Metal recovery from spent hydrodesulfurization catalysts using a combined acid-leaching and electrolysis process

Yi-Chieh Lai [a,b], Wen-Jhy Lee [a,b], Kuo-Lin Huang [c,*], Chung-Mou Wu [d]

[a] Department of Environmental Engineering, National Cheng Kung University, Tainan 70101, Taiwan
[b] Sustainable Environment Research Center, National Cheng Kung University, Tainan 70101, Taiwan
[c] Department of Environmental Engineering and Science, National Pingtung University of Science and Technology, Pingtung 91201, Taiwan
[d] Futran Inc., Taichung 40759, Taiwan

Abstract

This study focuses on recovering valuable metals from spent hydrodesulfurization (HDS) catalysts using a combined acid-leaching and fluidized-bed electrolysis process. The electrolytic cell was equipped with a glass bead medium, an iridium oxide mesh anode, and a stainless steel plate cathode. An acid solution consisting of concentrated $HNO_3/H_2SO_4/HCl$ with a volume ratio of 2:1:1 was found to be better than the other tested solution ($HNO_3/H_2SO_4 = 1:1$) to leach the metals. For the three-acid mixture, the best solid/liquid ratio and leaching time were 40 g/L and 1 h, respectively, at 70 °C; under this condition, the leaching yields of target metals (Mo, Ni, and V) in the 1st stage of leaching reached 90, 99, and 99%, respectively, much higher than those in the 2nd/3rd/4th stages. When this acid leachate was electrolyzed for 2 h at 2 A constant current (current density = ∼35.7 mA/cm^2), a stable cell voltage of 5 V was observed. The electrolytic recoveries of Mo, Ni, and V were ∼15, 61, and 66%, respectively, but extending the electrolysis time from 2 to 4 h did not increase the recoveries. For this operation, the total recoveries (leaching yield × electrolytic recovery) of Mo, Ni, and V were ∼14, 60, and 65%, respectively.
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1. Introduction

Hydrodesulfurization (HDS) catalysts, mainly made of molybdenum (Mo) with cobalt (Co) or nickel (Ni) promoters supported on porous Al_2O_3, are commonly used in petroleum refining processes for producing light oils from the cracking of heavy crude oil [1,2]. However, HDS catalysts may be deactivated by fouling the active surface with element (e.g., S, C, V, Fe, Ni, Si, Zn, and As) deposits during the cracking reactions [3–5]. As a result, large amounts of deactivated HDS catalysts become spent catalysts that need to be treated to meet environmental regulations because the predominant elements, such as V, Ni, Mo, and Co, in the catalysts are toxic and can be easily leached out with water to cause secondary pollution [3,6]. When land disposed, spent hydrocracking catalysts may pose hazards similar to those caused by spent hydrotreating and hydrorefining cata-

lysts that have been identified as hazardous wastes by USEPA since 1999 [7]. HDS catalysts may also be used in hydrotreating procedures [7]. Despite environmental concerns, more than 4800 t of spent HDS catalysts are discarded annually in Taiwan [8].

Studies on treatments of spent HDS catalysts have used different approaches, such as hydrometallurgy, stabilization and encapsulation, conversion of spent catalysts into useful products [9], and regeneration of spent catalysts with nitrogen-air or steam-air [3–6]. Among these methods, the hydrometallurgy process is an approach that has a good commercial potential to extract valuable metals due to the large amount of spent HDS catalysts and the high content of valuable metals (e.g., >11% Mo, >5% Ni, and >11% V) in the catalysts. Before conducting the hydrometallurgy process, the contaminants (i.e., oil residues, carbons, and sulfurs) present on the catalyst surfaces must be thermally removed [10].

Hydrometallurgy processes have been widely applied to metal recovery from industrial wastes, due to their flexible, environmentally–friendly, and energy-saving characteristics

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* Corresponding author. Tel.: +886 8 7703202x7092; fax: +886 8 7740256.
E-mail address: huangkL@mail.npust.edu.tw (K.-L. Huang).

[11]. The metal leaching of this process has been tested with a variety of reagents such as NaOH, NH$_3$, NH$_3$-(NH$_4$)$_2$SO$_4$, H$_2$O$_2$, H$_2$SO$_4$, HNO$_3$, HF, and aqua regia [1,10,12–15]. Aqua regia is usually used in hydrometallurgy processes to obtain high metal leaching yields because of its high oxidability and corrosiveness, but it may not be suitable for wide application [11,14,15]. Therefore, more research is necessary to examine if other acid mixtures are also suitable to extract metals from the spent HDS catalysts.

