



Metal valorization from the waste produced in the manufacturing of Co/Mo catalysts: leaching and selective precipitation

Mohammed F. Hamza, Jean-Claude Roux, Eric Guibal

► To cite this version:

Mohammed F. Hamza, Jean-Claude Roux, Eric Guibal. Metal valorization from the waste produced in the manufacturing of Co/Mo catalysts: leaching and selective precipitation. JOURNAL OF MATERIAL CYCLES AND WASTE MANAGEMENT, 2019, 21 (3), pp.525-538. 10.1007/s10163-018-0811-9 . hal-02425053

HAL Id: hal-02425053

<https://hal.science/hal-02425053>

Submitted on 4 Feb 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Metal valorization from the waste produced in the manufacturing of Co/Mo catalysts: leaching and selective precipitation

Mohammed F. Hamza^{1,2} · Jean-Claude Roux¹ · Eric Guibal¹

Abstract

Two different strategies have been designed for the acid and alkaline leaching steps of hydrodesulphurization catalysts. Tests have been performed on out-of-range catalysts issued from catalyst manufacturing process. Experimental conditions have been screened for these different processes considering the effects of concentration, temperature, solid/liquid ratio, etc. The best conditions have been used for producing two leachates that were treated by precipitation for recovery of valuable met-als such as cobalt and molybdenum. Post-treatments have also been designed for the selective separation of Co from Mo: X-ray diffraction analyses on selective precipitates (as sulfide) confirm the purity of produced materials. Two flow sheets are proposed that allow selectively recovering more than 95% of the valuable metals.

Keywords Hydrodesulfurization catalyst · Co and Mo selective recovery · Alkaline leaching · Acidic leaching · Sulfide precipitation

Introduction

The development of processes for the recovery of valuable metals from WEEE (waste electric and electronic equipment), spent catalysts, fly ash, and low-grade ores became a strategic research field for the last decade due to the high demand for critical metals and the rarefaction of metal resources. Pyrometallurgy and hydrometallurgy are the main processes for valorization of these mineral resources; gravimetric and magnetic separations of grinded materials are the first steps for the enrichment and separation of inorganic solids, prior to calcining, roasting or smelting (for pyrometallurgy) [1, 2] or to leaching (for hydrometallurgy) [3–5]. Hydrometallurgy can be applied after pyrometallurgy has produced enriched solid concentrates for further separation.

The leaching of spent catalysts from oil industry, waste electric, WEEEs, landfill deposits has retained a great attention for the last decades and an abundant amount of literature is available in this field [6–12]. Many techniques have been proposed using acidic leaching [3, 13–15], alkaline leaching [16, 17], chlorination process [18, 19] or bioleaching [20] for metal transfer from the solid waste or low-grade ore to the aqueous phase. The recovery of the valuable metals from leachates is frequently made complex by the presence of multiple metals, including elements like Si and Al that can strongly compete with valuable metals for recovery process, especially due to their very high concentration levels (these elements are the main constituents of the catalyst support or the ore). A wide range of processes can be used for metal recovery from precipitation [21–25] and solvent extraction [26] to binding on ion exchange or chelating resin (and similar materials like sorbents and biosorbents) [27–29]. The choice between the different strategies depends on the metal content in the solid, the presence of inert elements and/or poisoning compounds [5]. In the case of spent catalysts the poisoning of the catalyst surface with organic compounds, unburnt substances, carbon residues may cause a kind of inert effect that frequently requires preliminary calcination and/or oxidation of the solid with strong oxidizing agents.

In the industrial manufacturing of catalysts, the quality control of the products frequently leads to rejecting materials

✉ Eric Guibal
Eric.Guibal@mines-ales.fr

¹ C2MA, IMT Mines Ales, Univ. Montpellier, Alès, France

² Nuclear Materials Authority, PO Box 530, El-Maadi, Cairo, Egypt

that are out of tolerance range in terms of morphology aspects (shape, size), mechanical stability, and active catalyst metal content. These materials may contain valuable metals at relatively high mass concentration; their metal content is also limiting the possibility to discharge these out-of-range catalysts to the environment. In addition, in many countries, the regulations on waste management explicitly require recycling industrial products prior to their discharge into controlled deposits. The recovery of the metals from these materials is much less complex due to the relative purity of these supports (not contaminated with poisoning substances).

The objective of the present research consists of investigating the leaching of out-of-range hydrodesulfurization catalysts (mixed cobalt–molybdenum metals deposited on alumina/aluminosilicate support) before studying the selective separation of valuable metals (Co and Mo) from Al (and Si). Acid and alkaline leachings are successively investigated to evaluate the best process for achieving the selective separation of the metals (in the proper leaching process but also in the integrated process). The effects of reagent type and concentration, the influence of contact time, temperature and solid/liquid (S/L) ratio are investigated. In a second step, the recovery of metals is carried out using pH control (metal hydroxide precipitation) and alternatively by sulfide precipitation, with the objective to be the most selective possible in the separation of valuable metals against Al and Si, but also in the separation of Mo from Co metals. The leaching and recovery efficiencies are systematically evaluated by metal analysis in the aqueous phases, while the composition of products (pristine catalyst, treated material, and final metal precipitates) is evaluated by SEM-EDX analysis.

Materials and methods

Materials and catalyst

The hydrodesulfurization (HDS) catalyst used in this study is a material whose dimensions and/or metal contents were out of the tolerance ranges for industrial use. The raw material is characterized by a rod/slab-like shape (with lateral grooves) with 2 mm lateral dimension and 5–15 mm length. The stock of catalyst was coned and quartered (sample splitter) for preparing identical samples (Figure AM1, see Additional Material Section) [30]. The material was also tested as crushed material (using a ball mill Retsh Bioblock, Ilkirsh, France): the final size after sieving was 100–200 mesh (75–150 μm). A new step of quartering was operated to prepare crushed identical samples that were processed for analysis and leaching.

Reagents of analytical grade were supplied by SigmaAldrich (Taufkirchen, Germany): HCl, H_2SO_4 , HNO_3 , oxalic

acid, and by VWR-Prolabo (Fontenay-sous-Bois, France): sodium carbonate, sodium bicarbonate, sodium sulfide, and hydrogen peroxide.

Characterization of materials

The structure of the catalyst was characterized by X-ray diffraction analysis using a XRD Bruker D8 Advance diffractometer in a θ - θ configuration; the Cu $\text{K}\alpha$ radiation (1.54 \AA) was used with a fixed divergence slit size of 0.6° and a rotating sample stage. The samples were scanned between 5° and 180° with a lynx-eye-1 detector. The qualitative analysis was performed with the X'Pert High Score Plus software (v. 2.1), with the knife edge off.

The textural properties of the catalyst were determined using a surface area and porosity analyzer (Micromeritics TriStar II Plus, Micromeritics Instrument Group, Norcross, GA, USA). The sample (1.05 g) was degassed at 60°C for 48 h prior to processing the N_2 adsorption/desorption cycle.

The elemental composition of the catalyst was determined by acid attack using an aqua regia (1:3 HNO_3/HCl mixture) digestion method [31]: 1 g of crushed catalyst was mixed with aqua regia at 120°C for 40–45 min, the final volume of solution after sample digestion was 27 mL. After cooling, the solution was double-filtrated on 0.45 μm pore-size membrane filter and then diluted with Milli-Q water for further analysis of Mo, Co and Al using an inductively coupled plasma atomic emission spectrometer (ICP-AES, Activa M Horiba Jobin–Yvon, Longjumeau, France).

The materials were also characterized by SEM-EDX analysis using a Quanta FEG 200 (FEI France, Thermo Fisher Scientific, Merignac, France), equipped with an Oxford Inca 350 energy dispersive X-ray micro-analyzer (Oxford instruments France, Saclay, France). The SEM-EDX analysis was performed on the raw catalyst but also on the intermediary products (after leaching operations) and on final products for evaluating the efficiency of leaching, precipitation and the purity of elaborated products.

Procedures for metal leaching

For the testing of metal leaching, different methods (acid leaching and alkaline leaching) were used. With organic and inorganic acids, the catalyst sample (m, 5 g) was introduced in a four-neck glass flask equipped with a condenser, an agitator and a thermometer. Different parameters have been tested such as: particle size (grain, raw rod/slag), acid concentration, solid/liquid ratio (S/L, g L^{-1}), contact time and temperature. For alkaline leaching, the sodium carbonate/sodium bicarbonate mass ratio was varied as well as the concentration of the alkaline mixture (w/w, ratio with total amount of carbonate/bicarbonate mixture, for example, ratio 1:2 for a 10% concentration: 3.33 g of Na_2CO_3 + 6.67 g of

NaHCO₃ for 100 mL of water), the *S/L* ratio, the contact time and the temperature. It is noteworthy that for the study of *S/L* ratio, the wetting of dry catalyst represented a volume of leaching agent almost equivalent in mass to the amount of catalyst, and the *S/L* ratio will actually correspond to the ratio of solid to residual volume of leachate. As a consequence, the *S*/leachate volume = 1/*n* corresponds to the experimental *S*/leaching agent = 1/(*n* + 1).

