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CHLORIDE–HYPOCHLORITE OXIDATION AND LEACHING OF REFRACTORY SULFIDE GOLD CONCENTRATE

Mehdi Ghobeiti HASAB, Fereshteh RASHCHI, Shahram RAYGAN

School of Metallurgy and Materials, College of Engineering, University of Tehran, Tehran, Iran
rashchi@ut.ac.ir)

Abstract.: In this research, oxidation of sulfide minerals and leaching of gold from a gold–bearing sulfide concentrate using chloride–hypochlorite solution was investigated. The effects of calcium hypochlorite concentration, sodium chloride concentration and initial pH of leachant on changes of the slurry pH and Eh were examined. Then, considering the stability range of the gold complex (Eh ~ 1000 mV) and formation of chlorine gas (pH < 3.5), the optimum leaching parameters were determined. The optimum conditions were obtained at 200 g/dm^3 calcium hypochlorite, 200 g/dm^3 sodium chloride and initial pH 11 (with 200 g/dm^3 concentrate, stirring speed 600 rpm and temperature 25°C) at which about 82% gold was extracted in 2 h.

Keywords: *refractory gold ore, oxidative pre–treatment, non–cyanide leaching*

Introduction

Although cyanide has been used commercially for the extraction of gold, investigations are being made on alternative non–toxic lixiviants, such as thiosulfate (Abbruzzese et al., 1995; Aylmore and Muir, 2001), thiourea (Farinha et al., 1992; Ubaldini et al., 1998; Murthy et al., 2003), thiocyanate (Kholmogorov et al., 2002; Li et al., 2012) and halides (Davis et al., 1993; Van Meersbergen et al., 1993; Pangum and Browner, 1996; Vinals et al., 2006; Baghalha, 2012), mainly due to the failure of cyanidation for extracting gold from the refractory ores, long leaching times (more than 24 hours) and the environmental and safety issues (Senanayake, 2004). These lixiviants have not been widely used, because they also have disadvantages (Kai et al., 1997; Aylmore, 2005; Feng and Van Deventer, 2007; Li et al., 2012). The use of chloride is a proven technology in gold refining (Feather et al., 1997). However, no current large scale applications of leach plants are known. The use of the halogen of the halide itself as

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oxidant (chlorine gas), would lead to higher capital investment costs for the prevention of corrosion and the use of a closed system. Perhaps the biggest drawback in the use of the chloride/chlorine lies in the handling. Thus, it is important to select an effective substitute for chlorine.

For extraction of gold from the refractory ores in which gold is surrounded by sulfide minerals, oxidative pretreatment of the ore is essential to oxidize the sulfides and expose gold. Pyrometallurgical oxidation by roasting is encountered with environmental limitations; thus hydrometallurgical methods are preferred. These methods include pressure oxidation (Long and Dixon, 2004), bio–oxidation (Hansford and Chapman, 1992), oxidation by nitric acid (Gao et al., 2009) and chlorine species (Ikiz et al., 2006). Chlorine gas in aqueous solutions, depending on pH, can form three oxidizing species: aqueous chlorine ($Cl_2(aq)$), hypochlorous acid (HOCl) and hypochlorite ion (OCl^-). These three species also can be generated by the addition of sodium hypochlorite (NaOCl) or calcium hypochlorite ($Ca(OCl)_2$) to an aqueous solution (Puvvada and Murthy, 2000). Calcium hypochlorite is more stable than sodium hypochlorite and contains a higher chlorine concentration. These salts are ionized in water, Under acidic conditions ($pH < 7.5$) the hypochlorite ion is converted to hypochlorous acid. Under highly acidic condition ($pH < 3.5$) and in the presence of chloride ion, aqueous chlorine is formed. All of the chlorine species are powerful oxidants but HOCl is the most effective. Thus, pH should be maintained in the range of HOCl stability (Black and Veatch Corporation, 2010).

