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Solvometallurgical Process for the Recovery of Tungsten from Scheelite

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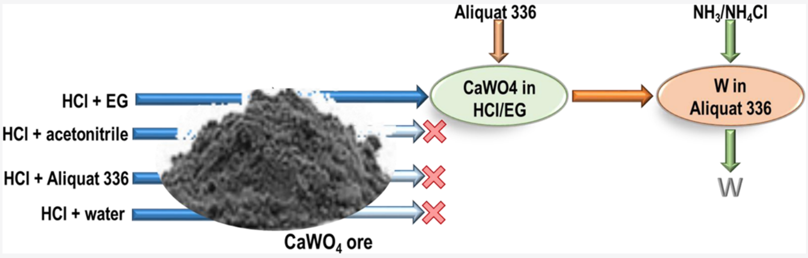

ABSTRACT: The industrial state-of-the-art processes to extract tungsten from scheelite ($CaWO_4$) require high pressures and temperatures. These flowsheets consume a large excess of chemicals (which are very hard to recycle) and generate up to 25 tons of high-salinity wastewater per ton of ammonium paratungstate product. In this work, a more sustainable conceptual flowsheet for the recovery of tungsten from high-grade (55.0 wt % W) and medium-grade (3.3 wt % W) scheelite ores was developed at the lab scale. Leaching of $CaWO_4$ was tested in solutions of 37.0 wt % aqueous HCl in organic solvents (ethylene glycol, poly(ethylene glycol) 200, acetonitrile) and ionic liquids (Aliquat 336). The tungstate ($H_xW_yO_z^{n-}$) generated by the reaction between $CaWO_4$ and HCl was only solubilized in the ethylene glycol system with an appropriate amount of 37.0 wt % aqueous HCl, whereas in all other solvents, it either precipitated or $CaWO_4$ did not dissolve. After the dissolution of tungsten, nonaqueous solvent extraction was used to separate tungsten from calcium, by means of a solvent consisting of 20 vol % Aliquat 336 in the aliphatic diluent GS190 with 10 vol % 1-decanol as a modifier. Scrubbing with water removed the co-extracted iron. Finally, tungsten was recovered as ammonium tungstate $(NH_4)_2WO_4$, the precursor of ammonium paratungstate, by stripping in a mixture of aqueous ammonia and ammonium chloride. Paratungstate is the most common intermediate for the production of tungsten oxide or tungsten metal. One drawback that needs to be adequately addressed, prior to further upscaling of this conceptual flowsheet, is the potential formation of trace levels of 2-chloroethanol in the leaching stage. It is hypothesized that this problem can be circumvented by further optimizing process conditions to enhance the mass transfer and reduce the reaction time, such as better mixing of the solid and the lixiviant.

■ INTRODUCTION

Tungsten is a critical commodity mainly employed as tungsten carbide (WC) which, in turn, is used in metalwork tools, a very large base application for sectors such as construction, metalworking, mining, and oil and gas drilling.[1] In addition, the economic importance of tungsten is increasing, due to its very high substitution index and its application in crucial, fast-developing technologies such as robotics, drones, and 3D printing.[2,3] In 2019, the U.S. had an import reliance on tungsten above 50% and the supply of secondary sources, mostly via recycling of WC, would not meet the demand for this metal.[1] To increase the resilience of the tungsten supply chain, the U.S. Geological Survey has recently launched the first study of domestic tungsten resources and mineral potential in over 20 years.[4] Appreciable amounts of tungsten resources were found to be economically suitable for exploitation, although the increasingly low grade of the primary sources necessitates preconcentration steps and renders the primary extraction increasingly complex.[5] In this work, we developed a process to efficiently recover tungsten from scheelite, $CaWO_4$, present in high-grade (55 wt % W) and medium-grade (3.3 wt %) ores, relevant to the exploitation of primary tungsten sources.

Scheelite and wolframite, (Fe, Mn)WO_4, are the two main tungsten ores, with scheelite being the easiest to dissolve. The core step in the flowsheet of the conventional industrial processing of scheelite is digestion with NaOH or Na_2CO_3 to convert $CaWO_4$ into Na_2WO_4, followed by the removal of impurities and acidification of the Na_2WO_4 solution (pH 2−3). Tungsten is then recovered via solvent extraction with protonated trioctylamine (or its commercial mixture Alamine

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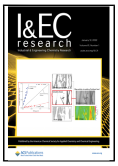

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336) and stripped with an aqueous ammonia solution to obtain ammonium paratungstate (APT), $(NH_4)_{10}(H_2W_{12}O_{42})\cdot 4H_2O$. The latter salt is crystallized and calcined to tungsten(VI) oxide and, finally, reduced by hydrogen gas to metallic tungsten powder.[6] The current industrial process was established more than 60 years ago, and at the time, it significantly increased tungsten recovery yields, while optimizing the energy efficiency and labor costs.[6] Nevertheless, it still has several drawbacks, including the need for digestion in NaOH or Na_2CO_3. Although being necessary to obtain a water-soluble form of tungsten, this step implies working in an autoclave at pressures between 1.2 and 2.6 atm, temperatures around 200 °C, and the large excesses of reagents, which are not or hardly recycled and generate at least 25 tons of high-salinity acidic wastewater per ton of APT product in the solvent extraction step.[7,8]

In the literature, different approaches to avoid the formation of Na_2WO_4 and high-salinity wastewater have been suggested. A first series of alternatives were the processes using H_3PO_4 as a chelating agent to recover tungsten as a heteropolytungstate $(NH_4)_3PW_{12}O_{40}\cdot 9H_2O$, which also include attempts to recycle the acidic solutions.[9−13] The use of H_2SO_4 or of mixtures of H_2SO_4/H_3PO_4 to dissolve scheelite was also investigated, obtaining soluble Na_2WO_4 and insoluble $CaSO_4$.[14−16] A more innovative technology was developed by Li and co-workers, based on roasting and $(NH_4)_2CO_3$ leaching, with the main advantages being the recyclability of the chemicals used in the process and the lack of discharged wastewater.[17,18] Recently, a process was developed, which entails H_2SO_4 conversion of $CaWO_4$ to H_2WO_4 followed by $(NH_4)_2CO_3$ leaching.[19,20] It is based on a patent comprising $CaWO_4$ leaching in H_2SO_4 (followed by leaching and separation of the formed H_2WO_4 in ethylene glycol).[21] APT was obtained without the formation of Na_2WO_4, and the reagents were recycled. Although this process is very promising, it still includes the formation of solid intermediates such as H_2WO_4 and $CaSO_4$ with consecutive dissolution−filtration−dissolution steps. More innovative resin-enhanced acid leaching of $CaWO_4$ from high-grade ores has also been developed, but the separation and purification of the formed H_2WO_4 and the cost-effectiveness of the process were not evaluated.[22] Optimization of tungsten recovery from $CaWO_4$ in alkaline media has also been extensively investigated: those processes are usually based on leaching in NaOH solutions to convert the tungsten into the water-soluble Na_2WO_4, although large excess of NaOH, temperatures above 100 °C, and high pressure are required for recovery efficiency ≥90%.[23−28] In fact, tungsten compounds cannot be leached in aqueous HCl since tungsten precipitates as H_2WO_4 on the particle interfaces, limiting the dissolution of the particles themselves. Martins and co-workers studied the leaching of scheelite in aqueous HCl solutions at a controlled pH, concluding that it can be possible with a large excess of leaching reagent.[29,30] Other factors that can facilitate the process are: (i) a smaller particle size, to enhance the mass transfer; (ii) a heated ball mill, to destroy the H_2WO_4 layer; (iii) the use of complexing agents, such as H_3PO_4 or organic acids (tartaric acid or citric acid); and (iv) the use of alcoholic solvents to solubilize the H_2WO_4. The use of a heated ball mill is difficult to scale up and organic acids are too expensive. By contrast, the use of HCl−alcohol mixtures, in particular of HCl−ethanol−water, to recover tungsten as H_2WO_4 was patented in 1966[31] and was then further studied by Girgin and co-workers.[32,33] Partial or total substitution of water by alcohols suppresses hydrolysis and allows us to control the reaction chemically rather than by diffusion. Unfortunately, all of these processes lead to the formation of solid H_2WO_4, which limits the dissolution of the particles themselves.

