

Article

Extraction and Recovery of Metals from Spent HDS Catalysts: Lab- and Pilot-Scale Results of the Overall Process

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Abstract: The present study proposes an overall recycling process for spent hydrosulfurization (HDS) catalysts. The process put together stages already known in the technical literature, tested again with samples coming from the roasting stage in a pilot kiln, which is the most limiting stage of metal recovery from spent catalysts. These catalysts contain valuable metals such as cobalt (Co), molybdenum (Mo), nickel (Ni), and vanadium (V). In particular, a dry Co-Mo catalyst was used and treated in order to optimize the roasting step (time, soda ash, and temperature) at a pilot scale and thus maximize the extraction yield of molybdenum (Mo) and vanadium (V). In particular, a dry Co-Mo catalyst was used. After roasting at 700 °C for 2.5 h, the best conditions, the catalysts underwent water leaching, separating Mo and V from Co and the alumina carrier, which remained in the solid residue. The pregnant solution was treated to remove arsenic (As) and phosphorus (P), representing the main impurities for producing steel alloys. V was precipitated with NH₄Cl, and further calcined to obtain commercial-grade V₂O₅, whereas Mo was recovered as molybdic acid by further precipitation at a pH of around one. Thus, molybdic acid was calcined and converted into commercial-grade MoO₃ by calcination. The hydrometallurgical section was tested on a lab scale. The total recovery yield was nearly 61% for Mo and 68% for V, respectively, compared with their initial concentration in the spent Co-Mo catalysts.

Keywords: catalyst; molybdenum; vanadium; cobalt; hydrosulfurization; HDS; recycling; circular economy



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1. Introduction

Since 2009, the maximum sulfur content in petrol and diesel fuels has been limited to 10 ppm in the European Union [1]. Based on this strict regulation, oil companies must perform thorough hydrosulfurization (HDS) consisting of removing sulfur from petrol; this process is carried out in the presence of a catalyst [2,3]. Catalysts are essential in petroleum refining, especially in hydrotreating; they are used to produce distillates like gasoline, naphtha, jet fuel, kerosene, and gas oils. Such catalysts commonly consist of molybdenum (Mo) supported on an alumina or silica carrier together with promoters such as cobalt (Co) or nickel (Ni). Hydrosulfurization (HDS), hydrodenitrogenation (HDN), and hydrodemetallization (HDM) are typical reactions in which various impurities such as sulfur, nitrogen, and metals, for instance, vanadium (V) are removed [4,5]. The remarkable flexibility of the catalytic chemistry allows the refiners to have rapid production to respond to market needs and product specifications. The volume of spent catalysts discharged from different process units depends on several factors, such as the volume of fresh catalysts used, their activity, and the poisoning deposits formed, and thus on their deactivation and regeneration cycles [6]. In most refineries, a considerable amount of the spent catalyst wastes come from the hydrosulfurization stages [4]. After several cycles,

the activity of the catalyst decreases below the acceptable level, so it is usually regenerated and reused. After some thousand working hours, the catalyst activity may decrease to deficient levels after several cycles. Further regeneration may not be economically feasible: the spent catalysts are discarded as solid wastes [7]. Among secondary industrial resources, spent catalysts are undoubtedly most important for their economic value and environmental concerns when discharged, as they have been classified as hazardous wastes [8]. Furthermore, Mo and V are widely used for preparing different types of steel, whereas Co, besides the steelmaking industry, is also extensively used for manufacturing Li-ion accumulators [9,10].

Various methods for recovery of HDS catalysts have been proposed in the literature: acid leaching followed by solvent extraction [11], primary leaching of spent catalyst, and then separation of metals through selective precipitation [12] recovery from biotechnological routes [13,14], carbon adsorption [15], polyelectrolyte extraction [16] and solvent extraction [17–19]. To all methods mentioned above, the recovery of metals was at different rates; however, the extraction of metals can achieve around 90% [11–13]. Presently, vanadium recovery is always greater than 90% concerning the concentration in spent catalysts [8,20]. Considering that these catalysts contain sulfur, coke, and sometimes hydrocarbons like naphtha, a thermal pre-treatment is required to convert these metals into oxides and enhance the leaching yield. The hydrometallurgical way is still the most used over the pyrometallurgical one [21]. Spent HDS catalysts are classified as hazardous materials: their disposal causes environmental threats because of the potential release of heavy metals into the soil and the groundwater table [20–22].

The present work reports the results of a one-step industrial process that includes roasting catalysts in the air at 700 °C in the presence of soda ash (Na_2CO_3) in a pilot-scale rotary kiln furnace, i.e., under operating conditions much close to those of industrial applications. The rest of the process was tested in the laboratory, whose hydrometallurgical trials are much easier to scale up on pilot and thus full scale. The aim is the conversion of molybdenum and vanadium oxides into soluble sodium molybdate and vanadate, easily leached by hot water [23–25]. Although sodium hydroxide, sodium bicarbonate, and sodium sulfate have been used in direct salt roasting, sodium carbonate is the most used due to its lower cost [26,27]. This method allows the separation of Mo and V from Co, Ni, and Al directly in the leaching stage, facilitating the downstream recovery. Other research groups tested the acid leaching, but in this case, all metals are leached, i.e., Co, Mo, and Ni (and V if present), together with a consistent amount of aluminum contained in the carrier: this makes the further separation and recovery of each metal difficult, often with a low grade of the recovered oxides/salts [8,28,29].

