Efficient rhenium recovery from molybdenite roasting dust leach solution using tributyl phosphate solvent extraction

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Extraction of rhenium from molybdenite roasting dust leach liquor was systematically studied through a hydrometallurgical process utilizing a solvent extraction technique. To prepare the leach solution, distilled water was used as the leach lixiviant at a liquid-to-solid ratio 3.5, temperature 85 °C, leaching time 90 min, and stirring speed of 400 rpm. Under these leaching conditions, the concentration of rhenium in the leachate was approximately 650 mg/L. Solvent extraction studies were conducted utilizing tributyl phosphate (TBP) as the organic extractant, diluted in kerosene. The paper aimed to assess the extraction efficiency of the extractant for rhenium separation from the aqueous solution using various operational parameters, including pH, TBP concentration, organic-to-aqueous (O/A) phase ratio, temperature, and contact time. The results demonstrated that under the specific experimental conditions of pH = 0, TBP concentration 40 v/v%, phase ratio O/A = 1, temperature 25 °C, and extraction time 6 min, more than 90% of rhenium could be efficiently extracted from the leach liquor. Additionally, based on the McCabe-Thiele diagram, a two-stage counter-current extraction process was simulated to estimate the extraction process in a continuous counter-current mixer-settler system. The results determined that more than 98% of rhenium could be extracted after a two-stage semi-batch counter-current extraction at a pH of 0.

Keywords: Molybdenite roasting dust, Rhenium, Leaching, Solvent extraction, Tributyl phosphate, Counter-current

INTRODUCTION

Rhenium (Re) stands out as a distinctive, valuable, and rare element. It holds significance as a scarce and essential metal, with its globally accessible resources projected to diminish within a century post-2050 (Shen *et al.,* 2021). Recognised by the USGS Mineral Resources Program as a critical rare metal for contemporary transportation, rhenium has also been consistently flagged by the British Geological Survey as a high-risk resource in their supply lists for 2011, 2012, and 2015; registering supply risk indexes of 6.5, 6.2, and 7.1, respectively (Shen *et al.*, 2021).

Rhenium holds significance in industry, serving as crucial components in high-temperature superalloys and as catalysts in the manufacture of high-octane, lead-free gasoline (Nebekar and Hiskey, 2012). Its widespread application spans various sectors including the chemical industry, metallurgy, aerospace, and national defence, owing to its physical and chemical attributes. These include a melting point of 3180 °C and the highest modulus of elasticity among refractory metals. Despite its importance, rhenium reserves on earth are notably scarce. Unlike some elements, rhenium is not found in isolation but rather occurs in association with other metal element minerals like copper, molybdenum, and uranium (Du *et al.*, 2022).

Rhenium is primarily extracted as a byproduct from the processing of molybdenite, which is associated with porphyry copper ores. Modern extraction methods involve recovering molybdenite as a byproduct during copper sulfide flotation. The final molybdenite concentrates typically contain 85–95% MoS_2, with a rhenium content ranging from 0.02% to 0.20% Re. These concentrates undergo roasting and purification to produce lubricant-grade MoS_2, albeit resulting in the loss of rhenium (Nebekar and Hiskey, 2012).

During the pyrometallurgical roasting of molybdenum concentrates with rhenium, rhenium is converted into rhenium heptoxide (Re_2O_7) through the following process:

$$2\ ReS_2(s) + 7.5\ O_2(g) \rightleftharpoons Re_2O_7(g) + 4\ SO_2(g)\ (\Delta G^{o}_{298K} = -406.5\ kcal) \quad (1)$$

Rhenium heptoxide is highly volatile, with a vapour pressure of 711 mmHg at 633 K. At roasting temperatures of 900-950 K, most rhenium is likely to vaporise. The volatile rhenium exits the furnace with the flue gases and is recovered as perrhenic acid ($HReO_4$) through a water scrubbing process:

$$Re_2O_7(g) + H_2O(aq) \rightleftharpoons 2\ HReO_4(aq)\ (\Delta G^{o}_{298K} = -15.16\ kcal) \quad (2)$$

The aqueous rhenium is then extracted using hydrometallurgical approaches, ultimately producing ammonium perrhenate (NH_4ReO_4) through crystallisation (Anderson *et al.*, 2013).

