



Simulated heap leaching and recovery of multiple elements from a mineralised black shale



H.R. Watling^a, D.M. Collinson^a, R.J. Watling^b, D.W. Shiers^{a,*}

^a CSIRO Mineral Resources, P.O. Box 7229, Karawara, W.A. 6152, Australia

^b TSW Analytical Pty Ltd., P.O. Box 240, Como, W.A. 6952, Australia

ARTICLE INFO

Article history:

Received 13 May 2016

Received in revised form 16 September 2016

Accepted 9 October 2016

Available online 11 October 2016

Keywords:

Bioleaching

Trace elements

Black shale

ABSTRACT

A pyritic, mineralised black-shale was used as a 'research resource' to investigate the range of elements amenable to acid and/or bioleaching, despite most elements not being present in economic concentrations. The shale was acid producing and amenable to heap bioleaching. Bioleaching of crushed shale in columns resulted in increased extraction of 44 out of 54 elements assayed, compared with an abiotic acid-leaching test. The importance of the microbial community in respect of heap closure was highlighted by the extent of pyrite oxidation during bioleaching (90%) compared with acid (abiotic) leaching. The leaching phase in a heap should be continued until the pyrite has been oxidised to minimise future acid generation within, and drainage from, the heap, whether or not the cost of continued heap management can be justified by further metals extraction.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Heap, dump and in-situ or in-place leaching technologies were developed to overcome the challenges of extracting metals from low-grade ores in circumstances where pyrometallurgical or other processing routes were marginal or uneconomic. Lixivants may be acidic or alkaline (e.g., Watling, 2006; La Brooy et al., 1994). Heap leaching is widely practised in the copper industry (e.g., Watling, 2006; Domic, 2007) but is applicable to the extraction of nickel/cobalt (Hunter, 2002; Wen et al., 2006; Steemson and Smith, 2009), zinc (Harlamovs et al., 2004), gold (Kappes, 2002; Logan et al., 2007; Wan and Le Vier, 2003) and uranium (Wadden and Gallant, 1985; Garcia, 1993; ANON, 2011). Two of many challenges in heap leaching are to know what metals can be recovered by (bio)leaching and to understand the chemistry and mineralogy of the large leached-ore beds, which must subsequently be treated and stabilised to prevent or minimise environmental damage.

Black shales are deposited under reducing conditions and containing low concentrations of base metals mainly hosted in the sulfides, and noble metals mainly hosted in an organic fraction (Tuttle et al., 2009). Genesis and weathering of black shales is a much researched topic of interest to geochemists and soil scientists (e.g., Grauch and Huyck, 1989; Petsch et al., 2005; Tuttle et al., 2009). However, in recent years there has also been strong interest in the hydrometallurgical extraction of metals from black shales leading to a number of multi-element commercial-scale developments (Li et al., 2010; Riekkola-Vanhanen, 2010;

Sabag, 2008; Beeson and Goodall, 2014; Continental Precious Minerals Inc., 2013; Western Areas Ltd., 2012) and laboratory- or pilot-scale research projects (d'Hugues et al., 2008a,b; Anjum et al., 2009, 2010).

Black shales differ from less complex ores in their chemical properties and recovery of metals. They are polymetallic (e.g., Loukola-Ruskeeniemi and Heino, 1996) and undergo a wide range of chemical transformations (Petsch et al., 2005). In addition, they are readily colonised by microorganisms (Watling et al., 2013) and amenable to bioleaching with high recoveries of some metals (Riekkola-Vanhanen, 2010). These characteristics facilitate the study of leaching patterns for multiple elements in the same test material and chemical and mineralogical compositions of the residues after leaching. In this study, an organic-rich, polymetallic black shale was leached and bioleached. The behaviour of multiple elements during leaching was monitored. The broader application of biohydrometallurgy for metals extraction is discussed, as is the composition of the leached shale with respect to heap closure.

