



Hydrometallurgical route to recover molybdenum, nickel, cobalt and aluminum from spent hydrotreating catalysts in sulphuric acid medium

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ARTICLE INFO

Article history:

Received 29 March 2007

Received in revised form 25 October 2007

Accepted 3 March 2008

Available online 8 March 2008

Keywords:

Spent catalysts

Metal recovery

Waste management

ABSTRACT

This work describes a hydrometallurgical route for processing spent commercial catalysts (CoMo and NiMo/Al₂O₃), for recovering the active phase and support components. They were initially pre-oxidized (500 °C, 5 h) in order to eliminate coke and other volatile species present. Pre-oxidized catalysts were dissolved in H₂SO₄ (9 mol L⁻¹) at ~90 °C, and the remaining residues separated from the solution. Molybdenum was recovered by solvent extraction using tertiary amines. Alamine 304 presented the best performance at pH around 1.8. After this step, cobalt (or nickel) was separated by adding aqueous ammonium oxalate in the above pH. Before aluminum recovery, by adding NaOH to the acid solution, phosphorus (H₂PO₄⁻) was removed by passing the liquid through a strong anion exchange column. Final wastes occur as neutral and colorless sodium sulphate solutions and the insoluble solid in the acid leachant. The hydrometallurgical route presented in this work generates less final aqueous wastes, as it is not necessary to use alkaline medium during the metal recovery steps. The metals were isolated in very high yields (>98 wt.%).

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1. Introduction

Hydrotreatment (HDT) is a group of catalytic hydrogenation reactions, which saturates olefinic and aromatic hydrocarbons, eliminates heteroatoms (such as nitrogen, sulphur and oxygen) and even metals in the feedstock to be treated. HDT is one of the most important catalytic processes and its catalysts correspond to about 10% of the worldwide catalyst market [1]. HDT has been extensively employed for processing heavy feedstocks (such as Chinese, Venezuelan and Brazilian petroleums), as well as to improve the quality of end products and intermediates for reforming and fluid catalytic cracking processes (FCC).

At present environmental directories impose severe restrictions concerning gas and particle emissions from refineries and fuels. These directories require the improvement of the petroleum refining (higher impurities removal). Sulphur removal (hydrodesulphurization) is essential to obtain more acceptable fuels for environment [2]. The maximum allowed sulphur content in diesel is 10 ppm in Europe (from 2008 [3,4]), 15 ppm in the USA (since 2006 [4]) and 50 ppm in Brazil (since 2007 [5]).

The most familiar HDT catalysts are CoMo, NiMo and NiW supported on alumina (Al₂O₃), normally modified by additives

that improve activity towards some HDT reactions (hydrogenation, cracking) or thermal resistance during its lifetime [1,6,7]. The increasing severity of the environmental directories concerning gas emissions (NO_x, SO_x, etc.) has been stimulating the development of a new generation of more efficient catalysts and the proposal of less drastic HDT conditions concerning energy and hydrogen consumption [1,8]. The studied parameters include: support preparation, inclusion of additives (P, B, Si, Mg, Ti, Pt, etc.), active phase deposition method [3,9,10] and manufacture of non-supported NiMo and CoMo samples of high surface area.

The North-American Environmental Protection Agency (EPA) [11,12] states that spent HDT catalysts may be pyroforic, spontaneously combustible and release toxic gases. The presence of sulphur is responsible for their flammability as its oxidation releases heat along the organic matter present. The presence of polyaromatic compounds in the coke deposited on the surface classifies these catalysts as a carcinogenic material. This situation is reinforced should nickel is present, since this metal is also carcinogenic to man. Although spent refinery catalysts correspond to about 4 wt.% of its overall waste [6,8], they are classified as one of the most dangerous wastes generated in petroleum refineries. Spent *in natura* HDT catalysts have proven to contain high amount of heavy metals (Ni, Co, Mo) that can be leached by water [13,14]. Leaching of catalysts in USA follows the toxic characteristic leaching procedure (TCLP) from the “American Society for Testing Materials”, and is based on the maximum amounts of elements in drinking water

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[19]: 7 ppb of Mo, 7 ppb of V, 0.3 ppm of Fe, 13.4 ppb of Ni and less than 0.7 ppb of Co. If one of the sample components surpasses 100 times the corresponding limit, the spent catalyst is a dangerous waste.

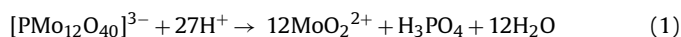
More than 90% of the European chemical industries [15] consider that definitive solutions for the spent catalyst must have been developed until 2012. The budget for this purpose and other refinery environmental challenges is US\$ 1.2 trillion (period 1997–2012). In USA the budget for the same purposes reaches US\$ 1.8 trillion (until 2015) [12]. It is expected that the greater severity of HDT reactions in the near future will increase generation of spent HDT catalysts [16].

The Resource Conservation and Recovery Act (RCRA) states [17] that a spent HDT catalyst must be previously oxidized at high temperatures (roasting) before sending it to an industrial dump because it is necessary not only to remove organic matter, but also insolubilize inorganic components. Incineration of spent catalysts is not a suitable practice [18] as this material has a low heat of combustion, thus requiring auxiliary fuel in order to ensure a full insolubilization of all its components.

