



Extraction of metals from spent hydrotreating catalysts: Physico-mechanical pre-treatments and leaching stage

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ABSTRACT

The present paper is focused on physico-mechanical pre-treatments of spent hydrotreating catalysts aimed at concentration of at least one of the valuable metals contained in such secondary raw material. In particular, dry Ni–Mo and Co–Mo as well as wet Ni–Mo catalysts were used. Flotation, grain size separation and attrition processes were tested. After that, a rods vibrating mill and a ball mill were used to ground the catalysts in order to understand the best mechanical pre-treatment before leaching extraction. The results showed that flotation is not able to concentrate any metals due to the presence of coke or other depressant compounds. The particle size separation produces two fractions enriched in Mo and Co when dry Co–Mo catalyst is used, whereas attrition is not suitable as metals are uniformly distributed in rings' volume. Roasting at 550 °C and vibrating grinding are the most suitable pre-treatments able to produce fractions easily leached by NaOH and H₂SO₄ after grain size separation.

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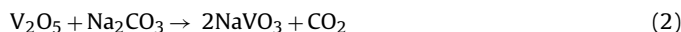
1. Introduction

Catalysts are widely used in petroleum refining and chemical industries; hydrotreating catalysts usually consist of molybdenum (Mo) supported on an alumina or silica carrier together with promoters such as cobalt (Co) or nickel (Ni): they enhance removal of undesirable impurities such as sulphur, nitrogen and metals like vanadium (V) in feedstocks by promoting hydrodesulphurization (HDS), hydrodenitrogenation (HDN) and hydrodemetallization (HDM) reactions [1,2]. The volume of spent hydroprocessing catalysts has increased significantly in recent years due to a rapid growth in distillates hydrotreating capacity to meet the increasing demand of ultra-low sulphur fuels, a steady increase in processing of heavier feedstock containing greater amount of sulphur and metals and a rapid deactivation with unavailability of reactivation processes for some of the hydroprocessing catalysts. After few cycles of regeneration, catalyst activity may decrease to very low levels and further regeneration may not be economically feasible or possible. Among secondary resources, spent catalysts are undoubtedly very important not only for their economic value but also for environmental concerns when disposed off, as they have been classified as hazardous wastes [2,3]. Several hydro- and pyrometallurgical processes have been proposed for metals recovery

from spent HDS catalysts. The most important metals recovered from HDS catalysts are Mo, Ni and Co, but Al (20–35 wt%) often represents a co-product which can be valorized avoiding dumping [4,5]. Furthermore, many of these catalysts contain V ranging from 0.5 to even 8 wt%, and this makes treatment of this material more viable.

A summary of the most important and recent studies on recovery of metals from hydrotreating catalyst is reported in Table 1. Recovery of vanadium, when present, is always greater than 90% with respect to the concentration in spent catalysts [4,5].

Since these catalysts contain sulphur, coke and sometimes hydrocarbons like naphtha, a pre-treatment is usually required to oxidize the organic matter. The two-steps process industrially used includes roasting of catalysts in air at 600 °C and a second roasting of the resulting material at 600–800 °C in presence of soda ash (Na₂CO₃): the aim is to convert molybdenum and vanadium oxides to soluble sodium molybdate and vanadate [16].



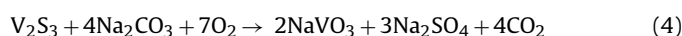
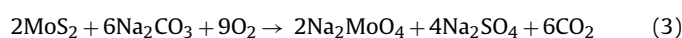
The roasted material is leached with water at 80–90 °C and atmospheric pressure to dissolve the soluble molybdenum and vanadium compounds. The insoluble Ni–Co–alumina filter cake is treated separately to recover those metals. Sometimes soda ash is directly mixed in a single roasting stage and this results in a greater

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Table 1
Summary of the most important experimental studies carried out on spent hydrotreating catalysts.

Catalyst	Pre-treatments	Leaching reagents	Co recovery, %	Mo recovery, %	Ni recovery, %	Reference
Co–Mo Ni–Mo	Roasting (500 °C, 5 h)	Leaching by H ₂ SO ₄ 9 mol L ⁻¹ , 90 °C, 2 h	98	99	98	[4]
Co–Mo Ni–Mo	Grinding	Fusion with KHSO ₄ (350–600 °C, 0.5–7 h)	87–90	96–99	91–94	[5]
Spent HDS catalyst	Washing (H ₂ O) Drying Grinding	– Na ₂ CO ₃ or NaOH (85 g L ⁻¹) + H ₂ O ₂ (10 vol%) – Ammonium molybdate precipitation – Roasting (450 °C)	–	85–97 MoO ₃	Not measured	[6]
Spent HDS catalyst (NiMo/γ-Al ₂ O ₃)	Washing (acetone) Drying Grinding	– Na ₂ CO ₃ (40 g L ⁻¹) + H ₂ O ₂ (6 vol%) – Carbon adsorption – Desorption (NH ₄ OH) – Roasting (450 °C)	–	99.4 MoO ₃	Not measured	[7]
Spent HDS catalyst (Co/Ni/Mo–Al ₂ O ₃)	Washing (acetone) Drying Roasting (500 °C)	– Na ₂ CO ₃ (30 g L ⁻¹) – H ₂ SO ₄ (6 mol L ⁻¹) – Solvent extraction of Al (Cyanex 272)	93%	98	90	[8]
Spent hydro-refining catalyst	–	– 600 °C air roasting + Na ₂ CO ₃ (12 wt%) for 30 min – Water leaching (90 °C) – Chemical treatment – Adsorption/desorption method	Not measured	92 Na ₂ MoO ₄	Not measured	[9]
Spent hydro-refining catalyst	–	– 900 °C air roasting + NaCl (20 wt%) – Water leaching (70–90 °C) for 60 min – Chemical treatment	Not measured	90 Na ₂ MoO ₄	Not measured	[10]
Co–Mo Ni–Mo	Roasting (450 °C, 2 h)	Two-steps alkali-acid procedure (1) Alkaline leaching → dissolution of Mo (10 g L ⁻¹ ; NaOH; 80 °C; 1/20 S/L) (2) Acidic leaching → dissolution of Co/Ni (10 g L ⁻¹ ; H ₂ SO ₄ ; 80 °C; 1/20 S/L)	80	97	80	[11]
Spent HDS catalyst	Heating (300 °C, 30 min)	– Acidic leaching, 70 °C (HNO ₃ /H ₂ SO ₄ /HCl = 2:1:1)	–	90	99	[12]
Spent HDS catalyst	Washing (toluene)	– Electrolysis Acidic leaching, 50 °C	–	90	65	[13]
Spent HDS catalyst	Heating (400 °C, 4 h)	0.5 mol L ⁻¹ H ₂ C ₂ O ₄ + 3 mol L ⁻¹ H ₂ O ₂ – Acidic leaching, 80 °C (H ₂ SO ₄ + H ₂ O ₂) – Alkaline leaching, 80 °C (NaOH + H ₂ O ₂) + Al precipitation at pH 8	81	72	Not measured	[14]
Ammonia leaching residue	Roasting with Na ₂ CO ₃	Water leaching (90 °C, 15 min, 50% S/L)	–	91	–	[15]

consumption of salt, since sulphur reacts with sodium according to the reactions:



