Leaching of blended copper slag in microwave oven

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Abstract: Leaching of blended slag (BS) was investigated in a microwave oven using hydrogen peroxide and acetic acid. The BS was a mixture of converter and flash furnace slag containing 51% Fe_2O_3, 3.8% CuO, and 3.2% ZnO. The important variables that influence the metal extraction yield were leaching time, liquid-solid ratio, H_2O_2 and CH_3COOH concentrations. The preferred leaching conditions were as follows: CH_3COOH concentration 4 mol/L; H_2O_2 concentration 4 mol/L; microwave power 900 W; leaching time 30 min; liquid-solid ratio 25 mL/g BS; leaching temperature 100 °C. Under these conditions, the metal extractions of 95% Cu, 1.6% Fe, and 30% Zn were obtained. The results were compared with the traditional leaching results. It is evident that microwave heating causes a reduction in the leaching time. Also, the extraction yield results indicate that selective leaching of BS can be achieved under the preferred conditions. The dissolution kinetic of BS in hydrogen peroxide with acetic acid is controlled by a shrinking unreacted core model equation. The apparent activation energy and reaction order were found to be 16.64 kJ/mol and 1.09, respectively.

Key words: slag; copper; microwave; selective leaching

1 Introduction

Copper is produced mostly from sulfide ores by pyrometallurgical techniques. Typical copper ores contain from 0.5% Cu (open pit mines) to 1%−2% Cu (underground mines). Chalcopyrite contains the least copper compared with other copper minerals [1,2]. The copper concentrate is typically fed to a smelter which includes melting−converting−refining−electrorefining stages. During the pyrometallurgical processing, various types of slags are generated containing significant amounts of some valuable metals such as Cu, Zn and Co. Slag containing valuable metals is generated during smelting and converting. The copper content of the slag is significant (average 4%) when the copper grade of the ore is considered.

Due to economical reasons, there has been growing interest in hydrometallurgical processes to recover the valuable metals from slag. In these studies, efforts have been mainly focused on the hydrometallurgical recovery processes. Recovery of valuable metals from slag can be classified as oxidative leaching [3−10], and roasting with various reagents [11−15]. The purpose of these research efforts is to offer an alternative hydrometallurgical method for slags because of selective leaching and low cost.

Although pyrometallurgical routes are available, the valuable metals from slags cannot be recovered economically. Also, it is difficult to recover valuable metals from these slags using froth flotation. The copper slag used in this study is a blended slag (BS) that is generated during flash smelting and converting. After cooling/solidification, these two slags (BS) are crushed, ground and treated by flotation. However, for reasons mentioned above, flotation recovery of valuable metals from BS is not effective with existing plant facilities. Therefore, treatment of the slag by a hydrometallurgical method involving microwave heating by hydrogen peroxide oxidation is considered.

Microwaves are electromagnetic waves. They are governed by the same physical laws as other waves (i.e., radio or radar waves), and therefore are reflected, transmitted or absorbed by materials. Microwaves cause molecular motion by migration of ionic species or rotation of dipolar species. The extent to which a material absorbs microwave energy is primarily determined by its conductivity. Materials with low

conductivities, such as insulators, are effectively transparent to the incident waves and thus, do not store any of the energy in the form of heat [16]. However, the permittivities of most materials are related with several variables such as the moisture content of materials, the frequency of the applied electric field, the temperature and the density and the structure of materials [17].

Compared to conventional heating, microwave heating offers a number of advantages which supplies non-contact heating, energy transfer (no heat transfer), rapid heating, material selective heating, heating start from interior of the material body. Materials which are excellent absorbers of microwave energy are easily heated and are classed as dielectrics [18].

The influence of microwaves on various hydrometallurgical processing has been widely reported in Refs. [16,19−22], also for sulphide ores [23−26]. The main reasons for using microwave energy are to reduce processing cost, process time, rapid heating of materials, and use of a controllable clean energy source.