Recovery of metals from spent catalysts depends on several factors: the nature of the sample (chemical composition) and the treated feedstock, the price of metals, the environmental directories, the distance between the refinery and the recycling industry and the operational costs [16,19]. Since the cost of transportation and disposal in industrial dumps, the severity of environmental directories, and the price of some metals (particularly cobalt) [20] have been rising, spent catalysts have been recognized as a secondary source of valuable metals [16,21–24]. This research field is very dynamic since the composition of a given catalyst may vary with time. Hydrometallurgical recovery routes require the maximum solubilization of the sample in an appropriate medium for the other central step, the separation of solubilized elements. For this purpose, it is necessary to pre-treat the sample in order to remove coke and other volatile species present. This step “cleans” the catalyst surface, thus reducing losses of recoverable metals by physical blocking. Care must be taken to avoid catalyst ignition during pre-treatment, thus forming refractory oxides that are difficult to solubilize in the leaching medium.

Extraction of metals with extractants dissolved in organic solvents has been gaining importance since the 1990s. Organophosphorous compounds are widely used [25–27] for treating effluents and leachates, especially in sulphuric acid medium. Extraction of molybdenum [28,29] with amines and organophosphorous compounds is possible in low pH (normally 1–2). Fe, Co, Ni and Al are not extracted. In pH below 2 MoO₂²⁺-type species predominate, whereas neutral or anionic species are dominant above this pH [30].

Molybdenum recovery presents a critical challenge—its separation from phosphorus, which is normally found as a support additive (this problem is also found when Mo is recovered as a by-product from uranium ores [31]). Mo forms heteropolyanions with P, V, Si and As. The challenge is to decompose them, for example:



Small amounts of a strong mineral acid play this role provided pH is below 2. It is easier to decompose phosphomolybdates than vanadomolybdates, whereas silicomolybdate [SiMo₁₂O₄₀⁴⁻] species are only decomposed in concentrated sulphuric acid [31]. Therefore, Mo recovery by solvent extraction depends on the presence or absence of P, Si, etc., and the settlement of experimental parameters (specially the concentration of the acid during sample leaching) to take into account the presence of such additives. In general, the influence of P on Mo recovery from spent catalysts is not discussed. Re-extraction of this metal to the aqueous phase is normally performed with NH₄OH [28,30].

Solvent extraction appears to be the most cited technique for separation of Ni or Co from complex matrixes. About 50% of the Co produced in the western world comes from solvent extraction [32]. In general, extractions are performed under pH between 4 and 7.5 [33], although there are some examples where these metals are extracted in ammonia solution [34]. Co is usually extracted in lower pH than Ni [35]. Ni separation is difficult as the ionic strength increases as pH increases [36]. Minerals, batteries, metallic nodules and standard solutions are the basic materials employed in these studies, where sulphuric acid is by far the most employed one. Under the pH for Ni/Co extraction Al precipitates (fully or partially). It would be suitable to recover Ni/Co by solvent extraction in lower pH (<2), which appears to be difficult with the present solvent extraction technology [37,38] (many stages are necessary to reach a high recovery of those elements).

This work presents a hydrometallurgical route for processing spent HDT catalysts in sulphuric acid solution. Recovery of components of the active phase (Mo, Ni or Co) and of the support (Al) was performed by a combination of several separation techniques in acid solution. The goal is to generate less final wastes as possible. The overall route present in this work was compared to those presented in the literature for the same catalysts.

2. Experimental

2.1. Catalysts

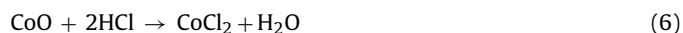
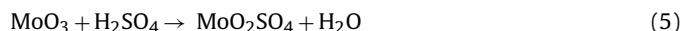
Spent NiMo and CoMo/Al₂O₃ catalysts were employed (5 mm cylinder extruded, 1.2 mm diameter). Chemical analyses are presented in Table 1. The catalysts were employed for at least 3 years in diesel/gasoline hydrotreaters in Brazilian refineries. For one of the CoMo catalysts this table also presents the analysis of its fresh sample. Samples were not ground and were dried at 110 °C for 2 h.

2.2. Pre-oxidation of samples

Samples were placed in identical ceramic crucibles. Since they were not ground, catalyst height in the crucible was fixed at 5 mm. Pre-oxidation was performed in a furnace following two heating rates: (i) 10 °C min⁻¹, from room temperature up to 500 °C (final time 5 h), according to previous studies in our laboratory [39,40]; (ii) 3 °C min⁻¹, from room temperature up to 500 °C (final time 5 h). The roasted mass was cooled down in the furnace and transferred to a dessicator before running the experiments. Chemical analyses of pre-oxidized samples are given in Table 1.