After acid-leaching, metals can be separated or recovered from the acid-leachate by separation processes such as solvent extraction, chemical precipitation, ion-exchange, and electrolysis [1,16]. Among these techniques, electrolysis is attractive for its versatility, energy efficiency, simple equipment, easy operation, and low operating cost [17,18]. Electrolysis processes have been utilized in heavy metal recovery from municipal incinerator fly ash [19], spent Ni–Cd batteries [15], printed circuit boards [20], and waste waters [16,21]. However, little information is available about recovering metals from spent HDS catalyst acid-leachate.

Accordingly, this work utilized a process that combined acid-leaching with electrolysis to recover mainly Mo, Ni and V (target metals) from spent HDS catalysts. Leachant [15], leaching time [11], and solid–liquid ratio are important parameters that may influence the metal leaching of spent HDS catalysts. In the metal-leaching stage, therefore, the effects of these metal-leaching parameters on leaching yield were examined. Then, the leachate (electrolyte) containing the acid-leached target metals was electrolyzed to investigate the recoveries of target metals in a fluidized-bed cell installed with a non-conductive bed medium, an iridium oxide mesh anode, and a stainless steel plate cathode. Compared to standard stirred reactors, the fluidized-bed reactor has the major advantages of improving mass transfer by circulating the electrolyte through turbulence promoters (i.e., nonconductive bed medium), providing a preferable environment for nucleation and crystal growth of metals [18,19], and enhancing metal recovery when their concentrations are lower than ∼1000 mg/L during electrolysis [22].

2. Experimental

2.1. Spent HDS catalysts

The spent HDS catalysts were obtained from a hydrotreating unit of a petroleum-refining plant in Taiwan. The catalyst specimens (cylindrical, with an average diameter of 4 and 8 mm in length) contained residual oils, sulfur, carbon and metallic V, Mo, and Ni supported on SiO$_2$–Al$_2$O$_3$ mixed oxides. Before metal acid-leaching, the residual oil, sulfur and carbon contaminants present on the surface of the catalysts were removed by heating at 300 °C for 30 min. The mass loss was about 19% for each catalyst specimen after the thermal treatment. The metal content of the heated catalyst specimen was determined using microwave-assisted acid-digestion method equivalent to USEPA SW846-3050b [23]. In this procedure, each specimen (0.05 g) was digested by a CEM digester using 10 mL HNO$_3$ (intra-

analyzed quality, J.T. Baker) assisted by a microwave system at 170 °C for 20 min to assure the complete digestion of the sample. Then, the obtained suspension was filtered through an ashless Whatman #41 filter, and diluted to 50 mL using ultra-pure water (specific resistance ≥ 18.3 MΩ cm) for metal analysis. The relative standard deviations of duplicate analyses were 0.17–2.89% below a control level of 5%. To identify the metal toxic hazard of spent catalysts, the specimens were tested (acetic acid leaching at pH 3.57) using the Toxicity Characteristic Leaching Procedure (TCLP) method (USEPA SW-8463) [24].

An inductively coupled-plasma mass spectrometer (ICP-MS Agilent 7500a) was employed to measure the content of 14 elements including Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mo, Ni, Pb, Se, V, and Zn in specimens. The ICP-MS system was calibrated before each run. The calibration was performed using multi-element (metal) standards (in 1% HNO$_3$). The standards also contained Li^6, Y^{89} and Ti^{205} elements to cover different mass regions. Acceptable R^2 values of the calibration curves were ≥0.999. In the leaching experiment, each batch of metal leaching was performed three times ($n = 3$) to assure the reproducibility of the method. For the duplicate analysis, samples taken from the same source of spent catalysts were leached simultaneously with the same procedure and then analyzed identically. The relative standard deviations of duplicate analyses were 0.21–3.02%.