Leachate samples were collected in the supernatant of the liquor of acid/alkaline leaching in the reactor. After filtration through 0.45 µm pore-size membrane filter metal concentrations were obtained by ICP-AES. The leaching efficiency was calculated by the mass balance equation.

Procedures for precipitation

The acidic leachates were treated by precipitation using sodium sulfide (40%), sodium hydroxide (5 M), while alkaline leachates were first neutralized using concentrated sulfuric acid then precipitated using sodium sulfide (40%, w/w). A fixed volume of leachate was pH controlled using the precipitating agent. The mixture was maintained under agitation in a jar test at the rotating speed of 200 rpm for 1 h. The metal concentration in the solution after filtration was analyzed using ICP-AES. The mass balance equation was used for calculating the precipitation efficiency and the recovery efficiency of the metal from the catalyst.

These characterizations were completed by SEM-EDX analysis for evaluating the purity of precipitates and the presence of residual amounts of metals in the catalyst at the different stages of the recovery processes.

Repeatability issues

Preliminary tests were performed on 5 g amounts of catalysts for evaluating the general impact of individual parameters and pre-selecting experimental conditions. In a second step of the study, the amounts of processed catalysts were increased to 50 and 100 g. The repeatability was evaluated. Tables AM1 and AM2 (see Additional Material Section) show a summary of the comparison of data considering the EDX analysis of precipitates obtained in the different compartments for both acidic and alkaline leaching processes. Tables AM3 and AM4 report the metal concentrations, leaching and precipitation efficiencies at different stages of the two leaching processes. These data confirm that the extraction and separation performances are reproducible. In most cases, the variation did not exceed 3–5% (for target metal subject to specific treatment). The selected optimum conditions have been used for treating an amount of 500 g of catalyst and preparing a sufficient amount of leachates for extensive study of selective metal precipitation and separation.

Results and discussion

Characterization of catalysts

The metal contents in the catalyst, as determined by aqua regia digestion, are 1.79, 8.51 and 27.45% for Co, Mo and Al, respectively (Table 1). These values are consistent with those found using SEM-EDX (Figure AM2a, see Additional Material Section): 1.68% for Co, 8.12% for Mo, 23.34% for Al, and 8.08 for Si. As a comparison, the fraction of these elements in the solid was also determined by concentrated nitric acid and hydrochloric acid treatments: the contents are consistent for Co and Al but slightly underestimated for Mo in the case of nitric acid.

Figure AM2b shows the XRD diffraction pattern of the catalyst. This diffractogram is poorly resolved. However, the most significant bands representative of ill crystallized alumina can be identified (with PDF reference: 00-004-0458). The presence of Si element (at a mass percentage of 8.08%, or 5.73% atomic percentage) shows that the support may also contain silicate or aluminosilicate. This could explain the poor resolution of X-ray diffraction pattern.

Textural analysis (not shown) allowed determining the principal characteristics of the catalyst material: BET surface area close to 245 m² g⁻¹, the pore volume close to 0.4 cm³ g⁻¹ and the pore size close to 65 Å. This confirms the high porosity of the catalyst and may explain the relatively facile access of the metal deposits to the leaching solutions.

The Co–Mo catalysts supported on alumina are usually prepared by successive impregnation steps of the alumina support with metal solutions in different orders of impregnation. In most cases, the cobalt is deposited on alumina support before impregnating the Al–Co material with molybdenum: the Co exists as a thin layer between the Mo layer and the Al support [32]. In the pristine HDS catalyst molybdenum is under the oxidized form (Mo(VI)) while after sulfidation (spent catalyst) the metal can be partially reduced [32].

Table 1 Metal content (% w/w) in the catalyst (concentrated acid treatment, digestion with aqua regia, 1:3 HNO₃/HCl solution, and EDX analysis on the solid) (solid: 1 g; final volume: 27 mL; contact time: 40–45 min; temperature: 120 °C)

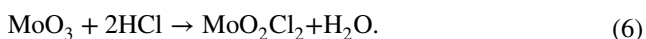
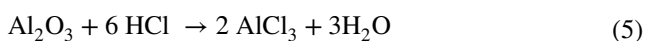
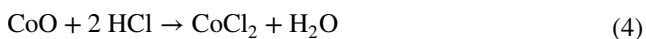
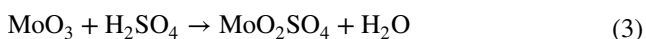
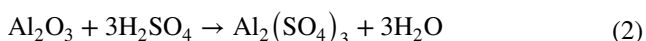
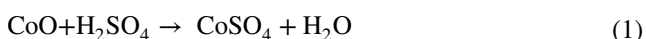
Metal	HNO ₃	HCl	Aqua regia	EDX analysis
Al	25.83	25.22	27.45	23.34
Mo	5.41	7.50	8.51	8.12
Co	1.68	1.62	1.79	1.68
Si	n.d	n.d	n.d	8.08

nd not determined

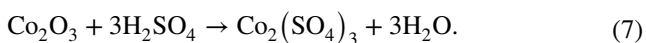
Metal leaching

Acid leaching

Effect of the type of acid Table 2 reports the effect of the acid used on the leaching of Al, Mo and Co. The tests were performed on both raw catalyst (R) and crushed catalyst (C) at two levels of concentration of the acid (50 and 100 g L⁻¹). The cross-variation show consistent trends: the leaching efficiency is slightly increased with increasing acid concentration, regardless of the metal. The acid does not affect Al leaching contrary to Mo and Co that are more efficiently leached by sulfuric acid than nitric or hydrochloric acid (which are equally recovered by these two acids). In the case of acidic leaching of spent hydrosulfurization catalysts, Valverde et al. [33] reported the formation of several species depending on the acid used (sulfuric acid vs. hydrochloric acid):



Lai et al. [12] concluded that a mixture of acids (2:1:1 HNO₃/H₂SO₄/HCl) is optimal for the recovery of Ni, Mo and V from spent HDS catalyst (with limited selectivity in the leaching). They commented that the introduction of concentrated HCl contributed to the formation of metal–chloride complexes that enhance metal leaching. The oxidation state of the metal in the catalyst may affect the reaction (and metal species present in the leachate); in the case of partially pre-oxidized HDs catalyst, Kim et al. [11] reported the additional reaction:



In most cases, the size of the material hardly changes the leaching efficiency (by a few %) except in the case of Co removal using sulfuric acid where decreasing the particle size significantly improves by 11% the efficiency of metal leaching (this means a relative increase of about 50% compared with raw material). The limited effect of particle size means that the metal sites are highly accessible: the porosity of the catalyst may explain this result (see above).

The efficiency in metal recovery is of the same order for Mo and Co and much higher than for Al. Al is the core and support of the catalyst (alumina and aluminosilicate): the proportion of aluminum is then much higher than that of the catalytic metals. This may explain the lower release of this metal under selected experimental conditions. The poor leaching of Al is interesting for the objective of separating valuable metals from the structural core of the catalyst. In addition, the catalytic metals are supposed to be deposited as a thin layer on the porous surface of the support; this means that metal sites can be well-accessed and better dissolved by the acid than the metal from core support.

These preliminary results show that sulfuric acid is the most efficient leaching agent for the treatment of these Co/Mo catalysts. Alternative acidic treatments have been tested for the recovery of metals from ores and catalysts or spent materials using organic acids [3, 34], including oxalic acid [35]. Some tests were carried out for the recovery of Al, Co and Mo from the catalyst material using oxalic acid at the concentration of 50 g L⁻¹; the leaching efficiency remained very low: 1.46–1.63% for Al, 1.55–2.62% for Mo and 1.30–2.59% for Co in raw and crushed catalysts. The efficiency of this alternative leaching agent is strongly increased using a strong oxidative agent: hydrogen peroxide has been successfully used for this purpose [6, 9, 36]. A complementary test was then performed using a higher concentration of oxalic acid (i.e., 100 g L⁻¹) in the presence of hydrogen peroxide (at the concentration of 0.2 M, and with a 1:25 S/L ratio). The leaching efficiency was strongly increased: 37.25% for Al, 28.52% for Co and up to 99.98% for Mo. This means that a huge amount of leaching agent is necessary for reaching the complete recovery of molybdenum, while significant amounts of Al and Co are simultaneously leached making complex the separation of the metals

Table 2 Effect of acid type (sulfuric acid, hydrochloric acid and nitric acid) and strength (50 g L⁻¹ or 100 g L⁻¹) on the efficiency of metal leaching (%) from raw material (R) and crushed (C) samples (Solid: 5 g; Acid volume: 5.2 mL; agitation time: 2 h; T: 23 ± 2 °C)

