

SELECTIVE RECOVERY OF METALS FROM SPENT DESULFURIZATION CATALYST

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Abstract – Valuable metals including V, Mo, Ni, Co, and Al were selectively recovered from spent desulfurization catalyst by means of extractive separation. Prior to selective metal recovery the spent catalyst was roasted at temperatures of 400–800 °C, and BET, SEM, and XRD data showed that roasting the spent catalyst at 550 °C gave birth to the surface and pore structures accounting for good extractibility of the roasted spent catalyst. A sequential scheme consisting of leaching and chelate extraction was developed to recover the metals from the spent catalyst roasted at 550 °C and oxygen space velocity of ca. 1800 hr⁻¹.

Key words: Extractive Separation, Selective Metal Recovery, Roasted Spent Catalyst, Surface and Pore Structures, Extractibility

INTRODUCTION

The spent catalyst removed from residue desulfurization process at the end of each cycle run contains several metals including vanadium (V), molybdenum (Mo), nickel (Ni), cobalt (Co), and aluminum (Al). Whereas Mo, Co, and Al are the constituents inherent from fresh desulfurization catalyst, V and most of Ni are those collected from demetalation of residue feed. The residue feed contains asphaltene-type molecules consisting usually of V- and Ni-porphyrins which decompose via hydrodemetalation to metals and hydrocarbon fragments. While the hydrocarbon fragments diffuse out of catalyst pores, the metals are accumulated in the form of metal sulfides within the catalyst pores [Tamm et al., 1981; Smith and Wei, 1991; Thakur and Thomas, 1985]. As process onstream hours increase, catalyst pores become gradually filled with these metal sulfides as well as coke (carbonaceous deposits), therefore the activity for residue desulfurization is lost eventually to such an extent that the aged catalyst needs to be replaced with fresh catalyst for another cycle run.

The metals in the spent catalyst are usually recovered by means of two different methods. One method is simply smelting the spent catalyst to metal alloys and slag in the gaseous environment [Howard and Barnes, 1991]. The other method is recovering the metals in the liquid environment, preceded by roasting or wet oxidation of the spent catalyst. The latter method has been studied and been in commercial use for the last decade by metal reclaimers in Japan and U. S. A.: the roasting or wet oxidation step is aimed at converting the metal sulfides to metal oxides and removing the residual oil and carbonaceous species in the spent catalyst; the metal recovery step proceeds usually via consecutive leaching of the spent catalyst or its derived compounds, coupled with selective precipitation [Cmojevich et al., 1990; Wiewiorowski et al., 1988; Wiewiorowski, 1987].

The principles of the metal recovery processes are classical,

however, the details are mostly protected by patents or yet to be investigated further for process improvement. For instance, in the case of roasting or wet oxidation of the spent catalyst, temperature and oxidant pressure reported in the literature [Tilley, 1988; Wiewiorowski et al., 1988] appeared to be unnecessarily high. Also, in the case of metal recovery, some metals were not completely recovered in the selective fashion [Wiewiorowski et al., 1988; Wiewiorowski, 1987]. In fact, not much of coherence has been published for the selective recovery of metals by means of extractive separation [Fischer and Van Savage, 1986; Nevitt, 1987; Tilley, 1988; Inoue, 1996]. As for the extractants, Fischer and Van Savage used the solutions of ligands including the salts of dithiolate, dithiocarbamate, and dithiocarbamate, while Nevitt used a complexing agent with multiple coordinating groups including at least two carboxylic acid type groups and at least one amino type group. Tilley reported the usage of alkyl phosphoric acids for recovering subvalent vanadium, and the usage of modified tertiary amines for recovering molybdenum. Inoue reported the usage of complicated organic mixtures for recovering nickel and cobalt: mixtures of diethyl hydroxy dodecanone oxime (LIX63) and acidic organophosphinates as well as mixtures of picolylamines and dinonylnaphthalene sulphonic acid.