Certified reference materials (CRMs) (Spex, Metuchen, USA) were used as quality control standards. The recoveries for the investigated metals from CRMs-spiked solutions ranged from 82% (Al) to 108% (Ni). The method detection limit (MDL) was estimated by repeatedly analyzing a predefined quality control solution and by replicate analysis of ICP-MS measurements. The MDL of each element was calculated by MDL $= 2.681 \times S_{\text{pooled}}$, with $S_A^2/S_B^2 < 3.05$. $S_{\text{pooled}} = [(6S_A^2 + 6S_B^2)/12]^{0.5}$, where S_{pooled} is the pooled standard deviation, S_A is the standard deviation of the prepared sample with the bigger F-test value, and S_B is the standard deviation of the other. The MDLs of these metals were between 0.05 μg/L (Ni) and 9.7 μg/L (Co).

2.2. Metal extraction from the spent catalyst by strong acid leaching

Two types of strong acid mixtures prepared from two to three strong acids (reagent grade) were used to extract metals on the spent catalyst specimens. One of the mixtures was 50 mL 70% HNO$_3$ + 50 mL of 96% H$_2$SO$_4$ (acid A) and the other was 50 mL 70% HNO$_3$ + 25 mL of 96% H$_2$SO$_4$ + 25 mL of 37% HCl (acid B). Each thermally treated catalyst specimen (with a given amount) was acid-leached using acid A or B (100 mL) in a Teflon breaker for 0.5–2 h at 70 °C. The acid leachate was filtered through a Whatman #42 filter to remove solid residues and then diluted to 100 mL with 0.5 M HNO$_3$. (The filtrate exhibited a dark green color generated mainly from Ni(II), V (III, IV, or V), and Fe(II).) Each type of metal leaching (extraction) batch experiment was performed three times ($n = 3$). The concentrations of 10 metal elements (Al, Co, Cr, Cu, Fe, Mo, Ni, Pb, V, and Zn) in the filtrate were also measured by ICP-MS.

2.3. Electrolysis

To recover the metals from the filtrate (filtered acid leachate) obtained in Section 2.2, electrolysis experiments were conducted using a fluidized-bed electrolytic cell installed with a nonconductive bed medium (glass beads, diameter = 0.5 mm) and two electrodes (anode and cathode) connected by a power supply (Fig. 1(a)). With the same dimensions of 70 mm (width) × 80 mm (length) × 2 mm (depth) (projected area = 56 cm^2), an iridium oxide mesh and a stainless steel plate were used as the anode and cathode, respectively.

The filtrate was used as the electrolyte with adjusted pHs of 2–4 by 10N NaOH. Prior to electrolysis, electrolyte was poured into the electrolytic cell and the nonconductive bed medium was static (Fig. 1(a)). During the electrolytic operation at a constant current of 2 A (current density = ∼35.7 mA/cm^2) for 2 to 4 hr, more electrolyte in a storage tank was pumped into the electrolytic cell from the bottom of the cell. The electrolyte was circulating at 5000 mL/min between the electrolytic cell and storage tank to fluidize the bed medium (Fig. 1(b)). The total electrolyte volume, including that in the electrolyte storage tank and electrolytic cell, was 1500 mL. The electrolyte pHs were monitored by a pH meter (Jenco 6173) and the electrolyte was sampled every 0.5 h. Again, the ICP-MS instrument was used to determine the metal concentrations of electrolyte samples, and the metal content in the precipitate and on the electrode.