In the present paper, we demonstrate how to successfully circumvent the formation of solid reaction products in the leachate by dissolving scheelite, $CaWO_4$, in 37.0 wt % aqueous HCl−ethylene glycol mixtures and purifying the tungsten by nonaqueous solvent extraction (NASX).

■ EXPERIMENTAL SECTION

Chemicals. $CaWO_4$ (98.0%) was supplied by Thermo Fisher GmbH (Kandel, Germany). Two grades of scheelite ores, i.e., a high-grade ore with a tungsten content of about 55 wt % (55-W) and a medium-grade preconcentrate containing about 3.3 wt % tungsten (3-W), were kindly provided by Saloro S.L. (Barruecopardo, Spain), and when required pretreated by gravimetric separation (ULiège, Belgium). Aqueous hydrochloric acid (HCl, 37.0 wt %), ultrapure NaCl for volumetric titration (99.99+%), and ammonia solution (NH_3, 25.0 wt % solution in water) were ordered from VWR Chemicals (Heverlee, Belgium); boric acid (H_3BO_3, ≥99.5%) was purchased from VWR International (Heverlee, Belgium). Ethylene glycol (99.0+%), 1-decanol (98.0+%), and Aliquat 336 TG were purchased from Acros Organics (Geel, Belgium); ICP metal standards (all 1000 mg L^{-1}), acetonitrile (a.r.), tri-*n*-butylphosphate (TBP, 99.0+%), $CaCl_2$ (99.0+%), silver nitrate titrant ($AgNO_3$, 0.1 mol L^{-1}), and nitric acid (HNO_3, 65.0 wt %) were supplied by Chem-Lab (Zedelgem, Belgium). Hydrofluoric acid (HF, 48.0 wt %) and poly(ethylene glycol) 200 (PEG-200, a.r.) were purchased from Merck (Steinheim, Belgium) and ICP standard uranium 10 mg L^{-1} from Merck KGaA (Darmstadt, Germany). Trioctylamine (TOA, 99.0+%) and deuterated dimethyl sulfoxide (DMSO-d_6 99.9% atom D for NMR) were purchased from Sigma-Aldrich (Diegem, Belgium). Cyanex 923, a mixture of four trialkylphosphine oxides, was purchased from Cytec (Vlaardingen, The Netherlands). ShellSol A150, ShellSol G70, ShellSol D70, Shell GTL Solvent GS190, and Shell GTL Solvent GS250 were supplied by Shell Chemicals Europe BV (Rotterdam, The Netherlands). Ultrapure water deionized to a resistivity of 18.2 MΩ·cm was produced using a Millipore Reference+ ultrapure water system. All chemicals were used as received without any further purification.

Lixiviant Preparation and Stability. The lixiviants were prepared by dilution of 37.0 wt % aqueous HCl in water, ethylene glycol, poly(ethylene glycol) 200 (PEG-200), and acetonitrile or by extraction of 37.0 wt % aqueous HCl in Aliquat 336. About 0.1 g of $CaWO_4$ in 2 mL of each solution was stirred at 60 °C and 1000 rpm for up to 4 h until a full dissolution was observed or yellow, solid H_2WO_4 was formed. The stability of the solutions under storage and process conditions was monitored via ^1H NMR spectroscopy on a Bruker Avance II+ 600 MHz spectrometer (solvent DMSO-d_6) and via gas chromatography/mass spectrometry (GC/MS) measurements (PerkinElmer Autosystem XL/Turbomass Kolom equipped with a PerkinElmer column of 60 cm length and 0.25 mm diameter, coating Perkin 5MS and film thickness of 1 μm). Other operational parameters were: injection volume = 1 μL; oven temperature = 45−230 °C; injection temperature = 220 °C; source temperature = 200 °C; helium pressure on the carrier = 15 psi; split flow = 15 mL min^{-1}. Unless otherwise stated, the samples studied by ^1H NMR and GC/MS consisted of 2 mol L^{-1} 37.0 wt % aqueous HCl in ethylene glycol. They were stirred for 8 and 24 h at 40 and 60 °C. The samples were diluted 5 times in ethanol and 20 times in DMSO prior to the GC/MS and ^1H NMR analysis, respectively.

Leaching Tests. The lixiviants, in which full dissolution of $CaWO_4$ was observed, were further investigated for the leaching of the high-grade or medium-grade pre-concentrated of scheelite ores, referred to as 55-W and 3-W, respectively. The 55-W and 3-W solids were characterized via analysis with ICP-OES (Optima 8300, PerkinElmer), after prior digestion using a microwave digester (Mars 6, CEM, equipped with EasyPrep iWave vessels) with 4.0 mL of 65 wt % HNO_3, 5.0 mL of 37 wt % HCl, and 3.0 mL of 48 wt % HF, followed by HF neutralization with 6.0 mL of 4 wt % H_3BO_3 per mL of HF. Calibration standards for the ICP-OES analysis ranged from 0.1 to 5.0 mg L^{-1}. Germanium and indium were used as internal standards for elements with I and II ionization state, respectively. The leaching tests were carried out on the solids (55-W or 3-W) at a liquid-to-solid (L−S) ratio of 20 mL g^{-1}. The samples were stirred in aluminum heating blocks at 1000 rpm at a temperature of 40, 60, 80, or 100 °C for 1−16 h. The blank of the lixiviant—with no addition of solid—was also stirred under the same conditions and was prepared for the ^1H NMR or GC/MS analysis (vide supra). At the end of the tests, the leachates were filtered and properly diluted for elemental analysis with ICP-OES (vide supra). All tests were performed in triplicate. The percentage of metal extraction in the leaching ($\%E_L$) was calculated as

$$\%E_L = \frac{n_{M,l}}{n_{M,max}} \times 100 \tag{1}$$

where $n_{M,l}$ denotes the number of moles of the metal in the leachate and $n_{M,max}$ represents the maximum number of moles of the metal after complete digestion of the solid.

