Hydrometallurgy 173 (2017) 50–56

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Recovery of rhenium from copper leach solutions using ion exchange with weak base resins

Bo Zhang, Hong-Zhao Liu*, Wei Wang, Zhao-Guo Gao, Yao-Hua Cao

Key Laboratory of Comprehensive Utilization of Gold Resource in Henan Province, Zhengzhou 450006, PR China
Zhengzhou Institute of Multipurpose Utilization of Mineral Resources, Chinese Academy of Geological Sciences, Zhengzhou 450006, PR China
Key Laboratory of Evaluation and Multipurpose Utilization of Polymetallic Ore, Ministry of Land and Resources, Zhengzhou 450006, PR China

ARTICLE INFO

Keywords:
Rhenium
Ion exchange
Weak base resin
Copper leach solution

ABSTRACT

This paper investigated the efficient extraction of rhenium from the leach solution generated by roasting the copper concentrates in a copper smelting plant by direct ion exchange process using weak base resins. The adsorption behaviors of rhenium with other coexisting impurity ions belonged to kinetic control by particle diffusion process, and the reaction rate constant was calculated. Then, the influences of temperature, pH value, stirring rate and calcium oxide dosage on the equilibrium adsorption capacity of rhenium were studied by batch experiments. To verify the process of extracting rhenium in industrial application, three ion exchange columns packing with 105 L resins were operated to recover rhenium by direct ion exchange method. In the adsorption process, the recovery rate of rhenium reached 97.13% after approximately 960 BVs of leach solution flow. The loaded resins were eluated using 2.5% concentration of aqueous ammonia, producing a rhenium-rich solution containing 1995 mg/L rhenium, in which the rhenium concentration enriched 309 times compared to the original leach solution.

1. Introduction

Rhenium is a silver-white transitions metal with the second highest melting point of any metal in periodic table. In the aerospace industry, rhenium is an indispensable component in the nickel superalloys for the production of turbine engine (Abisheva and Zagorodnyaya, 2002; Anderson et al., 2013; Lan et al., 2006; Xiong et al., 2011). Nevertheless, the concentration of rhenium in the earth crust is rather small, at approximately 1×10^{-9}. As rhenium possesses high value and is scarce, the price of rhenium is rather expensive. Thus, it is significative to investigate on efficiently recovering rhenium from rhenium bearing materials.

Most of rhenium deposits in molybdenum-copper ores with concentrations of up to 0.2% as ReS_2. In pyrometallurgical roasting process of copper concentrates, ReS_2 is oxidized to rhenium heptoxide (Re_2O_7) which is subsequently recovered as perrhenic acid ($HReO_4$) after being captured with water (Abisheva et al., 2011; Nebeker and Hiskey, 2012; Seo et al., 2012). Hence, the leach solution in the roasting process of copper concentrates is main raw material for recovering rhenium which is typically recovered using solvent extraction and ion-exchange processes. As the leach solution in copper smelting process contains lower Re concentration in the range of 2–30 mg/L and large amounts of impurities, the solvent extraction process is often complicated by lower concentration ratio, multi-stage cycles and extractant loss (Gerhardt et al., 2000; Cao et al., 2009; Gerhardt et al., 2001). The ion exchange process provides an effective and simple method, and the strong base anion exchange resin is extensively studied in previous research because of its excellent adsorption selectivity for rhenium. However, the eluting agent of these exchangers can be accomplished with ammonium thiocyanate or perchloric acid, which is quite expensive and complicate the following production process of perrhenate ammonium with high purity (Shariat and Hassani, 1998; Kholmogorov et al., 1999; Zagorodnyaya et al., 2013). From an economical and environmental viewpoint, there is continuous interest in investigating weak base resins to recovery rhenium since it is possible to desorb perrhenate ions with aqueous ammonia. In addition, most previous ion exchange experiments were conducted in pure solution system because it was difficult to recovery rhenium from the actual leach solution due to the low concentration of rhenium and the complexity of coexisting impurity ions (Mozammel et al., 2007; Zagorodnyaya and Abisheva, 2002; Agapova et al., 2001).

The purpose of this paper is to provide useful information for developing more efficient and economical technology of recovering rhenium from the copper leach solution in industrial application. The weak

* Corresponding author at: Zhengzhou Institute of Multipurpose Utilization of Mineral Resources, Chinese Academy of Geological Sciences, Zhengzhou 450006, PR China.
E-mail address: liuhongzhao1980@163.com (H.-Z. Liu).

http://dx.doi.org/10.1016/j.hydromet.2017.08.002
Received 14 March 2017; Received in revised form 26 July 2017; Accepted 5 August 2017
Available online 07 August 2017
0304-386X/

Table 1
Main chemical compositions of the leach solution.

Compositions	Re (mg/L)	As (mg/L)	Cu (mg/L)	S (g/L)	F (g/L)	Fe (mg/L)	Si (mg/L)
Amount	5.74	912	844	92.2	3.82	77	510

base anion exchange resins were chosen to selectively recovery rhenium from the low-grade leach solution of copper smelting process. Firstly, the kinetics properties of the adsorption process were investigated and the limiting step of rhenium adsorption process was determined. Then, the ability of the adsorbents to recovery rhenium was investigated as a function of temperature, initial solution pH, stirring rate and CaO dosage by batch technique in detail. Finally, the continuous tests with columns on adsorption and desorption properties of rhenium in leach solution were carried out in industrial scale.

