Nota Técnica

PROCESSING OF SPENT NiW/Al2O3 CATALYSTS

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Spent oxidized (500 °C, 5 h) commercial NiW/Al2O3 catalysts were processed using two different routes: a) fusion with NaOH (650 °C, 1 h), the roasted mass was leached in water; b) leaching with HCl or H_2SO_4 (70 °C, 1-3 h). HCl was the best leachant. In both routes, soluble tungsten was extracted at pH 1 with Alamine 336 (10 vol.% in kerosene) and stripped with 2 mol L^{-1} NH_4OH (25 °C, one stage, aqueous/organic ratio = 1 v/v). Tungsten was isolated as ammonium paratungstate at very high yield (> 97.5%). The elements were better separated using the acidic route.

Keywords: spent catalysts; metal recovery; Ni-W catalyst.

INTRODUCTION

At present, environmental directives impose severe restrictions concerning gas (NO_x, SO_x etc.) and particle emissions from refineries and fuels. More specifically, these directives require improvement of petroleum refining (higher impurities removal). Sulfur removal (hydro-desulfurization) is one of the reactions that take place during hydro-treatment (HDT). The reaction is essential to obtain more acceptable fuels for the environment.[1] The most familiar HDT catalysts are CoMo, NiMo and NiW supported on alumina (Al_2O_3), normally modified by additives that improve activity towards some HDT reactions (such as hydrogenation, cracking) or thermal resistance during its lifetime.[1-5]

The increasing severity of environmental directives has prompted the development of a new generation of more efficient catalysts and the proposal of less drastic HDT conditions concerning energy and hydrogen consumption.[2-4] The amount of spent non-reusable HDT catalysts has increased markedly in recent years[1] due to a steady increase in the processing of heavier feedstocks in the petroleum refining industries.

Spent refinery catalyst recycling is rapidly evolving due to the rapid evolution of environmental regulations in many countries and also the constant fluctuation of metal prices.[1] In view of the environ-mental and economic benefits, increasing attention has been paid to the development of technologies to recover valuable metals from these secondary sources.

There are significantly fewer studies on processing spent NiW catalysts than spent CoMo and NiMo catalysts. It appears that the methods used for the recovery of molybdenum can also be applied to tungsten recovery.[1] Both elements belong to group 6 of the Periodic Table, and their chemistry is very similar. Tungsten can be recovered from NiW catalysts by chlorination (typically at 450 °C for 30 min) as volatile WO_2Cl_2, which is hydrolyzed to WO_3.[6] Bioleaching of NiW catalysts has previously been studied in recent literature.[7,8]

Hydrometallurgical processing of concentrates from tungsten ores with strong acids (HCl, H_2SO_4) tends to keep it in solid residue.[9] Hydrometallurgical routes using aqueous NaOH or Na_2CO_3 and fusion with NaOH or Na_2CO_3 are also of practical interest.[10,11] The composition of spent NiW catalysts is very different and much simpler

than tungsten concentrates. Except for phosphorus, which is normally found as a support additive, the other usual interfering elements in tungsten recovery (Si, Mo, As) are absent in HDT catalysts.[1] However, the amount of aluminum is much higher (as aluminum oxide is the catalyst support), thus posing a challenge for tungsten recovery from these spent catalysts.

Recovery of tungsten via liquid-liquid extraction (LLE) in acidic medium has been gaining importance in recent literature. Aliphatic amines have been widely employed as extractants.[12,13] In general, the efficiency of amine decreases in the order quaternary > tertiary > secondary > primary under the same experimental conditions. Tertiary amines are the most cited in the literature.[14,15] Stripping is normally performed with NH_4OH. Akin to molybdenum,[16] tungsten recovery via LLE presents a critical challenge – its separation from phosphorus – because phosphotungstate ions ($PW_{12}O_{40}^{3-}$) are highly stable in acidic medium.[17] They are extracted by amines and also stripped by NH_4OH.[14,18-20] Tungsten can be separated from phosphorus in alkaline medium[9,13] via precipitation of magnesium phosphates in the presence of NH_4OH.

Taking into account that many commercial processes for spent NiMo/Al2O3 samples employ alkaline fusion and leaching with strong acids,[1] this work presents a route for processing spent NiW catalysts using these methods. Recovery of components of the active phase (nickel, tungsten) and of the support (aluminum) was performed by a combination of several separation techniques.