Nonaqueous Solvent Extraction, Scrubbing, and Stripping Tests. Nonaqueous solvent extraction (NASX) of metals was performed by shaking a certain volume of two immiscible organic phases in 4.0 mL vials, using a Nemus Life Thermo Shaker TMS-200 (Nemus LIFE AB, Lund, Sweden). The more polar feed (MP) contained tungsten, iron, calcium, and aluminum in 2 mol L^{-1} HCl and 2 mol L^{-1} $CaCl_2$ in ethylene glycol. The less polar organic phase (LP) was composed of an extractant, a diluent, and a phase modifier. Different extractants (i.e., Cyanex 923, tri-*n*-butylphosphate (TBP), Aliquat 336 chloride, and tri-*n*-octyl amine (TOA)); aliphatic and aromatic diluents (respectively, ShellSol G70, ShellSol D70, Shell GTL Solvent GS190, Shell GTL Solvent GS250, *n*-dodecane, and ShellSol A150; xylene, *p*-cymene, and toluene); and salting-out agent concentration in the MP (0−2 mol L^{-1} $CaCl_2$) were screened to optimize the NASX of tungsten. Unless stated otherwise, the experimental conditions were kept constant: MP/LP ratio = 1/1; temperature, T = 25 °C, mixing speed, r = 2000 rpm; mixing time, t_{mix} = 60 min. The McCabe−Thiele diagrams for W extraction were constructed using different MP/LP phase ratios from 1/5 to 5/1 to determine the theoretical number of countercurrent stages. After extraction, the phase disengagement was accelerated by centrifuging at 5000 rpm for 5 min with a Heraeus Labofuge 200 centrifuge (Thermo Fisher Scientific, Asse, Belgium). The MP raffinate phase was then diluted in a mixture of 2 vol % HNO_3 and 0.5 vol % HBF_4 as background solution to determine the metal content with ICP-OES. The concentration of the metals in the LP was calculated by mass balance. The percentage extraction of metals ($\%E_{SX}$) was calculated as

$$\%E_{SX} = \frac{n_{M,LP}}{n_{M,MP}} \times 100 \tag{2}$$

with $n_{M,LP}$ and $n_{M,MP}$ denoting the number of moles per metal in the LP and MP phases, respectively.

In a similar way to NASX, the scrubbing tests were performed by equilibrating the loaded LP phases with different scrubbing agent solutions (i.e., water, 0.5 mol L^{-1} HCl, and 0.25 mol L^{-1} H_2SO_4) at a phase ratio of unity. The percentage scrubbing of metals (%SB) was calculated as

$$\%SB = \frac{n_{M,aq}}{n_{M,org}} \times 100 \tag{3}$$

The selective stripping of tungsten from the scrubbed LP solvents was investigated using different stripping agent solutions of NH_3, NH_4Cl, or a mixture of NH_3 and NH_4Cl at a certain O/A phase ratio. The concentration of the stripping agents was varied from 0.0 to 2.5 mol L^{-1}. The percentage stripping of metals (%ST) was calculated as

$$\%ST = \frac{n_{M,aq}}{n_{M,org}} \times 100 \tag{4}$$

with $n_{M,aq}$ and $n_{M,org}$ denoting the number of moles per metal in the aqueous and organic phases, respectively. An overview of the parameters investigated in each process unit is displayed in Table 1.

Table 1. Overview of the Parameters Investigated for the Solvometallurgical Recovery of Tungsten from Scheelite

process unit	parameter
solvent preparation	stability over time
	stability over temperature
solvoleaching	HCl diluent
	temperature
	time
nonaqueous solvent extraction	extractant
	extractant concentration
	diluent and phase modifier
	O/A ratio
	number of stages
scrubbing Fe	scrubbing agent
stripping	stripping agent
	stripping agent concentration
	temperature
	number of stages

■ RESULTS AND DISCUSSION

Dissolution of $CaWO_4$. In conventional hydrometallurgy, the dissolution of scheelite ($CaWO_4$) in 37.0 wt % aqueous HCl, (HCl_{aq}), solutions would lead to the formation of solid tungstic acid (H_2WO_4), which deposits on the solid particles and passivates the particles for further leaching

$$(CaWO_4)_s + HCl_{aq} \xrightarrow{H_2O} (H_2WO_4)_s + CaCl_{2,aq} \tag{5}$$

Organic solutions (with less than 12 vol.% water) of hydrogen chloride in alcohols at atmospheric or superatmospheric pressure have been proven to dissolve $CaWO_4$ and to solvate H_2WO_4.[31−33] We have screened solvometallurgical solutions of 2 mol L^{-1} HCl_{aq} in ethylene glycol, poly(ethylene glycol) 200 (PEG-200), acetonitrile, and Aliquat 336 for the dissolution of synthetic $CaWO_4$ at 80 °C. Those solvents, both polar and apolar, were able to dilute the HCl and were stable at the tested reaction temperatures. The total water content in these solvometallurgical solutions was about 10.5 vol %. No tungsten precipitation occurred in ethylene glycol or in PEG-200, although it did happen in the acetonitrile and Aliquat 336 solutions, even at a low water content (see Figure S1). Similarly, H_2WO_4 also precipitated from ethylene glycol and PEG-200 solutions as the HCl_{aq} content was increased from 3 to 6 mol L^{-1} (Figure S2) because of the higher water content introduced with HCl_{aq}. Dissolution of $CaWO_4$ in 2 mol L^{-1} of HCl_{aq} in water was studied for comparison and the formation of yellow, solid H_2WO_4 was observed as well (Figures S1 and S2). The screening tests revealed that at 2 mol L^{-1} HCl_{aq} (water content of about 10.5 vol %), ethylene glycol and PEG-200 stabilize the dissolved tungsten in solution. However, the PEG-200 solution was discarded because of its higher viscosity, which would affect the further liquid−liquid extraction steps.

Characterization and Solvoleaching of Tungsten Ores. Two $CaWO_4$ ore samples 55-W and 3-W were digested by mineral acids in a microwave reactor, and the elemental composition was determined via ICP-OES analysis (Table 2).

