Leaching behaviors of Ni and V from spent catalyst

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Abstract

The leaching behaviors of Ni and V from a spent hydroprocessing catalyst were assessed in this study. The fractionations of Ni and V on the spent catalyst were determined. An automatic pH/ORP control apparatus was utilized to assess the leaching behaviors of Ni and V. When spent catalyst suspension was continuously aerated with nitrogen for 300 h, the pH did not change, and the redox potential decreased from 521 to 340 mV. Leached Ni and V concentrations did not change much during the aeration period, and were about 460 and 70 mg kg^{-1}, respectively. The leaching experiments under equilibrium were first conducted at a pH of 5.0 and various redox potentials (-100, 0, 100, 250, 330, 400 mV). Leached Ni concentrations did not change significantly with redox potential, while leached V concentrations decreased. At pH 8.0 and different redox potentials (-330, -300, -200, -100, 0, 150, 250 mV), leached Ni concentrations were relatively low, and increased with decreasing redox potential. Leached concentrations of V increased gradually with decreasing redox potential, and increased abruptly when the redox potential was changed from -300 to -330 mV. It is proposed that the exchangeable fraction of Ni was leached out, while the enhanced leaching of V could be attributed to both changes of fractionation and the reduction reactions of oxyanions of V. © 1997 Elsevier Science B.V.

Keywords: Fractionation; Leaching; Nickel; pH; Redox potential; Spent catalyst; Vanadium

1. Introduction

Spent catalysts contribute a significant amount of the solid wastes generated in the petrochemical industry. Hydroprocessing, reforming, and desulfurization all produce spent catalysts. It is estimated that more than 3000 tonnes of spent catalysts are annually generated by the China Petroleum Corporation in Taiwan.

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Spent catalysts are usually regenerated two or three times before being discarded. Various methods of handling these spent catalysts are available to refiners: they can be used as secondary raw material, or disposed of in land farming or land filling [1]. Since catalysts contain contaminants picked up in the processes for which they were used, there has been increasing concern about the land disposal of spent catalysts [2]. Some researches have focused on the long-term environmental impacts of petroleum industry hazardous waste land treatment [3,4]. Toxic components, such as Ni, Co, V, Mo, and some organic contaminants, render spent catalysts hazardous if improperly managed. Many parameters, such as pH, redox potential, solid–liquid ratio, and water content, will affect the leaching behaviors of heavy metal from landfilled spent catalysts. Among them, both pH and redox potential have long been recognized as critical parameters controlling the fate of pollutants in the environment. Theoretical predictions of heavy metal equilibria as affected by pH and redox potential have been extensively studied. In the meantime, an experimental apparatus controlling the redox potential and pH of soil suspension was developed [5]. The set-up was used to study the speciation and transformation of selenium and arsenic as affected by pH and redox potential in sediments and soil [6,7], heavy metal mobility from solidified fly ash and sludge [8], and solubilities of Pb, Cd, and Zn in a contaminated soil [9]. The major objective of the current study is to investigate the leaching behaviors of Ni and V as affected by pH and redox potential from spent hydroprocessing catalysts. This is critical to the assessment of leaching toxicity imposed by spent catalysts during land treatment, and is believed to be beneficial to regeneration technologies of spent catalysts.

2. Materials and methods

2.1. Characterization of the spent catalyst

Spent hydroprocessing catalysts were obtained from the Research Institute of China Petroleum Corporation in Chia-Yi County, Taiwan. The specific gravity was determined to be 2.56 by the weight difference method [10]. The specific surface area was determined to be 32 m^2 g^{-1} by the BET specific area analyzer (Micromeritics ASAP 2000). The total organic carbon content was determined to be 470 mg kg^{-1} by a TOC analyzer (Astro 2001). The size distribution of spent catalyst (Fig. 1) was determined utilizing a sizer (Malvern 2600C). Scanning electron microscope analysis (Cambridge S360) showed the spent catalyst to consist of aggregated small particles with diameters ranging from 0.4 to o.8 μm (Fig. 2(A)). Semiquantative analysis of the surface content by energy dispersion showed (Fig. 2(B)) that both Si and Al are major components, whereas Mg, Ti, V, Fe, Ni, and Zn are minor components.

