

## Selective Recovery of Molybdenum from Rhenium Containing Sulphate Model Solutions by Solvent Extraction with Organophosphorus and Oxime Reagents

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In various primary or secondary raw materials, for example in molybdenite or in so called “Theisenschlamm”, rhenium and molybdenum appear together. Consequently, processing of those materials can lead to aqueous solutions containing both elements. In order to obtain a separation of these elements the selective recovery of molybdenum by organophosphorus (D2EHPA, Cyanex 272) and oxime (LIX 63, LIX 84, LIX 860, LIX 984) reagents diluted in kerosene is investigated. The selectivity for the extraction of molybdenum over rhenium is compared and D2EHPA, Cyanex 272 as well as LIX 984 are chosen for extraction tests from sulphate model solutions containing zinc(II), iron(III), copper(II), molybdenum(VI), rhenium(VII), antimony(V), germanium(IV) and cobalt(II). Cyanex 272 achieves the highest selectivity for molybdenum. Due to that extraction isotherms of molybdenum with Cyanex 272 are constructed.

### 1. Introduction

The “Theisenschlamm” is a secondary raw material of the former copper shale processing in Germany. A total amount of 220,000 tons has been deposited between the years 1978 and 1990. Besides about 16 wt.-% zinc, 14 wt.-% lead and minor amounts of copper and tin, this material also contains valuable strategic elements, like about 0.05 wt.-% molybdenum and 100 ppm rhenium. Leaching tests in sulphate medium reveal that the acidic leaching solution contains both rhenium and molybdenum. Our results and also other investigations show that rhenium can be efficiently recovered with tertiary amines [1]. However molybdenum is co-extracted by these amines. The modification of the amine extraction system with tributyl phosphate (TBP) to selectively extract rhenium under alkaline conditions [2] or the separation of rhenium and molybdenum using only TBP as the active extractant [3, 4] have been reported. An approach that seems promising is the selective removal of molybdenum from rhenium containing solutions since there are a number of investigations reporting the ability of various extractants to recover molybdenum selectively over e.g. copper, iron, aluminium, uranium, cobalt or nickel. The applied extractants are, e.g. LIX 63 (5,8-diethyl-7-hydroxy-dodecan-6-oxime) [5, 6], LIX 84 (2-hydroxy-5-nonylacetophenone oxime) [7, 8], LIX 984N (1:1 mixture of LIX 84 and LIX 860N (5-nonylsalicylaldoxime) [3], LIX 622N (5-nonylsalicylaldoxime with tridecanol) [9], D2EHPA (di-(2-ethylhexyl)phosphoric acid) [10, 11], PC-88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) [12, 13] or Cyanex 272 (bis(2,4,4-trimethylpentyl)-phosphinic acid) [13, 14] all diluted in poorly water soluble organic diluents, e.g. kerosene. However,

reports including rhenium are rare. Valenzuela et al. found that PC-88A extracts molybdenum selectively from solutions containing rhenium, copper and iron [12]. Srivastava et al. reported the selective extraction of molybdenum over rhenium from chloride solutions with Cyanex 272 [14]. This study intends to further evaluate the suitability of organophosphorus and oxime reagents to selectively recover molybdenum over rhenium. For this purpose the following extractants are applied for extraction tests from acidic sulphate model solutions: LIX 63, LIX 84, LIX 860 (5-dodecylsalicylaldoxime), LIX 984 (1:1 mixture of LIX 84 and LIX 860), D2EHPA and Cyanex 272.

## 2. Experimental

### 2.1 Reagents

The model solutions were prepared by using the following chemicals:  $\text{NH}_4\text{ReO}_4$  (Alfa Aesar, 99.999%),  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (Merck,  $\geq 99.5\%$ ),  $\text{Fe}_2(\text{SO}_4)_3$  (VWR Chemicals,  $> 99\%$ ),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Merck,  $> 99.5\%$ ),  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (Merck,  $> 99\%$ ),  $\text{NaSbO}_3 \cdot 3\text{H}_2\text{O}$  (Alfa Aesar,  $> 98\%$ ),  $\text{GeO}_2$  (PPM Pure Metals GmbH, 99.999%),  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  (Alfa Aesar, 99.999%),  $\text{H}_2\text{SO}_4$  (Carl Roth GmbH, 98%), NaOH (pellets, Carl Roth GmbH,  $\geq 99\%$ ). Kerosene (light distillate, J.T. Baker) was used as diluent in the organic phase to dissolve the extractants: LIX 63 (BASF, 70%), LIX 84 IC (BASF, 65%), LIX 860 (BASF, 70%), D2EHPA (Alfa Aesar, 95%), Cyanex 272 (Cytec, 85%). The molar concentration of the respective extractant in the organic phase was adjusted considering the concentration of the active component in the supplied product (see percentage value in brackets). All chemicals were applied as supplied by the manufacturer.