3. Results and discussion

3.1. Characteristics of the thermally treated catalysts

For the thermally treated catalyst specimens, it was found that the content of Al (∼17%), Fe (∼1.5%), Mo (∼1.2%), Ni (∼5.1%), and V (∼16%) were much higher than those (∼1–510 mg/kg) of Co, Cr, Cu, Fe, Pb and Zn (Table 1). (Hg was not detected.) Al was the predominant metal in thermally treated catalyst specimens since it was one of the major components of the catalyst supporting material. The high content of target metals (Mo, Ni and V) observed proves
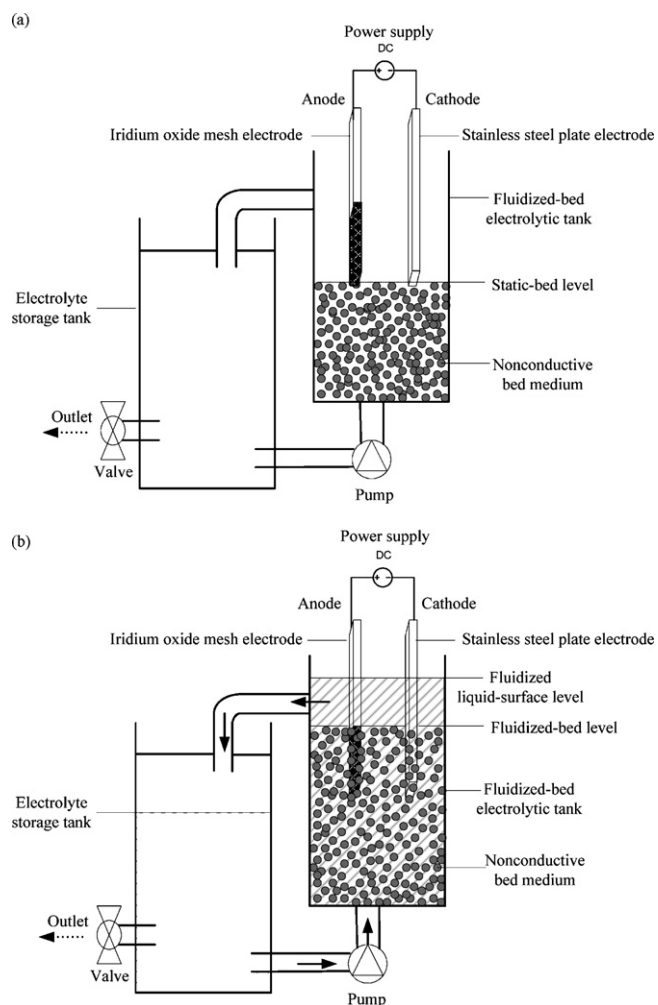

Fig. 1. Schemes of the experimental device used before (a) (static bed) and during (b) (fluidized bed) electrolytic operation.

that HDS catalyst is an excellent resource for target metal recovery.

Table 1 shows the concentrations of 12 elements (As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se, V, and Zn) of the thermally treated

Table 1
Metal content and TCLP-leaching metal concentrations of spent catalysts ($n = 3$)

Element	Metal content		Element	TCLP-leaching metal concentration	
	Mean (mg/kg)	R.S.D. (%)		Mean (mg/L)	R.S.D. (%)
Al	165,100	9.6	As	0.03	6.2
Co	315	0.1	Cd	0.01	2.6
Cr	102	8.6	Co	0.34	3.5
Cu	511	23	Cr	0.01	0.7
Fe	14,650	25	Cu	0.01	43
Mo	12,021	10	Hg	[a]	–
Ni	51,070	3.4	Mo	11	2.6
Pb	1.6	19	Ni	44	1.4
V	155,030	2.0	Pb	[a]	–
Zn	324	16	Se	<0.01	19
			V	28	0.8
			Zn	2.1	2.1

TCLP: toxicity characteristic leaching procedure.
[a] Below detection limit.

catalyst specimens in TCLP leaching tests. As can be seen from the table, Hg and Pb were not detected. The TCLP-leaching concentrations of the metals in specimens were below the regulated standards in Taiwan; however, the spent HDS catalysts without thermal treatment taken from the hydrotreating unit are considered hazardous wastes according to the USEPA [7]. The high TCLP-leaching concentrations of Mo (11 mg/L), Ni (44 mg/L) and V (28 mg/L), in accordance with their high content in the spent catalyst, also cause environmental concerns although they are not as toxic as some TCLP-guided metals (e.g., Hg, Pb, and Cd).

3.2. Effects of strong acid leaching parameters on metal leaching yield

In contrast to the weak acids employed in the TCLP metal leaching procedures, strong acid leachants were used to extract metals from the solid spent HDS catalysts. In general, leachant (strong acid), solid–liquid ratio, leaching time, and temperature are four major parameters that may affect the metal leaching yield ((leached mass/mass in spent catalyst for a metal species) × 100%).

3.2.1. Effect of strong acid leachant on metal leaching yield

Aqua regia (commonly 70% HNO_3:37% HCl = 1:3, v/v) is a strong acid leachant widely used to extract metals from solids. However, it was not employed in this study to avoid the possible formation of poisonous chlorine gas during electrolysis caused by the high Cl^- concentration in aqua regia. Instead, as mentioned in Section 2.2, acid A (HNO_3/H_2SO_4 = 1:1, v/v) and acid B (HNO_3/H_2SO_4/HCl = 2:1:1, v/v/v) were used as metal leaching agents. During the metal extraction, a soild–liquid (S/L) ratio (the weight of spent catalyst specimen/the volume of leachant) of 50 g/L was first tested at the leaching time of 1 h and temperature of 70 °C.