In order to analyze the total metal content [11], 2.5 g of spent catalyst was placed in a 250 cm^3 pyrex flask. 5 cm^3 of 4 N HNO_3 was added to the spent catalyst, and then placed on a heating plate (Corning PC-320) for digestion. A small amount of nitric acid was added intermittently to prevent spent catalyst from total dry-out, until the supernatant became clear and a brownish-colored fume was no longer generated. The suspension was cooled and filtered through a 0.45 μm membrane filter (MFS), and then
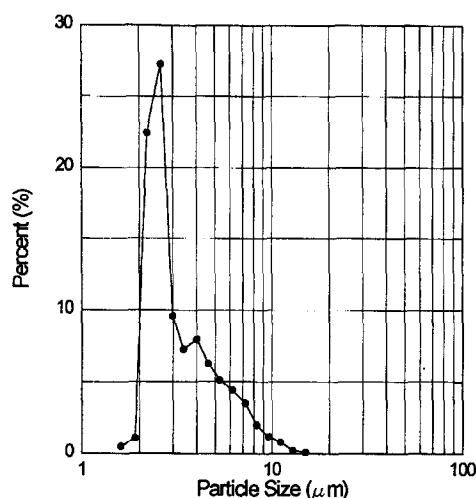
Fig. 1. Size distribution of spent catalyst.

measured by atomic absorption spectroscopy (GBC 904). The results are summarized in Table 1(A). In order to examine the toxicity of spent catalyst, a TCLP (Toxicity Characteristic Leaching Procedures, EPA, Taiwan) experiment was conducted. 100 g of spent catalyst was first weighed and placed in a 2 dm^3 polyethylene bottle. An appropriate amount of extractant (acetic anhydride solution at pH 2.88 ± 0.05) was added and then placed on a rotary shaker (ATCS DC-20S) for 18 h at 30 rpm. The spent catalyst suspension was then filtered through a 0.6–0.8 μm membrane filter (MFS). The concentrations of various metals in the filtrate were measured by atomic absorption spectroscopy and are shown in Table 1(B). The results show that the spent catalyst can be categorized as non-hazardous waste. Nevertheless, it is notable that high concentrations of Ni and V are present in the filtrate.

In the metal fractionation experiment, sequential extraction procedures [12] were utilized. The scheme is displayed in Table 2. Both Ni and V were partitioned into exchangeable, carbonate-bound, Fe–Mn oxide-bound, organic-bound, and residual fractions.

2.2. Experimental set-up and procedure

To study the effect of pH on the leaching behaviors of Ni and V from the spent catalyst, 10 g of spent catalyst and 150 cm^3 of 0.05 N $NaNO_3$ aqueous solution were put into a 250 cm^3 polyethylene bottle; the pH was adjusted with 1 N NaOH and 1 N HNO_3, and the suspension then placed on a shaker (Firstek B603). After shaking for 48 h, the pH was measured and the suspension then filtered through a 0.45 μm membrane filter (MFS). The Ni and V concentrations were determined by atomic absorption spectroscopy.