2. Materials and methods

2.1. Materials and methods

The mineralised black shale, rich in organic carbon (8.9 wt%), contained 8 wt% pyrite and <1 wt% sphalerite closely associated with pyrite grains in a mineral matrix comprised of calcite (10 wt%), intermixed muscovite ($KAl_3Si_3O_{10}(OH)_2$; 10 wt%) and sericite (a variety of muscovite in which some of the Al is replaced with Fe and/or Mg; 29 wt%), feldspar (4 wt%) and quartz (34 wt%). Trace amounts (<1 wt%) of pyrrhotite (approximate stoichiometry FeS), arsenopyrite

* Corresponding author.

E-mail address: Denis.Shiers@csiro.au (D.W. Shiers).

(FeAsS) and an unidentified, mixed iron-silicate-sulfate phase were also detected.

2.2. Microbial cultures

A mixed culture of microorganisms was enriched from solid and liquid samples collected from the Collie Coal Mine, Western Australia (WA). Cultures were grown in $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (10 g L^{-1}) medium or sulfur (5.0 g L^{-1}) medium, containing ammonium sulfate, magnesium sulfate, potassium dihydrogen phosphate, trace element solution (see DSMZ medium 882, www.dsmz.de) and yeast extract. Both media had sulfuric acid added to adjust the solution to pH 1.8, or in glucose-containing heterotrophic medium (DSMZ medium 269) pH 3.0. Microorganisms were adapted to the shale by replacing the ferrous sulfate or sulfur with pulverised shale (10 g L^{-1} , P_{80} 38 μm) or by adding the pulverised shale to the heterotrophic medium.

2.3. Leaching of ground shale in stirred tanks

Two batch leaching tests using ground shale ($-75 \mu\text{m}$, 15% solids loading) were conducted in air-sparged, temperature-controlled, stirred tanks containing 1800 mL acidified water (pH 2.5, H_2SO_4). The initial pH was chosen because the shale was expected to produce acid from the oxidation of pyrite. The ground shale was added to the tanks in small portions with stirring and the solution pH restored to pH 2.5 by intermittent measured additions of H_2SO_4 until all the shale had been added. The 100 g portion of ground ore consumed 14.3 g H_2SO_4 predominantly as a result of calcite dissolution. The solution temperature was raised to 35 °C and one of the tanks was inoculated with 200 mL of a mixed culture of iron(II)- and sulfur-oxidising acidophiles and heterotrophic acidophiles enriched from samples of acidic water from a Western Australian pyritic coal deposit, yielding an initial cell concentration of 6×10^7 cells mL^{-1} . The volume of the 'abiotic' tank was made up with 200 mL deionised water in place of inoculum. Sodium benzoate (biocide, 0.05 g L^{-1}) was added periodically to the second tank to prevent adventitious microbial colonisation. Tanks were sparged with air (0.1 mL min^{-1}) and stirred (300 rpm). Solution evaporation was compensated by weighing the tanks and adding deionised water to the correct mass before withdrawing solution samples. Tests were run for 28 days. The solutions and residues at the end of the tests were quantified, portions analysed and element extractions calculated.

2.4. Leaching of crushed ore in columns

Two small (100 mm ID) isothermal columns (35 °C) containing 4 kg crushed shale (100% passing a 25 mm screen) were aerated (1 L min^{-1}) and irrigated (1.2 mL min^{-1}) from individual reservoirs (5 L solution volume) maintained at pH 1.6 with H_2SO_4 . The amounts of H_2SO_4 required to establish a pH of 1.6 in the reservoir were 5.2 and 9.0 g for the bioleach column and the intended abiotic column, respectively, indicative of the inhomogeneity of the crushed ore with respect to calcite content, when small (4 kg) portions were used. One column was inoculated with a mixed culture containing iron- and sulfur-oxidising acidophiles and heterotrophic microorganisms. The inoculum was added directly to the top of the column to yield a cell concentration equivalent to 6×10^6 cells mL^{-1} in the 5 L of solution being circulated through the column. The second column was not inoculated and biocide (sodium benzoate) was added periodically to the solution reservoir. Solution samples were removed from reservoirs periodically for analysis. The solutions and residues at the end of the tests were quantified, portions analysed and element extractions calculated.