EXPERIMENTAL

Catalysts

Spent commercial NiW/Al2O3 catalysts were employed (5 mm extruded cylinder, 1.2 mm diameter). Chemical analyses are presented in Table 1. The catalysts were employed for at least 4 years in diesel hydrotreaters in a Brazilian refinery. Samples were milled to particle diameters < 0.106 mm and dried at 110 °C for 2 h.

Oxidation of samples

Samples were placed in ceramic crucibles. The height of the catalyst layer was set at 5 mm. The catalyst was placed in a furnace
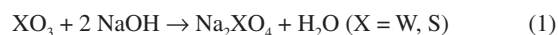
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Table 1. Chemical analysis (wt.%, dry basis) of the NiW/Al_2O_3 catalysts

Sample	Ni	W	Fe	Al	P	S	C	Si
Oxidized catalyst	2.7	10.2	0.2	39.3	2.2	1.1	Absent	Absent
Spent catalyst	2.4	9.2	0.3	32.0	2.0	3.7	10.5	<0.1

at room temperature and heated at 500 °C (10 °C min⁻¹) for 5 h, according to previous studies in our laboratory.[21,22] The roasted mass was cooled down in the furnace and transferred to a dessicator before running the experiments.
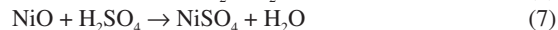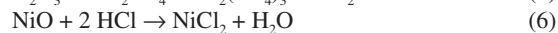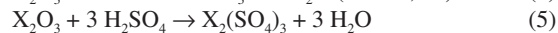
Fusion process

Fusion was carried out using sodium hydroxide. The stoichiometric amount of the reactant was calculated according to the following reactions:

$$XO_3 + 2\ NaOH \rightarrow Na_2XO_4 + H_2O\ (X = W, S) \qquad (1)$$
$$Al_2O_3 + 2\ NaOH \rightarrow 2\ NaAlO_2 + H_2O \qquad (2)$$
$$P_2O_5 + 6\ NaOH \rightarrow 2\ Na_3PO_4 + 3H_2O \qquad (3)$$

Based on data from Table 1, the theoretical NaOH/catalyst mass ratio is approximately 0.75:1. A 10 wt.% excess of NaOH was employed. Experiments were carried out using 10 g of sample in nickel crucibles. Fusion was performed at 650 °C in a furnace for 60 min.[23] The roasted mass was cooled down in the furnace and leached with distilled water (10 mL g⁻¹ solid, 60 °C, 200 rpm, 20 min). The insoluble matter was separated by filtration, washed with water (4 mL g⁻¹), dried at 150 °C for 2 h and weighed. The matter was then dissolved in HF + H_2SO_4 (1:2 v/v) at 60 °C for chemical analysis. The experiments were run in triplicate, and errors for each experiment were consistently below 4%.

Acidic leaching

6 mol L⁻¹ HCl and 6 mol L⁻¹ H_2SO_4 were used as leachants since they are the most cited in the literature.[1] The stoichiometric amount of these acids was calculated according to the following reactions:

$$X_2O_3 + 6\ HCl \rightarrow 2\ XCl_3 + 3\ H_2O\ (X = Al, Fe) \qquad (4)$$
$$X_2O_3 + 3\ H_2SO_4 \rightarrow X_2(SO_4)_3 + 3\ H_2O \qquad (5)$$
$$NiO + 2\ HCl \rightarrow NiCl_2 + H_2O \qquad (6)$$
$$NiO + H_2SO_4 \rightarrow NiSO_4 + H_2O \qquad (7)$$

WO_3 is insoluble in both leachants.[13,14] P_2O_5 reacts with water, and natural phosphates (for instance, monazite) are digested with hot strong mineral acids.[24] Based on data from Table 1, the theoretical HCl (H_2SO_4)/catalyst ratio is approximately 7.5 (3.75) mL g⁻¹. A 10 wt.% excess of the leachant was employed. Experiments were carried out using 10 g of sample in glass beakers. The experiments were run at 70 °C for 1-3 h. The insoluble matter was separated by filtration, washed with water (4 mL g⁻¹), dried at 150 °C for 2 h and weighed. The matter was then dissolved in HF + H_2SO_4 (1:2 v/v) at 60 °C for chemical analysis. The experiments were run in triplicate, and errors for each experiment were consistently below 4%.