2. Materials and Methods

2.1. Characterization of Samples

The shape of Co-Mo catalysts was cylindrical with an approximate size of $L = 4$ mm and $D = 2$ mm. Prior to the characterization, the catalyst was dried overnight in an oven at 100 °C. The sample was grounded in a mortar and sieved at 100 μm . Afterward, it was characterized by X-ray fluorescence (XRF) (Spectro Xepos) and X-ray diffraction (XRD) (X-Pert, Philips). Furthermore, 1 g of catalyst was immersed in 10 mL of aqua regia ($\text{HCl}:\text{HNO}_3 = 1:3$) at 80 °C for 2 h: the suspension was filtered, and the solution was transferred into a 10 mL calibrated flask. The concentration of metals, i.e., Mo, V, Al, Co, As, and P, was determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, Agilent 7900 spectrometer). The content of metals was quantified from Equation (1):

$$X = \frac{C \cdot V}{1000 \cdot p} \cdot 100 \quad (1)$$

where X is the concentration of metal, wt%; C is the concentration of metal in solution after dissolution in aqua regia, mg L^{-1} ; V is the final volume of solution (10 mL), L, and p is

the weight of the solid sample (unroasted catalyst), g. Sulfur, carbon, and hydrogen were quantified with a Fisons Instruments 1108 CHNS elemental analyzer.

2.2. Roasting of Samples

Unground samples were roasted at various temperatures in different time lapses to remove carbon, sulfur, and other impurities or organic compounds using a pilot rotary kiln (length 200 cm, inner diameter 18 cm). The kiln was used in a batch operating mode, filling around 15% of the cross-section to let the air flows throughout the catalysts bed and foster the oxidation. A 1 kW electric motor with a speed regulator put the kiln in rotation at around 4 rpm. The kiln was made up of AISI 316L stainless steel: the cylinder was surrounded by an alumina covering, housing the 15 kW resistances for heating the kiln to 650–700 °C, which was the optimal temperature range determined by tests in a muffle oven. The temperature was monitored and regulated by a temperature indicator and controller (TIC) that enabled or disabled the electrical resistances. One of the ends was covered by one small hood that sucked the flue gas and sent it to an alkaline scrubber before the release into the atmosphere via the chimney. Air was continuously insufflated by a small fan installed on the other edge. When the thermal process ended, the kiln was inclined to empty it. The roasted catalyst was recovered in a steel vessel after cooling in air. Some catalysts cylinder were manually broken to check that the inner part was not black anymore, i.e., the oxidation was complete even in the inner part where air takes more time to penetrate.

Soda ash (Na_2CO_3) was added to the catalyst to form sodium vanadate and sodium molybdate, water-soluble salts. They can be easily separated from other metals like Al and Co during the leaching stage.

The roasting temperature ranged from 400 to 750 °C. The amount of soda ash varied from 10 to 45%wt, referring to the catalyst's weight. The roasting time was tested from 40 to 180 min to optimize the thermal process, which is also one of the most energy-consuming stages of the recycling process.

Roasting time, soda ash concentration, and temperature were investigated to determine the best route of roasting catalyst to get as much metal extraction as possible in the leaching stage. The soda ash used during the roasting process was in excess concerning the stoichiometric amount required by Mo and V. This choice was made as most of it is consumed by the side reaction that captures SO_2 , converting into Na_2SO_4 .

2.3. Leaching Tests

Leaching tests with water were performed in 250 mL flasks at room temperature. Noteworthy, various temperatures (25–80 °C) were tried for optimization of leaching, but it didn't affect the leaching, so for further investigation, the room temperature was selected as the best option. Water was used as a solvent, and the mass was mechanically stirred at 250 rpm. The solid-to-liquid ratio (S/L) was 20% *w/v* for all experiments. Samples were taken after the end of the tests to monitor the extraction of the metals. The concentrations of Mo, V, Co, and Al were determined by ICP-MS, and the extraction yield was calculated by comparing the mass of the metals extracted with the initial mass contained in the catalysts and calculated by Equation (1).

2.4. Recovery Tests

The purification tests were carried out to remove As and P from the pregnant solution. These two elements, together with sulfur, lower the quality of steel and alloys. Their accumulation in steel is detrimental since they decrease toughness, increase temper brittleness, reduce corrosion resistance, and impairs welding.

Purification tests were performed in a 250 mL flask at 40 °C for 1 h under mechanical stirring at 200 rpm. Arsenic and phosphorus were precipitated via a chemical reaction with a stoichiometric amount of MgO and NH_4Cl (Equations (4) and (5)) [30–32]. A few drops of diluted HCl were added to adjust the pH in the range of around nine.