Reactions (3) and (4) can be considered as a first step of flue gas treatment (sulphur capture), giving a reduction of the amount of the alkaline reagent during desulphurization stage. However, the pregnant solution obtained after the water leaching is contaminated by huge amounts of sodium sulphate which can give problems during precipitation of Mo and V. Although sodium hydroxide, sodium bicarbonate and sodium sulphate have been used in direct salt roasting, sodium carbonate is the most used due to its lower cost. A good review on processes currently available for recovery of molybdenum and vanadium can be found in Zeng and Cheng [17,18]. The recycling processes can be classified as follows, according to the stages used:

1. **Acid leaching.** There are two main routes to treat spent catalysts: one is direct acid leaching under pressure and high temperature; the other is an acid leaching at atmospheric pressure and temperature lower than 100 °C after roasting. Untreated catalysts can also be leached by using an acid medium with one chemical oxidant such as H₂O₂ or HNO₃. Acid leaching is commonly used if recovery of all metals from the spent catalyst is required. Ni, Mo, V, Co and alumina dissolve whereas little dissolution of sil-

ica can take place. Sulphuric, hydrochloric, nitric or organic acids like oxalic and citric are used.

2. **Basic leaching.** Alkali leaching can be used to selectively dissolve molybdenum and vanadium from spent HDS catalysts. It also dissolves some aluminum but leaves nickel and cobalt in the solid residue. In most cases, metal sulphides are oxidized first by roasting; hence, soluble sodium molybdate, vanadate and aluminate form and dissolve in leaching solution. There are three main routes, including roasting followed by caustic leaching, direct hot caustic leaching under pressure and caustic/sodium aluminate leaching. Cobalt and/or nickel in solid residue can be extracted by acid. Alternatively, the residue can be sent to smelters or hydrometallurgical plants specialized in separation and recovery of nickel and cobalt. However, direct atmospheric leaching especially at low caustic concentration is not practicable because of low extraction of molybdenum and vanadium.

Several methods for separation, purification and recovery of molybdenum and vanadium from leach solutions are currently used; main techniques include sulphide precipitation, ammonium salt precipitation, carbon adsorption, ion exchange and solvent extraction [4–11,19–21]. Once nickel and cobalt are extracted from the solid residue of the water or alkaline leaching, they can be recovered by precipitation; however, due to their very similar physico-chemical properties, a concentrate is obtained only, otherwise a solvent extraction stage is required [22–25]. The aim of the present paper was to obtain one or more fractions concen-

trated in Mo, V, Ni or Co by using mechanical processes typical of mining industry in order to reduce material that undergoes hydrometallurgical processes. Furthermore, influence of two types of grinding as well as of different particle size was also investigated during roasting and leaching. This is the first research that studies flotation, attrition and grain size separation of spent hydrotreating catalysts before recycling. The present paper gives interesting information and results on which pre-treatments are the most appropriate to maximize extraction yields of leaching stage.

2. Materials and methods

2.1. Characterization of catalysts

Three different spent HDS catalysts were used in this study: in particular, a Ni–Mo and a Co–Mo black dry catalysts of different shapes (powder, spheres, cylinders and scraps) and a wet Ni–Mo (Lc-Finer) catalyst consisting of small pieces of cylindrical shape covered by naphtha. Catalysts were dried in oven (Mod. 780, Galli) at 105 °C for 24 h until constant weight was reached; then, weight loss was determined by an analytical balance (PE600, Mettler). Samples were ground by a lab-ball mill (PM100, Retsch) and screened to obtain the appropriate particle size of 100–125 µm for further characterizations. Catalyst samples were characterized by X-ray fluorescence (XRF) (Spectro, Xepos) and X-ray diffraction analyses (XRD) (X-Pert, Philips); moreover, the powdered samples were digested by aqua regia (HCl:HNO₃ = 3:1) and HF (1 g of catalyst in 20 mL of mixture) in a microwave digestion bomb (Mod. 4781, Parr Instruments) and the accurate concentration of Ni, Mo, V, Co and Al was determined by atomic absorption spectroscopy (AAS) (SpectrAA 240FS, Varian) by using the following equation:

$$X = \frac{C \cdot V}{1000 \cdot p} \cdot 100 \quad (5)$$

where X is the concentration of metal, wt%; C is the concentration of metal in solution, mg L⁻¹; V is the final volume of solution, L; and p is the weight of solid sample, g.

Sulphur, carbon and hydrogen were measured by an elemental analyzer (2400 Series II, Perkin Elmer). Aluminum represents the main element when acid leaching is carried out; in fact, Al concentration can reach 18 g L⁻¹ [26]. In this case, Al can easily be precipitated by NH₄OH or (NH₄)₂SO₄ at low pHs (2–2.5) and recovered as ammonium alum (NH₄Al(SO₄)₂·12H₂O). That salt can be valorized as a secondary product of the recovery process [26]. Regarding alkaline leaching, concentration of Al is lower but it can be precipitated at pH 8 as Al(OH)₃.

2.2. Grain size separation

Grain size separation tests were carried out on Ni–Mo and Co–Mo samples; 1 kg sample of each catalyst was used in an electric vibrating screen (Set.El, Erimaki) equipped with the following standard sieves: 5.6 mm, 3.35 mm, 2 mm, 1 mm, 500 µm, 250 µm, 75 µm, and <75 µm. After classification each fraction was weighted and concentration of metals was determined by XRF.

2.3. Attrition

The dry Ni–Mo catalyst was subjected to an attrition test to investigate whether one or more metals should be recovered by removal of external layers of rings. A lab-scale attrition grinder (Wemco, 1.5 L cell capacity) was fed by 1 kg of sample and 670 mL of demineralized water at 1200 rpm. After 20 min the material underwent wet screening at 208 µm; resulting granular fractions were dried at 105 °C for 24 h and weighted, whereas metal content was

determined by XRF. The test was repeated by using Lc-Finer (wet Ni–Mo) since it consisted on similar small cylinders and grain size separation does not make sense on untreated sample. Lc-Finer was previously dried in oven for 24 h at 105 °C to remove naphtha, and followed by the attrition test as described before. A pre-treatment step like drying or solvent extraction is required otherwise Lc-Finer cannot be ground (formation of a malleable paste).

