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Extraction of Valuable Metals from Spent Desulfurizing Catalyst[†]

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요 약

황산으로 탈황 폐촉매를 침출한 결과 황산농도 1 M, 반응시간 1 hr인 실험조건에서 Ni 및 V은 95% 이상, 그리고 Mo은 30%가 침출되었다. 탈황 폐촉매의 Mo matrix 특성으로 인하여 다른 금속에 비하여 Mo의 침출율이 낮았으며, 본 침출반응은 확산반응에 의하여 제어되는 것으로 판단된다. Mo을 완전히 침출하기 위하여 유황성분이 제거된 폐촉매로 침출실험을 실시하였다. 1 M 황산으로 처리후 탄산나트륨으로 세척시 Ni, Mo 그리고 V의 침출율은 99%이었다. Ni 2 g/L; V 9 g/L, Mo 0.6 g/L 조성의 침출액을 LIX 84I로 용매추출한 조건에서 A:O 비 5:2, 2단계로 처리시 Mo은 98% 이상 추출되었으며 A:O 비 5:3, 2단계로 처리시 V은 82%가 추출되었다.

주제어 : 침출, 폐촉매, 용매추출, 탈착

Abstract

Sulphuric acid leaching was conducted to extract the metal values from spent refinery catalyst. More than 95% of Ni and V and 30% of Mo could be leached out in 1 M sulphuric acid and 1 hr of leaching time. The decrease in Mo leaching was due to typical characteristic of Mo matrix. The activation energies of the leaching reactions showed the dissolution process follows a diffusion control mechanism. In order to leach out all Mo, further the leaching experiments were conducted with sulfur free spent refinery catalyst. For sulfur free spent refinery catalyst, a two step process of leaching with 1 M sulphuric acid followed by sodium carbonate washing showed better leaching than a two step leaching process with sodium carbonate followed by sulphuric acid washing, with almost 99% leaching of Ni, Mo and V. Solvent extraction using LIX 84I were conducted for a leach liquor containing Ni, 2 g/L; V, 9 g/L, Mo, 0.6 g/L. More than 98% of Mo was extracted from the leach liquor at A:O ratio of 5:2 in a 2 stage process. Similarly V was extracted at A:O ratio of 5:3 in a 2 stage process with 82% of total V extraction.

Key words : Leaching, Spent catalyst, Solvent extraction, Stripping

1. Introduction

Molybdenum, vanadium and nickel are important metals in human life and industry. These three metals

have wide applications in alloying elements, aircraft parts, electrical contacts, industrial motors, filaments.¹⁻⁵⁾ Apart from alloying, molybdenum, vanadium and nickel are widely used in the area of catalysis. In an estimate 90% of all commercial chemical products involve catalysts at some stage in the process of their manufacture.⁶⁾ Molybdenum and vanadium are used in

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chemical and aerospace industries because of their many superior performances.⁷⁾ In the petroleum refinery operations, solid catalysts are extensively used to improve the process efficiency.⁸⁾ The catalyst materials usually contain above metals and their oxides, which facilitate difficult hydrocarbons transformations with high selectivity and permit the refiners to produce the full range of clean transportation fuels with desired specifications from petroleum distillates and residues.⁹⁾ The requirements of such metals are full filled by metallurgical industries. Since primary resources of these metals are gradually depleting, metal recovery from secondary resources have been projected by several metal industries to fulfill the demand of the human being. These secondary resources include different solid wastes such as spent refinery catalysts, waste batteries, waste electronic equipments, municipal sold wastes, etc. These solid wastes are also hazardous in nature.

In South Korea spent refinery catalyst containing Al, Mo, V, Ni and Fe are estimated to be discarded annually around 15,000 tons, which looks sound as the secondary resources of metals.¹⁰⁾ In addition the waste catalysts are regarded as hazardous due to appreciable amounts of various heavy metal ions.¹¹⁾ A number of processes have been developed to recover metal values from waste petroleum catalyst.¹²⁻¹⁴⁾ The metal values can either be recovered through pyro or hydrometallurgical route. However, these two processes are not suitable when economics and environmental aspects are being concerned. In addition, these two routes have several drawbacks such as slow Mo kinetics and non-recovery of sulfur values.

On account of the above limitations, we have studied a smooth leaching process followed by a solvent extraction technique to recover all Ni, V and Mo from spent refinery catalyst.

2. Experimental

2.1. Pretreatment and characterization of spent catalyst

As such spent catalyst from the company was covered with a film of oils and organic pollutants. Since this spent catalyst looks like waxy material which cannot be used directly in our leaching purpose.

Acetone is chosen over all other organic solvents for the washing purpose. The spent catalyst was subjected to wash in acetone using a soxhlet to remove the oil coating. The spent catalyst washed by acetone was ground to powder size using a porcelain mortar and pestle followed by sieving to different size fraction. This powder material was used as a base material in all the leaching studies.

2.2. CS₂ washing of spent catalyst

As we discussed in our previous report¹⁵⁾ that leaching rate of Mo was lower than Ni and V due to hydrophobic elemental sulfur layer over Mo matrix, therefore, the acetone washed spent catalyst was further washed with carbon disulfide (CS₂) in a soxhlet. After removal of elemental sulfur, the dried material was ground and sieved for the leaching study.

2.3. Leaching

Leaching tests were conducted in a 500 mL volume stirred reactor containing 250 mL of solution. All leaching tests were carried out with 1 M H₂SO₄ as a lixiviant and 5% (v/v) H₂O₂ as oxidant for a duration of 1 hr, unless otherwise specified. Temperature of the system was controlled by using a thermostat. Oxygen was supplied into the lixiviant from an oxygen cylinder. Each leaching experiment was started after addition of required amount of spent catalyst and periodically 1.5 mL of samples were withdrawn for metal analysis. Prior to analysis, aliquot of sample was centrifuged then acidified with 10% (v/v) HCl and finally analyzed by ICP-AES (JOBIN-YVON JY 38).