Mo and V were recovered by sequential precipitations. The chemical reaction was conducted in a 250 mL Erlenmeyer flask at 2000 rpm. The temperature of the precipitation ranged from 25 to 100 °C. The amount of NH_4Cl and HCl was calculated by Equations (6)–(8) to know the stoichiometric concentration of the precipitating agent. The pH varied from 1–9, and the reaction time from 20–60 min. Precipitation of V occurred at pH around 9 and a temperature of 40 °C, whereas the precipitation of Mo was carried out at pH1 and a temperature of 90 °C. Mo and V were recovered with high-grade as oxides (MoO_3 and V_2O_5) (Equations (9) and (10)), respectively, by calcination of their salts (NH_4VO_3 and H_2MoO_4) in a muffle furnace for 1 h at 500 °C.

3. Results

3.1. Characterization of Samples

The concentration of the main metals, determined by ICP-MS and XRF and contained in the Co-Mo sample, is reported in Table 1.

Table 1. The concentration of metals in the spent unroasted catalyst (%wt, average values).

Sample	Mo	V	Co	Ni	Al	P *	As *
Co-Mo	8.7 ± 0.9	0.25 ± 0.04	2.6 ± 0.4	0.10 ± 0.02	19.2 ± 3.3	1.5 ± 0.3	0.5 ± 0.1

* XRF analysis.

Aluminum was found to have the highest concentration, around 19%, of the spent Co-Mo mass. Instead, the vanadium concentration was rather low. Molybdenum and cobalt are the most valuable metals in the sample. The vanadium content is certainly due to its presence in the oil feedstock treated in the hydrodesulfurization unit. Concentrations of carbon, hydrogen and sulfur in dried Co-Mo are listed in Table 2.

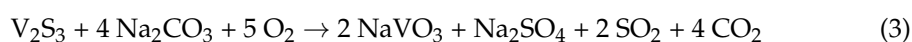
Table 2. The concentration of C, H, and S in the spent unroasted catalysts (%wt).

Constituents	C	H	S
Co-Mo	11.24 ± 1.4	2.18 ± 0.6	9.24 ± 1.1

Regarding the XRD analysis, some phases were identified, although the sample had low crystallinity and no well-defined peaks. The main probable crystalline phases were Al_2O_3 , $\text{Co}_{0.8}\text{V}_{1.6}\text{Mo}_{0.4}$, CoMoO_4 , MoS_2 and CoMoS_2 .

3.2. Roasting and Leaching Stages

Regarding molybdenum, based on XRD peaks, a hypothetical reaction that took place is described below in Equation (2). Concerning vanadium, we found it hard to identify any clear peaks from XRD. However, from the literature, it can be inferred that V_2S_3 is often present, together with other minor phases. The problem lies in the present sample, where the low vanadium concentration makes it difficult to find its main phase. Nevertheless, for our purposes, the reaction that usually takes place during roasting is given by Equation (3) [25]:



In the presence of Na_2CO_3 and O_2 , vanadium and molybdenum sulfide were converted into soluble salts, e.g., Na_2MoO_4 and NaVO_3 . Note of worth, gaseous SO_2 and CO_2 resulting from the reactions above were mainly captured in the kiln and converted into sodium salts (Na_2CO_3 and Na_2SO_4) before being scrubbed in a NaOH aqueous solution. During the leaching stage, additional Na_2CO_3 (5%wt) and H_2O_2 (5%wt) were added to the solution, as explained in Section 4.1. The best extraction yields obtained in the tests are listed in Table 3 (ICP analysis).

Co, Ni, and the alumina carrier were not leached by hot water, so they remained in the solid residue after filtration. Co and Ni could be recovered with further leaching with acids.

However, aluminum is leached contemporaneously, making the subsequent purification difficult and the final grade of the recovered metals. For this reason, such residue is often sent to metallurgical treatment by electric arc furnaces.

Table 3. Leaching of metals (%).

Sample	Mo	V	Co	Ni	Al	P	As
Co-Mo	80 ± 2.5	70 ± 3.7	-	-	-	<0.1	<0.05

3.2.1. Effect of Roasting Temperature

The percentage of molybdenum and vanadium extracted as a function of temperature is shown in Figure 1. The maximum recovery is observed around 700 °C, where the molybdenum leaching is 68%. On the other side, the leaching of vanadium is slightly higher, reaching 80% at 650 °C. A further increase in temperature decreases molybdenum's recovery, which may be attributed to the sublimation of MoO_3 . At variance, the increase in temperature did not affect vanadium leaching. Hence, an optimum temperature of 700 °C was chosen for further investigation.

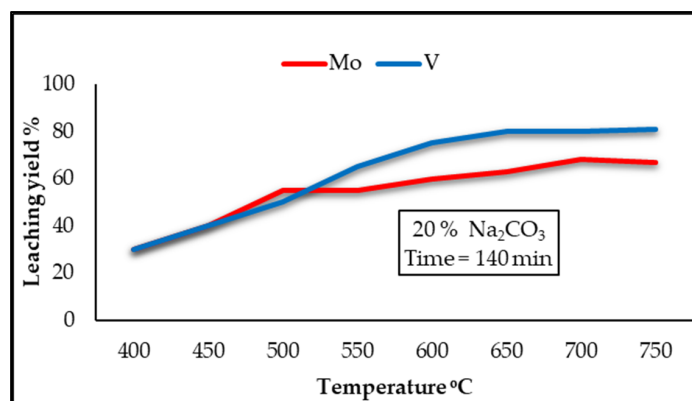


Figure 1. Leaching of molybdenum and vanadium vs. temperature.

