

# Sustainable Extraction and Separation of Rhenium and Molybdenum from Model Copper Mining Effluents Using a Polymeric Aqueous Two-Phase System

Lucy Muruchi,<sup>†</sup> Nicolas Schaeffer,<sup>‡</sup> Helena Passos,<sup>‡</sup> Carlos M. N. Mendonça,<sup>‡</sup> João A. P. Coutinho,<sup>\*,‡</sup> and Yecid P. Jimenez<sup>\*,†</sup>

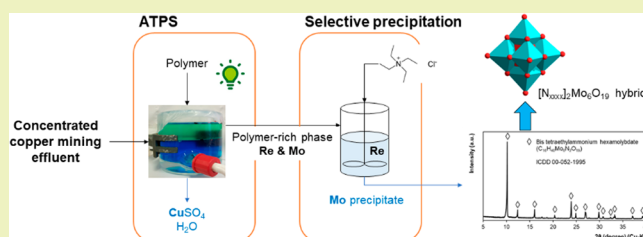
<sup>†</sup>Departamento de Ingeniería Química y Procesos de Minerales, Facultad de Ingeniería, Universidad de Antofagasta, Av. Angamos 601, Antofagasta, Chile

<sup>‡</sup>CICECO, Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

## Supporting Information

**ABSTRACT:** A sustainable and flexible approach for the extraction and separation of rhenium and molybdate species based on a polymeric aqueous two-phase system (ATPS) is proposed in which the high metal content in concentrated copper effluents is directly used as the driver of phase demixing. The partition coefficient and selectivity of Re, Mo, and Cu are studied in the proposed polymer-CuSO<sub>4</sub>-H<sub>2</sub>O ATPS as a function of additive concentration and polymer hydrophobicity. The electrolyte selection and concentration have a marked influence on the partition of Mo to the polymer phase, while increasing the hydrophobicity of the polymeric agent significantly improves the extraction of Mo. A selective precipitation based on the addition of quaternary ammonium salts directly to the polymer-rich phase is subsequently used for the quantitative recovery of Mo. A final polyoxometallate [N<sub>2222</sub>]<sub>2</sub>Mo<sub>6</sub>O<sub>19</sub> hybrid complex is obtained with high purity. The resulting process achieves high separation yields, relies exclusively on cheap chemicals with low toxicity and could be a more sustainable alternative for the extraction of Re and Mo from copper mine effluents. By using sulfate salts as the salting-out agent, the main component of the ore leachate drives the separation thereby avoiding the use of additional complexing agents.

**KEYWORDS:** Mining effluent, Oxyanion recovery, Polyoxometallate, Alternative separation medium, Critical metals



## INTRODUCTION

Rhenium and molybdenum are critical metals of high industrial importance due to their interesting physicochemical properties including their high melting points (3459 K for rhenium and 2896 K for molybdenum) and large number of stable valence states. As such, rhenium and molybdenum are integral components in specialist materials such as high-performance alloys, catalysts, and nanomaterials.<sup>1,2</sup> Furthermore, molybdenum is an essential building block of polyoxometallates, a class of inorganic compounds that is attracting significant interest due to their molecular, electronic, and structural versatility.<sup>3</sup> Hybrid organic molybdate compounds possess unique photochemical and photochromic properties and are touted as potential antitumor and anti-VIH agents.<sup>4</sup>

Chile is one the largest global producers of copper, rhenium, and molybdenum.<sup>5</sup> Rhenium is present in low concentrations in the Earth's crust (0.4 mg.t<sup>-1</sup>)<sup>2</sup> and is primarily produced as a byproduct of molybdenum and copper extraction at great environmental costs.<sup>6</sup> Rhenium is recovered during the pyrometallurgical processing of molybdenum sulfide and copper sulfide ores. This traditionally involves removing rhenium (VII) oxide, Re<sub>2</sub>O<sub>7</sub>, from the sulfurous gas phase

generated during hearth roasting (in molybdenum processing) and smelting (in copper processing).<sup>7–9</sup> An alternative process relies on the pressure leaching of molybdenite concentrates. Rhenium is solubilized during the pressure leaching step and can be subsequently recovered by a series of solution concentration and purification steps including ion exchange, solvent extraction, and electro dialysis to obtain pure ammonium perhenate crystals or rhenium metal.<sup>5</sup> In this context, there is a growing need for sustainable mining operations which alleviate the environmental burden while maintaining its efficiency and selectivity.

First proposed by Rogers and co-workers for the extraction of oxyanions,<sup>10–13</sup> a polymer-based aqueous two-phase system (ATPS) has emerged as an environmentally friendlier alternative to solvent extraction for the separation of metals.<sup>10,14,15</sup> Contrary to solvent extraction, ATPS occurs in fully aqueous media and relies on the difference in hydration energy between components in a ternary system, in this case