2.3. Leaching procedure

Sulphuric and hydrochloric acid solutions were tested, according to literature studies. The stoichiometric amount of each acid was calculated according to the following reactions:



From data of Table 1, the theoretical concentrated sulphuric acid/catalyst mass ratio is approximately 2.1:1 for all samples (or

Table 1
Chemical analysis (wt.%, dry basis) of the fresh, spent and pre-oxidized HDT catalysts

Sample	Ni/Co	Mo	Fe	Al	P	S	C	Si
NiMo spent	2.1 ± 0.2	9.5 ± 0.3	0.7 ± 0.1	31.3 ± 0.7	0.5 ± 0.1	3.1 ± 0.1	10.0 ± 0.2	<0.1
NiMo pre-oxidized	2.6 ± 0.1	10.6 ± 0.4	<0.1	32.1 ± 0.5	0.6 ± 0.1	0.5 ± 0.1	Absent	<0.1
CoMo 2 spent	2.7 ± 0.1	9.7 ± 0.2	0.7 ± 0.1	33.3 ± 0.5	2.9 ± 0.1	2.9 ± 0.1	12.0 ± 0.3	0.5 ± 0.1
CoMo 2 pre-oxidized	3.2 ± 0.2	10.5 ± 0.3	< 0.1	33.8 ± 0.2	3.1 ± 0.3	0.7 ± 0.1	Absent	0.6 ± 0.1
CoMo 1 fresh	2.9 ± 0.2	11.3 ± 0.2	Absent	33.7 ± 0.6	2.3 ± 0.1	Absent	Absent	3.2 ± 0.1
CoMo 1 spent	2.5 ± 0.2	9.9 ± 0.5	0.9 ± 0.1	33.3 ± 0.9	2.0 ± 0.2	3.4 ± 0.1	11.9 ± 0.2	2.9 ± 0.1
CoMo 1 pre-oxidized	2.8 ± 0.3	10.9 ± 0.4	< 0.1	33.9 ± 0.6	2.3 ± 0.2	0.9 ± 0.2	Absent	3.2 ± 0.2

1.15 mL acid g⁻¹ catalyst). The volume of acid was doubled with water in order to reduce viscosity of the leachate, ensure solubility of metal sulphates and allow an uniform stirring. Therefore, the final sulphuric acid concentration in the leachant is ca. 9 mol L⁻¹. For concentrated hydrochloric acid (12 mol L⁻¹), the acid/catalyst mass ratio is approximately 1.5:1 (3.5 mL acid g⁻¹ catalyst). This acid was not diluted with water since the leachate was easy to handle. A 10 wt.% excess of both acids was employed in the experiments. Since phosphate minerals (such as monazite, xenotime, etc.) are attacked by hot sulphuric acid [41], it is expected that phosphorus will be partially dissolved under leaching procedure. Si and some P-bearing compounds are the expected insoluble components to be found after acid leaching.

Experiments were carried out using 10–100 g of sample. Leaching was performed at 90 °C under magnetic stirring (200 rpm) in a heating–stirring plate for 30–120 min. The residue was separated from the liquid phase by filtration, washed with water (4 mL g⁻¹ solid), dried at 150 °C for 2 h and weighed. It was dissolved in HF + H₂SO₄ (1:2, v/v) at 60 °C for chemical analysis.

Some experiments were carried out with the original spent catalysts under the same experimental conditions, in order to determine the effect of coke on the acid leaching. The pre-oxidized fresh CoMo sample was also submitted to the above experiment, in order to assess the effect of pre-treatment conditions on the solubility of catalyst components in acid solution.

The experiments were run in triplicate, and errors for each experiment were always below 4%.

2.4. Analytical methods

Metal concentrations were determined by atomic absorption spectrometry. Phosphate ions were determined by ion-chromatography. A LECO analyzer determined carbon and sulphur contents. Crystalline phases in solid samples were identified by X-ray diffraction analysis. pH was measured by a digital pH meter.

3. Results and discussion

3.1. Effect of coke and other species on the catalyst surface

Data in Table 2 (experiments with H₂SO₄) show that previous oxidation of the catalyst was necessary to improve leaching. If we subtract the amount of carbon present in the spent samples (10–12 wt.%, Table 1), the amount of insoluble matter is higher

Table 2
Amount (wt.%) of the insoluble matter after pre-oxidation of catalysts at 500 °C (5 h) and leaching with 9 mol L⁻¹ H₂SO₄ (90 °C, 200 rpm, 70–90 min, 2.54 mL g⁻¹ catalyst)

Catalyst	Without pre-oxidation	Pre-oxidized at	
		3 °C min ⁻¹	10 °C min ⁻¹
CoMo1	38.3 ± 1.5	9.3 ± 1.0	75.6 ± 2.5
CoMo1 (fresh)	1.3 ± 0.3	4.8 ± 0.5	Not performed
CoMo2	25.6 ± 0.6	1.0 ± 0.2	8.7 ± 0.6
NiMo	22.5 ± 0.7	1.3 ± 0.3	9.9 ± 0.5

than the result found when the same catalysts were pre-oxidized at low heating rate. Coke (and other species on the catalyst surface) blocked the access of the acid to some reactive part of the sample. Loss of soluble matter reduced the amount of metals that can be recovered.

Another positive effect of the previous oxidation step is the quality of the leachate. For original spent catalysts it presented a dark color (organic matter in suspension) and an oily aspect. Besides problems related to safety and handling procedures, it was extremely difficult to prepare such leachate for the separation procedure. The leachate obtained after treatment of the pre-oxidized catalyst did not present any anomalous behavior. Pre-oxidation can be regarded as procedure which simplifies the sample composition since some components can be fully (carbon and water) or partially (sulphur) removed.

