

Application of encapsulation processes to stibnite mine wastes

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INTRODUCTION

The exploitation of antimony (Sb) ores to satisfy the growing demand and use of Sb and its compounds in numerous industrial applications represents a serious environmental issue (Zhang et al., 2021). Stibnite (Sb_2S_3) is the main exploitable form of Sb existing in nature (Shtangeeva et al., 2011). After ore extraction, large quantities of mine wastes are generated and exposed to the environment. Under atmospheric conditions stibnite oxidizes, releasing Sb to the surrounding mining area and environment, threatening the ecosystem and human health due to the toxic effects of this element on most organisms. There is an urgent need to develop methods to prevent the stibnite oxidation and the concomitant release of Sb from mine wastes so as to attenuate environmental pollution and preclude the negative impacts of this priority pollutant. The main objective of this study was to assess the application of encapsulation processes to stibnite to reduce its oxidation and/or to retain the released Sb.

MATERIALS AND METHODS

Stibnite samples of 2-5 mm particle size fraction were employed in this study. These samples were collected from the San Antonio mine in Badajoz (Spain), the most important Sb mine in Spain exploited until 1986 (Liso et al., 1991). Stibnite samples were characterized to determine their mineralogical composition and their leaching behavior. The mineralogical composition was determined by X-ray powder diffraction (XRD) using a Bruker D8 Advance diffractometer. The leaching behavior was evaluated according to two leaching tests: 1) the European leaching test EN 12457-4 (2002) and 2) the Toxicity Characteristic Leaching Procedure (TCLP) (EPA Test Method 1311, 1992), followed by analysis by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using a Varian 720-ES spectrometer.

The encapsulation processes of the stibnite samples were performed using FeSO_4 in an acid medium (HNO_3 0.1 M) as a precursor for coating and H_2O_2 (10%) as an oxidizing agent. A solid/liquid (kg/L) ratio of 1/7.5 and a $\text{Fe}/\text{Sb}_{\text{leachable}}$ molar ratio of 100 were employed. Following this process, a stirring stage for 30 minutes and a subsequent equilibration period for 24 h at room temperature were carried out. Then, the treated stibnite samples were filtered under vacuum and heat treated for 24 h in an oven at different temperatures (30 °C, 50 °C, 100 °C and 150 °C). Encapsulated stibnite samples were analyzed to determine their leachable Sb concentration according to the European standard EN 12457-4 (2002) and the TCLP (EPA Test Method 1311, 1992). The coating derived from the encapsulation process showing the best general behavior to mitigate the Sb leaching was analyzed for its mineralogy by XRD and for its chemical composition by microwave-assisted aqua regia digestion (conditions: 190 °C and 15 min) and further analysis by ICP-AES.

RESULTS AND DISCUSSION

As determined by XRD, stibnite samples were mainly composed of stibnite and quartz, together with some dolomite (Fig 1. (a)). According to the European standard EN 12457-4 (2002), the leachable Sb content of untreated stibnite samples showed an average value of 341.9 mg/kg, which greatly exceeds the limit value (5 mg/kg) established for the acceptance in landfills of hazardous waste (Council Decision 2003/33/EC). The Sb concentration released from stibnite samples pursuant the TCLP had an average value of 3.9 mg/L, which importantly surpasses the limit (0.6

mg/L) for the characterization of wastes as toxic, set at 100 times the US EPA drinking water standard (Guo et al., 2014).

All encapsulation processes significantly reduced the leachable Sb concentrations of stibnite samples; decreases reached values of approximately 99% (Fig 2). Furthermore, all values according to the standard EN 12457-4 (2002) (Fig 2. (a)) and the TCLP (Fig 2. (b)) were below the limit established for acceptance in hazardous waste landfills and below the limit set for the characterization of waste as toxic, respectively. In general, the best performance was achieved when the treated samples were heated at the lowest temperature (30 °C). Under these conditions, the Sb leaching showed average values of 1.4 mg/kg and 0.06 mg/L according to the standard EN 12457-4 (2002) and the TCLP, respectively.

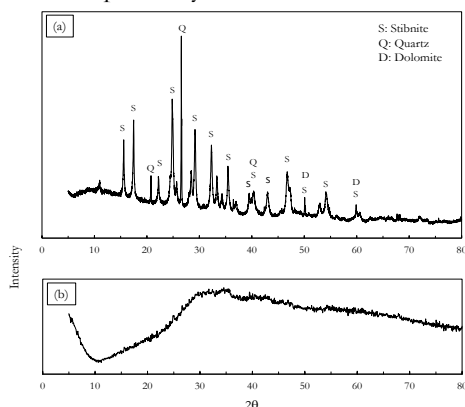


Fig 1. Representative XRD patterns. a) Stibnite samples and (b) Coating.

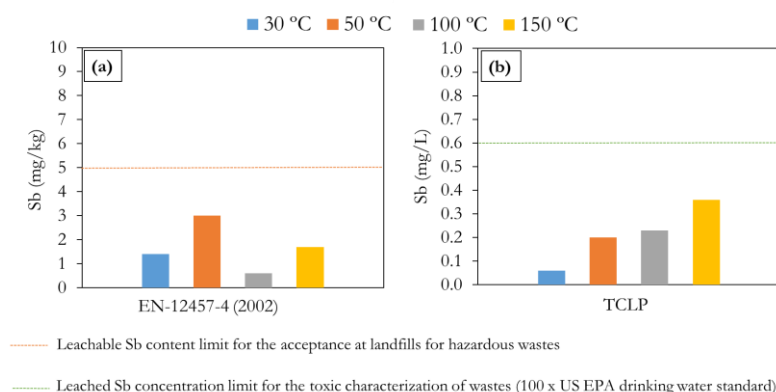


Fig 2. Leachable Sb contents in treated stibnite samples. (a) European Leaching Test EN 12457-4 (2002) and (b) TCLP.

The XRD of the orangish coating present on the treated stibnite samples heated at a temperature of 30 °C (Fig 1. (b)) revealed that it was composed by an amorphous phase. The corresponding chemical analyses showed that Fe, S, and Sb were the major elements composing such coating, with contents having values of 51.1 wt% Fe₂O₃, 25.2 wt% SO₃, and 7.2 wt% Sb₂O₅.

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