Next, pH/redox effects on the leaching behaviors of Ni and V from the spent catalyst were assessed by utilizing an apparatus based on a modification of the pH/redox control
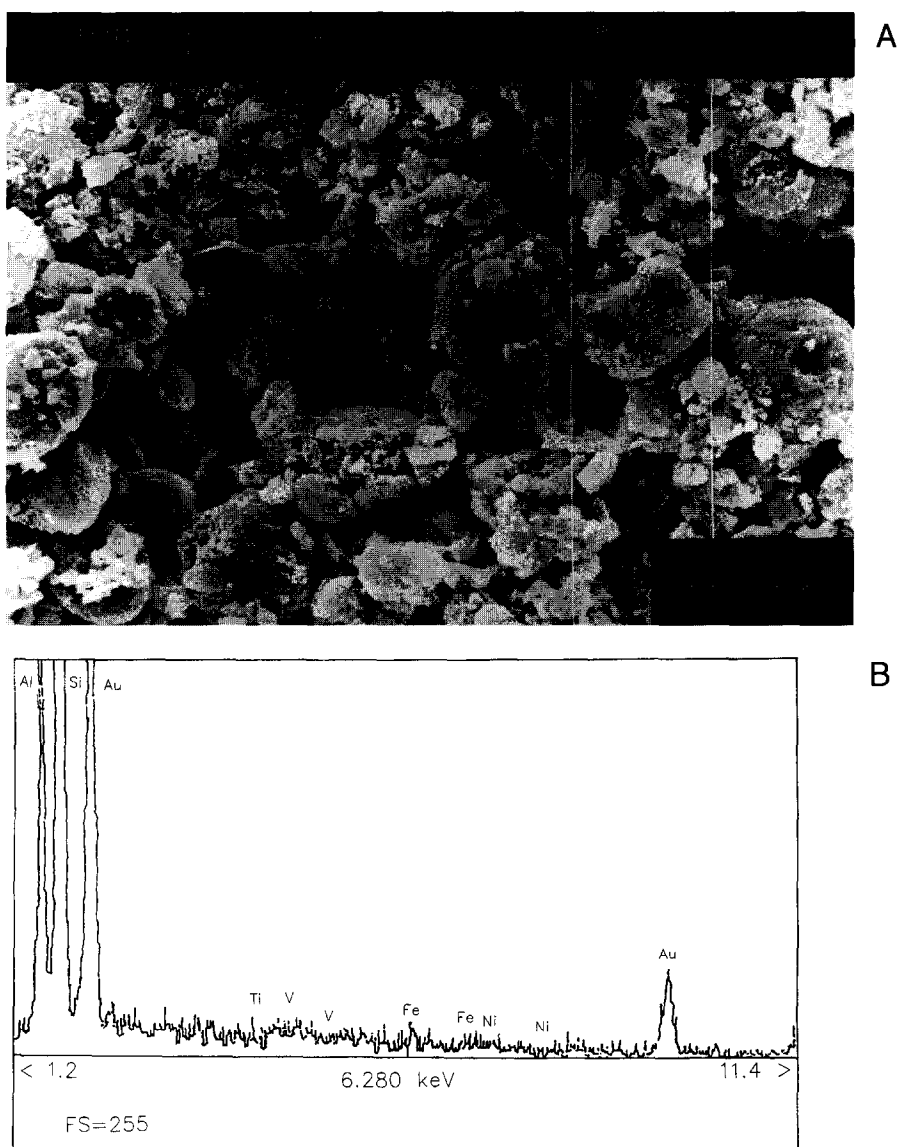
Fig. 2. (A) Scanning electron microscope picture of spent catalyst. (B) Energy-dispersive spectrometric analysis of the surface content of spent catalyst.

Table 1
Metal content of (A) spent catalyst (mg kg^{-1}) and (B) TCLP filtrate (mg dm^{-3})

	V	Cr	Fe	Co	Ni	Cu	Zn	Mo	Cd	Pb
(A)	8830	32.0	4440	12.8	4120	9.0	90	220	BDL	9.0
(B)	2.1	BDL	0.57	0.10	24.3	BDL	0.57	0.32	BDL	BDL

Table 2
Sequential extraction procedures

Fraction	Extractant	Extraction condition
Exchangeable	10 ml 1 M MgCl$_2$	Shaken 1 h at pH 7
Carbonate-bound	10 ml 1 M NaOAc	Shaken 5 h at pH 5
Fe–Mn oxide-bound	20 ml 0.04 M NH$_2$OH·HCl	Shaken 5 h at 85°C
Organic-bound	20 ml 30% H$_2$O$_2$ and 10 ml conc. H$_2$SO$_4$	Shaken 2 h and 3 h, respectively, at 85°C
Residual	20 ml conc. H$_2$SO$_4$	Mildly boiled for 1 h