3.2. Effect of heating rate

Data presented in Table 2 show a well-known result: the catalyst must be pre-oxidized at low heating rates in order to avoid serious losses of valuable components by formation of insoluble compounds in the leaching medium. This is due to ignition of coke present. The critical region appears to be between 400 and 500 °C. When heating rate was 10 °C min⁻¹ the catalyst bed temperature raised suddenly from 455 to 750 °C in about 8 min. When heating rate was limited to 3 °C min⁻¹, such phenomenon was not observed.

It seems to have a relationship between the amount of insoluble matter in sulphuric acid and the amount of Si present in the sample: the greater the amount the greater the losses, since this element tends to form insoluble silicates under sample ignition. It is remarkable that the CoMo1 spent sample presented more than 75 wt.% of insoluble matter in H₂SO₄ when it was pre-treated at 10 °C min⁻¹. It was not found a relationship between the amount of P and the insoluble matter in the acid medium. The X-ray diffractogram presented in Fig. 1 shows two crystalline phases: cobalt meta-silicate (CoSiO₃) and aluminium-silicon oxide, both insoluble in hydrochloric and sulphuric acids.

The mass loss after pre-oxidation at both heating rates was comprised in the 23–27 wt.% range (Table 3), thus agreeing with

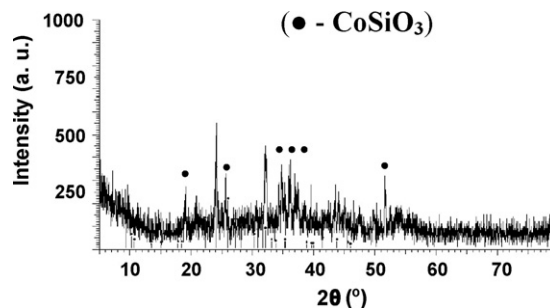


Fig. 1. X-ray diffractogram of the insoluble residue in H₂SO₄ of the CoMo1 catalyst pre-oxidized at 500 °C (3 °C min⁻¹), showing two crystalline phases: CoSiO₃ (assigned peaks) and an aluminium-silicon oxide (non-assigned peaks).

Table 3
Mass loss (wt.%) of samples pre-oxidized at 500 °C

Catalyst	3 °C min ⁻¹	10 °C min ⁻¹
CoMo1	27.4 ± 1.0	27.9 ± 1.3
CoMo2	27.3 ± 0.1	28.1 ± 0.5
NiMo	22.7 ± 0.6	23.0 ± 0.7

literature data [42,43]. Carbon was fully eliminated, (87 ± 3) wt.% of iron was eliminated as oxide and (25 ± 1) wt.% of sulphur remained in the catalyst as sulphate. No losses of other metals were observed.

Although there is only one fresh catalyst (CoMo1), data in Table 2 indicate that the amount of insoluble matter in this sample was about half of the spent sample treated at 3 °C min⁻¹. This demonstrates the importance of heating rate for coke removal with minimized loss of valuable components. This may explain why recovery of such elements in HDT catalysts generally did not reach 100 wt.% in literature studies [15,16] as the processes employed were not able to dissolve all components of the samples. The following results were obtained with samples pre-oxidized only at 3 °C min⁻¹.

3.3. Choice of the acid

Results of the Table 4 show that sulphuric acid was a better leachant than hydrochloric acid, according to the amount of insoluble matter found in each case. This demonstrates the best performance of sulphuric acid for dissolving the main components of the active phase/support and the additives/contaminants present, as mentioned in literature [21,41]. The insoluble matter in HCl was partially dissolved in H₂SO₄; qualitative tests [44–46] showed the presence of Al and P. HCl practically did not solubilize phosphorus-bearing species but sulphur (as sulphate) was dissolved over 99.0 wt.%.

Another disadvantage of HCl is its volatility (its azeotrope boils at 108 °C): it was slowly eliminated with time at 90 °C. It was necessary to add more HCl, which is a serious environmental pollutant, thus requiring measures to recover the acid that leaves the leachant (contacting the gas stream with water or an alkali solution). When sulphuric acid was used only water addition was necessary, as this acid has a high boiling point (338 °C). Finally, concentrated HCl (12 mol L⁻¹) presents lower hydrogen concentration than 9 mol L⁻¹ H₂SO₄: the same volume of the latter can react with more basic (NiO/CoO), amphoteric (Al₂O₃) and even acidic oxides (MoO₃). Therefore, H₂SO₄ is the best choice as leaching agent. It is also interesting to remember that the acid/catalyst ratio (including the 10 wt.% excess) for 9 mol L⁻¹ H₂SO₄ (2.54 mL g⁻¹) is lower than for concentrated HCl (3.85 mL g⁻¹).