Thus, it may be motivated to obtain the optimal process conditions and present another efficient scheme of metal recovery for the selective recovery of valuable metals from spent desulfurization catalyst. Prompted by this motivation, we performed a laboratory-scale study composed of roasting the spent desulfurization catalyst, dissolving the roasted catalyst in the leachants, and separating the constituent metals with the usage of relatively simple and inexpensive organic extractants.

EXPERIMENTAL

1. Roasting of Spent Catalyst

Samples of spent desulfurization catalyst were obtained from the spent catalyst removed from the vacuum residue desulfuri-

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zation (VRDS) unit of Yukong Limited at the end of its first cycle operation of VRDS process. In order to measure the elemental composition of the spent catalyst, a 0.5 g sample reduced to 80 mesh size was oxidized for 2 hours at 700 °C in a muffle furnace, and then was completely dissolved in a 15 N sulfuric acid solution at 120 °C for ICP (Shimadzu ICPS-1000III) analysis.

Roasting experiments were conducted in such a way that each 1 g of the samples in 80 mesh size was placed in a dispersive manner of 2-3 mm depth in a porcelain sample holder and was roasted in atmospheric oxygen flow in a tubular furnace. Prior to roasting, the sample was stripped in nitrogen flow of 100 ml/min for the temperature ramp of 5 °C/min from room temperature to 400 °C, followed by 1 hour hold at 400 °C. This nitrogen stripping was performed to remove the residual oil in the spent catalyst, thereby avoid the possible occurrence of violent exothermicity during roasting [Marafi et al., 1989]. A schematic diagram of the roasting apparatus is presented in Fig. 1.

1-1. Optimization of Roasting Temperature

Each 1 g sample was roasted for 90 minutes at each temperature of 400-800 °C in oxygen flow, and the roasted sample was characterized by means of BET adsorption (Micromeritics ASAP 2400), and SEM (Hitachi S-4100) and XRD (Rigaku D/max-2500) analyses. Residual sulfur content was measured using a sulfur analyzer (Perkin-Elmer Inc.). The rate of temperature ramp from 400 °C to the desired roasting temperature was 5 °C/min,

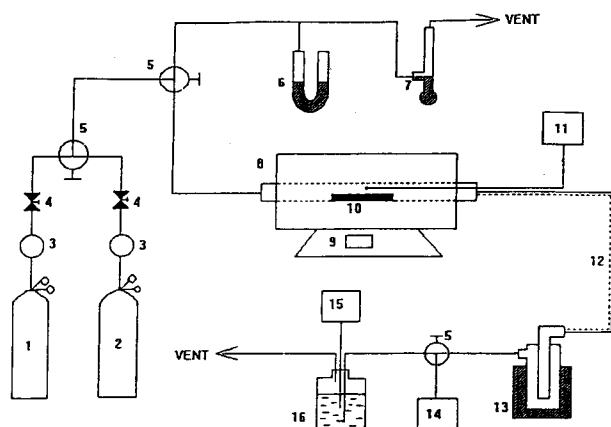


Fig. 1. Schematic diagram of spent catalyst roasting.

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|----------------------------|-----------------------------|
| 1. N ₂ cylinder | 2. O ₂ cylinder |
| 3. Line pressure regulator | 4. Needle valve |
| 5. Three way valve | 6. Manometer |
| 7. Soap film flowmeter | 8. Tubular furnace |
| 9. Temperature controller | 10. Spent catalyst sample |
| 11. Thermocouple | 12. Heating tape |
| 13. Cold trap | 14. Gas chromatograph |
| 15. pH meter | 16. NaOH scrubbing solution |

and the oxygen flow rate was maintained at 30 ml/min for roasting 1 g of the spent catalyst. In order to investigate the extractibility of roasted spent catalyst, each 0.8 g of the roasted samples was dissolved in 80 ml of 15 N sulfuric acid solution at 120 °C and its dissolution rate was measured in solubility (wt. %) vs. time. The sulfuric acid solution was used as the leachant, since it readily dissolved oxides of the metal components of the spent catalyst [Tilley, 1988; Kelebek and Distin, 1989; Inoue, 1996]. Based on the BET, SEM, XRD, and solubility data, the optimal roasting temperature was determined.