2.4. Flotation

Fifteen froth flotation tests were carried out on Ni–Mo catalyst to increase concentration of one or two metals in the concentrate. In fact, flotation is a process widely used to concentrate Mo, Ni and Co sulphides from primary ores. The sample was prepared by dry grinding and the resulting material was sieved at 100 µm. An aspirated-air flotation machine (Wemco) equipped with one 500 mL tank was fed by 20 g of sample per each test; after 10 min in contact with 250 mL of distilled water the collector was added as 0.5% (w/w) aqueous solution. After 5 min frother (polypropylene glycol, Aerofroth 65, Clariant) was added as 1% (w/w) aqueous solution. After 5 min 150 mL of distilled water were added and air was generated by increasing stirring rate to 1200 rpm. Total flotation time was 10 min. The following commercial collectors were experimented: ORFOM CO125, Aerofloat 25, 4-aminothiophenol (ATP), 4-aminothiophenol (ATP-SNC2), 2-mercaptobenzothiazole (MBT-DNC1), Aerofloat 242, Aero 3477, Aero 404, Aero thiocarbonilide 130, Aeropromoter 710, Aero 801, Flotisor P184, Flotisor SM15, Phosokresol C, Genamin 8R100D. pH was adjusted by NaOH and measured by a Mettler Toledo MP220 pH-meter. The two fractions recovered after each test were dried at 105 °C for 24 h and characterized by XRF.

2.5. Preparatory grinding stage

Tests of comminution were carried out using 210 kg of Ni–Mo and Co–Mo mixture. Before grinding, the sample was screened at 5 mm to remove biggest alumina rings and spheres, which accounted for 21.5 kg. The feed particle size distribution (PSD) was determined by a horizontal sieve (Electro Flux). The grinding stage was chosen for optimization of downstream operations for extraction of valuable metals in a future industrial plant, and for this purpose a vibrating mill (Palla, KHD H. Wedag) and a ball mill (ESM 326, Siebtechnik) were used.

2.6. Roasting tests

Some leaching tests of unroasted catalysts by NaOH and H₂SO₄ and different chemical oxidants (H₂O₂, NaClO, HNO₃) performed by authors demonstrated that good extraction yields can be achieved by using H₂SO₄/HNO₃ mixture only, although great amounts of NO_x are produced: thus, a thermal treatment is inevitable [26]. Ground and non-ground samples were roasted at 550 °C for 4 h to remove coke, sulphur and any other organic compound using a lab-scale rotary kiln (length 680 mm, diameter 150 mm, speed 3 rpm, Salvis AG). A certain aliquot of these two samples was collected for hydrometallurgical tests, whereas the rest underwent further roasting in presence of soda ash at 750 °C for 1 h. The following sets of pre-treatments were performed:

- A1 – Non-ground feed; roasting 550 °C, 4 h.
- B1 – Non-ground feed; roasting 550 °C, 4 h; followed by roasting + Na₂CO₃ 750 °C, 1 h.
- A2 – Ground feed; roasting 550 °C, 4 h.
- B2 – Ground feed; roasting 550 °C, 4 h; followed by roasting + Na₂CO₃ 750 °C, 1 h.

Variants for the leaching trials

A 1			B 1			A 2			B 2			A 3 - secondary grinding			B 3 - secondary grinding		
Non-ground roasted material (feed for the leaching trials)			Non-ground roasted material with soda ash (feed for the leaching trials)			Ground roasted material (feed for the leaching trials)			Ground roasted material with soda ash (feed for the leaching trials)			Non-ground roasted material (feed for the leaching trials)			Non-ground roasted material with soda ash (feed for the leaching trials)		
SET A 1			SET B 1			SET A 2			SET B 2			SET A 3			SET B 3		
Run	NaOH	Particle size	Run	NaOH	Particle size	Run	NaOH	Particle size	Run	NaOH	Particle size	Run	NaOH	Particle size	Run	NaOH	Particle size
A 1.1	1 M	-1.4+0.5	B 1.1	1 M	-1.4+0.5	A 2.1	1 M	-0.2	B 2.1	1 M	-0.2	A 3.2	1 M	-0.5+0.18	B 3.2	1 M	-0.5+0.18
A 1.2	1 M	-2.0+1.4	B 1.2	1 M	-2.0+1.4	A 2.2	1 M	-0.5+0.2	B 2.2	1 M	-0.5+0.2						
A 1.3	1 M	-2.8+2.0	B 1.3	1 M	-2.8+2.0	A 2.3	1 M	-1.4+0.5	B 2.3	1 M	-1.4+0.5						
			B 1.4	1 M	-0.5												
SET A 1			SET B 1			SET A 2			SET B 2			SET A 3			SET B 3		
Run	H ₂ SO ₄	Particle size	Run	Water	Particle size	Run	H ₂ SO ₄	Particle size	Run	Water	Particle size	Run	H ₂ SO ₄	Particle size	Run	Water	Particle size
A 1.1	1 M	-1.4+0.5	B 1.1	H ₂ O	-1.4+0.5	A 2.1	1 M	-0.2	B 2.1	H ₂ O	-0.2	A 3.2	1 M	-0.5+0.18	B 3.2	H ₂ O	-0.5+0.18
A 1.2	1 M	-2.0+1.4	B 1.2	H ₂ O	-2.0+1.4	A 2.2	1 M	-0.5+0.2	B 2.2	H ₂ O	-0.5+0.2						
A 1.3	1 M	-2.8+2.0	B 1.3	H ₂ O	-2.8+2.0	A 2.3	1 M	-1.4+0.5	B 2.3	H ₂ O	-1.4+0.5						
			B 1.4	H ₂ O	-0.5												

Fig. 1. Experimental plan of leaching trials (concentration: H₂SO₄ 1 mol L⁻¹; NaOH 1 mol L⁻¹; ground and non-ground refer to the catalysts feeding the rotary kiln).

A3 – Non-ground feed; roasting 550 °C, 4 h + secondary grinding.

B3 – Non-ground feed; roasting 550 °C, 4 h; followed by roasting + Na₂CO₃ 750 °C, 1 h + secondary grinding.

All roasted samples were analyzed by XRF. During the roasting tests at 550 °C and 750 °C the flue gas was analyzed by a non-dispersive infra-red detector to measure SO₂, NO_x, CO₂ and CO (Ultramat 23, Siemens).

2.7. Leaching tests

Leaching tests were performed in 250 mL screw flasks at 80 °C in a water bath (Dubnoff, ISCO) mechanically stirred at 200 rpm. The solid to liquid ratio (*S/L*) was selected to be 10% (w/v) for all experiments. Two samples were collected at 30 min and 4 h, filtered and diluted 1:10 in dilute HNO₃ solution after acidic leaching and in distilled water after alkaline leaching to avoid precipitation of metals during storage. The concentration of Mo, V, Co and Al in leach liquors was determined by AAS. In particular, samples roasted at 550 °C were screened and underwent alkaline or acidic leaching (set A, see Section 2.6, 1 mol L⁻¹ NaOH, 1 mol L⁻¹ H₂SO₄), whereas those roasted with soda ash underwent screening and alkaline or water leaching (set B, 1 mol L⁻¹ NaOH). The whole experimental plan is shown in Fig. 1.

Extraction yield of each metal was calculated as follows:

$$EY = \left(\frac{C \cdot V / 1000 \cdot p}{X / 100} \right) \cdot 100 \quad (6)$$

where *EY* is the extraction yield, %; *C* is the concentration of metal in solution, mg L⁻¹; *V* is the final volume of solution, L; *p* is the weight of solid sample, g; and *X* is the concentration of metal, wt%.