3.2.2. Effect of Soda Ash

The effect of soda ash addition on molybdenum and vanadium leaching from the spent catalyst was investigated for 140 min at 700 °C. The results are shown in Figure 2. As can be inferred from Figure 2, at 20 wt.% of soda ash content in the mass mixture, molybdenum leaching reaches 70% and vanadium 80%. Further increase in soda ash content did not improve the molybdenum and vanadium leaching yield. In light of this, 20 wt.% soda ash addition was considered to be the optimum value.

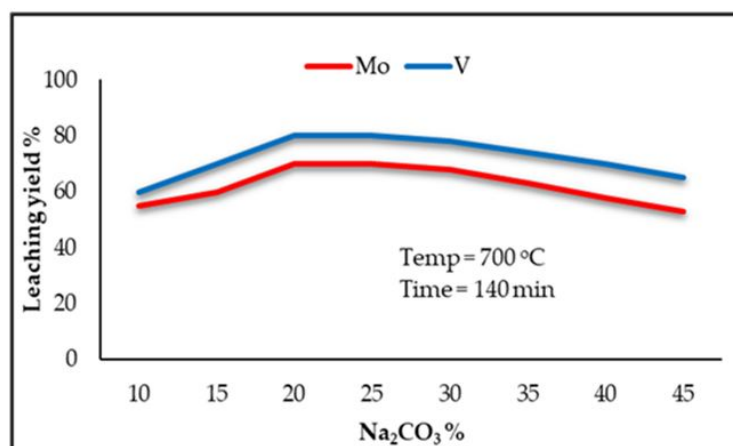


Figure 2. Leaching of molybdenum and vanadium vs. soda ash amount.

3.2.3. Effect of Roasting Time

The trials shown here refer to the soda ash content of 20%wt added in the feed mixture with a constant reaction temperature of 700 °C. The experimental results are given in Figure 3. It is possible to recognize that a roasting time of 140 min seems sufficient to leach about 70% of molybdenum and 80% of vanadium from the spent catalyst. The entire roasting was not completed within 140 min even though a further increase in this time does not affect the molybdenum leaching.

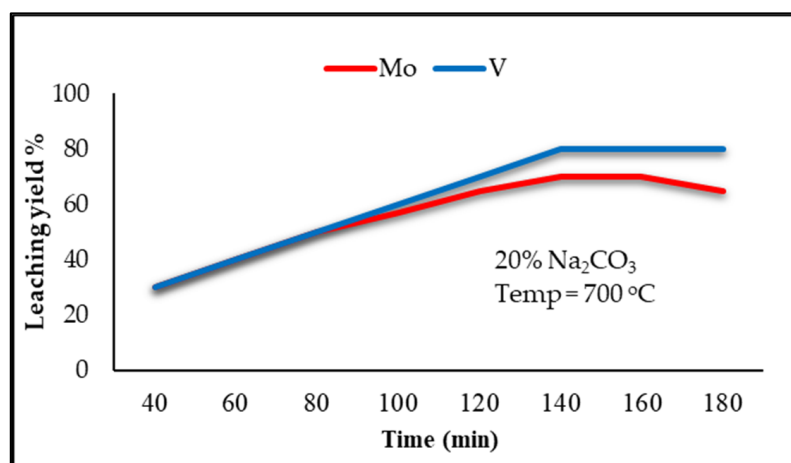


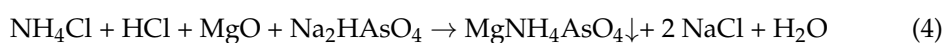
Figure 3. Leaching of molybdenum and vanadium vs. time (T: 700 °C).

The above parameters optimization reveals that, on a pilot scale, it is possible to extract around 70% of molybdenum and 80% of vanadium at 700 °C after 140 min roasting with 20%wt of soda ash. From the elemental analysis, it was clear that some fractions of sulfur and carbon were still present in the roasted catalyst, explaining the percentage of Mo and V extraction in water during the leaching step. Accordingly, around 20%wt of vanadium and 30%wt of molybdenum were still in the leaching solid, as the sulfides did not oxidize in the abovementioned conditions. Moreover, molybdenum and vanadium were found in the solid residue after leaching, after a chemical acid digestion was carried out to close the material balance.

After roasting, the carbon, hydrogen, and sulfur concentrations were 1.60%wt, 0.71%wt, and 1.40%wt, respectively. This was confirmed by a visual inspection of the roasted material. Some cylinders were randomly collected and manually broken to check the oxidation rate achieved in the inner core. All the cylinders showed a blue color on the surface, but some of those were still partially black inside. The roasting was thus not efficient at 100%.

