

## HYDROGEOCHEMICAL EVOLUTION OF THE AZNALCÓLLAR PIT LAKE DURING THE SPILL OF A PYRITIC WASTE PILE

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### Abstract

Since its closure in 1995 and the subsequent accident happened in 1998, the Aznalcóllar mine pit has been used as a disposal site for diverse metal-rich materials removed during the rehabilitation of polluted areas along the Guadiamar river and around the former ore processing facilities. At present, the mine pit is partly flooded and contains a highly acidic (pH 2.7) pit lake with ~6 Hm<sup>3</sup> of metal and sulphate-rich water. Detailed research performed in the area during recent years (November 2002 to present-day) has shown that the reaction of the lake water with the spilled wastes, in addition to mixing with two inflows of acid mine waters coming from a waste pile and a pool which collects acidic leachates generated in the mine area, are strongly modifying the water quality of the pit lake. A major and dramatic highlight in the water quality of the pit lake has been the spill of 1.4 Hm<sup>3</sup> of pyritic wastes from an adjacent waste pile during the period from November 2005 to November 2006. The oxidative dissolution of this pyrite has resulted in (i) a total consumption of dissolved oxygen, (ii) a notable increase of total dissolved solids (conductivity 8.6 to 12 mS/cm), and (iii) a strong acidification (pH 4.2 to 2.7). In addition, from January to October 2006 an important heating of the hypolimnion was observed. This heating is due to the exothermic nature of pyrite oxidation, and is three times greater than the one observed during a similar period in 2005 ( $\Delta T=5.3^{\circ}\text{C}$  vs.  $1.6^{\circ}\text{C}$ , respectively). Despite the virtually total lack of oxidizing agents such as O<sub>2</sub> and Fe(III) (Fe(III)<5% Fe<sub>total</sub>) in the pit lake, pyrite is being oxidized and dissolved at high rates, as evidenced by the continuous increase of the SO<sub>4</sub><sup>2-</sup> and Fe concentrations. The aim of this work was to investigate the hydrochemical evolution of the Aznalcóllar pit lake during this time interval, as well as to recognize the different geochemical reactions which are taking place in the water column.

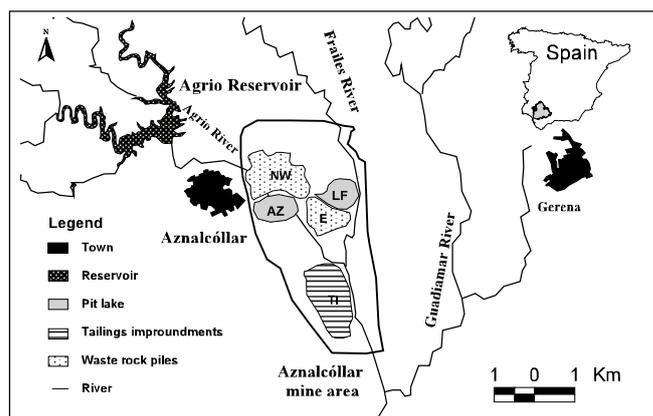
### Introduction

The Aznalcóllar mine is located at 35 km NW of Seville, Spain, in the eastern end of the Iberian Pyrite Belt (IPB). The Aznalcóllar mine site (formerly operated by Boliden Apirsa until 2001, and presently managed by an environmental management Division of Junta de Andalucía –Regional Government), includes two mine pits of considerable size (both partly flooded), Aznalcóllar (AZ, 1,200 m × 600 m × 275 m) and Los Frailes (LF, 800 m × 600 m × 265 m), in addition to two large waste piles locally known as Northwest pile (NW, 150 ha) and east pile (E, 115 ha), and a closed and sealed tailings impoundment (TI, 170 ha) (Fig. 1).

Since 1995 and up to date, the mine pit has been used as a disposal site for a number of waste materials and acid mine waters, namely: (i) waste-rock from the adjacent pit of Los Frailes in the period 1995-1998, (ii) pyritic sludge and contaminated soils in 1998 after the failure of the tailings dam, (iii) ~3 Hm<sup>3</sup> of metal-rich muds from the ore-processing facility between 1999 and 2001, (iv) metal-polluted soils from the Guadiamar river again in 2002, (v) ~1 Hm<sup>3</sup> of hematitic ashes from the pyrite processing facility between 2003 and 2004, and finally, (vi) ~1.4 Hm<sup>3</sup> of pyritic wastes from an adjacent waste pile from November 2005 to November 2006. The water level of the pit lake is artificially maintained below 0 meters a.s.l. (regulatory level imposed by regional authorities) by periodic pumping. The pumped water is neutralized in an adjacent chemical treatment plant (where the pH is raised to around 9.5 and dissolved metals are removed), and diverted to the Agrio river. The muds generated in this plant are again spilled to the pit lake.

