



Research article

Evaluation of strategies for mitigating risks associated with metals in pyrite ash

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ABSTRACT

The main objective was to evaluate and optimise strategies for the immobilisation or mobilisation of Cd, Cu, Cr, Ni, Pb, and Zn from pyrite ash. Alkaline amendments were used for the immobilisation test: cement, sandstone, marl, marble waste and calcareous crust. The amendments were mixed with pyrite ash at a 1:2 rate, incubated for 28 days, and leachates analysed at the beginning of the experiment (day 0) and after 2, 7, 14 and 28 days. The mobilisation experiment tested metal release from pyrite ash by four concentrations of H₂SO₄ (0.25 M, 0.5 M, 1 M and 2 M) and contact times (60, 120, 180 and 240 min). Results for the immobilisation/mobilisation tests for Cr and Ni are not presented due to the low concentration in pyrite ash. In the immobilisation test, optimum results across metals and amendments were obtained after two days with percentages of retention being about 90% compared to leachates from pyrite ash only. The release success (in % of total content) using sulphuric acid followed the order: Cd (75%) > Zn (62%) > Cu (37%) > Pb (7%). The concentration of acid was more important than contact time (release enhanced at higher concentrations) except for Zn. The two strategies tested were successful to reduce the risk posed by metals. In terms of optimization, all alkaline materials showed high efficiency for metal retention after a short contact time; for mobilisation, treatment with sulphuric acid at high concentration (up to 2 M tested) resulted to be the optimum with contact time having limited influence.

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1. Introduction

Legacy industry sites affected by metal contamination represent considerable environmental and human health risks. The production of sulphuric acid from pyrite ores roasting is responsible for the generation of roasted pyrite ashes (Lin and Quvarfort, 1996). Roasted pyrite ash is a waste rich in iron oxides (mainly hematite) typically containing high concentrations of metals (Oliveira et al., 2012). Effluents from this waste are acidic and rich in metals which poses high risk for surface and groundwater contamination (Lin and Quvarfort, 1996; Oliveira et al., 2012; Pérez-López et al., 2007).

Environmental risk management of areas affected by pyrite ashes represents a major challenge around the world (Hiji et al., 2014; Lin and Quvarfort, 1996; Oliveira et al., 2012; Pérez-López

et al., 2007). Such risk has been present for a long time (e.g. Bridgeford, 1922) and is far to be fixed in many areas (e.g. Domènech et al., 2017). In some areas the risk associated to roasted pyrite ash is due to current activities (Domènech et al., 2017). Different remediation techniques have been proposed in order to reduce the risks. They can be broadly classified in immobilisation and mobilisation techniques (Bolan et al., 2014). The immobilisation techniques aim to reduce the mobility of metals by their removal from solution through adsorption, complexation, absorption and precipitation reactions (Bolan et al., 2014; Lam et al., 2017a; Tack, 2010). This typically represents an *in situ* treatment characterized by its low cost, especially if locally available amendment materials are used (Lam et al., 2017b). The main disadvantage is related to the fact that pollutants are not removed and could be remobilised (Jia et al., 2016). In addition, amendments materials can be consumed over time reducing their ability to buffer pH, especially in cases where sulphides are present and continue to oxidise (Tiberg et al., 2017). Thus, there is a need to constantly monitor remediation projects under such treatments.

The objective of mobilisation techniques is to release metals into

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solution, subsequently removed by plants or recovered. The mobilisation process takes place through reactions (i.e. mechanisms) including solubilisation, desorption, chelation, or complexation (Bolan et al., 2014). This treatment recovers metals which can be then used for other processes. One of the options is to enhance metal leaching by treatment with sulphuric acid (Antonijević et al., 1997; Erust and Akcil, 2016; Mulligan, et al., 2001). The main disadvantage of the mobilisation treatments is the cost since the wastes are typically processed in specific facilities.

Few have been the attempts to test the efficiency of different immobilisation and mobilisation approaches to mitigate risks posed by pyrite ash. The main objective of this study was to test the efficiency of two different remediation alternatives to immobilise and recover metals (Cd, Cu, Cr, Ni, Pb, and Zn) from pyrite ash, and find the optimum operational remediation parameters. In terms of immobilisation, we were interested in the evaluation of the effect of contact time and type of alkaline material on metal retention. In the case of the mobilisation techniques, the focus was to find optimum concentration of H_2SO_4 and contact time values for metal release.

2. Material and methods

2.1. Study area

The study area is located in a legacy industry site of Cartagena (southeast Spain). The climate is Mediterranean with an annual average temperature of 18 °C, precipitation of 275 mm and evapotranspiration of 900 mm. The area was affected by the activity of a fertilizer company which ceased operation in 2001. This company produced phosphorus fertilizers from phosphoric rocks treated with sulphuric acid. The acid for this process was provided by the roasting of pyrite ores. As a result, large amounts of pyrites ash wastes were landfilled in the area over a number of ponds.

