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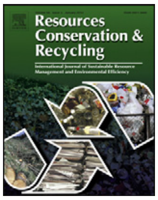

Utilisation of steel slags as neutralising agents in biooxidation of a refractory gold concentrate and their influence on the subsequent cyanidation

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ABSTRACT

A study on the possibilities to utilise steel slag as neutralising agent in biooxidation of a refractory gold concentrate has been done with reference to commercial grade slaked lime. The idea has been to reduce the operating costs for neutralisation in the biooxidation plant, which is known to be the second largest operating cost. Other benefits would be savings in cost for landfilling of slag, possibilities to recycle elements present in the slag and savings of virgin limestone deposits. The slags used were an EAF slag and a slag from ladle refining; both originating from Swedish scrap based steel-making. Continuous biooxidation of the refractory gold concentrate was conducted in a single-stage 5 L reactor at a retention time of 56 h. The neutralisation capacity was determined by comparing the amount needed, per ton of feed concentrate added, to maintain the desired pH of 1.5 during steady state operation. Slaked lime had the highest neutralisation capacity with 110 kg/ton feed followed by ladle slag and EAF slag with values of 152 and 267 kg/ton feed, respectively. Sulphide mineral oxidation was similar and high in all cases although the ladle slag results were slightly better. Gold recoveries after cyanide leaching on the residues obtained were also similar and were in the range of 86–89%. However, the cyanide consumption expressed as kilogram cyanide per ton of concentrate fed to biooxidation, was double in the case of ladle slag and three times as much for the EAF slag compared to the slaked lime experiment. The increased cyanide consumption could not be explained only by the increased amount of elemental sulphur obtained in the slag experiments. The elemental sulphur formed had different reactivities as seen from the thiocyanate formation and cyanide losses due to thiocyanate formation were 16%, 32% and 40% for EAF slag, slaked lime and ladle slag, respectively. It is concluded that the ladle slag could be a possible replacement for limestone if they are mixed in proper proportions so that the microbial carbon dioxide demand is met whereas the EAF slag is less suitable due to the very fine reaction products obtained which gave operational problems with filtration and washing. To come further, experiments with the normal multi-stage biooxidation set-up with total retention time of 120 h should be performed which would increase the sulphur oxidation and eventually also reduce the cyanide consumption.

1. Introduction

Steel industries produce large amounts of slags sometimes as a useful by-product but mostly as a waste material which is either disposed or dumped causing environmental problems by converting fertile land into barren and ground water contamination (Mayes et al., 2008). Accounting for the serious consequences caused by the steel slags and the loss of valuable metals as waste, much attention has been paid to find suitable recycling options aiming at the recovery of valuable metals and minerals and in return offer environmental safety. Various physical and chemical processing methods have been tried to recover the valuable metals, but most of the techniques aim to transform them from one form to another, either by stabilising or by extracting the valuable metals. Among the recycling options for steel slags are their use in building roads and pavements, as a base course and top course for asphalt roads or for the of production of reinforcing bars (CSIRO media release, 2001; Das et al., 2007). Shi and Qian (2000) reviewed the development of high performance cementing materials based on activated slags such as blast furnace slag, steel slag, copper slag and phosphorus slag and stated that these slags posses pozzolanic properties and therefore partially or fully could replace expensive portland cement. Durinck et al. (2008) analysed various case studies on Ca_2SiO_4 (dicalcium silicate) driven slag disintegration and chromium-leaching and stated that smaller or larger additives to the high temperature slag or changes in the cooling path could

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significantly enhance the functional properties of the cooled slag without interference on the metal extraction. As most steel slags contain large amounts of lime together with regulus, some steel making industries are using furnace linings to promote low waste generation, which enables them to produce a new product called recycled lime suitable for injection into electric arc furnaces. This new technology allows the steel industry to recover 500–700 kg lime per 1.0–1.5 tons steel slag formed in one heat (Danilov, 2003). In a hydrometallurgical approach to recycle blast furnace slag by sulphuric acid leaching a silica gel with 90% purity was obtained which could be utilised to increase the strength of cement and/or in ceramics (Seggiani and Vitolo, 2003).

Biohydrometallurgy/biomining is today a well-established technology operating in full-scale for biooxidation of refractory gold concentrates in continuous stirred tank reactors together with copper and nickel extraction via heap bioleaching technology (Rawlings and Johnson, 2007). Competing technologies for pre-treatment of refractory gold concentrates for gold and silver recovery by cyanide leaching are roasting and pressure leaching where the latter is the dominating technology (Reith et al., 2007). However, biooxidation has proven to be economically competitive as well as environmental friendly compared to the conventional methods and is therefore gaining market shares (Liu et al., 1993; Brierley and Brierley, 2001; Rawlings et al., 2003; Lindström et al., 2003; Ehrlich, 2004; van Aswegen et al., 2007; Brierley, 2008, 2010). Gold field's proprietary BIOX^{TM} technology and Canadian-based BacTech Mining Company's BACOX process are widely used today for bioprocessing of refractory gold (Rawlings et al., 2003). These technologies utilises acidophilic bacteria in the mesophile and moderate thermophile temperature range, i.e. with optimum temperatures of 35–50 °C. Biooxidation plants for treatment of refractory gold concentrates have reported higher cyanide consumption compared to when roasting and pressure leaching techniques were used which influenced the operation costs negatively. Hackl and Jones (1997) explained the reasons for increased cyanide consumption as the formation of thiocyanate (SCN^-) due to the reaction of CN^- with incompletely oxidised, meta-stable sulphur compounds. Lindström et al. (2003) showed that by combining a moderate thermophilic pre-leaching stage with a thermophilic leaching at 65 °C, resulted in a considerable reduction in cyanide consumption in the subsequent cyanide leaching due to lower final concentrations of elemental sulphur and other reduced sulphur species in the biooxidation residue. BIOX^{TM} co-workers and others (van Aswegen et al., 2007; Ciftci and Akcil, 2010) have later confirmed the reduced cyanide consumption obtained by using thermophiles in the last biooxidation stage.

