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TECHNICAL NOTE

Improvement of the Solvent Extraction of Rhenium from Molybdenite Roasting Dust Leaching Solution using Counter-current Extraction by a Mixer-settler Extractor

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P A P E R   I N F O

A B S T R A C T

Continuous counter-current extraction of rhenium from roasting dust leach liquor was carried out using a mixer-settler extractor. Tributylphosphate was used as the extractant diluted in kerosene. The effects of the flow rates and extraction stages were investigated. The extraction efficiency was affected by the flow rates of the aqueous and organic phases, and its mechanism was qualitatively discussed on the basis of the stoichiometric relations of the extraction. Rhenium extraction mass balance and simulation in the mixer-settler was also studied. A high rhenium extraction percentage (95.43%) in the phase ratio 1:1 was achieved using a counter-current four-stage extraction process. The continuous counter-current extraction technique was used in this research work showed to be effective for rhenium extraction from the leach solutions of the dust of the molybdenite roasting furnaces.

1. INTRODUCTION

Rhenium is a less common metal with special properties and is widely used in the petrochemical industry, aviation, electronics, medicine, metallurgy, etc.[1, 2]. It is a member of the group of high-melting temperature metals that includes molybdenum, tungsten, niobium, and tantalum [3]. Because of the higher commercial value of rhenium compared to molybdenum, the recovery of rhenium from rhenium bearing materials has both economic and environmental advantage [1, 2]. The best sources of rhenium are molybdenite concentrate and flue dust from molybdenite roasters [4]. The processing of these concentrates by pyrometallurgical and hydrometallurgical techniques leads to rhenium recovery in the form of molybdic and perrhenic acid solutions [5]. As the molybdenum concentration in these solutions is always high, small amounts of rhenium is separated from a relatively large amount of molybdenum. Some hydrometallurgical methods such as precipitation, ion exchange [6], chlorination [7], adsorption on activated carbon [8] and solvent extraction [9] is used for selective metal

extraction. Among them, solvent extraction provides an effective and simple separation method. Liquid-liquid extraction is a process of separating components of a solution by their distribution between two immiscible liquids[10, 11]. Solvent extraction has many applications in the petrochemical and pharmaceutical industries as well as in hydrometallurgy (copper, cobalt, nickel and zinc). In hydrometallurgy, the most applicable solvent extraction equipment is mixer-settler [12]. The main ideas in the development of the solvent extraction mixer-settler are focused on achieving clean phase separation, minimizing the loss of reagents and decreasing the surface area of the settlers [13-15]. In the mixer-settler, aqueous and organic phases are pumped into a mixer to achieve homogeneous dispersion. After mixing, the dispersion is fed into a settler where the aqueous and organic phases are separated by gravity. Generally, there are three methods for two-phase mixing in the mixer settler: counter-current, cross-current and co-current (Figure 1). Counter-current separation is applied to achieve a multi-stage treatment. In this context, separation reduces the necessary amount of separation agent and increases the concentration of product in streams. Counter-current operation in a separation device reduces the amount of necessary

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solvent, increases throughput, and enables higher extract concentrations in the solvent and lower residual concentrations in the raffinate than does single-stage or multi-stage cross-current operation. Counter-current operation is therefore useful for separations with high separation factors for example, the extractions from solid substrates. But, counter-current operation is absolutely necessary for achieving a reasonable separation between two substances with a relatively low separation factor [16].

In the present work, the separation of rhenium from roasting dust leach liquor using solvent extraction technique by employing tributylphosphate (TBP) as an extractant diluted in kerosene was studied by using a multi-stage horizontal type counter-current mixer-settler extractor. The effects of the flow rates of the aqueous and organic phases, the total number of stages and the feasibility of a mixer-settler pilot plant operation were tested in order to obtain a higher efficiency. Also, simulation for predicting the behavior of extraction stages was carried out by assuming constant stage efficiencies. A comparison of simulated and experimental results is also reported.