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water, polymer, and salt.<sup>11,14</sup> Concretely, ATPS allows for the predictable and reversible transition from a monophasic system to a biphasic one, composed of two phases with differing polarities, by manipulation of the system composition through the addition of an inorganic salt, for example. The partition of ions in ATPS is influenced by pH, temperature, surface properties, concentration, and the type of polymers and salts employed. Extraction of  $\text{ReO}_4^-$  using polyethylene glycol (PEG) 2000 and  $\text{Na}_2\text{MoO}_4$ ,  $\text{Na}_2\text{WO}_4$ , and  $\text{NaOH}$  as phase formers was reported to increase with increasing salt concentration at alkaline pH.<sup>13</sup> In accordance with the greater charge density of  $\text{OH}^-$  compared to the tested oxyanions, the distribution coefficient was primarily controlled by  $\text{NaOH}$  addition with a small contribution from the additional phase-forming salts ( $\text{Na}_2\text{MoO}_4$  or  $\text{Na}_2\text{WO}_4$ ).<sup>13</sup> The partition of  $\text{MoO}_4^{2-}$  in ATPS composed of the nonionic surfactant Triton-100 and  $(\text{NH}_4)_2\text{SO}_4$  is strongly dependent on the pH of the aqueous solution due to the change of molybdate speciation and the formation of species with variable charge densities.<sup>15</sup> Previously reported results on the mechanism of ATPS formation with  $\text{CuSO}_4$  in the presence of  $\text{MoO}_4^{2-}$  and  $\text{ReO}_4^-$ , respectively, as a function of pH and temperature serve as the basis for this work.<sup>16,17</sup> In the ATPS composed of  $\text{CuSO}_4$ -PEG 4000- $\text{H}_2\text{O}$ , a maximal molybdenum extraction of 93% was achieved in the pH range 1.5–2.5 at  $T = 35\text{ }^\circ\text{C}$ .<sup>17</sup> In contrast, temperature and pH did not have a significant effect on rhenium partitioning, and optimal rhenium extraction was obtained by increasing the PEG 4000 and  $\text{CuSO}_4$  concentration, yielding a final ATPS composition of 13.7 wt.% PEG 4000 and 13 wt.%  $\text{CuSO}_4$ .<sup>16</sup>

In the present study, the ability of PEG and polypropylene glycol (PPG) in  $\text{CuSO}_4$  solutions to extract polyoxomolybdates and  $\text{ReO}_4^-$  is assessed, and a simple and efficient method for the separation of rhenium from molybdenum is proposed. First, the partition behavior for rhenium and molybdenum as well as their mutual selectivity was determined as a function of salt additive addition, molecular weight and nature of the polymer. In a second part, quantitative and selective stripping of molybdenum directly from the polymer-rich phase after extraction was achieved in one step by addition of quaternary ammonium salts, yielding a molybdenum polyoxometalate of high purity. The selective recovery of molybdenum was optimized with regards to the nature and concentration of the precipitant, pH, and temperature.

## METHODOLOGY

**Chemicals and Instrumentation.** A detailed description of the compounds used as well as the instrumentation employed is provided in the “Methodology” section of the Supporting Information. The chemicals were used as received without further purification.

**Optimization of Re/Mo Extraction by ATPS  $\text{CuSO}_4$ -Polymer- $\text{H}_2\text{O}$ .** The ATPS phase diagram formed by  $\text{CuSO}_4$ -PEG 4000- $\text{H}_2\text{O}$ , taken by Claros et al. and presented in Figure S1,<sup>18</sup> was used as the starting point for metal partition tests. The effect of pH, temperature, and PEG 4000 and  $\text{CuSO}_4$  concentrations on the partition of the  $\text{ReO}_4^-$  anion was previously reported.<sup>16</sup> In light of these results, the composition of the ATPS  $\text{CuSO}_4$ -polymer- $\text{H}_2\text{O}$  was kept constant at 13 wt.%-13.7 wt.%-73.3 wt.% (total system mass of 20 g) at the conditions of  $T = 35\text{ }^\circ\text{C}$  and pH 2 for all extraction tests. A constant rhenium and molybdenum salt concentration of 0.3

wt.% for  $\text{NH}_4\text{ReO}_4$  and 0.85 wt.% for  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  was used for all partition experiments.

To further complement this, the effect of strong electrolytes as additives as well as the hydrophobicity of the polymer-rich phase on the distribution and selectivity of Mo and Re extraction was studied. The additives used were the chloride salts  $\text{LiCl}$ ,  $\text{NaCl}$ , and  $\text{KCl}$ . For the given ATPS condition employing PEG 4000, their presence was studied at two concentrations: a low concentration of 0.17 wt.% and a high concentration of 0.5 wt.%, referred to as systems L and H, respectively hereafter. The influence of the molecular weight of the PEG polymer (from 2000 to 20000  $\text{g}\cdot\text{mol}^{-1}$ ) on the metal partitioning in the absence of additives was also determined at the ATPS composition described previously. Furthermore, the distribution of the studied metals in mixed polymeric systems containing varying weight ratios of PEG 4000 to PPG 400 was also ascertained to provide a deeper insight into the relation between the polymer hydrophobicity and metal partition. All tests were performed at a fixed total polymer concentration of 13.7 wt.%.

All solutions were prepared gravimetrically using a Mettler Toledo analytical balance (model AX204) with a precision of  $\pm 0.1\text{ mg}$ . The prepared solutions were agitated in a temperature-controlled cell with an uncertainty of  $\pm 0.01\text{ }^\circ\text{C}$  (Julabo bath F25-ME refrigerated/heating circulator) until complete dissolution of all components. After complete dissolution, the pH system was adjusted by adding  $8\text{ mol}\cdot\text{L}^{-1}$  sulfuric acid. The obtained biphasic solutions were allowed to settle for 3.5 h at a constant temperature. Longer periods of agitation and sedimentation did not affect the results. Following equilibration, the top and bottom phases were separated, and the metal concentration (copper, rhenium, and molybdenum) was determined in each phase by inductively coupled plasma-mass spectroscopy (ICP-MS). Experiments were performed in duplicate with an average standard deviation ( $\sigma$ ) of  $\sigma(K_{\text{Cu}}) = 0.007$ ,  $\sigma(K_{\text{Mo}}) = 2.60$ , and  $\sigma(K_{\text{Re}}) = 0.33$ . Results were evaluated by the distribution coefficient ( $K_M$ ) for a given metal (M) in the aqueous two-phase system and the extraction selectivity ( $S_{M1/M2}$ ), defined as

