Recovery of Rhenium and Molybdenum from Molybdenite Roasting Dust Leaching Solution by Ion Exchange Resins

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Ion exchange separation of rhenium using Purolite A-170 and Purolite A-172 was carried out from the dust leach solution of molybdenite concentrate. Different parameters such as effect of contact time, equilibrium pH, and solid liquid ratio were investigated. The optimum absorption condition for Purolite A-172 resin was determined, and the absorption efficiency of Re and Mo were obtained to be about 90 and 0%, respectively. From results, it was evident that, the performance of Purolite A-172 resin was more effective than Purolite A-170 resin, towards the selective recovery of Re from the molybdenite dust leach solution. [doi:10.2320/matertrans.M2012200]

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1. Introduction

Rhenium (Re) is a rare metal with a high melting point and often being used in making super alloys to improve the characteristic feature such as creep strength. It is also used as a catalyst in petroleum refining industries for making of lead-free, high-octane gasoline. The wide industrial applications of rhenium and its low availability relative to demand, makes it expensive. Hexabutyltriamide of phosphoric acid dissolved in kerosene used as promising extractant for extraction of Re(VII) and Mo(VI) from mineral acids such as sulfuric, hydrochloric and nitric acid solutions were reported. And the reports consists fundamental experimental parameters like time effect, temperature effect and extractant concentration influence on title metal ions and found that, 5 min time is more than enough for extraction equilibrium. The possible separation of Rh and Mo by using Amberlite IRA-400 (ClO₄⁻) was studied by Meloche and Preuss. Thus a small quantity of rhenium can be obtained as a by-product during roasting molybdenites. Hydrometallurgical methods have been adopted to recover rhenium in order to meet the increasing industrial demand. The flowsheet developed for Re recovery by precipitation methodology followed by decomposition and final product formed as crude NH₄₂ReO₄. Resin-in-pulp process established for Re separation from molybdenite calcine and they successfully leached 95% Re with selectivity of Mo. The chemical leaching of rhenium using different acids namely sulfuric acid or nitric acid provides an economic and efficient process. On the other hand, bioleaching can also be another aspect where microorganisms play an important role to solubilize rhenium into the solution phase. Hydrometallurgical methods such as precipitation, chlorination, adsorption on activated carbon, solvent extraction (liquid-liquid extraction) and ion exchange are used for selective rhenium extraction from these solutions. Fisher and Meloche (year 1952) reported on the separation of rhenium from molybdenum in the form of perrhenate by using Amberlite IRA-400 and used 2.5 N sodium hydroxide and 7 N hydrochloric acid solutions, for removal of the molybdate and perrhenate, respectively. In more recent work rhenium concentration and molybdenum separation from sulfuric and nitric-sulfuric acid solutions were accomplished using weak base anion exchangers.

In the present study ion exchange behavior of rhenium and molybdenum were conducted using Purolite A-170 and Purolite A-172. The complete investigation includes the adsorption of metals in bench scale method followed by elution process. The key parameters such as effect of contact time, equilibrium pH and solid liquid (S/L) ratio are examined. The performance for loading of title metals (molybdenum and rhenium) for both of the ion exchange resins i.e., Purolite A-170 and Purolite A-172 were compared.

The optimum conditions for each resins (Purolite A-170 and Purolite A-172), were established by investigating the effects of various parameters namely equilibrium pH (E. pH), solid liquid (S/L) ratio and contact time. In the elution study, different elution agents were introduced for observing stripping behavior of Re.

2. Experimental Procedure

2.1 Preparation sample

After precipitating the major amount of molybdenum from molybdenite dust leaching solution, the remaining filtrate containing 109 mg/dm³ Re, 63 mg/dm³ Mo, 16 mg/dm³ Cu and 3.1 mg/dm³ Ca was used for adsorption of Re by ion exchange resins.

2.2 Procedures and analysis

The resins viz. Purolite A-170 and Purolite A-172 used in the experimental study were subjected to the pretreatment using H₂SO₄. Weighed amount of resins were kept with 2 kmol/m³ H₂SO₄ for 48 h and subsequently leads to the swelling of resin. Thereafter, the treated resins were filtered.
followed by washing with deionized water till a constant value of pH was achieved and later were dried by an oven at 323 K duration next 24 h. Desired quantity of resin was introduced to a conical flask (100 cm³) containing molybdenite dust leached solution and then it was placed in horizontal shaker for a definite time period. A sample of 5 cm³ was withdrawn in a regular time interval and the resin separated from the slurry and was returned to the original slurry. The loaded resin was separated from the slurry, which was later washed and eluted. The concentration of the metal remaining in the slurry and in elute were analyzed by ICP-AES (JOBIN-YVON JY 38). Prior to the elution study the metal loaded resin was washed with deionized water and dried. A desired quantity of loaded resin was treated with the specific reagents in a 50 cm³ conical flask for elution of the respective metal ions from the resin phase.