Analytical methods

Metal concentrations were determined by atomic absorption spectrometry (Perkin Elmer AAS 3300). The following wavelengths were employed: tungsten, 255.1 nm; nickel, 231.1 nm; aluminum, 396.2 nm. The following detection limits were determined experimentally:

1 mg L⁻¹ (aluminum), 0.5 mg L⁻¹ (nickel and tungsten). Phosphate ions were determined by ion-chromatography (Dionex DX-100). Solids were dissolved in a mixture of 2 mol L⁻¹ HF + 2 mol L⁻¹ HNO_3 at 60 °C prior to the analysis. A LECO analyzer determined carbon and sulfur contents. Acidity of aqueous solutions was determined by potentiometry using an Ag/AgCl reference electrode (Orion 2AI3-JG). Phase identification of the insoluble matter in the leachates was performed by X-ray diffraction (XRD) analysis (Bruker-AXS D5005) by the continuous scanning method at 35 kV and 40 mA, using Co Kα as the radiation source.

RESULTS AND DISCUSSION

After oxidation, the volatile matter corresponds to around 15 wt.% of the spent catalyst. This value agrees with the amounts reported in the literature for spent HDT catalysts[1,8,25] (12-30 wt.%). The volatile matter is basically due to coke burning (CO_2, H_2O). Also, sulfur was oxidized and partially eliminated as SO_x.[21,22]

Alkaline fusion and acidic leaching

After fusion with NaOH, most tungsten and aluminum was leached with water, whereas phosphorous partially reacted with NaOH (Table 2). The average tungsten concentration in the leachate is 5 g L⁻¹, which falls within the range for LLE of the element with amines.[12,13] pH of the leachate is 11.9 ± 0.1, where tungsten is present as WO_4^{2-}.[14] Iron and nickel remained in the insoluble matter. XRD data indicate that this solid is a poorly crystalline material. Small peaks corresponding to $AlPO_4$ and $NiWO_4$ were identified. XRD of the oxidized spent catalyst only contains small peaks corresponding to γ-Al_2O_3 phase.

Table 2. Chemical composition of the insoluble residue and the leachate after fusion of NiW catalysts with NaOH (650 °C, 1 h), followed by leaching with water (60 °C, 200 rpm, 20 min, 10 mL g⁻¹ solid)
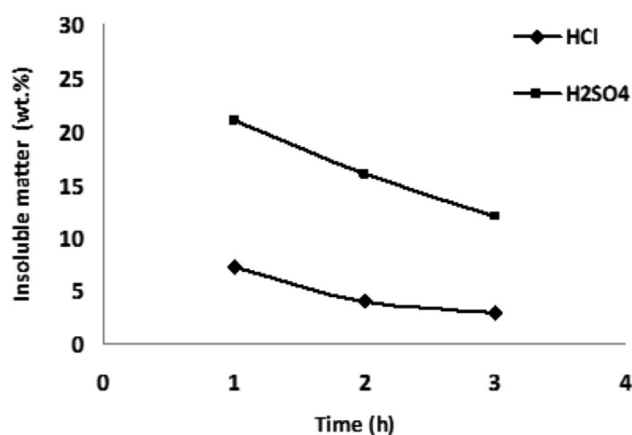
Element	Insoluble residue		Leachate	
	Relative amount (%)	Amount in the residue (%)	Relative amount (%)	Concentration (g L⁻¹)
Ni	~100	29.9	<0.1	-
W	1.5	1.7	98.5	5.0
Al	7.5	51.8	92.5	10.6
P	27	12.2	73	0.8
Fe	~100	1.8	<0.1	-
S	10	2.5	90	0.5

Data in Table 3 and Figure 1 show that the oxidized spent catalyst was almost completely dissolved in HCl after 3 h at 70 °C despite the insolubility of WO_3 in acids.[13,14] The insoluble fraction contains mainly phosphorus (Table 3). XRD data showed that this solid is amorphous. The presence of a considerable amount of soluble phosphorous may explain the solubilization of WO_3 in HCl according to the following reaction:

$$24\ WO_3 + 2\ H_3PO_4 \rightarrow 2\ H_3PW_{12}O_{40} \qquad (8)$$

Table 3. Chemical composition of the insoluble residue and the leachate after leaching NiW catalysts with HCl or H$_2$SO$_4$ (70 °C, 3 h)