Table 2. Elemental Composition of the Solid Samples 55-W (55.0 wt % W) and 3-W (3.5 wt % W) determined by ICP-OES

wt % metal	55-W	RSD%	3-W	RSD%
W	54.9	1.83	3.3	0.50
Al	n.d.	0.84	4.8	1.87
As	1.9	1.32	1.5	4.09
Ca	16.8	0.46	2.1	0.98
Fe	4.8	0.84	4.7	1.47
K	n.d.		2.8	1.79
Mn	0.4	0.19	0.2	2.72
Na	n.d.		1.3	2.21
P	1.9	0.08	0.6	2.77
S	n.d.		2.6	3.00
Ti	1.4	0.04	0.2	2.36

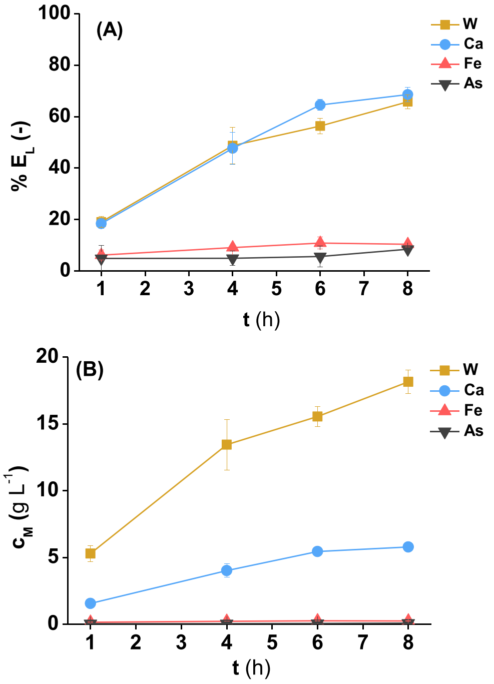

Figure 1. (A) Leaching efficiency, $\%E_L$, and (B) metal concentration, c_M (g L^{-1}), as a function of leaching time, t (h), for the 55-W sample. Working conditions: lixiviant: 2 mol L^{-1} HCl_{aq}/EG; L−S ratio = 20 mL g^{-1}, T = 60 °C, and r = 1000 rpm. See Table 2 for 55-W composition.

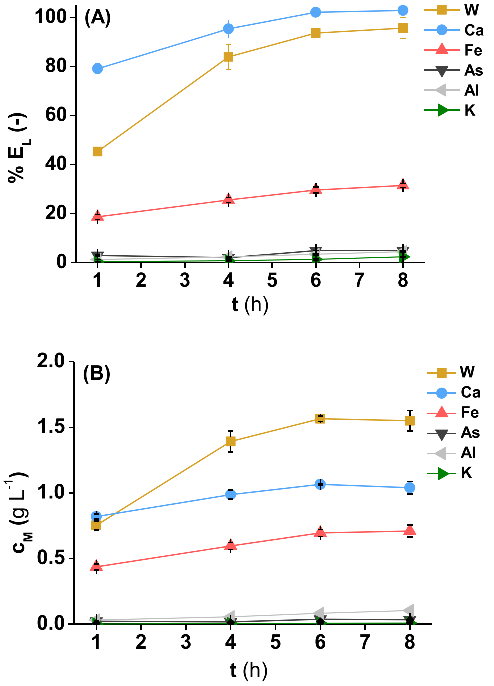

Figure 2. (A) Leaching efficiency, $\%E_L$, and (B) metal concentration, c_M (g L^{-1}), as a function of the leaching time, t (h), for the 3-W sample. Working conditions: lixiviant: 2 mol L^{-} HCl_{aq}/EG; L−S ratio = 20 mL g^{-1}, T = 60 °C, and r = 1000 rpm. See Table 2 for 3-W composition.

$CaWO_4$ dissolved completely in 2 mol L^{-1} HCl_{aq}-EG within 1 h at 60 °C and in excess of 3 h at 40 °C. Given this considerable difference in dissolution time, the leaching of 55-W and 3-W solids was carried out only at 60 °C. An aliquot of 2.0 mL of 2 mol L^{-1} HCl_{aq}-EG was used to leach, in triplicate, 0.1 g of 55-W or 3-W solid at 60 °C and 1000 rpm for 1, 4, 6, and 8 h. The leaching efficiency, $\%E_L$, and the leachate composition, c_M (g L^{-1}), are depicted in Figures 1 and 2 for, respectively, 55-W and 3-W. After 8 h, ≥95.0% tungsten from the 3-W sample was leached with a final concentration of 1.6 g L^{-1}, whereas, given the different composition (cf. Table 2) of the 55-W leachate, the latter had a higher tungsten content (18.0 g L^{-1}) although the leaching efficiency was lower (67.0%). In both cases, the main impurity was calcium with contents of ca. 1.1 and 5.8 g L^{-1} in the 3-W and 55-W leachates, respectively. The former also contained iron(III) at a significant concentration (0.7 g L^{-1}). The calcium dissolved was higher than that corresponding solely to the $CaWO_4$ dissolution since calcium is also present, in both ore samples, in other minerals such as apatite and calcite.

The shelf-life stability of the 2.0 mol L^{-1} HCl_{aq}/EG solution stored in the fridge at 2.0 °C was monitored via ^1H NMR analysis with a high-field (600 MHz) spectrometer on the as-prepared solution and after 1, 2, and 4 weeks: no decomposition products were detected, and fridge storage was considered safe (Figures S3−S6). However, a trace-level formation of 2-chloroethanol or dichloroethane could happen, following eqs 6 and 7; this was investigated on blanks of water-lean HCl_{aq} in ethylene glycol, stirred for 8 h at 40, 60, and 80 °C. The 600 MHz ^1H NMR spectra showed that 2-chloroethanol only formed at 80 °C (at about $\delta = 3.55$, (m, CH_2)), whereas dichloroethane did not form at any temperature (Figures S7−S9).

$$HOCH_2CH_2OH + HCl \rightarrow HOCH_2CH_2Cl + H_2O \quad (6)$$

$$HOCH_2CH_2Cl + HCl \rightarrow ClCH_2CH_2Cl + H_2O \quad (7)$$

Additionally, blanks of 2 mol L^{-1} HCl_{aq} in ethylene glycol were stirred for 8 and 24 h at 40 and 60 °C and analyzed by GC/MS. Dichloroethane was not detected, whereas traces of 2-chloroethanol were detected (see Table S1). The disagreement between the results from ^1H NMR and GC/MS analyses is explained by the higher detection limit (∼5%) of the ^1H NMR. For further study, it can be therefore recommended to consider different process conditions to prevent the formation of undesired products.

Nonaqueous Solvent Extraction and Purification of Tungsten. Further processing steps were necessary to separate the tungsten from metal impurities in the leachate. NASX was used for the purification of the tungsten. Screening tests were carried out on a synthetic solution, which was prepared by adding a known amount of $CaWO_4$, $CaCl_2$, $AlCl_3$, and $FeCl_3$ in 2 mol L^{-1} HCl_{aq} in ethylene glycol. Solvating (neutral) extractants (i.e., TBP and Cyanex 923) and basic extractants (i.e., TOA and Aliquat 336) were diluted in Shell GTL Solvent GS190, and with 10 vol % 1-decanol as a phase modifier, and they were used as the less polar (LP) phase. The effect of adding $CaCl_2$ to the MP phase as a salting-out agent was investigated as well (Figure 3).