For acid A, the leaching yields of Mo, Ni and V (target metals) reached 86, 48, and 70%, respectively; among the metals tested, Co (91%) and Pb (2.8%) exhibited the highest and lowest leaching yields, respectively, whereas the leaching yields of the other metals ranged between 23 and 73% (Table 2). When using acid B, the leaching yields of Al and Pb (with the highest and lowest content in the spent catalyst, respectively) were raised by approximately 3- and 15-fold, respectively. The leaching yields of Ni and V both reached ∼98%, significantly higher than those in acid A, respectively, although the leaching yields of Mo for acids A and B were similar. It is inferred that the introduction of concentrated HCl to the metal extraction led to the formation of metal-chlorine ion complexes and thus enhanced the metal leaching, although some other factors (e.g., types of metal compounds present in the spent catalyst specimen) also need to be considered. Accordingly, acid B was more efficient than acid A in target metal extraction despite its high leaching of Al (the most abundant metal in the catalyst support). Although Al is not one of the target metals in this study, it is also valuable and deserves to be recovered, but a separation operation is necessary. Cu is possibly easier to electro-deposit onto a cathode surface than the target metals because the standard (reduction)

Table 2
Metal leaching concentrations and yields of spent catalysts in acids A and B (S/L = 50 g/L) (n = 3)

Metal	Acid A		Acid B	
	Concentration (mg/L)	Yield (%)	Concentration (mg/L)	Yield (%)
Al	1555	31	4421	89
Co	8.7	91	8.8	93
Cr	2.2	70	2.7	87
Cu	3.5	23	3.3	21
Fe	287	65	374	85
Mo	311	86	316	87
Ni	736	48	1499	98
Pb	<0.01	2.8	0.02	44
V	3253	70	4571	98
Zn	7.1	73	8.6	88

Acid A: 50 mL 70% HNO_3 + 50 mL of 96% H_2SO_4. Acid B: 50 mL 70% HNO_3 + 25 mL of 96% H_2SO_4 + 25 mL of 37% HCl. Leaching yield: (leached mass/mass in spent catalyst for a metal species) × 100%.

electrode potential is more positive for Cu than it is for the target metals. As a result, the low leaching yield of Cu along with its low content in the spent catalyst was favored for the electrolytic recovery process of the target metals.

3.2.2. Effect of solid–liquid ratio on metal leaching yield

Acid B was used in solid–liquid (S/L) ratio tests at the S/L ratios of 10–50 g/L, for 1 h leaching at 70 °C. It was found that metal leaching yield roughly increased with increasing S/L ratio from 10 to 40 g/L, expect that for Al, Cu, and Mo (Fig. 2). When the S/L ratio raised from 40 to 50 g/L, only the leaching yields of Cu and Zn were improved; however, those of the other metals decreased or changed slightly. At the S/L ratio = 40 g/L, the Mo, Ni, and V target metals exhibited high leaching yields of ∼90, 99, and 99%, respectively. Moreover, Cu and Zn had leaching yields of ∼15 and 85%, respectively but their masses were low, so their interference in the following electrolytic metal recovery should be small. In contrast, the high leaching yield (91%) of Fe and its high content in the spent catalyst was a concern during the electrolysis process because it was possible that Fe might
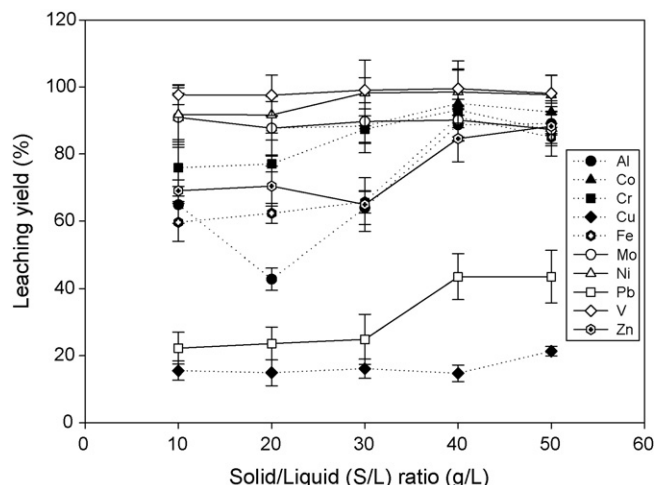

