

Supporting Information

Sustainable extraction and separation of rhenium and molybdenum from model copper mining effluents using a polymeric aqueous two-phase system

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Methodology

The ATPS studied in this work were established by various aqueous solutions of synthesis-grade PEG with an average molecular weight of 2000, 4000, 6000, 8000, 10000 and 20000 respectively and PPG of average molecular weight 400, all purchased from Sigma Aldrich. Ammonium perrhenate (NH_4ReO_4) with a purity 99.98% was procured from Molymet. Sodium molybdate di-hydrated ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) with a purity of 99.5% and copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) with a purity of 99.0% were obtained from Merck. The effect of additives on metal partition was studied by addition of chloride salts including LiCl (99% pure from Merck), NaCl (99.9% pure from BDH Chemicals) and KCl (99.5% pure from Chem-Lab). The solution pH was adjusted using technical grade sulfuric acid (95-97%) purchased from VWR. Ammonium chloride (99.8% pure from Merck) and tetraalkylammonium chloride with a general formula $[\text{N}_{\text{xxxx}}]\text{Cl}$ ($x=1-4$) purchased from Sigma Aldrich with a minimum purity of 97% were investigated for the selective precipitation of molybdenum from rhenium. All chemicals were used without further purification. Ultrapure, double distilled water, passed through a reverse osmosis system and further treated with a Milli-Q plus 185 water purification apparatus, was used for all experiments.

Copper, molybdenum and rhenium concentrations in solution were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using an Agilent Technologies 7700 Series spectrometer. Special care was taken to adequately dilute the polymeric phase to prevent interferences in the analysis. Solution pH was monitored using an Accumet pH meter 50 with a measurement range from -2 to 20 between -5 and 105 °C and a relative accuracy of ± 0.002 °C. The morphology of the obtained molybdenum precipitate was analysed by scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS) using a Hitachi SU-70 microscope. The crystal structure of the precipitate was determined by X-ray powder diffraction using a Bruker AXS; the resulting spectra were analysed using the X'pert Highscore Plus software package.

Figures

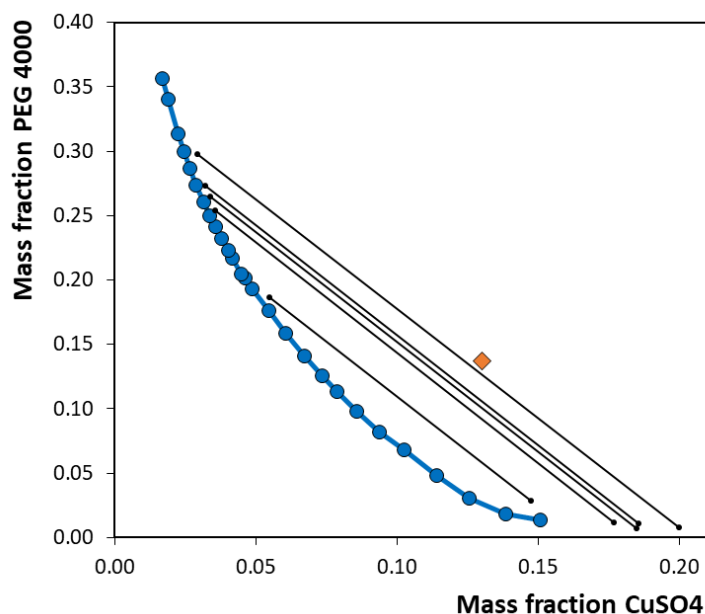


Figure S1. Phase diagram of the CuSO₄- PEG 4000-H₂O ATPS at 35 °C along with obtained tie-lines (data from Claros et al. (2014)). Operational mixture point used in this work indicated in orange.