As an oxidant, hydrogen peroxide is a good oxidizing agent for leaching studies because its oxidation potential (1.77 V) is adequate for oxidizing almost all metal sulfide minerals. The oxidative action of hydrogen peroxide in acidic solution may be represented by [27]

$$H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O \tag{1}$$

Furthermore, hydrogen peroxide can also behave as a reducing agent:

$$H_2O_2 \rightleftharpoons O_2 + 2H^+ + 2e \tag{2}$$
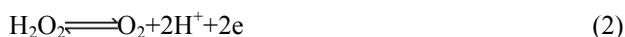
Hydrogen peroxide is an unstable compound, whose decomposition can be catalyzed by certain factors such as the presence of acid, base, mineral surface or soluble ions. Due to rapid exothermic decomposition of hydrogen peroxide in solution, isothermal leaching conditions may disappear and the active oxygen may not be sufficiently used for oxidation of sulfide minerals in the leaching system. To avoid rapid decomposition of hydrogen peroxide, some stabilizers have been used such as glycol, phosphoric acid, oxalic acid, citric acid, and acetic acid in the leaching solution [28−33]. However, acetic acid is known to be a good complexing agent as well as a stabilizer for hydrogen peroxide and reduces the rate of decomposition.

The aim of this study is to investigate the leaching of blended slag (BS) with microwave energy in the presence of hydrogen peroxide and acetic acid.

2 Experimental

2.1 Materials

Blended slag (BS) was obtained from the Karadeniz Copper Plant, Samsun, Turkey. The BS used in these experiments was from converter and flash furnace slag.

First, the BS was cooled in air by water. The cooled material was crushed, ground and fed to froth flotation to recover precious metals. Although it was intended to reduce the economic losses, the BS material thus prepared was floated with a low yield.
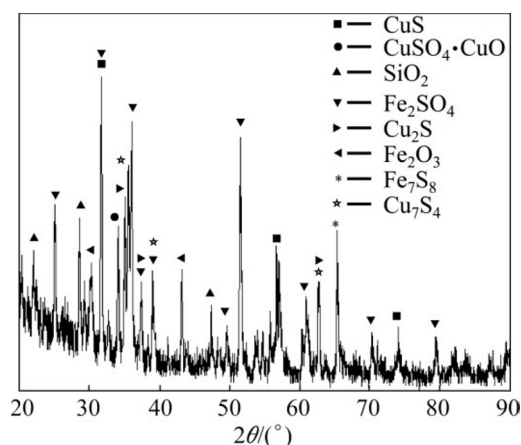
For the research program, the BS sample was crushed, ground, and sieved to <0.074 μm. Constant particle size was used in all experiments because it represented similar size in flotation plant. Subsequently, this sample was dried in a furnace, and it was stored in a closed vessel for later use.

2.2 Characterization of sample

Chemical analyses of the BS were carried out by AAS in clear supernatant that was obtained by the digestion process. Also, the results of chemical analysis were supported with XRF, to quantify the chemical composition of the oxidized metals. The results of the chemical analyses are shown in Table 1. BS contains various mineral phases as shown from the XRD analysis (Fig. 1). As seen in Fig. 1, there are mostly copper and iron−sulfur compounds in BS. The presence of these mineral phases indicates that non-oxidized minerals are collected in slag phase during copper production process. On the other hand, the presence of silicon is observed in some parts of SEM image in BS. SEM result of BS is shown in Fig. 2. Mapping and EDX analysis show that iron and silicon are dominant phases; however, these analyses did not provide information about the liberalization of metals. Particle size distribution measurement of the BS was carried out by using the laser scattering technique. According to particle size distribution analysis, $d_{0.1}$, $d_{0.5}$ and $d_{0.9}$ values are 4.939, 32.056 and 77.161 μm, respectively (Table 2).

Table 1 Chemical analyses of BS (mass fraction, %)

Fe_2O_3	Al_2O_3	SiO_2	SO_3	K_2O	CaO	TiO_2	CuO	ZnO
51	3.5	32	2.4	0.5	0.7	0.1	3.8	3.2

Fig. 1 XRD pattern of BS