The leachate got a pink (Co) or green (Ni) color. After (80 ± 10) min the insoluble matter reached a constant amount (Table 2). It had a bluish (Co) or greenish (Ni) aspect. The pH of the final solutions after catalyst leaching, filtration and washing of the insoluble matter (washing waters were added to the leachate) are very close: NiMo, 0.1; CoMo1, 0.5; CoMo2, 0.3. Table 5 shows the amount of

Table 4
Amount (wt.%) of insoluble matter after leaching of pre-oxidized catalysts (500 °C, 3 °C min⁻¹, 5 h) with 9 mol L⁻¹ H₂SO₄ or 12 mol L⁻¹ HCl (90 °C, 200 rpm, 70–90 min)

Catalyst	Acid	wt.% Insoluble
CoMo1	HCl	42.0 ± 1.4
	H ₂ SO ₄	9.3 ± 0.5
CoMo2	HCl	3.0 ± 0.3
	H ₂ SO ₄	1.0 ± 0.1
NiMo	HCl	7.2 ± 0.4
	H ₂ SO ₄	1.3 ± 0.2

Table 5
Amount of solubilized elements (wt.%) in 9 mol L⁻¹ H₂SO₄ (90 °C, 200 rpm, 70–90 min) after previous oxidation of catalysts (500 °C, 5 h, 3 °C min⁻¹)

Element	Catalyst		
	NiMo	CoMo1	CoMo2
Ni or Co	99.5 ± 0.6	90.5 ± 0.5	99.0 ± 0.4
Mo	99.5 ± 0.3	97.8 ± 0.2	99.2 ± 0.4
Al	99.7 ± 0.1	97.2 ± 0.2	99.5 ± 0.3
P	75.5 ± 1.4	72.7 ± 1.1	82.4 ± 1.8
Si	<0.1	<0.1	<0.1

metals solubilized. In general, metal losses were low, except for the CoMo1 sample, where insoluble matter reached 10 wt.% of initial mass (Table 2). Co loss reached around 10 wt.% (this is the sample with the highest Si content). 3/4 of P was solubilized, whereas Si remained in the insoluble matter.

Analysis of the solubilized portion of the catalyst (or the amount of insoluble matter) is of utmost importance for a given hydrometallurgical process. The literature indicates the metals recovered by hydrometallurgical routes are normally quoted as solubilized fraction in the leachate, rather than the total amount present in the original processed sample [8,16,21]. Efficiency of a given process must be evaluated as a whole (preparation and leaching of the sample and characterization of the insoluble residue obtained), not only the processing of the solubilized portion.

3.4. Metals recovery

3.4.1. Recovery of molybdenum

Fig. 2 presents the overall scheme for processing the metals in the leachate. The first step was the Mo recovery by solvent extraction. Two extractants were tested: Alamine 304 (tridodecylamine) and Alamine 336 (tricaprylamine), dissolved in deodorized kerosene. The extractant concentration varied between 2.5 and 10.0 vol.%. Experiments were performed at room temperature in a decantation funnel with an aqueous/organic phase ratio (A/O) equal to 1 (v/v). The influence of acidity on Mo extraction was also studied (pH 0, 1, 2, 3 and 4), by adding 6 mol L⁻¹ NaOH. When pH was above 1, it was necessary to filter a white precipitate, which was washed with water (3 mL g⁻¹) and the washing waters were added to the filtrate, being pH readjusted by adding 0.1 mol L⁻¹ H₂SO₄. Mo re-extraction was tested with the following compounds: NaCl, (NH₄)₂SO₄, H₂SO₄ and NH₄OH. This procedure was carried out at room temperature in a decantation funnel with an aqueous/organic phase ratio (A/O) equal to 1 (v/v).

The first tests intended to determine the optimum pH for Mo extraction and the choice of the extractant. The initial concentration was fixed at 5 vol.% as it corresponds to the average concentration issued in the literature (2.5–10.0 vol.%) [28–30]. The equilibrium between phases was reached in about 3 min. There was no contraction or expansion of both liquid phases after the experiment.

According to Figs. 3 and 4, the optimum pH for Mo recovery is about 1.8 for both extractants. The best performance was found for Alamine 304, and this extractant has been proposed for Mo recovery in aqueous acid media [47]. The optimum pH found in this study is in agreement with literature data [47,48]. After a two-stage process, using 5 vol.% Alamine 304, more than 99.99 wt.% of Mo was recovered under the optimum experimental conditions for all samples under study.

Data in Table 6 and Fig. 5 show that 5 vol.% Alamine 304 was the best extractant concentration. The extraction yield decreased when dilute solutions were used (thus requiring several stages for a complete Mo extraction). Amounts over 5 vol.% generated an intermediate phase, whereas emulsification was observed when concentration was 10 vol.%. The organic phase takes a strong green-olive color, thus Mo extraction can be easily followed.