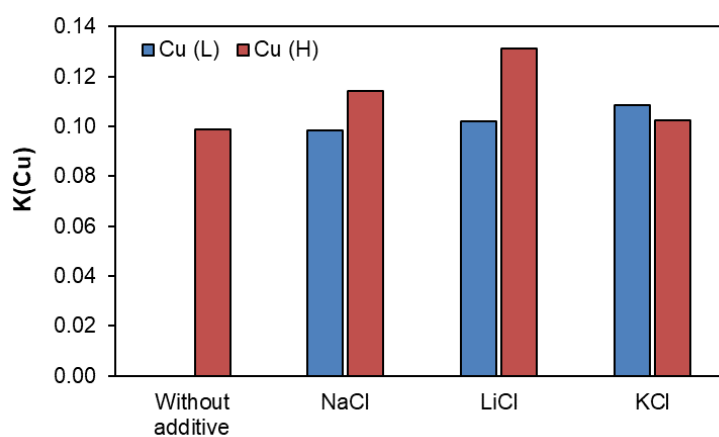


Figure S2. Effect of inorganic chloride additives (LiCl, NaCl, KCl) on the partition coefficient of Cu (K_{Cu}) at a low (blue) and high (red) concentration of 0.17 wt.% and 0.5 wt.% respectively in the ATPS CuSO₄-PEG 4000-H₂O, at 35 °C and pH=2.

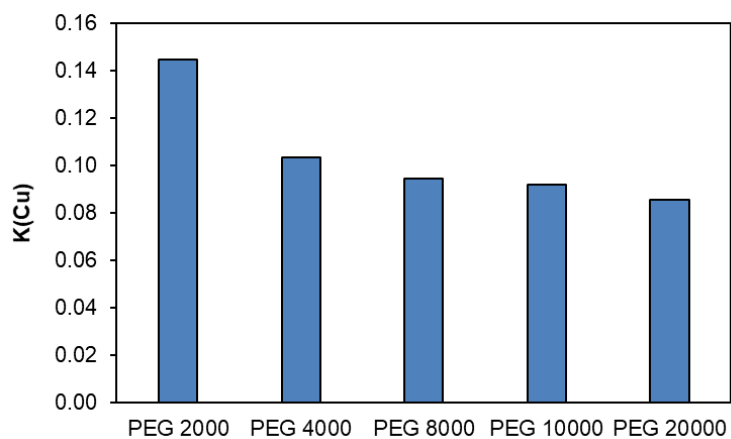


Figure S3. Effect of the molecular weight of PEG on the partition coefficient of Cu (K_{Cu}) in the ATPS composed of CuSO_4 -polymer- H_2O (pH=2, T=35°C).

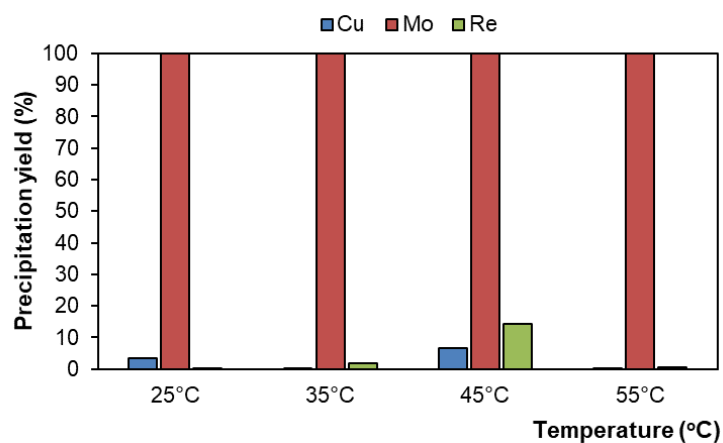


Figure S4. Effect of temperature on the precipitation yield of Re, Mo and Cu from the polymer-rich phase at $[\text{N}_{2222}]\text{Cl}$ = 5.0 wt.% and pH=2.