1-2. Optimization of Oxygen Flow Rate

After the roasting temperature was optimized, the oxygen flow rate was varied at 15-60 ml/min for roasting each 1 g of the spent catalyst at the optimal roasting temperature. The effect of oxygen flow rate upon roasting was investigated by measuring pH change of NaOH solution scrubbed with the effluent gas stream from the tubular furnace in which the spent catalyst was roasted. For each oxygen flow rate, SO₂ concentration of the effluent gas stream was also monitored with a gas chromatograph (Shimadzu GC-14A). The pH change of the scrubbing solution and the stability of the temperature profile of the roasting bed were the major aspects considered in determining the optimal oxygen flow rate.

2. Recovery of Metals from Roasted Spent Catalyst

The spent catalyst roasted at the optimal temperature and oxygen flow rate was dissolved in 1 N Na₂CO₃ solution at 120 °C for 2 hrs. Using the Na₂CO₃ solution as the leachant was due to the preferential dissolution of V and Mo into the liquid phase, with other metals undissolved in the solid phase. In order to dissolve the solid phases obtained subsequently, 15 N sulfuric acid solutions in appropriate volumes were used with the temperature and duration determined on the trial-and-error basis. Liquid phases were isolated from solid-liquid mixtures by filtration, and were treated with the organic extractants listed in Table 1 for extractive separation of metals into the organic phases. Selection of the extractants as well as the separation conditions was due to the literature [Jeffery et al., 1989; Ritcey and Ashbrook, 1979] and laborious searching by trial and error. For each metal recovered, a crossflow extractive separation up to 3 stages was employed, and recovery fraction was estimated by ICP analysis of the organic phases [Ritcey and Ashbrook, 1979].

RESULTS AND DISCUSSION

1. Roasting of Spent Catalyst

Elemental composition of spent desulfurization catalyst is presented in Table 2. Since the spent catalyst was removed from the hydrodemetalation reactor of VRDS process, V and Ni contents were high, and small amount of Fe was also detected ow-

Table 1. Extractive separation of metals using organic extractants

Metal extracted in organic phase	Organic extractant	Extractant preparation	Other reagents
Mo V	8-hydroxyquinoline sol'n acetyl acetone sol'n	8-hydroxyquinoline, 2 g+ethanol, 100 ml	chloroform, HCl pyridine, 1 M NaHSO ₃ , CH ₂ Cl ₂ , HCl, NH ₄ OH
Ni Co	dimethyl glyoxime sol'n 1-nitroso-2-naphthol sol'n	dimethyl glyoxime, 0.5 g+NH ₄ OH, 250 ml+H ₂ O, 500 ml 1-nitroso-2-naphthol, 1 g+50 % CH ₃ COOH (filtered solution)	chloroform, NH ₄ OH chloroform, NH ₄ OH

ing to either demetalation of the residue feed or corrosion scale deposit [Tilley, 1988; Smith and Wei, 1991].

BET data of roasted spent catalyst are listed in Table 3. The spent catalyst samples roasted at 500, 550, and 600°C exhibited relatively large surface area and pore volume, indicative of satisfactory removal of sulfur and carbon impurities. SEM analysis of roasted spent catalyst is presented in Fig. 2. As the roasting temperature increased, the particle size increased most likely due to sintering of the particles occurring at elevated temperatures [Twigg, 1989]. This is demonstrated by comparing the particle size after roasting at 550°C and 800°C, as the particle size shown in photograph (d) is much larger than that shown in photograph (b). Sintering of the particles usually decreases surface area and pore volume, which is consistent with the BET data. XRD analysis of roasted spent catalyst presented in Fig. 3 indicates that raising the roasting temperature resulted

in major alteration of the surface structure. The alteration included the followings.

(1) Molybdenum was lost from the surface as the roasting temperature exceeded 650°C.

(2) Vanadium migrated to the surface as the roasting temperature increased. Also, dramatic migration of nickel to the surface occurred at 800°C.