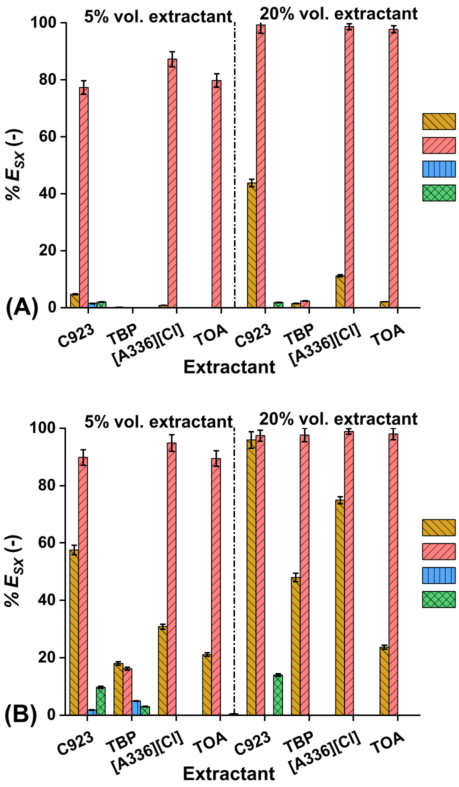

Figure 3. (A) Solvent screening for the NASX of tungsten without addition of $CaCl_2$ and (B) with $CaCl_2$ from a synthetic leachate (1.92 g L^{-1} tungsten, 1.40 g L^{-1} iron, 1.11 g L^{-1} calcium, and 1.34 g L^{-1} aluminum in 2 mol L^{-1} HCl_{aq}/EG). Working conditions: [$CaCl_2$] = 2 mol L^{-1}; diluent = Shell GS190; phase modifier = 10 vol % 1-decanol; MP/LP ratio = 1/1; t = 1 h; r = 2000 rpm; T = room temperature.

Good phase separation was achieved for all of the solvents tested as the LP phase due to the presence of the phase modifier, 1-decanol. Appreciable tungsten extraction, $\%E_{SX} \geq 60.0$, was achieved only in 20 vol.% Aliquat 336 or Cyanex 923 both with 2 mol L^{-1} $CaCl_2$. The majority of iron(III) was co-extracted by all extractants except TBP. Other impurities like Ca(II) and Al(III) were poorly extracted, yielding a first mechanism of process selectivity. Moreover, the addition of $CaCl_2$ enhanced the extraction of iron(III) even by TBP and, most importantly, the extraction of tungsten by all LP solvents. Scrubbing of iron(III) was a critical step for tungsten purification. Table 3 shows the percentage scrubbing of iron(III) using individual scrubbing agent solutions (i.e., water, 0.5 mol L^{-1} HCl and 0.25 mol L^{-1} H_2SO_4).

Iron(III) could be efficiently scrubbed with water and with 0.25 mol L^{-1} H_2SO_4 in one step from the loaded Aliquat 336 but not from the loaded Cyanex 923. In addition, the quantitative scrubbing of iron(III) from loaded Aliquat 336 is possible using water at O/A = 2/1 in a single contact. As for the other impurities, aluminum and calcium were not extracted with Aliquat 336 and were, hence, not scrubbed. In the case of the Cyanex 923 solvent, aluminum was scrubbed with any of the investigated scrubbing agents. However, a poor phase separation was observed during the scrubbing of impurities from loaded Cyanex 923. For further studies, water was preferred over H_2SO_4 because it is obviously a more sustainable scrubbing agent. Regarding the tungsten stripping from the loaded solvents, solutions of 1.0 mol L^{-1} NH_3, 1.0 mol L^{-1} NH_4Cl, and mixtures of 1.0 mol L^{-1} NH_3 with 1.0 mol L^{-1} NH_4Cl were evaluated (Figure 4).

Table 3. Scrubbing Percentage, %SB, of Metals in Water, 0.5 mol L^{-1} HCl, and 0.25 mol L^{-1} H_2SO_4 from the Loaded Aliquat 336 and Cyanex 923[a,b]

		%SB		
loaded organic	elements	water	0.5 mol L^{-1} HCl	0.25 mol L^{-1} H_2SO_4
Aliquat 336	Fe	82.0	41.0	90.0
	Al	<1	<1	<1
	Ca	<1	<1	<1
Cyanex 923	Fe	63.0	30.0	78.0
	Al	100.0	97.0	99.0
	Ca	<1	<1	<1

[a] Working conditions: O/A ratio = 1/1; t = 1 h; r = 2000 rpm; t = room temperature. [b] Tungsten scrubbing was 0% in all cases.

As for the loaded Cyanex 923, also NH_3 could recover the tungsten, but with a poor phase separation, whereas, as for the loaded Aliquat 336, all stripping agents showed good phase separation with the loaded solvent, but only the binary mixture of NH_3 and NH_4Cl could strip the tungsten. The latter findings suggest an important role of both NH_3 and NH_4Cl during the tungsten stripping. In fact, NH_3 guarantees the proper equilibrium pH >9 to convert the extracted tungsten species to ammonium tungstate, $(NH_4)_2WO_4$; meanwhile,

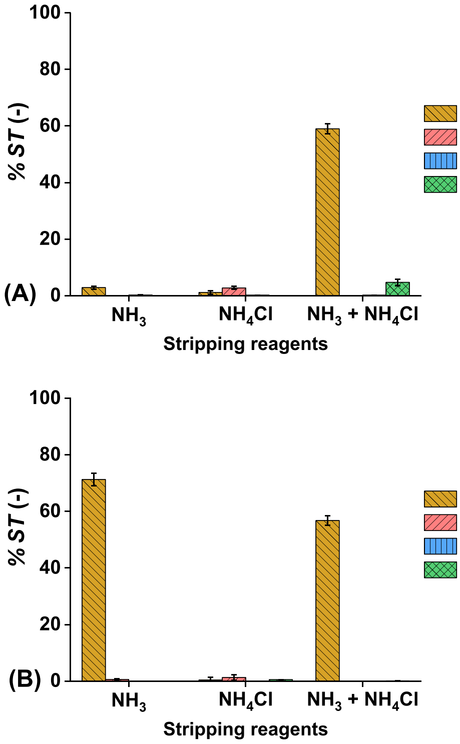

Figure 4. Stripping percentage, %ST, of metals in 1.0 mol L^{-1} NH_3, 1.0 mol L^{-1} NH_4Cl, or mixture of 1.0 mol L^{-1} NH_3 and 1.0 NH_4Cl from (A) the loaded Aliquat 336 and (B) Cyanex 923 in GS190 with 10 vol % 1-decanol. Working conditions: MP/LP ratio = 1/1; t = 1 h; r = 2000 rpm; T = room temperature.

NH_4Cl provides the chloride as counterions for the Aliquat 336 regeneration.

As a result of the NASX screening tests from model solutions, Aliquat 336 was chosen as an extractant over Cyanex 923 because of the more efficient iron(III) scrubbing and the good stripping efficiency using a buffer solution of NH_3/NH_4Cl. Subsequently, the NASX process to recover tungsten from a 2 mol L^{-1} HCl_{aq}/EG real leachate was optimized for the Aliquat 336 solvent.[34−39] The effects of several diluents and the addition of a phase modifier are shown in Figure 5.

The nature of the diluent has a negligible effect on the $\%E_{SX}$ of W and Fe, while it was observed that the presence of a phase modifier suppresses the extraction of impurities such as calcium and aluminum. The aromatic A-grade solvents provided a better phase separation. However, the aliphatic diluent, for example, Shell GTL Solvent GS190 was selected for further study because it has a lower environmental impact thanks to its high purity, low aromatic, low naphthenic contents, and low odor level. Once the diluent was selected, the concentration of extractant was optimized (Figure 6) and the stoichiometric ratio of extractant/metal for the NASX of tungsten via Aliquat 336 was estimated via slope analysis (Figure 7).

