Behavior of Extraction, Stripping, and Separation Possibilities of Rhenium and Molybdenum from Molybdenite Roasting Dust Leaching Solution Using Amine Based Extractant Tri-Otyl-Amine (TOA)

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The main objective of the present study is to separate the rhenium and molybdenum as well as recovery of the targeted metal ion. The behavior of extraction, stripping and separation possibilities of rhenium and molybdenum from molybdenite roasting dust leaching solutions using tri-octyl-amine (TOA) as an extractant has been investigated. From the results, 5 vol% TOA dissolved in kerosene is found to be selective for extraction of rhenium as compared with molybdenum. It extracted, molybdenum with extraction efficiency of less than 30%, whereas rhenium with extraction efficiency of more than ~99%. The optimum extraction conditions have been determined as: 5 vol% TOA, 900 s of contact time, 298K temperature, 250 ppm agitation speed, phase ratio (organic/aqueous = 2/1) of 0.4 at equilibrium pH 0.0. Stripping (back extraction of loaded metal) of rhenium from loaded organic phase with 5 kmol/m³ HNO₃ was proved as efficient and the rhenium stripping efficiencies were obtained about 99% under conditions of O:A ratio of 1, for 900 s time, at 298K temperature, at the same experimental condition whereas molybdenum stripped ~31%.

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1. Introduction

Rhenium is a less common metal with special properties and it is widely being used in several industrial processes such as petrochemical industry, aviation, electronics, medicine and metallurgy. Because of high costing value of rhenium while compared to molybdenum, the recovery of rhenium from molybdenum bearing materials has received much attention towards economic as well as environmental benefits. Moreover, the separation of rhenium from molybdenum in aqueous solution is a difficult task in hydrometallurgy owing to their adjacent position, in the periodic table and having similar chemical properties. "

The current industrial practice for recovery of rhenium from its bearing materials can be described as leaching—extraction and leaching ion exchanging resin, absorbing—eluting processes reported by several researchers. The resin-in-leaching solution (RIL) followed by selective elution processes is an effective process for rhenium recovery. However, the long leaching and absorbing operations, less selectivity of ion exchange resin and lower capacity of absorption makes the process cost higher. Solvent extraction technique receives considerable interest with high extraction efficiency especially for the recovery of rare metal ions from numerous aqueous solutions.

In general, extraction of metal anions with amines is regarded as a common method for the recovery of molybdenum and rhenium. The common amine extractant like tri-n-octylamine, provides high extent of extraction of metal anions since it is being applied in number of separation process for selective extraction of metal ions such as Mo, V and W from aqueous media. The extraction efficiency of metal ions using amine based extractants follows the order: quaternary > tertiary > secondary > primary while extracting the metal ions at the same experimental conditions. Certain difficulties like crud formation in the organic phase (which leads for low stripping efficiency) is encountered while stripping i.e., back extraction of the targeted metals using quaternary ammonium compounds. On the other hand, tertiary amines are found to be suitable one, which is widely being applied in practical extraction systems and these amines extracts the metal ion by an anion-exchange reaction.

Solvent extraction method is reportedly very successful which is used especially for separation of rhenium from aqueous solutions in presence of other components: arsenic, tungsten or molybdenum. Gerhardt et al. investigated for extraction of rhenium various organic extractants namely tri-n-octylamine, bis-isododecylamine, pyridine, Aliquat 336, tributyl phosphate, trioctylphosphine oxide and ethyl xanthate andmesityl oxide. Solutions of both acids and alkalis i.e., aqueous chloride, sulfate and ammonium solution (for ammonium perhenate separation) or aqueous solutions of NaOH and KOH (to separate suitable rhenium salts, i.e., NaReO₄ and KReO₄), were used in the process of rhenium back extraction (stripping process) from the loaded organic phase. Recently, Zhan-fang et al. used the mixture of TOA and TBP for extraction of Re and Mo (synthetic ammonium solutions containing metal composition: Mo = 15 g/L, Re = 0.1 g/L) and 20% N₂35 (Tri-octyl-amine) extracted 96.7% Re, 1.6% Mo, with separation factor: β_{Re/Mo} = 2.5 × 10³. Further the stripping studies carried out with 18% ammonia and reached 99.3% Re.

