Assessment of amorphous aluminum oxide as amendment to immobilize antimony in mine wastes

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

(1) Department of Environmental Geochemistry, IRNASA (CSIC), C/ Cordel de Merinas 40-52, 37008 Salamanca (Spain)
* corresponding author: esther.alvarez@irnasa.csic.es

Palabras Clave: Sb, Óxido de Al, Estabilización, Residuos mineros. **Key Words:** Sb, Al oxide, Stabilization, Mine wastes.

INTRODUCTION

The exploitation of antimony (Sb)-bearing deposits has resulted in an important legacy of mine wastes within the environment. In general, these wastes have been poorly handled, especially in the case of former mine exploitations, causing the pollution of surrounding areas. Moreover, unless appropriate measures are implemented to mitigate the off-site migration of Sb from mine wastes, they constitute nowadays an ongoing source of this potentially toxic element (Guo et al., 2014). Several approaches have been proposed to manage these mine wastes, including encapsulation processes, aimed to confine wastes within a matrix that restricts their weathering, and stabilization methods, aimed to immobilize the Sb labile forms occurring in wastes. Different materials have been proven to retain Sb, comprising inorganic materials, organic products, and biosorbents (Long et al., 2020). Thus, they could act as feasible amendments to stabilize Sb mine wastes. Of them, metal oxides such as iron, aluminum, or manganese oxides highlight for their important role in controlling the mobility of Sb in the environment. Moreover, it has been found that Sb is mostly adsorbed on them via the formation of inner-sphere complexes (Mitsunobu et al., 2010; Ilgen & Trainor, 2012; Sun et al., 2019), thus strongly binding Sb. The main objective of this work was to assess the potential of an amorphous aluminum oxide as stabilizing agent of Sb mine wastes, studying its performance to attenuate Sb leaching from them.

MATERIALS AND METHODS

The aluminum oxide used as an adsorbent in this study was synthesized using the method described by Sims & Bingham (1968). Accordingly, a 2 M NaOH solution was slowly added to a 1.5 M $AlCl_3$ solution in a volume ratio of 2:1 under continuous stirring. The obtained precipitate was washed thoroughly with deionized water, centrifugated, and dried at 70 °C for 24 h. The prepared solid was characterized by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer. Mine wastes resulting from the former San Antonio mine were considered in this study. This mine exploited the most important stibnite (Sb_2S_3) ore deposit in Spain from 1940 to 1986. Its main mineral association is constituted by quartz–stibnite–scheelite ($CaWO_4$). Mine wastes were collected from a small mine dump where small-sized rocks (< 10 mm) are accumulated. Mine waste rocks were sampled from the dump surface at different places, put together, and homogenized to generate a single composite sample. The minerals composing these mine waste rocks mainly include silicates and carbonates together with minor/trace amounts of iron oxyhydroxides and sulfides, as previously determined (Álvarez-Ayuso et al., 2022). Stabilization studies were carried out by adding increasing amounts of the synthetized solid to a fresh determined amount of mine waste rocks in order to obtain aluminum oxide/mine waste ratios of 0, 1, 2, 5, 10, and 25%. The obtained mixtures were shaken for homogenization during 5 min by means of a vertical rotary shaker. The treatment effectiveness was assessed by leaching studies. Thus, amended mine waste rocks were subjected in triplicate to the European leaching standard test EN-12457-4 (2002). Accordingly, treated wastes were shaken with deionized water at a liquid/solid ratio of 10 L/kg for 24 h using a vertical rotary shaker working at 10 rpm. After sedimentation and filtration, the extracts derived from this test were analyzed for Sb by inductively coupled plasma-atomic emission spectrometry using a Varian 720-ES instrument.

RESULTS AND DISCUSSION

According to the XRD analysis performed on the synthesized solid (Fig. 1), no minerals were detected, indicating its amorphous character.