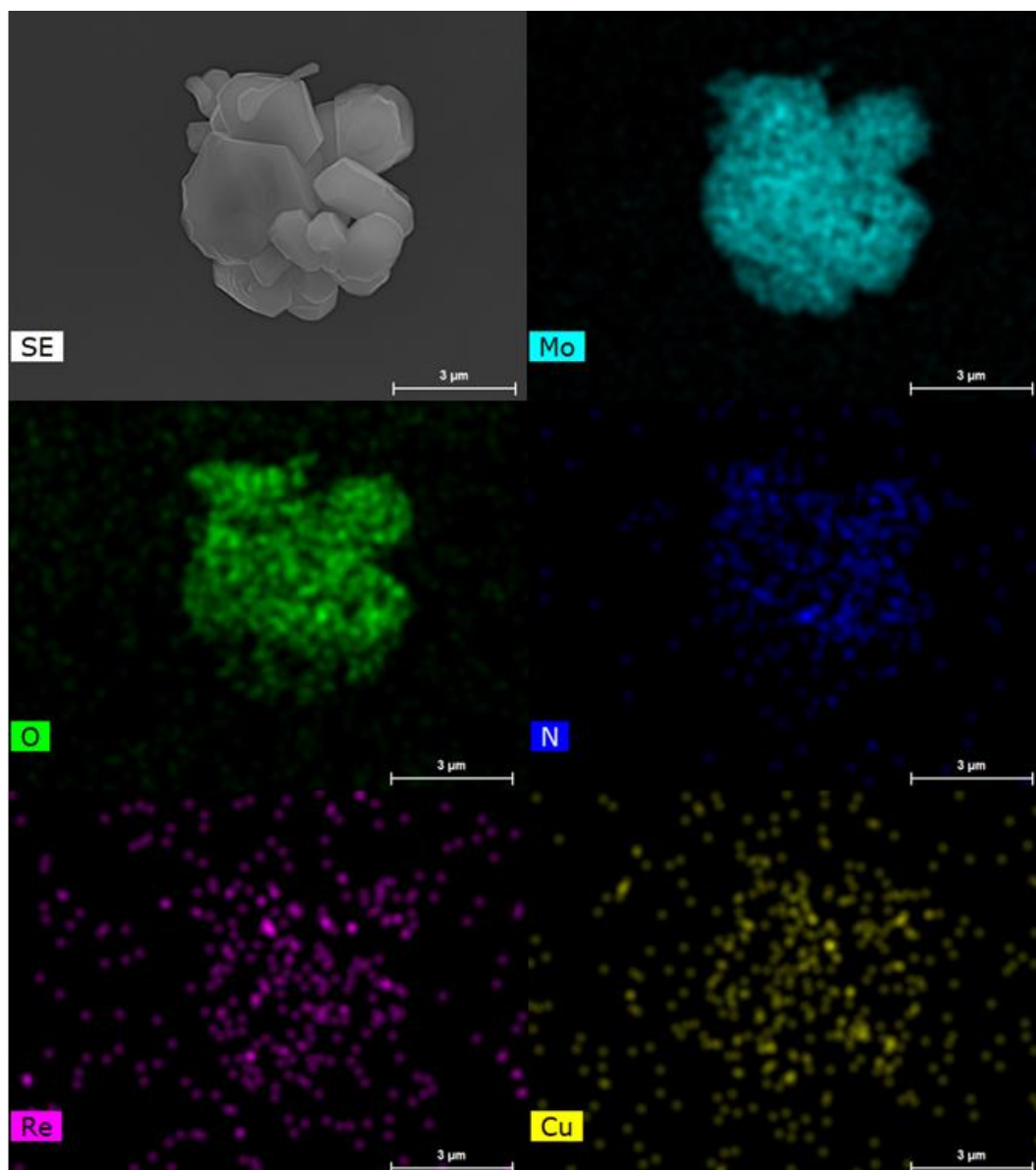


Figure S5. SEM analysis with elemental mapping of the precipitate obtained from the polymeric phase after addition of $[N_{2222}]Cl$ at $35^{\circ}C$ and $pH=2$.