$$K_M = \frac{C_{M,t}}{C_{M,b}} \quad (1)$$

$$S_{M1/M2} = \frac{K_{M1}}{K_{M2}} \quad (2)$$

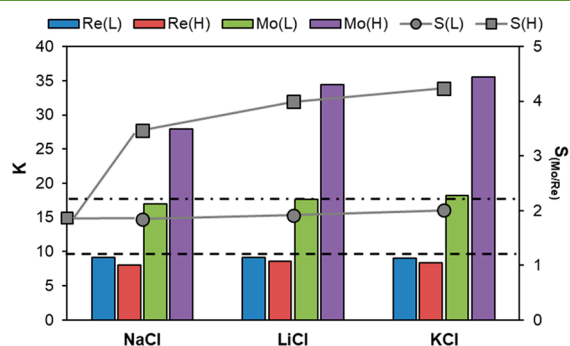
where  $C_{M,t}$  and  $C_{M,b}$  are concentrations of metal M in the top and bottom phase ( $\text{g}\cdot\text{L}^{-1}$ ), respectively, and  $K_{M1}$  and  $K_{M2}$  are the distribution coefficients for metal 1 and metal 2, respectively.

**Stripping of the Organic Phase by Precipitation with Ionic Liquids.** To ensure that all stripping experiments were performed under identical metal loading conditions, a large ATPS  $\text{CuSO}_4$ -PEG 4000- $\text{H}_2\text{O}$  extraction system of total mass 150 g was prepared. Extraction occurred at the standard concentrations and conditions described previously in the absence of additives. Following system equilibration and phase separation, aliquots of the polymer-rich phase (8 g) were taken to study the effect of the nature and concentration (2.4–9.2 wt.%) of the quaternary ammonium salt, temperature (25–55  $^\circ\text{C}$ ), and pH (0.94–4.44) on the selective precipitation and separation of molybdenum from rhenium. Unless otherwise stated, standard conditions were of pH 2,  $T = 35\text{ }^\circ\text{C}$ , and a

precipitant concentration of 5 wt.%, with each parameter varied individually while keep the others constant. Following an initial screening,  $[N_{2222}]Cl$  was selected as the precipitating agent. After addition of the precipitating agent, the system was left to settle for 12 h prior to ICP-MS analysis of the liquid phase following a 100-time dilution. The solid phase was recovered by vacuum filtration, washed with water several times, and dried in the oven for 24 h at 60 °C yielding an insoluble precipitate ranging in color between green, yellow, and white depending on the test conditions. Selected samples were further analyzed by X-ray diffraction (XRD) and SEM-EDS to obtain compositional and crystallographic analysis.

## RESULTS AND DISCUSSION

**Effect of Inorganic Additives on Selectivity  $S_{Re/Mo}$  in ATPS  $CuSO_4$ -PEG 4000- $H_2O$ .** The partition of rhenium, molybdenum, and copper in the ATPS composed of PEG 4000,  $CuSO_4$ , chloride salt additives (LiCl, NaCl, and KCl), and water is presented in Figure 1. Partition results in the



**Figure 1.** Effect of inorganic chloride additives (LiCl, NaCl, KCl) on the partition coefficient ( $K$ ) and the Mo/Re selectivity ( $S_{Mo/Re}$ ) at a low (L) and high (H) concentration of 0.17 and 0.5 wt.%, respectively, in the ATPS  $CuSO_4$ -PEG 4000- $H_2O$ , at 35 °C and pH 2. The dashed lines indicate the partition of Re (—) and Mo (—•—) in the absence of additives.

absence of additives indicate that Re and Mo are both successfully extracted to the PEG 4000-rich phase under the tested experimental conditions. Both partition coefficients ( $K_M$ ) for Mo and Re in the absence of additives are superior to 1 indicating their preferential partitioning to the polymer-rich phase, with  $K_{Re} \approx 10$  and  $K_{Mo} \approx 20$ . For all studied systems,  $K_{Cu}$  is always low and does not exceed 0.14 even for high additive concentrations (Figure S2). It was previously shown that the partition of metal ions in PEG-based ATPS could be correlated to their molar entropy of hydration ( $\Delta S_{Hyd}^\circ$ ).<sup>19</sup> Ions which interact strongly with water, i.e., have large  $\Delta S_{Hyd}^\circ$  values, will salt-out PEG 4000 and partition preferentially to the salt-rich phase, while ions with small  $\Delta S_{Hyd}^\circ$  values will partition to the PEG-rich phase. The low  $\Delta S_{Hyd}^\circ$  of  $Cu^{2+}$  ( $\Delta S_{Hyd}^\circ = -275.5 \text{ J.K}^{-1}.\text{mol}^{-1}$ ) and  $SO_4^{2-}$  ( $\Delta S_{Hyd}^\circ = -244.8 \text{ J.K}^{-1}.\text{mol}^{-1}$ ) enable them to act as efficient salting-out agents in the proposed ATPS.<sup>20</sup> In contrast, the higher  $\Delta S_{Hyd}^\circ$  of perrhenate ( $\Delta S_{Hyd}^\circ = -92.7 \text{ J.K}^{-1}.\text{mol}^{-1}$ )<sup>20</sup> reflects its preferential partition to the polymer-rich phase. The case of molybdenum is more complex and is addressed further on.

For all studied systems,  $K_{Mo} > K_{Re}$ . The additives used were selected as follows: (i) they are not known to directly complex the metal ions present in the system at the conditions and concentrations studied<sup>21</sup> and (ii) they do not induce phase

separation of PEG 4000 by themselves, thereby minimizing their effect on the system properties. There is no notable increase in  $K_{Mo}$  and  $K_{Re}$  for low LiCl, NaCl, or KCl additive concentrations of 0.17 wt.%. Increasing the ATPS chloride salt content to 0.5 wt.% has no appreciable effect on  $K_{Re}$  but results in a noticeable increase in  $K_{Mo}$  (Figure 1) by a factor of over 2. Correspondingly, the selectivity of the molybdenum/rhenium pair ( $S_{Mo/Re}$ ) increases from 1.84 when no additive is present to 4.24 after addition of 0.5 wt.% KCl at the studied pH and temperature conditions. The results presented in Figure 1 indicate that the proposed ATPS system is not only capable of extracting Mo and Re from concentrated copper effluents but can also be used for the mutual separation of oxyanions.