2. MATERIALS AND METHODS

2. 1. Materials and Reagents   The outgoing dust of the roasting furnace was obtained from the Karmania Co. (Kerman, Iran). Tributylphosphate (Fluka, Switzerland) was the extractant, Kerosene (Tehran Refinery, Tehran) was diluents and sulfuric acid and ammonium hydroxide (Merck, Germany) were pH adjusting solutions used in this study.

2. 2. Preparation of Aqueous Phase   The leaching experiments were carried out in a 3L beaker placed in a water bath and equipped with an overhead mixer. Experiments were performed by distilled water as leachant at the solid to liquid ratio of 1:3.5 at 85 $^{\circ}$C for 90 min with the agitation rate of 400 rpm. The bath temperature was digitally controlled within ±0.5 $^{\circ}$C. The obtained pulp was then filtered and the liquor analyzed for Re, Mo and other compositions. Under these conditions, the amount of rhenium obtained in the aqueous solution was 600-700 mg/L (Table 1). Then, the leach liquor was prepared for solvent extraction process in the mixer-settler in order to investigate the effects of flow rates of both phases and the number of extraction stages.

2. 3. Batch Equilibrium Experiments   For selective extraction of rhenium from the leach liquor, solvent extraction experiments were performed by 40 vol.% TBP diluted in kerosene as organic solvent and leach liquor at pH=0 and ambient temperature for 60

min to approach equilibrium. The above data were selected based on previously published results [17-19] and our previous work (data not published). According to a previous study [17], small amounts of Mo were extracted in these conditions which can be removed later by selective stripping. Also, it was found that Cu and Fe extraction is impossible by TBP in this media. In the case of Mn, Mg, Pb, As and Se which are present in ionic forms in the solution, TBP cannot extract these elements. After the two phases were separated, the aqueous phase was analyzed for determination of rhenium. McCabe-Thiele plot for rhenium was constructed with the mixtures of leaching solution and organic solvent with specific volume ratios. V_a/V_o ratios of McCabe-Thiele construction were in the range of 1:10–10:1. Extraction simulation was performed by optimum phase ratio obtained in continuous counter-current experiments.

**TABLE 1.** Elemental compositions of roasting dust leach liquor used in this research

| Element	Concentration(mg/L)
Re	710
Mo	5050
Cu	170
Fe	940
S	1150
As	130
Zn	60
Ni	1
Co	5.4
Pb	<1
Se	<1
W	<1
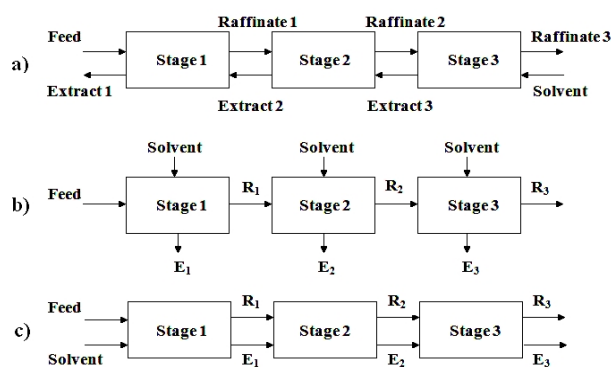
Figure 1. Arrangements of solvent extraction stages: (a) counter-current; (b) cross-current; and (c) co-current
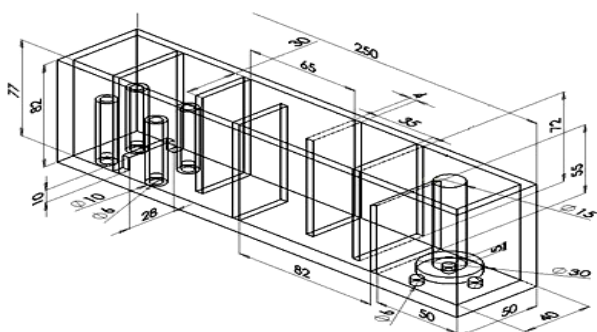
Figure 2. Schematic diagram of the mixer-settler used in the experiments (unit of length: mm)
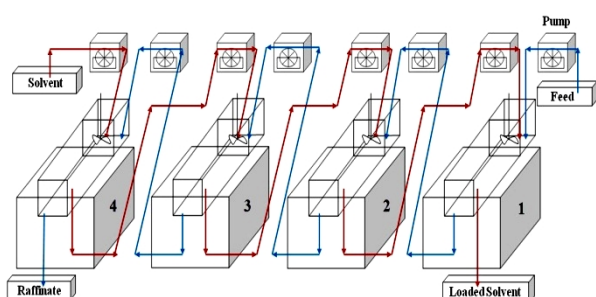
Figure 3. Flow sheet of the counter-current extraction in a four-stage horizontal type mixer-settler
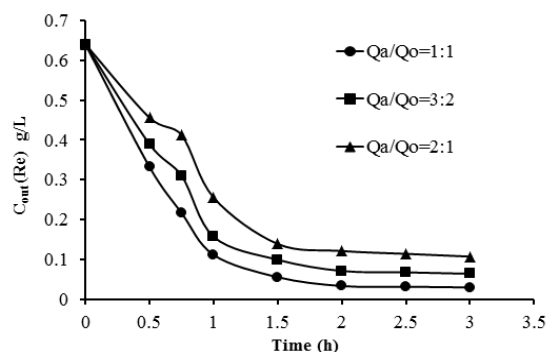
Figure 4. Evolution of the Re concentration in the outlet aqueous phase of the mixer settler (T=25±1 ^{o}C, N=4)