Currently the primary methods for rhenium recovery in industrial applications are ion exchange and solvent extraction. However, the extraction process has several drawbacks, including complexity, difficulty in back extraction, and environmental pollution. Additionally, the adsorption capacity of the ion exchange resin is limited and decreases with each cycle of regeneration (Du *et al.*, 2022).

Solvent extraction presents an efficient and uncomplicated method for separation, particularly in the isolation of rhenium from other elements like arsenic, tungsten, and molybdenum. Various extractants, including tri-n-octylamine, bis-isododecylamine, pyridine, Aliquat 336, tributyl phosphate, trioctyl phosphine oxide, cyclohexanone, ethyl xanthate, and mesityl oxide, are commonly utilised in rhenium extraction processes. Tributyl phosphate (TBP), extensively utilised in hydrometallurgical operations, plays a pivotal role as both an extractant and a modifier in the separation of rhenium (Hosseinzadeh *et al.*, 2014b).

Truong *et al.*, (2017) investigated solvent extraction experiments to separate Mo(VI), V(V), Re(VII), and W(VI) from two synthetic solutions: one with 1–5 M HCl, containing Mo(VI), V(V), and Re(VII), and the other with these metals in a pH of 2–10 range. Initially, LIX 63 extracted Mo(VI) and V(V) from the 1 M HCl solution, leaving Re(VII) behind. Later, V(V) was selectively stripped using a 6 M HCl solution. In the second scenario, LIX 63 extracted Mo(VI) and V(V) from the solution with an initial pH of 2, leaving Re(VII) and W(VI) in the raffinate. Alamine 336 selectively extracted W(VI) over Re(VII). Based on results, a separation process was proposed using solvent extraction and stripping.

Srivastava *et al.*, (2015) explored the extraction of rhenium(VII) from HCl solutions using Cyanex 923 in kerosene. They investigated various factors such as extractant type, acid and chloride concentrations, and organic-to-aqueous phase ratio on Re extraction. It was found that higher HCl concentrations notably enhanced extraction efficiency. The $HReO_4$ species formed a complex with Cyanex 923 in the organic phase at 2.0 M HCl. McCabe–Thiele simulations indicated 99.2% extraction efficiency in a two-stage counter-current process with a 2:3 organic-to-aqueous phase ratio. Loaded Cyanex 923 showed over 99% stripping efficiency with a 1.5 M NH_4OH solution at unit phase ratio and 298 K. Hence, Cyanex 923 displayed potential as a proficient extractant for Re(VII) from acidic chloride solutions.

The literature highlights the importance of efficient rhenium recovery from molybdenite roasting dust and emphasizes various methods and challenges associated with the extraction process. While the existing studies focus on solvent extraction to isolate rhenium from complex mixtures, there remains a need to optimise these processes to enhance recovery efficiency and reduce operational difficulties.

Therefore, this study aims to address these gaps by systematically investigating the solvent extraction of rhenium from molybdenite roasting dust leach liquor, utilizing tailored experimental conditions to maximise rhenium recovery. The objective is to refine the extraction process and provide practical insights for improving industrial rhenium recovery methods. In this context, tributyl phosphate is selected for its proven effectiveness in separating rhenium from other elements and its compatibility with the leach solution. TBP's historical success in hydrometallurgical applications and its ability to meet the extraction efficiency requirements make it an ideal choice for improving rhenium recovery from complex leach solutions obtained from molybdenite roasting dust.

Materials and methods

The aqueous solution for conducting solvent extraction experiments was prepared using the leaching solution derived from molybdenite concentrate roasting dust originated from the Khatunabad Copper Smelting Factory in Kerman, Iran. The results from the XRF analysis of the solid sample are presented in Table I.

