MINERALOGICAL CHARACTERIZATION OF A REACTIVE TANK IN A PASSIVE AMD TREATMENT SYSTEM AT MONTE ROMERO (IBERIAN PYRITE BELT, SW SPAIN)

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Abstract

An acid mine drainage passive treatment system, consisting in three alkaline reactive tanks and six decanter ponds, has been installed at the Monte Romero mining area (Iberian Pyrite Belt, south-western Spain). This study is focused on the chemically induced precipitates formed in the calcite-base first alkaline reactive tank, (T1), of the treatment after one year of operation. For this purpose all the reactive material and precipitates from the first tank were extracted, and samples at different depths were collected. Solid samples were analyzed using conventional methods, including XRD and differential XRD (DXRD), calcimetry, SEM-EDS, sequential extractions and wet chemical analysis by ICP-OES. The study reveals the existence of three mineralogical zones in the precipitates that were formed in the first upper 30 cm of the tank's reactive material. These zones have been named on the basis of the main mineralogy as: 1) "Schwertmannite >> Goethite", 2) "Goethite >> Schwertmannite", 3) "Hydrobasaluminite + Gypsum". An important finding for the optimization of the treatment is that limestone is just consumed through the first 30 cm of the reactive material of T1; however an armouring process is localized at 10-15 cm depth due to the precipitation of hydrobasaluminite coating the limestone grains´ surface.

Introduction

Acid Mine Drainage (AMD) is considered as one of the biggest environmental problems caused by mining activities, mainly in sulfide deposits mining (Akcil and Koldas, 2006) and in coal mines (Nordstrom and Alpers, 1999). At the Tinto and Odiel basins, this problem is specially intense and ubiquitous because these two rivers drain the Iberian Pyrite Belt, (IPB), one of the most famous and richest sulfide mining regions of the world, whose original reserves are in the order of 1700 million tonnes (Sáez et al., 1999). Large-scaled exploitation of this region did not start until the second half of the 19th century (Leblanc et al., 2000), although there are vestiges of mining activity in the IPB dating back to prehistoric times (Nocete et al., 2005). Nowadays there are not many active mines in this region; however both rivers continue to carry high levels of contaminants due to mining wastes´ oxidation produced by the ancient workings and to the long-lived of the contamination processes of AMD.

The great number of contaminant focus present at the IPB make necessary, for a future restoration of the area, the use of passive treatment system, which once built only requires infrequent maintenance, as the unique economical option to improve water quality in this region.

There are lots of experiences of passive treatment systems carried out in many countries during the last two decades (see for example Gagliano et al., 2004; Whitehead et al., 2005; Barrie et al., 2005). The objective of this study is not to show in detail the passive treatment system that we have constructed at the Monte Romero field site, but to determine the secondary mineralogy precipitated in the first tank of the system after one year of acid water treatment.

Materials and Methods

1. Field Site and Treatment Description

The present study was carried out at the Monte Romero abandoned mining area, in south-western Spain (Fig. 1). The Monte Romero mineralization is a massive pyrite deposit with minor amounts of Zn, Pb and Cu sulfides. The enclosing rocks are low grade phyllites with no carbonate beds present. The AMD emerging from the adit has a mean pH of 3.3, an acidity of over 2300 mg/L as $CaCO_3$ equivalents, and contains 400 mg/L Zn, 350 mg/L Fe (83% Fe(II)), 260 mg/L Mg, 210 mg/L Ca, 130 mg/l Al, 18 mg/L Mn, 11 mg/L Cu and 1200 mg/L sulfate. Flow rate is usually around 2 L/s (Rötting et al., 2006).

The passive AMD treatment system at the Monte Romero field site was originally consisting of only one reactive tank (T1 in Fig.1), and after one year of operation the second and third reactive tanks (T2 and T3 in Fig. 1) were installed. Tank 1 (photograph in Figure 1) contains 1 meter of 80 wt %, (25 vol %) of calcite gravel and 20 wt %, (75 vol %) of wood chips reactive mixture in the upper part, and 10 cm of quartz gravel in bottom. Inflow water comes directly from the adit and feeds the tank by gravity flow.
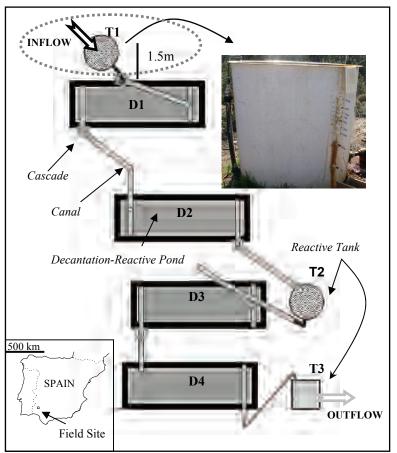
Figure 1. Location and schematic representation of the experimental passive system treatment developed at Monte Romero field site.