3. Results and discussion

3.1. Characterization of samples

Moisture of original samples ranged from 1 to 2% for Ni–Mo and Co–Mo. The Lc-Finer sample showed a weight loss close to 13% due to the naphtha content, whereas the amount of water is negligible. XRD spectra are characterized by low counts and this means that

phases are not crystalline. The most probable compounds identified by spectra were:

- Ni–Mo: Al₂O₃–MoS₂–Ni₂S₃–(V_{0.07}Mo_{0.93})₅O₁₄.
- Co–Mo: Al₂O₃–CoMoS₄–CoV₂O₆.
- Lc-Finer: Al₂O₃–Ni₃S₄–NiV₂S₄–Mo₄O₁₁.

The Lc-Finer's XRD analysis revealed that molybdenum is present as an oxide rather than sulphide (~65%): this fact was confirmed by bioleaching tests by means of Fe/S oxidizing bacteria where molybdenum follows a dissolution pattern not associated to sulphides oxidation [27]. XRF and AAS analyses of the three catalysts are listed in Table 2.

The Ni–Mo and Co–Mo elemental analysis showed the following results: *S* = 6.6–6.8 wt%, *C* = 6.4–6.9 wt%, *H* = 1.4–1.7 wt%, where carbon is due to coke deposition during refinery operations. The Lc-Finer analysis showed the following values: *S* = 5.5 wt%, *C* = 28.5 wt%, *H* = 3.5 wt%, where carbon and hydrogen are mainly due to naphtha content. The low heating value (LHV) of Ni–Mo/Co–Mo and Lc-Finer was 3.73 and 13.76 MJ kg⁻¹, respectively.

3.2. Grain size separation

3.2.1. Ni–Mo

Results of the grain size separation tests are listed in Table 3, where XRF analysis of each fraction is also reported.

Around 50% of the Ni–Mo catalyst size is represented by the 1 and 2 mm fractions, whereas another 12% is retained by the 500 μm screen. The retained material at 5.6 mm accounts for 17.4% of the incoming material but concentration of Ni, V and Mo is negligible since this fraction is composed by big rings where the main component is alumina. However, there is not a significant concentration of metals in any grain size, and this means that the active metals for catalysis are well dispersed in the huge specific area of the rings.

3.2.2. Co–Mo

The results of the second separation test carried out on the Co–Mo catalyst are showed in Table 4.

Table 2
XRF and AAS analysis of the samples.

	(wt%, dry basis)										
	Mo	V	Ni	Co	Al	Fe	S	Si	P	Mg	As
Ni–Mo											
XRF	13.4 ± 0.6	1.86 ± 0.6	2.72 ± 0.3	–	22.3 ± 0.5	1.53	5.67	2.59	2.18	1.16	0.23
AAS	12.1 ± 0.2	2.50 ± 0.2	3.15 ± 0.1	n.m.	24.3 ± 0.3	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Co–Mo											
XRF	11.7 ± 0.5	0.3 ± 0.1	0.3 ± 0.1	2.7 ± 0.2	22.9 ± 0.4	0.16	6.36	–	0.02	2.31	0.17
AAS	12.8 ± 0.3	0.4 ± 0.1	0.2 ± 0.1	2.6 ± 0.1	23.4 ± 0.3	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Lc–Finer											
XRF	5.3 ± 0.4	7.6 ± 0.4	3.7 ± 0.5	–	20.9 ± 0.5	0.15	7.67	–	0.22	0.41	0.28
AAS	4.4 ± 0.1	8.4 ± 0.1	4.5 ± 0.1	n.m.	22.8 ± 0.3	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.

n.m. = not measured.

Table 3
Results of grain size separation of Ni–Mo catalyst.

Screen	Retained solid (%)	(wt%, dry basis)										
		Ni	Mo	V	Mg	Al	Si	P	S	Ca	Fe	As
5.60 mm	17.4	0.05	0.10	0.07	13.27	29.80	0.11	0.26	0.33	0.36	0.13	0.01
3.35 mm	7.8	2.31	4.12	2.11	1.21	37.14	1.20	0.33	3.86	0.04	0.25	0.38
2 mm	25.2	2.61	5.68	2.49	0.89	34.11	1.61	0.61	5.51	0.01	0.27	0.44
1 mm	25.1	2.68	5.56	2.46	0.78	33.91	1.71	0.68	5.29	0.01	0.29	0.47
500 μm	11.9	2.23	4.52	1.96	0.57	22.85	1.75	1.50	3.42	0.11	0.91	0.41
250 μm	5.1	2.64	4.51	2.57	0.21	11.55	2.98	4.67	3.69	0.39	2.06	0.54
75 μm	5.5	1.57	2.33	1.51	1.16	4.91	4.76	9.42	3.27	1.06	12.37	0.41
<75 μm	2.0	1.00	0.84	1.17	1.49	4.38	5.38	10.36	3.10	1.43	17.06	0.34

Table 4
Results of grain size separation of Co–Mo catalyst.

Screen	Retained solid (%)	(wt%, dry basis)										
		Ni	Mo	V	Co	Mg	Al	Si	P	S	Ca	Fe
5.60 mm	25.7	0.02	0.03	0.03	0	13.91	30.49	0	0	0.25	0.38	0.10
3.35 mm	21.2	1.24	5.70	0.10	0.01	0.36	30.31	0	0	2.25	0	0.09
2 mm	7.6	2.22	10.57	0.14	0.04	0.37	28.43	0	0.42	4.16	0	0.17
1 mm	45.0	0.15	17.48	0.30	2.84	0.37	22.75	0	0	6.37	0.08	0.02
500 μm	0.3											
250 μm	0.0											
75 μm	0.1	0.92	10.39	0.57	0.96	1.16	11.21	0.86	1.78	3.53	0.42	4.81
<75 μm	0.1											

As it can be noted, the material below 1 mm only accounts for 0.5% of the total sample weight: hence, the finest fractions were grouped together and analyzed by XRF. The greatest fraction in terms of weight is that one retained at 1 mm (45%), where Mo and Co concentrated to around 17.5 and 2.8%, respectively. The 5.6 mm fraction accounts for 25.7% of the total weight, but concentration of Co and Mo is negligible: this is due to the fact that this fraction is composed by big alumina rings. Another interesting result shows that Co is practically absent in fractions above 1 mm: a pre-treatment flow-sheet of Co–Mo catalyst could expect a grain size separation to eliminate the 5.6 mm fraction and another step at 2 mm: the finest fractions (–2 mm) will be used to recover both Co and Mo in the hydrometallurgical section, whereas –5.6 + 2 mm fractions could undergo leaching for recovery of Mo.

3.3. Attrition

XRF analysis of fractions obtained by attrition of Ni–Mo and Lc–Finer samples is reported in Table 5, where the most important elements are listed only.