Hypochlorite solutions within the pH range at which hypochlorous acid dominates, will readily oxidize all sulfides commonly associated with gold. Pyrite is more stable than other metallic sulfides. It means that when in the aqueous media pyrite is oxidized, other sulfides are surely oxidized. The Pourbaix diagram of Fe–S shows that pyrite is decomposed to iron hydroxide and sulfate in the range of hypochlorous acid (grey area in Fig. 1). Oxidation of sulfides by hypochlorite solutions has an advantage of sulfate formation instead of elemental sulfur; since elemental sulfur causes passivation of minerals surfaces (Marsden and House, 2005). In hypochlorous acid solutions, gold is also dissolved as the $[AuCl_4]^-$ complex. Therefore it is possible to oxidize sulfides and leach gold simultaneously by this oxidant (Welham and Kelsall, 2000). Leaching of gold with hypochlorous acid follows reaction (1) (Jeffrey et al., 2001):

$$2Au + 3HOCl + 3H^+ + 5Cl^- \rightarrow 2[AuCl_4]^- + 3H_2O. \tag{1}$$

Controlling solution pH and Eh is important for stabilizing the gold complex. Failing to do this would cause the gold to reprecipitate, after it is dissolved from the ores (Baghalha, 2007; Soo Nam et al., 2008). The stability region of $[AuCl_4]^-$ is determined by the Pourbaix diagram of the Au–Cl system.

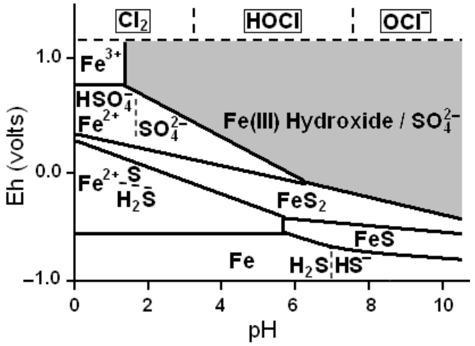

Fig. 1. The Pourbaix diagram of Fe–S at
[Fe] = 10^{-4} M, [S] = 10^{-4} M and 25°C
(the chlorine species regions are also marked)
(Marsden and House, 2005)

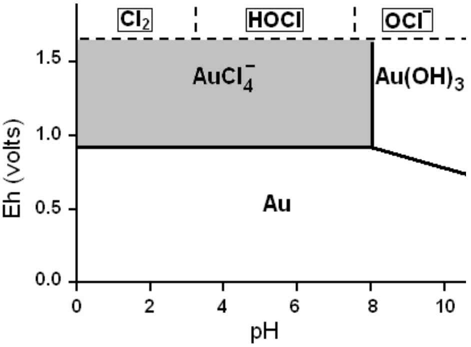

Fig. 2. A part of the Au–Cl Pourbaix
diagram in the $[AuCl_4]^-$ domain
at [Au(III)] = 10^{-6} M, $[Cl^-]$ = 1 M and 25°C
(Marsden and House, 2005)

A part of the Pourbaix diagram of Au–Cl in the $[AuCl_4]^-$ domain is shown in Fig. 2. This region is bounded by equations (2) and (3). According to these equations, increasing the Cl^- concentration results in the extension of $[AuCl_4]^-$ domain to the lower Eh and higher pH. The $[AuCl_4]^-$ is stable in the 0–8 pH range and in potentials greater than 0.9 volts, depending on the concentration of gold and chloride ion (Nesbitt et al., 1990; Welham and Kelsall, 2000).

$$Au + 4Cl^- \rightarrow [AuCl_4]^- + 3e$$

$$Eh = 1.00 + 0.02\,(\log\,[AuCl_4]^- - 4\log\,[Cl^-]\,) \tag{2}$$

$$Au(OH)_3 + 3H^+ + 4Cl^- \rightarrow [AuCl_4]^- + 3H_2O$$

$$pH = (18.38 - \log\,[AuCl_4]^- + 4\log\,[Cl^-])/3 \tag{3}$$

The present paper is a study about the changes of slurry pH and Eh during simultaneous oxidative pretreatment and gold leaching of a sulfide concentrate using the chloride/hypochlorite solution at various conditions of calcium hypochlorite concentration, sodium chloride concentration and initial pH. Then considering the suitable pH and Eh, optimum conditions are determined.

