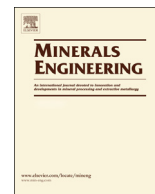




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Short communication

# A preliminary study of the formation of efflorescent sulfate salts in abandoned mining areas with a view to their harvesting and subsequent recovery of copper

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## ARTICLE INFO

## Keywords:

Acid sulfates

Efflorescences

Harvesting

Copper cementation

## ABSTRACT

The study focuses on the mineralogy and geochemistry of efflorescent sulfate salts formed every summer close to the Tinto River, located near the municipality of Nerva (Huelva, Spain). Two types of efflorescences were tested. The most acidic efflorescences, with a rate of production of approximately 120 t/ha, are mainly composed of coquimbite and showed the highest Fe content. The closest to the river, still in formation in July, reaching 24 t/ha, are richer in Al and Mg, because of the predominance of rozenite and pickeringite. Despite their different mineralogies both types of efflorescences have similar elevated Cu and Zn content, in a range between 3600 and 5600 mg/kg, that were fully dissolved in deionized water. A laboratory copper cementation experience was performed in order to measure the recovery of copper from 1 kg of salt dissolved at 25 °C in 20 L of water to which iron nails were added. After 90 min, 95% of the copper was precipitated. The rate of copper cementation followed first order kinetics.

## 1. Introduction

In dry climates, soluble sulfate salts precipitate as efflorescences (efflorescent salts) from the evaporation of waters rich in sulfates. After the dry period, the first rains dissolve these efflorescences, releasing acidity and metals to the environment.

A highly significant historical mining area is the Rio Tinto district. The waters of the Tinto River are affected by acid mine drainage containing extremely high concentrations of iron, sulfates, and metals (Hudson-Edwards et al., 1999; Galán et al., 2003). Evaporation of the river water causes precipitation of iron sulfate salts, with high concentrations of Zn and Cu, on the river sides and floodplains during summer (Buckby et al., 2003). These authors estimated that, on average, more than 200 tonnes of Zn and more than 150 tonnes of Cu exist in these salts which equate to the transient storage of 10% and 22%, respectively, of the total discharge of Zn and Cu from this river to the Huelva estuary.

Several studies have suggested the recovery of metals from efflorescent sulfate salts given their high solubility. In ancient times in Spain, copper was recovered from acid mine drainage by iron precipitation (natural cementation). Natural cementation was introduced

in the Rio Tinto area in the mid-18th century (Ortiz, 2003). Copper-enriched acidic water was pumped through channels containing iron scrap. The cementation of copper on iron scrap produced an average content of 78% copper in precipitates (Domínguez and Ortega, 2012).

This study focuses on the characterization of the mineralogy and geochemistry of efflorescent sulfate salts formed over the alluvial soils of the Tinto River in the vicinity of Nerva (Huelva, SW Spain), as well as of the materials on which sulphate salts are deposited on (hereinafter called substrates). This characterization identifies, the elements of interest for recovery. A laboratory-scale cementation of copper over iron nails was performed to evaluate the feasibility of copper recovery.

## 2. Materials and methods

### 2.1. Location

The study zone of 14 ha is located near the municipality of Nerva (Iberian Pyrite Belt, Huelva, Spain). The study zone is covered in summer by an important layer of saline efflorescences. The accumulation of salts on this site is favored by the flat topography of the alluvial plain of the Tinto River, after having collected acidic mine waters since

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<https://doi.org/10.1016/j.mineng.2018.09.014>

Received 8 May 2018; Received in revised form 13 September 2018; Accepted 17 September 2018

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Fig. 1. Photographs of the efflorescences studied: NER-1 (left) and NER-2 (right).

their origin in the Peña del Hierro open pit and after passing by the base of many waste dumps, such as those located east of the Cerro Colorado open pit.

## 2.2. Sampling and analytical methods

In the study area, two sampling zones were differentiated: NER-1, more distant to the Tinto River, showing greenish to yellowish efflorescences and NER-2, closest to the river, whit white to pale blue (Fig. 1). All efflorescences had a popcorn texture. The average production of efflorescences, on a dry basis, was estimated at 120 t/ha/annum for NER-1, and at 24 t/ha/annum for NER-2.

A total of 8 samples of efflorescences (4 in each zone) and 2 of their corresponding composite substrates (SUS-1 and SUS-2) were collected. pH was measured by mixing 1 part of solid to 1 part of deionized water. Major elements (Al, Ca, Fe, K, Mg, Mn, Na) were determined by X-ray fluorescence. Trace elements (As, Cd, Co, Cu, Ni, Pb, Zn) were determined by tri-acid digestion followed by ICP-MS. The potential of solubilization of trace elements from efflorescences and substrates was evaluated using leaching extracts (solid-water ratio of 1:10), as described by the European standard EN 12457-2 (ECS, 2002). Electrical conductivity and pH of the leachates were also measured. Trace elements present in leachates were analyzed by ICP-MS. For the determination of anions, UV-Vis absorption spectrophotometry was used. Mineralogy was examined using powder X-ray diffraction (XRD).

