

# AMD Passive Treatment using DAS at an Old Tin Mine in France

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## Abstract

Tailings from a closed Sn mine in Abbaretz (France) produce an AMD containing high concentrations of Fe and Al, but also a few mg/L of Mn, Zn, Ni and Co. A passive water treatment based on a DAS with a high ratio of limestone sand to wood chips (37%<sub>v/v</sub>) was tested on site at pilot scale during 5 months. Over the study period, removal rates were 88% for net acidity, 100% for Al, 82% for Fe, 71% for Zn, 23% for Co, 24% for Ni and 0% for Mn. After 122 days, the pilot was stopped due to excessive clogging.

**Keywords:** AMD, DAS, Clogging, Passive Treatment

## Introduction

The treatment of acid mine drainage (AMD) is a complex and challenging issue, especially when the water is very acidic or the flow rate is too high for classical passive treatment methods (Trumm 2010). Anoxic limestone drain is a common treatment method used for moderately acidic mine drainages, but it may not be effective in treating partially oxidized or aluminium-containing AMD (Watzlaf *et al.* 2000). With technological advancements in the field of mine drainage treatment, efforts have been made to push the limits of the applicability of passive treatment methods. Moreover, the traditional binary division between passive and active treatments is increasingly being replaced by a more nuanced continuum of treatments, ranging from fully passive to semi-passive (Kleinmann *et al.* 2023). DAS technology is clearly part of the progress made in this area in recent years (Ayora *et al.* 2013).

In this study, we focus on the treatment of AMD from a closed Sn open-pit mine using a dispersed alkaline substrate reactor (DAS). The lifespan of a DAS is limited by two phenomena: limestone depletion and clogging. Increasing the proportion of limestone in the packing material can delay its depletion, but accelerates pressure drop by reducing the porosity of the mixture, increasing the specific surface area, and increasing the amount of metals that can precipitate in the packing material. The aim of this study is to determine the optimal design

of a full scale treatment plant for Abbaretz AMD with the longest possible service life and to predict its service life before failure, regardless of the cause.

## Methods

### Site

The tin deposit in the Abbaretz region near Nantes (west of France) has been mined industrially from 1952 to 1957 after producing 3750 tonnes of cassiterite (SnO<sub>2</sub>). It is located onto a carboniferous quartz vein of the Armorican massif. The mineralisation is in the form of cassiterite associated with other minerals: mispickel (FeAsS), beryl (Be<sub>3</sub>Al<sub>2</sub>Si<sub>6</sub>O<sub>18</sub>), molybdenite (MoS<sub>2</sub>) and chalcopyrite (CuFeS<sub>2</sub>). The mineral is associated with inter-layered quartz in micaschists that form the bedrock of the area. The tailings produce an AMD (pH 2.9) containing high concentrations of Fe (300 mg/L at 85% Fe<sup>2+</sup>), Al (24 mg/L), Mn (4.3 mg/L), Zn (4.5 mg/L), Ni (2.1 mg/L), Co (1.8 mg/L), As (190 µg/L) and sulfate (1270 mg/L) at a mean flow rate of 5 m<sup>3</sup>/h.

### Water treatment system

The components of the pilot scale treatment system are: a DAS reactor, followed by an aeration stage, then a settling stage (fig. 1). The DAS is a downflow PMMA square column (0.3 m x 0.3m x 1.5 m) filled with a 64 L of mixture (porosity 55%) of 63%<sub>v/v</sub> wood chips (grain size 0-30 mm) and 37%<sub>v/v</sub> limestone sand (grain size 0-4 mm). The reactor was

equipped with 2 sampling ports (at 8 cm and 38 cm) and 2 transparent graduated tubes for measurement of pressure drop at 8 cm and 38 cm (total thickness 73 cm). The outlet pipe was adjusted to maintain 15 cm of supernatant and 30 cm of freeboard to handle the build-up of pressure drop. The aeration step was composed of one, then 2 pseudo-cylindrical PVC reactors (working volume respectively 5.5 L and 3.2 L) supplied with 3 L/min of air each. The settling step consisted of 3 rectangular PP containers in series of 77 L each. A peristaltic pump (Watson-Marlow QDOS120) fed the treatment system at 1.3 L/h. The only modification of operating condition was the addition of a 2<sup>nd</sup> aeration reactor after day 60, increasing residence time in the oxidation step from 2.4 h to 6.5 h. Residence time was 36h in the DAS and 7.4 days in the settling stage. The pilot scale treatment system operated for 122 days from October 2022 to March 2023 and was shut down due to excessive clogging.

