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Investigation on the recovery of gold and silver from cyanide tailings using chlorination roasting process

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In this work, a chlorination roasting method for the extraction of precious metals (gold and silver) from the cyanide tailings (CT) was investigated. The decomposition mechanism of the $CaCl_2$ used as chloride agent was presented during the chlorination roasting. The Au and Ag recovery as high as 91.6% and 54.7% under the optimum experiment conditions would be achieved. The optimal process conditions were identified to be a $CaCl_2$ content 4%, chlorination temperature 1323 K and chlorination duration of 2 h. The microstructures of CT before and after roasting were examined by using scanning electron microscopy (SEM), and the volatilization process of the chloride of Au and Ag was assessed. The chlorination behaviors of all the phases in the CT in air atmosphere was analyzed using the thermogravimetric analysis (TGA), and the phase transformation of the main phase during roasting were analyzed by using X-ray diffraction (XRD). The chlorination roasting process shows unique advantage for treating the secondary sources of CT, additionally being environmentally benign.

1. Introduction

Gold has been an important metal in home and industrial application throughout the human history. The very significant properties of gold such as high melting point, strong acid resistance, good electrical conductivity, good ductility and resistance to x-ray [1,2] has made it widely useful in aerospace, electrical, electronic and various other industries [3,4]. With the development of modern industry, the comprehensive utilization of natural resources have become more and more popular, and remnants of gold in the tailings makes it have great economic value [5–7].

Gold bearing ores from the refractory are typically classified based on their metallurgical response to cyanide leaching [8–10]. The resources of CT can still be economical to recycle as it contains gold 5–25 g/t [11]. However in practice CT are being sold to the cement plant to be used as ingredients of low cost cement. Many conventional methods such as pyro-technologies [12], hydro-technologies [13,14] and bio-technologies [15,16] have been applied for treatment of the CT to separate Au and Ag. Puvvada and Murthy [17] have reported utilization of sodium hypochlorite for selective extraction of Ag and Au from a copper concentrate. With aqueous pressure oxidation followed by hypochlorite leaching, it was possible to selectively recover 90.0% of gold and 92.5% of silver from the copper concentrate. Wen et al. [18] have investigated the leaching behaviors of gold from ores by using alkaline sodium polysulphide solutions. Sodium polysulphides were prepared by hydrothermal method using sulfur and sodium sulphide nonahydrate ($Na_2S \cdot 9H_2O$) as precursor under alkaline condition. An optimal gold-extraction efficiency of 85% was reported. Although the recovery of precious metals from cyanide tailings has been industrialized, the high cost and the generation of a large amount of waste effluent and waste gas are still the key issues that cannot be

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solved.

The literature clearly indicates the presence of gold as small particles, highlighting the difficulties of extraction of precious metals from CT [19–21]. In this work, a new chlorination roasting process for the extraction of precious metals (gold and silver) from the CT was attempted. Chlorination process, harness the feature of low boiling point and high volatile of metal chlorides. It demonstrates that $CaCl_2$, as a chlorination reagent, effectively break small particles and release gold [22]. It is based on the high chemical affinity of the chlorinating agents towards gold and silver which can be achieved at relatively moderate temperatures compared to other methods (oxidation or reduction processes). This approach has many merits as compared to contemporary popular technologies: 1. Low energy consumption. In general, chlorides have lower melting and boiling points than oxides and sulphates. So we only need to heat to a very low temperature to get the product [23]. 2. Highly selectivity. A wide range of noble metals were recovered by chlorination process selectively and can separate them from oxides such as iron oxides and silica, effectively [24]. 3. Environmental protection. When chlorinating agents such as NaCl and $CaCl_2$ are used, not only the cost can be reduced but also the generated chlorine gas and hydrogen chloride gas can be easily controlled by the content of the chlorinating agent, thereby achieving no exhaust gas generation effect. At the same time, it can be seen in the subsequent part of this article that no toxic waste liquid was newly generated before and after the reaction. It was confirmed in principle that chlorination roasting is a green treatment process [25]. Unfortunately, there are few studies regarding chloridizing roasting of CT using solid chlorinating agent.

In this paper, a novel one-stage selectively chlorinating process to recovery noble metals from CT was investigated. The microstructure of CT was revealed using scanning electron microscopy (SEM). The phase transformation in the roasting process was confirmed using fire assay, X-ray fluorescence (XRF), thermogravimetric analysis (TGA) and X-ray diffraction (XRD). The effect of roasting temperature and the chlorination agent dosage were optimized. Moreover, this paper will describe some thermodynamics and experimental results were studied by the preliminary reaction mechanism.