(3) Alloy phases were formed by roasting at 800°C, as evidenced by the peaks at 2 theta values of 34.9, 52.2, and 57.3 which could not be ascribed to any single metal in the spent catalyst.

SEM and XRD analyses indicate that in case of roasting at excessively high temperature, large particles and alloy phases were formed due to sintering as well as vanadium and nickel migra-

Table 2. Elemental composition of spent desulfurization catalyst after oxidation at 700°C for 2 hours

Element	wt%
V	22.6
Ni	5.5
Mo	2.8
Co	0.8
Al	24.7
Fe	0.2
O	balance

Table 3. Surface area and porosity of spent desulfurization catalyst roasted at various temperatures

Roasting temp. (°C)	Sp. surface area (m ² /g)	Pore volume (cc/g)	Avg. pore diameter (Å)
400	35.9	0.17	180
500	36.8	0.18	190
550	38.6	0.19	190
600	37.7	0.20	210
650	34.1	0.18	210
700	24.3	0.13	220
800	3.4	0.02	160

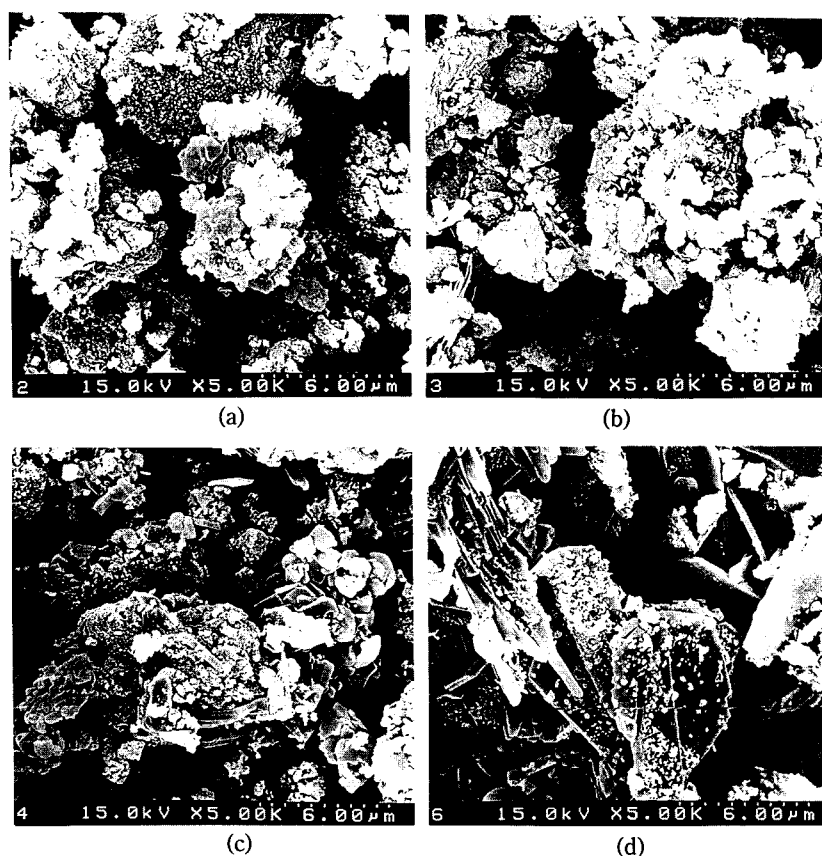


Fig. 2. SEM photographs of spent desulfurization catalyst.