TABLE 2. Flow rates of aqueous and organic phases inlet to the mixer-settler

Q_a/Q_o	Q_a (ml/min)	Q_o (ml/min)
1:1	10	10
3:2	12	8
2:1	14	7

2. 4. Continuous Counter-Current Extraction

Figure 2 shows one unit of a mixer-settler extractor with 25.0×5.0×8.2cm dimension. The aqueous and organic phases flowed into the bottom of the mixer and were discharged from different points of the settler bottom. For the multi-stage experiments, the mixer-settler units were counter currently connected. The aqueous and organic phases were transported to the system inlets by separate peristaltic pumps (Figure 3). The agitation speed in each mixer was maintained at 500 rpm. All the experiments were done at room temperature, and the liquid temperature, T, was measured by an alcohol thermometer immersed in the settler. The aqueous phase in each system outlet was sampled in specific time intervals. The mixer-settler experiments were tested at the ratio of the flow rates, Q_a/Q_o, 1:1, 3:2 and 2:1 in 4 stages.

Based on our previous study [data not published], the extraction time in the mixer-settle was selected as 6 min. Thus, regarding mixer operational volume (120 ml), the ratio of the flow rates, Q_a/Q_o in the continuous counter-current extraction experiments in the mixer-settler is listed in Table 2. Here, Q_a and Q_o are the flow rates of the aqueous and organic phases, respectively. In all the experiments, the total flow rate of the input mixer was chosen such that the mean residence time of the two phases in the mixer was equal to the mean residence time of phase ratio 1:1.

2. 5. Analytical Methods The concentration of rhenium in the aqueous phase was determined by an Inductively-Coupled Plasma (ICP) instrument. The concentration of rhenium in the organic phase was calculated through mass balance calculations. The extraction percentage at the steady state was calculated using Equation (1):

$$E(\%) = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \tag{1}$$

where C is the mg/L concentration of rhenium, and the subscripts, in and out, denote the inlet and outlet in the aqueous phase, respectively.

3. RESULTS AND DISCUSSION

3. 1. Attainment of Steady State Figure 4 shows the effect of time on C_{out} (Re) during the continuous counter-current extraction experiments using conditions of Table 2. N is the total number of stages.

The C_{out} (Re) values rapidly decreased initially, and then slowly approached a constant value at t= 3 h. The data of the raffinate analysis showed that the steady state conditions were obtained after about 2h of continuous operation. On the basis of these facts, the system was considered to reach a steady state at 3h under this condition.

