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Effect of operational parameters and internal recycle on rhenium solvent extraction from leach liquors using a mixer-settler

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Mostafa Hosseinzadeh [a,b,∗], Mohammad Ranjbar [a], Mehdi Alizadeh [b]

[a] Mining Engineering Department, Engineering Faculty, Shahid Bahonar University of Kerman, P.O. Box 7618868366, Kerman, Iran
[b] Materials and Energy Research Center (MERC), P.O. Box 3177983634, Karaj, Iran

A B S T R A C T

The extraction of rhenium from molybdenite roasting dust leach solution was performed using a mixer-settler extractor by tributyl phosphate (TBP) diluted in kerosene as the extractant. In the single-stage extraction experiments, effect of the aqueous to organic phase ratios, Q_a/Q_o, and the number of extraction stages, N, on the rhenium extraction was studied. It was found that using the phase ratio of 1:1 in a two-stage extraction, 87.5% depletion of rhenium was obtained. The comparison of experimental results with the continuous co-current extraction showed a good agreement. The effect of internal recycle of organic phase was investigated in the phase ratio of 1:1 by changing the flow rate ratio of recycle-to-fresh organic phase, Q_{ro}/Q_{fo}. The optimum performance was achieved in the phase ratio, Q_{ro}/Q_{fo}, equal to 3:7. It was found that improvement in the performance of the mixer-settler for the rhenium-TBP system can be obtained in the phase ratio of 1:1 when $Q_{ro}/Q_{fo} = 3:7$.

1. Introduction

Rhenium (Re) is one of the most interesting transition elements due to its properties that have been useful mainly in the petroleum-reforming industry and in the production of special metal alloys (e.g. nickel-based super alloys, refractory alloys, high performance alloys for aerospace application, among others) [1]. This element and its compounds (ammonium perrhenate-NH_4ReO_4 and perrhenic acid-$HReO_4$) are produced in Chile (53% of the world production in 2010) as a byproduct from porphyry copper-molybdenum ores [2]. Nevertheless, rhenium is present in nature in very low concentration (0.4 mg/t) which makes it a very valuable metal [3]. Hydrometallurgical techniques such as solvent extraction [4], adsorption [5], ion exchange [6], supported liquid membrane [7], precipitation [8], etc., have been used extensively for the recovery of rhenium from various solutions. Amongst these, solvent extraction method is one of the most effective methods and especially used for separation of rhenium from other components, such as arsenic, tungsten or molybdenum [9]. Solvent extraction has been used in the minerals processing industry since the 1950s. It involves contacting two immiscible phases, usually an organic phase as an extractant and an aqueous phase containing the metal values. With energy input into the solvent extraction system, the two immiscible phases form an emulsion to provide an interfacial area for chemical reaction or mass transfer. As a result, the metal ions are extracted from the aqueous phase into the organic phase to achieve separation, purification, and concentration [10].

Over the past 20 years mixer-settlers have been intensively used in chemical, pharmaceutical, and hydrometallurgical industries [11]. Mixer-settler extractor has been widely used in the rare earth element separation industry [12]. The main advantages of this equipment are: strong operational loads, easy operation and maintenance, and simple start-up [11]. In hydrometallurgical solvent extraction systems, in addition to purification, a metal value concentration effect between the feed and strip aqueous streams are usually required. This means that the feed-to-strip flow rate ratio (A/A') is usually large. A large A/A' value would result in either a small O/A or a large O/A' value or both (O is the organic phase flow rate). In such cases the resulting mixture in a mixer-settler will tend to emulsify and be difficult to separate. One way to overcome this problem is to recycle the minor phase from the settler back to the mixer. Recycle is also often practiced

∗ Corresponding author. Materials and Energy Research Center (MERC), P.O. Box 3177983634, Karaj, Iran. Tel.: +98 26 3628 0032; fax: +98 26 3620 1887.
E-mail address: mta.hosseinzadeh@yahoo.com (M. Hosseinzadeh).

to reduce the entrainment of the organic phase in the aqueous stream or of the aqueous phase in the organic stream, or both [13]. In the present work, the separation of rhenium from molybdenite roasting dust leach solution using solvent extraction technique by tributyl phosphate (TBP) as an extractant diluted in kerosene was studied. The investigation was carried out in a laboratory-scale mixer-settler. The objectives of the present work are: (i) optimization of operation parameters such as flow rate ratio of the two phases, Q_a/Q_o, and the number of extraction stages, N, in a single-stage mixer-settler; (ii) to study the effect of internal recycle on rhenium extraction; and (iii) eventually to investigate the agreement between single-stage experimental results with continuous co-current extraction experiments in a multi-stage mixer-settler.