The $\%E_{SX}$ of tungsten progressively increased, in a single stage, from 38.0 to 93.0 when the Aliquat 336 concentration increased from 0.1 to 0.8 mol L^{-1} (Figure 6). Meanwhile, a slight increase in extraction efficiency from 93.0 to 95.0 was achieved by varying the Aliquat 336 concentration in the range of 0.8−1.0 mol L^{-1}. It should be noted that the higher the extractant concentration, the higher the increase of the viscosity of LP. To avoid problems in phase separation and mass transfer, a concentration ranging between 0.47 and 0.71 mol L^{-1} Aliquat 336 (corresponding to 20 and 30 vol %, respectively) was chosen as optimum to ensure a good $\%E_{SX}$ of tungsten and a feasible solvent viscosity. Iron(III) was, unfortunately, efficiently extracted at any concentration of Aliquat 336, confirming the high affinity of this extractant for iron(III) and for other light transition metals in general.[40−43]

The mechanism of NASX entails an interesting research question and, so far, no conclusive answer has been reported. The composition of the extracted species was determined using the slope method. As shown in Figure 7, the plot of log D vs log[Aliquat 336] shows a straight line with a slope of 1.3,

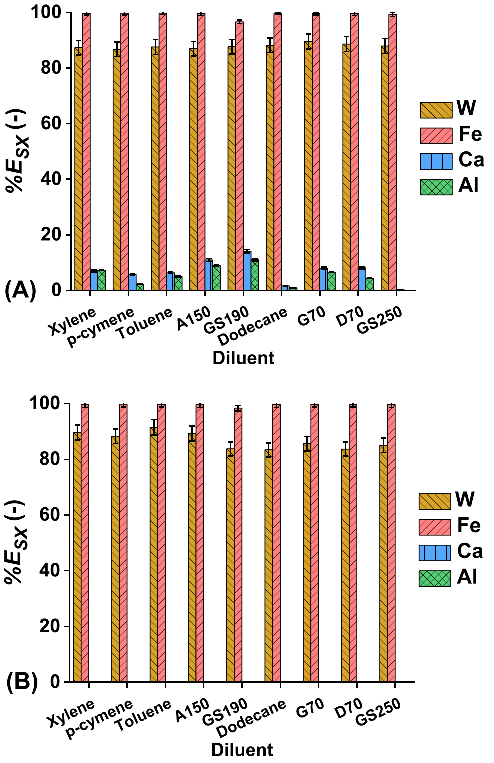

Figure 5. (A) Effect of aromatic and aliphatic diluents without phase modifier and (B) of addition of 10 vol % 1-decanol on the NASX in Aliquat 336 of tungsten, iron, calcium, and aluminum from a 2 mol L^{-1} HCl_{aq}/EG leachate with 2 mol L^{-1} $CaCl_2$. Working conditions: MP/LP ratio = 1/1; t = 1 h; r = 2000 rpm; T = room temperature.

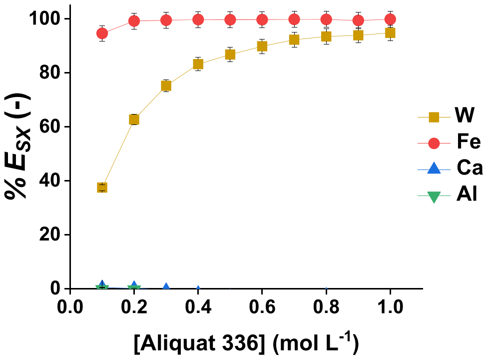

Figure 6. Effect of Aliquat 336 concentration in GS190 with 10 vol % 1-decanol on the NASX of on the NASX of tungsten, iron, calcium, and aluminum from a 2 mol L^{-1} HCl_{aq}/EG leachate with 2 mol L^{-1} $CaCl_2$. Working conditions: MP/LP ratio = 1/1; t = 1 h; r = 2000 rpm; T = room temperature.

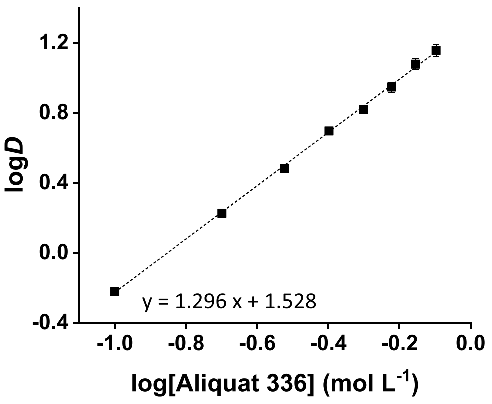

Figure 7. Log D vs log[A336] for the NASX of tungsten in Aliquat 336 diluted in GS190 with 10 vol % 1-decanol from a 2 mol L HCl_{aq}/EG leachate with 2 mol L^{-1} $CaCl_2$. Working conditions: MP/LP ratio = 1/1; t = 1 h; r = 2000 rpm; T = room temperature.

suggesting that at least one mole of Aliquat 336 is needed to extract and coordinate one mole of the extracted species in the LP phase. The determined stoichiometric ratio tungsten/Aliquat 336 for the NASX mechanism matches well with the one reported in traditional solvent extraction of tungsten via anion exchange.[34,44−46] In aqueous solutions, tungsten tends to form isopolyanions and it is, in fact, extracted as isopolytungstate.[45,46] No evidence exists that the same isopolytungstate species form in EG media, and the NASX mechanism can be assumed as reported in eq 8 for a generic tungstate anion. Equation 8 was postulated on the assumption that the linear behavior of the curve in Figure 7 likely implies that the tungsten species does not change upon extraction, or at least the number of tungsten centers per extracted species does not. The number of theoretical stages for NASX of tungsten was estimated by constructing McCabe−Thiele diagrams for concentrations of 20 vol.% (Figure 8A) and 30 vol.% (Figure 8B) Aliquat 336 in GS190.

$$H_xW_yO_z^{n-} + n\overline{[R_3R'N]Cl} \rightarrow \overline{[R_3R'N]_n[H_xW_yO_z]} + nCl^- \qquad (8)$$

Increasing the Aliquat 336 concentration from 20 to 30 vol.% only has an effect on the number of theoretical stages at an LP/MP phase ratio of 1/2, i.e., when attempting to concentrate the tungsten through the NASX step, but not at the LP/MP ratio of 1/1. Under similar conditions, the use of 30 vol.% Aliquat 336 required fewer stages (4 instead of 5) than those required with 20 vol.% Aliquat 336. Taking into account the extraction efficiency, the number of theoretical countercurrent stages, the solvent losses per stage, and the chemical consumptions, 20 vol.% Aliquat was considered as the optimum concentration at an LP/MP ratio of 1/1. Subsequently, a batch-wise simulation of extraction with three countercurrent stages confirmed that tungsten and iron(III) were quantitatively extracted from the MP feed solution, leaving trace amounts of 0.03 g L^{-1} tungsten and 0.001 g L^{-1} iron in the MP raffinate phase. As for the scrubbing, 90% iron(III) is removed by contacting the loaded Aliquat 336 solvent with water at an O/A phase ratio of 1/1. Complete back-extraction of iron(III) can be achieved using either two stages (O/A = 1/1) or single stage (O/A = 1/2) for 1 h, at room temperature, and 2000 rpm. Note that although the reaction rates for NASX and scrubbing were rather fast (within 5 min), all experiments were performed for 1 h to ensure that full equilibrium was achieved.