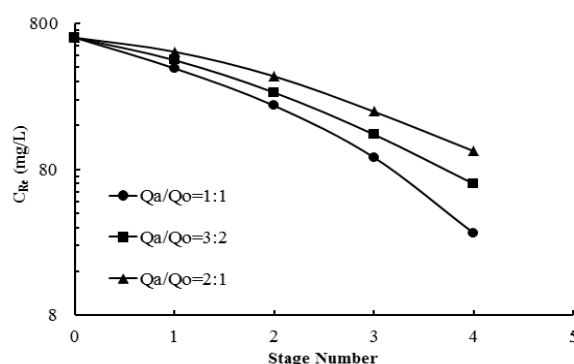**3. 2. Effects of Flow Rates and Total Number of Stages on the Extraction Efficiency**   The conditions used for the continuous counter-current extraction experiments are given in Table 3 and represented as a detailed flow sheet in Figure 3. Table 4 shows the effects of the ratio of flow rates and number of extraction stages vs. time. As can be seen, with increasing Q_a/Q_o, rhenium concentration decreases at the end of the fourth stage. This indicates that more number of stages is required to reach a suitable depletion of rhenium in a higher phase ratio. Samples from aqueous phase were taken after attaining the steady state conditions and the results is presented in Table 4. From this table, it is clear that the aqueous concentration of rhenium decreases gradually from Stage 1 to 4 reaching 29 mg/L in phase ratio 1:1. Figure 5 shows the effects of the ratio of the flow rates, Q_a/Q_o, and N on rhenium concentration in the raffinate under the following conditions: Q_a/Q_o=1:1, 3:2, 2:1; T=25±1 °C; t=3 h, N=1-4.

Figure 5. Concentration profile of Re in the extraction banks
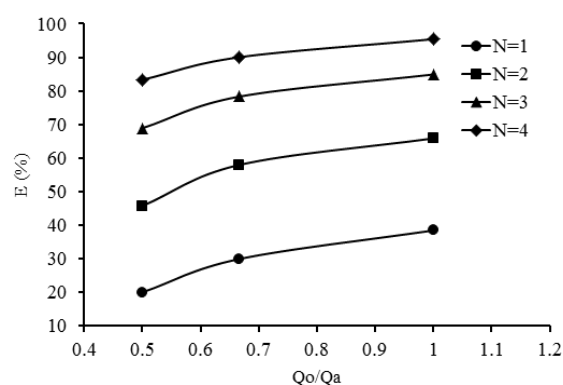
Figure 6. Effects of Q_O/Q_a and N on E

TABLE 3. Conditions for counter-current Re extraction in the mixer-settler

Situation	Data
Aqueous feed	640 mg Re/L
Organic	40% TBP/ kerosene
Temperature, °C	25±1
Number of stages	4
Time of run, h	3
Mixer speed, rpm	500

TABLE 4. Equilibrium results of the continuous counter-current extraction of Re

Stage No.	Q_a/Q_o=1:1	Q_a/Q_o=3:2	Q_a/Q_o=2:1
Re concentration in the aqueous phase, mg/L, after 2 h			
1	389	461	526
2	212	262	357
3	104	144	191
4	33	71	121
Re concentration in the aqueous phase, mg/L, after 3 h			
1	394	449	512
2	219	269	347
3	97	139	199
4	29	64	107

Maximum E values of the ratio of the flow rates, Q_a/Q_o, 1:1; 3:2 and 2:1 in N=4 were 95.43%, 90.05% and 83.32%, respectively. According to the batch experiment, the equilibrium E value was 96.54% at the equal phase volume; however, the experimental E value for the continuous experiments monotonically decreased from 95.43 to 83.32% with the increasing phase ratio (Figure 6). In all phase ratios, which correspond to the mean residence time of both phases of 7.1 min [20], the E value did not reach the equilibrium E value, although vigorous batch agitation for 6 minutes was sufficient to attain equilibrium [data not published]. This would be mainly attributed to the residence time distribution caused by the vigorous mixing during continuous experiments. On the other hand, a monotonous decrease in E with increasing the flow rate would result from the reduction in the residence time of both phases, although the increase in the flow rate of both phases would cause a minor positive effect on E due to the rise in the organic phase hold up, and thus the enhancement of the interfacial area as indicated by Takahashi and Takeuchi [21]. When Q_a is too low, a sufficient throughput is not obtained, while a sufficient recovery is not obtained when Q_a is too high. Thus, the phase ratio 1:1 in four

stages would be sufficient for the extraction of rhenium from roasting dust leach liquor.