### 2.2 Methods

The extraction experiments were carried out by mixing aqueous and organic phase in a beaker with an overhead stirrer followed by separation in separating funnels and analysis of the aqueous phase with ICP-OES. Unless otherwise specified the experiments were performed with 100 mL of each phase (phase ratio A/O = 1), 10 min mixing time, a stirring speed of  $400 \text{ min}^{-1}$  and a temperature of  $20 \pm 2^\circ\text{C}$ . The pH value was adjusted with 9.2 M  $\text{H}_2\text{SO}_4$  and 15 M NaOH. The percentage extraction (E) was calculated with Eq. (1) and the element concentration in the organic phase ( $c_{\text{org}}^n$ ) for a certain loading stage (n) with Eq. (2).

$$E = \left( 1 - \frac{V_{\text{aq}}^t \cdot c_{\text{aq}}^t}{V_{\text{aq}}^\circ \cdot c_{\text{aq}}^\circ} \right) \cdot 100 \% \quad (1)$$

$$c_{\text{org}}^n = \sum_{i=1}^n \left( \frac{V_{\text{aq}}^{\circ i} \cdot c_{\text{aq}}^{\circ i} - V_{\text{aq}}^{t i} \cdot c_{\text{aq}}^{t i}}{V_{\text{org}}^i} \right) \quad (2)$$

(with: V – volume, c – concentration, aq – aqueous phase, org – organic phase, ° – initial state, t – state after a certain mixing time, n – loading stage of the organic phase)

## 3. Results and Discussion

### 3.1 Selectivity for Mo(VI) over Re(VII) comparing different extracting agents

In order to decide a suitable extractant to efficiently separate Mo(VI) and Re(VII), extraction tests with a model solution containing 1400 mg/L Mo(VI) and 150 mg/L Re(VII) are performed. The Mo(VI) concentration is chosen to include the possibility of polymolybdate formation whereas the

Re(VII) concentration refers to the intended concentration after cross-current Theisenschlamm leaching.

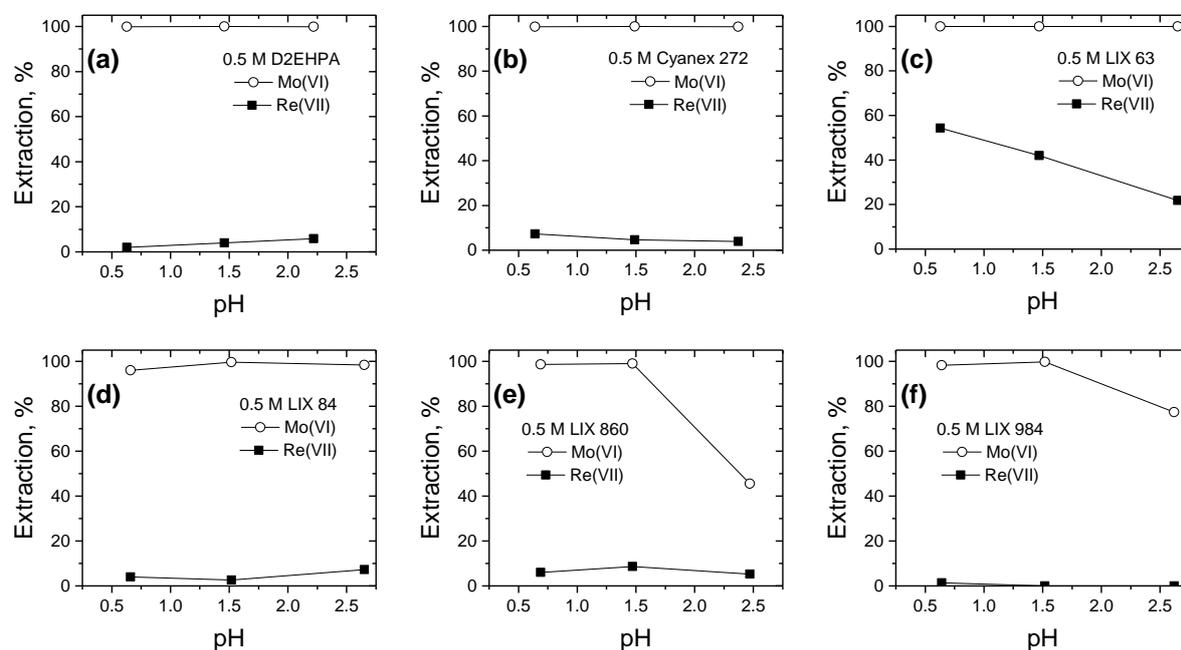
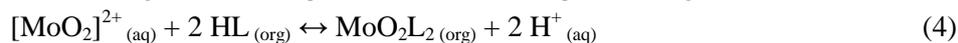