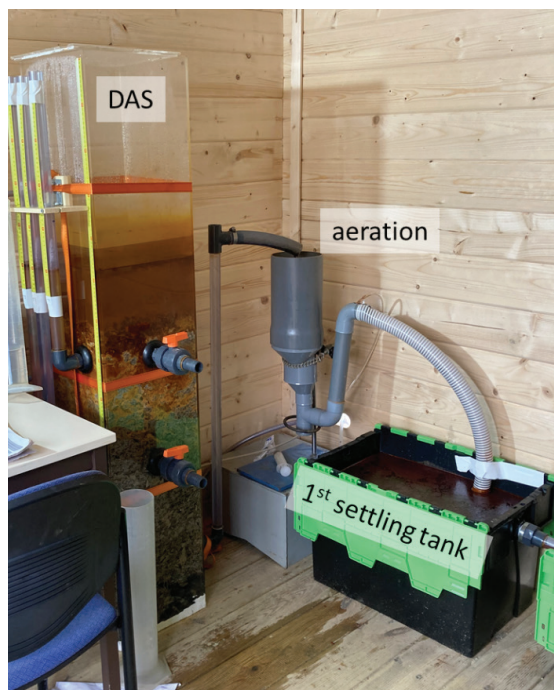
#### *Sampling and analytical techniques*

Sampling and measurements were made every weeks at the inlet and at the outlet of

the DAS reactor, in the aeration reactors and at the outlet of the 3<sup>rd</sup> settling tank. In total, 19 measurement and sampling campaigns were carried out. Redox, pH and temperature, conductivity and dissolved oxygen were measured using a WTW Multi 3620 with Sen Tix 950, Sen Tix ORP-T900, TetraCon 925 and FDO925 probes respectively. Samples were immediately filtered using 0.45 µm filters and acidified at pH 2 with nitric acid (HNO<sub>3</sub>) 67%. Ferrous iron was analysed on site with Merck® Spectroquant kits. Dissolved Iron, Ca, Al, Mn, Ni, Co, Zn and Mn were quantified by Agilent 4210 MP-AES (microwave plasma atomic emission spectroscopy). Flow rates were checked using a graduated container and a stopwatch.

#### **Results and discussion**

The physico-chemical characteristics of the AMD before and during treatment in the pilot plant, as well as the removal percentage of metals and net acidity, are summarized in Table 1. These are averages over the entire study period. An important increase in pH is observed between the inlet and outlet of the DAS, followed by a more moderate increase in



*Figure 1 AMD pilot plant on site*

the aeration step likely due to CO<sub>2</sub> degassing, and finally a decrease in pH in the settling step, probably due to residual Fe hydroxide precipitation.

Regarding the metals, in the treatment system, there is: a total removal of Al ; only a partial removal of iron (82%), caused by insufficient oxidation of Fe II to Fe III in the aeration step; and various removal for other metals, Zn (71%), Co (23%), and Ni (24%). After the DAS, the soluble Fe is

almost exclusively composed of Fe II, as Fe III is insoluble at these pH levels. There is no removal of Mn, probably due to the presence of residual Fe II which is known to prevent Mn precipitation. Metals removal is mainly concentrated in the DAS, except for iron, for which 42% of the removal occurs in the aeration and settling steps.