According to the results of continuous experiments overlaid in Figure 6 as a function of the ratio of the organic to aqueous flow rates, Q_o/Q_a, the initial rapid increase in E in the continuous system was explained in terms of the stoichiometry of the extraction reaction [22]:

$$ReO_4^- + H^+ + TBP = ReO_4^-.H^+.TBP$$
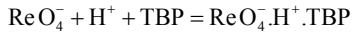
It can be concluded that the increase in Q_o would positively affect E from the hydrodynamic as well as stoichiometric viewpoints [23, 24]. Also, it was found that the difference between curves became smaller by increasing N, indicating that it is reached to convenient depletion of rhenium with increasing number of extraction stages.

3. 3. Counter-current Extraction Simulation
McCabe–Thiele plot was constructed applying 40 vol.% TBP at pH close to zero to estimate the number of stages required for the isothermal rhenium extraction (Figure 7). The concentration of rhenium in the leach liquor reaches to 0.64 g/L by adjusting pH to around zero. The data plotted in Figure 7 shows that the organic phase is loaded with rhenium up to 0.63 g/L at two stages where the V_a/V_o is 1:1, while the raffinate is completely depleted. A simulated counter-current extraction under these conditions for two stages was carried out. The results obtained for concentration of rhenium is depicted in Figure 8. As can be seen, the values of rhenium are close to the theoretical values predicted by the McCabe-Thiele equilibrium isotherm. In the continuous counter-current extraction in the phase ratio 1:1 in the mixer-settler, if the extraction rate at each stage is considered (Figure 9), input and output concentrations of each unit of mixer-settler can be obtained with solving the system of following equations:

$$\begin{cases} C_{a_0} - C_{a_1} + C_{o_3} - C_{o_4} = 0 \\ C_{a_1} - C_{a_2} + C_{o_2} - C_{o_3} = 0 \\ C_{a_2} - C_{a_3} + C_{o_1} - C_{o_2} = 0 \\ C_{a_3} - C_{a_4} + C_{o_0} - C_{o_1} = 0 \\ 0.3841C_{a_0} + 1.3841C_{o_3} - C_{o_4} = 0 \\ 0.4455C_{a_1} + 1.4455C_{o_2} - C_{o_3} = 0 \\ 0.5581C_{a_2} + 1.5581C_{o_1} - C_{o_2} = 0 \\ 0.6972C_{a_3} + 1.6972C_{o_0} - C_{o_1} = 0 \end{cases} \rightarrow$$

$$\begin{cases} C_{a_1} = 0.2878 \, , \, C_{o_1} = 0.0252 \\ C_{a_2} = 0.1138 \, , \, C_{o_2} = 0.1028 \\ C_{a_3} = 0.0362 \, , \, C_{o_3} = 0.2769 \\ C_{a_4} = 0.0110 \, , \, C_{o_4} = 0.6290 \end{cases}$$
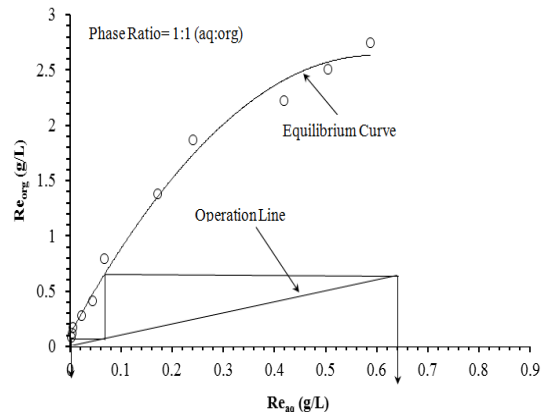
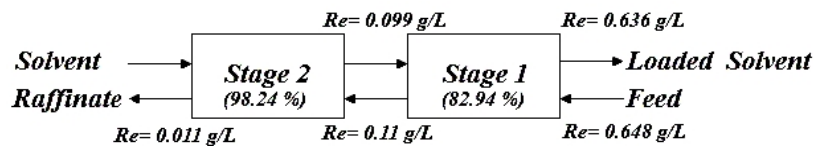**Figure 7.** McCabe–Thiele diagram for extraction of Re by 40 vol.% TBP in kerosene.