Metal	Sample	Sulfuric acid		Hydrochloric acid		Nitric acid	
		50 g L ⁻¹	100 g L ⁻¹	50 g L ⁻¹	100 g L ⁻¹	50 g L ⁻¹	100 g L ⁻¹
Al	R	4.98	5.50	4.70	5.02	4.43	4.73
	C	4.06	7.27	4.71	5.08	5.15	5.36
Mo	R	25.95	26.74	17.56	21.96	16.54	18.11
	C	27.94	30.55	13.79	15.56	17.09	18.33
Co	R	19.39	24.61	19.50	21.44	18.26	21.97
	C	31.06	35.48	17.42	19.81	19.25	20.49

Table 3 Effect of sulfuric acid concentration (g L^{-1}) on the efficiency of metal leaching from raw (R) and crushed (c) materials (Solid: 5 g; Acid volume: 5.2 mL; agitation time: 2 h; T: 23 ± 2 °C)

Metal	Sample	Sulfuric acid concentration (g L^{-1})							
		50	100	150	200	250	300	400	500
Al	R	5.21	2.11	8.59	10.13	11.57	11.61	12.97	13.81
	C	3.58	6.86	10.21	10.18	10.85	15.03	15.18	15.25
Mo	R	25.95	26.74	33.20	31.77	35.53	37.11	38.64	38.53
	C	27.94	30.55	29.05	28.11	31.44	38.11	39.09	38.99
Co	R	19.39	24.61	36.71	36.92	39.72	40.31	40.42	42.68
	C	31.06	35.48	39.38	31.31	31.66	41.45	39.02	36.93

in the next step of the process for metal recovery (i.e., precipitation): the precipitation of huge amounts of aluminum will probably co-precipitate substantial amounts of valuable metals. Beside the consumption of large quantities of oxalic acid (2.5 kg per kg of catalyst) and the dilution of the metals (due to the S/L ratio of 1:25), it is a non-selective leaching that makes this process not really competitive, despite the complete recovery of molybdenum. For these reasons, the study was focused on sulfuric acid because of the relatively good leaching performance and the less expensive cost of this reagent.

Effect of H_2SO_4 concentration The influence of sulfuric acid concentration on the leaching efficiency is reported on Table 3. As expected, increasing acid concentration enhances metal recovery. However, the table clearly shows that Al recovery increases with acid concentration while for Co and Mo the leaching yield tends to stabilize when the concentration of sulfuric acid reaches $250\text{--}300 \text{ g L}^{-1}$: the benefits of increasing acid concentration on metal recovery is almost negligible and uneconomic. In addition, an excessive amount of acid will require using higher concentrations or volumes of alkaline solutions for further metal precipitation in the next step of the recovery process. Crushing the catalyst has a limited effect on leaching yield except for Co recovery at low sulfuric acid concentration: milling the catalyst hardly affects the equilibrium performance and it is expected that the main effect of material size is associated to leaching kinetic, although the porosity of this material probably minimizes this effect. An acidic concentration of 300 g L^{-1} is selected for further studies: the leaching efficiencies reach 11.6–15.0, 37.1–38.1, and 40.3–41.4% for Al, Mo and Co, respectively.

Effect of S/L ratio The S/L ratio is an important criterion that may influence both the efficiency of leaching but also the metal concentration in the leachate. Increasing the volume of leaching solution usually improves the yield of dissolution but at the expense of a dilution of metal ion in the final solution. The optimization of the process should then take into account the efficiency and the dilution effect. Table 4 summarizes the results obtained varying the volumes of sul-

Table 4 Effect of solid/liquid ratio (S/L) (g L^{-1}) on the efficiency of metal leaching with sulfuric acid (300 g L^{-1} solution) from crushed material (Solid: 5 g; Acid volume: 5.2–25.2 mL; agitation time: 2 h; T: 23 ± 2 °C)

Metal	Acid volume (mL) S/L ratio (1:N)				
	5.2	10.2	15.2	20.2	25.2
	1:1	1:2	1:3	1:4	1:5
Al	15.03	16.21	19.16	24.03	27.11
Mo	38.11	45.60	51.62	62.49	71.92
Co	41.45	44.72	50.20	59.31	67.72

Table 5 Effect of contact time (h) on the efficiency of metal leaching with sulfuric acid (300 g L^{-1} solution) from crushed material (Solid: 5 g; Acid volume: 20.2 mL; T: 23 ± 2 °C)

Metal	Agitation time (h)				
	2	3	4	5	6
Al	24.03	26.39	37.25	37.40	41.60
Mo	62.49	81.03	90.43	92.20	98.55
Co	59.31	75.52	83.43	86.44	90.48

furic acid (300 g L^{-1}) used for the treatment of 5 g of catalyst. Dissolution yield continuously increases with the volume of acid for the three metals. However, when the volume exceeds 15 mL, leaching efficiency tends to stabilize around 24% for Al, 62.5% for Mo and 59.3% for Co. The concentrations of the metals in the leachates approach 15 g Al L^{-1} , 10.8 g Mo L^{-1} and 2.4 g Co L^{-1} when using S/L ratio of 1:4. Above $S/L = 1:4$, the concentration in the leachate tends to decrease while dissolution is only slightly increased. A good compromise between metal concentrations in the leachate and desorption efficiency is obtained setting S/L ratio to 1:4, this value was selected for investigating the effect of leaching time.

Effect of leaching time Maintaining the suspension in agitation for a longer time obviously allows increasing the leaching of metal ions (Table 5). After 6 h of agitation, Al recov-

ery reaches 41.6%, while for Mo and Co the leaching yields 98.5 and 90.5%, respectively. Increasing the contact time has a main drawback on the practical point of view since it decreases the volumetric flux of treatment and/or increases the dimension of the treatment unit. The potential advantage of increasing the contact time should be measured taking into account the flux of treatment of the solid. Actually, the increase in contact time only allows slightly increasing the efficiency of leaching. With a contact time of 4 h the leaching efficiencies reach up to 37.2, 90.4 and 83.4% for Al, Mo and Co, respectively. This compromise was selected for optimizing the temperature effect.

The effect of contact time on the leaching efficiency was modeled using the shrinking core model (SCM) with different control modes (i.e., film diffusion, particle layer diffusion control, and reaction rate) [37]. Table AM5 (see Additional Material Section, for data exploitation and reminder on kinetic equations) reports the kinetic parameters (rate coefficients) and the correlation parameters (ordinate intercept in the linearization of model equations, and determination coefficient, R^2). The best correlation was obtained with the SCM associated to particle layer diffusion control (highest relative R^2 , and lowest ordinate intercept), which plays the major role in the kinetic control. However, the fits were not perfect and the leaching kinetic is probably controlled by a combination of different mechanisms. A more sophisticated model could be used [37], but it would require extending the number of experimental data. Another way to confirm this analysis would consist of testing the effect of particle size on the kinetic profile: crushing the catalyst slabs did not change the leaching yield but the kinetics were not compared for raw and crushed catalyst. It is noteworthy that in the acid leaching process the rate coefficients for the three metals were ranked according: Mo (0.122 h^{-1}) > Co (0.078 h^{-1}) > Al (0.011 h^{-1}), while the equilibrium values were of the same order of magnitude for Mo and Co leaching.

Effect of temperature Table 6 compares the leaching efficiencies at three temperatures 25, 50 and 100 °C. The yield of metal removal drastically increases between 25 °C and 50 °C up to 65.6% for Al, 99.9% for Mo and 98.8% for Co. Increasing again the temperature to 100 °C is counter-productive: the marginal increase in Mo and Co recovery (which are complete) are accompanied by the simultaneous complete recovery of Al. The leachates at 100 °C will then

Table 6 Effect of temperature (°C) on the efficiency of metal leaching with sulfuric acid (300 g L⁻¹ solution) from crushed material (Solid: 5 g; Acid volume: 20.2.2 mL; agitation time: 4 h)

Metal	Temperature (°C)		
	23 ± 2	50 ± 2	23 ± 2
Al	37.25	65.59	99.71
Mo	90.43	99.92	100
Co	83.43	98.81	99.23

contain huge amounts of aluminum that will make more complex the selective separation of Mo and Co from Al without being justified by a beneficial recovery of valuable metals. It seems that a temperature close to 50 °C will be sufficient for reaching the efficient recovery of target metals without overloading the composition of the leachates with Al, in the perspective of selective precipitation post-treatment.