system [9]. The first experiment was conducted to examine the leaching of Ni and V under continuous nitrogen aeration. First, 100 g of spent catalyst and 1500 cm^3 of 0.05 N NaNO$_3$ aqueous solution were mixed in the 2 dm^3 pyrex reactor. The spent catalyst suspension was continuously stirred and nitrogen was bubbled through. The redox potential and pH were measured and recorded on-line. Samples were taken at regular time intervals. In each instance, 50 cm^3 of spent catalyst suspension was taken and filtered through a 0.45 μm filter paper (MFS) under a nitrogen atmosphere. The leached concentrations of Ni, V and Fe were analyzed by atomic absorption spectroscopy. In the second experiment, spent catalyst suspensions were equilibrated under controlled redox potential and pH conditions. The automatic pH/redox control apparatus allowed either oxygen or nitrogen to flow into the reactor to adjust the redox potential to the preset value. Meanwhile, 1 N HNO$_3$ and 1 N NaOH aqueous solution were automatically pumped into the spent catalyst suspension to maintain the pH at the preset value. Equilibrium conditions were assumed when both pH and redox potential were maintained at constant values for three days. Both slightly acidic (pH 5.0) and slightly alkaline (pH 8.0) conditions were chosen for investigation. The amount of metal leached under acidic conditions (pH 5.0) and six different redox potentials (−100, 0, 100, 250, 330, 400 mV) was first investigated. Additionally, the leaching of metals under slightly alkaline conditions (pH 8.0) and seven different redox potentials (−330, −300, −200, −100, 0, 150, 250 mV) was also examined. Since −330 mV was the lowest achievable redox potential by nitrogen bubbling, sodium thioglycollate was added to decrease the redox potential further. The solubilizing effect of sodium thioglycollate on Ni and V through complexation was calculated on the basis of stability constants [13] and proved to be negligible. Samples were not taken until both redox potential and pH reached preset values for at least three days. The error of the redox potential was within ±10 mV, and that of the pH, ±0.1 unit. The electrodes were calibrated intermittently during each experiment.

3. Results and discussion

The results of Ni and V fractionation are shown in Table 3. Residual element comprises the major fraction of Ni, while the exchangeable fraction (480 mg kg^{-1}) accounts for 12%. Fe–Mn oxide-bound V is the predominant fraction of this metal, the other major fractions being organic-bound and residual V. The highest amount of Ni in

Table 3
Fractions of Ni and V in spent ROC catalyst

Fraction	Concentration (mg kg^{-1})		Percentage (%)	
	Ni	V	Ni	V
Exchangeable	480	11	12	0.1
Carbonate-bound	10	150	0.2	1.7
Fe–Mn oxide-bound	70	5040	1.7	57.1
Organic-bound	23	1330	0.6	15.1
Residual	3540	2300	85.9	26.0

sludge has been found in either the Fe–Mn oxide-bound fraction or the residual fraction [14,15]. The fractionation pattern has been shown to be related to the uptake of metals and their capacity for leaching out from soils [14,16,17]. It has been indicated [18] that the exchangeable and carbonate-bound fractions represent the more mobile parts of metals. Therefore, the leaching potential of the exchangeable fraction of Ni on spent catalyst is expected to be high. Little information is available on the fractionation of V on solid surfaces. However, it has been indicated that pH, redox potential, and organic content exert a profound influence on the fate of V in soil systems [19].

The dissolution of Ni and V from the spent catalyst as affected by pH is shown in Fig. 3(A) and Fig. 3(B). Ni solubility under acidic conditions was about 600 mg kg^{-1}, and decreased rapidly when the pH value was higher than 5.0. Only a negligible amount of Ni was dissolved when the pH was higher than 6.0. The solubility of V decreased as the pH increased from 2.0, and showed minimum values in the pH range of 4.0–8.0. The solubility of V increased rapidly when the pH was higher than 9.0. This is expected, since both V_2O_5 and V_2O_4 have been recognized as highly soluble under acidic as well as alkaline conditions [19–21].

When the spent catalyst suspension was continuously aerated by nitrogen, the initial redox potential of spent catalyst suspension was 521 mV (Fig. 4). The redox potential rapidly decreased and stabilized at 340 mV within 24 h under aeration. It did not then change within 300 h. The changes of redox potential during aeration represented reduction reactions of trace amounts of oxidizing reagents by nitrogen. Meanwhile, the pH value fluctuated between 4.0 and 4.2, and did not change significantly from the initial value of 4.1. The total concentration of leached Ni during nitrogen aeration was about 460 mg kg^{-1} as aeration proceeded (Fig. 5), and that of leached V was about 70 mg kg^{-1}. Neither the leaching of Ni and nor that of V was affected significantly by the changes of redox potential brought about by continuous nitrogen aeration,.