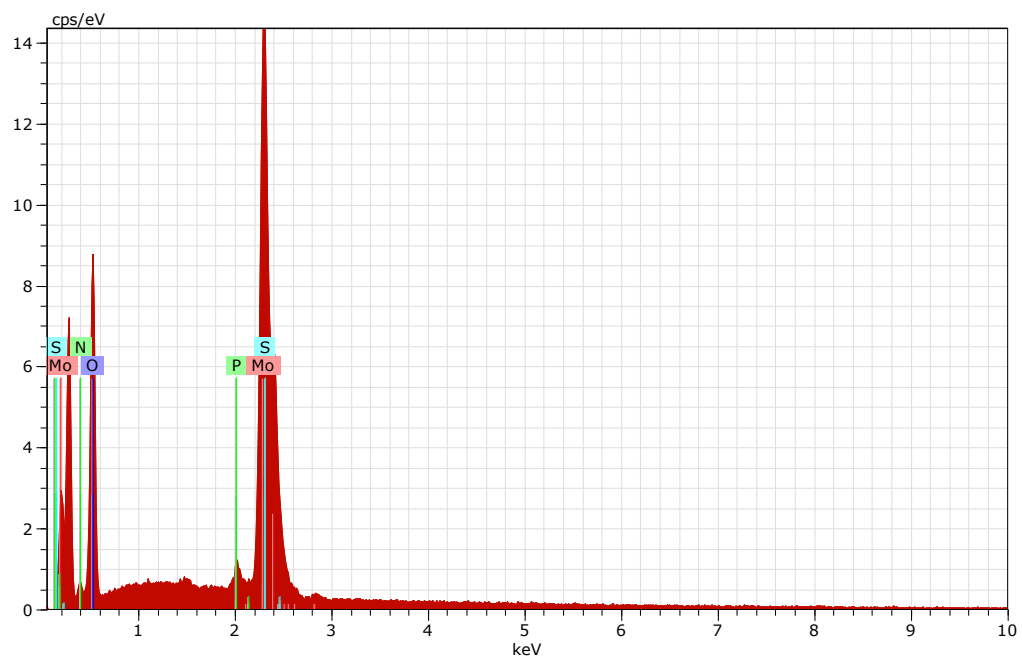


Figure S6. EDS spectra of the precipitate presented in Figure S5 obtained after precipitation at $[N_{2222}]Cl = 2.4$ wt.%, $T = 35$ °C and $pH = 2$.