As it can be inferred from Table 5, no metals were concentrated in any fraction. Thus, this confirms that metals are present in the porous structure of alumina and their concentration is approximately constant in the entire volume.

3.4. Flotation

Results obtained in the flotation tests are shown in Table 6, where pH of conditioning operation, amount of collectors and

Table 5
Results of the attrition tests.

Screen	Retained solid (wt%)	(wt%, dry basis)					
		Al	V	Ni	Co	Mo	S
Ni–Mo							
–0.208	21.8	16.58	1.36	2.01	–	11.08	5.95
+0.208	78.2	20.98	0.86	1.97	–	14.74	6.29
Lc–Finer							
–0.208	32.6	19.50	7.77	3.39	–	5.37	7.75
+0.208	67.4	21.26	6.37	3.31	–	5.43	7.58

Table 6
XRF analysis of froth and gangue of seven flotation tests on Ni–Mo.

	pH	C (kg t ⁻¹)	FA (g t ⁻¹)	F (wt%)	G (wt%)	Mo (wt%)		V (wt%)		Ni (wt%)		Al (wt%)		Si (wt%)		S (wt%)	
						F	G	F	G	F	G	F	G	F	G	F	G
ORFOM CO125	7	4	100	18.4	81.6	4.58	11.21	0.30	0.89	0.86	1.55	80.54	15.38	8.20	1.94	6.09	5.63
ATP	10	1	600	5.1	94.9	3.08	9.10	0.29	0.76	1.35	1.96	81.15	14.60	8.10	1.72	6.26	4.21
ATP-SNC2	10	4	900	9.7	90.3	2.63	9.41	0.25	0.76	1.05	2.05	82.70	15.44	8.30	1.81	5.60	4.20
MBT-DNC1	10	4.2	–	12.6	87.4	2.89	7.78	0.26	0.61	1.21	1.60	81.25	12.38	7.99	1.40	6.83	3.56
AEROFLOAT 242	10	4	300	10.3	89.7	3.14	9.68	0.32	0.81	1.28	2.02	82.21	13.79	7.92	1.57	5.75	4.19
AERO 3477	10	4	300	16.7	83.3	2.84	11.92	0.33	0.82	1.20	1.20	82.43	17.61	7.99	1.93	5.90	5.20
AERO 404	10	4.5	300	20.8	79.2	3.52	9.66	0.32	0.82	1.52	2.15	81.03	17.93	7.63	2.01	6.29	4.79

C: collector; FA: foaming agent (frother); F: froth; G: gangue.

frother, quantity and XRF of froth and gangue are listed. Eight of the fifteen tests were characterized by weak results in terms of froth formation; moreover, in some tests the required amount of collector was huge and scum was not firm: for this reason they are not shown in Table 6.

As previously said, the catalyst was ground and screened at 100 μm , that is enough to achieve the degree of liberation for Mo, Ni or Co sulphides. However, quantities of froth were very low even for tests shown in Table 6 (maximum 20.8%), whereas the amount of collectors was large anyhow (4–5 g t⁻¹). This could be due to the large amount of carbonaceous residues (coke deposition) that strongly inhibit the rising of hydrophobic particles to the surface. Many sulphides like MoS₂ are recovered by flotation from primary ore bodies, but in this case it may be possible that MoS₂ represents a small percentage of the total molybdenum, or other elements/compounds in spent catalysts act as depressant avoiding flotation. At this stage the great consumption of chemicals as well

as the small quantity of froth do not justify this technology as a pre-treatment of spent catalysts.

3.5. Roasting tests

Fig. 2 shows the PSDs of the feeding material of rotary kiln and vibrating mill after different times. As it can be noted, 40% of the incoming material has a size lower than 1 mm.

In general, size reduction by impact forces is predominant in the Palla vibrating mill; after 2 min, 80% of the incoming sample was reduced below 100 μm , whereas after the same time around 70% of the feed was ground below 100 μm by the ball mill.

As regards roasting tests, XRF analyses of the resulting roasted samples are listed in Table 7 (see Section 2.6 for conditions).

Comparing the results of A1 (non-ground feed, 550 °C, 4 h) and A2 (ground feed, 550 °C, 4 h), it is clear that the ground material is better oxidized since the surface area of catalyst is greater and

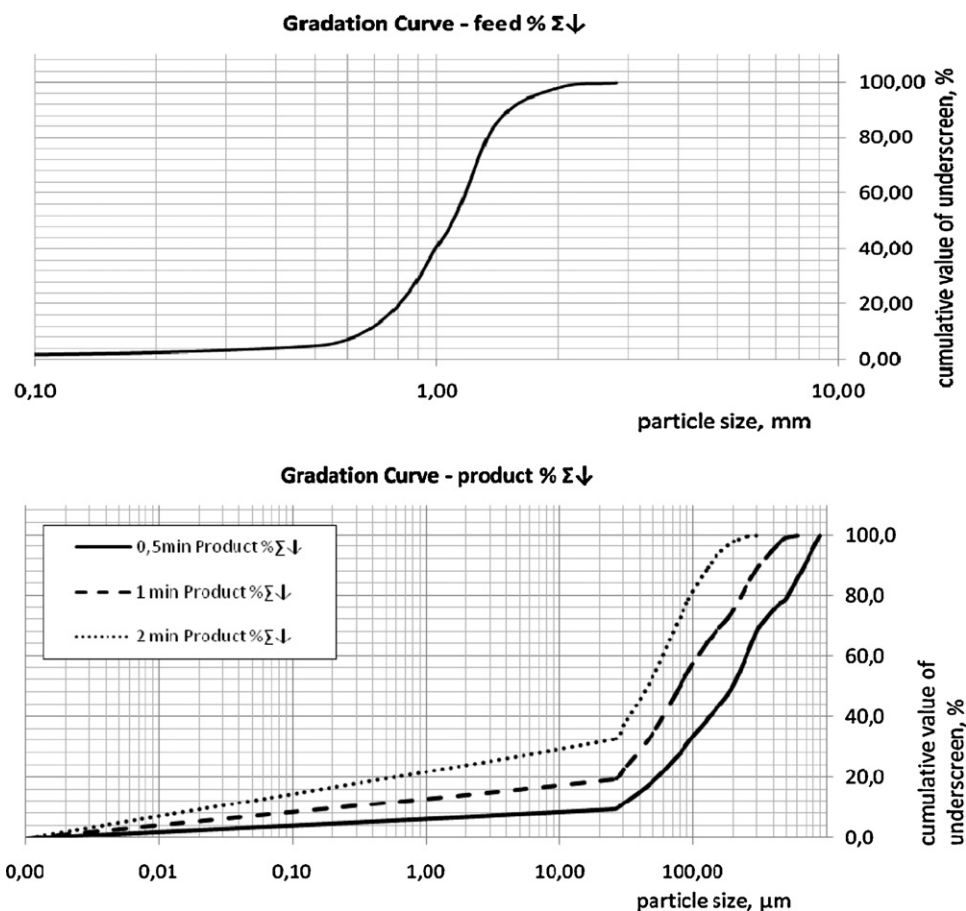


Fig. 2. PSD of feed material and vibrating mill products at different operating times.