2.2. Pyrite ash sampling and characterization

Pyrite ash samples were sourced from one of the ponds. This pond has been kept under unsaturated conditions, and has an approximate extension of 6000 m² and volume of wastes of 17320 m³. Ten surface samples (0–30 cm) were taken. Samples were dried at 45 °C, sieved to 2 mm and ground in a mechanical mortar (Retsch RM 100) for 15 min. Ground samples were thoroughly mixed to get a composite sample used for further tests.

Waste pH, redox potential (Eh) and electrical conductivity (EC) were measured in deionised water (1:2.5 w/v and 1:5 w/v, respectively). Equivalent calcium carbonate (ECC) was determined by a volumetric method using Bernard's calcimeter. Leachable metals were analysed according to the lixiviation protocol UNE-EN 12457/Part 4 (method prEN14405). This protocol consists in the addition of deionised water in a 1:10 ratio, shake for 24 h, settle for 15 min, centrifuge at 5000 rpm for 2 min and filtrate through a 0.45 µm filter. Total metal concentration was determined by digestion of 0.5 g of sample in a MARS 6 microwave oven using 10 ml of nitric acid (EPA 3051). A sequential extraction of metals was performed according to the Tessier method (Tessier et al., 1979) modified by Li et al. (1995). One gram of soil was weighted and the following reagents were used for each fraction: 1) exchangeable (0.5 M $MgCl_2$ (8 mL)); 2) specifically adsorbed (1 M NaOAc (8 mL)); 3) reducible or bound to Fe and Mn oxides (0.04 M NH_2OHCl (20 mL)); 4) oxidisable (0.02 M HNO_3 (3 mL), H_2O_2 30% (5 mL) and 3.2 M NH_4OAc in 20% (v/v) HNO_3 (5 mL)); and 5) residual (HNO_3 65% (10 mL). Metal concentrations (Cd, Cr, Cu, Ni, Pb and Zn) in the different solutions were measured using atomic absorption spectrometer AAnalyst 800 (Perkin Elmer, United States). Instrument

optimization evaluation and quality control included the use of reference soil material from the Federal Institute for Material Research (BAM-U110), blanks and reference standards during the analyses, and sample replicates. For each analyte three replicates of the pyrite ash were measured and mean values provided which were characterized by small standard deviation values due to homogenization of the ground waste material.

The mineral composition of pyrite ash was determined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). X-ray diffraction analysis was conducted on randomly oriented ground samples, using a D8 X-ray diffractometer (Bruker, Germany) with Cu-K α radiation operated at 40 kV and 30 mA. The morphology and the *in situ* chemical composition of samples were observed and determined using a XLS-30 SEM (Philips, The Netherlands) equipped with energy dispersive system (EDS). The sample for SEM analysis was mounted on an aluminum stub and coated with platinum for 3 min using a Denton™ vacuum system prior to submicroscopic observations. The SEM was operated at 15 keV and 1.94 A filament current. *In situ* chemical composition of particles was recorded in EDAX spectrum collected either in spot (~1 µm) or full field of view mode for 400 s. Semi-quantitative ($\pm 5\%$) elemental composition of particles was corrected for Z (atomic number), A (absorption), and F (fluorescence) factors.

2.3. Immobilisation and mobilisation tests

The following alkaline amendment materials were used for the immobilisation test: cement (CE), sandstone (SA), marl (MA), marble waste (MW) and calcareous crust (CC). These materials were selected due to their alkalinity, availability and proximity. They were processed and characterized for pH, EC, carbonate content and mineralogy (see Section 2.2).

As a previous step, a pH neutralisation test was performed. The alkaline materials were mixed with pyrite ash at increasing concentrations (i.e. from 5% to 200%) to derive neutralisation curves. Such curves were used to derive the optimum amendment rate to raise the pH of pyrite mixture, at least, up to neutrality, which was the rate used for the metal immobilisation test. Samples were incubated in plastic containers and maintained at, approximately, 60% of the water holding capacity under laboratory conditions (mean temperature value of 22 ± 2 °C) for 28 days. A total of 15 samples were incubated per amendment material and sampled (per triplicate) at the beginning of the experiment (day 0), and after 2, 7, 14 and 28 days of incubation. At each sampling day, samples were analysed following the lixiviation protocol UNE-EN 12457/Part 4. pH, EC, Eh and metals (Cd, Cr, Cu, Ni, Pb and Zn) were analysed in the extract as per protocols described in Section 2.2.

The mobilisation test was carried out under the same laboratory conditions but using H_2SO_4 for metal release into soil solution (Antonijević et al., 1997; Erust and Akcil, 2016). Pyrite samples (in triplicate for each treatment) were placed in 100 mL plastic containers and mixed with H_2SO_4 (1:10 ratio) at four concentrations (0.25 M, 0.5 M, 1 M and 2 M) and contact times (60, 120, 180 and 240 min) under constant shaking speed (170 rpm) as used in Erust and Akcil (2016). Metal content at each obtained solution was analysed by Atomic Absorption spectrometer AAnalyst 800 (Perkin Elmer, United States). A metal mass balance was performed to produce the percentage of metal released for each sulphuric acid concentration and contact time treatments. For this calculation, the original total content of metals in pyrite ash was considered and compared with the amount released.

Data and plots were processed in Excel (2016) (Microsoft, USA).

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