The results of equilibrium leaching under acidic condition (pH 5.0) are shown in Fig. 6. The leached Ni concentration (540 mg kg^{-1}) at 250 mV was the highest. However, leaching of Ni was not significantly affected by changes in redox potential, and no systematic pattern was found. The results indicated that the leached V concentration increased when the redox potential became more reducing. A similar pattern was found for the effect of redox potential on Fe leaching. Under slightly alkaline conditions (pH 8.0), the leached Ni concentration was very low for redox potentials higher than −100 mV (Fig. 7). It then gradually increased with decreasing redox potential to 27 mg kg^{-1}
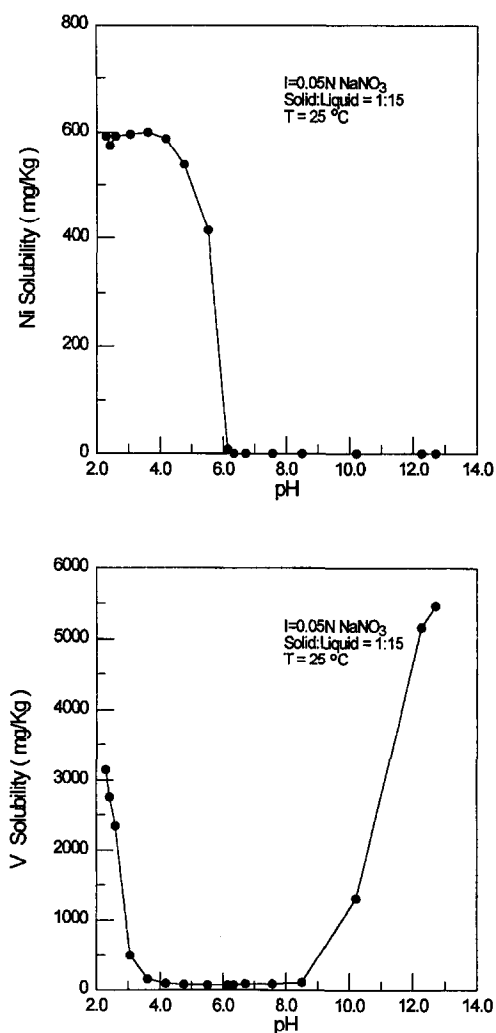
Fig. 3. (A) Ni solubility as affected by pH: solid:liquid ratio = 1:15, I = 0.05 N NaNO$_3$, 25°C. (B) V solubility as affected by pH: solid:liquid ratio = 1:15, I = 0.05 N NaNO$_3$, 25°C.

at −330 mV. A similar pattern was found for Fe leaching. Significant leaching of Fe was found only when the redox potential changed from −200 to −300 mV, and then to −330 mV. Concerning the leaching of V, the pattern was quite different. The leached concentration of V increased gradually when the redox potential changed from 250 to −300 mV. An abrupt increase in the leaching of V was then observed as the redox potential was further decreased from −300 to −330 mV. Additionally, the concentration of leached V was obviously much lower under alkaline than under acidic conditions at an identical redox potential.

In order to investigate the leaching mechanism and changes of metal speciation after
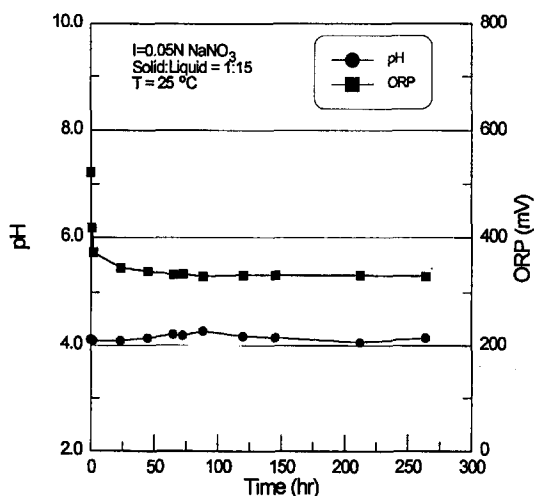
Fig. 4. Changes in the pH and redox potential of spent catalyst suspension under continuous nitrogen aeration.