Biooxidation of refractory gold ores or concentrates is normally an acid producing process (Eqs. (1) and (2)).

$$2FeAsS + Fe_2(SO_4)_3 + 6O_2 + 4H_2O \rightarrow 4FeSO_4 + 2H_3AsO_4 + H_2SO_4 \tag{1}$$

$$FeS_2 + Fe_2(SO_4)_3 + 3O_2 + 2H_2O \rightarrow 3FeSO_4 + 2H_2SO_4 \tag{2}$$

To maintain pH at for the microorganisms optimum pH of 1–2 limestone is generally used as neutralising agent. After S/L separation where the residue is sent for gold and silver recovery further neutralisation is needed to precipitate iron and arsenic and to obtain a neutral effluent with a pH of 7–8. In this second stage a combination of initially limestone and later slaked lime is used (Stephenson and Kelson, 1997). Together, the need of neutralisation in biooxidation plants constitutes approximately one third of the operation cost in a biooxidation plant (van Aswegen et al., 2007). When available nearby cheaper neutralising agents like dolomite, ankerite or calcrete (a low-grade limestone) are used to make the process economical (van Aswegen and Marais, 1999). To investigate if industrial oxidic by-products like dust, slag and ash could be used for neutralisation a series of studies have been performed by the authors with the aim of improving biooxidation operational costs, recycle metal and mineral (e.g. lime) values and to save virgin limestone deposits (Cunha et al., 2008a,b; Gahan et al., 2008, 2009, 2010).

The aim with the present investigation has been to investigate if slag generated in Swedish steel industries could serve as neutralising agents in the biooxidation of refractory gold concentrate. The slags used were a slag produced in an electric arc furnace (EAF) from scrap based steel making (EAF slag) and a steel slag generated during ladle refining (ladle slag). Special focus has been on eventual negative effects on biooxidation performance, gold and silver recoveries and cyanide consumption.

2. Materials and methods

2.1. Microorganisms, growth medium and culture conditions

A mixed mesophilic microbial culture comprising of both iron oxidising bacteria, sulphur oxidising bacteria and archaea were used in the study. The culture was growing continuously on a modified 9 K nutrient medium ($(NH_4)_2SO_4$, 3.0 g/L; KCl, 0.1 g/L; K_2HPO_4, 0.5 g/L; $MgSO_4 \cdot 7H_2O$, 0.5 g/L; $Ca(NO_3)_2 \cdot 4H_2O$, 0.01 g/L) supplemented with 4.5 g/L Fe^{2+} and 2 mM potassium tetrathionate at a dilution rate of 0.021 h^{-1} (Silverman and Lundgren, 1959). The pH and the temperature were maintained at 1.45 ± 0.05 and 37 °C, respectively, while the redox potential was 740 ± 5 mV versus the Ag/AgCl reference electrode. The microbial population in the mixed culture, determined by Q-PCR analysis at Bioclear B.V., The Netherlands showed a dominance of *Leptospirillum ferriphilum* followed by *Acidithiobacillus caldus* and with approximately the same numbers of *Acidithiobacillus thiooxidans*, *Sulphobacillus* sp. and *Ferroplasma* sp. (Gahan et al., 2008, 2009, 2010).

2.2. Analytical procedures and instrumentation techniques

A platinum electrode against Ag, AgCl reference electrode was used to measure the redox potential of the bioleaching pulp and a Lange LDO^{TM}/sc100 was used to measure the dissolved oxygen level. The concentration of iron, arsenic and zinc was analysed by atomic absorption spectrometry (AAS) on the samples drawn from the biooxidation tank. Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)/Quadrupole Mass Spectrometry (ICP-QMS)/Sector Field Mass Spectrometry (ICP-SFMS) was used to determine the elemental composition of the refractory gold concentrate, neutralising agents, bioleach liquors and the bioresidues. Powder X-ray diffraction (XRD) analysis was carried out on a Siemens D5000 automatic diffractometer with Cu Kα radiation of 40 kV and 30 mA with a sample rotation of 30 rpm to analyse the mineralogical composition of the solid samples. The diffraction patterns were measured in the 2θ range of 10–90° and the crystalline phases were identified using the Joint Committee for Powder Diffraction Standards (JCPDS) database of the instrument.

2.3. Refractory gold concentrate

A refractory gold concentrate from the Petiknäs North mine, owned by Boliden Mineral AB, was used in the study. The wet concentrate received was dried and divided in a rotary divider into 1 kg packets each, prior to its use in the experiments. The refractory gold concentrate contained 10.8 g Au/ton, 91 g Ag/ton, 34.9% Fe, 39.9% S, 5.0% Si and 10.2% As (Table 1). Mineralogical examination by XRD revealed the presence of pyrite (FeS_2), arsenopyrite (FeAsS), sphalerite (ZnS), pyrrhotite (FeS) and quartz (SiO_2). In a previous unpublished study, it was shown that the majority of the