

Preliminary study on encapsulation processes of antimony mine wastes

Marina Campos-Ballesteros (1), Ascensión Murciego (2), Esther Álvarez-Ayuso (1*)

(1) Department of Environmental Geochemistry. IRNASA (CSIC), C/ Cordel de Merinas 40-52, 37008 Salamanca (Spain)

(2) Department of Geology. University of Salamanca, Plaza de los Caídos s/n, 37008 Salamanca (Spain)

* corresponding author: esther.alvarez@irnasa.csic.es

Palabras Clave: Antimonio, Residuos mineros, Encapsulación, Lixiviación. **Key Words:** Antimony, Mine Wastes, Encapsulation, Leaching.

INTRODUCTION

Antimony (Sb) is a potentially toxic element found in water, soils, and sediments from our immediate environment (Herath et al., 2017). Antimony can reach the environment from different sources. Some sources are associated with natural processes, such as erosion and weathering of antimony-containing rocks and volcanic activity. Other sources are associated with anthropogenic activities (Li et al., 2018). Antimony and its compounds have diverse industrial applications; thus, is increasingly being demanded. Antimony mainly occurs naturally as stibnite (Sb_2S_3) and valentinite ($\beta\text{-Sb}_2\text{O}_3$) (Filella et al., 2002). Antimony also forms part of many copper, silver, and lead ores. The weathering of mine wastes produced by the exploitation of antimony-bearing ores is the main cause of the presence of antimony in the environment (Herath et al., 2017).

Many studies in areas affected by antimony mining confirm that the surrounding water and soils show a significant increase in antimony concentration (Herath et al., 2017). Antimony can exist in different oxidation states: -III, 0, III, and V, but the two main ones are III and V (Herath et al., 2017). Sb(III) compounds are more toxic than Sb(V) compounds. In contrast, the mobility and solubility of Sb(V) are higher than that of Sb(III) (Li et al., 2018). Factors such as temperature, pH, and Eh of the environment determine the solubility of antimony species. Antimony is not an essential element in living organisms and is considered toxic for the majority of them above certain threshold concentrations (Herath et al., 2017). Particularly in humans, it can cause various respiratory, cardiac, and gastrointestinal diseases and is believed to be carcinogenic (Li et al., 2018). The exploitation of antimony deposits has caused a serious environmental issue. It is necessary to develop methods to avoid or minimize the release of antimony generated from these mine wastes and its negative impact on the surrounding ecosystems. The main aim of this study was to test the feasibility of generating coatings on mine wastes able to diminish environmental Sb release.

MATERIALS AND METHODS

This study targeted samples of mine waste rocks collected from the San Antonio mine in Badajoz (Spain), the most important Sb mine in Spain exploited until 1986 (Liso et al., 1991). The particle size fraction of 1.5-5 mm was used to perform their characterization and the encapsulation tests.

The mineralogical composition of mine waste rocks was determined by X-ray powder diffraction (XRD) using a Bruker D8 Advance diffractometer. Their leachable Sb content was evaluated according to the European leaching test EN 12457-4 (2002) followed by analysis by inductively coupled plasma-atomic emission spectrometry (ICPAES) using a Varian 720-ES spectrometer. The encapsulation process of these mine wastes was performed using FeSO_4 in acid medium (HNO_3 0.1 M) as a precursor for coating and H_2O_2 (10%) as oxidizing agent. A solid/liquid (kg/L) ratio of 1/7 and different Fe/Sb_{leachable} molar ratios (0.1, 1, and 10) were employed. The treated mine wastes were left in agitation for 30 minutes. After 24 h of equilibration at room temperature, they were filtered by vacuum and put in reactors with ultrapure water adjusted to pH 2.5 using a solid/liquid (kg/L) ratio of 1/10. The reactors were subjected to thermal treatment processes during 24 h in an oven at different temperatures (50 °C, 100 °C, and 150 °C). Afterwards, the treated mine wastes were filtered by vacuum, washed with acidified ultrapure water, and dried in an oven for 72 h at 30 °C. Then, the leachable Sb content of treated mine wastes was determined according to the European standard EN 12457-4 (2002) and their mineralogical composition by XRD.

RESULTS AND DISCUSSION

As determined by XRD, mine waste rocks consist of: silicates (quartz, muscovite, and chlorite) and carbonates (calcite and dolomite). After the encapsulation processes a very thin coating of orange-red colors appeared on their surface; the coating thickness increased with the increasing $\text{Fe}/\text{Sb}_{\text{leachable}}$ molar ratio (Fig. 1a). The XRD analysis of coated mine wastes revealed the occurrence of silicate, carbonate, and calcium sulphate minerals. No iron (oxyhydr)oxides or antimony minerals were detected, pointing out their amorphous character or their minor/trace level.