Figure 1. (a) – (f): Comparison of extracting agents based on the extraction of Mo(VI) and Re(VII) at different pH values from a model solution containing 1400 mg/L Mo(VI) and 150 mg/L Re(VII).

Figure 1 shows the results of the extraction of Mo(VI) and Re(VII) with D2EHPA, Cyanex 272, LIX 63, LIX 84, LIX 860 and LIX 984 with a concentration of 0.5 M each. Besides LIX 63 all of the tested extractants show a low Re(VII) extraction between 0% and 8.7% in the pH range 0.6 to 2.2. In the same pH range the organophosphorus reagents Cyanex 272 and D2EHPA extract Mo(VI) quantitatively. Regarding the oxime reagents LIX 84 and LIX 63 show quantitative Mo(VI) extraction in the considered pH range. However with LIX 860 Mo(VI) extraction decreases at pH values > 1.5 from 99% to 45% at pH 2.5. Since LIX 860 is one component of LIX 984 the effect of a decrease in Mo(VI) extraction at pH values > 1.5 appears as well but less distinct. However compared to LIX 84 and LIX 860 the Re(VII) extraction is lower with LIX 984.

The poor Re(VII) extraction can be explained with the presence of the  $[\text{ReO}_4]^-$  anion. Neither the cation exchange mechanism of Cyanex 272 and D2EHPA nor the mechanism of chelate formation of the oxime reagents extract the negatively charged Re(VII) complex. In contrast to rhenium, molybdenum forms a variety of species, e.g. at pH < 2.5 and 21.2 mM Mo(VI):  $[\text{H}_6\text{Mo}_2\text{O}_8]^{2+}$ ,  $[\text{H}_3\text{MoO}_4]^+$ ,  $\text{H}_2\text{MoO}_4$  and  $[\text{Mo}_7\text{O}_{21}(\text{OH})_3]^{3-}$  [15]. The species formation depends on both the molybdenum concentration and the pH value. However, it is often assumed that at low pH values the  $[\text{MoO}_2]^{2+}$  cation is extracted by the organic reagents [7, 16]. So the Mo(VI) extraction can be expressed by Eqs. (3) and (4) according to the cation exchange mechanism of the dimeric organophosphorus reagents  $(\text{HR})_2$  and the chelate formation mechanism for the oxime reagents (HL).



### 3.2 Mo(VI) extraction from multi element sulphate model solution

Due to the results shown in Figure 1 Cyanex 272, D2EHPA and LIX 984 are chosen for further investigations. A multi element sulphate model solution (MES I) is prepared based on first results of the Theisenschlamm leaching. Table 1 shows the composition of this solution. The Re(VII) content has not reached the intended concentration yet.

Table 1. Composition of the multi element sulphate model solution (MES I).

	Zn(II)	Fe(III)	Cu(II)	Mo(VI)	Co(II)	Re(VII)	Sb(V)	Ge(IV)
Concentration, mg/L	3190	1765	250	150	12	9	9	6

This multi element model solution is used to further characterise the selected extractants regarding the selectivity for Mo(VI) depending on the pH value. The investigations are performed with extractant concentrations of 0.1 M and 0.5 M respectively.