The objective of the present study is extraction, stripping and the separation of rhenium and molybdenum from alkaline leach solutions of molybdenite roasting dust by
solvent extraction technique and TOA using as an extractant. Chemical composition of the sample solution for solvent extraction tests with TOA was follows: 186 mg/dm³ Re, 150 mg/dm³ Mo, 11 mg/dm³ Cu and 4.6 mg/dm³ Ca.

2. Experimental Procedure

2.1 Reagents

The commercial amine based extractant such as TOA, supplied by Cognis company, USA and was used as received without further purification. Commercial grade extra-pure kerosene (bp.453–543 K) was supplied by Junsei Chemicals Co. Ltd., Japan. It was used as a diluent for all sets of experiments. A stock solution of TOA was prepared by TOA with kerosene at a predetermined mass ratio, respectively. All preliminary experiments were carried out at ambient temperature (298 ±1 K) to examine the effect of pH, concentration of extractant, and phase ratio (O/A).

2.2 Analytical procedure

The equilibrium pH and metal concentrations in the aqueous phase were measured after separation of the aqueous and organic phases in both extraction and stripping experiments. All the aqueous samples were analyzed to read the metal ion concentration by ICP-AES (JOBIN-YVON JY 38) and pH of the solutions were measured by a pH meter (Orion, USA). The sample solution was immediately filtered through phase separation paper (IPS). The stripping of Rhenium and molybdenum from loaded organic phases were carried out by NaCl, NH₄OH and HNO₃.

3. Results and Discussions

3.1 Extractant (TOA) effect on rhenium and molybdenum

Influence of the TOA concentration on rhenium and molybdenum extraction was tested and the extractant concentration varying from 0.1 to 5 vol%. The other experimental conditions were kept constant: temperature 298 K shaking time 900 s, shaking speed 250 rpm, phase ratio (O/A) of 0.4 and recorded the equilibrium pH 2.5. As shown in Fig. 1, with increasing in the concentration of TOA, the extraction efficiency of rhenium and molybdenum were also increased. The initial increase of the extraction of rhenium and molybdenum were steady (up to 1 vol% TOA concentration) and complete extraction was obtained with using 5 vol% TOA. Therefore, 5 vol% TOA concentration was fixed for further experimental investigations.

3.2 pH effect on rhenium and molybdenum extraction process

The effect of equilibrium pH (from 0 to 10.0) for extraction of rhenium and molybdenum was performed at 298 K, shaking time 900 s, shaking speed 250 rpm, O/A ratio 0.4, by using 5 vol% TOA. The complete extraction of of rhenium was obtained at the solution equilibrium pH 0, whereas molybdenum was extracted only 20% at the same equilibrium pH (Fig. 2). The low extraction of molybdenum at the equilibrium pH 0 may be due to the reason that molybdenum exist as an anionic form beyond equilibrium pH 1 and cation species below equilibrium pH 1 which is further supported by data reported in literature. Therefore, the selective extraction of rhenium was obtained with low co-extraction of molybdenum at the equilibrium pH 0.

3.3 Possible extraction reaction mechanism

The reaction mechanism of the protonation followed by extraction of Re and Mo with TOA can be explained based on eqs. (1), (2) and (3). Overall extraction and stripping reaction mechanism of rhenium and molybdenum in acidic medium follows according to eqs. (4) and (5), respectively is given below.

\[
R_3N_{(org)} + H^+_{(aq)} + HSO_4^-_{(aq)} \leftrightarrow R_3NH^+_{(org)}[HSO_4^-_{(aq)}] \quad (1)
\]

\[
[R_3NH^+][HSO_4^-_{(aq)}] + [ReO_4^-_{(aq)}] \leftrightarrow [R_3NH^+][ReO_4^-_{(aq)}] + HSO_4^- \quad (2)
\]

\[
2[R_3NH^+][HSO_4^-_{(org)}] + MoO_4^{2-}_{(aq)} \leftrightarrow 2[R_3NH^+][MoO_4^{2-}_{(org)}] + 2HSO_4^- \quad (3)
\]

\[
R_3N_{(org)} + H^+_{(aq)} + ReO_4^-_{(aq)} \leftrightarrow [R_3NH^+][ReO_4^-_{(aq)}] \quad (4)
\]

\[
2R_3N_{(org)} + 2H^+_{(aq)} + MoO_4^{2-}_{(aq)} \leftrightarrow 2[R_3NH^+][MoO_4^{2-}_{(org)}] \quad (5)
\]