Table I. Elemental composition of the roasting dust utilised in this study

Element	wt.%
Re	0.61
Mo	61.8
Cu	0.45
Fe	0.62
W	0.56
Rh	0.032
Nb	0.016
S	23
Mn	0.1
Te	0.028
Ti	0.23
Hf	0.012
Bi	0.077

A Heidolph RZR 2102 control (Germany) mechanical agitator was used for the leaching experiments. To measure the pH of the solutions, an 826 pH mobile meter from Metrohm was used. The aqueous solution for the solvent extraction experiments was achieved from leaching the molybdenite roasting furnace dust at liquid-to-solid ratio 3.5, temperature 85 °C, stirring speed 400 rpm for 90 min using distilled water as the lixiviant (Hosseinzadeh *et al*., 2014b). The obtained pulp was filtered to achieve a high-purity solution free of solid particles. Under these conditions, the concentration of rhenium and molybdenum in the leach solution was roughly 650 mg/L and 5700 mg/L, respectively. Since the amount of impurities in the dust was very low and the leaching reagent was water, it was assumed that the impurities transferred into the leach solution were also very low. Based on this knowledge, it was decided to analyse only rhenium for all the tests, while molybdenum was analysed only for the pH investigation.

Tributyl phosphate (Fluka, Switzerland) diluted in kerosene (Tehran Oil Refining Company, Iran) was employed as the organic phase in the solvent extraction experiments. Sulfuric acid 95-98% (Merck, Germany) and ammonium hydroxide 25%, (Merck, Germany) were utilised to modify the pH of the leaching solutions.

To determine the amount of metal transferred to the organic phase, distribution factor (D), extraction percentage (E), separation factor (S), and McCabe-Thiele diagram, equations (3), (4), (5), (6), and (7) were respectively employed.

$$\frac{V_o}{V_a} = \frac{[(X_a)_0 - (X_a)_n]}{[(Y_o)_1 - (Y_o)_{n+1}]} \tag{3}$$

Where V_o and V_a are the volume of the organic and aqueous phases, respectively. $(X_a)_0$ and $(X_a)_n$ are the concentration of the metal ion in the aqueous phase of the input and output of the system, respectively. And $(Y_o)_1$ and $(Y_o)_{n+1}$ are the concentration of the metal ion in the organic phase of the output and the input to the system, respectively.

The distribution factor, D, was calculated as the concentration ratio of metal ion in the organic phase $[A]_o$ to that in the aqueous phase at equilibrium condition $[A]_a$:

$$D = \frac{[A]_o}{[A]_a} \tag{4}$$

The extraction percentage of metal ion was calculated using the following:

$$E = \frac{D}{(D + \frac{V_a}{V_o})} \times 100 \tag{5}$$

The separation factor was studied using the equation below:

$$S = \frac{D_A}{D_B} \tag{6}$$

Where D_A and D_B are the distribution factors of metal ions A and B, respectively. And the equation 7 was applied to plot the operational line in the McCabe-Thiele diagram:

$$Y_1 = \frac{A}{O}(X_0 - X_n) + Y_{n+1} \tag{7}$$

Extraction equilibrium experiments involved agitating equal volumes (50 mL) of the feed solution and organic phase for 60 min to reach equilibrium at room temperature (25 °C). To construct the rhenium extraction isotherm, various ratios of organic to aqueous phases were employed. All experiments were conducted at room temperature, except for the temperature tests, which explored the range of 25 to 60 °C. All data points in the paper refer to single experimental results, and no reproducibility tests were conducted. Upon reaching equilibrium, the two phases were separated in a separation funnel, and the concentrations of Re and Mo in the aqueous phase were then analysed using inductively coupled plasma-optical emission spectrometry (ICP-OES).

Simulation of solvent extraction process

Figure 1 shows a model simulating the solvent extraction process using the counter-current method in a two-stage extraction. Since final separation conditions cannot be achieved in just one repetition (Hosseinzadeh *et al.*, 2014c), additional two-stage repetitions are necessary to reach stable equilibrium conditions. In this figure, each node represents a contact between the aqueous and organic phases in a discontinuous state, where the phases meet in a certain and constant ratio to reach complete equilibrium. The arrows indicate the aqueous and organic phases that come into contact at each node. The number of extraction steps is determined from the McCabe-Thiele diagram. Repetitions should continue until the concentrations of final raffinates remain unchanged, ensuring the final equilibrium state is obtained. If the number of extraction steps is indicated by i and the number of repetitions by j, the simulation model can be applied for different numbers of extraction steps (i) and repetitions (j). Initially, the results of the experiments are unstable when the two phases come into contact. However, after several repetitions of the extraction process, a steady state is achieved, ultimately leading to the final separation condition, which is similar to the results of the counter-current operation in a mixer-settler system.