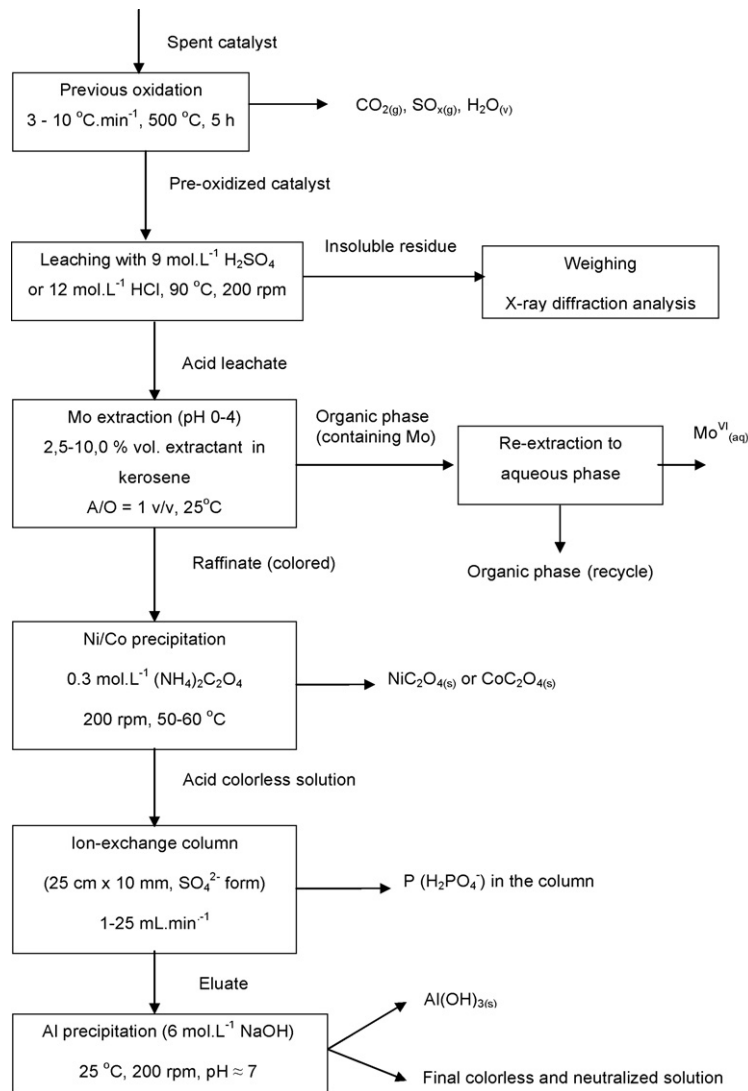


Fig. 2. General scheme for recovery of Mo, Ni(Co) and Al from spent HDT catalysts after pre-oxidation and leaching with $9 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$.

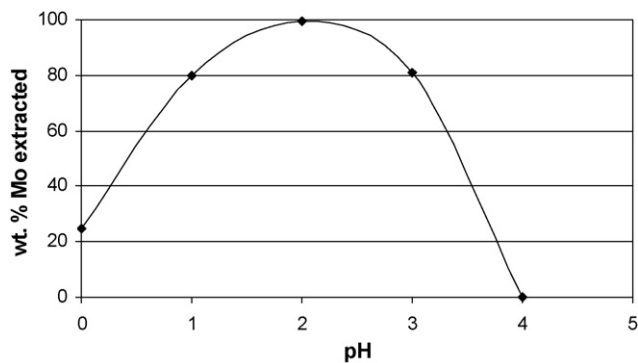


Fig. 3. Mo extraction with 5 vol.% Alamine 304 as a function of pH (CoMo1 catalyst, A/O 1:1, v/v, 25°C).

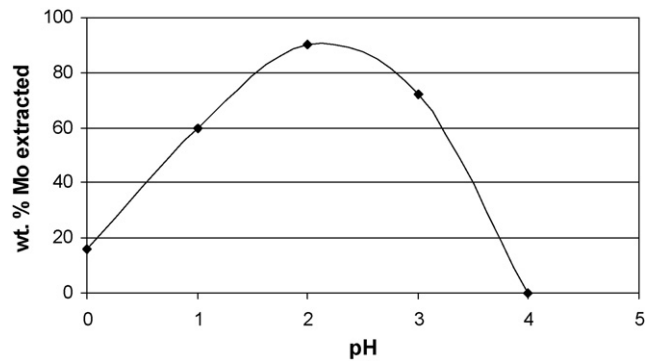


Fig. 4. Mo extraction with 5 vol.% Alamine 336 as a function of pH (CoMo 2 catalyst, A/O 1:1, v/v, 25°C).

Table 6
Influence of Alamine 304 concentration on Mo extraction (CoMo1 catalyst, A/O 1:1, v/v, 25°C , pH 1.8)

vol.% Alamine 304 in kerosene	wt.% Mo extracted into the organic phase	Remarks
2.5	54.4 ± 0.6	Insufficient extraction
5	99.5 ± 0.8	Optimum concentration
7.5	61.6 ± 1.3	Intermediate phase formation
10	Not determined	Emulsification

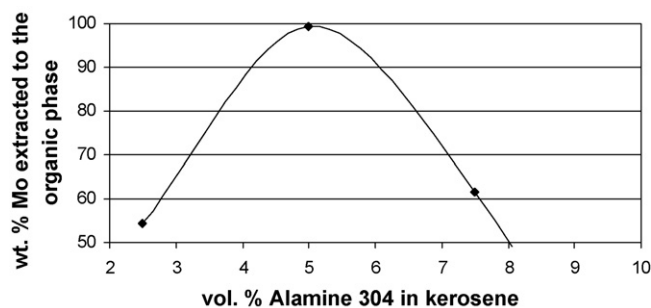


Fig. 5. Influence of Alamine 304 concentration on Mo extraction (CoMo1 catalyst, pH 1.8, A/O 1:1, v/v, 25 °C).

The precipitate isolated when pH was above 1 was solubilized in 0.01 mol L⁻¹ H₂SO₄, giving a colorless solution. Qualitative testes indicated the presence of Al with traces of Fe, which was present in low amounts in the spent samples (Table 1) and was mainly eliminated after pre-oxidation. The solution obtained above was added to the raffinate.

