Ding W, Xu J, Chen T, Liu C, Li J, Wu F. (2018). Co-oxidation of As(III) and Fe(II) by oxygen through complexation between As(III) and Fe(II)/Fe(III) species. *Water Research*, Volume 143, 2018, pp. 599-607, ISSN 0043-1354, https://doi.org/10.1016/j.watres.2018.06.072.
- Edwards M, Patel S, Chen H, Frey M, Eaton A.D, Antweiler R, Taylor H.E. (1998) Considerations in As analysis and speciation. *Journal AWWA*. Vol 90 issue 3. pp. 103-113, March 1998. https://doi.org/10.1002/j.1551-8833.1998.tb08402.x
- Ficklin, W. H. (1983). Separation of arsenic (III) and arsenic (V) in ground waters by ion-exchange. *Talanta*, Volume 30, Issue 5, 1983, pp. 371-373, ISSN 0039-9140, https://doi.org/10.1016/0039-9140(83)80084-8.
- Halder D, Lin J, Essilfie-Dughan J, Das S, Robertson J, Hendry M. J. (2018). Implications of the iron(II/III)-arsenic ratio on the precipitation of iron-arsenic minerals from pH 2.5 to 10.5. *Applied Geochemistry*, Volume 98, 2018, pp. 367-376, ISSN 0883-2927, https://doi.org/10.1016/j.apgeochem.2018.10.012.
- Jally B. (2018). Développement d'un procédé de traitement semi-passif pour une eau de mine arsénisée – Internship report. INP ENSIACET.
- Montiel A, Weté B. (1996). Elimination de l'arsenic dans les eaux destinées à la consommation humaine. Colloque spécialisé AIDE ; « Micropolluants d'origine naturelle – arsenic et autres composés. Vienne.
- Senn A. C, Hug S. J, Kaegi R, Hering J. G, Voegelin A. (2018). Arsenate co-precipitation with Fe (II) oxidation products and retention or release during precipitate aging. *Water Research*, Volume 131, 2018, pp. 334-345, ISSN 0043-1354, https://doi.org/10.1016/j.watres.2017.12.038.
- Vaxelaire S, Jally B, Battaglia-Brunet F, Jacob J (2019). The Development Of A Treatment Process For The Mine Water Containing Arsenic And Thiocyanate From Lab Scale To Pilot Plant Scale. *Proceedings of the IMWA 2019 Conference*.