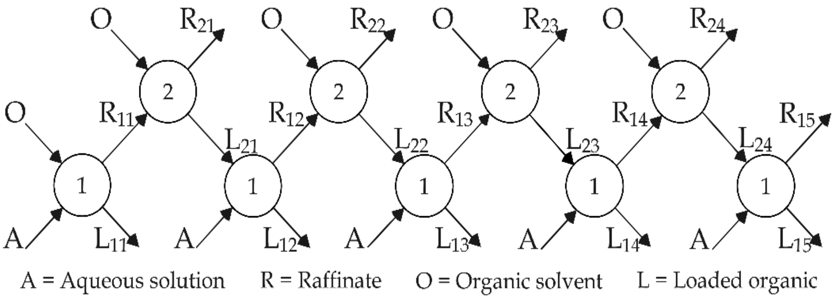

Figure 1. Applied a model to simulate rhenium solvent extraction in a mixer-settler system using a two-stage counter-current extraction.

Results and Discussion

Effect of pH

Figure 2 illustrates the extraction trends of Re and Mo using 40 v/v% TBP as an extractant across different pH levels.

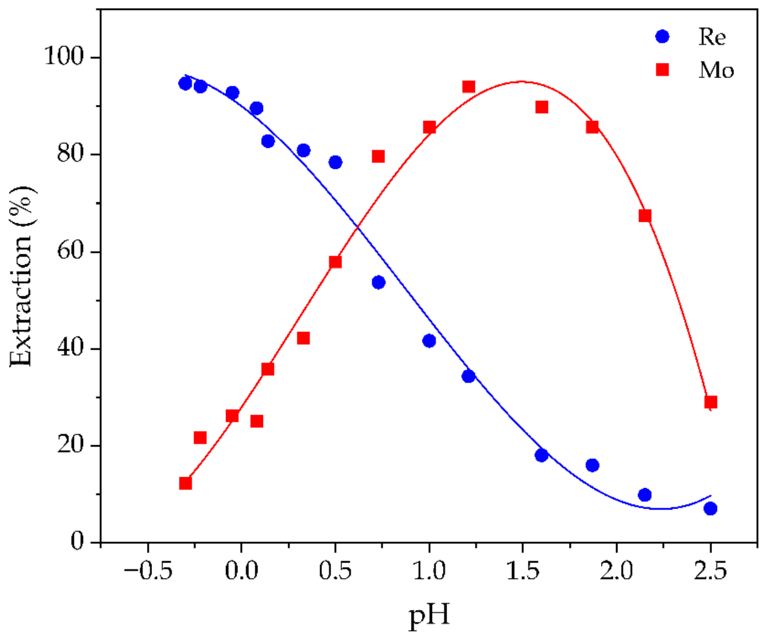

Figure 2. Effect of pH on Re and Mo extraction percentage using TBP = 40 v/v%, $V_o/V_a = 1$ at 25 °C for 1 h.

It is observed that an increase in the H^+ concentration in the leaching solution corresponds to a rise in the extraction percentage of Re. Conversely, the lowest extraction of Mo is noted at pH levels close to zero. This variation in extraction behaviour is ascribed to distinct extraction reactions of Re and Mo (Lee *et al.*, 2008). Mo experiences transformation from anionic to cationic states due to pH influences on extraction reactions and Mo concentration, resulting in the coexistence of MoO_4^{2-} and MoO_2^{2+} ions in the aqueous solution (Zeng and Cheng, 2009; Park *et al.*, 2010; Valverde Jr. *et al.*, 2008). Moreover, the stronger hydrogen bond between TBP and H^+ in perrhenic acid compared to molybdate, (Lee *et al.*, 2008), enhances the selectivity and extraction of Re with higher H^+ concentrations in the leach liquor, suggesting Re extraction is favourable at low pH values (Hosseinzadeh et 2014b). In the case of Mn, Mg, Pb, As, and Se which are present in ionic forms in the solution, TBP cannot extract these elements.