To verify the reproducibility of the experiments and to also evaluate the impact of temperature on Co and Mo leaching kinetics, additional kinetic experiments were performed at 25 °C, 50 °C and 100 °C (Fig. 1). As the temperature increases the required contact time decreases and 4 h are sufficient in most cases for removing more than 90% of the total amount of metal that can be leached. Molybdenum is slightly faster released than cobalt. This is confirmed by Table AM6 (see Additional Material Section) that reports the modeling of kinetic profiles with the FDC, PLDC and

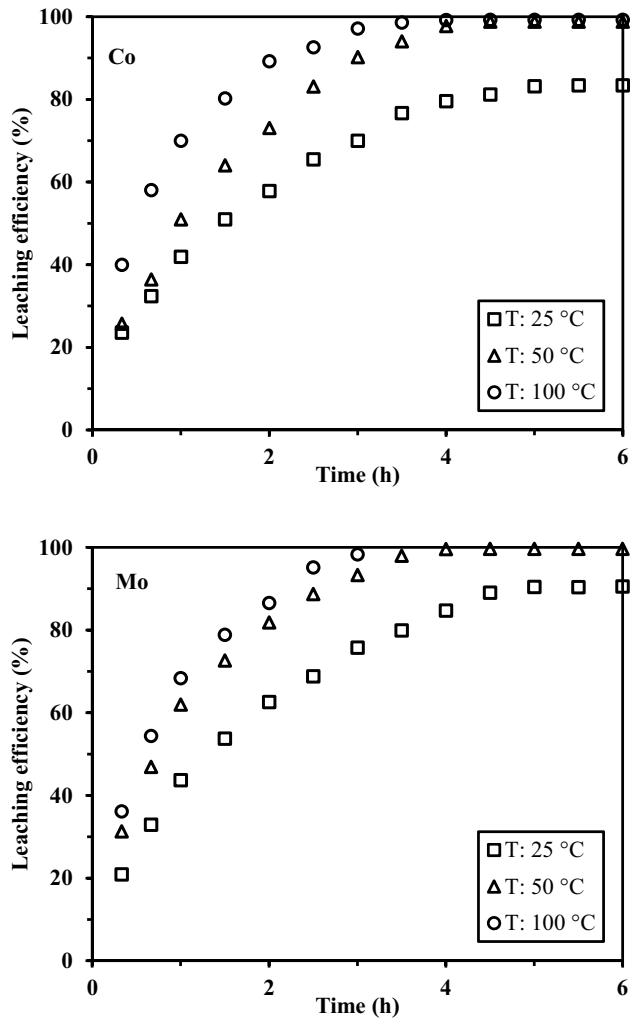


Fig. 1 Kinetics of Co and Mo acid leaching at different temperatures (300 g L⁻¹ H₂SO₄, Solid: 5 g; Acid volume: 15.2 mL)

RC modes of the SCM model. Again, the FDC model failed to fit experimental profiles and the leaching curves are best fitted by the SCM-PLDC and the SCM-RC equations. The rate coefficients for PLDC and RC (k_i , h) have been used for calculating the activation energy (E_a , kJ mol⁻¹) for the acid leaching of Co and Mo [Tanda, 2018 #2630]:

$$k_i = Ae^{-E_a R/T}, \quad (8)$$

where A is a frequency factor, T the absolute temperature (K) and R the universal gas constant (J mol⁻¹ K⁻¹).

The activation energies (average values calculated using the rate coefficients of both SCM-PLDC and SCM-RC) are close to 12.3 (± 0.12) and 10.7 (± 0.21) kJ mol⁻¹ for Co and Mo, respectively (Figure AM3, see Additional Material Section). This confirms that Mo can be slightly more readily leached from the catalyst than Co.

Alkaline leaching

Acid leaching can be well-controlled and maintained at a lower cost, but the process generates leach liquor with significant concentrations of aluminum, which complicates downstream processing [38, 39]. Alkaline leaching may be an alternative or complementary leaching process making profit of the differences in the chemistry of the target metals. Indeed, alkali carbonates (sodium or less commonly ammonium) are used for selective leaching of some elements that form stable soluble carbonate complex. Alkali carbonate leaching has several important advantages over acid leaching like its selectivity: comparatively pure solutions are readily obtained beside its non-corrosive nature [40]. Also, the consumption of the reagent by the ore is low and some elements can be readily recovered from the leach liquors. Finally, the carbonate solutions can be readily regenerated for further recycling of the leaching agent [41]. However, there are some limitations to the use of carbonate leaching due to its mild nature: some minerals are not solubilized by carbonate leach solutions. Moreover, it requires fairly fine grinding of the ore to obtain reasonable reaction rates [42]. Alternatively, carbonate leaching could be performed under relatively high pressure and temperature in suitable autoclaves [43]. Generally, sodium chlorate is used in carbonate leaching circuit [30, 44]. Sodium hydroxide resulting from the reaction may contribute to increase the pH of the solution pH, which, in turn, causes the precipitation of some elements. Therefore, to prevent an excessive rise of the pH (and unwanted metal re-precipitation), sodium bicarbonate is frequently used to the reactive media.

Effect of Na₂CO₃/NaHCO₃ ratio Molar ratio between carbonate and bicarbonate was varied by increasing the amount of bicarbonate with fixed concentration of carbonate (Table 7). The recovery of aluminum and cobalt is negligible and

Table 7 Effect of Na₂CO₃/NaHCO₃ ratio on the efficiency of metal leaching from crushed material (Solid: 5 g; alkaline concentration: 10% (w/w); alkaline solution volume: 5.3 mL; agitation time: 2 h; T: 23 \pm 2 °C)

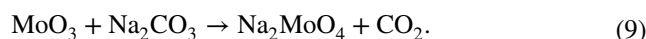
Metal	Na ₂ CO ₃ /NaHCO ₃		
	1:1	1:2	1:3
Al	0.09	0.12	0.10
Mo	18.47	21.53	20.15
Co	0.01	0	0

Table 8 Effect of solid/liquid ratio (S/L) on the efficiency of metal leaching from crushed material using alkaline solution (Solid: 5 g; alkaline concentration: 10% (w/w); Na₂CO₃/NaHCO₃: 1:2; alkaline solution volume: 5.3–25.2 mL; agitation time: 2 h; T: 23 \pm 2 °C)

Metal	Na ₂ CO ₃ /NaHCO ₃ (mL) S/L ratio (1:N)				
	5.3	10.2	15.4	20.3	25.2
	1:1	1:2	1:3	1:4	1:5
Al	0.12	0.29	0.34	0.32	0.35
Mo	21.53	43.98	53.87	53.81	59.94
Co	0.00	0	0	0	0

S/L ratio represents the mass of solid divided by the actual volume of leachate; the wetting of the catalyst with the leaching solution represented 2.5 mg of solution and this means that compared to the used volumes of leaching solutions the S/L ratio could be written 1:2, 1:3, 1:4, 1:5 and 1:6

poorly affected by this molar ratio. On the opposite hand, the alkaline leaching allows recovering 18.5–21.5% of Mo with a limited effect of the ratio between carbonate and bicarbonate: molybdenum leaching is slightly higher with a 1:2 Na₂CO₃/NaHCO₃ ratio. Alkaline solutions readily dissolve Mo(VI), which is the oxidized form present on the catalyst [32], to form molybdate species while the other metals on the catalyst cannot be dissolved in alkaline conditions. These conditions allow recovering selectively Mo from the catalyst. This is consistent with the comments of Ferella et al. [45] who reported the selective extraction of Mo and V from HDS catalysts using alkali leaching; partial leaching of alumina was reported while cobalt was segregated in the solid residue. Mo was dissolved through the reaction:



Effect of S/L ratio Increasing the volume of alkaline leaching solution does not affect Al and Co leaching while the recovery of Mo from the catalyst is increased (Table 8). The highest increase in metal recovery is observed when volume of leaching agent is increased from 5 mL to 15 mL (S/L ratio increasing from 1:1 to 1:3). Above, the increase in Mo leaching is not sufficient for justifying the increased consumption of the reagent. In addition, the concentration of molybdenum in the leachate progressively decreases when increasing the volume of leaching agent. A good compromise between Mo desorption yield and concentration crite-

Table 9 Effect of $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ concentration (g L^{-1}) on the efficiency of metal leaching from crushed material (Solid: 5 g; alkaline concentration: 10–30% (w/w); $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$: 1:2; alkaline solution volume: 15.4 mL; agitation time: 2 h; T: 23 ± 2 °C)

Metal	$\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ concentration (% w/w)				
	10	15	20	25	30
Al	0.34	0.47	0.45	0.45	0.43
Mo	53.87	72.63	69.77	69.76	66.39
Co	0	0	0	0	0

Table 10 Effect of temperature (°C) on the efficiency of metal leaching from crushed material using alkaline solutions (Solid: 5 g; alkaline concentration: 15% (w/w); $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$: 1:2; alkaline solution volume: 15.4 mL; agitation time: 2 h; T: 25–100 °C)

Metal	Temperature (°C)		
	23 ± 2	50 ± 2	100 ± 2
Al	0.47	1.11	1.92
Mo	72.63	80.47	86.05
Co	0	0.27	0.86

tion appears to be using a 1:3 S/L ratio with the 1:2 molar ratio $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ (10% w/w carbonate/bicarbonate concentration): the leaching yields almost 54% while the concentration of Mo in the leachate reaches up to 12.4 g Mo L^{-1} .

