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Technological scheme for copper slag processing

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ABSTRACT

A technological scheme for copper slag processing is proposed. It comprises 5 stages, namely: (i) air oxidation of the copper slag at a temperature above 800 °C for 2 h; (ii) hydrothermal treatment of the oxidized slag with sodium hydroxide solution (140 g/l) at 190 °C for 3 h; (iii) separation of the solid from the liquid phase by hot filtration; (iv) gel formation through hydrolysis of the liquid silicate phase by changing pH; (v) obtaining of amorphous SiO_2 (silica gel) by drying at 80 °C. The processes used for slag manipulation were elucidated and optimized for silicon extraction. It was established that the increase in the oxygen partial pressure in the oxidizing gas does not change the mechanism nor significantly intensifies the oxidizing process. A decisive factor for the extraction of SiO_2 during hydrothermal treatment was the concentration of NaOH. Its increase from 60 to 140 g/l reduced the amount of residual SiO_2 more than half and significantly decreased the formation of analcime ($NaAlSi_2O_6 \cdot H_2O$) in the solid phase. Hydrolysis of the liquid silicate phase by changing pH is an appropriate process for gel formation.

1. Introduction

Copper is derived mainly from copper–iron–sulphur minerals such as chalcopyrite ($CuFeS_2$) and bornite (Cu_5FeS_4), as well as chalcocite (Cu_2S) and enargite (Cu_3AsS_4) (Ayres et al., 2002). They usually are not found in pure form, but combined with each other and with different impurities (especially FeS). Since copper ores typically contain no less than 95% of silicate compounds, the raw materials are subjected to comminution and flotation to produce copper concentrate, which is then sent to a smelter. The purpose of the smelting is to eliminate as much of the unwanted iron, sulphur and gangue minerals as possible, while minimizing the loss of copper (Davenport et al., 2002). This is achieved by: (i) adding appropriate amount of silica, so that a separate fayalite ($2FeO \cdot SiO_2$) phase is formed that captures the iron (Hayes, 1993); and (ii) blowing air to remove the sulphur at high temperature as sulphur dioxide. The latter is captured and used for production of sulphuric acid, thus copper smelters have become integrated with acid plants that utilize offgas (Biswas and Davenport, 2013). But, for every ton copper produced, roughly two tons of iron - silicate slags are generated (Kim et al., 2013). They are considered as wastes irrespectively of their significant content of valuable components including FeO (35–49%), SiO_2 (28–40%), CaO (1–10%), MgO (1–3%), Al_2O_3 (2–15%), Cu (about 1%), as well as Mn, Ni, Zn, Co below 1% (Gorai et al., 2003). Deposition of this slag causes loss of valuable metals and creates environmental issues, owing to the occupation of large quantities of land (Gonzalez et al., 2005) and the acidification of surrounding waters and soils (Rabadjieva et al., 2009). A more sustainable approach would be to reduce the amount of copper slag and to recycle it into useful products.

With minimal treatment, the slag is often used in the production of cement and concrete (Toshiki et al., 2000; Moura et al., 1999; Shi and Qian, 2000), glass (Dongping et al., 1997), abrasive materials (Wozniak and Herman, 1988), bricks, tiles and roof tiles (Marghussian and Maghsoodipoor, 1999). Various methods have also been developed to treat the slag for the recovery of the residual Cu and valuable metals such as Fe, Zn, Ni and Co, by ammonium chloride treatment (Nadirov et al., 2013), by oxidative acid leaching (Yang et al., 2010; Yunjiao et al., 2008), by hydrometallurgical methods (Chen et al., 2012; Rudnik et al., 2009), etc. However, no significant reduction in the slag volume was achieved by these methods, as the silicate components remain untapped. If the fayalite slag were to be decomposed into two phases, silica and mixture of iron oxides, the silica itself could be utilized.

A new approach has been proposed for recycling the copper slag into iron oxide concentrate, alkali metal silicate or a solution of silicon in alkali metal hydroxide, which can be used to produce water glass and

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silica gel (Gyurov et al., 2012 EU patent No. 2 331 717 B1). The proposed method consists of thermal decomposition of the main mineral component of the copper slag - fayalite ($2FeO \cdot SiO_2$) through oxidation in air atmosphere and subsequent hydrothermal treatment with alkali hydroxides or carbonates. The hydrothermal process is carried out at 160 °C for 6 h resulting in roughly 30% extraction of silicon.

Silica gel is a hydrophilic absorbent, with a wide range of applications in the chemical and construction industries. We believe that a more in-depth study of the utilization of silicon containing slag is needed to achieve better extraction of silicon in the form of silica gel. Thus, integrated production of sulphuric acid, silica gel and iron concentrates could be developed eventually leading to the full utilization of all waste products and the minimization of environmental pollution.