2. Materials and methods

2.1. Sample and reagents

The outgoing dust of the roasting furnace was obtained from the Karmania Co. (Kerman, Iran). Chemical analysis of the dust used in this research is listed in Table 1. The organic phase was composed of Tributyl phosphate (TBP) and kerosene. TBP is produced by the Fluka Factory in Switzerland and the kerosene was the product of the Tehran Refinery in Tehran. For pH adjusting, sulfuric acid and ammonium hydroxide (Merck, Germany) were used in this study.

2.2. Leaching

Operational conditions used for the leaching of dust in this research were as following: distilled water as leachant at the solid to liquid ratio of 1:3.5 at 85 °C for 90 min with the agitation rate of 400 rpm. The bath temperature was digitally controlled within ±0.5 °C. Under these conditions, the value of rhenium in the aqueous solution 600–700 mg/L was obtained. Then, the leach liquor was prepared for the solvent extraction experiments of rhenium in the mixer-settler.

2.3. Solvent extraction experiments

For selective extraction of rhenium from the leach liquor, the 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 the equilibrium. The solvent extraction data were selected based on previously published results [14–17]. According to previous study [14,15]; small amounts of Mo were extracted in these conditions which can

Fig. 1. Schematic diagram of the mixer-settler used in the experiments (unit of length: mm).

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 presence, TBP is useless. After the two phases were separated, the aqueous phase was analyzed for determination of rhenium. The concentration of rhenium in the aqueous phase was determined by an Inductively-Coupled Plasma (ICP) instrument.

2.4. Experimental apparatus

A box-type mixer-settler made of plexiglas was used as the extraction equipment. The dimension of the mixer-settler is 25 × 5 × 8.2 cm (Fig. 1). The aqueous and organic phases flowed into the bottom of the mixer and were discharged from different points of the settler bottom.

2.5. Operating conditions

All the solvent extraction experiments were performed through a single-stage mixer-settler other than continuous co-current extraction experiments, which was carried out through a four-stage mixer-settler. The experiments were conducted at the flow rate ratios, Q_a/Q_o, 1:1, 3:2, 2:1, and 5:2. Based on our previous study [data not published], the extraction time in the mixer-settler was selected 6 min. In these experiments, in each phase ratio the values of volumetric flow rates of aqueous and organic phases were set at one hour. Therefore, with the completion of the feed of phases in each vessel, the raffinate and pregnant organic phase was returned

Table 1
Elemental compositions of roasting dust used in this research.

Element	wt.%
Re	0.61
Mo	61.80
Cu	0.45
Fe	0.62
W	0.56
Rh	0.03
Nb	0.02
S	23.00
Mn	0.10
Te	0.03
Ti	0.23
Hf	0.01
Bi	0.08

Fig. 2. Process scheme for operational parameters optimization on Re extraction.

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
5:2	15	6

Table 3
Conditions used for single-stage extraction of Re by the mixer-settler.

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

again to re-extract (Fig. 2). This was performed four times for each flow rate ratio, Q_a/Q_o. The aqueous and organic phases were moved to the system inlets by the separate peristaltic pumps. Regarding the mixer operational volume (120 ml), the value of flow rate ratios, Q_a/Q_o, in the semi continuous co-current extraction experiments in a single-stage mixer-settler are listed in Table 2.

Where Q_a and Q_o are the flow rates of the aqueous and organic phases, respectively. In all experiments, the total flow rate input to the mixer was chosen such that the mean residence time of the two phases in the mixer to be equal to the mean residence time of the phase ratio of 1:1.

In order to verify the results obtained in the single-stage extraction experiments, continuous extraction experiments in the flow rate ratios, Q_a/Q_o, 1:1 and 2:1 was performed in a multi-stage mixer-settler. In these experiments, the mixer-settler units were concurrently connected by four stages. All the experiments were done at room temperature and the impeller rotational speed was kept at 500 rpm. The liquid temperature, T, was measured by an alcohol thermometer immersed in the settler. In order to determine rhenium concentration in the raffinate, sampling was performed from the aqueous phase in certain time intervals.

After achieving the optimum condition of flow rate ratio and the numbers of extraction stages, the effect of internal recycle on rhenium extraction and mixer-settler performance was investigated. In these experiments, a part of the pregnant organic stream outlet of the settler was returned to the mixer for the re-extraction (Fig. 3). The experiments were carried out in a single-stage continuous form. Regarding the optimum flow rate ratio obtained, the recycle stream was regulated in different values. The sampling was performed at three time intervals.