The pit lake presents two inflows of acid mine drainage (AMD): (1) the Northern Drainage (ND) drains the NW pile and enters the pit lake by its northern wall, and (2) a western inflow discharges pumped AMD from a pool which collects all the acidic leachates generated in the mine area (Acid Mine Drainage Dam, AMDD).

The Aznalcóllar pit lake contains at present 6.05 Hm<sup>3</sup> of highly acidic and metal-rich water, occupies a surface of 284,000 m<sup>2</sup>, and presents a maximum depth of 37 m and a relative depth of around 6% (according to Doyle and Runnells, 1997). Such low relative depth is usually associated to *holomictic* lakes in which a complete mixing of the water column takes place during some period of the year (Wetzel, 2001). Recent research carried out in this lake since 2002 indicates that the homogenization of the Aznalcóllar pit lake usually takes place during the period from November to February (Schultze et al., 2006).



**Figure 1. Location of the study area. AZ, Aznalcóllar pit lake; LF, Los Frailes pit lake; TI, tailings impoundments; NW, northwestern waste rock pile; E, eastern waste rock pile.**

## Methods

The field measurements and water sampling were carried out at different seasons and every two months from October 2005 to November 2006. Depth measurements and vertical profiles of pH, Eh, temperature (T), dissolved oxygen content (DO), and electric conductivity (EC) were taken with a Hydrolab<sup>®</sup> Quanta multi-parametric probe. The quantitative measurement of acidity was performed *in situ* with titration-based test kits (*HACH Instruments company*) using the digital titration methods 8201 (bromophenol blue) and 8202 (phenolphthalein (total) acidity). The Fe(II) concentration was measured by reflectometry (reflectance photometry), with a RQflex10 reflectometer (*Merck*) and Reflectoquant<sup>®</sup> analytical strips. Two different reagents were used depending on the Fe(II) concentration (Ferospectral<sup>®</sup> for 0.5 mg/L < Fe(II) < 20 mg/L, and 2,2'-bipyridine for 20 mg/L < Fe(II) < 200 mg/L). Water samples were taken in an opaque, 2.2 L-capacity, BetaPlus<sup>®</sup> PVC bottle (*Wildlife Supply Company*) to obtain water samples at different depths. All samples were filtered on site with 0.45 µm membrane filters (*Millipore*), stored in 125 ml-polyethylene bottles, acidified with HNO<sub>3</sub>, and refrigerated at 4°C during transport.

Water samples were analyzed by AAS for Na, K, Mg, Ca, Fe, Cu, Mn, Zn and Al, by ICP-AES for Ni, and by ICP-MS for As, Cd, Co, Cr, Pb and U. Sulphate was gravimetrically measured as BaSO<sub>4</sub>. The detection limits for trace elements were 10 µg/L for Zn, 2 µg/L for Ni, Co, Cr, Pb and U, 0.4 µg/L for As, Cd and Cu. The detection limit for major cations (Na, K, Ca, Mg, Mn, Fe, Al) was <1 mg/L in all cases.

## Results and Discussion

### 1. Hydrochemistry of pit lake before the spill of the pyritic waste pile

Before the spill of the pyrite-rich wastes (October 2005), the pit lake showed an average conductivity of 8.7 mS/cm, with a slight increase in the upper epilimnion due to evapoconcentration processes (evaporation rates of up to 6 mm/day were measured), a slight thermal stratification was still observed (20°C and 15°C in the epi- and the hypolimnion, respectively), and the entire water column showed oxygenic conditions (near-saturation in the epilimnion, and around 60% sat., equivalent to around 6 mg/L, in the hypolimnion) (Fig. 2). At that moment, the water column was clearly stratified with respect to the pH value, with the epilimnion showing a pH of 3.6 (buffered by the hydrolysis of dissolved Fe(III)), and the hypolimnion exhibiting a pH of 4.2 (partly buffered by the hydrolysis of dissolved Al) (Fig. 3A).

