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Green process for selective extraction: Superchaotropic foam flotation of tungsten from soft leaching conditions of scheelite ores.

Valentin LEGRAND[1] , Pierre BAUDUIN[1] , Stephanie SZENKNECT[1] , Luc GIRARD[1] and Olivier DIAT[1]

ICSM, Univ Montpellier, CEA, CNRS, ENSCM, Marcoule, France

This study explores a sustainable method for extracting tungsten (W) from scheelite mining residues using a new concept, the superchaotropic flotation, leveraging the formation tungsten ionic nanometre-size clusters during the dissolution process, to be selective in ion flotation recovering.

Context and purpose: Scheelite ($CaWO_4$) (see figure 1) and wolframite ($Fe,MnWO_4$) are the main tungsten ores. After concentration, they are processed using hydrometallurgical methods to extract and purify the tungsten.

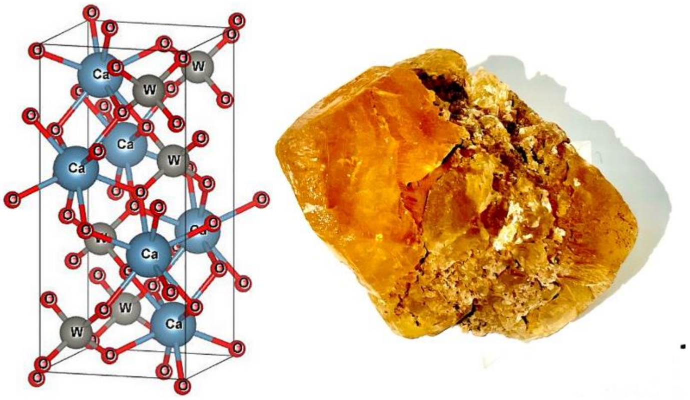

Figure 1: a) Crystalline structure of scheelite $CaWO_4$: this mineral crystallizes in space group $I4_1/a$ (88) with lattice parameters a = 5.243(2) Å, c = 11.376(3) Å, having Z = 4 units per lattice at ambient pressure and temperature [1]. An ionic crystal with Ca^{2+} cations and $[WO_4]^{2-}$ tetrahedra forming a face-centred cubic lattice could give a suitable description of the scheelite structure [2]. b) Scheelite crystal from Mohave Co. Arizona (Peabody Museum Harvard).

Because high-grade deposits are depleted, it is now important to concentrate our effort of W-recovery on low-grade deposits (<0.3%) using sustainable and efficient processes, a challenge. Scheelite – the ore on which this study is dedicated - often requires pre-concentration, with froth flotation (using surfactant collectors) being the standard extraction and concentration method since the 1970s.[3] Then, industrially, scheelite ore concentrates are usually decomposed with alkaline reagents (NaOH or Na_2CO_3) in autoclaves to form sodium tungstate (Na_2WO_4),[4] which is further purified into ammonium paratungstate ($(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$). However, these processes demand high temperature and pressure and generate large volumes of secondary by-products such as $Ca(OH)_2$ or $CaCO_3$, posing environmental and technical challenges.[5] Alternative hydrometallurgical routes exist to directly dissolve scheelite to tungstic acid using common mineral acids (HCl, HNO_3, H_2SO_4); they require lower acid consumption and milder conditions than alkaline decomposition.[6] However, HCl and HNO_3 generate corrosive and polluting gases, while H_2SO_4 produces solid by-products (gypsum and tungstic acid) that passivate the ore surface and halt dissolution. The intimate mixing of gypsum and tungstic acid further complicates phase separation, limiting process efficiencies.

It is important to note that tungsten, the metal of interest, is a transition metal with extensive redox chemistry. Depending on the environment, it can adopt several oxidation states. States VI and V govern most aqueous chemistry. This redox variability results in hydrolysis, condensation, and precipitation sequences that are however difficult to predict and control as a function on the surrounding medium. This point is well addressed by speciation reviews on isopolytungstate systems as those of Gumerova and Rompel.[7] The literature distinguishes between unstable, stable, and metastable species and mentions oxides that have been little studied due to their low stability. At basic pH, the dominant form is the tungstate anion (WO_4^{2-}), while acidification to a pH close to zero leads to the formation of tungsten trioxide hydrates, the pale yellow $WO_3{\cdot}2H_2O$ or $WO_3{\cdot}H_2O$ which are pale-yellow, until a yellow hydrated solid commonly known as tungstic acid (H_2WO_4).[8] Between a pH of 1 and 8, the chemistry is even more complex as tungstate condenses in a variety of polytungstate ionic cluster, forming the polyoxometalate family (see figure 2a). The protonation and oligomerization equilibria of these ions are highly dependent on pH, ionic strength, and total tungsten concentration.[7, 9] n the presence of phosphate and at stoichiometric concentrations, the heteropolyoxometalate ion $[PW_{12}O_{40}]^{3-}$ hetero-polyoxometalate (see figure 2b) is a dominant chemical species at low pH and low ionic strength. This species is very interesting because of its superchaotropic property, but what does that mean?