the leaching experiment, spent catalyst which had been leached pH 8.0 and a redox potential of -330 mV for three days was examined on metal fractionation. The results are shown in Table 4. The exchangeable fraction of Ni decreased significantly, while that of both carbonate-bound and Fe–Mn oxide-bound Ni increased. The organic-bound and residual Ni did not change during the leaching procedure. Again, a dissimilar pattern was found for V. All fractions of V changed after being leached under alkaline and reducing conditions. Both exchangeable and carbonate-bound fractions of V increased, while the other three fractions decreased. It is likely that the leaching behavior of V was
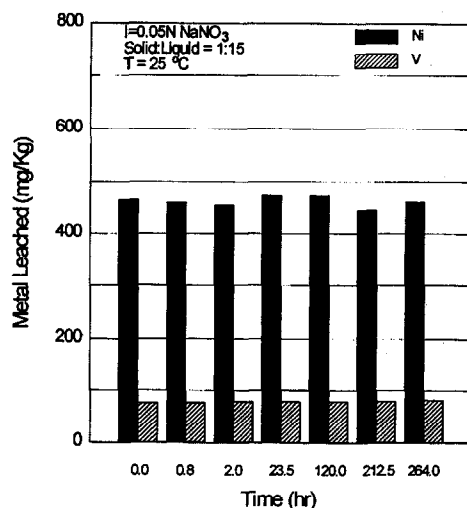

Fig. 5. Leached concentrations of Ni and V from spent catalyst suspension under continuous nitrogen aeration.
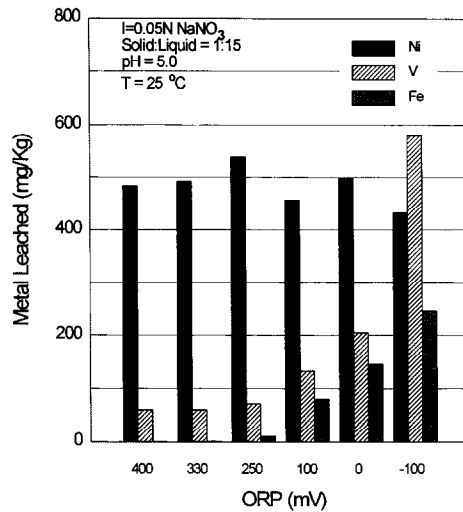
Fig. 6. Leached concentrations of Ni, V, and Fe from spent catalyst suspension at pH 5.0 and six different redox potentials.

affected by changes of fraction in the current work. In studying lake sediment, oxidation has been found to cause changes of fraction, and the related mobility of heavy metals [22]. Similar findings have also been shown among tannery waste and sludge-amended soils [23]. Little work has been conducted on the effect of reduction reaction on changes of fraction and the mobility of heavy metals. However, judging from the significant
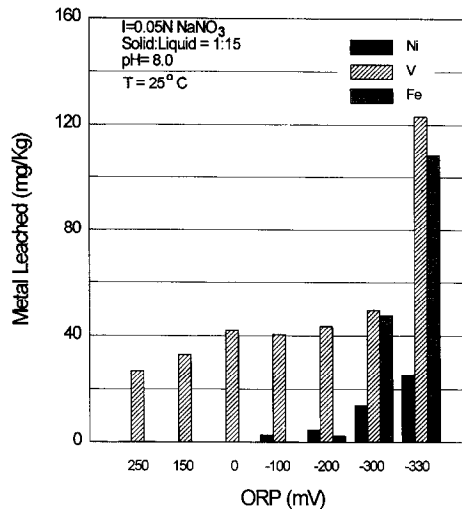

Fig. 7. Leached concentrations of Ni, V, and Fe from spent catalyst suspension at pH 8.0 and seven different redox potentials.