The preferential selectivity of ATPS  $CuSO_4$ -PEG 4000- $H_2O$ , with and without additives, for molybdenum over rhenium is attributed to the difference in the oxyanion speciation at a pH of 2. Previous solvent extraction studies of rhenium(VII) from solutions of varying acidity confirmed that Re exists exclusively as the perrhenate anion  $ReO_4^-$  in the pH range from 2 to 7.<sup>22</sup> In contrast, the speciation of molybdenum(VI) is known to vary as a function of pH, temperature, and ionic strength among others.<sup>21,23–27</sup> Upon addition of acid,  $MoO_4^{2-}$  ions are easily protonated and have a strong tendency to form polyoxoanions by oxygen bridging and the release of water molecules, this becoming the predominant mechanism in the pH range from 1 to 5.<sup>27</sup> In this pH range, various polymerization reactions occur between  $MoO_4^{2-}$  and the hydrogen ion, and consequently, diverse polynuclear species such as  $Mo_7O_{23}OH_5^-$ ,  $Mo_7O_{22}(OH)_2^{-4}$ ,  $Mo_7O_{21}(OH)_3^{-3}$ , and  $Mo_8O_{26}^{-4}$  were reported.<sup>27</sup>

Upon polymerization, the charge density of the resulting complex varies accordingly. It is well known that anions with lower charge densities favorably partition to the polymer-rich phase in ATPS.<sup>28</sup> Thus, the extent of partition depends on the charge density of the species present, which in turn depends on the experimental conditions, namely, pH, temperature, and the presence of additives. The studied  $CuSO_4$ -PEG 4000- $H_2O$  system has a pH = 2,  $T = 35 \text{ °C}$ ,  $[Mo] = 34 \text{ mM}$ , and an ionic strength of 5.24 considering the  $CuSO_4$ ,  $NH_4ReO_4$ , and NaCl concentrations. The speciation of molybdenum under these conditions was investigated using the Visual MINTEQ software package,<sup>29</sup> with the results presented in Table S1. Visual MINTEQ is a chemical equilibrium model for the calculation of metal speciation based on an inbuilt library of stoichiometries, equilibrium constants, and reaction enthalpies for each species.<sup>29</sup> Simulation results indicate  $Mo_8O_{26}^{-4}$  as the predominant species along with lower concentrations of heptamolybdate complexes. These results are to be taken as more qualitative than quantitative at the elevated ionic strength used. The charge densities, defined as the net charge ( $|z|$ ) divided by the molecular weight ( $M_w$ ) for a given complex of  $Mo_8O_{26}^{-4}$  along with the most commonly reported heptamolybdate complexes identified in the literature, are listed in Table 1.<sup>21,23–27</sup> From the results listed in Table 1, the significantly lower charge density of hepta- and octamolybdate complexes compared to  $ReO_4^-$  and particularly to the  $MoO_4^{2-}$  monomer translates to an increased hydrophobic character of these macro-ions, ultimately resulting in their preferential partition to the more hydrophobic polymer-rich phase.

In addition to ionic strength, the ionic medium was also found to influence the formation of various polyoxometalate complexes. Larger polyanions were found to be less stable at lower ionic strength, with higher ionic strength promoting the

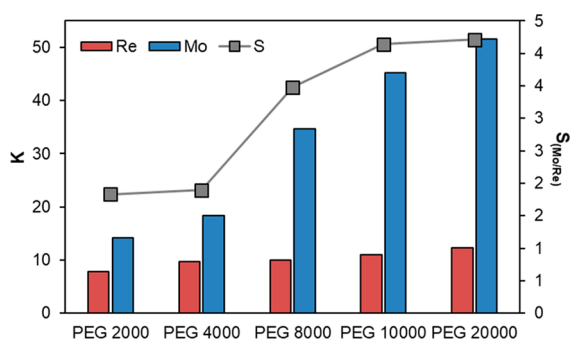


**Table 1.** Charge Density ( $|z|/M_w$ ) for Rhenium and Molybdenum Species

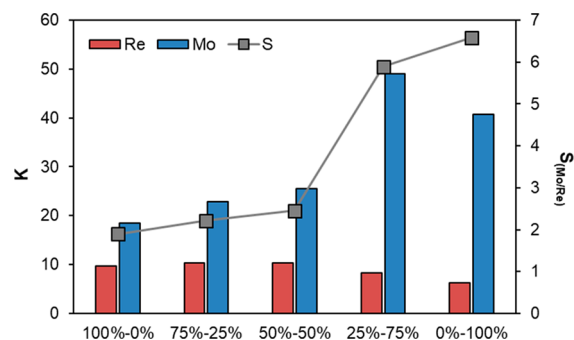
Species	$ z /M_w$
$H_{11}Mo_7O_{28}^{-3}$	$2.65 \times 10^{-3}$
$H_3Mo_7O_{24}^{-3}$	$2.83 \times 10^{-3}$
$Mo_8O_{26}^{-4}$	$3.38 \times 10^{-3}$
$Mo_7O_{24}^{-6}$	$5.68 \times 10^{-3}$
$MoO_4^{2-}$	$1.25 \times 10^{-2}$
$ReO_4^-$	$3.99 \times 10^{-3}$

formation of polyoxomolybdate species at higher pH values. This effect is more significant if the cation of the ionic medium is different ( $Na^+$  and  $K^+$ ). For example, the formation of  $(MoO_4)_7H_{10}^{-4}$  was reported to decrease in  $3.0 \text{ mol.L}^{-1}$  KCl solution in favor of the less charge dense  $(MoO_4)_7H_{11}^{-3}$  at pH 2. Furthermore, the species  $(MoO_4)_7H_{11}^{-3}$  represented 80% of Mo in solution compared to 57% in  $3.0 \text{ mol.L}^{-1}$  KCl and NaCl, respectively.<sup>27</sup> As such, the difference in Mo partition in the studied ATPS for different additives (LiCl, NaCl, and KCl) presented in Figure 1 is tentatively assigned to the difference in the predominance area of the various hepta- and octamolybdate species for different additive cations, with KCl emerging as the best additive tested for the enhanced extraction of Mo.