(a) roasted at 400°C, (b) roasted at 550°C, (c) roasted at 700°C, (d) roasted at 800°C

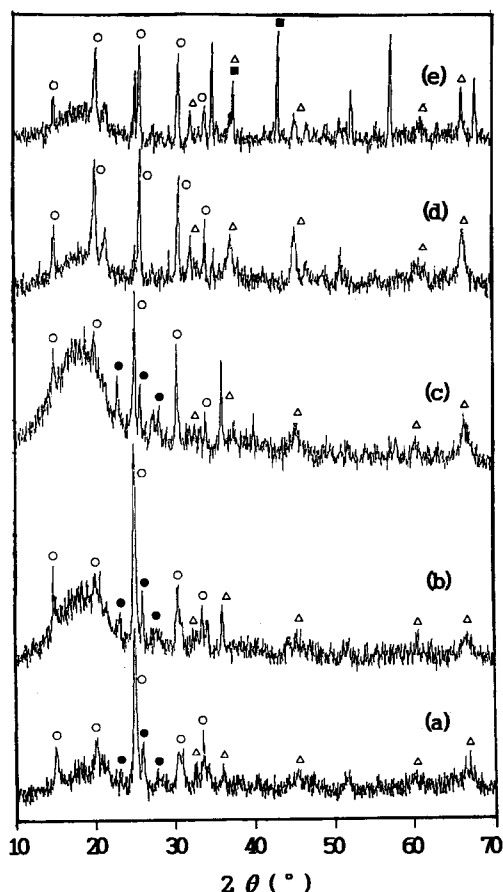


Fig. 3. XRD pattern of spent desulfurization catalyst.

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|-----------------------|-----------------------|
| ○: vanadium | △: aluminum |
| ●: molybdenum | ■: nickel |
| (a) roasted at 400°C, | (b) roasted at 550°C, |
| (c) roasted at 650°C, | (d) roasted at 700°C, |
| (e) roasted at 800°C. | |

tion to the surface.

Extractibility of roasted spent catalyst is shown in Fig. 4, with the samples roasted at 500, 550, and 600°C exhibiting relatively high dissolution rate in the sulfuric acid leachant. For example, by leaching for 100 minutes, the sample roasted at 550°C was completely dissolved while the samples roasted at 650°C and 800°C were dissolved in 87% and 60%, respectively. Extractibility of spent catalyst roasted at 400°C was not included in Fig. 4 due to its samplewise inconsistency presumably attributed to incomplete or inhomogeneous removed of sulfur and carbonaceous species. The extractibility data together with BET, SEM, and XRD data implied that 500-600°C was the temperature range preferable for spent catalyst roasting since the surface and pore structures obtained by roasting at those temperatures facilitated dissolution of roasted spent catalyst in the leachant.

With the roasting temperature fixed at 550°C, the effect of oxygen flow rate on roasting was investigated by comparing the pH change of NaOH scrubbing solution vs. oxygen flow rate for roasting 1 g (ca. 1 cc volume) of the spent catalyst. Fig. 5 represents pH decrease of the scrubbing solution for the oxygen flow rate of 15, 30, and 60 ml/min. As the oxygen flow rate was decreased to 15 ml/min, pH decrease of the scrubbing

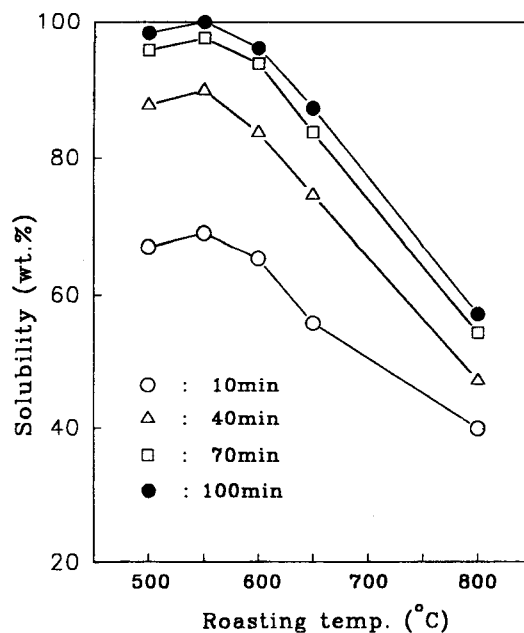


Fig. 4. Extractibility of roasted spent catalyst.

(The legend denoted the time lapsed in dissolving each 0.8 g sample in 80 ml of 15 N H₂SO₄ leaching solution at 120°C.)