Effect of carbonate/bicarbonate concentration When varying alkaline concentration from 10% to 30%, Al leaching does not exceed 0.47% while cobalt is not recovered at all from the catalyst, on the opposite hand the maximum Mo leaching (i.e., 72.6%) is obtained at 15% w/w (Table 9). Molybdenum recovery decreases again when the concentration of the alkaline leaching agent exceeds 15% (w/w).

Effect of temperature Carbonate/bicarbonate mixture being a mild leaching agent, playing with temperature may influence the efficiency of the process. This is confirmed by Table 10: increasing the temperature from 23 to 100 °C allows dissolving very small amounts of Al and Co (less than 2 and 1%, respectively); on the opposite hand, molybdenum leaching is significantly increased from 72.6% to 86.0%. The concentrations of Al, Co and Mo reach up to 1.63 g Al L^{-1} , 47.5 mg Co L^{-1} and 19.95 g Mo L^{-1} . The leaching conditions are remarkably selective for Mo over Co but significant amounts of the support element (i.e., Al) are simultaneously leached.

Effect of leaching time Increasing the reaction time slightly increased Al and Co leaching (Table 11); however, even after 6 h of contact the leaching efficiencies do not exceed 2.3 and 1.9%, respectively. For Mo the leaching efficiency increases up to 95.2% after 5 h of reaction while above

Table 11 Effect of agitation time (h) upon the leaching efficiencies of metal values from crushed material using alkaline solutions (Solid: 5 g; alkaline concentration: 15% (w/w); $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$: 1:2; S/L ratio: 1:4; alkaline solution volume: 15.4 mL; T: 100 °C (± 2 °C))

Metal	Agitation time (h)				
	2	3	4	5	6
Al	1.92	1.92	1.98	2.09	2.25
Mo	86.05	88.32	91.36	95.19	95.12
Co	0.86	0.95	1.5	1.68	1.86

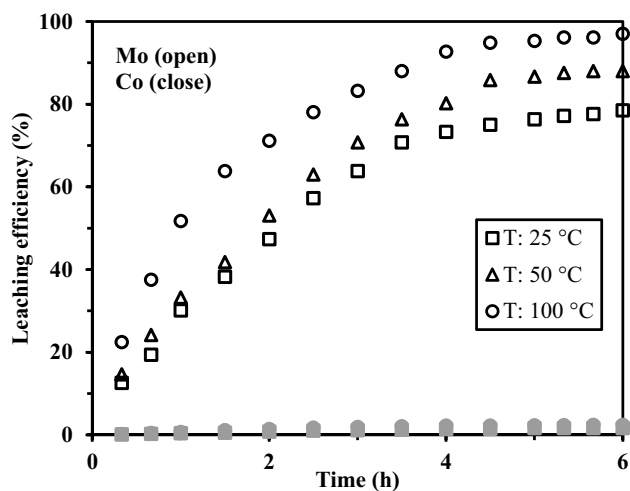


Fig. 2 Kinetics of Co and Mo alkaline leaching at different temperatures (Solid: 5 g; alkaline concentration: 15% (w/w); $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$: 1:2; alkaline solution volume: 15.4 mL; T: 25–100 °C)

metal recovery tends to stabilize. Then, it is not necessary increasing the reaction time above 5 h: the metal concentrations in the leachate approach 1777 mg Al L^{-1} , 92.5 mg Co L^{-1} and up to 22.07 g Mo L^{-1} . As for acidic leaching, the equations for SCM controlled by film diffusion, particle layer diffusion and reaction rate have been tested (see Table AM5, Additional Material Section). None of the models fits experimental profiles for Mo (the leaching of other metals was negligible and the kinetic profiles are not meaningful).

Complementary tests were performed to evaluate the impact of temperature on leaching kinetics (Fig. 2). Table AM7 reports the rate coefficients for Co and Mo leaching using the different equations. Co leaching is limited to less than 3% (consistently with previous results): increasing the temperature to 100 °C did not change the leaching efficiency and the kinetics were not significantly changed (overlapping of the curves). The rate coefficients for Mo were analyzed using the Arrhenius equation (Eq. 8; Figure AM4, see Additional Material Section) and the coefficients obtained for both SCM-PLDC and SCM-RC equations: the activation energy reaches 9.0 (± 0.33) kJ mol^{-1} ; this is slightly lower

than the activation energy for sulfuric acid leaching (i.e., 10.5 kJ mol⁻¹).

Precipitation of metals from pregnant leaching liquors

Acid leachates

Production and characterization of acid leachate The optimization of the acidic leaching concluded that the best conditions for metal recovery of metals from catalysts correspond to the use of sulfuric acid solution (2.5 L) at the concentration of 300 g L⁻¹ with *S/L* ratio of 1:5 maintaining the temperature to 50 ± 2 °C under agitation for 4 h. The leaching efficiencies reach up to 65.6% for Al, 98.8% for Co and 99.9% for Mo. These experimental conditions have been applied for treating 500 g of catalyst under an agitation speed of 400 rpm. At the end of the process, the aqueous phase was recovered by filtration under vacuum and the metal concentrations were determined: 42.485 g Al L⁻¹, 4.097 g Co L⁻¹ and 17.27 g Mo L⁻¹. This corresponds to leaching efficiencies of 66.6, 99.0 and 99.1% for Al, Co and Mo, respectively: these results are consistent with the results obtained on small-size tests. This is also consistent with the SEM-EDX analysis of the residue of acidic leaching (Figure AM5, see Additional Material Section): Co and Mo have disappeared from the SEM-EDX spectra, while Al content is decreased to 4.39% (compared to 23–27% in the pristine catalyst material). The residue is mainly constituted of silicate that was not dissolved by sulfuric acid solution [46]; Si represents 30.45% of the residue contrary to only 8.1% for pristine catalyst. It is interesting to observe that the values of leaching efficiencies are remarkably consistent with the values obtained in the preliminary optimization study (see Sect. 3.2.1.5.).

Precipitation of metal ions from acidic leachates by pH control The pH of acid leachates was controlled between pH 1 and 5 using NaOH or H₂SO₄ (5 M) solutions (Figure AM6, see Additional Material Section). The precipitation of the different metals increases with pH: metal precipitation is negligible at pH 1–2 and becomes appreciable at pH 5. It is noteworthy that the three metal ions have very similar precipitation profiles: the metal ions cannot be separated by a simple precipitation method.

Selective separation by sulfide precipitation Sulfur dissociation properties and metal sulfide precipitation are strongly influenced by the pH of the solution. This may explain that sulfide precipitation process is widely used for metal separation [47]; this method is usually more selective than simple pH-controlled alkali precipitation. Different metal sulfides/bisulfides may be formed depending on the metal and the

pH, including M(SH)⁺, M₂(SH)³⁺ and M₃(SH)⁵⁺ [48], or simple sulfur complexes MS [49]. In the separation of Mo and Co from spent HDS catalysts, Vemic et al. used sodium sulfide for the selective precipitation of metal ions [21]. The precipitation of the metal ions with sodium sulfide was first investigated at pH 2 using increasing amounts of sulfide (10–40%, w/w) (Fig. 3). Increasing sulfide concentration slightly increases metal precipitation: with 40% Na₂S concentration the precipitation leads to the recovery of 8.9, 97.0 and 97.6% for Al, Co and Mo, respectively. This means that the precipitate contains significant amounts of aluminum that cannot be easily separated from the precipitate. Decreasing the pH to 1 (and maintaining the same sodium sulfide concentrations) decreases the precipitation of Al to about 1.2% (Figure AM7, see Additional Material Section) while maintaining almost constant the precipitation of Co and Mo, at a very high level (i.e., 99.7% and 99.9% for Co and Mo, respectively). Controlling the pH to 1 with a Na₂S concentration close to 40% is a solution for selectively recovering the valuable metals. In the sulfide precipitation of Mo, Co and Ni from synthetic leachates, Vemic et al. [21] suggested processing the precipitation of Ni and Co (as sulfide precipitates) at pH 4, before precipitating Mo at pH 1. With real acidic leachates, the presence of zinc decreases the efficiency of the process. In the present case, the leachates contain Al, processing the precipitation of Co at higher pH (i.e., 4–5) would also lead to co-precipitation of Al and make difficult the separation of the different metals. For these reasons, it is preferred separating Mo and Co as precipitates at pH 1 while maintaining aluminum in solution.