Table 7
XRF analysis of catalyst after different roasting steps.

Set	Weight loss (%)	Concentration (wt%)									
		Al	Si	P	S	V	Fe	Co	Ni	As	Mo
A1	19.3	28.80	2.21	1.11	2.40	1.12	0.30	1.77	1.37	0.30	10.68
A2	22.5	29.32	1.67	0.97	0.17	1.48	0.30	1.96	1.58	0.39	11.54
B2	5.8	15.22	1.19	0.60	0.17	1.34	0.25	1.67	1.42	0.35	10.79

then the sulphur content is lower (0.17 vs. 2.40%). Considering the high roasting time, the residual sulphur could be due to sulphides oxidized to sulphate instead of SO_2 . In the B2 set concentration of metals decreases because of dilution effect of sodium. Concentration of compounds in flue gas is shown in Fig. 3:

The stoichiometric amount of Na_2CO_3 (monohydrate, Merck) was calculated using reaction (1) and (2) and 30% more was added to take into account further consumption of Na_2CO_3 due to remaining sulphides from the first roasting.

Fig. 3a and b shows the behaviour of gaseous compounds during roasting of Ni–Mo/Co–Mo mixture without (a) and in presence (b) of soda ash (test A2 and B3, respectively; see Section 2.6 for experimental conditions). In the latter soda ash was added after

nearly 4 h of roasting at 550°C . Furthermore, the feeding material was ground (a) and non-ground (b). Other graphs are here not shown. During flow-gas monitoring of case (b), CO and NO_x were detected in very low range (around 1–3 ppm). Maximum production of SO_2 during roasting of non-ground catalysts with soda ash at 550°C corresponds to 230 ppm, whereas in case of ground material (a) the maximum corresponds to 1000 ppm, then the particle size is very important in SO_2 generation. After addition of soda ash, a prompt increase in CO_2 formation occurs due to decomposition of carbonate ions; in Fig. 3b it can be noted that SO_2 concentration strongly decreases with soda ash addition: this is due to remaining sulphur when is captured by sodium, according to reactions (3) and (4). In Fig. 3a CO and NO_x concentrations (8–12 ppm) are

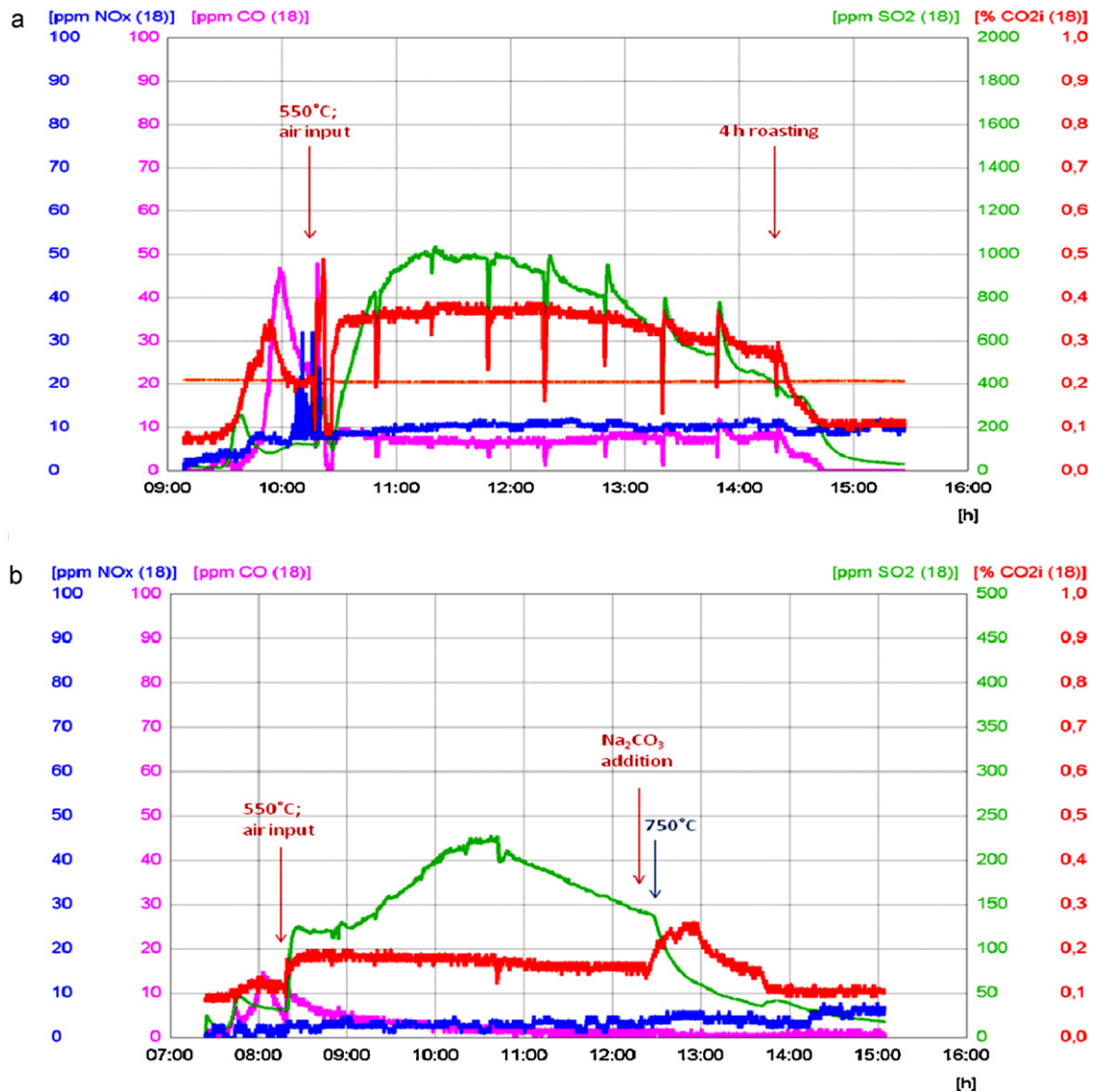


Fig. 3. Results of flue gas monitoring ((a) ground feed, roasting at 550°C , 4 h and (b) non-ground feed, roasting at 550°C , 4 h + roasting with Na_2CO_3 at 750°C , 1 h).