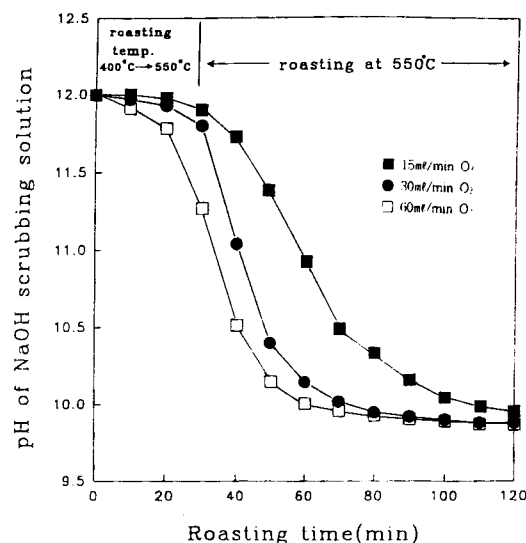


Fig. 5. pH change of NaOH scrubbing solution for roasting 1 g spent catalyst at 550°C.

solution was significantly retarded so that roasting time greater than 90 minutes was required for pH of the scrubbing solution to get down to the level reached by roasting in 30 ml/min oxygen flow for 90 minutes. For the oxygen flow rates greater than 30 ml/min, pH decrease of the scrubbing solution was somewhat accelerated, however, the temperature profile of the roasting bed became quite unstable compared to those observed in 15 and 30 ml/min oxygen flows. For example, in the early part of roasting in 60 ml/min oxygen flow, the bed temperature fluctuated rapidly in a random fashion in the range of 630-750°C, that is, 80-200°C greater than the preset roasting temperature. Therefore, the optimal oxygen space velocity was preferably estimated as 30 ml/min oxygen flow for 1 ml spent catalyst, i.e.,

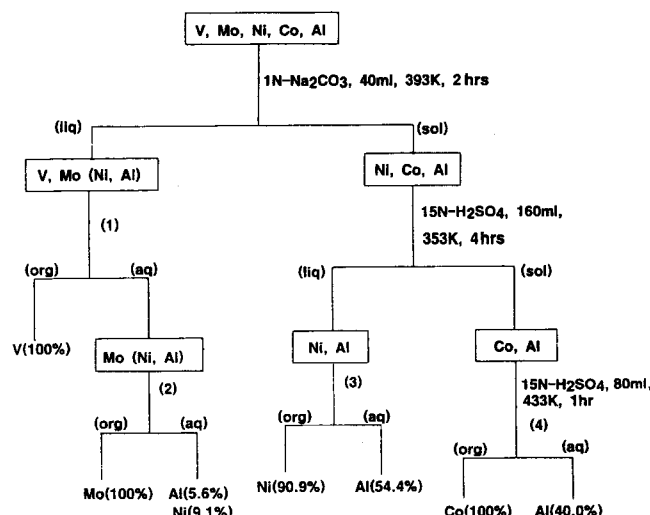


Fig. 6. Selective recovery of metals from a 0.8 g sample of roasted spent catalyst.

(liq) liquid, (sol) solid, (org) organic, (aq) aqueous

(1) acetylacetone sol'n, (2) 8-hydroxyquinoline sol'n,

(3) dimethyl glyoxime sol'n, (4) 1-nitroso-2-naphthol sol'n.

1800 hr⁻¹.

2. Recovery of Metals from Roasted Spent Catalyst

Selective recovery of metals from spent desulfurization catalyst utilized a sequential network of leaching and extraction. The sequential recovery scheme presented in Fig. 6 can be explained as follows. 0.8 g of the spent catalyst sample roasted at 550 °C and oxygen space velocity of 1800 hr⁻¹ was dissolved in 40 ml of 1 N Na₂CO₃ solution at 120 °C for 2 hrs. This leaching treatment was followed by filtration isolating the dissolved (liquid) phase from the undissolved (solid) phase. The liquid phase contained all of the Mo and V contents with small fractions of the Ni and Al contents. Addition of acetylacetone solution to the liquid phase led to organic-aqueous phase separation, by which all of the V content was extracted to the organic phase. Addition of 8-hydroxyquinoline solution to the aqueous phase led to another organic-aqueous phase separation, extracting all of the Mo content to the organic phase. The remaining aqueous phase, which is the final raffinate of the first dissolved phase, contained 5.6 % of the Al content and 9.1 % of the Ni content.