Experimental

The concentrate used in this study was obtained by flotation of an ore located in north-western Iran (Barika Mine in Sardasht). Flotation was conducted at 25°C with a laboratory flotation machine at 25% solid by weight, 40 g/Mg of PEX (potassium ethyl xanthate as collector) and 25 g/Mg of MIBC (methyl isobutyl carbinol as frother). The pH of the slurry was about 7 and agitation rate was set at 1200 rpm. The slurry was conditioned in the flotation cell for 5 minutes before air was introduced. Concentrate collecting time was set at 5 minutes. About 200 g concentrate was obtained from each 1 kg sample. The particles size of the concentrate was examined with a laser particle size analyser. Mineralogical studies were also carried out with an optical microscope (polished and thin sections) and X-ray diffractometer (XRD). Major elements analysis was determined by X-ray florescence (XRF). Gold and silver were analysed by Fire Assay and Atomic absorption spectroscopy (AAS), respectively. For leaching experiments the required reagents were added to a beaker containing deionized water (all the reagents used such as sodium chloride, calcium hypochlorite and sulfuric acid (H_2SO_4) were of analytical grade, purchased from Merck). Then, the concentrate was added into the leachant solution in the beaker and stirred by a magnetic stirrer at 600 rpm at 25°C for 2 h. The solid–liquid ratio was maintained at 1:5. During the leaching, slurry pH and Eh were controlled by two multi–meters with pH and ORP electrodes. Before starting every test, pH and ORP electrodes were calibrated. Solution samples were taken at different intervals by a syringe and filtered. Then clear solutions were analysed for gold by Inductively coupled plasma (ICP). The solid residues were washed and then dried in an oven at 80°C for 2 h and after drying, they were ground, then analysed by XRF, AAS and Fire Assay.

Results and discussion

Particles size analysis of the concentrate showed that 90% of particles are smaller than 37.4 μm (~ 400 mesh) in size (Fig. 3). Mineralogical studies by optical microscope on polished and thin sections showed that the major components of the concentrate are quartz (SiO_2), pyrite (FeS_2), muscovite ($H_2KAl_3(SiO_4)_3$) and barite ($BaSO_4$). Sphalerite (ZnS), calcite ($CaCO_3$) and galena (PbS) constitute the minor phases of the concentrate. Small amounts of pyrrhotite (FeS), chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), tetrahedrite ($(Cu,Fe)_{12}Sb_4S_{13}$) and arsenopyrite (FeAsS) were also detected. More than 90% of the minerals were separated from each others. Gold was not observable in this concentrate because of its small amount. The XRD analysis of the concentrate showed main phases of quartz and pyrite along with minor phases of muscovite and barite (Fig. 4). Major elements composition of the ore and floated concentrate are presented in Table 1. As shown in this table, by flotation of the ore with 3.770 g/Mg gold, a concentrate containing 20.451 g/Mg gold was obtained.

After 24 hours, direct cyanide leaching of the initial ore resulted in only 54.8% gold recovery. However, cyanidation after dissolving the ore sample in hydrochloric acid (HCl), sulfuric acid (H_2SO_4), ferric chloride ($FeCl_3$) and nitric acid (HNO_3), respectively, increased the gold recovery to 98.1%. This shows that the ore is a sulfide refractory gold ore (Saba et al., 2011).