2.5. Analyses

The element composition of the shale was determined using inductively-coupled plasma atomic emission spectroscopy (ICP-AES) and

ICP-mass spectrometry (ICP-MS) following acid digestion with nitric/perchloric/hydrofluoric acids (twice) and nitric/hydrochloric acid dissolution of the digest residue. Total and organic carbon and total sulfur were determined using a Leco carbon sulfur analyser. X-ray diffraction analysis and Rietveld refinement of the XRD patterns (QXRD) gave quantitative estimates of major mineral phases. These analytical methods were also applied to the insoluble residues from the bioleaching tests. Trace and ultra-trace element occurrences in discrete mineral particles in the shale were identified using qualitative laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). This was accomplished through repeated laser ablations at 2 s intervals to generate 'depth' profiles in selected mineral grains. Mean counts (not concentrations) for each element were recorded for that part of the profile indicative of the target phase (beneath a weathered surface). Mineral associations in particles were visualised using scanning electron microscopy-energy dispersive spectrometry (SEM-EDS) using a JEOL JSM-7001F field emission SEM.

The solution oxidation-reduction potentials (ORP) and pH values were measured periodically during leaching. A pH meter (TPS-Smartchem model) and glass membrane electrode (Ionode PBFC), calibrated using pH 1.68 and 4.00 buffers, were used to measure pH. Solution potentials were measured using a redox electrode (Ionode PRFO, Ag/AgCl_(ref)). Microbial cells in tank solutions were examined using phase contrast microscopy but could not be enumerated because of the presence of fine mineral particles. Solution samples were filtered and analysed using ICP-AES and ICP-MS.

3. Results

The goals of this research were (i) to determine what elements could be acid leached from mineralised black shale with and without microorganisms, and (ii) to measure element concentrations in leached residues that would ultimately be 'stored' in the environment. In undertaking the work, it was assumed that the technology of choice would be heap leaching because element concentrations in the shale were low and an economic process would therefore need to be low-cost. In respect of the first goal, tests were conducted on ground material ($-75 \mu\text{m}$) so that mineral liberation and surface areas for reaction were maximised. A moderate temperature (35 °C) was employed to accelerate reaction rates during leaching, thus emphasising differences between acid leaching and bioleaching. With the second goal in mind, it was important also to leach particles of a size appropriate to heap leaching, to generate residues similar to those that might be encountered at heap closure. Therefore complementary leaching and bioleaching tests were undertaken in small columns using crushed shale (particle size up to 25 mm).

3.1. Mineralised black shale characteristics

By definition (Huyck, 1989), a black shale is "a dark-coloured (gray or black), fine-grained (silt sized or finer), laminated rock that generally is argillaceous and contains appreciable carbon (>0.5 wt%)". The mineralised black shale used in the current study exhibited the definitive characteristics gray to black colour, fine-grained, and rich in mica (muscovite, 10 wt% and sericite, 29 wt%) and organic and inorganic carbon (8.95 and 1.4 wt%, respectively). The element 'signature' of the test shale (Fig. 1) corresponded closely to that reported for the global averages for trace element distributions in black shales (Ketris and Yudovich, 2009).

There was clear delineation between the mixed organic-mica phase and veins of quartz with pyrite and sphalerite (Fig. 2). On the basis of SEM-EDS and LA-ICP-MS analyses, it is hypothesised that there are three forms of pyrite, (i) a crypto-crystalline first-generation pyrite that was formed during deposition of the organic-mica phase under reducing conditions, (ii) a second generation pyrite (P2) produced by in situ crystallisation and aggregation within the organic-

Download English Version:

<https://daneshyari.com/en/article/4769385>

Download Persian Version:

<https://daneshyari.com/article/4769385>

[Daneshyari.com](https://daneshyari.com)