Figure 2 shows the results of the mainly extracted elements of the model solution (MES I). In the investigated pH range of  $0.5 < \text{pH} < 2.0$  Co(II) is not extracted with these extractants. LIX 984 shows the lowest affinity for Zn(II) with a maximum of 5% extraction and D2EHPA as well as Cyanex 272 achieve the best selectivity over Cu(II) with a maximum of 5% Cu(II) extraction.

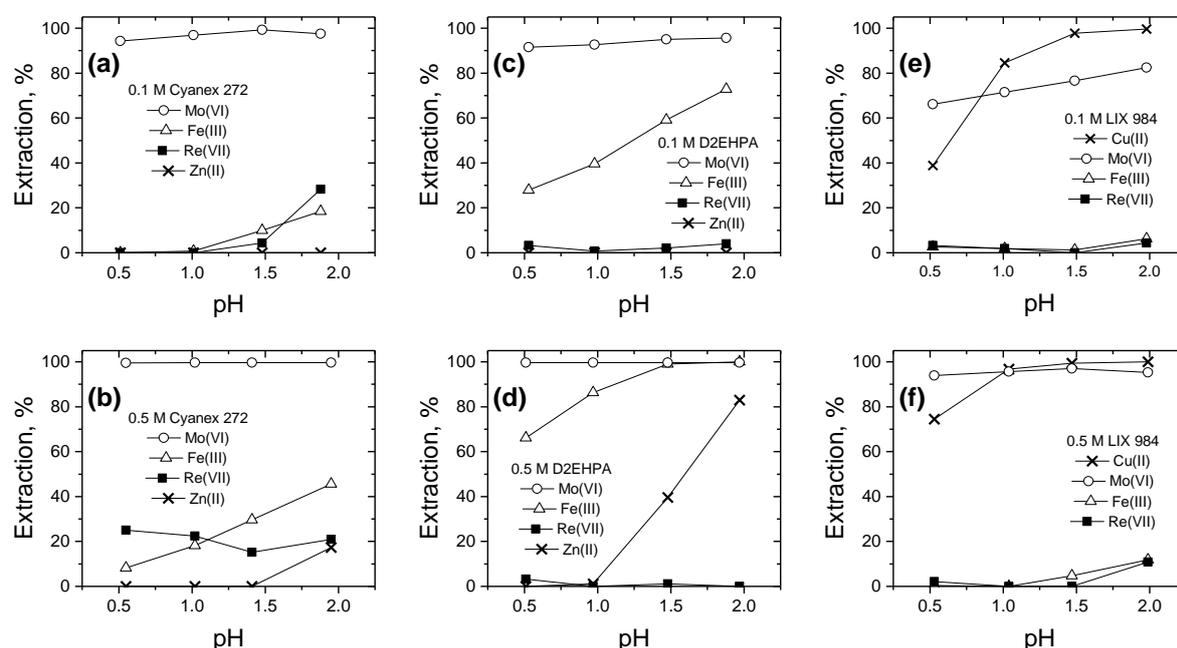


Figure 2. (a) – (f): Comparison of Cyanex 272, D2EHPA and LIX 984 based on the extraction of various elements from the multi element model solution (MES I).

Figures 2 (a) and (b) indicate that Cyanex 272 achieves the most selective Mo(VI) extraction at  $\text{pH} \leq 1$

with both 0.1 M and 0.5 M extractant concentrations. An increase in Cyanex 272 concentration leads to an increased extraction of Fe(III) and Re(VII) as well as Zn(II) co-extraction at  $\text{pH} > 1.5$ , as shown in Figure 2 (b). Figures 2 (c) and (d) show that with D2EHPA the Re(VII) co-extraction is the lowest among these extractants and within the investigated pH range. However, D2EHPA intensively co-extracts Fe(III) even at a low extractant concentration. At a D2EHPA concentration of 0.5 M and  $\text{pH} > 1$  also Zn(II) is co-extracted. As shown in Figures 2 (e) and (f) LIX 984 achieves good selectivity over Fe(III) and Re(VII) at  $\text{pH} < 1.5$ . But it is also a well-known Cu(II) extractant so that Mo(VI) and Cu(II) are co-extracted. Figure 2 (e) indicates that a concentration of 0.1 M LIX 984 is not sufficient to extract Mo(VI) quantitatively. With an increase in LIX 984 concentration to 0.5 M a Mo(VI) extraction of  $> 95\%$  can be achieved.