A chaotropic ion (or salting-in agent) weakens the structured hydrogen-bond network of water due to weak hydration and high polarizability.[11] They usually lead to enhanced solubility of hydrophobic molecules and altered interfacial or biochemical processes. Recently, it has been shown that inorganic nanometre-size anions (nano-ions, NIs) with low charge density weakens even more the structured hydrogen-bond network and then adsorb onto hydrated, neutral molecules (macrocycles, polymers, and co-solvents) and surfactant assemblies in aqueous phases.[12] This specific ion association, called superchaotropicity, is driven by the enthalpy gained from recovering the hydrogen bonds of water molecules that have desorbed from molecules (or assemblies) and nano-ions. The resulting apparent attractive force competes with and equilibrates the electrostatic repulsion (Born energy) occurring between the adsorbed nano-ions.[13] In 2015, we demonstrated that the most common Keggin-type POMs, tungstosilicate ($SiW_{12}O_{40}^{4-}$) and tungstophosphate ($PW_{12}O_{40}^{3-}$), display an unexpectedly strong affinity for polar and electrically neutral interfaces.[12e] This interfacial behaviour was investigated at systems such as micelles in water and water/air foam's interfaces stabilized by non-ionic surfactants. The pronounced enrichment of POMs in non-ionic foams highlighted their strong potential for ion separation and water decontamination applications. In 2023, we have indeed demonstrated that, using neutral foaming agents, superchaotropic isopolyoxomolybdates could be selectively extracted.[14] This study demonstrated a proof-of-concept for superchaotropic flotation, where non-ionic surfactants extract and separate superchaotropic polyoxometalate nano-ions from other ions in solution. For example, at pH 1 and with 1.5 mM BrijO10 and 100 mM of Molybdenum salt, up to 25% interfacial ion recovery was achieved, underscoring the efficiency of this approach. Combined flotation mass balance, Raman spectroscopy and small angle x-ray scattering analyses allowed us to show that $Mo_{36}O_{112}^{8-}$ and $Mo_6O_{19}^{2-}$ species were adsorbed at the air–water interface in non-ionic foams and that att pH 3, only $Mo_6O_{19}^{2-}$ was stabilized at the air–water interface, suggesting that surfactants can promote the conversion of $Mo_7O_{24}^{6-}$ and $Mo_8O_{26}^{4-}$ into the superchaotropic $Mo_6O_{19}^{2-}$ form. Through this pioneering and innovative research, we achieved selective separation of molybdate from tungstate at pH 2, reaching a Mo/W separation factor of ~20, confirming the strong potential of this innovative flotation concept.

Finally, coming back on the W issue, the work of Zhao et al of these last ten years on scheelite dissolution in a H_2SO_4-H_3PO_4 mixture to form the phosphotungstate $[PW_{12}O_{40}]^{3-}$ hetero-polyoxometalate in solution[4, 15] were extremely very inspiring to revisit this approach, via the superchaotropic flotation.As Zhao et al, we have first successfully dissolved scheelite in a H_2SO_4-H_3PO_4 mixture, thus preventing the formation of insoluble tungstic acid. Indeed, Zhao et al showed that scheelite dissolution can be enhanced by adding small amounts of phosphoric acid to sulfuric acid, which simultaneously produces gypsum and soluble Keggin-type phosphotungstate (POT) a W-speciation under the form of superchaotropic ions while limiting scheelite passivation by tungstic acid. The formation of POT, confirmed by NMR spectroscopy in their studies, drives indeed this synergistic process but was restricted to strongly acidic conditions (pH < 1.5). However, and despite its importance, POT identification was rarely performed in studies of scheelite leaching kinetics, leaving process optimization incomplete. However, we used to do as referred to our previous publications in performing, among others, SAXS technique to identify POT formation.