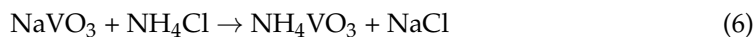
3.3. Purification of Leach Liquor

Equations (4) and (5) are the reactions that take place in the purification stage. Taking into account the pH of the leach solution, which is alkaline, the addition of a stoichiometric quantity of MgO, and performing a reaction for 1 h under gently warming, almost all of As and P were removed since such elements were not found in the solution after the precipitation. Additionally, the loss of Mo and V that might have been co-precipitated altogether with As and P is very small, i.e., 0.5% of Mo and 0.3% of V, compared to the amount contained in the pregnant solution.

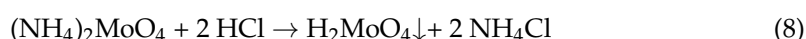


3.4. Precipitation of Metals and Their Separation

Vanadium is precipitated as NH_4VO_3 by mixing NH_4Cl into the hot water-leached solution from the Na_2CO_3 -roasted waste catalysts. The precipitation occurs as per the reaction in Equation (6), as explained in [33]:



After precipitation, around 0.4%wt of the total vanadium mass contained in the solution after As and P purification remained dissolved; afterward, molybdenum was precipitated by adding HCl to very acidic pH and high temperature, i.e., pH around 1 and 90 °C [34,35]. The reactions proposed are the following:



3.4.1. Effect of Time on Vanadium and Molybdenum Precipitation

Figure 4 shows the impact of reaction time on the precipitation of vanadium and molybdenum from the leaching solutions under specific conditions (precipitation of V at pH 9 and 40 °C; precipitation of Mo was precipitated at pH 1 and approximately 90 °C). Vanadium precipitates quickly, reaching 60% after 20 min, but after that, it climbs steadily, achieving 95% after 60 min with no positive impact on response time. In these conditions, molybdenum remained dissolved in solution. However, when the pH was lowered to 1 in a boiling solution, molybdenum precipitation occurred at the same rate as vanadium.

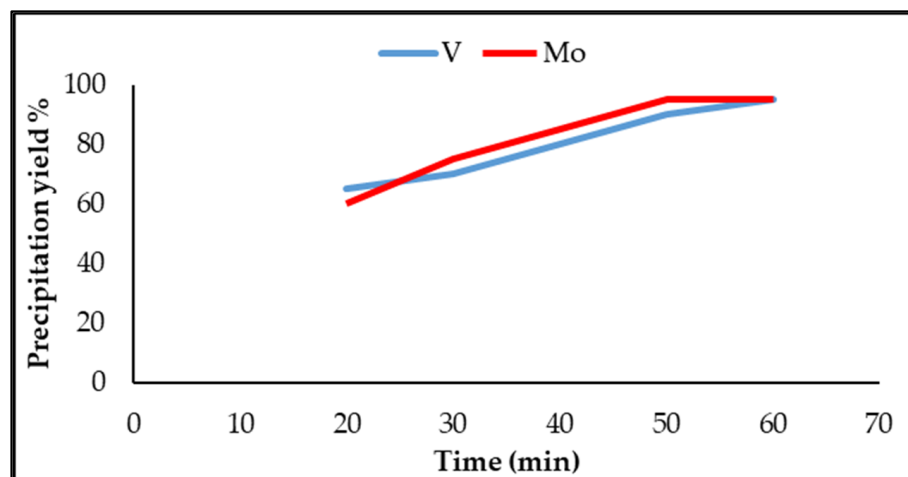


Figure 4. Precipitation yield of molybdenum and vanadium vs. time (V: pH 9, 40 °C; Mo: pH 1, 90 °C).

3.4.2. Effect of Temperature on Vanadium and Molybdenum Precipitation

As seen in Figure 5, the influence of temperature on the precipitation of vanadium and molybdenum was studied in the range of 20–100 °C. The effects of temperature on molybdenum precipitation are significant (pH = 1 and reaction time of 1 h at 90 °C with over 95% of Mo precipitate). Under these conditions, precipitation of vanadium did not take place. However, at 40 °C and pH = 1, 95% of the V precipitation was unaffected by temperature change. A higher temperature did not impact the amount of vanadium that precipitated, and it has the opposite effect at very high temperatures close to the boiling point.