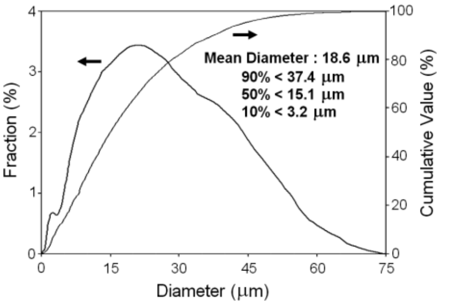

Fig. 3. Particles size analysis
of gold concentrate

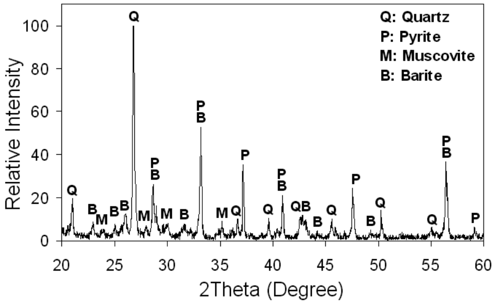

Fig. 4. XRD analysis of gold concentrate
obtained by flotation

Table 1. Major elements composition of the ore and floated concentrate

Analysed Sample	Si (%)	S (%)	Al (%)	K (%)	Ba (%)	Ca (%)	Fe (%)	Zn (%)	Pb (%)	Cu (ppm)	Sb (ppm)	As (ppm)	Ag (ppm)	Au (ppb)
Ore	23.89	5.87	8.07	3.87	7.75	0.99	5.81	0.76	0.31	981	771	751	364	3770
Concentrate	17.76	13.68	5.93	2.26	1.84	0.75	12.79	1.79	0.51	3994	1870	1689	1650	20451

During leaching of concentrate by the chloride/hypochlorite solution, the changes of pH and ORP were detected to determine the optimum calcium hypochlorite concentration, sodium chloride concentration and initial pH.

Effect of hypochlorite concentration

The calcium hypochlorite powder, at various amounts of 2.5, 5, 10, 15, 20 and 25 g, was placed in a beaker containing 10 g of sodium chloride powder. Then, deionized water was added and the mixture was stirred to form a homogenous milky solution with a volume of 100 cm^3. Initial pH of all these solutions was about 11. Then, a 20 g of concentrate was added into the stirring solution. Changes in the slurries pH and Eh during leaching are shown in Fig. 5 (a) and (b).

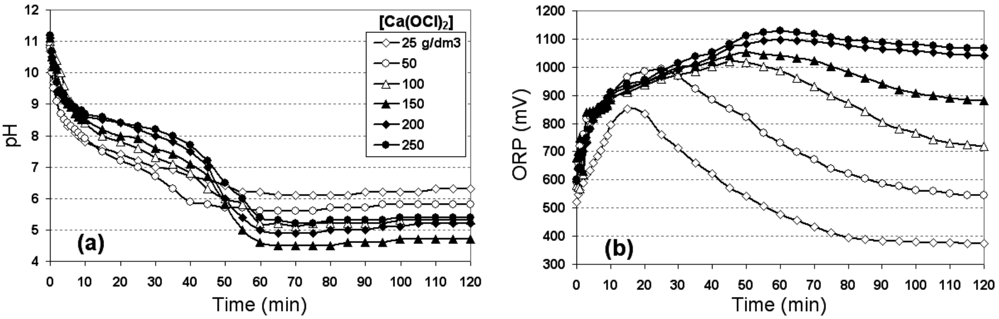

Fig. 5. Changes of (a) pH and (b) Eh of the slurries containing 100 g/dm^3 sodium chloride
and 25, 50, 100, 150, 200 and 250 g/dm^3 calcium hypochlorite during 2 h

According to the results of Fig. 5a it was clear that for all the samples when the concentrate was added, pH decreased during the dissolution. Decreasing the pH is due to the oxidation of sulfides and generation of sulfuric acid. The rate of sulfides oxidation is indicated by the rate of the pH drop. With decreasing pH to below 7.5, hypochlorous acid becomes dominant oxidant and Eh is at its highest value. Due to the hypochlorous acid consumption in reaction with sulfides, its concentration in the slurry reduces and Eh drops (Fig. 5b). According to Fig. 5a and b, it seems that the 200 g/dm^3 calcium hypochlorite is adequate for obtaining an oxidizing media with Eh about 1000 mV to stabilize the gold complex during 2 h. Higher concentration of calcium hypochlorite (250 g/dm^3) has not significant effected changes of pH and Eh. At high hypochlorite concentrations, pH drops slowly due to hypochlorite/hypochlorous acid buffer solution.