The separation factor of Re and Mo indicates that at lower pH values, the ability of the investigated extractant to selectively extract rhenium from the leach solution increases significantly (Table II).

Table II. Re and Mo separation factor at different pHs

pH	$S = D_{Re}/D_{Mo}$
-0.30	184.72
-0.22	69.91
-0.05	36.50
0.08	19.16
0.14	9.86
0.33	7.32
0.50	2.79
0.73	0.29
1.00	0.12
1.21	0.03
1.60	0.02
1.87	0.02
2.15	0.03
2.50	0.06

Effect of TBP concentration

Figures 3 depicts the effect of varying TBP concentrations from 10 to 60 v/v% on the extraction percentage and distribution factor of Re.

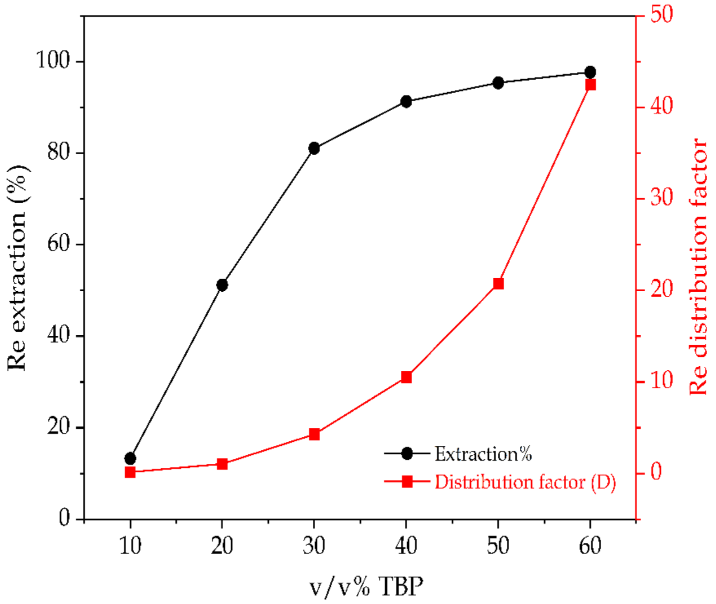

Figure 3. Effect of TBP concentration on extraction percentage and distribution factor of Re using pH = 0, V_o/V_a = 1 at 25 °C for 1 h.

It was found that as the concentration of TBP increased, both the extraction percentage and distribution factor of Re also increased. In solvent extraction, it is essential to utilise an extractant that offers high selectivity and minimal solubility and consumption. Decreasing the extractant concentration offers several advantages, including reduced solvent consumption costs, lower solvent viscosity, decreased formation of third phase compounds, and improved selectivity in the metal ion extraction process. Based on the results obtained, it was noticed that increasing the TBP concentration beyond 40 v/v% did not significantly affect Re extraction. Therefore, a concentration of 40 v/v% TBP was selected for the rhenium solvent extraction experiments.

Effect of temperature

The temperature parameter has a varied impact on the extraction process in SX, primarily determined by the endothermic or exothermic nature of equilibrium processes. Generally, increasing temperature adversely affects extraction but benefits stripping. In the case of rhenium, temperature elevation is observed to impede extraction, indicative of an exothermic reaction where higher temperatures decrease the distribution factor of rhenium (Figure 4).