The temporal evolution of Fe and Al in the treatment system is presented in Figure 2. There were relatively minor variations in

Table 1 AMD characteristics and treatment performances in the pilot plant

Parameter	Measured values				Removal rate	
	Inlet	DAS	Aeration	Settling	DAS	DAS+Settling
pH	3.0	6.5	6.8	5.9		
Conductivity (µS/cm)	1766	1739	1612	1621		
Dissolved O <sub>2</sub> (mg/L)	8.9	0.8	11.2	7.1		
Temperature (°C)	8.8	9.1	8.5	8.1		
Eh SHE (mV)	627	166	190	347		
Net acidity (mg/L eq. CaCO <sub>3</sub> )	726	256		90	65%	88%
Fe (mg/L)	279	146		49	48%	82%
Fe II (mg/L)	235	153	87	51	35%	78%
Al (mg/L)	24	<0.25		<0.25	>99%	>99%
Zn (mg/L)	3.19	1.31		0.91	59%	71%
Co (mg/L)	1.25	1.04		0.97	17%	23%
Ni (mg/L)	1.42	1.12		1.08	21%	24%
Mn (mg/L)	3.68	3.93		4.07	-7%	-11%
Ca (mg/L)	20	254		263		

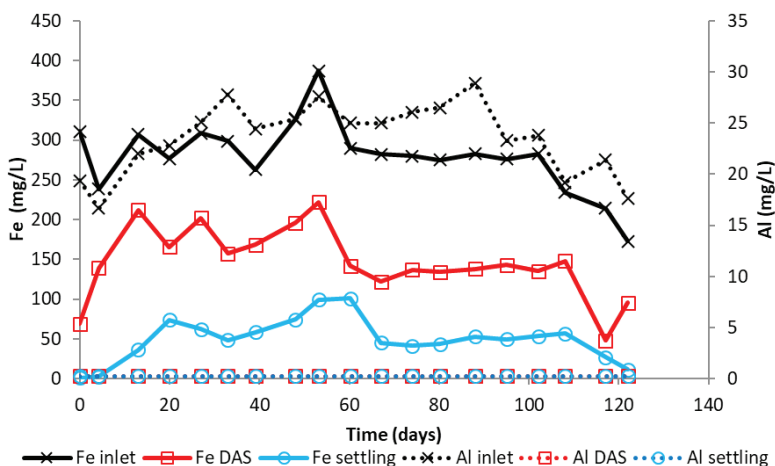


Figure 2 Dissolved Fe and Al in the pilot plant

Fe and Al concentrations during the study period. However, it is worth noting that the addition of a 2<sup>nd</sup> aeration reactor on day 60 led to an average decrease in Fe concentration at the pilot outlet from 74 mg/L to 49 mg/L. Additionally, during the last two measurement campaigns, Fe concentrations throughout the system were lower, likely due to a reduction in the treatment load resulting from dilution of the AMD by heavy rainfall.

Figure 3 shows the evolution of net acidity in the pilot as well as the amount of CaCO<sub>3</sub> that has dissolved in the DAS, calculated based on Ca concentration difference between the outlet and the inlet. This calculation assumes no gypsum precipitation, as sulfate concentrations do not decrease between the inlet and outlet of the DAS (data not shown). It is observed that the alkalinity produced in the DAS by calcite dissolution is almost always lower than the net acidity of the AMD, and there is a regular decrease in the amount of dissolved calcite. The net acidity removed averages 473 mg/L (65%) in the DAS and 638 mg/L (88%) in the entire system. The amount of dissolved limestone in the DAS shown in Figure 3 corresponds to an increase in Ca concentration from 20 to 250 mg/L. In the literature, limestone dissolution can be greater, for example, Ca concentration in DAS increases from 200 to 700 mg/L in the study of Rotting *et al.*

(2008a) and in the paper of Carabello *et al.* (2011b), while also experiencing gypsum precipitation. These studies also show much greater reduction in net acidity (from 900 to 1600 mg/L), indicating greater metal removal and hence more clogging. The generation of proton during metal precipitation in the DAS is a factor that promotes the dissolution of limestone, the kinetics of which depend on pH.

Figure 4 shows the temporal evolution of Ca dissolution along DAS depth as percent of total Ca dissolution. At the beginning of the experiment, the majority of the calcite was dissolved within the first 8 cm of the DAS. However, this zone became less effective over time and starting from day 102, it no longer contributed much to the dissolution of calcite. The middle zone (8-38 cm) became predominant starting from day 74 and remained so until the end of the pilot. The deepest zone of the pilot started to produce an important amount of alkalinity from day 102 onwards, but at the end of the pilot, it remained a minor contributor. The reasons for this shift in activity could be limestone passivation, depletion of the fine fraction of the calcite, and/or partial clogging that reduces water residence time. Limestone depletion can be ruled out since at the end of the pilot study, only 30% of the limestone initially present in the 1<sup>st</sup> layer (0 – 8 cm) was consumed.