Fig. 2 shows the leaching behavior of treated mine waste rocks determined according to the European leaching standard test EN-12457-4 (2002). The incorporation of the amorphous aluminum oxide progressively decreased the leachable Sb content in mine wastes with the increasing amendment application, ranging from 30.0 mg/kg (0% amendment) to 9.2 mg/kg (25% amendment). The Sb leaching decreases achieved values of 6.8, 14.6, 18.7, 24.4, and 69.5% when the amorphous aluminum oxide was applied at doses of 1, 2, 5, 10, and 25%, respectively. Despite the important reduction in the leachable Sb content in mine waste rocks treated with the highest amendment dose, the limit value (5 mg/kg) established for the acceptance of wastes at hazardous waste landfills (Council Decision 2003/33/EC) was still exceeded. Higher amendment applications would be necessary to further decrease the leachable Sb content in mine waste rocks and thus make them acceptable at controlled landfills. Therefore, the amorphous aluminum oxide shows a great potential to stabilize Sb mine wastes, albeit relatively important amendment doses (> 25%) are required if their acceptance at controlled landfills is the goal.

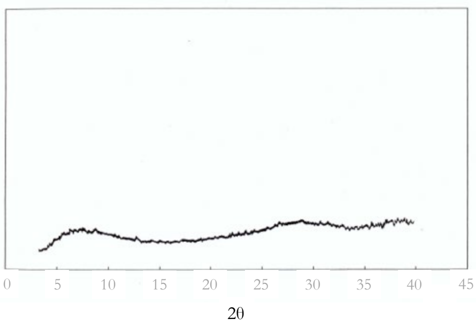

***Fig 1**. XRD pattern of synthetized solid.*

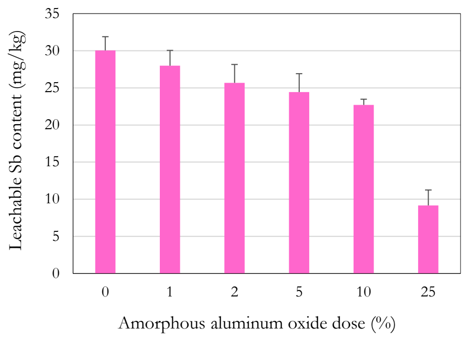

***Fig 2.** Leaching behavior of treated mine waste rocks.*

ACKNOWLEDGMENTS

The present study was carried out under the project PURVAL (Grant number: PID2022-141352OB-I00) funded by Ministerio de Ciencia e Innovación (MCIN), Spain/Agencia Estatal de Investigación (AEI), Spain/Fondo Europeo de Desarrollo Regional (FEDER) "A way of making Europe", European Union (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

Álvarez-Ayuso, E., Murciego, A., Rodríguez, M.A., Fernández-Pozo, L., Cabezas, J., Naranjo-Gómez, J.M., Mosser-Ruck, R. (2022): Antimony distribution and mobility in different types of waste derived from the exploitation of stibnite ore deposits. Sci. Total Environ., **816**, 151566.

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., L**11**, 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.

Guo, X., Wang, K., He, M., Liu, Z., Yang, H., Li, S. (2014): Antimony smelting process generating solid wastes and dust: Characterization and leaching behaviors. J. Environ. Sci. (China), **26**, 1549-1556.

Ilgen, A.G. & Trainor, T.P. (2012): Sb(III) and Sb(V) sorption onto Al-rich phases: hydrous Al oxide and the clay minerals kaolinite KGa-1b and oxidized and reduced nontronite NAu-1. Environ. Sci. Technol., **46**, 843-851.

Long, X., Wang, X., Guo, X., He, M. (2020): A review of removal technology for antimony in aqueous solution. J. Environ. Sci. (China), **90**, 189-204.

Mitsunobu, S., Takahashi, Y., Terada, Y., Sakata, M. (2010): Antimony(V) incorporation into synthetic ferrihydrite, goethite, and natural iron oxyhydroxides. Environ. Sci. Technol., **44**, 3712-3718.

Sims, J.R. & Bingham, F.T. (1968): Retention of boron by layer silicates, sesquioxides, and soil materials. II. Sesquioxides. Soil Sci. Soc. Am. Proc., **32**, 364-369.

Sun, Q., Cui, P.-X., Liu, C., Peng, S.-M., Alves, M. E., Zhou, D.-M., Shi, Z.-Q., Wang, Y.-J. (2019): Antimony oxidation and sorption behavior on birnessites with different properties (Δ-MnO_2 and triclinic birnessite). Environ. Pollut., **246**, 990-998.