3. Results and discussion

3.1. Effects of flow rates and total number of stages

The conditions used for the single-stage extraction experiments have been given in Table 3. Table 4 shows the effects of the flow rate ratios and the number of extraction stages vs. time. As can be seen, with increasing Q_a/Q_o, rhenium concentration decreases at the end
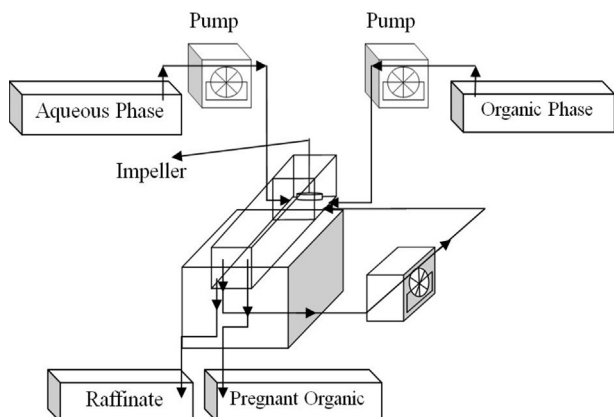
of the extraction process. It was found that more stages are required to reach a suitable depletion of rhenium in higher phase ratios, A/O. Also, it was found that increasing the number of extraction stages at a fixed phase ratio had no effect on rhenium extraction. Therefore, it can be reduced without much change on the final concentrations. Fig. 4 shows the effects of Q_a/Q_o and N on the rhenium concentration in the raffinate under the following conditions: $Q_a/Q_o = 1:1$, 3:2, 2:1, and 5:2; $T = 25 \pm 1$ °C; $t = 4$ h. It is clear that the initial rapid decrease in the rhenium concentration can be explained by the stoichiometry of the extraction reaction [18]:

$$ReO_4^- + H^+ + TBP = ReO_4^- \cdot H^+ \cdot TBP$$
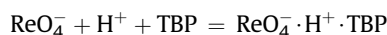
It can be concluded that the increase in Q_o would positively affect efficiency from the hydrodynamic as well as stoichiometric viewpoints [19,20]. The maximum concentration values of rhenium in the flow rate ratios, Q_a/Q_o, 1:1, 3:2, 2:1, and 5:2 in $N = 4$ were 89.06%, 79.68%, 75.16%, and 57.81%, respectively. In all the phase ratios, the mean residence time of both phases is 7.1 min [21]. On the other hand, a monotonous decrease in the rhenium concentration by increasing the flow rate ratio, Q_a/Q_o, would be resulted from the reduction in the residence time of both phases, although the increase in Q_o/Q_a would cause a minor positive effect on concentration due to the rise in the organic phase hold up and thus the enhancement of the interfacial area as indicated by Takahashi and Takeuchi [22]. When Q_a is too low, throughput is not sufficient while recovery is not high enough when Q_a is too high. Thus, the

Table 4
Results of the single-stage extraction experiments.

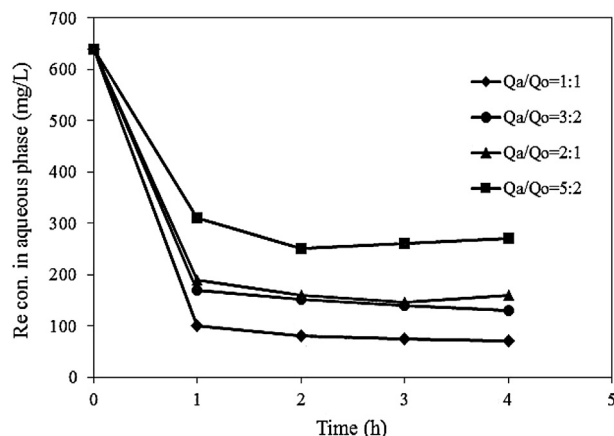| Time (h)	$Q_a/Q_o = 1:1$	$Q_a/Q_o = 3:2$	$Q_a/Q_o = 2:1$	$Q_a/Q_o = 5:2$
Re concentration in the aqueous phase, mg/L				
1	100.032	169.984	190.016	310.016
2	80	152.64	160	249.984
3	75.008	140.032	145.024	260.032
4	70.016	130.048	158.976	270.016

Fig. 3. Process scheme for investigation of internal recycle effect on Re extraction.

Fig. 4. Effect of Q_a/Q_o and t on Re concentration.

Table 5
Results of the continuous co-current extraction ($t = 3$ h, Re in aqueous $= 640$ mg/L).