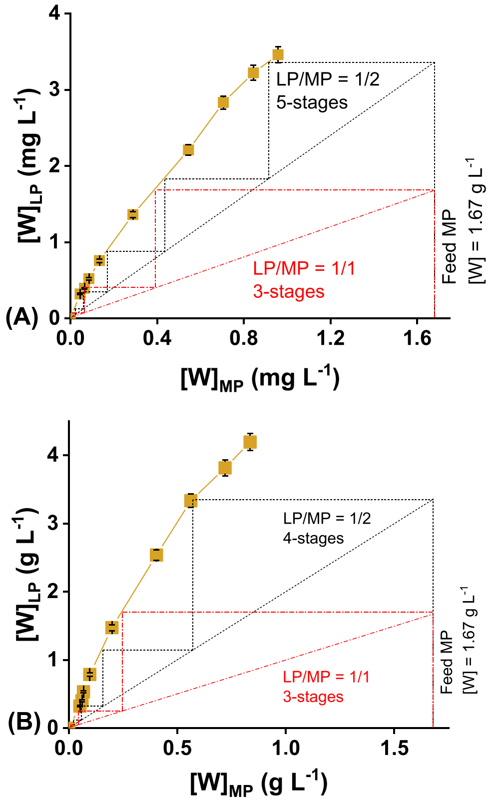

Figure 8. McCabe−Thiele diagrams for the NASX of tungsten in (A) 20 vol % and (B) 30 vol % Aliquat 336 in GS190 with 10 vol % 1-decanol from a 2 mol L^{-1} HCl_{aq}/EG leachate with 2 mol L^{-1} $CaCl_2$. Working conditions: t = 1 h; r = 2000 rpm; T = room temperature.

Finally, stripping of tungsten was optimized. It has been already shown (Figure 4) that mixtures of NH_3−NH_4Cl efficiently strip tungsten from the loaded Aliquat 336 solvent. In addition, the concentrations of both NH_3 and NH_4Cl were separately optimized, keeping the concentration of one component at 1.0 mol L^{-1} while varying the other. The results are shown in Figure 9.

A plateau is reached for both NH_3 and NH_4Cl and at the same concentration of 1.0 mol L^{-1}, indicating that tungsten is efficiently stripped in solutions of both NH_3 and NH_4Cl. In the case of tertiary amines, such as TOA, aqueous NH_3 is enough to recover tungsten because the conjugate acid of the tertiary amine will deprotonate at a high pH, inhibiting further extraction. Charge neutrality is preserved by co-stripping of these protons. Quaternary ammonium compounds, such as Aliquat 336, require the presence of chloride anions, which are efficiently exchanged for the highly hydrated tungstate dianions, hence preserving the charge neutrality of both phases upon stripping by anion exchange. We targeted to obtain $(NH_4)_2WO_4$, which can subsequently be converted to APT by evaporation and crystallization. The stripping mechanism was first described by Gaur and is given in eq 9.[46] This equation refers, similarly to eq 8, to a generic polytungstate $H_xW_yO_z^{n-}$ as the extracted species; moreover, the equation does not include the stripping agents NH_3 and NH_4Cl but the OH^- and Cl^- ions, provided by, respectively, NH_3 and NH_4Cl. NH_3 works to provide OH ions, which decompose the polytungstate species.

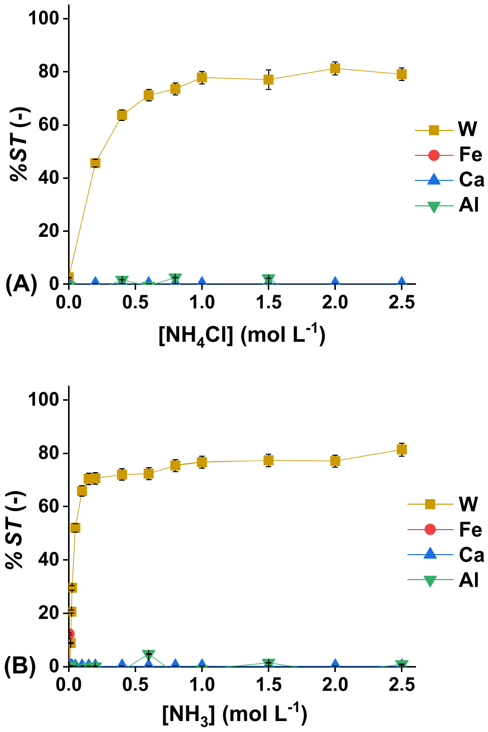

Figure 9. (A) Optimization of NH_4Cl concentration ([NH_3] = 1 mol L^{-1}) and (B) NH_3 concentration ([NH_4Cl] = 1 mol L^{-1}) for the selective stripping of tungsten from loaded 20 vol % Aliquat 336 in GS190 with 10 vol % 1-decanol. Working conditions: O/A ratio = 1/1; *t* = 1 h; *r* = 2000 rpm; *T* = room temperature.

Once the stripping solution was defined as 1.0 mol L^{-1} NH_3 with 1.0 mol L^{-1} NH_4Cl, McCabe–Thiele diagrams systems were constructed to calculate the theoretical number of stages at two different O/A ratios, 1/1 and 3/1 (Figure 10).

$$m\overline{[R_3R'N]_n[H_xW_yO_z]}_{org} + qOH^-_{aq} + (m\cdot n)Cl^-_{aq} \rightarrow WO^{2-}_{4\ aq} + rH_2O + (m\cdot n)\overline{[R_3R'N][Cl]}_{org} \qquad (9)$$

The diagrams showed an intersection of the stripping isotherm with the operating lines at both O/A ratios 1/1 and 3/1. It means that it is challenging to get less than about 0.30 g L^{-1} tungsten in the organic phase using a mixture of 1.0 mol L^{-1} NH_3 and 1.0 mol L^{-1} NH_4Cl in a countercurrent system. Similarly to the NASX step, a countercurrent process was simulated in batch at O/A = 3/1, confirming that, after three stages, the tungsten concentration is 0.33 g L^{-1} in the loaded solvent and 2.71 g L^{-1} in the NH_3–NH_4Cl stripped phase. However, quantitative stripping will be possible if operating in cross-current mode. Furthermore, the stripping efficiency of tungsten can be enhanced by increasing either the concentration of NH_3/NH_4Cl or the temperature up to 60 °C (Figure S10).