A laboratory cementation experience was performed in order to measure the recovery of copper from 1 kg of efflorescences dissolved (25 °C) in 20 L of water to which iron nails were added. Filtered samples were taken at regular intervals during the reaction and were analyzed for copper by ICP-MS. At each sampling, the pH was measured. The amount of cemented copper was calculated as the difference between the initial and final copper concentration in solution.

## 3. Results and discussion

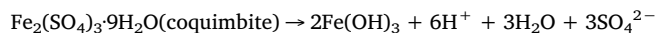
Both substrates (SUS-1 and SUS-2) had quartz and phyllosilicates as major minerals, and traces of jarosite, goethite, pyrite, galena and barite. Both substrates had high acidity (pH: 2.1–2.4). In the NER-1 area the dominant mineral phase was coquimbite ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ) and, secondarily, magnesiocopiapite ( $\text{MgFe}_3^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$ ), minerals in which iron exists in its ferric state, and, pentahydrate ( $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ ). Romero et al. (2006) reported the association of coquimbite and magnesiocopiapite in efflorescences formed in the more acidic zones affected by effluents with high ferric iron contents and acid mine drainage from Peña del Hierro, located next to the study zone. According to these authors, the occurrence of magnesiocopiapite instead of copiapite would confirm the low occurrence of ferrous iron in drainage waters. NER-2 showed that rozenite ( $\text{Fe}^{2+}\text{SO}_4 \cdot 4\text{H}_2\text{O}$ ) and pickeringite

( $\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ ) were the main minerals with copiapite ( $\text{Fe}^{2+}\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$ ) as a secondary mineral, which indicates the formation of salts from waters high in aluminum and ferrous iron.

Sulfur in the substrates ranged from 1.7 to 2.2%, and from 14 and 17% in the efflorescences. The efflorescences were mainly composed of Fe, Mg and Al sulfates with little Ca, K and Na. Romero et al. (2006) observed high Fe and low Al and Mg in waters where coquimbite precipitates, and higher Al and Mg in waters where pickeringite precipitates. The NER-1 efflorescences contained significantly less Al and Mg than the NER-2 efflorescences.

There was no significant difference in the content of trace elements in both zones. Cu (3603–5604 mg/kg) and Zn (3794–5377 mg/kg) were most abundant, followed by Mn (2478–4259 mg/kg), Pb (96–988 mg/kg), As (30–480 mg/kg), Co (64–114 mg/kg), Ni (30–70 mg/kg) and Cd (14–17 mg/kg). The trace elements were not necessarily found in mineral sulfates which may have been low crystallinity sulfates not detected by XRD. The ratio between the mean concentration of trace elements in efflorescences to that in their substrates was: Cd (28) > Zn (20) > Ni (18) > Co (16) > Cu (10) > Mn (9)  $\gg$  As (0.15) > Pb (0.06). As and Pb were preferably concentrated in the substrates, through adsorption/coprecipitation with Fe oxyhydroxides (goethite) and hydroxysulfates (jarosite).

Dissolution of efflorescences generated very acidic solutions: pH of 0.2–0.6 for NER-1 and 1.5–1.8 for NER-2.  $\text{Fe}^{3+}$  bearing minerals, such as coquimbite, copiapite, Mg-copiapite, and the  $\text{Al}^{3+}$  bearing minerals such as pickeringite, produce acidity when dissolved due to the hydrolysis of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ , respectively (Cravotta, 1994; Jambor et al., 2000). An example of this effect is the dissolution of coquimbite (Blowes et al., 2005), a major mineral in NER-1 efflorescences:



The electrical conductivity values of the leachates were also very high (16–25 mS/cm at 20 °C), due to elevated concentrations of sulfate (28–47 g/L). The dominant elements leached from the efflorescences were Fe (6–11 g/L) and Al (17–3.4 g/L). These solutions far exceeded normally acceptable for Effluent Discharge Requirements (WBG, 1998) (Table 1).

The NER leachates were more concentrated in Cu, Mn and Zn than the river waters around the study zone (Table 1). Cu, Mn and Zn could be worth recovery. These elements existed in highly soluble sulfate minerals. The average dissolution was: 96% and 84% for Cu, 82% and 79% for Mn, and 97% and 87% for Zn, for NER-1 and NER-2, respectively.

The quantity of valuable metals in efflorescences was estimated to be about 830 kg Cu/ha and 790 kg Zn/ha for NER-1, and 138 kg Cu/ha and 140 kg Zn/ha for NER-2. Taking into account that the efflorescent salts are generated during high evapotranspiration and that, with the

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