Table 4
Fractions of Ni and V in spent ROC catalyst equilibrated at pH 8.0 and ORP = − 330 mV

Fraction	Concentration (mg kg^{-1})		Percentage (%)	
	Ni	V	Ni	V
Exchangeable	11	42	0.3	0.5
Carbonate-bound	230	710	5.6	8.2
Fe–Mn oxides-bound	300	5300	7.3	60.8
Organic-bound	22	520	0.5	6.0
Residual	3530	2140	86.2	24.6

decrease of portions of the two least mobile fractions, i.e. organic-bound and residual fractions, as well as the leaching of Fe under reducing conditions (Fig. 7), it is proposed that the leaching of V could well be related to changes of fractionation.

The leaching of Ni under continuous nitrogen aeration did not change with respect to changes in redox potential. Similarly, equilibrium leaching at pH 5.0 and various redox potentials was not significantly affected by the redox potential. The pH value seems to have a stronger effect than the redox potential on the leaching of Ni. This is in conformity with the proposed theory that pH is the most important factor determining the distribution of Ni between solid and solution phases [17]. Evidenced by the proximity of leached Ni concentrations and fractionation analysis, it is proposed that Ni leaching under both conditions can be attributed to the mobilization of the exchangeable fraction of Ni. Additionally, the reduced leaching of Ni at pH 8.0 could also be explained in terms of the transformation of exchangeable Ni to both carbonate-bound and Fe–Mn oxides-bound Ni. Namely, leached Ni either precipitated as hydroxides or was readsorbed onto solid surfaces.

The leaching of V was more complicated owing to the existence of different chemical species as affected by pH and redox potential. The leaching of V has been found to increase with decreasing redox potential from stabilized fly ash and sludge [8]. Nevertheless, the immobilization of V under reducing conditions has also been indicated [19]. In addition, it has also been pointed out that controversy exists concerning the E_h/pH chemistry of V [8]. According to the thermodynamically predicted E_h/pH diagram [21,24], $H_2VO_4^-$ is the most stable species at pH < 5.0 and in an oxidizing environment. Reduction of $H_2VO_4^-$ to VO^{2+} would occur when the redox potential was reduced from 400 to − 100 mV. It is speculated that VO^{2+} is more soluble than $H_2VO_4^-$. Likewise, the reduction of $H_2VO_4^-$ to $HV_2O_5^-$ when the redox potential was reduced from − 300 to − 330 mV [24] could possibly explain the enhanced leaching of V from the spent catalyst. As stated in the current work, changes in the fractionation of V could also possibly influence its leaching behavior. Further study is required to elucidate the mechanism of V leaching.

4. Summary

As land disposal of petrochemical wastes continues to represent an attractive option in Taiwan, questions regarding the short-term and long-term environmental impact may

be raised. Little information has been published on the leaching behaviors of metals from spent catalyst. Based on results obtained from the current work, the following conclusions are made.

1. The spent catalyst could meet TCLP standards, and be categorized as a non-hazardous waste. However, notably high concentrations of Ni and V were found in TCLP filtrate.
2. Results from sequential extraction showed that residual and exchangeable fractions constituted the majority of Ni, whereas Fe–Mn oxide-bound V was the dominant portion. Fractionation is believed to affect the leaching of Ni and V.
3. Ni solubility was negligible when the pH was higher than 6.0. Minimum solubility was found for V in the pH range of 4.0–8.0.
4. The leached concentrations of Ni and V were about 460 and 70 mg kg^{-1}, respectively, under continuous nitrogen aeration. Neither were significantly affected by redox potential.
5. No systematic pattern was found for Ni leaching at pH 5.0 and various redox potentials. The leaching of V increased with decreasing redox potential.
6. The leached concentration of Ni was very low at pH 8.0 and different redox potentials. The leaching of V increased gradually as the redox potential decreased, and abruptly increased when the redox potential was reduced from -300 to -330 mV.
7. The leaching of Ni from spent catalyst is proposed to be largely related to the exchangeable fraction of Ni. However, the leaching of V was speculated to be related to both changes of fractionation and reduction reactions.