**Effect of Polymer on the Selectivity  $S_{Re/Mo}$ .** The lower charge density of polyoxometalate complexes results in a greater affinity for the more hydrophobic polymer-rich phase of the proposed ATPS. Considering this, the effect of increasing polymer hydrophobicity on the partition of rhenium and molybdenum in the ATPS with  $CuSO_4$  in the absence of additives was studied. ATPS conditions were maintained constant for all polymers. The polymers assessed were PEG of varying molecular weight from 2000 to 20000 as well as the mixture of PEG 4000 with PPG 400 at different weight ratios. The results are presented in Figures 2 and 3.

**Figure 2.** Effect of the molecular weight of PEG on the partition coefficient ( $K$ ) of Re and Mo and the Mo/Re selectivity ( $S_{Mo/Re}$ ) in the ATPS composed of  $CuSO_4$ -polymer- $H_2O$  (pH 2,  $T = 35^\circ C$ ).

Similarly to the results presented in Figure 1, increasing the PEG molecular weight, and hence its phase relative hydrophobicity, promotes the extraction of molybdenum and to a lesser extent rhenium (Figure 2), while decreasing copper extraction (Figure S3). The behavior of  $ReO_4^-$  is in accordance with that previously reported for the monovalent pertechnetate anion, which also exhibited an increased distribution in PEG-based ATPS at higher molecular weight.<sup>12</sup> The effect of polymer molecular weight is more pronounced for Mo due to the more hydrophobic nature of the

**Figure 3.** Effect of the polymeric phase composition between PEG 4000 and PPG 400 on the partition coefficient ( $K$ ) of Re and Mo and the Mo/Re selectivity ( $S_{Mo/Re}$ ) in the ATPS composed of  $CuSO_4$ -polymer- $H_2O$  (pH 2,  $T = 35^\circ C$ ).

polymolybdate complexes existing in solution at the studied conditions. However, a significant industrial hurdle to the application of higher molecular weight PEG is the resulting high solution viscosity. This in turn lowers mass transfer kinetics and decreases the ease of handling, traditionally a major advantage of ATPS.

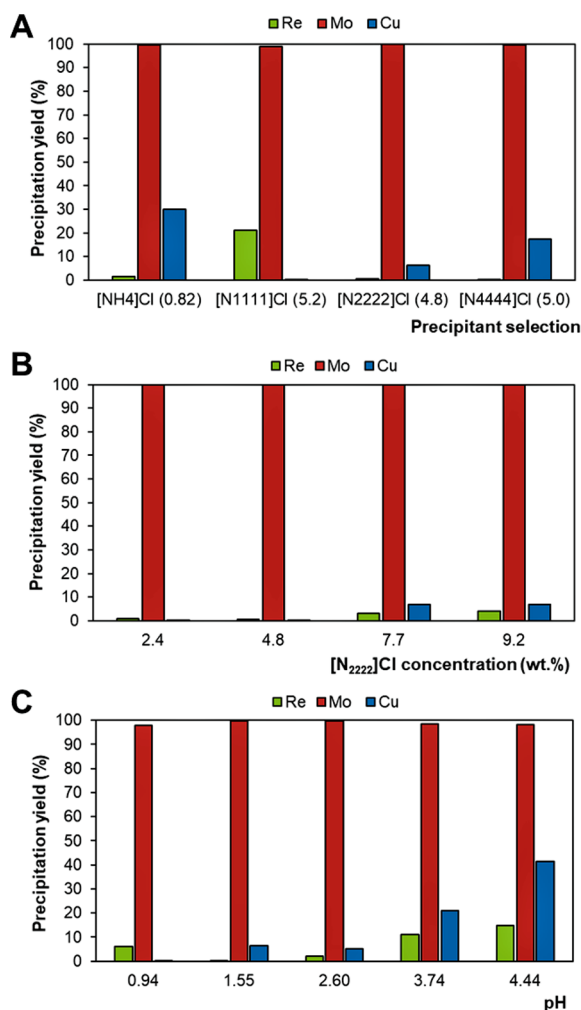
To overcome this limitation while maintaining a high relative hydrophobicity in the polymeric phase, mixtures of PEG 4000 and PPG 400 were studied, with the results presented in Figure 3. Gradual substitution of PEG 4000 by PPG 400 promotes the extraction of polyoxomolybdate complexes while reducing the distribution of  $ReO_4^-$ . A similar decrease in the extraction of  $ReO_4^-$  upon substitution of PEG with PPG was previously reported for the structurally similar  $TcO_4^-$ .<sup>12</sup> Substitution of PEG 4000 by PPG 400 increases  $K_{Mo}$  from 18.41 to 40.8 and the selectivity of Mo/Re separation from  $S_{Mo/Re}$  of 1.9 to 6.6, further validating the versatility of the proposed ATPS, which can act as an extraction and separation system. Interestingly, the combination of high KCl additive with a mixed polymeric phase (50:50 wt.% PEG 4000 to PPG 400) did not result in a synergistic improvement in Mo extraction and selectivity (Table S2), highlighting the delicate balance of forces dictating the extraction.