As regards to the water chemistry, the pit lake presented, as an example, 1,150 mg/L Mg, 530 mg/L Ca, 194 mg/L Mn, 37 mg/L Cu, 7.8 mg/L Co, 2.6 mg/L Ni, and 1.9 mg/L Cd, which were constant with depth. There existed, however, slight differences between the epilimnetic and hypolimnetic concentrations of several elements like SO<sub>4</sub><sup>2-</sup> (8.0 and 7.8 g/L, respectively), Fe (3.4 and 0.6 mg/L, respectively), and Al (81 and 75 mg/L, respectively). The variation of the sulphate content is in accord with the observed conductivity increase and seems to be related to evapoconcentration, whereas the observed differences between the Fe and Al concentrations would be a direct consequence of their respective hydrolysis pK for each element (pK<sub>1</sub>(Fe<sup>III</sup>)~2.2, pK<sub>1</sub>(Al)~4.5; Nordstrom and Alpers, 1999). The epilimnetic Fe content and pH value were also influenced by the ND and AMDD inflows, which transfer significant amounts of dissolved Fe to the pit lake (Table 1). The hydrolysis and precipitation of this Fe is probably taking place in the form of schwertmannite, which is the most stable mineral phase under which Fe(III) precipitates in most AMD systems between pH 2.5 and 4 (Bigham et al., 1996).

## 2. Chemical characterisation of the spilled wastes and water inputs

The chemical composition of the sludges resulting from the treatment plant (which are systematically spilled into the pit lake; ~50,000 m<sup>3</sup> in 2005) included, on average, 20.3% CaO, 10.6% MgO, 1.61% Al<sub>2</sub>O<sub>3</sub>, 1.6% MnO, and 1.26% Zn, in addition to ~40% of sulphated interstitial water (October 2005). Thus, the partial redissolution of these muds in the pit lake can imply a significant enrichment in SO<sub>4</sub><sup>2-</sup>, Ca, Mg, and metals like Al, Mn and Zn.

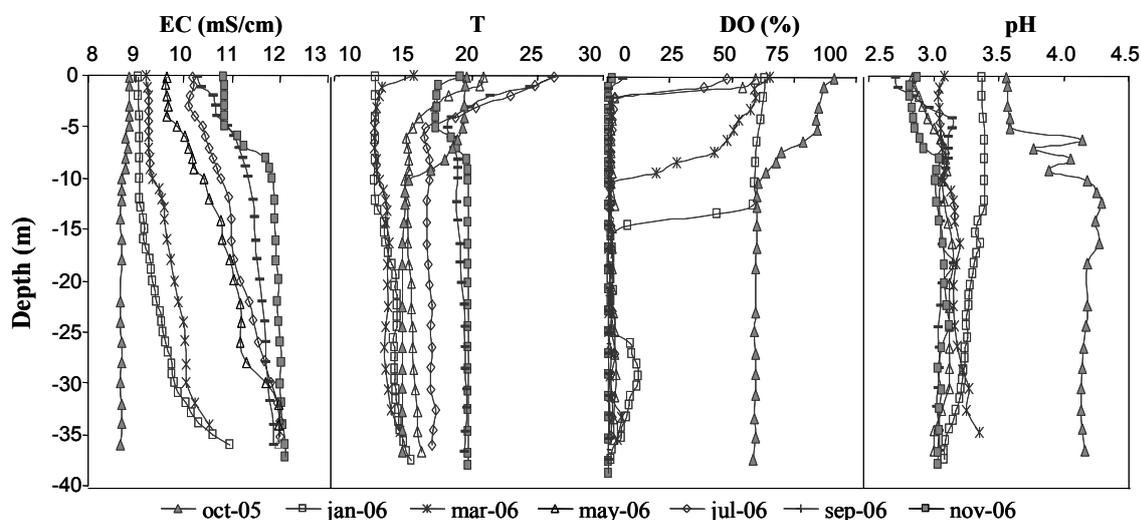
**Table 1. Average aqueous composition of the ND and AMDD inflows.**

