

15th Water-Rock Interaction International Symposium, WRI-15

## Metal/loid release from cyanidation wastes in response to rainfalls

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### Abstract

Cyanide heap leach operations developed in Tharsis (SW Spain) from 1982 to 2001 left the legacy of a huge amount of cyanidation wastes deposited over a total area of 47 ha without any type of isolation. The main goals of this work are to study the release of metals and metalloids under rainfall occurrence and the potential impact on the aquatic life. A vertical profile was sampled in the leaching heap and the chemical and mineralogical composition of these wastes was analyzed. In addition, the response of these wastes to rainfalls was studied by leaching with water at different solid-liquid ratios. The cyanidation wastes are mainly composed by Fe oxides/oxyhydroxides (i.e. goethite and hematite), oxyhydroxysulfates (i.e. jarosite), and quartz as well as gypsum in different levels. Although the alkaline conditions of the cyanidation wastes precluded the mobilization of most metals, some elements such as As, Zn, Ni and Pb showed concentrations which may pose a significant risk to aquatic life if chronic exposure is maintained. For this reason, a safe disposal of these wastes is needed in order to reduce the release of metals into the environment.

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Peer-review under responsibility of the organizing committee of WRI-15

**Keywords:** leaching test; alkaline conditions; criterion continuous concentration; aquatic life; safe disposal

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### 1. Introduction

Cyanide leaching is currently the dominant process used by mining companies to extract precious metals (i.e. Au and Ag) from ores. This cost-effective process based on the selective dissolution of precious metals by cyanide solutions generates large amounts of cyanide-bearing wastes. In order to assure an effective performance of cyanide solutions, the pH of solutions has to be maintained at alkaline values of around 10.3, which often requires the addition of lime or other alkaline materials<sup>1</sup>. The cyanide anion not only dissolves Au and Ag but also other metals and metalloids (e.g. As, Cd, Co, Cu, Fe, Ni, Pb and Zn), however most of them are present as secondary minerals

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that are insoluble at these alkaline pH values. As a result, large quantities of alkaline cyanidation wastes are usually stockpiled in the vicinity of processing plants. Unlike acid generating wastes, cyanidation residues has attracted less interest among the scientific community due to the lower capacity for releasing metals at weathering conditions. However, metalloids are mobile at alkaline pH and thus, elements such as As and Sb can be present in strongly elevated concentrations.

The Iberian Pyrite Belt (IPB) is one of the most important polymetallic sulfide-mining regions in the world. The long history of metal mining in the region has left a legacy of derelict mines and an enormous amount of mining wastes. Among them, it stands out the occurrence of large piles of cyanidation wastes in the surrounding of Tharsis Mine, which has been scarcely studied. Cyanide heap leach operations were developed in Tharsis from 1982 to 2001. The processed ores correspond mainly to Fe oxides (i.e. goossan and roasted pyrite) from derelict exploitations of the area. Minerals were crushed and milled until reaching a grain size between 0.1 and 7 mm. Then, lime and cement were added to the minerals and afterwards the mixture was transported to the leaching heaps. During the mineral processing performed until 2001, cyanidation wastes were stockpiled over 47 ha in different levels of variable height. No remediation measures were performed on the leaching heaps and thus were subjected to weathering agents after the cease of the activity. The main goals of this work are to study the release of metals and metalloids under rainfall occurrence and the potential impact on the aquatic life.