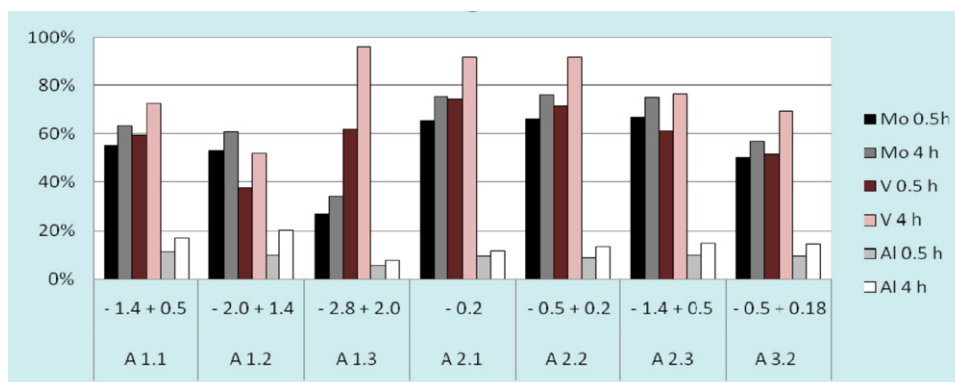


Fig. 4. Extraction yields at 0.5 h and 4 h by NaOH leaching of roasted catalysts (NaOH 1 mol L⁻¹, pulp density 10% (w/v), 80 °C).

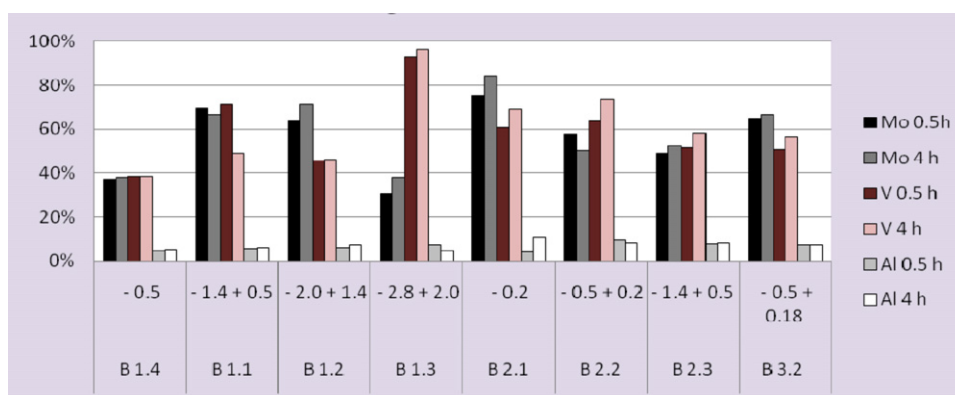


Fig. 5. Extraction yields at 0.5 h and 4 h by NaOH leaching of catalysts after roasting with soda ash (NaOH 1 mol L⁻¹, pulp density 10% (w/v), 80 °C).

also greater than those of Fig. 3b, so this leads to the conclusion that the lower particle size, the higher the production of gaseous compounds; hence, kinetics of oxidations and vanadate/molybdate formation is quicker.

3.6. Leaching tests

Results of leaching tests in terms of extraction yields are shown in Figs. 4–7 (see Fig. 1 for experimental conditions).

Fig. 4 shows extraction yields of Mo, V and Al after 0.5 h and 4 h by NaOH leaching of roasted feed. Considering Mo and V extraction, it is recommended to mill catalysts to $-500 \mu\text{m}$ before the roasting stage. Wet Ni–Mo catalyst must be roasted before any further treatment, because of the presence of naphtha. However, the smaller dimension of the rings does not influence so much the roasting time. The results obtained in trial A.1.3 ($-2.8+2.0 \text{ mm}$) and A.2.2

($-0.5+0.2 \text{ mm}$) show that the greatest V and Mo extraction yields are 96% and 77%, respectively. Aluminum is not the preferable metal to be leached, because of further purification of leach liquor: Al has amphoteric nature, so it is partially dissolved in alkaline medium. However, the greatest extraction yield is 20%. As regards Mo, results are very similar to those obtained by Park et al. [6,7] (85% by 40 g L⁻¹ NaOH or Na₂CO₃ + 6 vol% H₂O₂, 1 h, 20% (w/v) pulp density at room temperature). On the contrary, our preliminary tests at 30 °C did not show good extraction yields (<50%) [26]. Angelidis et al. [11] extracted 80–86% of Mo using 10 g L⁻¹ NaOH, a solid to liquid ratio of 5% at 100 °C for 2 h. The solid residue of that leaching underwent acid leaching by H₂SO₄, increasing the total recovery of Mo up to 97%, whereas extraction of Co and Ni was around 80%.

In case of roasting with soda ash and leaching by NaOH (Fig. 5), the best extraction yield of V is achieved again with the $-2.8+2.0 \text{ mm}$ fraction (trial B.1.3) whereas 85% of Mo can be

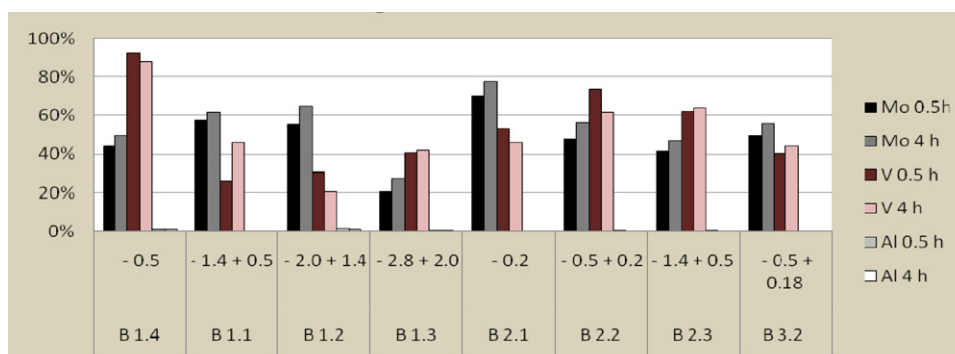


Fig. 6. Extraction yields at 0.5 h and 4 h by water leaching of catalysts after roasting with soda ash (pulp density 10% (w/v), 80 °C).

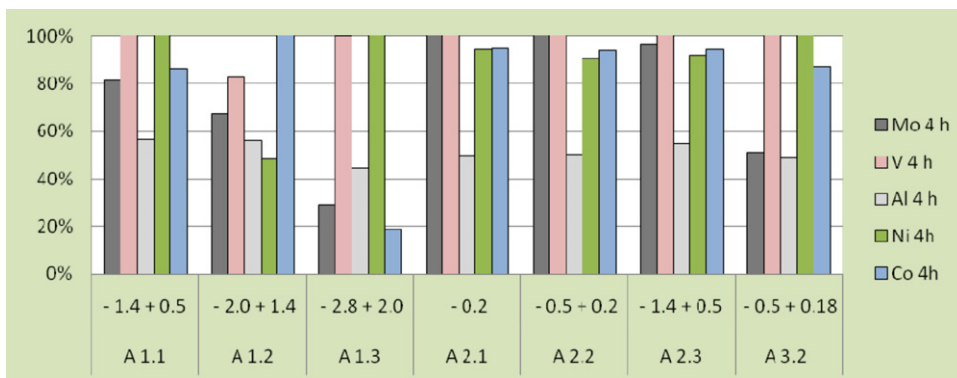


Fig. 7. Extraction yields at 4 h by H₂SO₄ leaching of roasted catalysts (H₂SO₄ 1 mol L⁻¹, pulp density 10% (w/v), 80 °C).

extracted by using the -0.2 mm fraction (B.2.1). Al extraction yields range from 5 to 10%. No previous studies were found in the literature since roasting with soda ash is usually followed by water leaching.