Results for Mo re-extraction from organic phase are presented in Table 7. The equilibrium between phases was reached in 5 min, and no contraction/expansion of both phases was observed. Among the several options the best choice is NH₄OH, as addition of foreign metals and anions is avoided. Moreover, ammonium heptamolybdate [(NH₄)₆Mo₇O₂₄·4H₂O], the most current Mo salt, can be easily obtained by evaporation of the ammonia solution, releasing NH₃, which can be absorbed in water, giving a new NH₄OH solution. The roasting of the above salt at 360 °C gives MoO₃ [1].

The critical parameter for Mo re-extraction is the concentration of the elution agent: higher concentrations (particularly of acids or hydroxides) favor the process but risk of emulsification (or formation of an intermediate phase) is considered. This may explain the need to use two or more stages in order to avoid/minimize such risks in some studies mentioned in the literature.

3.4.2. Recovery of cobalt and nickel

From the raffinate Co (or Ni) was isolated by adding dropwise 0.3 mol L⁻¹ (NH₄)₂C₂O₄ at 50–60 °C, under stirring (200 rpm), until the solution became colorless. The solid was washed with 0.01 mol L⁻¹ (NH₄)₂C₂O₄ and dried at 110 °C for 2 h.

Ni or Co recovery was very high (98.0 ± 0.3 wt.% for both metals). Phosphorous-bearing species were not detected. In the pH where oxalates were precipitated (1.8) Ni/Co phosphates are soluble under the concentration range of such ions in the leachates [44–46].

Al³⁺ forms very stable complexes with oxalate ions ([Al(C₂O₄)₃]³⁻, K_{est} = 2 × 10¹⁶), whereas Ni and Co complexes are much less stable ([Co(C₂O₄)₂]²⁻, K_{est} = 8 × 10⁶; [Ni(C₂O₄)₂]²⁻, K_{est} = 7 × 10⁶) [46]. This avoids co-precipitation of Al together with Ni/Co. The amount of Al in the precipitated oxalates is 0.05 wt.% or below.

An excess of oxalate ions should be avoided, as Al will be partially complexed. The best way to avoid this inconvenience is to

Table 7
Mo re-extraction from the organic phase

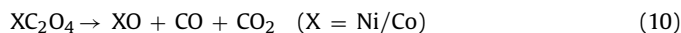
Re-extraction with	Concentration (mol L ⁻¹)	wt.% Mo re-extracted
NaCl	2.0	>99.99
(NH ₄) ₂ SO ₄	1.0	>99.99
H ₂ SO ₄	6.0	Emulsification
H ₂ SO ₄	4.5	>99.99, Slight emulsification
H ₂ SO ₄	2.0	≈95, Two-stage process required
NH ₄ OH	6.0	Emulsification
NH ₄ OH	2.0	>99.95

Table 8
Retention of phosphorus in the ion-exchange column (pH 1.8, 25 °C)

Sample flow (mL min ⁻¹)	wt.% P retained	Residence time (min)
3 (or lower)	99.8 ± 0.2	>8
5	93.5 ± 0.3	5
8	82.0 ± 0.9	3.5
10	68.1 ± 0.7	3
15	52.2 ± 1.0	1.7
20	34.4 ± 0.6	1.3
25	14.6 ± 0.8	1

add dropwise the ammonium oxalate solution, according also to the procedure described elsewhere [38].

The oxalates can be easily thermally decomposed, giving the corresponding oxides (NiO/CoO or even Co₂O₃):



The oxalate precipitation technique avoids the problems predicted should Ni/Co were extracted by organic extractants: the extraction is performed in a less acid solution, where Al partially precipitates, thus requiring additional steps (filtration, washing) and increasing risk of Ni/Co losses by co-precipitation/occlusion. This situation is typical of spent HDT catalysts in view of their chemical composition.

3.4.3. Recovery of aluminum

When the acid solution is neutralized P tends to co-precipitate with Al; therefore, the idea was to remove it before Al precipitation. A commercial ion-exchange resin (Amberlite IRA-400 AR, Cl⁻ form), containing quaternary ammonium groups, was used. This resin has been used for removing P species in aqueous effluents and standard solutions [49,50]. The resin was converted into sulphate form by treating it with two volumes of 2 mol L⁻¹ H₂SO₄, followed by elution with two volumes of 0.01 mol L⁻¹ of the same acid. The column was 25 cm long and 10 mm diameter. The influence of flow on P retention in the column was investigated (2–25 mL min⁻¹). Eluate samples were placed in a mixture of concentrated HNO₃ and 0.1 mol L⁻¹ NH₄NO₃ at 40 °C; the appearance of a yellow precipitate of ammonium phosphomolybdate, (NH₄)₃PMo₁₂O₄₀, confirms the presence of P [44–46].

In pH 2, about 50% of P is found as H₂PO₄⁻ anion [46]. Therefore, it was necessary not only to retain H₂PO₄⁻ but also to displace the equilibrium of H₃PO₄–H₂PO₄⁻ to produce more H₂PO₄⁻ until full removal of P. Thus, the flow along the column is a very important parameter. Another point is the presence of high amounts of SO₄²⁻ species, which compete favorably with H₂PO₄⁻ for adsorption in the resin.