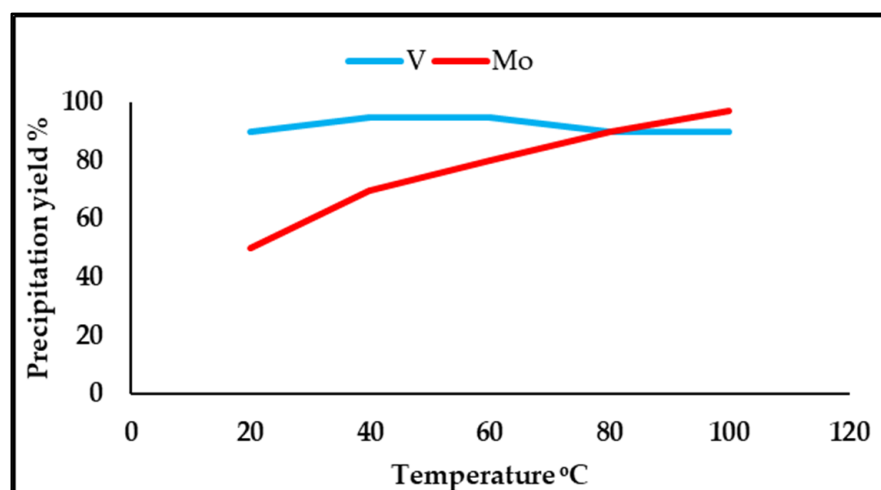


Figure 5. Precipitation yield of molybdenum and vanadium vs. temperature (V: pH 9, time 60 min.; Mo: pH 1, time 60 min.).

3.4.3. Effect of pH on Vanadium and Molybdenum Precipitation

The effect of pH on the precipitation of V and Mo is reported in Figure 6. As shown, pH plays a fundamental role in precipitating metals from the leach solution. At pH 9 (reaction time of one hour and 40 °C as explained above), with over 95% vanadium precipitate. On the other hand, molybdenum requires a highly acidic environment and higher temperatures. At pH 1 (reaction time of one hour and 90 °C), almost all molybdenum in the solution precipitated at a high rate.

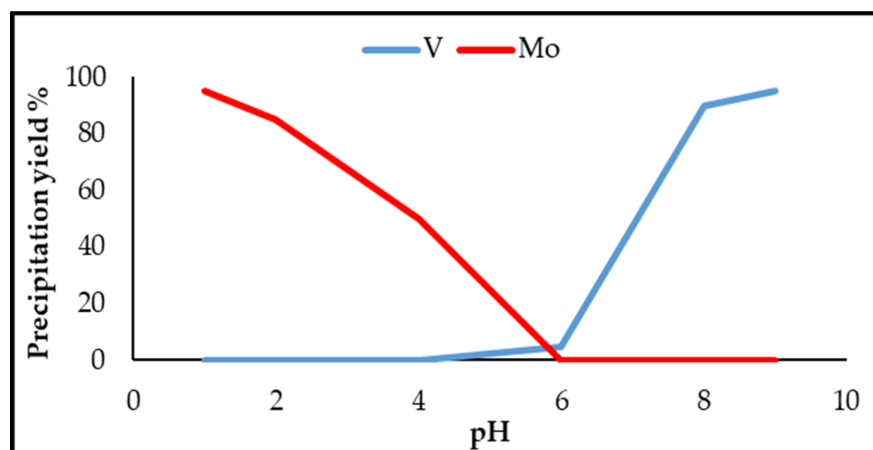
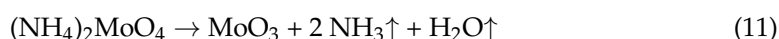
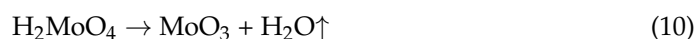


Figure 6. Precipitation yield of molybdenum and vanadium vs. pH (V: 40 °C, time 60 min; Mo: 90 °C, time 60 min.).

3.5. Production of MoO_3 and V_2O_5

Equations (9) and (10) describe the decomposition of molybdate and vanadate. Ammonia and water were released because of the decomposition of these compounds, i.e., NH_4VO_3 and $(\text{NH}_4)_2\text{MoO}_4$ [36]. Different temperatures and times were tried to get the best possible parameters on these recovery steps, and the best option was calcination at 500 °C for 1 h.



There is also some ammonium molybdate that can precipitate together with molybdic acid: this does not represent a problem as that salt is also decomposed during the calcination, according to Equation (11).

Once roasted, both Mo and V salts were cooled down and manually ground; the two products were analyzed by XRD, which showed that the products were V_2O_5 and MoO_3 , as expected (XRD patterns not reported). 0.2 g of each sample were dissolved by aqua regia to measure Mo and V quantitatively in the two oxides recovered according to the procedure reported in Paragraph 2.1: the results showed the grade of the V_2O_5 and MoO_3 was 98.2%wt and 98.4%wt, respectively. Besides that, a further qualitative ICP scan was carried out to detect the highest absorbance relevant to the other elements. The most concentrated impurities were aluminum, sodium, and magnesium, probably in the form of oxides and sulfur (as sulfates).

4. Discussion

4.1. Roasting and Leaching Process

Among various recovery processes already published in the literature [5], we wanted to find an economically and environmentally feasible way. In this context, roasting spent catalysts in a rotary kiln furnace in the presence of Na_2CO_3 , turning Mo and V into soluble salt, and later leaching with water might be an alternative approach. Based on the results, leaching did not achieve high yields for both metals even though different parameters for the roasting were investigated. Elemental analysis of the roasted catalyst revealed the presence of carbon and sulfur, suggesting an unroasted fraction of the catalyst. Moreover, pH is a critical parameter during the leaching and further recovery of metals. Maintaining a pH above eight-nine during the leaching is fundamental to avoiding the partial dissolution of other metals like Co and Ni. In light of this data, powdered Na_2CO_3 (5% wt) was added to keep the pH alkaline, together with an oxidizing agent such as H_2O_2 (5% wt), to try to break the remaining metal-S bond [23]. As a consequence of this new strategy, leaching was improved by 80% for V and 70% for Mo. A further improvement was not possible, and a significant fraction of V and Mo remained in the residue.