Sample	Field measurements					Major elements							Trace elements			
	pH	Eh mV	EC mS/cm	DO mg/L	DO %	Mg mg/L	Fe mg/L	SO <sub>4</sub> g/L	Al mg/L	Mn mg/L	Cu mg/L	Zn mg/L	Ni µg/L	Cd µg/L	Co µg/L	Pb µg/L
ND	3.0	700	12	8	90	2,000	200	15	950	225	75	950	6,100	2,550	6,650	250
AMDD	2.7	600	8.5	5	60	600	750	6.5	280	150	16	300	1,600	730	3,000	400

As previously stated, the two AMD inflows (ND and AMDD) represent an important input of acidity and metals for the water quality of the pit lake. These waters are acidic (pH 3.0 and 2.7, respectively; Table 1), with high contents of dissolved solids (EC~12 and 8.5 mS/cm, respectively), and sulphate and metal concentrations which were significantly higher than those of the pit lake in October 2005 (Table 1). The flow rates of both inflows are highly dependent on the rainfall discharge, but their respective water volumes during the studied time interval have been estimated to be around 0.47 Hm<sup>3</sup> (ND) and 0.55 Hm<sup>3</sup> (AMDD).

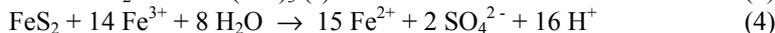
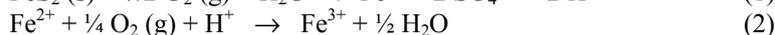
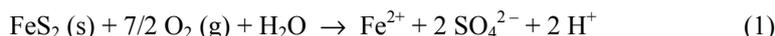
## 3. Hydrochemical evolution of the pit lake during the pyrite waste spill

The spill of pyritic wastes during 2006 has resulted in a strong and progressive modification of the pit lake water chemistry. During this period (November 2005 to November 2006), the water has experienced drastic changes in EC (from 8.6 to 12 mS/cm), T (from 13 to 20°C), DO (from 75% sat. to 0% sat.), pH (from 3.2 to 2.7; Fig. 2), and Eh (from 700 to 500 mV; data not shown), as well as drastic increases in the concentration of most elements, as for example sulphate (from 7.8 to 11.3 g/L), Fe (from 300 to 1,500 mg/L, Fig. 3B), Al (from 150 to 300 mg/L), and As (from 60 to 2,300 µg/L; Fig. 4).

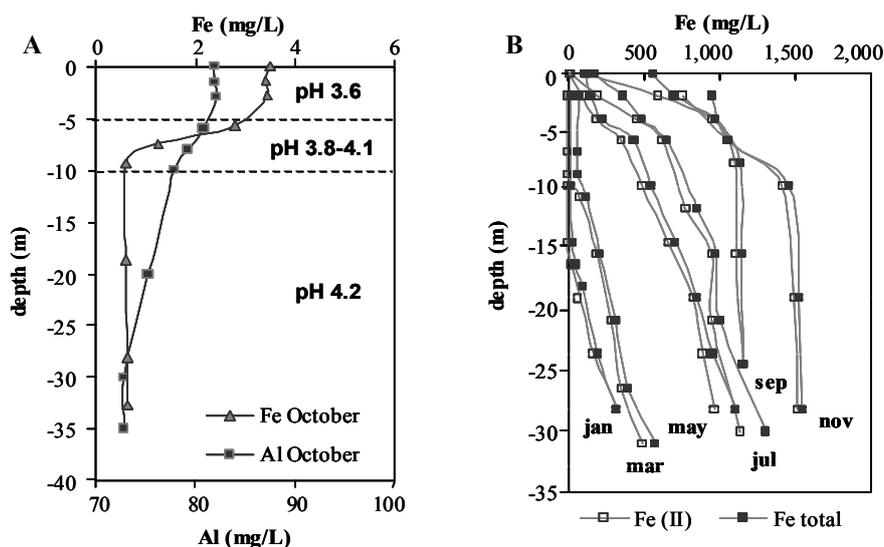


**Figure 2. Vertical profiles showing the variation of electric conductivity (EC), temperature (T), dissolved oxygen (DO) and pH with depth. Data from October 2005 to November 2006.**