Leaching Experiment: Choosing various acidic conditions (H_2SO_4 concentration from 0.1 up to 3.5M and H_3PO_4 concentration from 0.003 up to 0.3), temperature (from 20 up to 80°C) and fixing three W:P ratios via the control of the mass of scheelite added to the solution, tungsten and calcium concentrations in eluted solution were quantified by ICP-AES (Spectro Arcos) - at multiple wavelengths to reduce spectral interferences and as a function of dissolution time. More details are given in reference [17]. Based on these concentrations, relative mass loss ($\Delta m_i/m_0$) and normalized mass loss (NL(i,t)) were calculated as a function of time, taking into account the sample's initial specific surface area and elemental composition. We indeed tried to find the optimizing conditions for $[PW_{12}O_{40}]^{3-}$ formation. POT formed in solution were characterized (see figure 2c) and quantified by SAXS ($\lambda = 0.071$ nm wavelength, Mo x-ray radiation) on a XENOCS experimental bench. Experimental spectra were fitted using SASView software and applying a spherical form factor over q-range between 0.03 and 0.8 $Å^{-1}$, and we could precisely determine the POT volume fraction as a function of various step along the dissolution process (see figure 2c). To confirm POT speciation, complementary ^{31}P NMR spectra were acquired on a Bruker Avance400 (DMSO-d_6 solvent and δ referenced to H_3PO_4), with long acquisition times (~17 h) for dilute samples.

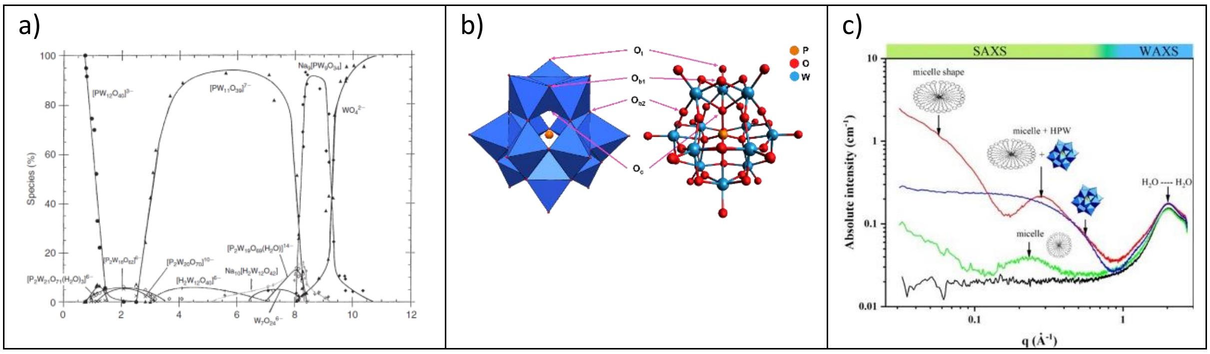

Fig. 2: a) Speciation diagram of heteropolyoxotungstates and also including some isopolyoxotungstates as a function of pH at ≈100 mM initial $H_3PW_{12}O_{40}$.[7] b) Representation of the polyhedral and atomic structure of the most common Kegging POM anion, $PW_{12}O_{40}^{3-}$. c) SAXS/WAXS scattering signature in absolute scale of 5 mM of $PW_{12}O_{40}^{3-}$ in solution (blue curve) water scattering black curve, micelles of C8G1 foaming agent, 100 mM (green curve) and POT (5mM) + foaming agent (100 mM) micelle scattering (red curve).

The effect of the various thermodynamical conditions on the POT formation was summarized hereafter. The effect of sulfuric acid concentration on $CaWO_4$ dissolution kinetics was studied at constant concentration of phosphoric acid: An enhanced dissolution until a saturation effect over the molar regime in [H_2SO_4], with a rate that decreases, likely due to H_2WO_4 precipitation, is consistent with literature trends. Then, fixing the H_2SO_4 concentration in the molar range, the scheelite dissolution rate increases with [H_3PO_4], between 0.003 and 0.3 mol L^{-1}. This effect stems both from higher proton activity and from enhanced phosphate activity, which promotes POT formation. SAXS analysis confirmed these macroscopic observations, with the maximum dissolution rate that depends on the W:P ratio: at 12:1 it occurs near 1 mol L^{-1} H_2SO_4, at 12:10 near 1.5 mol L^{-1}, and at 12:100 near 2.5 mol L^{-1}. Moreover, POT yield rises from 12 wt.% at 0.003 mol L^{-1} of H_3PO_4 to 96 wt.% at 0.03 mol L^{-1} of H_3PO_4 in 2.5 mol L^{-1} H_2SO_4 solution. At too low [H_3PO_4], tungstic acid forms instead (yellow gel). Overall, 0.03 mol L^{-1} H_3PO_4 (W:P = 12:10) appears as the optimal concentration for rapid and complete scheelite dissolution without saturation effects. In all these cases, high rates correlate with ~90% yield of soluble polyoxotungstate (POT). They can be considered as mild conditions.[16]