Where, R stands for Octyl group.
3.4 Phase ratio effect on rhenium and molybdenum

Effect of phase ratio variation (O/A) on extraction of rhenium and molybdenum was investigated by changing O/A ratio in the range of 0.2 to 1 and results are presented in Fig. 3. The experimental parameters such temperature 298 K, shaking time 900 s, shaking speed 250 rpm, equilibrium pH 0 and TOA 5 vol%, were kept constant during the study. As shown in Fig. 3, with change in O/A ratio up to 0.4, the extraction efficiency of rhenium and molybdenum were approximately more than 99% and less than 30%, respectively. However with increase in the higher phase ratio, there is a partial increase in co-extraction of molybdenum along with rhenium.

3.5 Stripping of rhenium and molybdenum from loaded TOA

In any solvent extraction processing back extraction phenomena plays key role for metal recovery technologies establishment. The 5 vol% TOA successfully loaded the 186 mg/L of Re and 45 mg/L of Mo at 25°C temperature, 900 s equilibrium time, unit phase ratio (O/A = 1) with 250 rpm speed of shaker. The stripping behavior of loaded organic with TOA was investigated. It was performed for possibility of selective stripping of rhenium and molybdenum using several stripping agent such as NH₄OH (10 to 50 vol%), NaCl (1 to 5 kmol/m³) and HNO₃ (1 to 5 kmol/m³). The stripping behavior of rhenium and molybdenum with different concentration of HNO₃ (in the range of 1 to 5 kmol/m³) as a stripping solution was examined while keeping rest the of the parameters constant as: temp. 298 K, shaking time 900 s time, 250 rpm. As shown in Fig. 4, all Re was stripped with 5 kmol/m³ HNO₃ and at the same time, co-stripping of Mo was obtained to be less than 30%. Stripping efficiency of Re was increased with increasing of HNO₃ concentration, where as Mo stripping efficiency was remained independent at any concentration of HNO₃. After stripping with HNO₃, concentration of final solution: 186 mg/L Re (99% over), 13.5 mg/L Mo (30%). The representative and possible stripping chemical reactions are given below:

\[
\frac{1}{2} R_3N_2H^+ ReO_4^- \text{org} + [NH_4^+ + OH^-]_{aq} \\
\rightarrow [R_3N]_{org} + [H^+] + [H_2O]_{aq} + [NH_4ReO_4]_{aq} \quad (6)
\]

\[
\frac{1}{2} R_3N_2H^+ ReO_4^- \text{org} + [Na^+ + Cl^-]_{aq} \\
\rightarrow [R_3N]_{org} + 2[H^+]_{aq} + [Cl^-]_{aq} + [NaReO_4]_{aq} \quad (7)
\]

\[
\frac{1}{2} R_3N_2H^+ ReO_4^- \text{org} + [H^+ + NO_3^-]_{aq} \\
\rightarrow [R_3N]_{org} + [NO_3^-]_{aq} + 2[H^+]_{aq} + [HReO_4]_{aq} \quad (8)
\]

3.6 Separation possibilities of rhenium and molybdenum by TOA

Based on the developed experimental methodology on extraction as well as stripping (back extraction from loaded organic phase) of rhenium and molybdenum we checked the separation possibilities in between title metals. It was clearly shows that pH 0 is better experimental conditions to separate both metals with highest separation factor (Fig. 5).

4. Conclusions

The recovery of rhenium and molybdenum from sulfuric acid leaching solution of molybdenite roasting dust was performed by using TOA as an extractant system. Extraction efficiency of rhenium and molybdenum were obtained as 99 and 30%, respectively, using 5 vol% TOA at the solution equilibrium pH of 0 and O/A ratio of 0.4. HNO₃ proved
efficient stripping reagent for Re and Mo. Selective extraction of Re was accomplished with 5 vol% of TOA followed by selective stripping from metal loaded TOA using 5 kmol/m³ HNO₃.

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