The undissolved (solid) phase consisted of the remainders of Ni and Al contents together with a whole of Co content of the sample. Dissolution of the solid phase in 160 ml of 15 N sulfuric acid solution at 80 °C for 4 hrs gave birth to another liquid phase (the second dissolved phase) containing Ni and Al, as well as a solid phase containing Co and Al. The liquid phase was treated with dimethyl glyoxime solution in order to envelop Ni in the organic phase. Al recovered in the aqueous phase accounted for 54.4 % of total Al content. The solid phase containing Co and Al was thoroughly dissolved in 1 hr by addition of 80 ml of 15 N sulfuric acid solution at 160 °C. 1-nitroso-2-naphthol solution was added to the resultant solution in order to isolate Co into the organic phase, with 40 % of total Al content collected in the aqueous phase.

Owing to the sequential recovery scheme described above, V, Mo, Co, and 91 % of Ni could be recovered in the organic

phases via extractive separation. Moreover, by adding the final raffinate of the first dissolved phase to the second dissolved phase, the overall fraction of Ni recovery could be increased to 100 %. These two dissolved phases could be extracted together, since both were aqueous and contained Ni and Al. The metals recovered in the organic phases should be in the form of metal chelates since addition of each organic extractant to the aqueous phase led to isolation of the corresponding metal into the organic phase [Jeffery et al., 1989; Ritcey and Ashbrook, 1979]. In contrast, aluminum was collected as aluminum sulfate in the aqueous phase.

The extractive metal recovery scheme developed in this study has the distinction from the processes in commercial use which utilize mainly consecutive leaching or dissolution of the salts formed by addition of sodium carbonate or caustic soda solution at high temperatures and pressures, and usually end up with incomplete separation of Ni and Co mixtures [Sebenik et al., 1985; Wiewiorowski et al., 1988; Wiewiorowski, 1987]. In this study each component metal of the spent desulfurization catalyst could be selectively recovered via sequential separation utilizing inexpensive leachants as well as relatively simple and inexpensive organic extractants compared to the previous studies [Fischer and Van Savage, 1986; Nevitt, 1987; Tilley, 1988; Inoue, 1996]. The selective metal recovery scheme developed in this study consisted of leaching and extraction at moderate temperatures below 200 °C and under atmospheric pressure, rendering the potential of its commercial application competitive, although recycle or disposal of spent sulfuric acid solution as well as spent organic extractants would leave the economic and/or environmental problems to deal with further.

CONCLUSIONS

From the results discussed above, the following conclusions could be drawn for the selective recovery of metals from spent desulfurization catalyst by means of roasting followed by extractive separation.

1. Roasting could be optimized with respect to temperature and oxygen flow rate. Roasting at the temperature range of 500–600 °C and oxygen space velocity of 1800 hr⁻¹ gave birth to good surface and pore structures of roasted spent catalyst, to which good extractability in leaching the roasted spent catalyst was attributed.

2. In recovering the metals selectively, Na₂CO₃ solution was used to leach the roasted spent catalyst for the purpose of extracting V and Mo preferentially, and H₂SO₄ solutions were the leachants used to dissolve the solid phases obtained subsequently.

3. By extractive separation Mo, V, Ni, and Co were recovered as metal chelates in the organic phases, while Al was recovered as aluminum sulfate in the aqueous phases.

4. The selective metal recovery scheme developed in this study comprised leaching and extraction operated at moderate temperatures below 200 °C and under atmospheric pressure, therefore its potential of commercial application appeared competitive, although recycle or disposal of spent sulfuric acid solution as well as spent organic extractants would leave the economic and/or environmental problems to deal with further.

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