The versatility of the proposed ATPS for coextraction of oxoanions molybdenum and rhenium from model copper solutions is successfully demonstrated. Using only economical and nonhazardous components, the developed ATPS can coextract Mo and Re from solutions with a high Cu concentration. Furthermore, the same system can also be used to enhance the Mo partition by varying the solution ionic strength and the hydrophobicity of the polymeric phase.

**Selective Recovery of Molybdenum from PEG 4000-Rich Phase by Induced Precipitation with Ammonium Salts.** The selective precipitation of molybdenum from the polymer-rich phase after extraction is presented in the following section. To highlight the flexibility and robustness of the developed process, the ATPS composed of  $CuSO_4$ -PEG 4000- $H_2O$  was used as this system presented the lowest Mo to Re selectivity, i.e., the largest concentration of coextracted metals. This ensures that the effectiveness and selectivity of the proposed precipitation method can be extrapolated to the other systems studied which displayed greater selectivity toward Mo. The application of organic ammonium-based shrink-wrapping cationic precursors for the precipitation and isolation of polyoxometalate clusters is well documented.<sup>24,30</sup> Applying the same principle concepts but in a different ambit,

the use of quaternary ammonium salts was assessed for the selective separation of Mo from Re by induced precipitation from the polymer-rich phase. To this end, multiple factors were studied including pH, temperature, precipitant concentration, and nature of the precipitant. The average initial composition of the polymer-rich phase prior to precipitation is of 11.4 g.L<sup>-1</sup> of Cu, 7.0 g.L<sup>-1</sup> of Mo, and 4.4 g.L<sup>-1</sup> of Re.

Counter ions play a decisive role in the isolation of polyoxoanions,<sup>24</sup> with large organic counterions favoring the formation of polymolybdates containing tetrahedrally coordinated Mo(VI) not observed in the presence of small counterions.<sup>31</sup> As such, conditions favorable for the precipitation of polymolybdates from the polymer-rich phase using ammonium chloride ([NH<sub>4</sub>]Cl) or tetraalkyl ammonium chloride salts ([N<sub>1111</sub>]Cl, [N<sub>2222</sub>]Cl, and [N<sub>4444</sub>]Cl) were determined, with the results presented in Figure 4A. These salts were selected (i) as they are all soluble in aqueous PEG 4000 solutions and (ii) to assess the relative importance of hydrogen-bond and electrostatic interactions on the precipitation of polymolybdate complexes. Based on the trend in the phase-forming abilities of these salts to create ATPS with PEG,



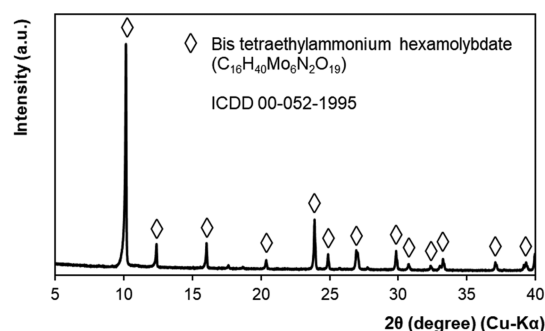
**Figure 4.** Effect of (A) precipitant selection (concentration indicated in wt.%), (B) [N<sub>2222</sub>]Cl precipitant concentration (2.4 to 9.2 wt.%), and (C) pH (5 wt.% [N<sub>2222</sub>]Cl) on the precipitation yield of Re, Mo, and Cu from the polymer-rich phase at 35 °C and pH 2 unless otherwise stated.

Silva et al.<sup>32</sup> demonstrated that [N<sub>1111</sub>]Cl and [N<sub>2222</sub>]Cl behaved like salts in which Coulombic interactions dominated, while [N<sub>4444</sub>]Cl behaved like an ionic liquid. Furthermore, the ammonium cation is a good hydrogen bond donor, whereas the other tested cations have limited H-bonding abilities due to their alkyl moieties. The results in Figure 4A indicate that ≥97 wt.% precipitation yield for Mo is achieved at all investigated conditions. However, the use of [NH<sub>4</sub>]Cl promoted the formation of a gel-like polymeric phase which became difficult to handle, a fact not observed for the other precipitants studied. This prevented the use of [NH<sub>4</sub>]Cl concentrations greater than 0.82 wt.%. Comparison of [N<sub>1111</sub>]Cl, [N<sub>2222</sub>]Cl, and [N<sub>4444</sub>]Cl reveal minimal Re coprecipitation in the case of [N<sub>2222</sub>]Cl and [N<sub>4444</sub>]Cl but an increase Cu precipitation for [N<sub>4444</sub>]Cl. An additional benefit of [N<sub>2222</sub>]Cl over [N<sub>4444</sub>]Cl is its lower cost. Problematically, the addition [N<sub>1111</sub>]Cl yielded the greatest coprecipitation of rhenium. In light of these results, [N<sub>2222</sub>]Cl was selected as the precipitant for the subsequent experiments.

The influence of [N<sub>2222</sub>]Cl concentration on the precipitation of the various metals present in the polymer-rich phase is presented in Figure 4B. For all tested [N<sub>2222</sub>]Cl concentrations, from 2.4 to 9.2 wt.%, quantitative Mo precipitation was achieved, while Re concentration in the PEG-rich phase remained practically constant. However, [N<sub>2222</sub>]Cl concentrations above 4.8 wt.% promote the coprecipitation of Cu. Cu precipitation yield increases 4 fold from under 2% for [N<sub>2222</sub>]Cl = 4.8 wt.% to approximately 9% for [N<sub>2222</sub>]Cl = 7.7 wt.%. For an initial Mo concentration of approximately 7.0 g/L in the polymer-rich phase, a low precipitant concentration of 2.4 wt.% emerges as the most selective option. Given the initial [Mo] = 7.0 g.L<sup>-1</sup> in the polymer-rich phase, addition of 2.4 wt.% [N<sub>2222</sub>]Cl results in an approximate 1:2 Mo to [N<sub>2222</sub>]Cl molar ratio excess.