Stage no.	$Q_a/Q_o = 1:1$	$Q_a/Q_o = 2:1$
Re concentration in the aqueous phase, mg/L		
1	113.344	161.344
2	101.632	155.136
3	98.496	164.864
4	86.784	164.928

Table 6
Conditions used in the internal recycle experiments.

Test no.	Q_{fo} (ml/min)	Q_{ro} (ml/min)
1	10	0
2	7	3
3	4	6
4	1	9

phase ratio of 1:1 by two stages would be sufficient for the extraction of rhenium from the roasting dust leach liquor in a co-current approach in the mixer-settler. In order to determine the accuracy of the approach used in the investigation of the effects of the flow rate ratios and the number of extraction stages on the rhenium extraction, continuous co-current extraction experiments in the flow rates ratio, Q_a/Q_o, 2:1 and 1:1 were performed by the mixer-settler in 4 stages (Table 5). As can be seen, the results obtained from the continuous extraction are in a good agreement with the single-stage experiment results. Therefore, a single-stage mixer-setter can be used instead of a multi-stage one when it is needed to study the effect of flow rate ratios, Q_a/Q_o, and the number of extraction stages, N, in the co-current method. By this way, the number of mixer-settler units and required equipment for the operational parameters optimization can be reduced.

3.2. Effect of internal flow

Regarding the phase ratio of 1:1, the effect of internal recycle of organic phase in four different conditions was studied (Table 6). Where Q_{fo} and Q_{ro} are the flow rates of the fresh and recycle organic phases to the mixer, respectively. It was found that the increase in the internal recycle of organic phase reduces the recovery of rhenium (Table 7). Fig. 5 shows that applying the phase ratio of 1:1 and the recycle flow of 3 ml/min in the first stage of a multi-stage extraction, 75% of rhenium was extracted. Therefore, using the flow rate ratio, of $Q_a/Q_{fo} = 10:7$ in the first extraction stage of continuous co-current extraction experiments, can reduce organic phase consumption without much decline in the rhenium extraction.

The approach used in the investigation of the effect of internal recycle cannot be used in the counter-current method because in the counter-current approach, it is needed that all the mixer-settler units to be in use so that the effect of recycle flow in the first stage can be examined. As a result, the co-current method is a useful

Table 7
Results of the recycle flow of organic phase on Re extraction ($t = 2$ h, Re in aqueous $= 640$ mg/L).

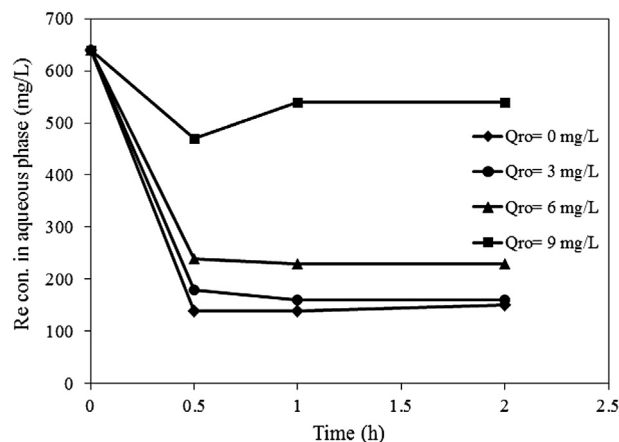| Time (h)	$Q_{ro} = 0$	$Q_{ro} = 3$	$Q_{ro} = 6$	$Q_{ro} = 9$
Re concentration in the aqueous phase, mg/L				
0.5	140.032	180.032	240	470.016
1	140.032	160	230.016	540.032
2	150.016	160	230.016	540.032

Fig. 5. Effect of recycle flow of organic phase (Q_{ro}) on Re extraction.

method in the study of the effect of internal recycle for the continuous extraction experiments in a multi-stage mixer-settler.

4. Conclusions

The single-stage extraction experiments were performed in order to study the effect of the flow rates on rhenium extraction in the phase ratios of 1:1, 3:2, 2:1, and 5:2. Results showed that in the phase ratio of 1:1 a convenient depletion of rhenium was obtained. Effect of the recycle flow was studied for different flow rate ratios. The best one was in the phase ratio of $Q_{ro}/Q_{fo} = 3:7$. The continuous co-current extraction experiments were performed in the phase ratios of 1:1 and 2:1. The results were in a good agreement with the single-stage results. Therefore, it was found that the performance of the mixer-settler can be improved by recycling without much change on rhenium extraction in the phase ratio of 1:1 under the experimental conditions used in this study. Eventually, it has been experimentally shown that the present technique can be effectively applied to investigate the effect of operating parameters on the rhenium extraction form roasting dust leach liquor by a mixer-settler.

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