Element	Insoluble residue				Leachate			
	Relative amount (%)		Amount in the residue (%)		Relative amount (%)		Concentration (g L^{-1})	
	HCl	H$_2$SO$_4$	HCl	H$_2$SO$_4$	HCl	H$_2$SO$_4$	HCl	H$_2$SO$_4$
Ni	<0.1	8	<0.1	3	~100	92	3.2	5.5
W	<0.1	5	<0.1	6	~100	95	11.9	21.5
Al	0.4	7	10	48	99.6	93	46	81
P	27	40	90	40	73	60	1.9	2.9
Fe	<0.1	10	<0.1	<0.1	~100	90	0.2	0.4
S	<0.1	5	<0.1	3	~100	95	1.3	2.3

Figure 1. *Amount on insoluble matter after acidic leaching of spent NiW catalysts*

Taking into account the composition of the oxidized spent catalyst (Table 1) the amount of phosphorus is much greater than that necessary to react with WO$_3$.

H$_2$SO$_4$ was a poorer leachant than HCl (Figure 1, Table 3). The amount of insoluble matter was higher, nickel and aluminum were partially leached and the amount of tungsten solubilized via reaction 8 was also lower. This result is the same as that found when a Brazilian tungsten concentrate was treated with these acids.[26] The difference between HCl and H$_2$SO$_4$ can be at least partially explained by the concentration of the latter (6 mol L^{-1}). In general, concentrated H$_2$SO$_4$ (> 9 mol L^{-1}) is used as the leachant for processing tungsten concentrates.[9]

Processing of leachate after fusion with NaOH

Figure 2 illustrates the overall scheme. The first step is of utmost important in order to separate tungsten from phosphorus. The pH of the leachate was adjusted from 11.9 to ~9 by adding 6 mol L^{-1} HCl, after which the leachate was heated to 70 °C. A mixture of 0.1 mol L^{-1} MgCl$_2$ + 5 mol L^{-1} NH$_4$OH was added dropwise under stirring (200 rpm) until no white precipitate is formed.[9] This solid was filtered. More than 99% of phosphorus precipitated as MgNH$_4$PO$_4$,[9,13] but aluminum (> 99.5%) also co-precipitated. No attempt was made to separate aluminum and phosphorus in this precipitate.

Tungsten was isolated by LLE. Alamine 336 (mixture of trioctyl and tridecylamine) was employed as the extractant (10 vol.% in kerosene). This presented very good results for tungsten recovery from Brazilian wolframite concentrates.[23] Experiments were performed at 25 °C, with an aqueous/organic phase ratio (A/O) = 1 (v/v). The equilibrium between phases was reached within around 5 min. The influence of pH (1-3) on tungsten extraction was studied by adding
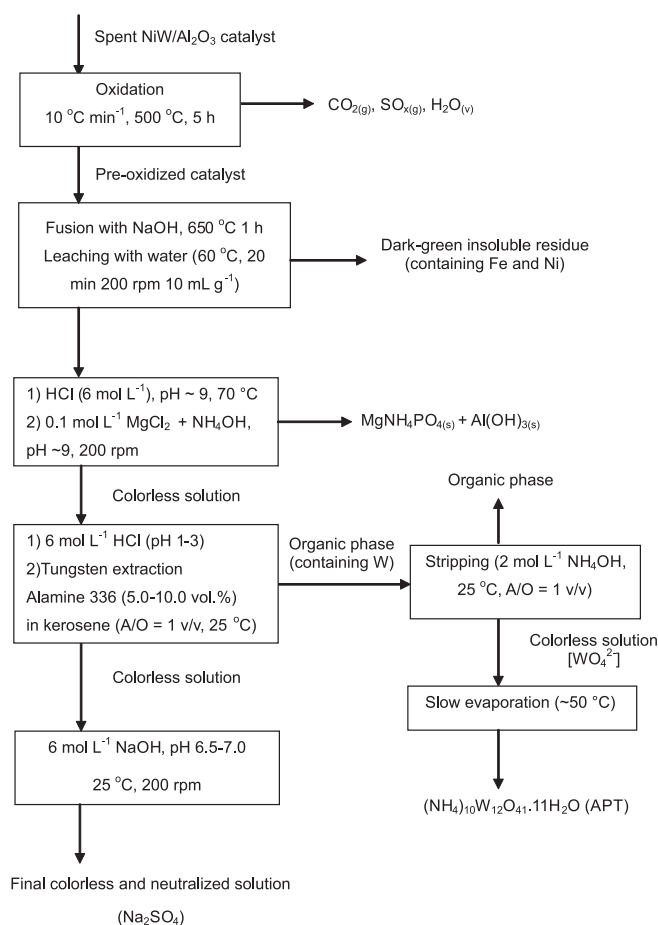
Figure 2. *General scheme for recovery of elements from spent NiW catalysts after oxidation, fusion with NaOH and leaching with water (A/O = aqueous/organic phase ratio)*

6 mol L^{-1} HCl to adjust the pH. According to Table 4, more than 99% of the element was extracted in one stage at pH 1. At pH 3, efficiency of the amine was greatly reduced.