3. Results and Discussions

3.1 Effect of time

The effect of contact time was investigated in the range of 600 to 3,600 s in the following experimental conditions: solid liquid (S/L) ratio, 40 kg/m³; temp., 298 K; shaking speed, 130 rpm. The results show that the adsorption equilibrium was achieved just after 2,400 s of the reaction time and there after the percentage of metal adsorption remained constant. The maximum adsorption efficiency of Re and Mo with Purolite A-170 was obtained to be ~99 and 95%, respectively (Fig. 1(a)). Whereas with Purolite A-172 adsorption of Re was not significantly affected with increase in the time and just after 1200 s of reaction time the adsorption rate remained the same. On the other hand the adsorption efficiency of Mo was found to be increasing from 8 to 35% during 600 to 3000 s and remained constant on further increase in the contact time (up to 3600 s). From the results, the optimum contact time for selective adsorption Re was 1200 s and the adsorption efficiency of Re and Mo were found to be 99 and 20%, respectively (Fig. 1(b)).

3.2 Effect of pH

In case of Purolite A-170, the adsorption behavior of Re and Mo were examined as the function of E. pH. The other conditions adopted in this test were: S/L ratio 40 kg/m³, 298 K, agitation speed: 130 rpm, contact time: 2,400 s for Purolite A-170 and 1,200 s for Purolite A-172.

Fig. 1 Adsorption efficiency of Re and Mo by contact time with Purolite A-170 (a) and Purolite A-172 (b). (Solid/Liquid ratio: 40 kg/m³, Temp.: 298 K, agitation speed: 130 rpm, pH: 2.5).

Fig. 2 Adsorption efficiency of Re and Mo by equilibrium pH with Purolite A-170 (a) and Purolite A-172 (b). (Solid/Liquid ratio: 40 kg/m³, Temp.: 298 K, agitation speed: 130 rpm, contact time: 2,400 s for Purolite A-170 and 1,200 s for Purolite A-172).
The Purolite A-172 adsorption process pH effect was shown in Fig. 2(b). It is found that over 95% adsorption is taking place at the solution E. pH 8, and later being decrease on further increase of the E. pH (up to 10.0). Meanwhile, the adsorption efficiency of Mo was reached to about 50% between E. pH of 4 and a sharp decrease of the Re adsorption is observed on further increase of the pH value up to 10.0. At E. pH 0, the adsorption efficiency of Re and Mo were 95 and 3%, respectively.

3.3 Effect of solid liquid (S/L) ratio
The absorption behavior of Re and Mo were examined as function of solid liquid (S/L) ratio. The other experimental conditions were adopted viz. temperature 298 K, shaking speed 130 rpm, contact time 2400 s for Purolite A-170 whereas 1200 s for Purolite A-172 and initial pH 0 were kept constant for both resins. From Fig. 3(a), it is seen that adsorption efficiency of both the metals were steadily increased with an increase in the Solid liquid ratio. The maximum adsorption efficiency of Re and Mo at Solid liquid ratio 40 is about 90 and 20%, respectively with Purolite A-170. The adsorption percentage of Re was increased from 38 to 90% with an increase in the solid liquid ratio from 13 to 40 kg/m³ and the adsorption of Mo was not observed at the studied solid liquid ratio range by Purolite A-172 (Fig. 3(b)).

3.4 Elution behavior of Re and Mo from Purolite A-170 and Purolite A-172
Various reagents such as ammonium hydroxide, sodium chloride, nitric acid were used as elution process and the elution profile for Re and Mo above said reagents was presented in Fig. 4(a) for Purolite A-170 and Fig. 4(b) for Purolite A-172 resins. The loaded Purolite A-170 resin having 100.6 mg/dm³ of Re and 17 mg/dm³ of Mo, whereas in case of second resin Purolite A-172 having 84 mg/dm³ of Re and 1 mg/dm³ of Mo. The conditions like solid liquid (S/L) ratio 40 kg/m³, temp. 298 K, shaking speed 130 rpm and contact time 2400 s are kept fixed during experimental study. In case of loaded Purolite A-170 resin, it was cleared that almost all Re adsorbed in the loaded resin was eluted at all label concentration of NH₄OH, but at the same time the elution of Mo was found to be very low (<10 mg/dm³) which showed a selective separation of Re from Mo from the metal loaded resin phase. On the other hand in case of second metal loaded resin i.e., Purolite A-172 the obtained results clearly demonstrates that, elution amount of Re was increased while increasing the NH₄OH concentration from 1 to 5 whereas nitric acid was eluted the Re 30 to 45 mg/dm³ (Fig. 4(b)).
4. Conclusions

The investigation for the recovery of rhenium was carried out using two types of anion exchange resins Purolite A-170 and Purolite A-172. In case of Purolite A-170 resin, the absorption efficiency of Re and Mo were about 90 and 20\% at E. pH 0, contact time 40 min, Solid liquid ratio 40 g/m^3, 298 K, whereas the absorption efficiency of Re and Mo were about 90 and 0\%, respectively using Purolite A-172 resin. Although the adsorption performance for both type of resins found to be similar with respect to adsorption metal Re, however, Purolite A-172 was found to be effective for selective adsorption of Re. Among the eluting reagents, NH_4OH showed a best reagent for quantitative elution of Re. Elution amount of 100.6 mg/dm^3 Re and 5 mg/dm^3 Mo obtained using 1 to 5 mol/dm^3 NH_4OH. On the other hand, the elution amount of Re and Mo were obtained to be 50 and 1 mg/dm^3, respectively, for the case of Purolite A-172. Among the both of the resins, the overall the adsorption behaviour of Purolite A-172 was found to be significant in terms of the selective as well as effective separation of Re from the molybdenite dust leach solution.

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