4.2. Purification and Selective Precipitation of V and Mo

It is conceivable for some alumina, As, and P to be leached during the leaching process. As and P may then react with molybdenum and vanadium in solution to produce a variety of different compounds that strongly influence the subsequent recovery process, despite the amounts of the components above being very low [30]. ICP data from leached solution revealed small quantities of As and P in the solution. The following route applied elsewhere [30,31] was taken into consideration. After optimization of all reaction parameters, it was highlighted that As and P were no longer present in the solution.

Regarding the selective precipitation of Mo and V, the experiments tested were carried out under specific conditions (see Paragraphs 3.4 and 3.5). Before adjusting the molybdenum parameters, a small amount of vanadium remains in the solution. Nevertheless, vanadium did not precipitate with molybdenum. Otherwise, V should have been reduced from V^{5+} to V^{4+} to avoid precipitation. Molybdenum precipitates with a very high yield at a strongly acidic pH under boiling. Calcination of precipitated salt produces good grade and purified V_2O_5 and MoO_3 .

The overall recovery process is shown below in Figure 7. Table 4 shows the material balance of the whole process based on data from a pilot- and lab-scale test conducted under carefully chosen processing conditions. Molybdenum and vanadium were recovered at 67.9% and 60.8%, according to the initial concentration of metals in the HDS catalyst. The suggested roasting, leaching, and separation methods offer an affordable option for handling the water-leaching waste of used catalysts and may be used in the thorough processing of spent catalysts generated as hazardous waste [37].

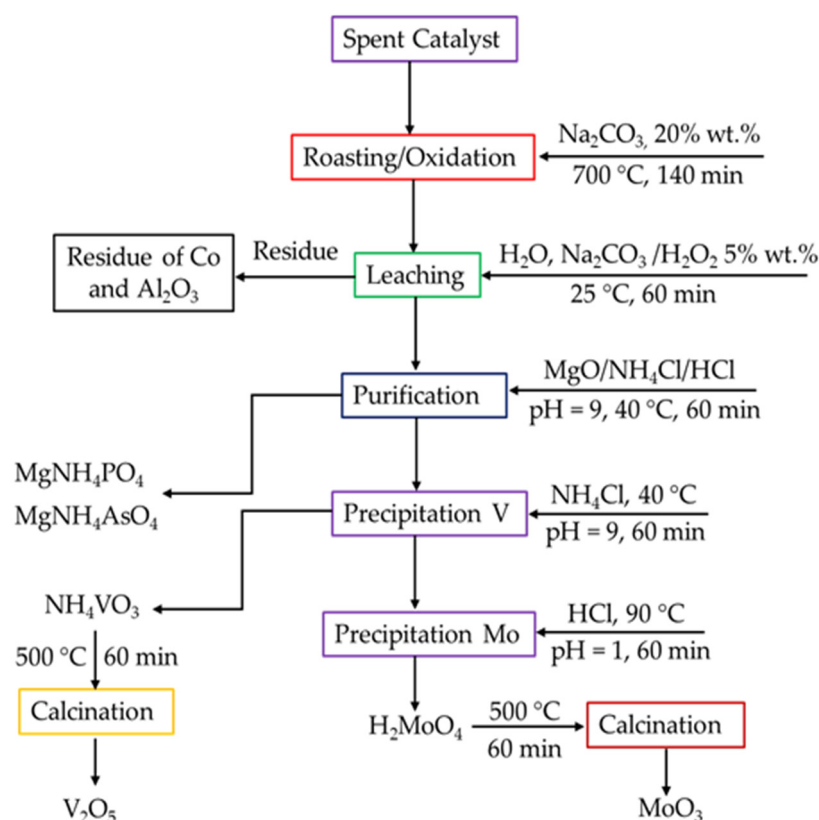


Figure 7. Flowsheet of the overall process.

Regarding the upscaling of the process, it would be necessary to test the hydrometallurgical section on a pilot scale. This way shall be pursued to have more reliable data for robust profitability analysis of the overall recycling route.

The most challenging stage, i.e., roasting, was already tested with a pilot rotary kiln, as described in the present paper. Roasting results are usually very different from simple trials carried out with a laboratory muffle oven, where a small mass is roasted. Thus air can diffuse efficiently through the heap.

Compared to the overall extraction and Mo reported in the most recent literature, higher yields were obtained using oxidative acid leaching with H_2O_2 without roasting as pre-treatment, i.e., 90% of Mo and 83% Co [38]. Park et al. [34] tested alkaline oxidative leaching with Na_2CO_3 and H_2O_2 , recovering about 85% of Mo by carbon adsorption. An alkaline leaching of Co-Mo catalyst with a NaOH solution was tested by Ruiz et al. [39] after roasting at 800 °C. An overall Mo extraction yield of 90% was achieved. Other authors conducted a preliminary roasting with different time and temperature conditions, followed by alkaline leaching with NH_3 , Na_2CO_3 , and NaOH: the extraction yield of Mo—roasting plus leaching—was in the range of 90–98%, compared to the initial concentration in the spent catalyst [40–46].