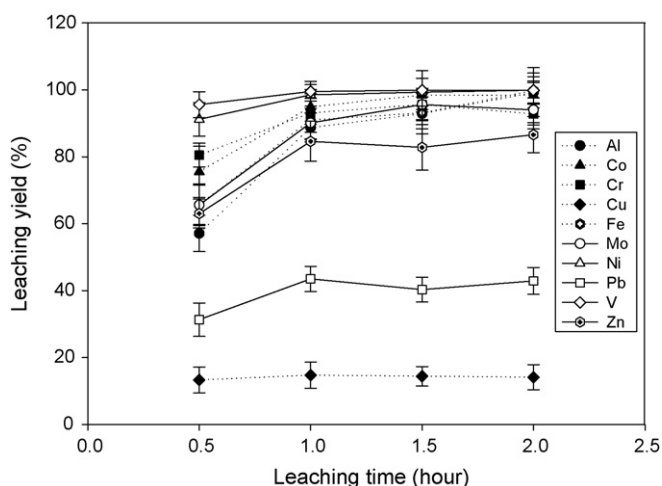Fig. 2. Metal leaching yields in acid B at various solid–liquid (S/L) ratios.

Fig. 3. Metal leaching yields against leaching time (S/L = 40 g/L).

Table 3
Metal leaching yields of spent catalysts in acid B at four-stage leaching (S/L = 40 g/L) (n = 3)

Metal	Leaching yield (%)				Unleached percent (%)
	1st stage	2nd stage	3rd stage	4th stage	
Al	89	10	1.1	0.5	0.1
Co	95	3.3	–	–	1.8
Cr	93	5.2	–	0	1.6
Cu	15	1.9	2.5	12	69
Fe	91	7.9	0.3	–	0.8
Mo	90	7.2	2.2	–	0.5
Ni	99	1.2	0.2	–	–
Pb	43	–	–	–	57
V	99	0.1	–	–	0.5
Zn	85	12	1.2	–	2.5

co-deposit with the target metals onto the cathode surface and decrease the current efficiencies for the electrolytic recovery of target metals. Nevertheless, the S/L ratio of 40 g/L was adopted in the leaching time experiments.

3.2.3. Effect of leaching time on metal leaching yield

For leaching time experiments, the leaching time varied from 0.5 to 2 h at a fixed temperature of 70 °C. The leaching yields of most metals tested dramatically increased when the leaching time increased from 0.5 to 1 h, but the leaching yield increase of each metal was small after >1 h of leaching (Fig. 3). At the leaching time of 1 h, the leaching yields of both Ni and V reached ~99%, while that of Mo was ~90%, which was raised to ~96% at 1.5 h. Unwanted metals such as Al, Co, Cr, and Fe also displayed ≥93% leaching yields for leaching time of ≥1.5 h; again, as mentioned in Section 3.2.2, Fe was a bigger concern than the other three unwanted metals in the electrolysis process because the content of Co and Cr was low in the spent catalyst. Although the Al concentration was high in the leachate, Fe and the target metals were much more competitive than Al for the electrolytic recovery (for more discussion see Section 3.4). Thus, the leaching time chosen was 1 h for the four-stage metal leaching tests.

3.3. Four-stage leaching procedure

Four-stage leaching tests (at 70 °C, 1 h for each stage) were conducted to study the metal leaching from the spent catalysts in the leaching process. For this type of test, a thermally treated spent catalyst specimen (4 g) was first leached with 100 mL of acid B solution (1st stage) (S/L ratio = 40 g/L). Using 100 mL of acid B, the 2nd stage leaching was performed by extracting metals from the solid residues obtained by filtering the 1st-stage leachate. The 3rd stage and the 4th-stage metal leaching processes followed the same procedures.