Stripping (> 99.5%) was easily accomplished in one stage with 2 mol L^{-1} NH$_4$OH (25 °C, A/O = 1 v/v). The equilibrium between phases was reached within 5 min. Concentrations of over 4 mol L^{-1} led to emulsification (Table 4). The aqueous solution was slowly evaporated (~50 °C) in a fume hood, yielding crystals of ammonium paratungstate (APT), (NH$_4$)$_{10}$W$_{12}$O$_{41}$.11H$_2$O. According to Table 5, its purity grade is very good. Only traces of phosphorous were found. 97.5% of tungsten present in the oxidized spent catalyst was recovered as APT.

Table 4. Tungsten extraction*,** and stripping data**

Leachate	pH 1	pH 2	pH 3
Alkaline fusion	99.9%	56.0%	6.0%
Acidic leaching	99.5%	55.0%	5.0%
Stripping with NH_4OH	2 mol L^{-1}	4 mol L^{-1}	6 mol L^{-1}
Alkaline fusion	>99.9%	emulsification	emulsification
Acidic leaching	>99.9%	>99.9%	emulsification

*10 vol.% Alamine 336 in kerosene. **One stage, aqueous/organic ratio = 1 v/v, 25 °C.

Table 5. Chemical analysis of ammonium paratungstate

Element (as oxide)	wt.%	
	Alkaline fusion	Acidic leaching
WO_3*	85.59 ± 0.16	85.31 ± 0.15
P_2O_5	0.05 ± 0.02	0.10 ± 0.03
Al_2O_3	0.04 ± 0.01	0.02 ± 0.01

*Theoretical value for ammonium paratungstate: 85.86 wt.%.

The overall process of LLE and stripping of tungsten reported in this work agrees with literature data[15,27] for tungsten alloy scrap and tungsten concentrates[14,23] (which also contain phosphorus) in terms of yield and optimal experimental conditions.

The acidic solution after tungsten extraction is colorless. Neutralization with 2 mol L^{-1} H_2SO_4 formed a final colorless and neutralized solution.

Processing of acidic leachate

Figure 3 depicts the overall scheme. The first step was to separate tungsten via LLE using the tertiary amine (Alamine 336) under the same conditions applied to the alkaline leachate except for a different A/O ratio (1/2 v/v) because tungsten concentration is higher (Table 3). Upon acidification, tungsten was converted to $PW_{12}O_{40}^{3-}$ ions that were extracted[18,19] in one stage (99.5%) under the best experimental conditions shown in the previous section (Table 4). Stripping was also easily performed in one stage with 2 mol L^{-1} NH_4OH (25 °C, A/O = 1 v/v) without emulsification. The aqueous solution was heated to 70 °C after which a mixture of 0.1 mol L^{-1} $MgCl_2$ + 5 mol L^{-1} NH_4OH was added[9] dropwise under stirring (200 rpm) until no white precipitate ($MgNH_4PO_4$) was formed.[9,13] This solid was filtered. APT was isolated after slow evaporation of the filtrate. Its purity (Table 5) is comparable to APT obtained via the alkaline route. 99% of tungsten present in the oxidized spent catalyst was recovered as APT.

The raffinate was added dropwise to 6 mol L^{-1} NaOH at 25°C (200 rpm). pH was kept at around 12 by adding further NaOH. A green solid precipitated. XRD data showed that this solid is amorphous, but its chemical analysis (Table 6) suggests that this solid is $Ni_3(PO_4)_2$. The amount of soluble phosphorus is much higher than that necessary to precipitate soluble nickel and iron (Table 3). Nickel phosphate is more insoluble in water than its hydroxide, whereas iron phosphate is more soluble than its hydroxide.[28,29]