In most of the studies handling the treatment of Co-Mo catalysts and reviewed in the scientific literature, vanadium extraction was seldom considered.

Vanadium was recovered with Mo from spent Ni-Mo catalysts by Chen et al. [47], after NaOH roasting, by adding barium hydroxide and barium aluminate to the leaching solution: a final recovery of nearly 95% and 93% for V and Mo was achieved, respectively.

A similar process using Na_2CO_3 roasting and water leaching was reported by Chen et al. [48], but Mo and V were extracted and purified by solvent extraction. 88.2% molybdenum and 87.1% vanadium were recovered from such catalysts.

Other researchers used solvent extraction, even after the preliminary roasting obtaining Mo and V extractions up to 98% [49–55].

Acid leaching is another recycling route tested after roasting: the main drawback is that aluminum, cobalt, or nickel are extracted in addition to vanadium and molybdenum: this makes the downstream recovery and separation operations more complicated and expensive [56].

These works were all performed on a laboratory scale, including the most critical stage, i.e., roasting. All the methods tested in the literature show some critical issues compared to our process, in the perspective of upgrading to a bigger scale: acid leaching dissolves Al, Co, and Ni together with Mo and V, so the purification stages are complicated and expensive; moreover, solvent extractions need expensive reagents that have to be reused, producing several spent solutions to treat. After roasting, alkaline leaching consumes more Na_2CO_3 or NaOH, the latter being more expensive.

The thermal process by the rotary kiln is undoubtedly more efficient in removing carbon, sulfur, and hydrocarbons from a big amount of catalyst mass. Nevertheless, a further second stage will be required to improve the leaching stage. In the first roasting stage, C, S, and HC are burnt off quantitatively, whereas, in the second one, soda ash is added: this choice will allow an enhanced reaction between Na and Mo/V ions, leading to the formation of more Na_2MoO_4 and NaVO_3 [21]. After the optimization, the recycling route proposed in this paper could be entirely updated to a pilot scale. It shows clear technical advantages over other recycling methods, as hot water is used as a lixiviant, and high-grade Mo and V are recovered by selective precipitation.

Table 4. Yields of the process stages.

Stage (Yield, %)	V	Mo	Al	Si	P	As	Co	Ni
Leaching	80.0	70.2	ND	ND	<0.1	<0.05	ND	ND
After purification	79.5	69.7	-	-	ND	ND	-	-
Precipitation of V	95.2	-	-	-	-	-	-	-
Precipitation of Mo	-	97.3	-	-	-	-	-	-
Calcination of V (V_2O_5)	89.5	-	-	-	-	-	-	-
Calcination of Mo (MoO_3)	-	90.1	-	-	-	-	-	-
Recovery of V and Mo in the whole process %	67.9	60.8	-	-	-	-	-	-

5. Conclusions

In the present paper, an overall process for the recovery of Mo and V from spent HDS catalysts was reported. The thermal pre-treatment stage was tested by a pilot rotary kiln, whereas the laboratory carried out hydrometallurgical trials.

Spent catalysts generated from refining and petrochemical plants can be a secondary source of molybdenum, vanadium, cobalt, and aluminum. Roasting with soda ash is efficient and cheap for industrial applications and allows the extraction of molybdenum and vanadium after the leaching of the roasted catalyst in water. Under selected experimental conditions, i.e., roasting at 700 °C and adding 20 wt.% soda ash for 140 min, 70% molybdenum, and 80% vanadium were extracted from a Co-Mo catalyst.

After leaching, the pregnant solution was purified by the precipitation of As and P, which represent harmful impurities in steel alloys, as Mo and V are mainly used in the steelmaking industry. Cobalt and nickel remain in the leaching residue, together with the alumina carrier: this material needs further treatment for the extraction of Co and Ni.

V is recovered by selective precipitation at 40 °C and pH 9 as ammonium vanadate, which is thus calcined to obtain commercial-grade V_2O_5 . In the last stage, Mo is mainly recovered as H_2MoO_4 after precipitation at 90 °C and pH 1: molybdic acid is thus calcined at 500 °C for 1 h to get commercial grade MoO_3 . The total recovery yields were around 68% and 61% for V and Mo, respectively.

Regarding future work, a two-stage calcination treatment on the pilot scale is foreseen: the goal is to remove all carbon, coke, sulfur, and residual hydrocarbons before the second treatment with soda ash and enhance the conversion into sodium molybdate and vanadate.

The present work demonstrated that the limiting step in achieving high Mo and V recovery yields, commercially required for the development to the full scale, is the roasting stage.

This double stage will result in an enhancement of the leaching yield and, thus, of the overall process. Furthermore, metals have to be concentrated more in the pregnant solutions, as the precipitation yield certainly improves; for this reason, a counter-current leaching stage must also be tested in future work.

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