2. Materials and methods

2.1. Materials

The cyanide tailings used in this work were received from a Gold smeltery in Yan Tai of China. The major elements of the CT were determined with X-ray fluorescence (XRF), as shown in Table 1, are O, Fe, Si, Al, C and Ca. The contents of Au and Ag determined by fire assaying are 10.8 and 24.8 g/T (see Table 1), respectively. The X-ray diffraction (XRD) pattern, as shown in Fig. 1, indicates that Fe_3O_4, Fe_2O_3, SiO_2, $MgAl_2Fe_{1.8}O_4$, and Fe_2MgO_4 are major minerals presented in the CT. Fig. 2 shown that the CT sample mainly exists in three typical structures: light grey and dark grey parts (points A and B) and mixed parts (point C). The light grey and dark grey parts are mainly iron oxide (point A) and silicon dioxide (point B), and gangue minerals with Zn, Fe, O, Pb, Al was primarily found in the CT. At the same time, the light grey, dark grey and mixed parts are

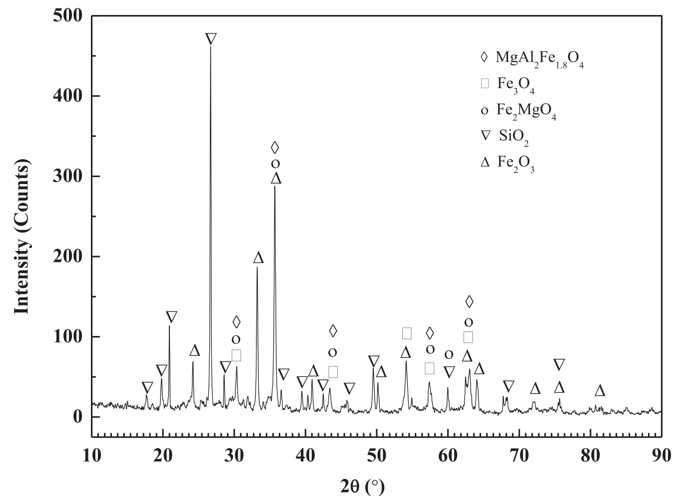

Fig. 1. X-ray diffraction pattern of the cyanidation tailing.

nested each other. Combined with Figs. 1 and 3, it was found that the disseminated ore with large amount of Fe_3O_4, Fe_2O_3, SiO_2, and relatively small amounts of Al_2O_3. It is worth mentioning that due to the extent of the present research, the following discussion is focused on the particles found in greatest abundance. Anhydrous $CaCl_2$ was purchased from Tian Jin Rui Jin chemicals Co., Ltd. (China). The other chemical reagents used in this work were of analytical grade.

2.2. Product identification

Scanning electron microscopy (SEM-XL30ESEM-TMP, Philips Company, Holland) with energy-dispersive X-ray spectroscopy (EDS-GENESIS, EDAX Company, America) measurements of CT sample were performed to understand the structure, morphology and chemical composition, as shown in Figs. 2 and 3. The chemical compositions of CT and roasted powders were analyzed by X-ray fluorescence (XRF, Lab-X3500, Oxford, British). The XRD patterns were taken by a scan rate of 10° min^{-1} was applied to record a pattern in the 2θ range of 10°–90°. The XRD patterns were recorded on a Rigaku D/max-3B powder X-ray diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) and a graphite monochromator in the diffracted beam, and the operating voltage was 32 kV and the current was 0.5 mA. A thermal analysis technique for measuring the relationship between the mass and temperature of the sample under test temperature is used for studying reaction process during chlorination roasting. TGA was measured on a Seraram TGA 92 (Setaram Calure, Cedex, France BP34-69641) system. The test conditions were as follows: air atmosphere, heating rate 20 °C/min, temperature range: 0–1323 K. Fire assaying is a classical method determined gold, silver and platinum group metals by adding solvent (sodium carbonate, lead oxide, silica, sodium borate, etc.) in a crucible, and melting. At the same time, the melt has a good slag flow by adding an oxidizing agent or a reducing agent, and the noble metal and lead form a composite alloy particles separated from the raw material [26]. Fire assay is one of the simple and effective means of integrating metallurgical technology and principles into analytical chemistry, enriching precious metals such as gold, silver and platinum. It is considered as the most reliable analytical method in metallurgy at home and abroad. It has been widely used in related fields and has become an international arbitration method for gold content [27,28].

Table 1
Elemental composition of the CT sample. (mass fraction, %).

Au(g/t)	Ag(g/t)	O	Fe	Si	Al	C	Mg	Ca
10.8	24.8	44.79	25.86	12.08	5.45	3.11	1.12	1.08