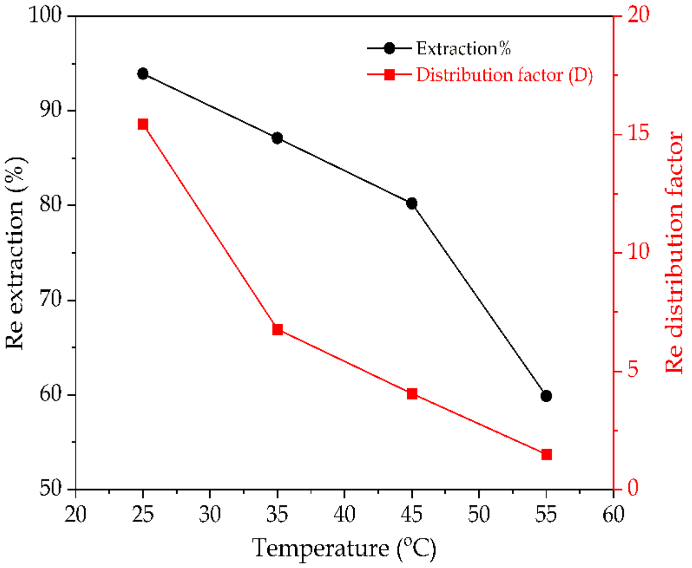

Figure 4. Effect of temperature on extraction percentage and distribution factor of Re using pH = 0, TBP = 40 v/v%, $V_o/V_a = 1$ for 1 h.

Effect of phase ratio

Figure 5 shows that with an increasing organic-to-aqueous phase ratio, the distribution factor of Re rises. This increase in the availability of TBP molecules to extract the metal ion enhances the mass transfer between the two phases. This factor significantly impacts the solvent extraction process. While reducing the ratio of organic-to-aqueous phase is economical in terms of organic consumption, it increases the number of extraction stages, requires larger facilities, and consumes more energy. Conversely, elevating the organic-to-aqueous phase ratio enhances extraction but also raises organic chemical consumption and associated costs. Therefore, it is crucial to choose a ratio that optimises extraction efficiency while also being economically feasible. Although the distribution factor typically increases with the organic-to-aqueous phase ratio, careful consideration is necessary when determining this parameter in the initial designs of the mixer-settler extraction process. In general, at lower O/A ratios, the distribution factor is not significantly affected by the phase ratio.

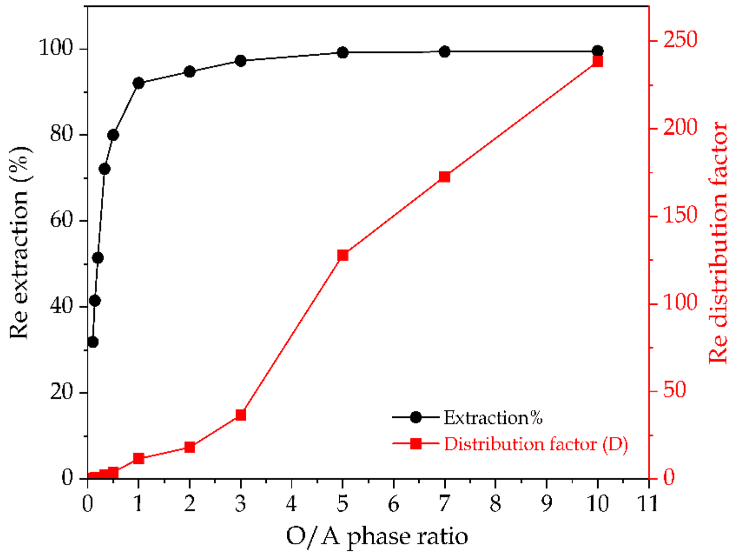

Figure 5. Effect of phase ratio, V_o/V_a, on extraction percentage and distribution factor of Re using pH = 0, TBP = 40 v/v% at 25 °C for 1 h.

Effect of time

The research explored the duration needed to extract Re using 40 v/v% TBP in kerosene, ranging mixing times from 0.5 to 14 min at a phase ratio of 1:1 (Figure 6). Within the first 30 seconds, over 90% of Re was extracted, and the extraction process stabilised after 5 min. Therefore, a 6 min contact time was selected to reach equilibrium. Extending this contact time did not negatively impact extraction efficiency (Alizadeh and Hosseinzadeh, 2013).