Effect of initial pH

To investigate the effect of the initial pH, solutions with 100 g/dm^3 sodium chloride and 200 g/dm^3 calcium hypochlorite were prepared and their pH were adjusted to 10, 9, 8 and 7, by adding sulfuric acid. Figures 6a and b shows the changes of pH and Eh of these slurries during 2 h leaching. As shown, at initial pH of below 11, pH and Eh drop are faster and higher. It was found that the optimum initial pH was 11. In other words, decreasing the initial pH is not useful, neither for the desired reaction nor for the safety issues.

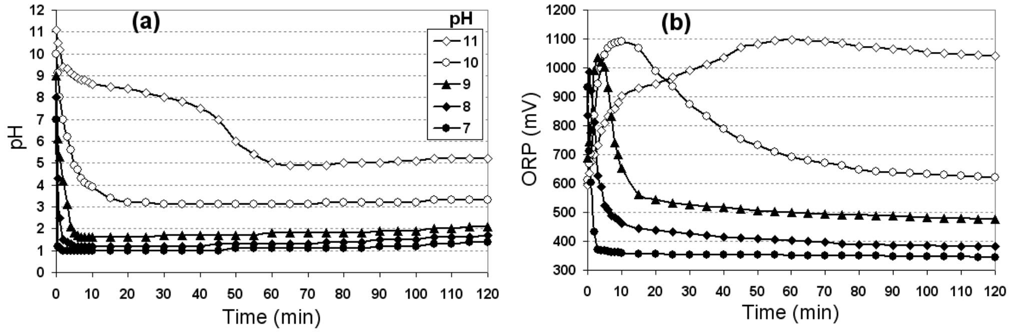

Fig. 6. Changes of (a) pH and (b) Eh of the slurries containing 100 g/dm^3 sodium chloride and 200 g/dm^3 calcium hypochlorite at various initial pH during 2 h

Effect of chloride concentration

Various quantities of sodium chloride in solution (100, 150, 200, 250 and 300 g/dm^3) were used to determine the effect of chloride concentration on pH and Eh. The obtained results are given in Figs 7a and b. Higher levels of sodium chloride were found to significantly enhance the rate of pH drop, i.e. the rate of sulfides oxidation reaction. When the sodium chloride concentration was increased, conversion reaction of hypochlorous acid species to chlorine species occurred at higher pHs. Thus, chlorine gas could be formed easier, and due to escaping of the chlorine oxidant from the solution, Eh drops rapidly.

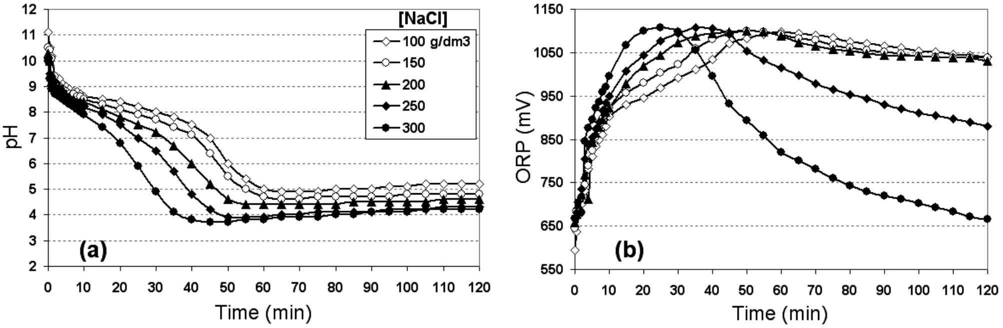

Fig. 7. Changes of (a) pH and (b) Eh of the slurries containing 200 g/dm^3 calcium hypochlorite at initial pH 11 and various concentrations of sodium chloride during 2 h.

In all the experiments, it was observed that after the pH drop, it slowly increased again since the acid generated from the oxidation reaction was consumed by minerals such as $CaCO_3$, which could also increase the slurry viscosity (Marsden and House, 2005). Other gangue minerals such as quartz, muscovite and barite have a low reactivity in the chloride/hypochlorite system. Based on the results at the pH range of 4–7, Eh is at high levels. This indicates that the hypochlorous acid is the dominant oxidant in this pH range. Due to the oxidant consumption at dissolution reactions, Eh drops again. Two important points should be notified here. Dropping of the pH to the values below 3.5 and thus the formation of chlorine gas; dropping of the Eh to the values less than ca. 1000 mV and thus the instability of the gold complex. Therefore 200 g/dm^3 sodium chloride is the optimum amount required.