After Mo and Co precipitation at pH 1, the filtrate, which contains an Al concentration close to 41.99 g L⁻¹, is treated by alkaline precipitation using 30% NaOH (w/w) solution and adjusting the pH to 5. A white precipitate

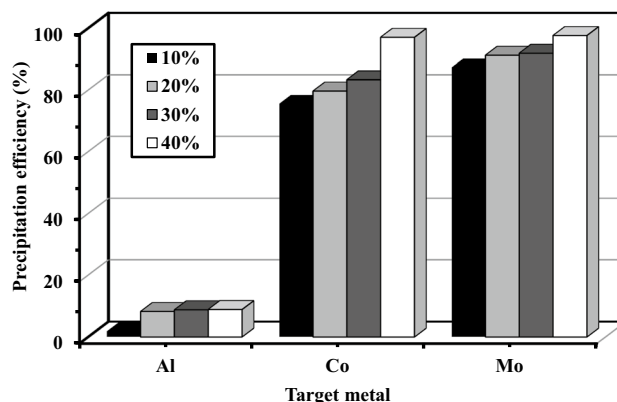
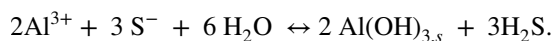
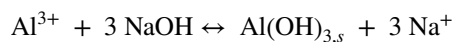


Fig. 3 Effect of sodium sulfide concentration (10–40%, w/w) on precipitation of Al, Co and Mo at pH 2 (volume of solution: 130 mL per L of leachate, T: 23 ± 2 °C; agitation time: 1 h; pH control with 5 M NaOH/H₂SO₄ solutions; C₀: 40.45 g Al L⁻¹, 4.09 g Co L⁻¹ and 17.25 g Mo L⁻¹)

appears, the SEM-EDX analysis of this precipitate (Figure AM8, see Additional Material Section) confirms that molybdenum and cobalt are correctly separated from aluminum since the elements do not appear on EDX spectrum. Al content reached 20.1% (accompanied by O element: 70.9%) and there are traces of sulfide (i.e., 8.8%) and Na element (i.e., 0.2%). It is noteworthy that the presence of sulfide ions contributes to improve the precipitation of aluminum hydroxide according to [50]:



Selective separation of Co and Mo from sulfide precipitate Figure AM9 (see Additional Material Section) shows the EDX analysis of the sulfide precipitate of acidic leachate [pH 1, 40% (w/w) Na_2S]. Al is not appearing in the EDX spectrum as a confirmation of the selective separation of valuable metals from the metal of the catalyst support: Co element reaches 9.9% (against 40.3% for Mo element). The Mo/Co mass ratio in the pristine catalyst (close to 4.8) is of the same order than in the mixed precipitate (i.e., 4.1); however, after metal leaching and selective reprecipitation the Mo/Co atomic ratio decreases from 2.9 to 1.2.

To separate Mo from Co, an alkaline leaching of the precipitate was carried out. The Co/Mo cake (109.7 g, resulting from the acidic leaching and final sulfide precipitation of 500 g of pristine catalyst) is mixed with 440 mL of 15% (w/w) alkaline solution (1:2 carbonate/bicarbonate mixture) for 4 h (under agitation, 400 rpm) at 100 ± 2 °C. The filtrate was recovered for further precipitation of Mo using Na_2S after neutralization by sulfuric acid solution while the insoluble product consists of Co precipitate, which was washed up two times with hot water to remove unreacted carbonate and purify the insoluble Co precipitate (about 22 g). The filtrate (390 mL) is neutralized using sulfuric acid before processing the precipitation of molybdenum with sodium sulfide (150 mL of a 40% w/w Na_2S solution for 1 h). Figure AM10 (see Additional Material Section) shows the EDX analysis of the precipitate obtained after carbonate leaching of Co/Mo cake (Mo dissolving) and final acidic Mo precipitation (after calcination at 900 °C). These spectra show relatively pure products despite the presence of traces of sodium (i.e., around 0.4%) in molybdenum sulfide precipitate.

Figures AM11 (see Additional Material Section) shows the EDX spectra of the solid residue after alkaline leaching of Mo from the Co/Mo, after two successive steps of solid washing of Co-based solid. After the second step of purification, the traces of aluminum disappear and a relatively pure Co-based product (cobalt sulfide) is obtained (Co elements counts for 43.0% and S element for 14.4%); the presence of O element (about 42.6%) is probably associated to an

incomplete drying of the precipitate or the moistening of the material.

Alkaline leachates

Production and characterization of alkaline leaching liquor The production of the alkaline pregnant leaching liquor was performed in a reactor maintained under agitation and under reflux at 100 ± 2 °C for 5 h. The catalyst (500 g) was mixed with 2.5 L of 15% $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ solution (1:2 mixture). The remaining solid was washed three times with 500 mL of hot water (i.e., $S/L = 1:1$) for 30 min; this step is supposed to dissolve any carbonate present in the solid. The pre-treatment allows reducing the amount of acid to be used in the next step for acid leaching and contributes to improve the competitiveness of Mo recovery. It is noteworthy that washing solution can then be recycled for preparing the leaching step for the processing of alkaline leachates. Figure AM12 (see Additional Material Section) shows the residue after carbonate leaching process indicating removal of Mo; the residue contains mainly Si, Al and Co.

Selective Mo recovery

In a second step, Na_2S was added to the solution to reach a 40% (w/w) concentration. The step allows precipitating Mo from the alkaline leachate as molybdenum sulfide (producing about 46 g of solid, corresponding to precipitation efficiency close to 98.2%). Figure AM13 (see Additional Material Section) shows the SEM-EDX analysis of the molybdenum sulfide precipitate (S element is in the range 61.0–62.2%, and Mo element between 35.9 and 39.0%); small traces of sodium can be detected (around 1.5%); however, other elements initially present in the catalyst are negligible. This is consistent with the ICP-AES analysis that shows negligible concentrations of Al, Si, and Co in the alkaline leachate, this also confirms the results obtained in the preliminary study. After burning/roasting at 900 °C, the molybdenum sulfide residue only contains molybdenum (Figure AM14, see Additional Material Section).

Selective recovery of Si

The residue of alkaline leaching (after water washing) that represents an amount of 455 g (over the initial amount of 500 g of catalyst) was mixed with 2.3 L of sulfuric acid (300 g L^{-1} concentration) for 4 h at 50 °C under agitation (speed 400 rpm). The pH of the filtrate was controlled to 2 using concentrated sulfuric acid. Acidic treatment allows (a) completely removing cobalt, (b) removing the last traces of Mo, and (c) removing most of Al. After vacuum filtration, the solid residue was collected and analyzed by SEM-EDX (Figure AM15, see Additional Material Section, after drying

at 100 °C for 10 h): silicate-based compound is predominant in the solid phase (i.e., Si: 35.5% and O: 58.5%) with traces of aluminum (about 0.71%, w/w) and carbon (around 5.3%). The filtrate is supposed to contain aluminum, and cobalt.

Selective recovery of Co

The sulfuric acid filtrate (after Mo and Si removal) was precipitated by controlling the pH to 1 and adding sodium sulfide (200 mL of 40% w/w Na_2S) under agitation for 2 h, at room temperature. This step allows producing cobalt sulfide with high purity, as shown on Figure AM16 (see Additional Material Section). The weight fractions of Co and S elements are close to 34.9% and 24.6%, respectively, the remaining major element is oxygen (around 40.5%).

Selective recovery of Al

A final filtration step (after Co removal) allowed recovering a white precipitate by pH control at 5 (using 450 mL of 30% NaOH w/w solution) under agitation (agitation speed: 400 rpm) for 1 h. SEM-EDX analysis confirms the purity of the aluminum hydroxide (Figure AM17, see Additional Material Section, after drying at 100 °C for 10 h). Aluminum represents 22.8–25.0%, while oxygen varies between 69.4%