It is hypothesized that the first reaction taking place during the initial stages of the spill process was the dissolution of highly soluble, efflorescent sulphate salts of Fe(II) (e.g., melanterite, rozenite, szomolnokite, halotrichite), Fe(II)-Fe(III) (roemerite, copiapite) and Fe(III) (e.g., coquimbite, rhomboclase), which are commonly formed during the pyrite oxidation and which usually store large quantities of acidity and trace metals like Cu or Zn in their crystalline lattices (Nordstrom and Alpers, 1999). This salt solubilization could explain the rapid increase of the total dissolved solids content (as indicated by a shift of the electric conductivity from 8.7 to 9.3 mS/cm) in January 2006. Subsequently, the pyrite of the spilled wastes would have reacted with the oxygen-rich water of the pit lake, according to the following overall reactions (Nordstrom and Alpers, 1999):



The oxidation of pyrite is highly exothermic and explains the observed heating of the pit lake. The result of the above cited reactions was evidenced by a shift of all measured parameters (EC increase and pH decrease in all the water column, O<sub>2</sub> consumption and T and Fe(II) increase in the lower layer; Figs. 2 and 3B). The shift of these parameters with depth points to the presence of a “reactive front” of pyrite oxidation in the pit lake bottom.



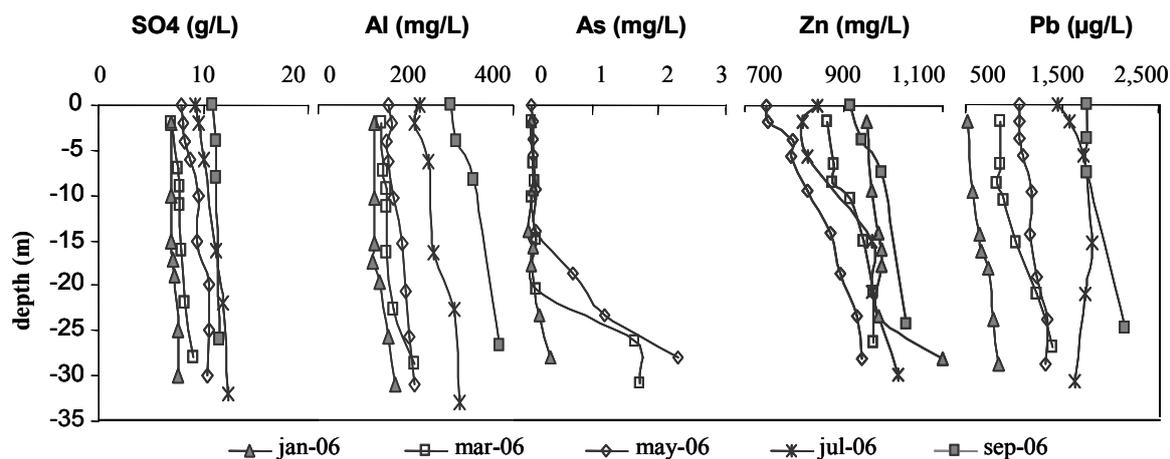
**Figure 3. Vertical profiles showing the variations with depth in the concentration of (A) Fe<sub>total</sub> and Al in October 2005, and (B) Fe(II) and Fe<sub>total</sub> from January 2006 to November 2006, in the Aznalcóllar pit lake.**

From November 2005 to February 2006, two opposite and competing processes were simultaneously taking place, namely: (i) progressive cooling of the surface water, which favoured the mixing and homogenization processes, and (ii) oxidative dissolution of pyrite, which gradually increased the density of water in the lower layer, thus impeding the mixing and enhancing the stratification of the pit lake. This is illustrated in the vertical distribution of DO (Fig. 2). The oxygen consumption by pyrite oxidation could not be compensated by oxygen transport (by mixing) from the lake surface to the lake bottom, and an anoxic front progressively rose towards the lake surface during January-March 2006, and finally reached the epilimnion in May 2006.

Despite the fact that the pyrite wastes became immersed in an anoxic environment during January to November 2006, both EC and T continued to increase, and pH also decreased, which suggests that the oxidative dissolution of pyrite proceeded through reaction (4) with Fe(III) (instead of O<sub>2</sub>) as oxidizing agent. A low but measurable content of Fe(III) (20-50 mg/L) was always detected in the dominantly ferrous lower layer in all sampling seasons. Although the anaerobic microbial oxidation of Fe(II) should not be ruled out, the presence of Fe(III) could be explained either by (i) dissolution of Fe(III)-sulphates associated with the pyritic wastes, and/or (ii) redissolution of previously formed Fe(III) precipitates due to the acidification of the pit lake.