Aluminum ($Al(OH)_4^-$) was precipitated as $Al(OH)_3$ after adjusting pH to 6.5-7 by adding 2 mol L^{-1} HCl. The precipitate was filtered and washed with 0.01 mol L^{-1} NH_4OH (4 mL g^{-1}) and water (6 mL g^{-1}).[28,29] The solid was dried at 150 °C for 2 h and weighed. This precipitate does not contain nickel and tungsten (Table 6) but iron was co-precipitated. On the basis of phosphorus content, around 1.0 wt% of aluminum was precipitated as $AlPO_4$.
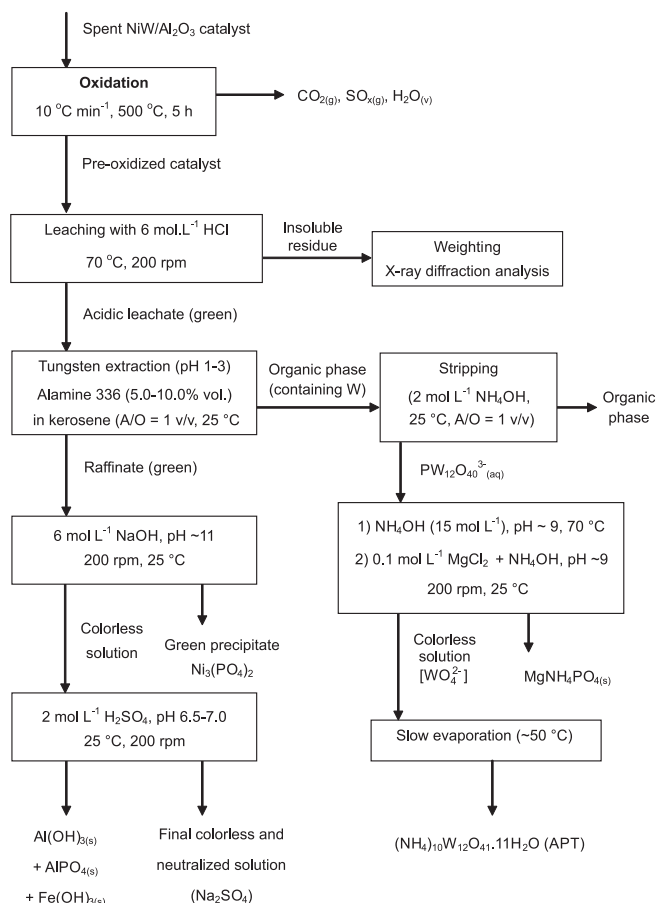
Figure 3. *General scheme for recovery of elements from spent NiW catalysts after oxidation and leaching with HCl (A/O = aqueous/organic phase ratio)*

Table 6. Chemical analysis of Ni and Al precipitates

Element (as oxide)	Amount (wt.%)	
	Ni precipitate	Al precipitate
Al_2O_3	0.03 ± 0.01	98.50 ± 0.21
Fe_2O_3	<0.01	0.23 ± 0.06
P_2O_5	38.66 ± 0.09	1.45 ± 0.09
NiO	61.05 ± 0.11	<0.01

CONCLUSIONS

Oxidized spent NiW/Al_2O_3 catalysts can be processed in a similar way as oxidized spent $NiMo/Al_2O_3$ samples. Alkaline fusion (NaOH, 650 °C, 1 h) converted 98.5% of tungsten as water-soluble WO_4^{2-}. Aluminum was also extensively leached (> 90%) whereas nickel and 30% of the phosphorus remained in the insoluble matter. Acidic leaching was best conducted with HCl (70 °C, 3 h). Samples were almost fully dissolved but tungsten was present as $PW_{12}O_{40}^{3-}$ ions.

Processing of the acidic leachate allowed recovery of tungsten (APT) and nickel ($Ni_3(PO_4)_2$), whereas aluminum was precipitated as $Al(OH)_3$ with minor amounts of $AlPO_4$ and iron. Processing of the alkaline leachate allowed recovery of tungsten by LLE without the presence of phosphorus but the latter and magnesium were co-precipitated with aluminum. Metals separation from the acidic leachate was more successful than from the leachate after alkaline fusion. High amounts of aluminum did not interfere in tungsten recovery, but phosphorus made separation steps more difficult, particularly aluminum recovery.

Despite the similarity of the chemistry of molybdenum and tungsten, LLE of the latter with tertiary amines in the presence of phosphorus occurred in a different way. At pH 1-2, while molybdenum is extracted as MoO_2^{2+} (phosphomolybdates are decomposed),[21] tungsten was extracted as phosphotungstate ions, thus requiring an additional step to recover it as a pure APT.

ACKNOWLEDGMENTS

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