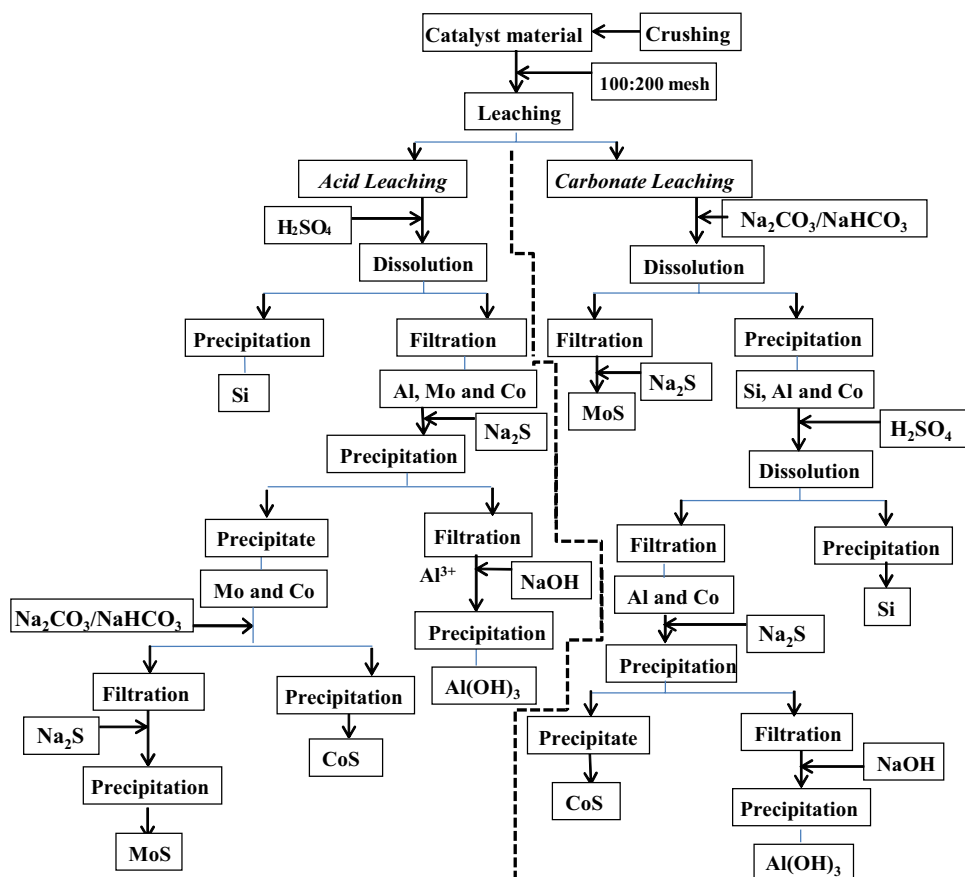
and 70.9%. Traces of S element (i.e., 3.8–4.4%) and Na element (i.e., 1.2–2.5%) are also observed.

Suggested flowsheet for metal recovery from waste products

Baes and Mesmer [51] deeply investigated the hydrolysis of cations. Aluminum has a minimal solubility close to neutral pH: in acidic conditions Al(III) is solubilized; in alkaline conditions the solubilized aluminum appears under the form of Al(OH)_4^- . On the other hand, cobalt is poorly soluble in alkaline conditions, requiring acidic conditions for increasing the solubility. In the case of molybdenum, a broad range of pH conditions is favorable to metal solubilization; however, in very acidic conditions the solubility of molybdenum is decreased (formation of MoO_3). Obviously, these general trends may be affected by the composition of the solution, the oxidation state of the metal in the catalyst, and the type of acid or alkaline agent used for metal leaching. Metal sulfate precipitation or carbonate complexation of metals (respectively) can affect the overall solubility of target metals.

Figure 4 shows the flowsheet of catalyst treatment for the selective recovery of metals. The sequence of operating steps is briefly reminded for both acid and alkaline leaching

Fig. 4 Flowsheet for the separation of Al, Co and Mo from the crude catalyst material



strategies. Tables 12 and 13 show the percentage distribution of target metals (i.e., Al, Co, and Mo) in the different compartments, i.e., liquid and solid phases or residues generated in the process. The mass balance is respected in most cases: a little variation is observed for Mo in the acid leaching process (total balance differs by 1%). The recovery of valuable metals (i.e., Co and Mo) is almost quantitative: higher than 99% for Co, and higher than 97% for Mo. In addition, the recovery of these metals is very selective as identified on EDX spectra of cobalt and molybdenum sulfides (pure products); the distribution of Co and Mo in the different compartments is also clearly showing that Co and Mo are selectively recovered in the two compartments, though some traces can be found in some liquid and solid phases the relative loss amount does not exceed a few percent. The flowsheet clearly shows that both the acid and alkaline leaching processes allows recovering selectively the target metals, providing an appropriate selection of precipitation and purification steps are applied.

Table AM8 (a&b) (see Additional Material Section) summarizes the main costs for expenditures (reagents and energy for thermal control) for both the acid leaching and the alkaline leaching processes. These data (which can be only considered as rough estimates of the operative costs; requiring more rigorous calculations for commercial application) demonstrate that the acidic leaching is slightly cheaper than the alkaline leaching; the difference represents only 4 € per kg of processed catalyst.

Conclusion

A series of leaching (acid or alkaline), selective precipitation (using sulfide) and purification steps (alkaline leaching and precipitation) can efficiently be used for selective recovery of cobalt and molybdenum from hydrosulphurization catalysts (non-spent but out-of-range materials). Both the acidic and the alkaline leaching procedures

Table 13 Distribution of metals (Al, Co and Mo) in the different compartments of the alkaline leaching process (normalized values)

Compartment	#	Al	Co	Mo
Aqueous phase after MoS precipitation	C1	2.0	1.0	2.4
Aqueous phase after final Al(OH) ₃ precipitation	C2	0.6	2.3	0.5
Solid residue after acid leaching of Co/Mo cake	C3	0.9	0.1	0.0
Solid phase in MoS precipitate	C4	0.0	0.0	95.5
Solid phase in CoS precipitate	C5	0.6	94.5	0.0
Solid phase in Al(OH) ₃ precipitate	C6	95.9	2.0	1.6
Effective metal recovery in selective compartment ^a		95.9	94.5	95.5

Bold values identify the compartments where the greatest amounts of selected metal ions are recovered

^a: calculated by comparison to initial metal amount in 500 g of catalyst; mass balance close to 100%

can be used for quantitative recovery of valuable metals. SEM-EDX characterization on the selective precipitates and residue confirm the high efficiency in both recovery and selectivity (purity of elaborated solids). The possibility to use both acid and alkaline treatment lines offers great flexibility in the selection of methods, depending on the characteristics of the waste products. These different strategies provide useful information for the valorization of metals from out-of-range products during the manufacturing of catalysts. This information could be also useful for the treatment of spent catalyst although the presence of poisonous substances, unburnt residues may alter the efficiency of the recovery process. This may help in the design of processes for metal recycling from industrial manufacturing of catalysts and other metal-bearing systems, in coherence with the international policies and politics for waste recycling.

Table 12 Distribution of metals (Al, Co and Mo) in the different compartments of the acid leaching process (normalized values)

Compartment	#	Al	Co	Mo
Aqueous phase after Na ₂ S precipitation of acid leachate	A1	66.6	0.3	0.1
Aqueous residue (End of the process)	A2	0.0	1.0	0.6
Solid residue after acid leaching	A3	33.4	1.0	0.9
Solid phase in CoS precipitate	A4	0.0	97.7	1.8
Solid phase in MoS precipitate	A5	0.0	0.0	96.6
Effective metal recovery in selective compartments ^a		66.6	97.7	95.7

Bold values identify the compartments where the greatest amounts of selected metal ions are recovered

^aCalculated by comparison to initial metal amount in 500 g of catalyst; mass balance on Al and Co close to 100%, and close to 99% for Mo

Acknowledgements Authors acknowledge the financial support of French Government (Institut Français d'Égypte, French Embassy in Egypt) through the fellowship granted to M.F. Hamza.