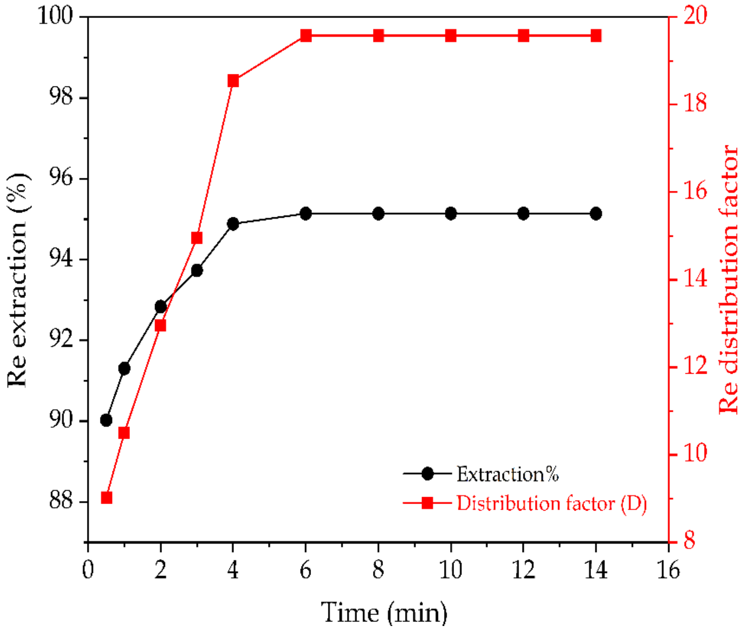

Figure 6. Effect of contact time on extraction percentage and distribution factor of Re using pH = 0, TBP = 40 v/v%, V_o/V_a = 1 at 25 °C.

Solvent loading capacity and rhenium extraction isotherm

Different ratios of V_o/V_a were employed between 10:1 and 1:10 to establish the equilibrium isotherm of Re extraction from leach liquor. As shown in Figure 7, the peak concentration of Re in the organic phase is achieved at V_o/V_a = 1:10, reaching 2.75 g/L. Beyond this ratio, the Re concentration in the organic phase remains steady with no further increase.

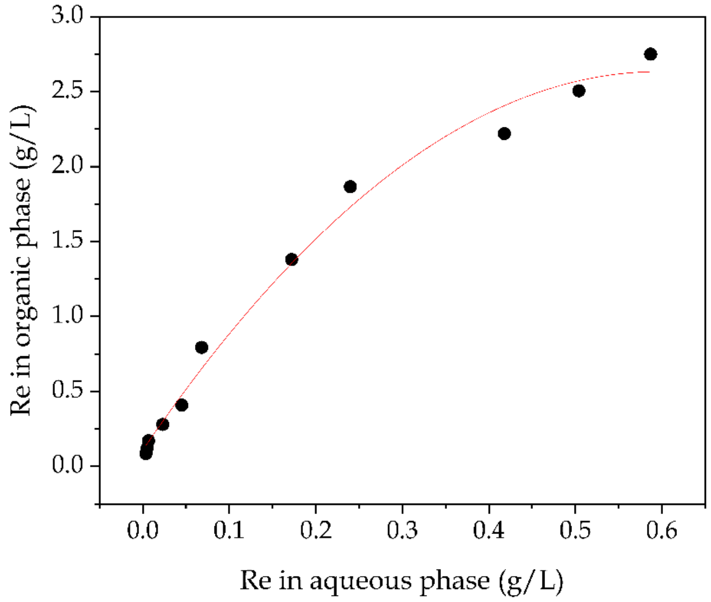

Figure 7. Re extraction isotherm using pH = 0, TBP = 40 v/v% at 25 °C for 6 min.

The McCabe-Thiele diagram was employed to estimate the number of stages necessary to complete the extraction process using a 40 v/v% extractant at pH = 0. As illustrated in Figure 8, after two stages, the rhenium concentration in the aqueous phase decreases from 0.648 g/L to 0.005 g/L at a pH close to 0, resulting in an extraction efficiency of 99.23%. The results shown in the McCabe-Thiele diagram indicate that the rhenium concentration in the organic phase exceeds 0.640 g/L after the two-stage extraction.