Consequently, D2EHPA is not suitable for the selective extraction of Mo(VI) if the solution contains Fe(III) and/or Zn(II) and also LIX 984 is not suitable in case the solution contains Cu(II). Hence Cyanex 272 is chosen for more detailed investigations.

### 3.3 Time dependence with Cyanex 272

Figure 3 shows the influence of the mixing time on the extraction of Mo(VI) and the mainly co-extracted elements with Cyanex 272 at pH 1.5. The results in Figure 3 reveal that a short mixing time is favourable since an increase leads to higher co-extraction of Fe(III) and Re(VII). This behaviour is more distinct for 0.5 M than for 0.1 M Cyanex 272. However, to reach a Mo(VI) extraction  $> 95\%$  mixing times of 5 min and 1.5 min are necessary in case of 0.1 M and 0.5 M Cyanex 272, respectively.

### 3.4 Extraction isotherms with Cyanex 272

Extraction isotherms are constructed by using the method of contacting the organic phase several times with a fresh aqueous multi element sulphate model solution (MES II) with the composition shown in Table 2 [17, 18]. For all loading stages the aqueous to organic phase ratio is 1:1 and the equilibrium  $\text{pH} = 1$ . A mixing time of 5 min is adjusted to reduce co-extraction of Re(VII) and Fe(III) but still achieve a high Mo(VI) extraction with 0.1 M Cyanex 272. The element concentration in the organic phase after n loading stages is calculated according Eq. (2). Due to the low Mo(VI) concentration in the MES II the maximum loading capacity is not reached after 10 loading stages.

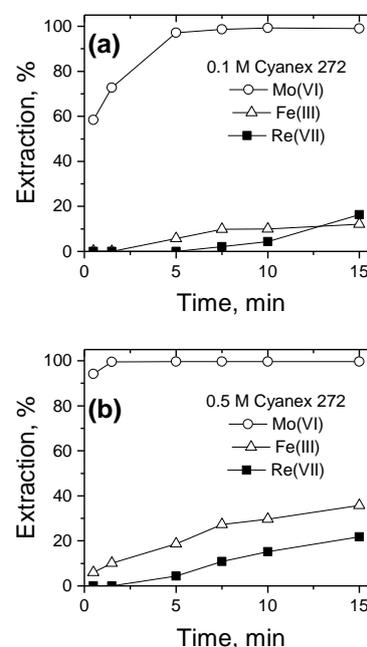


Figure 3. Influence of the mixing time on the extraction with (a) 0.1 M and (b) 0.5 M Cyanex 272 at pH 1.5.

Table 2. Composition of the multi element sulphate model solution (MES II).

	Zn(II)	Fe(III)	Cu(II)	Mo(VI)	Co(II)	Re(VII)	Sb(V)	Ge(IV)
Concentration, mg/L	3650	1930	242	146	10	10	10	5

So only the first part of the extraction isotherms is constructed. Figure 4 shows that in the range of low Mo(VI) concentrations in the aqueous phase the extraction isotherms for Cyanex 272 concentrations of 0.3 M and 0.5 M are considerably steeper compared to that of 0.1 M. The higher slope is favourable because a low Mo(VI) concentration in the raffinate can be achieved with less extraction stages. Table 3 indicates that after 10 loading stages a cumulative Mo(VI) extraction of respectively 74.2%, 95.9% and 98.2% is reached with 0.1 M, 0.3 M and 0.5 M Cyanex 272. Thus an increase in Cyanex 272 concentration enables a more efficient Mo(VI) extraction and enrichment in the organic phase. However the increase from 0.3 M to 0.5 M leads only to a slightly improved Mo(VI) extraction. Table 3 also shows that, besides Mo(VI), other elements of the MES II accumulate in the organic phase as well. As already stated in Figures 2 (a) and (b), an increase in

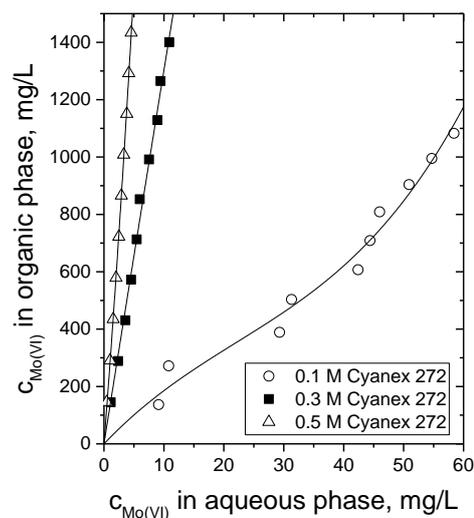


Figure 4. Extraction isotherms for Mo(VI) from multi element model solution (MES II) and 0.1, 0.3 and 0.5 M Cyanex 272,  $\text{pH}_{\text{eq}} = 1$ ,  $V_a:V_o = 1$ , mixing time: 5 min.