The present study is an extension of the method proposed by Gyurov et al. (2012) for utilization of the copper slag for the preparation of silica gel and iron rich residue. The processes used for slag manipulation have been elucidated and optimized for silica extraction. As a result, a technological scheme for copper slag processing is proposed, which comprises: (i) oxidation of the copper slag; (ii) hydrothermal treatment of the oxidized slag with sodium hydroxide or carbonate; (iii) separation of the solid from the liquid phase; (iv) gel formation through hydrolysis of the liquid silicate phase; (v) obtaining of amorphous SiO_2 (silica gel).

2. Experiments and methods of characterization

2.1. Oxidation of the copper slag

Two types of experiments were performed.

2.1.1. Non-isothermal oxidation

The non-isothermal oxidation of copper slag was carried out using the computerized combined thermal analysis apparatus LABSYS evo (SETARAM Company, France) in the temperature range 25–1000 °C. Gas mixtures of nitrogen and oxygen with an oxygen content of 18, 42, 63 and 100 vol% were used as the oxidant. Alumina crucibles with diameter of 4 mm and height of 10 mm were used. The sample weight in all tests was 80 ± 1 mg. The experiments were carried out under dynamic conditions, with a heating rate of 10 °C min^{-1} and an oxidizing gas flow rate of 30 ml min^{-1}.

2.1.2. Isothermal oxidation

The isothermal oxidation was carried out at temperatures of 250, 400, 600, 800 and 1000 °C for 2 h in an air atmosphere. Approximately 1 g of slag was placed in an alumina crucible and was heated in a laboratory furnace at each temperature.

2.2. Hydrothermal treatment of the copper slag

The oxidized slag was treated with a solution of sodium hydroxide or a mixture of sodium hydroxide and sodium carbonate in an autoclave installation under continuous stirring. The system was set to operate at temperatures up to 250 °C and corresponding autogenous pressure of water vapor. Both temperature and pressure were controlled. The optimum parameters of the process of extracting the silicon phase were obtained by varying the temperature, duration of the process and concentration of the alkaline solutions (Table 1).

The resulting mixture of solid iron rich residue and liquid silicate was separated by hot filtration. Then the solid residue was treated again with water in the autoclave in order to achieve additional extraction of the silicon.

Table 1
Conditions of the experiment for hydrometallurgical treatment of the copper slag.

		Concentration of alkali reagent, g/l	
T, °C	t, h	NaOH	Na_2CO_3
160	3	140	–
180	3	140	–
190	3	60	–
	3	80	–
	2	100	–
	3	100	–
		80	20
		70	30
	4	100	–
	3	140	–
200	3	140	–

Note: The amount of the copper slag was 200 g and the solid to liquid ratio – 1:5 g/ml in all experiments.

2.3. Gel formation through hydrolysis of the liquid silicate phase

Two methods were used for carrying out the gelation of the silicate phase:

- Natural formation of gel from the hydrosol extracted from the alkaline filtrate at room temperature for ten days;
- Changing the pH of the liquid phase by acidification with hypo chloric acid down to pH 7–9 or pH 2–3.

2.4. Characterization of the solid and liquid phases

2.4.1. XRD analysis

The phase composition of the solid phases was determined by XRD analyses using an automatic Bruker D8 Advance powder X-ray diffractometer with CuKα radiation (Ni filter) and registration by LynxEye solid-state position-sensitive detector. The X-ray spectra were recorded in the range from 5.3 to 100° 2θ with a step of 0.02° 2θ. A rotating speed of 30 rpm was found to provide sufficiently accurate measurements. Qualitative phase analysis was performed using the PDF-2 (2014) database of the International Centre for Diffraction Data (ICDD) by means of the DiffracPlusEVA software package. Rietveld based quantitative phase analysis was performed with the use of the TOPAS 4.2 software (TOPAS V4, 2008). The total quantity of SiO_2 was calculated by summation of its contents in the silicon-containing phases.

2.4.2. SEM analyses

SEM images were recorded and the distribution of the chemical elements was determined using a JEOL JSM 35 CF scanning electron microscope with a TRACOR NORTHERN TN – 2000 X-ray microanalyser using JEOL standards.

2.4.3. IR analysis

Infrared spectra of the samples were recorded in KBr tablets (13 mm) using Thermo Nicolet Scientific iS5 FTIR spectrometer at a spectral resolution of 2 cm^{-1}. Processing and analysis of the spectrum were made using the OMNIC software.

2.4.4. Chemical analysis

The silicon content in the liquid phases was determined spectrophotometrically in the form of soluble complex β-silicomolybdic heteropolyacid at $\lambda_{max} = 400$ nm, using UV–vis spectrophotometer Evolution 160 of Thermo Scientific Company, USA.