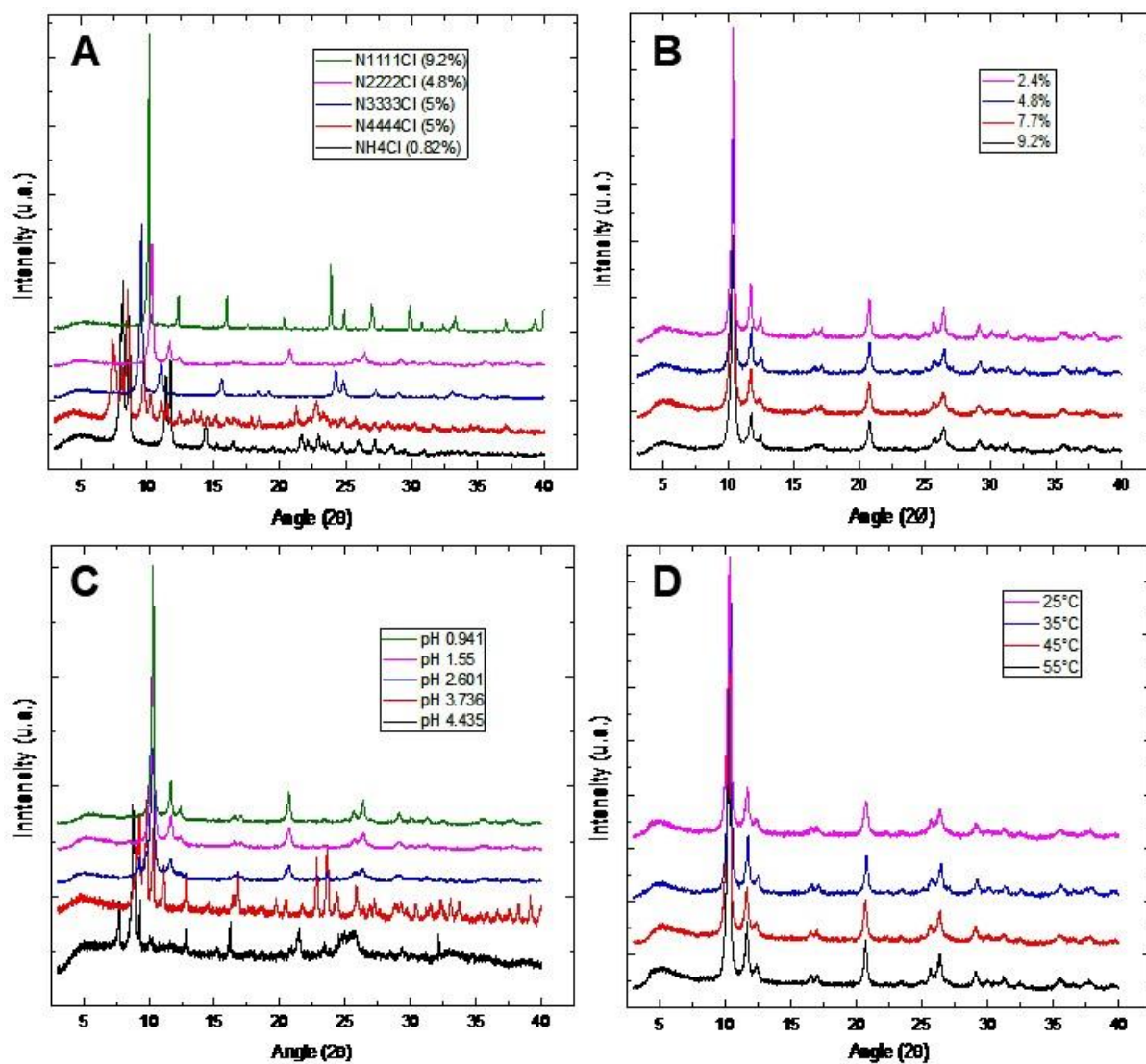


Figure S7. Effect of (A) precipitant selection (concentration indicated in wt.%), (B) [N₂₂₂₂]Cl precipitant concentration (2.4 to 9.2 wt.%), (C) pH (5 wt.% [N₂₂₂₂]Cl) and (D) temperature on the crystal structure of the obtained precipitate from the polymer-rich phase using [N₂₂₂₂]Cl as precipitating agent, at 35°C and pH=2 unless otherwise stated.

Tables

Table S1. Speciation results from software Visual Minteq 3.1 in the PEG 4000-CuSO₄-H₂O ATPS at a pH=2 and T=35 °C, [Mo]= 34mM and the ionic strength is of 5.24 considering CuSO₄, NH₄ReO₄ and NaCl concentrations.

Component	% of total concentration	Species name
Cl ⁻¹	88.4	Cl ⁻¹
	11.6	NaCl (aq)
MoO ₄ ⁻²	95.9	Mo ₈ O ₂₆ ⁻⁴
	0.04	H ₂ Mo ₆ O ₂₁ ⁻⁴
	0.21	HMo ₇ O ₂₄ ⁻⁵
	3.8	H ₃ Mo ₈ O ₂₈ ⁻⁵
Na ⁺¹	93.4	Na ⁺¹
	6.6	NaCl (aq)

Table S2. Distribution coefficients (K) of Re, Mo and Cu and the separation selectivity (S) of the Mo/Re pair in three different systems

Polymer	Additive	K Re	K Mo	K Cu	S Mo/Re
PEG 4000	KCl (H)	8.39	35.57	0.10	4.24
50% PEG 4000 - 50% PPG 400	None	10.40	25.56	0.08	2.46
50% PEG 4000 - 50% PPG 400	KCl (H)	7.45	28.86	0.05	3.88

Table S3. EDS compositional analysis of the precipitate presented in Figure S5 obtained after precipitation at [N₂₂₂₂]Cl= 2.4 wt.%, T=35 °C and pH 2.

Element	Series	Normalised Concentration [wt.%]	Atomic Concentration [mol.%]	Error (3 Sigma) [wt.%]
Molybdenum	L-series	45.93	12.30	4.72
Oxygen	K-series	50.05	80.37	17.93
Phosphorus	K-series	0.05	0.04	0.09
Nitrogen	K-series	3.97	7.29	2.50

References

Claros, M., Taboada, M. E., Galleguillos, H. R., Jimenez, Y. P., Liquid–liquid equilibrium of the CuSO₄+PEG 4000+H₂O system at different temperatures. *Fluid Phase Equilibria*, 2014, 363, 199-206.