Once the leachate contains POM of W, flotation process can be implemented using here non-ionic foaming agent. One of the crucial points is to choose the suitable surfactant molecules in order to i) avoid any precipitation of the foaming agent in the acidic condition, even mild and ii) minimize the transport of solution, optimizing the interfacial recovery factor versus the total recovery factor.[17] Indeed, a minimal transport guarantees a concentration of ions within the collapsed foam solution. The initial operation conditions were those used in previous works from Naskar et al, Micheau et al and Skorzevska et al.[12e, 14, 17] Non-ionic polyethoxylated surfactants are in general more sensitive to acidic pH conditions than sugar-based foaming agent. POT adsorption onto foaming agent micelles was investigated independently (see figure 2c). Preliminary flotation tests allowed us to achieve up to about 60% of W recovery from dissolved scheelite in mild acidic conditions (0.2 mol L^{-1} H_2SO_4, 0.03 mol L^{-1} H_3PO_4 and minimizing the transport below 10% (see table 1). Of course, the surfactant choice, its initial concentration (around its critical micellar concentration) as well as the injected N_2 gas flow-rate are processing factors that have to optimized but the preliminary results are very encouraging.

Table 1: C_W^0 (mmol.L^{-1}) the initial tungsten concentration in the solution before flotation, I_w (%): percentage of tungsten extraction at the interface. T (%): Transport factor. I_S (%): Percentage of surfactant extraction to the floated phase. $[S]/[HPW]_{0\text{-}r}$: Molar ratio between concentration of extracted surfactant and that of the extracted polyoxometalates (HPW), reflecting the number of adsorbed HPW per surfactant. Time (h): Approximate duration for each flotation experiment.

C_W^0 (mmol.L^{-1})	I_W (%)	T (%)	I_S (%)^a	$[S]_{0\text{-}r}/[HPW]_{0\text{-}r}$	Temps (h)
4,6	64,0 ± 2,0	6,4 ± 0,2	92,9 ± 0,8	24,6 ± 0,6	≈ 24

Conclusion: This study demonstrates that H_2SO_4–H_3PO_4 synergistic dissolution offers a robust and sustainable route for scheelite processing. Complete dissolution is achieved at mild conditions (60 °C) with gypsum as the only benign by-product, easily recovered for reuse. The process reduces energy demand, waste management costs, and reagent consumption and phosphoric acid is effective even at low concentrations. Compared with conventional alkaline or strong acidic methods, this approach delivers clear economic and environmental advantages, paving the way for integration into full and efficient tungsten extraction workflows. Preliminary superchaotropic flotation tests demonstrated already very promising alternative in case of W-recovery from a pure scheelite leachate. The W-selective flotation process achieved nearly 100% extraction efficiency, separating superchaotropic species from calcium using non-ionic surfactants. This robust method (see figure 3) will enable mild leaching and sustainable tungsten recovery from complex and W-poor ores, even under other metal-rich conditions, as ongoing studies confirm.

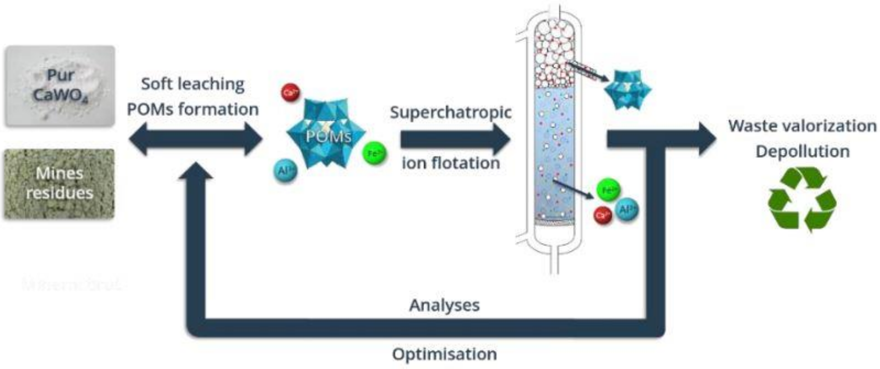

Fig. 3: Tungsten extraction from tailings: an original approach using superchaotropic foam flotation

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