References

- Mohapatra D, Park KH (2007) Selective recovery of Mo, Co and Al from spent Co/Mo/gamma-Al₂O₃ catalyst: Effect of calcination temperature. *J Environ Sci Health Part A Toxic/Hazard Subst Environ Eng* 42(4):507–515
- Le H-L, Yamasue E, Okumura H, Ishihara KN (2014) Improving sustainable recovery of metals from waste printed circuit boards by the primary copper smelter process. *J Mater Cycles Waste Manag* 16(2):298–305
- Huang K, Inoue K, Harada H, Kawakita H, Ohto K (2011) Leaching of heavy metals by citric acid from fly ash generated in municipal waste incineration plants. *J Mater Cycles Waste Manag* 13(2):118–126
- Rudnik E, Pierzynka M, Handzlik P (2016) Ammoniacal leaching and recovery of copper from alloyed low-grade e-waste. *J Mater Cycles Waste Manag* 18(2):318–328
- Navarro R, Guzman J, Saucedo I, Revilla J, Guibal E (2007) Vanadium recovery from oil fly ash by leaching, precipitation and solvent extraction processes. *Waste Manag (Oxford)* 27(3):425–438
- Liu J, Qiu ZF, Yang J, Cao LM, Zhang W (2016) Recovery of Mo and Ni from spent acrylonitrile catalysts using an oxidation leaching-chemical precipitation technique. *Hydrometallurgy* 164:64–70
- Pinto ISS, Soares H (2012) Selective leaching of molybdenum from spent hydrosulphurization catalysts using ultrasound and microwave methods. *Hydrometallurgy* 129:19–25
- Barik SP, Park KH, Parhi PK, Park JT (2012) Direct leaching of molybdenum and cobalt from spent hydrosulphurization catalyst with sulphuric acid. *Hydrometallurgy* 111:46–51
- Szymczycha-Madeja A (2011) Kinetics of Mo, Ni, V and Al leaching from a spent hydrosulphurization catalyst in a solution containing oxalic acid and hydrogen peroxide. *J Hazard Mater* 186(2–3):2157–2161
- Ruiz V, Meux E, Schneider M, Georgeaud V (2011) Hydrometallurgical treatment for valuable metals recovery from spent Co/Mo/Al₂O₃ catalyst. 2. Oxidative leaching of an unroasted catalyst using H₂O₂. *Ind Eng Chem Res* 50(9):5307–5315
- Kim HI, Park KH, Mishra D (2009) Sulfuric acid baking and leaching of spent Co-Mo/Al₂O₃ catalyst. *J Hazard Mater* 166(2–3):1540–1544
- Lai YC, Lee WJ, Huang KL, Wu CM (2008) Metal recovery from spent hydrosulfurization catalysts using a combined acid-leaching and electrolysis process. *J Hazard Mater* 154(1–3):588–594
- Wu Y, Wang B, Zhang Q, Li R, Sun C, Wang W (2014) Recovery of rare earth elements from waste fluorescent phosphors: Na₂O₂ molten salt decomposition. *J Mater Cycles Waste Manag* 16(4):635–641
- Zhang X, Xie Y, Lin X, Li H, Cao H (2013) An overview on the processes and technologies for recycling cathodic active materials from spent lithium-ion batteries. *J Mater Cycles Waste Manag* 15(4):420–430
- Zhang P, Ma Y, Xie F (2013) Impacts of ultrasound on selective leaching recovery of heavy metals from metal-containing waste sludge. *J Mater Cycles Waste Manag* 15(4):530–538
- Pinto ISS, Soares HMVM (2013) Recovery of molybdates from an alkaline leachate of spent hydrosulphurization catalyst - proposal of a nearly-closed process. *J Cleaner Prod* 52:481–487
- Alonso F, Ramirez S, Ancheyta J, Mavil M (2008) Alternatives for recovering of metals from heavy hydrocarbons spent hydrotreating catalysts a case of study. *Rev Int Contamin Amb* 24(2):55–69
- Zeng L, Cheng CY (2009) A literature review of the recovery of molybdenum and vanadium from spent hydrosulphurization catalysts Part I: metallurgical processes. *Hydrometallurgy* 98(1–2):1–9
- Gaballah I, Djona M, Mugica JC, Solozobal R (1994) Valuable metals recovery from spent catalysts by selective chlorination. *Resour Conserv Recycl* 10(1–2):87–96
- Li J, Liang C, Ma C (2015) Bioleaching of gold from waste printed circuit boards by *Chromobacterium violaceum*. *J Mater Cycles Waste Manag* 17(3):529–539
- Vemic M, Bordas F, Comte S, Guibaud G, Lens PNL, van Hullebusch ED (2016) Recovery of molybdenum, nickel and cobalt by precipitation from the acidic leachate of a mineral sludge. *Environ Technol* 37(17):2231–2242
- Chen T, Lei C, Yan B, Xiao XM (2014) Metal recovery from the copper sulfide tailing with leaching and fractional precipitation technology. *Hydrometallurgy* 147:178–182
- Fernandes A, Afonso JC, Dutra AJB (2013) Separation of nickel(II), cobalt(II) and lanthanides from spent Ni-MH batteries by hydrochloric acid leaching, solvent extraction and precipitation. *Hydrometallurgy* 133:37–43
- Cibati A, Cheng KY, Morris C, Ginige MP, Sahinkaya E, Pagnanelli F, Kaksonen AH (2013) Selective precipitation of metals from synthetic spent refinery catalyst leach liquor with biogenic H₂S produced in a lactate-fed anaerobic baffled reactor. *Hydrometallurgy* 139:154–161
- Zhang H, He P-J, Shao L-M, Li X-J (2008) Leaching behavior of heavy metals from municipal solid waste incineration bottom ash and its geochemical modeling. *J Mater Cycles Waste Manag* 10(1):7–13
- Fernandes A, Afonso JC, Dutra AJB (2012) Hydrometallurgical route to recover nickel, cobalt and cadmium from spent Ni-Cd batteries. *J Power Sources* 220:286–291
- Pinto ISS, Sadeghi SM, Izatt NE, Soares H (2015) Recovery of metals from an acid leachate of spent hydrosulphurization catalyst using molecular recognition technology. *Chem Eng Sci* 138:353–362
- Zawierucha I, Kozłowski C, Malina G (2013) Removal of toxic metal ions from landfill leachate by complementary sorption and transport across polymer inclusion membranes. *Waste Manag (Oxford)* 33(10):2129–2136
- Soukand U, Kangsepp P, Kakum R, Tenno T, Mathiasson L, Hogland W (2010) Selection of adsorbents for treatment of leachate: batch studies of simultaneous adsorption of heavy metals. *J Mater Cycles Waste Manag* 12(1):57–65
- Habashi F (1997) Handbook of extractive metallurgy. Wiley-VCH, Weinheim
- Niemela M, Pitkaaho S, Ojala S, Keiski RL, Peramaki P (2012) Microwave-assisted aqua regia digestion for determining platinum, palladium, rhodium and lead in catalyst materials. *Microchem J* 101:75–79
- Portela L, Grange P, Delmon B (1995) XPS and NO adsorption studies on alumina-supported Co-Mo catalysts sulfided by different procedures. *J Catal* 156(2):243–254
- Valverde IM Jr, Paulino JF, Afonso JC (2008) Hydrometallurgical route to recover molybdenum, nickel, cobalt and aluminum from spent hydrotreating catalysts in sulphuric acid medium. *J Hazard Mater* 160(2–3):310–317
- Erust C, Akcil A, Bedelova Z, Anarbekov K, Baikonurova A, Tuncuk A (2016) Recovery of vanadium from spent catalysts of sulfuric acid plant by using inorganic and organic acids: Laboratory and semi-pilot tests. *Waste Manag (Oxford)* 49:455–461

35. Nguyen TH, Lee MS (2015) Development of a hydrometallurgical process for the recovery of calcium molybdate and cobalt oxalate powders from spent hydrosulphurization (HDS) catalyst. *J Cleaner Prod* 90:388–396
36. Aydogan S, Aras A, Ucar G, Erdemoglu M (2007) Dissolution kinetics of galena in acetic acid solutions with hydrogen peroxide. *Hydrometallurgy* 89(3–4):189–195
37. Tanda BC, Eksteen JJ, Oraby EA (2018) Kinetics of chalcocite leaching in oxygenated alkaline glycine solutions. *Hydrometallurgy* 178:264–273
38. Chander S (1982) Atmospheric-pressure leaching of nickeliferous laterites in acidic media. *Trans Indian Inst Met* 35(4):366–371
39. Terekhov DS, Emmanuel NV (2013) Direct extraction of nickel and iron from laterite ores using the carbonyl process. *Miner Eng* 54:124–130
40. Schortmann WE, DeSesa MA (1958) Kinetics of the dissolution of uranium dioxide in carbonate-bicarbonate solutions. In: National Lead Co., Inc. Raw Materials Development Lab., Winchester, Mass. page(s): 17, Medium: X
41. Beverly RG, Charles WD (1958) Pilot Plant alkaline leaching of uranium ores. US Government Printing Office
42. Sohn HY, Wadsworth ME (1979) Rate processes of extractive metallurgy. Springer US, New York
43. Aly MM, Hamza MF (2013) A Review: studies on uranium removal using different techniques. *Overview J Dispers Sci Technol* 34(2):182–213
44. Merritt RC (1971) The Extractive Metallurgy of Uranium. Colorado School of Mines Research Institute, [Golden
45. Ferella F, Ognyanova A, De Michelis I, Taglieri G, Veglio F (2011) Extraction of metals from spent hydrotreating catalysts: Physico-mechanical pre-treatments and leaching stage. *J Hazard Mater* 192(1):176–185
46. Svehla G (1996) Vogel's qualitative inorganic analysis. Addison Wesley Longman Ltd, Harlow
47. Lewis AE (2010) Review of metal sulphide precipitation. *Hydrometallurgy* 104(2):222–234
48. Luther GW, Rickard DT, Theberge S, Olroyd A (1996) Determination of metal (bi)sulfide stability constants of Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} by voltammetric methods. *Environ Sci Technol* 30(2):671–679
49. Bhattacharyya D, Jumawan AB, Grieves RB (1979) Separation of toxic heavy metals by sulfide precipitation. *Sep Sci Technol* 14(5):441–452
50. Shapiro L (1975) Rapid analysis of silicate, carbonate, and phosphate rocks. In: U.S. Geol. Surv. Bull., Vol. 76, pIII, Report Number 1401, pp. 88
51. Baes CF Jr, Mesmer RE (1976) Hydrolysis of cations. Wiley, New York