Acknowledgements

References

[1] G. Berrebi, P. Dufresne and Y. Jacquier, Recycling of spent hydroprocessing catalysts: EURECAT technology. Environ. Prog., 12 (1993) 97–100.
[2] R.A. Corbett, Refiners, petrochem. plants focus on new waste challenges, Oil Gas J., March 5 (1990) 33–38.
[3] R.C. Loehr, L.A. Rogers and D.C. Erickson, Mobility of residues at petroleum industry hazardous waste land treatment sites, Water Sci. Tech., 25 (1992) 191–196.
[4] R.C. Loehr, D.C. Erickson and L.A. Kelmar, Characteristics of residues at hazardous waste land treatment units, Water Res., 27 (1993) 1127–1138.
[5] W.H. Patrick, Jr., B.G. Williams and J.T. Moraghan, A simple system for controlling redox potential and pH in soil suspensions, Soil Sci. Soc. Am. Proc., 37 (1973) 331–332.
[6] P.H. Masscheleyn, R.D. Delaune and W.H. Patrick, Jr., Transformations of selenium as affected by sediment oxidation–reduction potential and pH, Environ. Sci. Technol., 24 (1990) 91–96.
[7] P.H. Masscheleyn, R.D. Delaune and W.H. Patrick, Jr., Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil, Environ. Sci. Technol., 25 (1991) 1414–1419.

[8] D.C. Dusing, P.L. Bishop and T.C. Keener, Effect of redox potential on leaching from stabilized/solidified waste materials, J. Air. Waste Manage. Assoc., 42 (1992) 56–62.

[9] M.C. Chuan, G.Y. Shu and J.C. Liu, Solubility of heavy metals in a contaminated soil: effects of redox potential and pH, Water Air Soil Pollut., 89 (1996) 1–14.

[10] Standard Methods for the Examination of Water and Wastewater, 16th edn., APHA, AWWA, WPCF, Washington, DC, 1985.

[11] J.T. Sims and J.S. Kline, Chemical fractionation and plant uptake of heavy metals in soils amended with co-composted sewage sludge, J. Environ. Qual., 20 (1991) 387–395.

[12] A. Tessier, P.G.C. Campbell and M. Bisson, Sequential extraction procedures for the speciation of particulate trace metals, Anal. Chem., 51 (1979) 844–851.

[13] R.M. Smith and A.E. Martell, Critical Stability Constants, Vol. 4, Plenum, New York, 1976.

[14] T.E. Clevenger, Use of sequential extraction to evaluate the heavy metals in water treatment sludges, Water Air Soil Pollut., 50 (1990) 241–250.

[15] S. Dudka and A. Chlopecka, Effect of solid-phase speciation on metal mobility and phytoavailability in sludge-amended soil, Water Air Soil Pollut., 51 (1990) 153–160.

[16] D.B. Levy, K.A. Barbarick, E.G. Siemer and L.E. Sommers, Distribution and partitioning of trace metals in contaminated soils near Leadville, Colorado, J. Environ. Qual., 21 (1992) 185–195.

[17] S.P. McGrath and S. Smith, Chromium and Nickel, in B.J. Alloway (Ed.), Heavy Metals in Soils, Blackie, London, 1990.

[18] H.A. Elliot, B.A. Dempsey and P.J. Maille, Content and fractionation of heavy metals in water treatment sludges, J. Environ. Qual., 19 (1990) 330–334.

[19] K.C. Jones, N.W. Lepp and J.P. Obbard, Other Metals and Metalloids, in B.J. Alloway (Ed.), Heavy Metals in Soils, Blackie, London, 1990.

[20] G. Gonzalez, S.M. Saraiva and W. Aliaga, Isoelectric points of niobium and vanadium pentoxides, J. Dispersion Sci. Technol., 15 (1994) 123–132.

[21] A.J. Bard, Encyclopedia of Electrochemistry of the Elements, Marcel Dekker, New York, 1976.

[22] K. Saeki, M. Okazaki and S. Matsumoto, The chemical phase changes in heavy metals with drying and oxidation of the lake sediments, Water Res., 27 (1993) 1243–1251.

[23] R. Milacic and J. Stupar, Fractionation and oxidation of chromium in tannery waste and sewage sludge-amended soils, Environ. Sci. Technol., 29 (1995) 506–514.

[24] D.R. Diercks and D.L. Smith, Stress-corrosion cracking susceptibility of V–15Cr–5Ti in pressurized water at 288°C, J. Nucl. Mater., 26 (1988) 995–1007.