Mo, Ni, and V exhibited high leaching yields (~90, 99, 99%, respectively) in the 1st stage of leaching, much lower leaching yields in the 2nd stage, and negligible ones in the 3rd and 4th stages (Table 3). Furthermore, unwanted metals were predom-

inantly present in the 2nd-stage leaching solution. Therefore, only the 1st-stage leaching solution was used in the target metal recovery by electrolysis.

3.4. Metal recovery from the 1st-stage leachate

The filtered 1st-stage leaching solution with high concentrations of Mo (433 mg/L), Ni (2012 mg/L), and V (6168 mg/L) was used as the electrolyte for electrolytic metal recovery. The initial electrolyte pH values were adjusted to 2–4 by a NaOH solution to evaluate the effect of initial electrolyte pH on the recovery of the target metals under constant current operation (2 A for 2 h).

The electrolytic recoveries of Mo at initial electrolyte pHs of 2.0, 2.5, 3.0, and 4.0 were ~15, 14, 13, and 13%, respectively, whereas those of Ni were ~61, 60, 40, and 38%, respectively, and those of V were ~66, 56, 38, and 32%, respectively. The maximum recoveries of Mo, Ni, and V were obtained from the electrolyte with an initial pH value of 2.0. However, Orhan et al. [16] reported that maximum Ni recoveries from plating bath rinsing water were obtained within a pH range of 5.45–5.55. The discrepancy between their work and this study is mainly due to the different systems used (i.e., electrode, electrolyte, and operation mode, etc.). Moreover, we found that the co-precipitation of several compounds occurred, when the electrolyte pH values were higher than 3.0.

Fig. 4(a) shows the variation of electrolytic recoveries with time for Mo, Ni, and V in an electrolyte with an initial pH of 2.0. The recoveries of these target metals all dramatically increased from 0 to 2 h, but only slightly increased from 2 to 4 h (constant current at 2 A, current density = ~35.7 mA/cm²). A similar trend was observed for electrolyte pH variation, although only from 2 to 2.3, probably due to the consumption of protons in the electrolysis process. The electrolytic recoveries of Mo, Ni, and V at 4 h were ~16, 68, and 70%, respectively; however, the recoveries reached ~15, 61, and 66%, respectively, at 2 h. The electrolytic recovery was lower for Mo than it was for Ni and V. One explanation for this finding is that the initial concentration of Mo (642 mg/L) was lower than those of Ni (2501 mg/L) and V (4368 mg/L). More critically, it was lower than 1000 mg/L so it is expected to have low electrolytic metal recoveries [22]. The
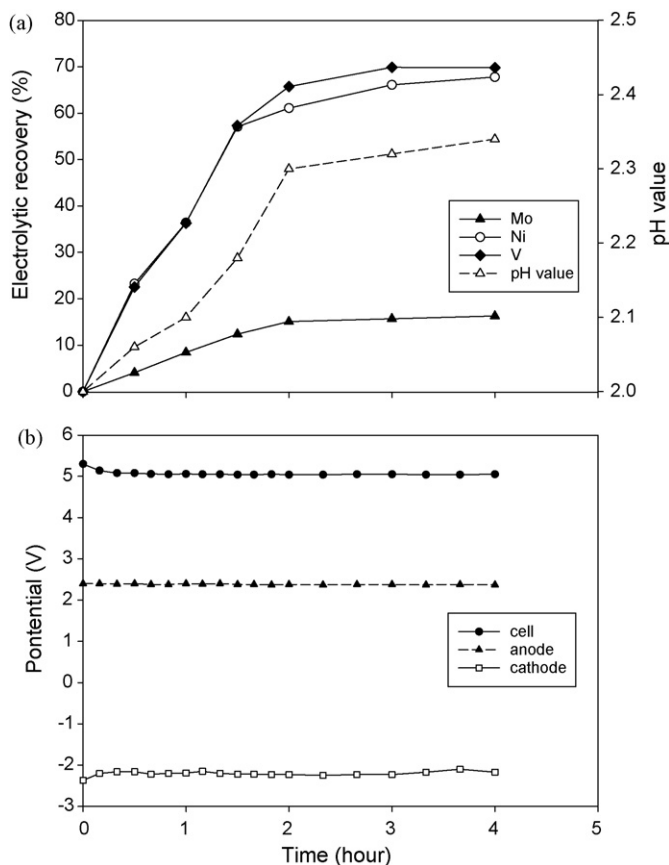
Fig. 4. Electrolytic recoveries of Mo, Ni and V (a) and potentials of cell, anode, and cathode (b) against electrolytic time (initial electrolyte pH 2).

fluidized-bed (nonconductive small glass beads) cell adopted in this study was used to improve the recoveries of target metals when their concentrations were lower than 1000 mg/L. (The concentrations of Mo, Ni, and V in the electrolyte were 562, 973, and 1498 mg/L, respectively, after 2 h of electrolysis.)