Cyanex 272 concentration also increases the co-extraction of not only Fe(III) but also Zn(II), Re(VII) and Sb(V). Less than 1 mg/L of Ge(IV), Cu(II) and Co(II) is present in the organic phase after 10 loading stages without being influenced by the Cyanex 272 concentration. In order to improve the purity of Mo(VI) in the organic phase previous investigations show that scrubbing of the loaded organic phase with sulfuric acid can reduce the Fe(III) content significantly [13]. Other approaches to reduce the impurity content in 0.3 M and 0.5 M Cyanex 272 are a shorter mixing time, compare Figure 3, and/or lowering the equilibrium pH value, compare Figures 2 (a) and (b).

Table 3. Concentration in the organic phase ( $c_{\text{org}}$  in mg/L) and cumulative extraction (E in %) after 10 loading stages with MES II,  $\text{pH}_{\text{eq}} = 1$ ,  $V_a:V_o = 1$ , mixing time: 5 min.

Elements	Concentration of Cyanex 272 in kerosene					
	0.1 M		0.3 M		0.5 M	
	$c_{\text{org}}$	E	$c_{\text{org}}$	E	$c_{\text{org}}$	E
Mo(VI)	1082.7	74.2	1400.2	95.9	1433.8	98.2
Fe(III)	180.0	0.9	830.0	4.3	890.0	4.6
Zn(II)	0.0	0.0	130.0	0.4	150.0	0.4
Re(VII)	1.2	1.2	4.1	4.2	5.2	5.4
Sb(V)	1.0	1.0	2.9	3.0	3.1	3.1
Ge(IV)	0.5	0.9	0.3	0.6	0.0	0.0
Cu(II)	0.0	0.0	0.0	0.0	0.0	0.0
Co(II)	0.0	0.0	0.0	0.0	0.0	0.0

#### 4. Conclusion

The investigation reveals that among the considered extractants Cyanex 272, D2EHPA and LIX 984 are the most promising ones for a selective extraction of Mo(VI) over Re(VII). Comparing the Mo(VI) extraction with these extractants from sulphate model solutions containing Zn(II), Fe(III), Cu(II), Mo(VI), Re(VII), Sb(V), Ge(IV) and Co(II) it is found that Cyanex 272 is the most selective. D2EHPA shows a significant co-extraction of Fe(III) and Zn(II) and LIX 984 extracts Cu(II) better than Mo(VI). The highest selectivity for Mo(VI) can be obtained with low Cyanex 272 concentrations (e.g. 0.1 M) at  $\text{pH}_{\text{eq.}} \leq 1$  and short mixing times (e.g. 5 min). In order to improve selectivity the mixing time has to be adjusted depending on the Cyanex 272 concentration (e.g. 1.5 min at 0.5 M Cyanex 272). The construction of extraction isotherms for Mo(VI) by repeated loading of the organic phase shows that Cyanex 272 concentrations of 0.3 M and 0.5 M are more favourable for an efficient Mo(VI) extraction than a concentration of 0.1 M. With 0.1 M, 0.3 M and 0.5 M Cyanex 272 cumulative extractions of respectively 74.2%, 95.9% and 98.2% Mo(VI) and a low extraction of respectively 1.2%, 4.2% and 5.4% Re(VII) are achieved after 10 loading stages. Similar to Re(VII) also Fe(III) co-extraction increases with increasing Cyanex 272 concentration. Therefore a scrubbing step with sulfuric acid is required. These results form a basis for further investigations with real leaching solutions and the aim to achieve a Mo(VI) enrichment in the organic phase as well as an improvement of the selectivity which could be possible by e.g. reducing the contact time and/or lowering the  $\text{pH}_{\text{eq.}}$  value.

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