Considering the increase in dissolved sulphate during the studied period ( $\Delta[\text{SO}_4]=3.5 \text{ g/L}$ ), as well as the volume of the pit lake ( $6 \times 10^9 \text{ L}$ ), and assuming that all the gained sulphate came from the pyrite dissolution, the amount of dissolved pyrite would be of  $1.1 \times 10^8 \text{ moles}$  ( $1.32 \times 10^4 \text{ tons}$ ). Considering an average density of  $5.02 \text{ g/cm}^3$ , this quantity would be equivalent to a volume of  $2.6 \times 10^3 \text{ m}^3$ , which would represent around 0.2% of the total volume of spilled wastes.

The heat input due to the exothermic pyrite oxidation is evidenced by comparing the net heat input to the hypolimnion from January 2005 to October 2005 ( $\sim 7.2 \times 10^9 \text{ kcal}$ ,  $\Delta T=1.6^\circ\text{C}$ , chiefly due to solar radiation), with that of the period January 2006-October 2006 ( $\sim 2.4 \times 10^{10} \text{ kcal}$ ;  $\Delta T=5.3^\circ\text{C}$ , solar radiation plus pyrite oxidation). In coherence with the dissolution of pyrite, both Fe(II) and  $\text{SO}_4^{2-}$  are the substances which most importantly have been increased in concentration (Figs. 3 and 4). However, some other trace elements such as Cu, As and Pb have also been considerably enriched, as a result of dissolution of other sulphides (sphalerite, chalcopyrite, galena, arsenopyrite) and sulphosalts (tetrahedrite-tennantite) which were also common in the mineralizations.



**Figure 4. Variation in the concentration of  $\text{SO}_4^{2-}$ , Al, As, Zn and Pb, with depth in the Aznalcóllar mine pit lake. Data from January to September 2006.**

The increases of Al and Mg (80 to 300 mg/L and 1,150 to 1,300 mg/L, respectively) probably result from the dissolution of aluminosilicates (chlorite, muscovite, feldspar) and/or Al precipitates (e.g., alunite, basaluminite). Conversely, from January to May 2006, Zn and Cd exhibited a striking behaviour, being reduced in their respective concentrations in the upper (oxygenated) layer of the pit lake (e.g., Zn decreased from 970 to 850 mg/L, but was again increased until its initial (pre-spill) content in November 2006; Fig. 4). This could be the result of the precipitation of Fe(III) as schwertmannite, which has been shown to be an efficient adsorbant of anionic metal species in AMD systems of the IPB (Sánchez-España et al., 2006). Such sorption could have effectively sequestered these metals, which have been shown to be significantly complexed with sulphate, forming  $\text{Zn}(\text{SO}_4)_2^-$  and  $\text{Cd}(\text{SO}_4)_2^-$  species (Sánchez-España et al., 2006). After May 2006, the pit lake became anoxic, and reaction (2) did not take place, so that no additional input of Fe(III) occurred, and the formation of schwertmannite was no longer possible. Under these new conditions, both Zn and Cd increased again (Fig. 4). Finally, the spill of the pyrite wastes has resulted in an important increase of the total (mineral) acidity of the pit lake (from 2,000 to 6,400 mg/L  $\text{CaCO}_3$  eq.), which should be considered in any future remediation attempt.

### Conclusions

The spill of 1.4  $\text{Hm}^3$  of pyritic mine wastes to the Aznalcóllar pit lake has resulted in a drastic decrease of its water quality. The oxidative dissolution of pyrite has provoked a total consumption of the oxygen dissolved in the lake, a sharp increase in the concentration of  $\text{SO}_4^{2-}$ , Fe(II), and other elements (Al, Cu, As, Pb), and a net pH decrease. The exothermy of this reaction has resulted in a more important heating of the hypolimnion than the one observed during the previous year ( $\Delta T=5.3$  vs.  $1.6^\circ\text{C}$ ). Dissolved iron in the lower (anoxic) layer of the pit lake is >95% Fe(II). However, pyrite dissolution seems to continue anaerobically due to the presence of Fe(III), which could be provided by dissolution of sulphates present in the wastes, and/or previous Fe(III) precipitates.

### Acknowledgements

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