Analysis of the resulting leach solution and the solid residue

Three clear filtrate solutions (with calcium hypochlorite–sodium chloride concentrations of 200–100, 250–100 and 200–200 g/dm^3) were analyzed by ICP to determine the amount of leached gold. The results are presented in Fig. 8. It is evident that increasing the concentration of calcium hypochlorite had no significant effect on the recoveries of gold. However, increasing the concentration of sodium chloride had a considerable effect. Approximately 82% of gold had been leached during 2 h under experimental conditions of 200 g/dm^3 calcium hypochlorite, 200 g/dm^3 sodium chloride, 200 g/dm^3 concentrate, initial pH 11, stirring speed 600 rpm and temperature 25°C. For this sample, after 30, 60, 90 and 120 min, the filter cake was analysed by XRF, AAS and Fire assay. The results are shown in Table 2, where it is evident that most of sulfides and gold have been extracted from concentrate during leaching. Remained sulfur in solid residue is related to $BaSO_4$ which was not dissolved during leaching and $CaSO_4$ which can form during reaction of Ca(II) with generated sulfate. After 2 h, the slurry colour was converted from dark–grey to light–creamy, which is due to the metal sulfides removal.

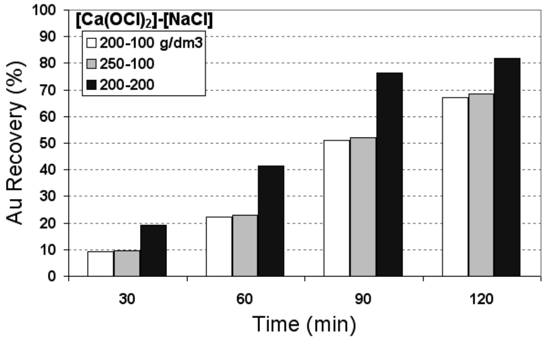

Fig. 8. Percentage recoveries of gold obtained at different concentrations of calcium hypochlorite and sodium chloride during 2 h (concentrate 200 g/dm^3, initial pH 11, 600 rpm and 25°C)

Table 2. Major elements composition of filtrate cake after leaching at different times (200 g/dm^3 calcium hypochlorite, 200 g/dm^3 sodium chloride, 200 g/dm^3 concentrate, initial pH 11, 600 rpm and 25°C)

Time of leaching	Si (%)	S (%)	Al (%)	K (%)	Ba (%)	Ca (%)	Fe (%)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Sb (ppm)	As (ppm)	Ag (ppm)	Au (ppb)
30 min	20.72	8.03	7.58	3.46	2.38	4.80	10.35	6317	4697	3430	1265	1214	1320	16019
60 min	21.54	5.76	7.83	3.68	2.64	6.59	9.27	173	4659	2846	137	57	988	11732
90 min	21.53	5.79	7.91	3.71	2.71	6.63	9.22	67	4571	2673	78	38	403	4631
120 min	21.54	5.81	7.93	3.72	2.73	6.66	9.21	44	4563	2648	51	36	274	3065

Conclusions

Combining sulfides oxidation and gold leaching processes using chloride/hypochlorite solution was a successful method for leaching of a refractory sulfide concentrate containing 20.451 g/Mg gold. Leaching tests at different concentrations of calcium hypochlorite and sodium chloride and also various initial pHs were performed. It was observed that for 200 g/dm^3 concentrate, initial pH 11, stirring speed 600 rpm and temperature 25 °C, at least 200 g/dm^3 calcium hypochlorite is required to achieve high potential values for the gold leaching. Increasing the sodium chloride concentration from 100 to 200 g/dm^3 resulted in an increase in the sulfide oxidation rate as well as the extent of extracted gold. Under optimum conditions 200 g/dm^3 calcium hypochlorite, initial pH = 11 and 200 g/dm^3 sodium chloride), the recovery of gold after 2 h of leaching was about 82%.

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