Using [N<sub>2222</sub>]Cl as the precipitating agent, no significant temperature effects were observed in the range from 25 to 55 °C (Figure S4). As such, the extraction temperature of T = 35 °C was maintained during the precipitation to avoid unnecessary temperature adjustments. However, the influence of pH on the purity and appearance of the precipitate is more pronounced. The effect of pH on the precipitation yield of Mo, Re, and Cu is presented in Figure 4C. Again, Mo precipitation is superior to 97 wt.% in the entire studied pH range from 0.9 to 4.4. Cu coprecipitation increases linearly with pH above 2.6 due to the precipitation of Cu(II) at higher pH values.<sup>33</sup> The Re precipitation is minimal in the pH range from 1.6 to 2.6 and increases with pH thereafter. Three different precipitate colors were obtained: yellow from 0.9 to 2.6, white for 3.7, and green for pH values of 4.4 and above. The latter is most likely due to the increased Cu concentration on the precipitate.

The precipitate obtained at the optimized conditions of [N<sub>2222</sub>]Cl = 2.4 wt.%, pH 2.6, and T = 35 °C was characterized by SEM-EDS and XRD with the results presented in Figures S5 and S6 and Figure 5, respectively. Elemental mapping of the precipitate (Figure S5) show it to be composed of 12.3 mol % Mo, 80.4 mol.% oxygen, and 7.3 mol.% nitrogen (when carbon is not considered) with no trace of Re and Cu detected. The full EDS spectra and composition are provided in Figure S6 and Table S3. Compositional results confirm the complete selectivity of the proposed separation method. Crystallographic analysis in Figure 5 reveals the exclusive presence of the tetragonal organic hybrid bis(tetraethylammonium)-hexamolybdate (ICDD 00-052-1995) crystalline state. XRD



**Figure 5.** XRD analysis of the precipitate obtained from the polymeric phase after addition of  $[N_{2222}]Cl$  at 35 °C and pH 2.

analysis of the precipitates obtained at all tested conditions (Figure S7) confirm this as the dominant crystalline phase in almost all cases. The resulting light-yellow precipitate was found to be insoluble in water but soluble in some organic solvents in accordance with previously reported for  $[N_{xxxx}]_2Mo_6O_{19}$  hybrid complexes.<sup>34</sup>

The yellow hexamolybdate ion  $[Mo_6O_{19}]^{-2}$  is not reported to exist in significant amounts in aqueous solution but is commonly identified in the solid state.<sup>35</sup> Despite its low surface charge density, multiple authors reported the synthesis of organic- $[Mo_6O_{19}]^{-2}$  hybrids similar to that obtained here. However, many of these syntheses required the use of aggressive conditions and/or organic solvents.<sup>34,36–42</sup> The use of an inexpensive and nontoxic polymer-rich phase as an alternative reaction media to replace the VOC solvents commonly used in organic polyoxometalate synthesis procedures is of great scientific interest. The synthesis of polyoxometalate clusters such as  $[Mo_6O_{19}]^{-2}$  is an area of active study as these polyoxoanions offer a fascinating diversity of structural, electrochemical, magnetic, and catalytic properties.<sup>43</sup> Furthermore, this synthesis was achieved in quantitative yield and elevated purity in the presence of high concentrations of impurities, highlighting the robustness of the proposed approach.

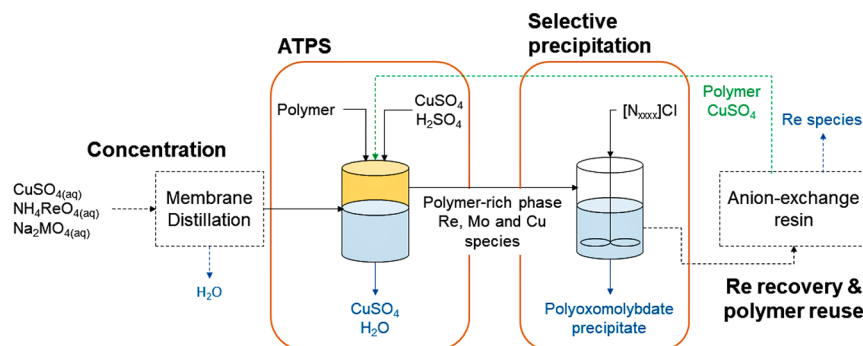
## DISCUSSION

By employing nontoxic and affordable chemicals, the proposed ATPS can act as medium for the concentration of Re and Mo from concentrated Cu solutions. In the potential process, which is conceptually illustrated in Figure 6, the primary solution component,  $CuSO_4$ , acts as the salting-out agent and represents a more sustainable alternative to the current solvent

extraction procedures currently applied for the separation of Mo, Re, and Cu from copper mine leachates. It is worth stressing that in this proof of concept, the copper concentration required at the studied mixture point far exceeds that of copper ore leachates.<sup>5,7,44</sup> To address this, a preconcentration step such as flash or membrane distillation is required to increase the metal content in solution, the extent and feasibility of which will depend on the polymer content of the ATPS, the nature of the polymer, and the inherent metal concentration of the leachate. As all points on a given tie-line have the same phase compositions, by “moving-up” along the tie-line, a lower  $CuSO_4$  requirement can be achieved at the expense of greater polymer content (Figure S1), a process not optimized in the scope of this work. Furthermore, the use of a more hydrophobic polymer will reduce the metal ion concentration required to induce phase separation while maintaining the selectivity of Mo and Re extraction as demonstrated in Figures 2 and 3.