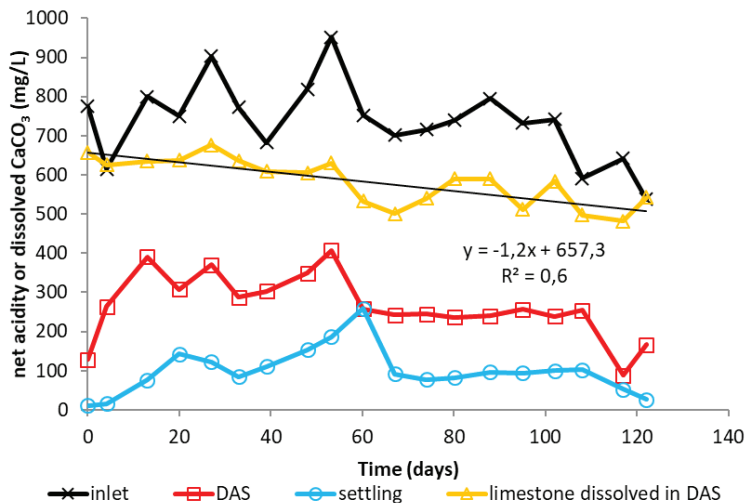


Figure 3 Net acidity and dissolved CaCO<sub>3</sub> in the DAS reactor

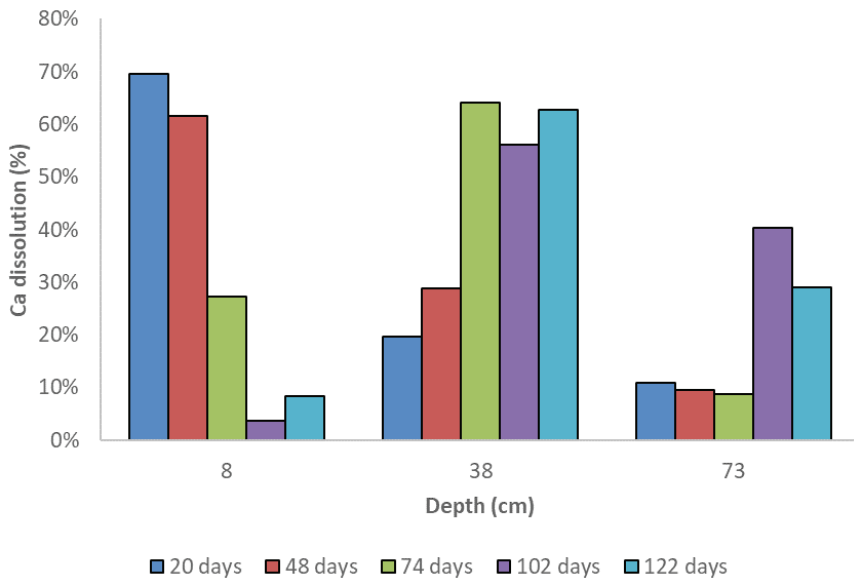


Figure 4 Evolution of Ca dissolution in the DAS

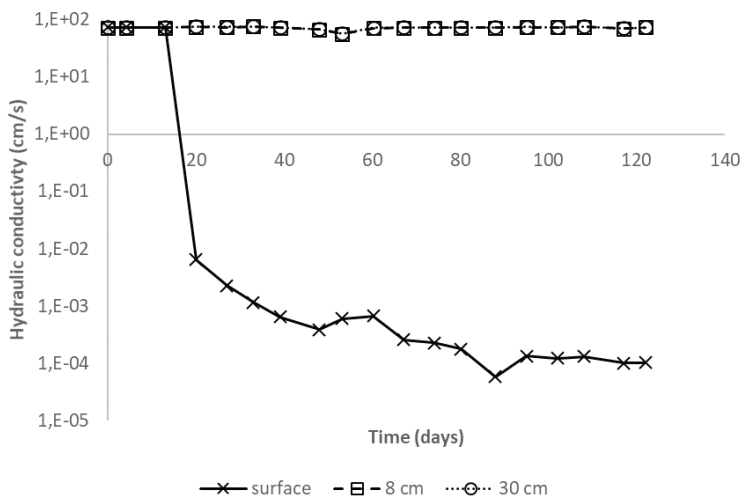


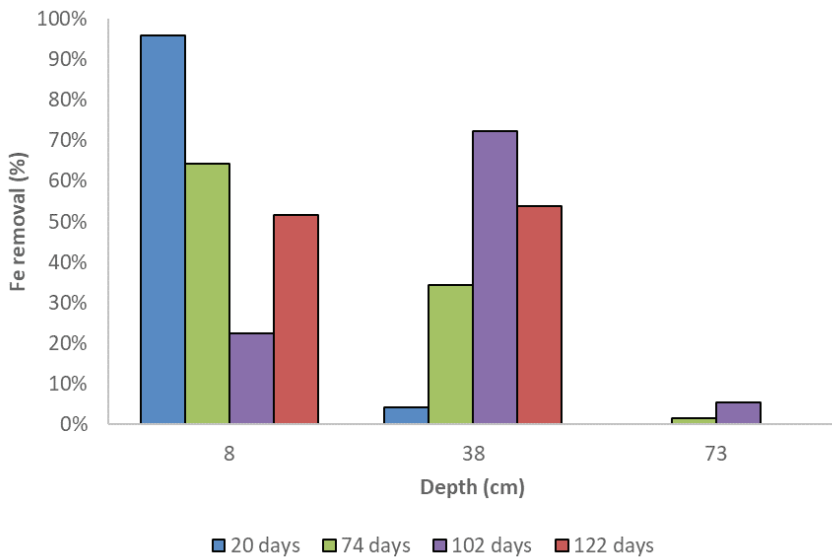
Figure 5 Evolution of hydraulic conductivity

Although the decrease in the amount of alkalinity produced is perfectly measured, it is difficult to estimate the lifetime of the DAS in this configuration as this amount has been insufficient (lower than AMD net acidity) since the beginning of the study, despite a high limestone fraction.

Hydraulic conductivity in the upper part of the pilot started to decrease 20 days after the beginning, and continued to decrease

steadily during the study period (fig. 5). By the end of the experiment, head loss had reached 300 mm H<sub>2</sub>O. Surprisingly, hydraulic conductivity remained constant in the middle and lower parts of the DAS.

As Fe is the contaminant present in the highest concentration, its precipitation is a major driver of head loss. Initially iron precipitation is concentrated almost exclusively in the first 8 cm of the DAS, then



*Figure 6 Evolution Fe precipitation in the DAS*

precipitation also takes place in the middle part of the reactor while remaining largely located in the upper part (Fig. 6). At the end of the experiment, there is still no Fe precipitation in the lower part. This explains why the pressure drop is concentrated in the 1<sup>st</sup> layer of the DAS and the absence of pressure drop in the 8-38 cm zone indicating that the iron precipitation might be more spread out there.

## Conclusions

This DAS configuration has achieved promising acidity and metals removal, but it can still be improved, both in terms of performance and lifespan. The first parameter to modify is obviously the proportion of limestone sand in the filling material. It must be reduced because using such a high limestone fraction not only causes rapid clogging, but also does not help to delay limestone depletion. Indeed, it was found that, after 100 days, there is no more limestone dissolution in the first layer of the DAS (0 to 8 cm) while only 30% of the initially present limestone has been consumed, meaning 70% of the limestone in it unused. A new DAS with much less limestone has recently been started: 18%<sub>v/v</sub> instead of 37%<sub>v/v</sub> and packing were added in the aeration reactors

to improve Fe II oxidation. To improve the system performance, several other measures could be taken, including increasing the residence time, oxidizing a small portion of Fe before the DAS and adding a 2<sup>nd</sup> DAS after the sedimentation step. A geochemical modelling is currently underway to validate the operating hypotheses and limitations of the pilot.

## Acknowledgements

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