Cementation processes of arsenic-bearing mine wastes to mitigate environmental risks

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INTRODUCTION

The accumulation of arsenopyrite (FeAsS)-bearing mine wastes in dumps exposed to the atmosphere entails a great risk of As release to the surrounding environment with the consequent pollution of impacted areas. Measures should be adopted to prevent or limit the off-side migration of As from mine wastes and the derived environmental risks. Among techniques proposed to deal with mine wastes, cementation can represent a suitable alternative due to its affordable cost and relatively easy application. The main goal of this study was to evaluate the use of cementation processes to treat arsenopyrite-bearing mine wastes at different weathering degrees.

MATERIALS AND METHODS

Mine waste rocks were collected from dumps of the former exploitation of the most important tungsten deposit in Spain, located in Barruecopardo (Salamanca). Two types of samples were subject of study: mine wastes with low weathering degree (LWD) and with high weathering degree (HWD). In the former the most abundant As mineral was arsenopyrite and in the latter the dominant As mineral was scorodite. Both were characterized as toxic and hazardous regarding their As leaching behavior. Ordinary Portland cement (OPC) and mixtures of OPC and calcium hydroxide (90:10 wt.%) were used as binders. The sampled mine wastes (at particle size < 5 mm) were mixed separately with the binder using binder/mine waste ratios of 15:85 and 30:70 wt.%. Then, ultrapure water was incorporated to the solid mixtures to reach a water content of 10-15%. Pastes were thoroughly mixed to complete homogenization. Afterwards, the different pastes were cast in ϕ 30 mm \times 60 mm polypropylene cylinders, sealed, and cured at room temperature for 28 days. After this period, the cured samples were removed from the molds and characterized. The mechanical behavior of cemented mine wastes was evaluated by the Unconfined Compressive Strength (UCS) test using a compressive strength testing apparatus. Their leachable As content was evaluated according to the European leaching test EN 12457-4 (2002) and their toxicity was established following the TCLP procedure. The mineralogical characterization of cemented mine wastes was performed by polarized light microscopy studying polished thin sections in transmitted and reflected light by means of a Nikon Eclipse E400 POL optical microscope.

RESULTS AND DISCUSSION

Cemented mine wastes presented compressive strength values within the range of 0.37-22.8 MPa (Fig. 1a). The highest values were shown by cemented materials obtained at a binder/mine waste ratio of 30:70 wt. % using only OPC as binder. In any case, all cemented mine wastes developed compressive strengths higher than that regarded suitable to maintain their physical integrity under the common overburden pressures in landfills (0.35 MPa; Choi et al., 2009). The leachable As content of cemented LWD and HWD mine wastes showed values of 1.85-11.1 mg/kg and 0.61-4.80 mg/kg, respectively. All these leachable As contents were below the limit value (25 mg/kg) for acceptance at hazardous waste landfills (Council Decision 2003/33/EC). Furthermore, the leachable As content showed by cemented materials obtained at a binder/mine waste ratio of 30:70 wt. % using both OPC and calcium hydroxide in the binder mixture were below the limit value (2 mg/kg) for acceptance at non-hazardous waste landfills (Council Decision 2003/33/EC). Additionally, the As concentration released from cemented LWD and HWD mine wastes following the TCLP procedure exhibited values of 0.66-2.28 mg/L and 0.44-3.91 mg/L, respectively. These concentrations were below the limit set for wastes to be classified as toxic (5 mg/L).



apy: arsenopyrite; CP: cementing phase; Fe Ox.: Fe (oxyhydr)oxides; qtz: quartz; ms: muscovite; sc: scorodite. Fig 1. (a) Compressive strength development of cemented mine wastes. (b) Microscopy images of cemented mine wastes.

Polarized light microscopy analyses (Fig. 1b) revealed the formation of red phases, likely corresponding to Feoxyhydroxides. They were present surrounded by the cementing phase, bordering arsenopyrite crystals and filling their cracks, adhered to quartz and muscovite, on scorodite borders and cracks, and forming thin coating on scorodite.

CONCLUSIONS

The cementation processes based on OPC and calcium hydroxide (90:10 wt.%) have proven their feasibility to treat arsenopyrite-bearing mine wastes at different weathering degrees. A binder/mine waste ratio of 30:70 wt.% was found suitable to reduce their leachable As contents at levels below the limit for acceptance at non-hazardous waste landfills and to reverse their toxic character. Also, at such conditions the compressive strengths developed by cemented materials were appropriate for disposal.

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REFERENCES

- Choi, W.-H., Lee, S.-R., Park, J.Y. (2009): Cement based solidification/stabilization of arsenic-contaminated mine tailings. Waste Manage., 29, 1766-1771.
- 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.