2. Sampling and Mineralogical Characterization Methods

After 6 months of operation (Feb-Jul 2006), T1 was sampled for the mineralogical characterization of the precipitates. Thirteen samples were collected from different depths to ensure a representative sampling of all the mineralogical differences observed in the precipitates and the reactive material. The different depths at which samples where collected were: 0-1 cm, 1-3 cm, 3-5 cm, 5-10 cm, 10-15 cm, 15-20 cm, and seven more samples every 10 cm until reach the quartz gravel base. During this sampling we observed in the cross section of the reactive tank that it was possible to differentiate macroscopically six different zones from top to bottom: 1) a "crunchy" reddish-dark brown level from 0 to1 cm; 2) a dark orange level from 1 to 3 cm; 3) a light orange-yellowish zone from 3 to 10 cm; 4) a colourless cemented zone from 10 to 15 cm; 5) a yellowish zone from 15 to 30 cm; 6) and from 30 cm to the bottom apparently unreacted substrate.

Around 1 kg of homogenized sample was collected at thirteen different depths, and the samples were stored in minigrip plastic bags until their chemical and mineralogical analysis.

All samples were subjected to a calcimetry test to know the amount of calcite consumed in the neutralization process of the inflow AMD water during the six month treatment.

The precipitates´ mineralogical composition was firstly evaluated by XRD analysis of randomly oriented powder samples using a Bruker D5005 X-ray Diffractometer with CuKα radiation, at the CSIC Institute of Earth Sciences "Jaume Almera" at Barcelona. Each sample was scanned from 4 to 60º 2θ for two hours.

Selected samples of the Fe-rich and Al-rich zones were examined with a JEOL JSM-5410 SEM fitted with an Oxford Link EDS at the Central Research Services of the Huelva University. Some of the samples were coated with gold to improve the observation of surface structures, and others were coated with carbon to obtain chemical information using the EDS.

Sequential Extraction and DXRD of selected samples (0-1 cm, 1-3 cm, 3-5 cm, 5-10 cm and 40-50 cm) was also carried out. A scheme of sequential extraction developed for Cu-sulfide mine waste (Dold, 2003) was adapted to our samples using just the first four steps of the extraction, and modifying the residual digestion step (Table 1). The chemical analysis of the extractants obtained at each step of the sequential extraction was carried out at the Central Research Services of the University of Barcelona using a Perkin Elmer Optima 3200 RL ICP-OES.

Table 1. Sequential Extraction sequence used in this study.

Simplified Sequential Extraction after Dold (2003)	Preferentially dissolved minerals according to Dold (2003)	Expected preferentially dissolved minerals in our samples
1) **Water soluble fraction**: 1.0 g sample into 50 ml deionizied H_2O, shake for 1 h, at room temperature (RT)	Secondary sulfates, e.g., bonattite, chalcanthite, pickeringite, magnesioauberite, Gy	Gypsum and other possible water soluble secondary sulfates.
2) **Exchangeable fraction**: 1 M NH_4-acetate, pH 4.5, shake for 2 h, at RT	Cc, vermiculite-type mixed-layer, adsorbed and exchangeable ions	Calcite predominantly
3) **Fe(III) oxyhydroxides**: 0.2 M NH_4-oxalate, pH 3.0, shake for 1 h in darkness, at RT	Sch, two-line Fh, secondary Jt, MnO_2	Schwertmannite, Al-Hydroxysulfates
4) **Fe(III) oxides**: 0.2 M NH_4-oxalate, pH 3.0, heat in water bath at 80 ºC for 2 h	Gth, Jt, Na-jt, Hm, Mt, higher ordered Fh's (e.g., six-line Fh)	Goethite
5) **Residual**: HNO_3, HF, $HClO_4$ digestion	Silicates, residual	Wood chips

Abbreviations: Cc: calcite, Fh: ferrihydrite, Gth: goethite, Gy: gypsum, Hm: hematite, Jt: jarosite, Mt: magnetite, Na-jt: natrojarosite, Sch: schwertmannite.
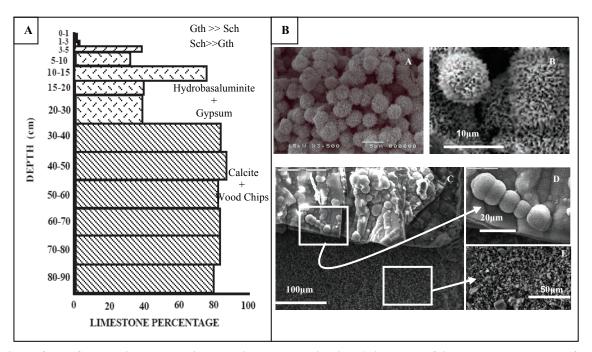

Figure 2. [A] Schematic cross-section showing the zonation in T1, in terms of limestone abundance, after six months of operation. [B] SEM images of the representative mineralogy of reactive tank T1: A) and B) schwertmannite from sample 0-1 cm; C) armouring of hydrobasaluminite on calcite in sample 10-15 cm; D) detail of hydrobasaluminite morphology; E) dissolution texture in calcite.