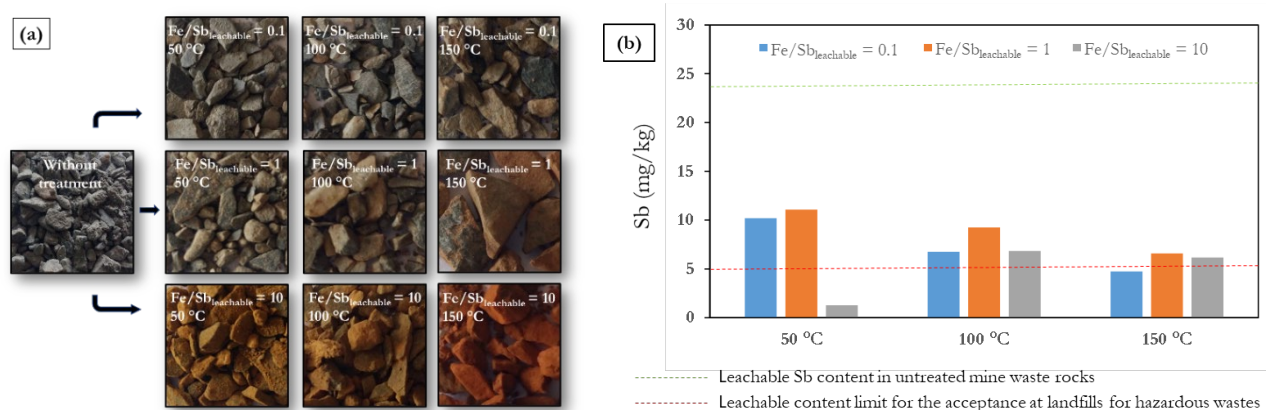


Fig 1. (a) Hand samples of untreated and treated mine waste rocks. (b) Leachable Sb contents in untreated and treated mine waste rocks.

The leachable Sb content of untreated mine wastes showed a value of 23.8 mg/kg (Fig. 1b), greatly exceeding the limit value (5 mg/kg) for acceptance at hazardous waste landfills (Council Decision 2003/33/EC). Hence, it is required a previous treatment to decrease their leachable Sb content below the established limit. All the tested encapsulation processes reduced importantly the leachable Sb content of mine wastes (Fig. 1b). Decreases were comprised in the range of 57-97%, with the highest decrease being attained by the encapsulation process performed at a $\text{Fe}/\text{Sb}_{\text{leachable}}$ molar ratio of 10 and a temperature of 50 °C. Under such conditions the leachable Sb content of mine wastes showed a value of 1.3 mg/kg, which is below the limit established by the European legislation for acceptance at hazardous waste landfills.

ACKNOWLEDGMENTS

The present study was carried out under the project TERMET (Grant number: RTI2018-095433-B-I00) funded by Ministerio de Ciencia, Innovacion y Universidades (MCIU), Spain/Agencia Estatal de Investigacion (AEI), Spain/Fondo Europeo de Desarrollo Regional (FEDER), EU, and the project “CLU-2019-05 – IRNASA/CSIC Unit of Excellence”, funded by the Junta de Castilla y León (Spain) and cofinanced by the EU (European Regional Development Fund (ERDF) “Europe drives our growth”).

REFERENCES

- Council Decision 2003/33/EC of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC. Off. J. Eur. Commun., **L11**, 27-49.
- EN-12457-4 (2002): Characterization of Waste - Leaching-Compliance Test for Leaching of Granular Waste Materials and Sludges - Part 4: One Stage Batch Test at a Liquid to Solid Ratio of 10 L/kg for Materials with Particle Size below 10 mm (Without or With Size Reduction). European Committee for Standardization, Brussels.
- Filella M., Belzile, N., Chen, Y. (2002): Antimony in the environment: A review focused on natural waters. I. Occurrence. Earth Sci. Rev., **57**, 125-176.
- Herath, I., Vithanage, M., Bundschuh, J. (2017): Antimony as a global dilemma: Geochemistry, mobility, fate and transport. Environ. Pollut., **223**, 545-559.
- Li, J., Zheng, B., He, Y., Zhou, Y., Chen, X., Ruan, S., Yang, Y., Dai, C., Tang, L. (2018): Antimony contamination, consequences and removal techniques: A review. Ecotoxicol. Environ. Saf., **156**, 125-134.
- Liso, M.J., Rincón, J.M., Casillas, R. (1991): Presencia de CaSbO_4 en La Codosera (Badajoz). Stvd. Geol. Salmant., **XXVII**, 197-206.