Chloride–hypochlorite leaching of gold from a mechanically activated refractory sulfide concentrate

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ABSTRACT

In this research, effect of mechanical activation on the chloride–hypochlorite leaching of gold from a refractory pyritic concentrate containing ca. 27 g/t gold was investigated for the first time. Results showed that after 30 min leaching, 100% of gold was extracted from a 45 min-milled sample while only 37.2% of gold was obtained from the un-milled sample after 480 min leaching (at 25 °C and 600 rpm). This improvement occurred due to the increase in specific surface and accumulated strain in the crystal structure of particles by mechanical activation. It was concluded from the experiments that sensitivity of leaching rate to the temperature decreased after mechanical activation. Results of kinetic study showed that there were two stages in the leaching rate of gold from un-milled sample. The rate of the first stage was controlled by chemical reaction and the second stage was mixed controlled (chemical reaction and diffusion through the $Fe(OH)_3$ layer formed on the pyrite particles). In the case of milled sample, there was one stage in which chemical reaction and liquid film diffusion controlled the rate of leaching.
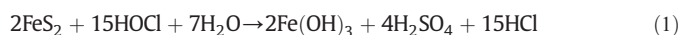
1. Introduction

Pyrite (FeS_2) is the most common sulfide host for gold. In refractory pyritic samples, gold is encapsulated in the pyrite matrix; thus, in hydrometallurgical extraction process, this matrix must be broken down prior to leaching in order to enhance accessibility of gold particles by the leachant (Eymery and Ylli, 2000).

Application of mechanical activation (intensive milling) as a pre-treatment step before leaching has been investigated in different sulfide samples by many researchers (Achimovicova and Balaz, 2005; Balaz et al., 1995, 2000; Ficeriova et al., 2005; Hashemzadehfini et al., 2011; Hu et al., 2004; Maurice and Hawk, 1998). The enhancement of leaching rate, due to mechanical activation, is attributed to the increase of specific surface and lattice strain.

Chloride–hypochlorite leaching represents an alternative route for non-cyanide leaching of gold. This leachant can dissolve gold as $[AuCl_4]^-$ complex (Baghalha, 2007; Ghobeiti Hasab et al., 2013; Puvvada and Murthy, 2000; Soo Nam et al., 2008). In a solution containing 100 g/L NaCl, this complex is stable in the pH range of 0–8 and oxidation–reduction potential (ORP) of greater than 900 mV (Nesbitt et al., 1990). In the hypochlorite solution, oxidant species change with pH. At pH > 7.5, pH = 3.5–7.5 and pH < 3.5 hypochlorite ion (OCl^-), hypochlorous acid ($HOCl$) and chlorine (Cl_2) are the dominant species, respectively. Among these species, hypochlorous acid is the most effective oxidizing agent (Jeffrey et al., 2001). This oxidant can also oxidize pyrite

(Ghobeiti Hasab et al., in press; Ikiz et al., 2006; Ravinder et al., 2010). Oxidation of pyrite and leaching of gold by hypochlorous acid may be expressed as Eqs. (1) and (2).

$$2FeS_2 + 15HOCl + 7H_2O \rightarrow 2Fe(OH)_3 + 4H_2SO_4 + 15HCl \tag{1}$$

$$2Au + 3HOCl + 3H^+ + 5Cl^- \rightarrow 2[AuCl_4]^- + 3H_2O \tag{2}$$

In this research, a gold-bearing pyritic concentrate was activated in a high-energy planetary mill and physicochemical changes of the particles (morphology, specific surface, crystallite size and lattice strain) were investigated. Then, the effect of mechanical activation on the chloride–hypochlorite leaching of gold was studied for the first time.

2. Experimental

2.1. Material

The concentrate used in this study was obtained from flotation of an ore located in north-west of Iran (Barika Mine). Size fraction of −75 + 53 μm (−200 + 270 mesh) from the concentrate was chosen. Fire assay technique indicated that the concentrate contained 27.15 g/t gold. Composition of major elements of the concentrate using XRF (Philips, PW1480) is given in Table 1, which shows S and Fe as the main elements present in the concentrate.

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Table 1
Composition of the concentrate used in this study.

S (%)	Fe (%)	Si (%)	Al (%)	K (%)	Zn (ppm)	As (ppm)	Ag (ppm)	Cu (ppm)	Pb (ppm)	Ba (ppm)	Ca (ppm)	Au (ppb)
46.51	40.61	4.16	0.59	0.23	6264	2614	1972	1499	959	896	143	27 154

Mineralogical studies using thin and polished sections under light microscopy (Leitz, Ortholux POL-BK) showed that pyrite (FeS_2) and quartz (SiO_2) were the major and minor minerals in the concentrate, respectively. Gold presented as electrum alloy (Au–Ag) was predominantly linked to pyrite. Muscovite ($H_2KAl_3(SiO_4)_3$), sphalerite (ZnS), arsenopyrite (FeAsS), chalcopyrite ($CuFeS_2$), galena (PbS), barite ($BaSO_4$), calcite ($CaCO_3$) and argentite (Ag_2S) were also presented at trace amounts.