Results and Discussion

The results of the calcimetery are synthesized in Figure 2A. As it can be seen in this figure, only in the first 30 cm of the reactive material the amount of limestone decrees as a result of the AMD neutralization process (with the exception of sample 10-15 cm where an armouring process inhibited the calcite dissolution), meanwhile from 30 cm to the bottom of the tank the proportion of limestone and wood chips remains unaltered. This observation is of great relevance for the optimization of future passive reactive treatments in the area, since the reactive material necessary for the treatment is an important economic factor for the design of the system.

XRD was chosen as a first approach to the mineralogy of the samples. However, as Figure 3 shows, only calcite and gypsum could be detected without any doubt. In sample 1-3 cm the presence of goethite was difficult to detect, in sample 0-1 cm schwertmannite could be just "suspected", and in sample 10-15 cm there was no evidence of any mineral phase responsible of the cemented zone. To improve this poor characterization of the low crystallinity mineral phases like schwertmannite, ferrihydrite, hydrobasaluminite, etc., a DXRD was carried out by obtaining the XRD patterns of the different samples after each step of the sequential extraction. As can be seen in Figure 3, after passing sample 0-1 cm through steps 1 to 3 and 1 to 4 of the sequential extraction, the XRD pattern change from one with almost only schwertmannite to a second one of schwertmannite + goethite, and a final one only with goethite. Something similar could be observed in the XRD patterns of sample 1-3 cm after steps 1 to 3 of the sequential extraction.
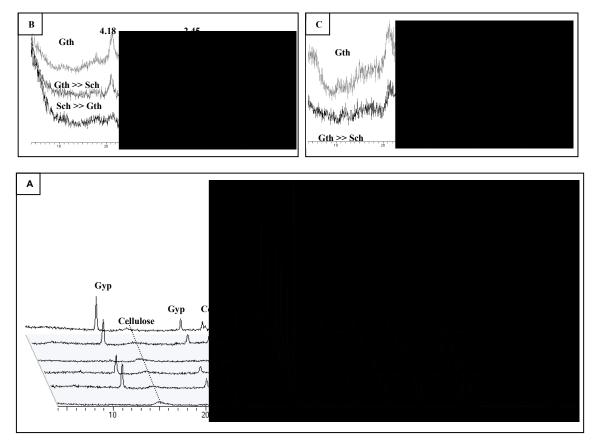

Figure 3. XRD pattern for some selected treated and untreated samples. A) From top to bottom: 3-5 cm, 5-10 cm, 10-15 cm, 15-20 cm, 20-30 cm, 30-40 cm. B) Sample 0-1cm after some steps of the sequential extraction. C) Sample 1-3 cm after some steps of the sequential extraction.

Figure 2B shows representative SEM images of the low crystallinity precipitates studied, where the characteristic "pincushion" morphology of schwertmannite from sample 0-1 cm can be observed, (A and B panels in Fig. 2B), with a ranging size for the sphere diameter of 5-10 μm. Panel C in this figure shows the armouring process affecting the limestone grains in sample 10-15 cm, and panel D the dissolution marks developed on the surface of the limestone grains.

The EDS and Sequential Extraction analysis suggests hydrobasaluminite, (Hybsl) as the best candidate for the Al-hydroxysulfate precipitates that caused the coating on the surface of the limestone grain.

Conclusions

The mineralogy of the AMD precipitates formed in the first reactive tank of the passive treatment system installed at Monte Romero site has been reliably determined although the DXRD scheme followed did not allow to obtain unambiguous results.

The mineralogical zonation of the cross section of the T1 has been characterized (Fig. 2.A). It can be seen that SO_4 precipitates along all the established precipitation zones, while Fe just precipitates at 0-1, 1-3 and 3-5 cm in

the form of schwertmannite and goethite. Calcium precipitates at zones 3-5, 5-10 and 15-30 cm as gypsum and Al precipitates at 3-30 cm in the form of hydrobasaluminite.

The mineral characterization carried out in this study is just the essential first step for future studies that will link hydrochemical analysis of the treated waters with possible mineral phases responsible of scavenge contaminant from the acid mine water.

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