Figure 8. The counter-current batch simulation of Re extraction in the mixer-settler
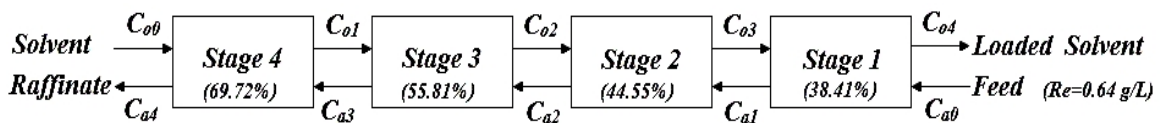
Figure 9. Mass balance of Re extraction in a continuous counter-current four-stage extraction in the mixer-settler

The results of this mass balance showed that the concentration of rhenium in the loaded organic phase is 0.629 g/L after four extraction stages. The concentration of rhenium after two extraction stages in the McCabe-Thiele diagram and simulation was up to 0.63 g/L. Thus, to achieve an optimum concentration of rhenium in the organic phase equal to concentration obtained after a two-stage extraction in the McCabe-Thiele diagram, four stages is required in the mixer settler.

4. CONCLUSIONS

The continuous solvent extraction using the mixer-settler were firstly applied to the extraction of rhenium from leaching solution of dust molybdenite roasting using an organic phase containing 40 vol.% TBP as the extractant diluted in kerosene. The effects of the flow rates and the total number of stages on the extraction efficiency were investigated, and the results are summarized as follows:

1. Chemical analysis of the withdrawn samples showed that the steady state conditions are reached after about 2h of continuous operation.

2. The extraction efficiency were affected by the flow rates of the organic and aqueous phases, which were qualitatively explained on the basis of the stoichiometry of the reaction, the average residence time and hydrodynamic properties of both phases.

3. The continuous extraction for rhenium was carried out using a horizontal type mixer–settler in which the feed solution (640 mg/L) and organic solvent (40 vol.% TBP in kerosene) were fed at the ratio of the flow rates, Q_a/Q_o, 1:1; 3:2 and 2:1 in N=4.

4. The highest percentage extraction, %E, of 95.43% was obtained when $Q_o=Q_a=10$ ml/min and in a continuous counter-current four-stage operation. Under these conditions, the remaining content of rhenium in leaching solution was reduced to 29 mg/L.

5. Simulation of a batch two-stage extraction and mass balance of rhenium was performed in order to estimate the number of extraction stages and the input and output concentrations of rhenium in the mixer-settler in the continuous scale. The results were satisfactory in comparison with continuous counter-current extraction experiments.

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چکیده

استخراج رنیوم از محلول لیچینگ غبار کوره تشویه مولیبدنیت توسط دستگاه استخراج کننده میکسر–ستلر به روش جریان متقابل در مقیاس پیوسته انجام شد. فاز آلی مورد استفاده در آزمایش‌ها شامل تری بوتیل فسفات رقیق شده در نفت سفید بوده است. تاثیر دبی‌ها و تعداد مراحل‌استخراج مورد بررسی قرار گرفت. در ادامه، بازدهی استخراج توسط دبی‌های فازهای آبی و آلی و مکانیزم آن براساس رابطه استوکیومتری واکنش استخراج بحث شد. همچنین، موازنه جرمی و شبیه سازی استخراج رنیوم در دستگاه میکسر–ستلر مورد مطالعه قرار گرفت.در نهایت، درصد استخراج ٪٤٣/٩٥ از رنیوم در نسبت فازی ١:١ طی چهار مرحله استخراج به دست آمد. این روش استخراج به صورت جریان متقابل در مقیاس پیوسته انتظار می‌رود برای جداسازی رنیوم از محلول‌های لیچینگ غبار کوره‌های تشویه مولیبدنیت در دستگاه میکسر–ستلر موثر باشد.