2.2. Mechanical activation

Mechanical activation of the concentrate was performed using a planetary ball-mill (Retsch, PM 400) with 25 g concentrate and 500 g tungsten carbide balls (BPR = 20, 7 balls with diameter of 20 mm and 7 balls with diameter of 10 mm) into a tungsten carbide chamber with volume of 250 mL. Then, the samples were subjected to dry milling at ambient atmosphere. The mill was run at 300 rpm at different milling times (15, 30, 45, 60, 120, 240 and 480 min). After each milling, the grinding chamber and balls were thoroughly cleaned by methanol into an ultrasonic bath (Retsch, 5 L) and dried for the next milling experiment. The obtained samples were sealed in a plastic pocket for the leaching experiments.

2.3. Physicochemical characteristics

Changes of particles' morphology, specific surface area, crystallite size and lattice strain introduced by mechanical activation were investigated by SEM/EDX (Cam Scan MV2300), BET (Micromeritics Gemini 2375) and XRD (Philips, X'PERT, Cu–Kα radiation) techniques, respectively.

2.4. Leaching experiments

Leaching tests were carried out in a 250 mL four-necked flask equipped with a reflux condenser, a thermometer, a pH meter and an ORP meter (vs. SHE). The flask was immersed in a water bath located on a magnetic stirrer equipped with a hot plate. The leachant was prepared by adding 100 g sodium chloride (NaCl) and 250 g calcium hypochlorite ($Ca(OCl)_2$) to 1000 mL deionized water (pH = 11). To run each leaching experiment, 100 mL leachant was added into the flask and heated up to a pre-set temperature under continuous stirring and then 5 g concentrate was added to the flask (S / L = 1 / 20). In a defined time intervals, 2 mL of the slurry was withdrawn and filtered. Gold content of the clear solutions was analyzed by ICP (Varian, VISTA-PRO). All the chemical materials used for the experiments were of analytical grade of Merck and deionized water was used throughout the work.

3. Results and discussion

3.1. Physicochemical changes of mechanically activated concentrate

Fig. 1 shows XRD patterns of the un-milled and milled samples. As can be seen, no new phase was produced by milling. The recorded XRD spectra were used for calculation of lattice strain and crystallite size from changes in the profile of the main peaks of pyrite, i.e. (200), (210) and (311). Increase of the profile width resulted from decrease

of the crystallite size and increase of the lattice distortion. These parameters could be calculated using the Williamson–Hall method after instrumental correction (Williamson and Hall, 1953). The Williamson–Hall equation is expressed as follows:

$$B\cos\theta = \frac{0.9\lambda}{t} + 2\varepsilon\sin\theta \qquad (3)$$

where B is the full width at half maximum (FWHM) of the XRD peaks, t is the crystallite size, λ is the wave length of the X-ray, ε is the lattice strain and θ is the Bragg angle. In this method, $B\cos\theta$ is plotted against $2\sin\theta$. Using a linear extrapolation to this plot, the intercept gives the crystallite size ($0.9\lambda/t$) and the slope gives the strain (ε).

Variation of crystallite size and strain with milling time is listed in Table 2. Specific surface area of pyrite particles measured by BET technique is also represented in Table 2. According to Table 2, with increasing the milling time, the crystallite size decreased and the lattice strain increased while the specific surface area increased from the original value of 0.18 m²/g to the maximum value of 3.36 m²/g after 45 min milling. With milling more than 45 min, the specific surface area was lowered; the reason of this was agglomeration of the particles. SEM images of the concentrate milled at different times demonstrated this issue (Fig. 2). A high magnification SEM image of the concentrate
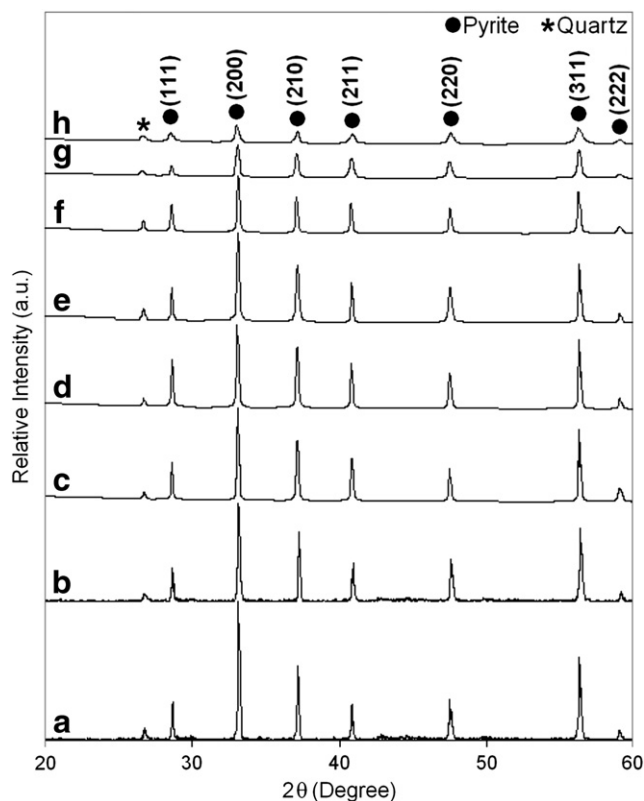
Fig. 1. XRD patterns of the (a) un-milled and milled samples at different times of (b) 15, (c) 30, (d) 45, (e) 60, (f) 120, (g) 240 and (h) 480 min.