A 3 mL min⁻¹ (or lower) flow allowed retention of P in the column but required a long residence time (>8 min, Table 8). The column tested retained P from 100 mL of leachate (without Ni or Co and Mo). It can be regenerated by applying the same procedure for conditioning as shown above.

The proposal of an ion-exchange column for P retention appears to be a simple way to separate it from Al in leachates of spent HDT catalysts, but further studies are required in order to improve this procedure (for example, the use of more specific resins for P).

The eluate was treated with 6 mol L⁻¹ NaOH, at room temperature, under stirring (200 rpm), until pH around 7. The Al(OH)₃ was filtered and washed with 0.01 mol L⁻¹ NH₄OH (4 mL g⁻¹) and water (6 mL g⁻¹) until full removal of SO₄²⁻ and Na⁺ ions. The washed solid was dried at 150 °C for 2 h and weighed. The purity of isolated aluminum hydroxide is high according to data in Table 9. The traces of Fe came from the catalyst as seen in Table 1 (chemical composition). P was not detected.

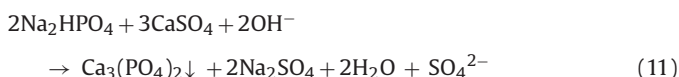
Table 9
Chemical analysis of Al(OH)₃ precipitate

Metal	wt.%
Al	99.60 ± 0.25
Na	0.20 ± 0.06
Fe	0.11 ± 0.03
Ni (or Co)	<0.05
Mo	<0.05

3.5. Final wastes management

The aqueous solution after Al recovery (pH ≈ 7) was colorless and presented no precipitate (no turbidity), as it contains Na₂SO₄. The amounts of Al and Mo are below the detection limit of the analytical method employed (atomic absorption).

The effluents obtained when the column was conditioned or regenerated can be neutralized with 6 mol L⁻¹ NaOH. The final solution contains Na₂SO₄ and Na₂HPO₄. P can be removed from it by adding CaSO₄:



the precipitate can be disposed in industrial dumps or co-processed.

For 1 g of processed spent HDT catalyst, about 8 mL of final effluent was generated, including the conditioning and regeneration steps of the ion-exchange column. This result is much more favorable than the ones found in most studies in the literature [16,19,39,40]. This is due basically: (i) to the use of a limited excess of the acid when the catalyst was leached; (ii) to the use of a separation scheme entirely in an acid medium. The use of alkaline solutions implies in using further acid for neutralization. This subject is not usually commented in studies on spent catalyst recycling processes found in the literature. However, this aspect, together with energy consumption and other costs and the market value of end products, may determine the economical viability of the recycling process.

The insoluble residue in H₂SO₄ can be co-processed (mineralizing raw material) according to the Directory No. 264/99 from the National Brazilian Environmental Council (CONAMA). This residue can account for a small portion of the original sample (Table 2).

4. Conclusions

It is of utmost importance to pre-oxidize spent HDT catalysts under a low heating rate (3 °C min⁻¹) in order to reduce possibility of coke ignition, thus avoiding losses of valuable elements when the pre-oxidized sample is leached (formation of refractory compounds). 9 mol L⁻¹ H₂SO₄ has proven to be good to treat spent HDT samples in about 80 min at 90 °C.

It is possible to recover the main components of the active phase (Ni or Co and Mo) and the support (Al) with high yield and good purity by an appropriate combination of separation techniques (solvent extraction, selective precipitation and ion-exchange column). Mo was better extracted (>99.5 wt.%) with Alamine 304 (5 vol.% in kerosene), in pH around 1.8, at room temperature and with an A/O phase ratio equal to 1 (v/v). It was re-extracted with dilute NH₄OH, giving ammonium heptamolybdate [(NH₄)₆Mo₇O₂₄·4H₂O] after concentration of its solution. The raffinate was treated with ammonium oxalate (50–60 °C), precipitating Ni/Co as oxalate. Soluble P was removed by passing the acid solution through an anionic ion-exchange column at low flow rate (3 mL min⁻¹) at room temperature, and Al was isolated by neutralizing the eluate with NaOH.

The advantage of the separation scheme described in this work is the use of only acid medium to isolate all elements, avoid-

ing alkaline solutions to recover Ni/Co in the presence of Al. This means lower reagent consumption and less generation of final salted wastes. The used solvents (Mo extraction) and the spent ion-exchange column (P removal) can be regenerated; the NH₃ generated when ammonium heptamolybdate was crystallized can be recovered to form new NH₄OH solutions, and the insoluble residue in H₂SO₄ can be co-processed. This implies in a lower waste generation by mass of catalyst processed.

Taking into account the market value of some metals present in HDT catalysts, which can be high nowadays, it is much more interesting to recover such elements instead of discarding or even co-processing the entire sample.

Acknowledgments

Ivam M.V. Jr. acknowledges Agência Nacional de Petróleo (ANP) for a M.Sc. fellowship. J.F. Paulino is grateful to PIBIC/CNPq/UFRJ for a fellowship. We are grateful to Centro de Tecnologia Mineral (CETEM/MCT) for X-ray diffraction analysis.

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