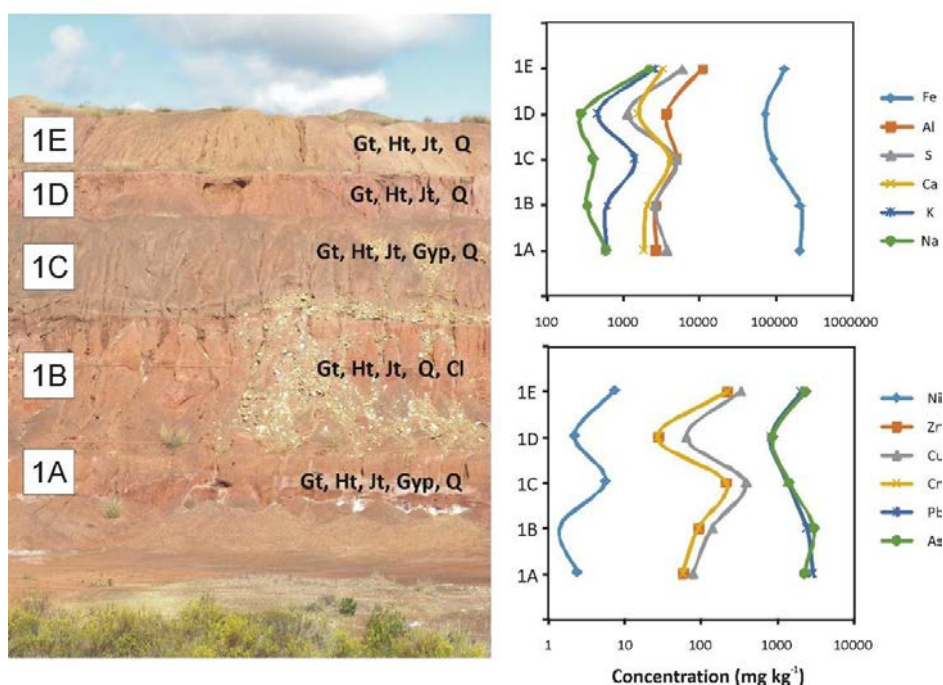


Fig.1. Mineralogical and chemical composition of the profile samples in the cyanidation wastes (Gt: goethite; Ht: hematite; Jt: jarosite; Gyp: gypsum; Q: quartz; Cl: clinocllore).

## 2. Methodology

A vertical profile was sampled in the leaching heaps in order to study the heterogeneity of the wastes. A composite sample of approximately 2 kg was collected from each level (Fig. 1) using a polypropylene shovel previously washed with distilled water, and transferred to polypropylene sterile bags. In the laboratory, the sample was oven-dried (30 °C), ground and stored in sterile polypropylene containers until analysis. Samples were chemically characterized by aqua regia digestion: 10 mL of aqua regia (12 mol L<sup>-1</sup> HCl and 15.8 mol L<sup>-1</sup> HNO<sub>3</sub> in the ratio 3:1) were added to 1 g of sample in Teflon reactors, which were allowed to stand for 20 h in a fume

cupboard, and then simmered on a hot plate for 1 h at 100 °C. X-ray diffraction (XRD) patterns were obtained with a Bruker D5005 X-ray Diffractometer with Cu K $\alpha$  radiation. Diffractometer settings were 40 kV, 30 mA, a scan range of 5-65° 2 $\theta$ , 0.02 2 $\theta$  step size, and 2.4 s counting time per step. The behavior of the heap leaching wastes during storm events was studied by performing a 24-h distilled water leaching (ratio 1:10) following the procedure contained in the Council Decision 2003/33/EC of the European Union. The effect of storm magnitude on metal release was studied by increasing the ratio to 1:20. The impact of both drainages on aquatic life was assessed according to the EPA's recommended aquatic life criteria<sup>2</sup>.

### 3. Results and discussion

The cyanidation wastes are mainly composed by Fe oxides/oxyhydroxides (i.e. goethite and hematite), oxyhydroxisulfates (i.e. jarosite), and quartz (Fig. 1). Gypsum was also identified in some levels (i.e. 1A and 1C) of the heaps. The low crystallinity and minor presence (below 5%) of other minerals precluded its identification by XRD. Accordingly, the wastes showed high concentrations of Fe (72-206 g kg<sup>-1</sup>; Fig. 1) with the highest values observed in the bottom piles. The evolution of total Ca and S along the profile is quite similar, with a saw-teeth evolution, which may be related to the different abundance of gypsum between levels.

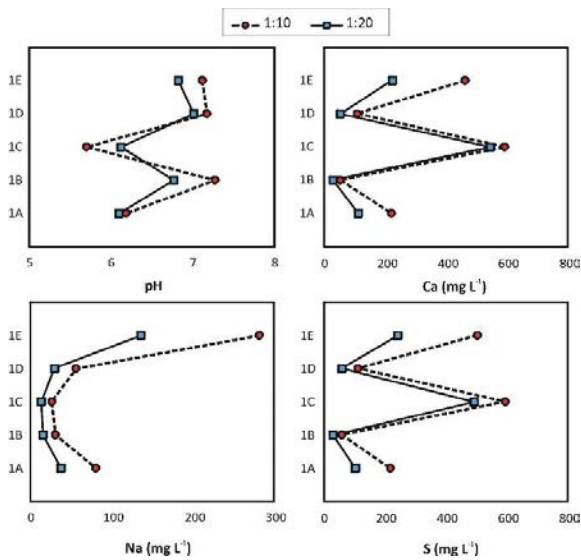


Fig. 2. Evolution of pH, Ca, S and Na during the leaching tests with distilled water (1:10 and 1:20 ratio S:L).