An additional consideration is that copper ore leachates contain a significant concentration of coextracted metal salts with high molar entropies of hydration other than  $Cu^{2+}$  including  $Zn^{2+}$  ( $\Delta S_{Hyd}^\circ = -273.2 \text{ J.K}^{-1}.\text{mol}^{-1}$ ),  $Mg^{2+}$  ( $\Delta S_{Hyd}^\circ = -286.8 \text{ J.K}^{-1}.\text{mol}^{-1}$ ),  $Fe^{2+}$  ( $\Delta S_{Hyd}^\circ = -318.0 \text{ J.K}^{-1}.\text{mol}^{-1}$ ),  $Fe^{3+}$  ( $\Delta S_{Hyd}^\circ = -489.9 \text{ J.K}^{-1}.\text{mol}^{-1}$ ), and  $Al^{3+}$  ( $\Delta S_{Hyd}^\circ = -471.7 \text{ J.K}^{-1}.\text{mol}^{-1}$ ).<sup>20</sup> The presence of these salts in conjunction with the large excess of sulfate anions contribute toward the salting out of the polymer as was demonstrated in previously reported ATPS,<sup>45</sup> thereby reducing the required  $CuSO_4$  input solely used in this study as simplification. For example, copper ore leachates (at pH  $\sim 2$ ) were reported to contain over 7 wt.%  $SO_4^{2-}$ , 7.0 g.L<sup>-1</sup> of  $Al^{3+}$ , 5.0 g.L<sup>-1</sup> of  $Mg^{2+}$ , 0.8 g.L<sup>-1</sup> of  $Mn^{2+}$ , and 0.4 g.L<sup>-1</sup> of  $Fe^{2+/3+}$  in addition to  $Cu^{2+}$ .<sup>7</sup>

A further advantage of ATPS is that all components are water miscible, opening the possibility for several recovery techniques such as selective precipitation, electrodeposition of Cu, or ion-exchange columns. The opposite charge of the  $Cu^{2+}$  and  $ReO_4^-$  anions results in a straightforward separation after the removal of Mo. Multiple commercially available anion-exchange resins were shown to selectively recover  $ReO_4^-$  from solutions containing excess of contaminants and as such the recovery of  $ReO_4^-$  is not discussed here.<sup>5,46–48</sup> Ongoing work aims at closing the loop on the presented ATPS process, separating and recovering Re and Cu independently, and regenerating the polymeric phase for reuse.



**Figure 6.** Conceptual process design for the separation of rhenium and molybdenum from concentrated copper-rich mining effluents. Dashed line represents process steps not investigated within this work; flows indicated in green correspond to recycle streams.



## CONCLUSIONS

In this work, a novel ATPS based in  $\text{CuSO}_4$ -PEG 4000- $\text{H}_2\text{O}$  is proposed for the recovery of oxyanions from concentrated copper model mining effluents, further allowing the separation of rhenium and molybdenum from copper mine leachates. The proposed ATPS is a sustainable alternative to current solvent extraction processes, employing only nontoxic reagents and using the high copper concentration as the driving force behind the ATPS formation and Re and Mo partition. In doing so, this reduces the need for additional phase-forming salts. This process could be easily integrated into existing copper mining operations. The possibilities of linear scale up, ease of use, and rapid phase separation without the formation of stable emulsions are other advantages of the ATPS-based process. At the tested conditions of pH 2 and  $T = 35\text{ }^\circ\text{C}$ , Re and Mo preferentially partition to the polymer-rich phase due to the formation of polyoxomolybdate complexes of low charge density in the case of Mo. The extraction of Mo and selectivity of the Mo/Re separation can be further enhanced by the presence of KCl as an additive and/or by varying the hydrophobicity of the polymeric phase, providing an additional degree of versatility to the proposed ATPS. Finally, quantitative and selective recovery of Mo was achieved directly from the polymer-rich phase after extraction by addition of quaternary ammonium chloride salts. At the optimized conditions of  $[\text{N}_{2222}]\text{Cl} = 2.4\text{ wt.}\%$ , pH 2, and  $T = 35\text{ }^\circ\text{C}$ , the organic hybrid bis(tetraethylammonium)hexamolybdate complex was obtained, a high value product of relevance for the growing field of polyoxometalate chemistry.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b05759.

Detailed list of chemicals and instruments used, phase diagram of the ternary  $\text{CuSO}_4$ -PEG-4000- $\text{H}_2\text{O}$  ATPS, copper partitioning as a function of additive concentration and polymer selection, speciation results from software Visual Minteq in the PEG 4000- $\text{CuSO}_4$ - $\text{H}_2\text{O}$  ATPS at a pH 2, partition coefficients of Re, Mo, and Cu and the separation selectivity (S) of the Mo/Re pair in three different systems, effect of temperature on the precipitation yield of Re, Mo, and Cu from the polymer-rich phase using  $[\text{N}_{2222}]\text{Cl}$ , SEM-EDS analysis of the final obtained precipitate, and XRD diffractograms of the obtained precipitate under different experimental conditions. (PDF)

## AUTHOR INFORMATION

### Corresponding Authors

\*J.A.P. Coutinho. E-mail: [jcoutinho@ua.pt](mailto:jcoutinho@ua.pt). Phone: +351 234 401 507.

\*Y.P. Jimenez. E-mail: [yecid.jimenez@uantof.cl](mailto:yecid.jimenez@uantof.cl). Phone: +56 (55) 2637 902.

### ORCID

Nicolas Schaeffer: 0000-0002-0747-2532

Helena Passos: 0000-0002-0573-093X

João A. P. Coutinho: 0000-0002-3841-743X

Yecid P. Jimenez: 0000-0001-6451-4615

## Author Contributions

All authors have given approval to the final version of the manuscript.

## Notes

The authors declare no competing financial interest.

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