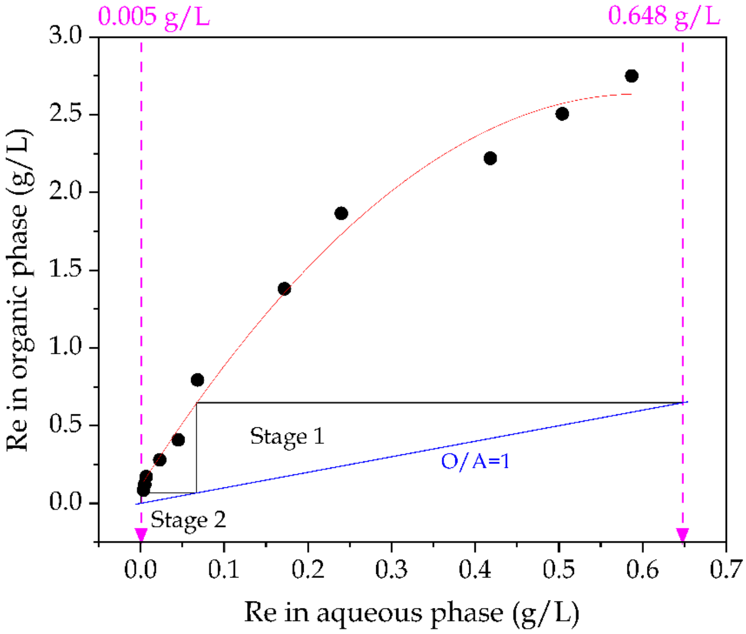

Figure 8. McCabe-Thiele diagram for Re extraction at V_o/V_a = 1.

Rhenium solvent extraction simulation

Based on the McCabe-Thiele diagram, with an aqueous to organic phase ratio of 1:1, two extraction stages are required to achieve over 99% rhenium extraction. Therefore, a two-stage extraction simulation (i=2) was performed to separate rhenium from the leach solution. Stable equilibrium conditions were achieved after four series of repetitions (j=4), resulting in a final rhenium extraction percentage of 98.24% from the roasting dust leach liquor (Figure 9). These results closely align with the predictions made by the McCabe-Thiele diagram. It was also found that in one stage, over 80% rhenium could be extracted with the same phase ratio.

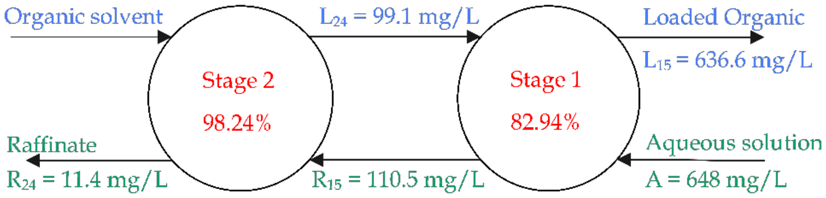

Figure 9. Results of Re extraction under steady state conditions using a two-stage semi-batch counter-current simulation with pH = 0, TBP = 40 v/v%, V_o/V_a = 1 at 25 °C for 6 min.

CONCLUSION

Solvent extraction of Re from molybdenite roasting dust leach liquor using TBP as an extractant diluted in kerosene was investigated. The effect of different parameters on achieving equilibrium conditions of Re separation was conducted. The pH experiments demonstrated that increasing the acidity of the leachate solution to nearly zero significantly enhances the separation factor of Re and Mo, thereby improving the selectivity of Re extraction from the leach liquor in the SX process. TBP concentrations above 40 v/v% did not significantly improve rhenium separation, and rasing the temperature had no positive impact on rhenium extraction. The optimum values for rhenium solvent extraction were found to be pH = 0, TBP concentration 40 v/v%, extraction time 6 min, and temperature 25 °C. The McCabe-Thiele diagram revealed that a two-stage counter-current extraction is needed to achieve an extraction percentage of rhenium greater than 99% from the leach liquor in a continuous contactor. To simulate the continuous solvent extraction process in a mixer-settler system, a two-stage semi-batch counter-current extraction process was developed, and the results demonstrated that more than 98% of Re could be extracted, which was consistent with the results of the McCabe-Thiele diagram.

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