From the viewpoint of cost-effectiveness, the best electrolysis time was 2 h. Combining the electrolytic recovery and leaching yield together, the total recoveries (leaching yield × electrolytic recovery) of Mo, Ni, and V were ∼14, 60, and 65%, respectively, using acid B at S/L = 40 g/L, one stage leaching, and 2-h electrolysis. After the electrolytic operation, no silver-like metal deposit was observed on the cathode surface, but the front and rear surfaces of the cathode displayed deposits with dominant colors of green, yellow, and brown, and minor ones of purple, red, and black, mainly reflecting the presence of target metal compounds. However, the electrodeposited compounds on the cathode could not be clearly identified using X-ray diffractometry (XRD) (Siemens XRD D-500) with Cu Kα radiation (scanning rate: 0.05° 2θ/s) due to the interference of high Ni content. The electrolyte ion speciation was not analyzed. As a result, the current efficiencies of these target metals were difficult to estimate. Although the concentration of Al ions was high in the electrolyte, its influence on the electrolytic recovery of target metals should be negligible because the standard electrode potential for Al reduction is much more negative than those of the target metals. The present process is suitable for

the recovery of target metal compounds (not silver-like metals). After drying, the cathode deposits can be scraped from the cathode surface and collected as powders which are valuable and recyclable depending on their purities. However, the collected metal oxide powders need subsequent separation which increases operation cost. Therefore, further research is necessary for obtaining materials with high target metal content. During constant current electrolysis, the stable cell voltage was about 5 V while the stable anode and cathode potentials were around +2.4 and −2.2 V vs. standard hydrogen electrode (SHE), respectively (Fig. 4(b)). This led to a 0.4 V deviation between the cell voltage and the anode–cathode potential difference chiefly due to the distances between the reference electrode (Ag/AgCl) and the anode/cathode. By rough estimation, the reward from metal oxide recovery is ∼3.43 times that of the operation cost (∼$7.5/kg-catalyst, including those of materials and power); however, the cost of metal oxide separation also needs to be included and thus the benefit is ∼$2.8/kg-catalyst, assuming the cost of metal oxide separation = 60% of the reward from metal oxide recovery. However, this value decreases to ∼$0.2/kg-catalyst if the separation cost is increased by 10%. Therefore, this process (regardless of capital costs) relies heavily on the cost of metal oxide separation and it may be economically viable if the electrolytic recovery is improved and the costs of metal oxide separation and leaching-acids are lowered (e.g., recycling the used acid mixture and/or the use of appropriate waste acids).

4. Conclusions

In this study, the influence of leachant, solid–liquid ratio, and leaching time on the metal leaching yields for heated spent catalyst specimens were investigated and the electrolytic recoveries of these metals were examined. Acid B with a volume ratio of concentrated $HNO_3/H_2SO_4/HCl = 2:1:1$, was found to be better than acid A ($HNO_3/H_2SO_4 = 1:1$) at leaching metals. At 70 °C, the best S/L ratio and leaching time were 40 g/L and 1 h, respectively, for acid B. At this condition, the first stage leaching yields reached 90, 99, and 99% for the target metals of Mo, Ni, and V, respectively; the leaching yields of these target metals were much lower in the 2nd stage of leaching, and negligible in the 3rd and 4th stages.

Using acid B at S/L = 40 g/L, one stage leaching, and 2-h electrolysis at a constant current = 2 A (current density = ∼35.7 mA/cm², with a stable cell voltage of 5 V), the electrolytic recoveries of Mo, Ni, and V at 2 h were ∼15, 61, and 66%, respectively. Extending the electrolysis time from 2 to 4 h did not increase the recoveries. For this operation, the total recoveries (leaching yield × electrolytic recovery) of Mo, Ni, and V were ∼14, 60, and 65%, respectively. Further research is necessary to improve the metal recoveries.

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