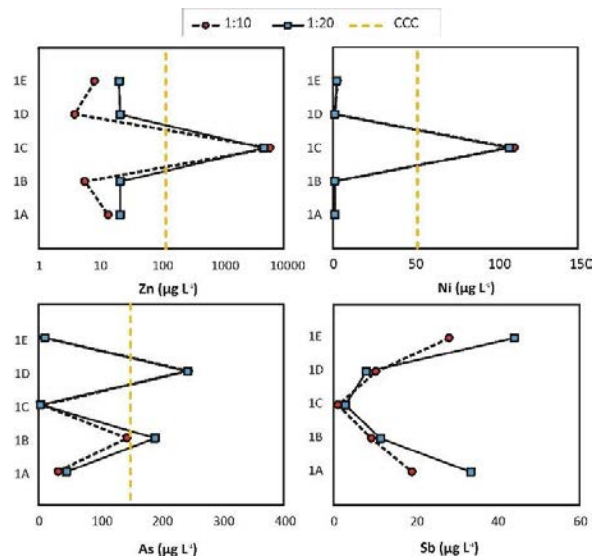


Fig. 3. Evolution of some metals and metalloids during the leaching tests with distilled water (CCC: criterion continuous concentration).

Other crustal elements such as Al and K also followed the same evolution. It is striking the high concentration of Na observed in the top level of the waste (2127 mg kg<sup>-1</sup>; 1E) compared to those found along the profile. The capacity of Fe minerals to retain As and Pb is evidenced by the high concentration of both elements (830-2956 mg kg<sup>-1</sup>; Fig. 1) and the evolution along the profile, similar to that observed for Fe. The cyanidation wastes also contain other elements such as Cu, Zn and Ni but at lower concentrations (Fig. 1). The contact of water with cyanidation wastes also released other metals although at lower concentrations. During the leaching test at 1:10 S:L ratio up to 7.8 mg L<sup>-1</sup> of Mn, around 80-300 μg L<sup>-1</sup> of Al, 13-764 μg L<sup>-1</sup> of Co and 2.5-117 μg L<sup>-1</sup> of Cu were released. The release during the 1:20 leaching test was slightly lower; a maximum value of 4.2 mg L<sup>-1</sup> was observed for Mn, 8.6-605 μg L<sup>-1</sup> for Co and 2.0-80 μg L<sup>-1</sup> of Cu. In turn, higher values were observed for Al, especially in the bottom piles (79-662 μg L<sup>-1</sup>). Despite the high concentration of Fe observed in the wastes (Fig. 1) both leaching tests did not release significant quantities of Fe, discarding the presence of Fe soluble salts. Concerning those elements considered toxic for the aquatic life, the interaction with water turned to be effective releasing metalloids such as Sb and As (maximum values of 44 and 245 μg L<sup>-1</sup>, respectively). Highest Sb concentrations were observed in the

bottom and top levels of the wastes while As followed a saw teeth evolution. In the case of As, samples from two levels (1B and 1D; Fig. 3) exceeded the criterion continuous concentration (CCC), that is, the threshold value above which a certain element pose a significant risk to the majority of species in freshwaters if chronic exposure is maintained. On the other hand, the level 1C also exceeded the CCC for Zn, Ni and Pb with maximum values of  $8.1 \text{ mg L}^{-1}$ ,  $111 \text{ } \mu\text{g L}^{-1}$  and  $7.5 \text{ } \mu\text{g L}^{-1}$ , respectively (the latter not shown in Fig. 3). No exceedance of the criterion maximum concentration (CMC) was observed for any element. This latter value represents the highest concentration which is not expected to pose a risk for aquatic life in case of acute exposure.

#### 4. Conclusions

Cyanide heap leach operations developed in Tharsis (SW Spain) from 1982 to 2001 left the legacy of a huge amount of cyanidation wastes deposited over a total area of 47 ha without any type of isolation. Thus, these wastes are, since the cease of the activity, subjected to weathering conditions. The response of these wastes to rainfalls was simulated by leaching the samples with distilled water at different solid:liquid ratios (1:10 and 1:20). The cyanidation wastes are mainly composed by Fe oxides/oxyhydroxides (i.e. goethite and hematite), oxyhydroxysulfates (i.e. jarosite), and quartz as well as gypsum in different levels. The dissolution of gypsum and reaction products from sodium cyanide caused the release of high concentrations of Ca, S and Na. The contact of water with cyanidation wastes also released other metals although at lower concentrations (e.g. Mn, Al, Co and Cu). The increase of solid:liquid ratio led to a general decrease of element concentration in the leachate, except in the case of Al, Zn and Sb. Although the alkaline conditions of the cyanidation wastes preclude the mobilization of most metals, some elements such as As, Zn, Ni and Pb showed concentrations which may pose a significant risk to aquatic life if chronic exposure is maintained. For this reason, a safe disposal of these wastes is needed in order to reduce the release of metals into the environment.

#### Acknowledgements

This work has been funded by the European Union's Seventh Framework Program, Marie Skłodowska-Curie actions and the Ministry of Economy, Innovation, Science and Employment of the Junta de Andalucía by the program TalentHub (COFUND — Grant Agreement 291780). R. Pérez-López would also like to thank the Spanish Ministry of Science and Innovation and the 'Ramón y Cajal Subprogramme' (MICINN-RYC 2011)

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