Leaching by water (Fig. 6) showed a V extraction yield of 95% after 30 min when using the -0.5 mm fraction (B.1.4), whereas the most appropriate particle size of feed material should be -200 μm in order to achieve the greatest Mo extraction yield (80%, trial B.2.1). Extraction of Al is negligible, as it does not exceed 1–2%. In their two studies Kar et al. [9,10] found that nearly 90% of Mo is extracted by water after roasting with Na₂CO₃ or NaCl. Chen et al. [15] extracted 91% of Mo and 90% of V after leaching by water (90 °C, 15 min, 50% S/L) of an ammonia leaching residue previously roasted with soda ash.

Fig. 7 shows metal extractions in acidic conditions (1 mol L⁻¹ H₂SO₄ at 80 °C) after 4 h only. The acid leaching of roasted catalysts is able to extract all metals even though it is not selective as that by water or NaOH: however, using the -0.2 mm fraction (A.2.1) 100% of Mo and V and nearly 96% of Ni and Co are extracted. When using sulphuric acid, up to 16 g L⁻¹ of Al can be present, making the downstream process more difficult. Nevertheless, Al can be separated as indicated in Section 2.1. Valverde et al. [4] obtained extraction yields of 90–99.5% for Co, Mo and Ni after 90 min by using 9 mol L⁻¹ H₂SO₄ solution at 90 °C. However, the huge amount of acid has to be neutralized before recovery of metals and this results in great consumption of an alkaline reagent. Mulak et al. [13] recovered 90% of Mo, 65% of Ni and 94% of V at 50 °C by H₂C₂O₄ and H₂O₂; the catalyst was simply washed by toluene without roasting. Anyhow, the solid to liquid ratio was 0.25%, too much low for industrial applications. Lai et al. [12] used a mixture of concentrated acids (HCl, HNO₃ and H₂SO₄ with 40% (w/v) S/L, 70 °C, 1 h) to extract 90% of Mo and 99% of Ni and V and to recover them by electrolysis, but the process is not economically viable.

Hence, the following conclusions are possible:

- Preliminary grinding before roasting is necessary for improving extraction of Mo.
- Roasting (550 °C; 4 h) followed by alkaline leaching (1 mol L⁻¹ NaOH, 80 °C, 4 h) – it is recommended to ground the feed material to less than 1 mm. Comparing Mo dissolution of non-ground feed (8.88 g L⁻¹, $-1.4 + 0.5$ mm) to the same of ground feed in the same size range (10.5 g L⁻¹), it is obvious that liberation of the molybdenum particles is essential for the process, as Mo is the most valuable metal. Therefore grinding for 1 min by using Palla vibrating mill will lead to 100% of the particles with -500 μm size.
- Roasting (550 °C; 4 h) followed by acidic leaching (1 mol L⁻¹ H₂SO₄, 80 °C, 4 h) – maximum extraction of Mo can be achieved

only if catalysts are preliminary ground to -500 μm . Therefore grinding by Palla mill is required.

- Roasting in the presence of soda ash, followed by alkaline or water leaching – in order to achieve Mo concentration of 11–12 g L⁻¹, the feed material has to be ground to -200 μm . Therefore grinding for 2 min by vibrating mill is required.
- Vanadium is not contained in Ni–Mo and Co–Mo samples at a high concentration. Maximum 1.8 g L⁻¹ of V can be dissolved in acidic conditions and this quantity represents 100% as extraction yield. To achieve this result the original sample has to be ground to -500 μm .
- Ni and Co are obviously not leached when alkaline or water leaching is carried out; maximum concentrations obtained in different acid tests were 1.43 and 1.52 g L⁻¹ for Ni and Co, respectively.
- As regards aluminum, non ground feed should be preferable to avoid a heavy contamination of pregnant solution in acid conditions, but it can be easily precipitated at very low pHs as ammonium alum. When using water, Al concentration is negligible but by NaOH its concentration is no greater than 6 g L⁻¹.

Considering a recycling process of spent hydrotreating catalysts, wastes are generated in physico-mechanical treatments and leaching stage, depending on specific procedures:

- Co–Mo catalyst: grain size separation only removes the +5.6 mm fraction, consisting of big rings. This fraction ($\sim 26\%$ of the total weight, see Table 4) can be landfilled or used as tar cracking catalyst in pyrolysis/gasification plants fed by biomass. In fact, that fraction is mainly composed by alumina and small amounts of Co and Mo, thus after a thermal treatment it can be ground and used to produce tar cracking catalysts [28,29].
- Dry and wet Ni–Mo catalysts: these catalysts are only ground at the desired fraction, so that pre-treatments do not generate any waste.

As regards leaching stage, alkaline and acid leachings produce solid residues that can be landfilled or, as said above, used for production of tar cracking catalysts.

4. Conclusions

In this paper several physico-mechanical tests were carried out on spent HDS catalysts with the aim to obtain concentrates before hydrometallurgical treatments. Moreover, effects of mechanical grinding and roasting on extraction of Ni, Mo, Co, Ni and Al were investigated. Results showed that flotation is not a suitable process for concentration of metals due to the presence of coke and/or other depressants. Large consumptions of both collectors (4–5 kg t⁻¹) and frother (up to 900 g t⁻¹) were detected, obtaining no more than 20%

of froth fraction. No concentrated metal fractions can be obtained by attrition since active metals are dispersed in the entire volume of rings. The wet Ni–Mo catalyst is the most difficult to handle since complete removal of the layer of naphtha by drying or solvent extraction is not possible, and this influences the floatability of material. Grain size separation is useful to remove the greatest rings in case of dry catalysts, mainly composed by alumina, whereas for Co–Mo it is also possible to produce two fractions enriched in Co and Mo. Further pre-treatments were tested: in particular, roasting is required to oxidize the organic fraction and vibrating grinding was found to be very effective in size reduction. A preliminary grinding was found to be very important to improve extraction of Mo in the leaching stage. As regards alkaline leaching, around 96% of V can be extracted by NaOH by using roasted feed (–2.8 + 2.0 mm fraction) and 85% of Mo (–0.2 m), whereas Al does not exceed 20%. Water leaching after roasting with soda ash extracted 90% of V (–0.5 mm fraction) and nearly 80% of Mo (–0.2 mm). Acid leaching by H₂SO₄ extracted 100% of Mo and V, as well as 96% of Ni and Co by using the –0.2 mm fraction. In terms of extraction is the most effective, although further purification is required due to the large amount of Al dissolved (50%). Some pre-treatments have given better results in terms of leaching extraction than those of the literature obtained in the same conditions; other results was found to be a bit different but this is due to the different catalyst samples used in the respective studies. However, comparing these results with those of the scientific literature, it can be stated that the preliminary procedures permitted to maximize the extraction of metals reducing the operating costs, mainly due to consumption of reagents.

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