2. Experimental

2.1. Materials

The rhenium stock leach solution was provided by one of the copper smelters in China. The results of the chemical analysis for the leach solution were given in Table 1.

It can be seen that the rhenium was dissolved in the leach solution as 5.74 mg/L, and brought into solution with various other impurities, including arsenic (912 mg/L), copper (844 mg/L), sulfur (92.2 g/L), fluorine (3.82 g/L), iron (77 mg/L) and Si (510 mg/L). The leach solution obtained from the copper smelting process was used for recovering rhenium by direct ion exchange process under laboratory and industrial conditions. All reagents were of analytical grade and were used without further purification.

The main parameters of the weak base anion exchange resins were listed in Table 2 and the functional group of the resins was complex amine. The weak base anion exchange resins ZS70 were purified from the alkaline and acidic impurities with sodium hydroxide and hydrochloric acid solutions respectively. Then, the resins were transformed from chloride form into sulfate form via washing with the sulfuric acid solution in dynamic conditions. Completing the transformation, the resins were washed with distilled water to nearly neutral pH.

2.2. Batch adsorption studies

A predetermined volume of the leach solution was charged to a conical flask and heated to a specific temperature while being magnetically stirred at a speed of 200 rpm (except for stirring rate experiments). Then, a measured amount of pretreatment rein was added to the flask and the reaction time was initiated. All equilibrium adsorption experiments were individually conducted for 24 h (except for the kinetics experiments) at ambient temperature (except for the temperature experiments). After the required time, the resins were separated from the leach solution by vacuum filtration and washed with distilled water. The amount of Re adsorbed per unit mass on the resins was calculated by using the following mass balance equation.

$$Q_e = (C_0 - C_e)\cdot V/W \quad (1)$$

where Q_e is the equilibrium adsorption capacity of metal ions (mg/g), C_0 is the initial concentration of metal ions (mg/L), C_e is the equilibrium concentration of metal ions measured in effluent (mg/L), V is the volume of leach solution (L), W is the amount of resins (g).

2.2.1. Adsorbing kinetics studies

The kinetics experiments of rhenium adsorption were carried out by adding 1 mL resin in 300 mL leach solution for 48 h at ambient temperature. The elution process was accomplished using 50 mL aqueous ammonia with various concentrations for 1 h at ambient temperature.

2.2.2. Temperature

The effect of temperature was conducted by adding 1 mL resins in 300 mL leach solution at varying temperatures of 293, 303, 313 and 323 K.

2.2.3. Initial pH value

For initial pH value of untreated leach solution was 0.94, four conical flasks were filled with 250 mL leach solution and different amounts of aqueous ammonia were employed to adjust the pH value to 2.24, 3.92, 6.14 and 8.20 respectively. Then, all solutions were diluted to 400 mL and 1 mL resins were added to the solution with given pH value.

2.2.4. Stirring rate

The effect of stirring rates was conducted by adding 1 mL resins in 300 mL leach solution at varying speed of 100, 150, 200 and 250 rpm.

2.2.5. CaO dosage

Different amounts of CaO were added to six conical flasks with 250 mL leach solution. The mixtures were shaken for 3 h and the solutions were filtered by vacuum filtration. Then, all solutions were diluted to 300 mL and 1 mL resins were added to the obtained solutions.

2.3. Continuous tests with columns

Following the batch experiments, pilot-scale continuous tests with columns were carried out in a copper smelting plant in China to evaluate the application of weak base resins for recovering rhenium from low-grade rhenium containing leach solution. Three ion exchange columns were consecutively operated for conducting the continuous tests with columns. The columns were fabricated of polymethyl methacrylate (inner diameter is 300 mm, height is 1200 mm) and packed with total 105 L of the resins. The leach solution which came from the copper concentrate roasted flue dusts was used as raw material. To prevent fouling of the ion exchange resins, these leach solutions were firstly sent to a Gore membrane filter to remove any solid particles and then sent to the ion exchange column, where rhenium was selectively adsorbed on the resins as perrhenate anions. The leach solution was fed at a constant flow rate of 700 L/h equivalent to 6.67 bed volumes per hour (BVs/h) through the column using a peristaltic pump. To elute the adsorbed metal ions, the loaded $1^{\#}$ column was first washed with water and then the aqueous ammonia with 2.5% concentration was fed to the column at the flow rate of 40 L/h equivalent to 1.14 bed volumes per hour. The eluted solution was collected at 20 min time intervals for measuring the metal concentration.

2.4. Analysis

The concentrations of metal ions in the leach solution, the effluent

Table 2
The main parameters of the weak base anion exchange resins.

Structure	Matrix	Functional group	Ionic form	Moisture retention	Specific gravity	Bead size
Macroporous	Polystyrene	Complex amine	Cl^- form	40%–45%	1.08	0.7–1.4 mm