In the light of the obtained results, a conceptual flowsheet has been suggested for the solvometallurgical recovery of tungsten from $CaWO_4$ contained in high-grade (ca. 55.0 wt % W) and medium-grade (ca. 3.3 wt % W) ores (Figure 11). The overall tungsten recovery is between 55 and 60% if operating the NASX in a single-stage process, but it will increase when running the process in multistages in mixer-settlers. One drawback is the potential formation of trace levels of 2-chloroethanol, in the leaching stage. However, this problem can be avoided by further optimizing process conditions, such as a better mixing of the solid and the lixiviant to enhance the mass transfer and reduce the reaction time.

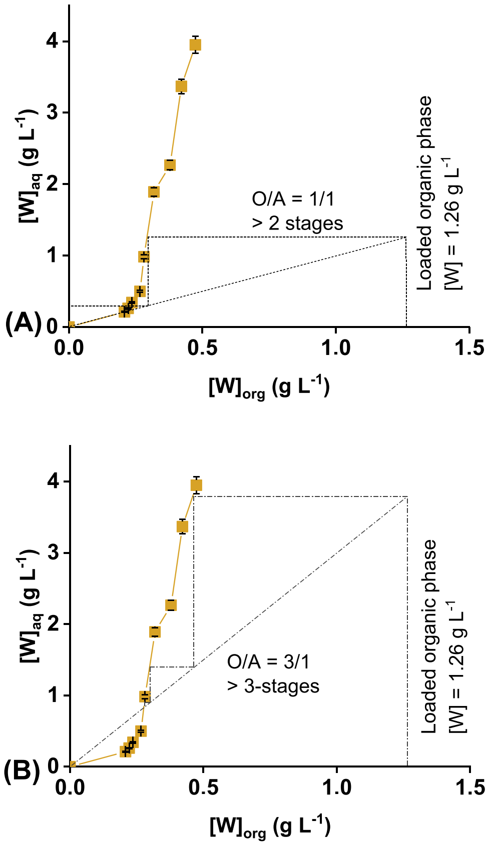

Figure 10. (A) McCabe–Thiele diagrams for the stripping of tungsten in a mixture of 1.0 mol L^{-1} NH_3 and 1.0 mol L^{-1} NH_4Cl from 20 vol % Aliquat 336 in GS190 with 10 vol % 1-decanol at O/A ratio = 1/1 and (B) at O/A ratio = 3/1. Other working conditions: *t* = 1 h; *r* = 2000 rpm; *T* = room temperature.

■ CONCLUSIONS

In the current paper, we developed a conceptual flowsheet that comprises solvoleaching of tungsten from scheelite ($CaWO_4$) in 2 mol L^{-1} HCl_{aq} in ethylene glycol, and nonaqueous solvent extraction of tungsten from the HCl–ethylene glycol leachate using 20 vol % Aliquat 336 in the aliphatic diluent Shell GTL Solvent GS190 with 10 vol % 1-decanol. Thereafter, tungsten is recovered as ammonium tungstate in solutions of 1.0 mol L^{-1} $NH_{3,aq}$ with 1.0 mol L^{-1} NH_4Cl. Compared to the industrial state-of-the-art process—in which recovery of tungsten from $CaWO_4$ is carried out in $NaOH/Na_2CO_3$ solutions in an autoclave at temperatures around 190–225 °C and large volumes of high-salinity acidic wastewater are generated (up to 25 tons per ton of produced APT)—the main advantages of the present conceptual flowsheet are: (i) ethylene glycol avoids the precipitation of tungsten even in the presence of 2 mol L^{-1} HCl_{aq}; (ii) consequently, no further steps of re-dissolution are required; (iii) selective NASX and scrubbing steps produce an organic phase with only tungsten present; and (iv) tungsten can be recovered from the loaded Aliquat 336 phase as ammonium tungstate, from which tungsten is commonly crystallized and purified as APT. Other advantages compared to the traditional industrial process are: (v) milder leaching conditions, i.e., no pressure

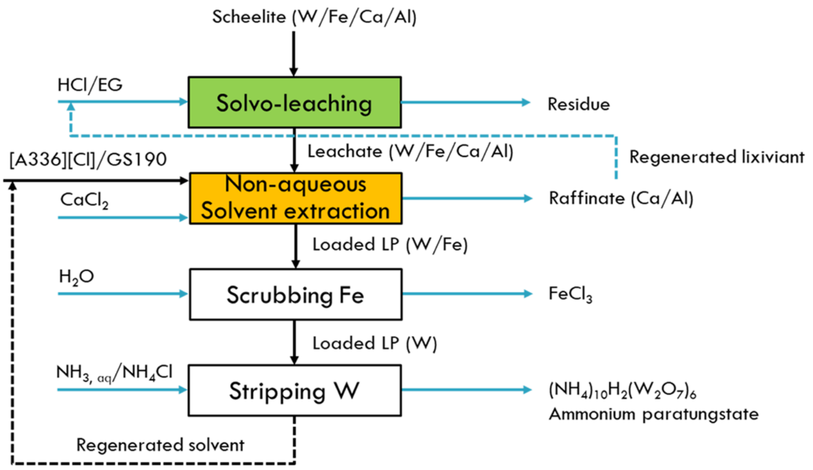

Figure 11. Conceptual flowsheet for the solvometallurgical recovery of tungsten from $CaWO_4$ in high-grade (W = 55 wt %) and medium-grade (W = 3.3 wt %) ores.

above atmospheric pressure and no temperatures above 100 °C, and (vi) no generation of high-salinity wastewater.

The nonaqueous solvent extraction system selectively extracts tungsten, leaving calcium in the raffinate. This is particularly convenient for streams like the scheelite leachates of this work, where calcium was the main impurity. In the case of streams such as the leachate of medium-grade scheelite, the other main impurity is iron and can be removed by scrubbing with water. The production of tungsten(VI) oxide or tungsten metal from the obtained ammonium tungstate has not been investigated since they can be carried out according to established industrial procedures. One drawback that needs to be adequately addressed, prior to further upscaling of this process, is the potential formation of trace levels of 2-chloroethanol in the solvoleaching step. It is hypothesized that this problem can be circumvented by further optimizing process conditions, such as the mixing to enhance the solid−liquid mass transfer and reduce the reaction time.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.1c03872.

> Photos of the screening tests with 2−6 mol L^{-1} HCl_{aq}, displaying the formation of yellow H_2WO_4 precipitate (Figures S1 and S2); ^{1}H NMR spectra of the 2 mol L^{-1} HCl_{aq}/EG solutions recorded in DMSO-d_6 with a Bruker Avance II+ 600 MHz (Figures S3−S9); and plot over the increased tungsten stripping efficiency at a higher NH_3/NH_4Cl concentration or a higher temperature (Figure S10). (PDF)

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Author Contributions

§M.O. and V.T.N. contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

55-W	55 wt % W sample
3-W	3.3 wt % W sample
APT	ammonium paratungstate
HCl_{aq}/EG	37.0 wt % aqueous HCl in ethylene glycol
LP	less polar phase
MP	more polar phase
NASX	nonaqueous solvent extraction
O/A	organic/aqueous ratio
WC	tungsten carbide

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