2.4. Solvent extraction

Solvent extraction studies were carried out using LIX-84I (2-hydroxy-5-nonylaceto-phenone oxime) as an organic extractant. Kerosene was used as a diluent. Metal salts used in this investigation were of analytical grade reagents. Initial aqueous solutions of known concentration were prepared by dissolving an appropriate amount of salt in de-ionized water. The pH was adjusted to the required levels by the addition of concentrated H₂SO₄ or NaOH solution. The actual leach liquor was obtained after sulfuric acid leaching of the spent catalyst. From the series of leaching experiments it was confirmed that vanadium exists in

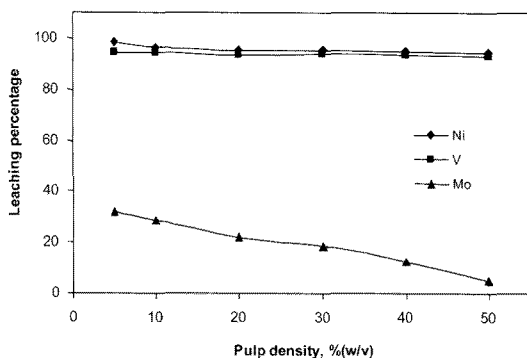


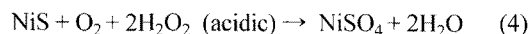
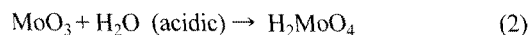
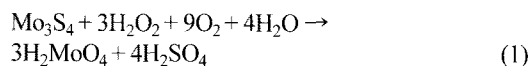
Fig. 1. Sulphuric acid leaching at different pulp density (H_2SO_4 : 1 M, H_2O_2 : 5% (v/v), temp.: 30°C, time: 1 hr).

the +4 oxidation and molybdenum in +6 state in leach solution. Therefore, ammonium molybdate and vanadyl sulfate were used in all solvent extraction tests concerning molybdenum and vanadium in the present study.

3. Results and discussion

3.1. Leaching of acetone washed spent catalyst

Leaching studies were carried out using acetone washed and CS_2 washed spent catalyst. But initially the experiments were conducted using acetone washed spent catalyst. The dissolution of sulfide requires an oxidant whereas oxide requires an acid. In our case the oxidant and acid used were H_2O_2 and dilute H_2SO_4 , respectively. The dissolution reactions for Mo, V and Ni in the spent catalyst are given in equations (1 to 4).¹¹⁾



Leaching studies were conducted by varying the pulp density from 5 to 50% (w/v). The leaching efficiency of Ni, V and Mo in terms of % are shown in Fig. 1. It can be observed that leaching percent of Ni and V was almost similar as more than 90% of these metals leached out at different pulp density. However, leaching percent of Mo was much lower than Ni and V.

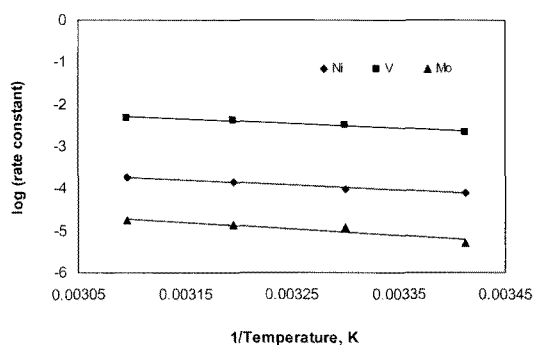


Fig. 2. Arrhenius plot for Ni, V and Mo.

Also it decreased with increase of pulp density from 5 to 50% (w/v). As leaching kinetics of Ni and V were higher than Mo at same condition, the decrease in leaching kinetics may be due to typical characteristic of Mo matrix as we have reported earlier.¹⁵⁾

Activation energy of the leaching reactions is an important parameter to evaluate the leaching kinetics. To find out the activation energy, the leaching temperature was varied from 20°C to 50°C. The activation energies for Ni, V and Mo were calculated using Arrhenius equation as follows:

$$k = Ae^{-E/RT} \quad (5)$$

where, k = reaction rate constant
A = frequency factor
E = activation energy
T = absolute temperature

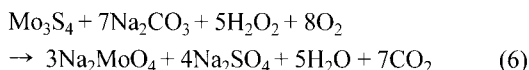
The slope of the plot log (reaction rate constant) versus 1/Temperature would be the activation energy. The Arrhenius plot is shown in Fig. 2. The activation energies of Ni, V, and Mo were found to be 2.3, 2.06, and 3.06 kJ/mole, respectively. From the values of activation energy it can be predicted that the dissolution process followed a diffusion control mechanism.¹⁶⁾ By varying the parameters such as pulp density and temperature, it was observed that the Mo leaching kinetics is different from that of Ni and V due to sulfur layer over Mo matrix. Therefore the elemental sulfur should be dissolved prior to leaching process.

3.2. Leaching with CS_2 washed spent catalyst

The acetone washed spent catalyst was further

washed with CS₂ to dissolve the elemental sulfur present in the spent catalyst. After dissolving in CS₂, the sulfur free spent catalyst was subjected to leaching process using both alkali and acid. Leaching studies were conducted using the same reactor size and same solution volume as discussed earlier for acetone washed spent catalyst.

Mo₃S₄ can be easily dissolved in Sodium carbonate (Na₂CO₃) to give (Na₂MoO₄) as following reaction shown in equation¹¹:



So leaching experiments were carried out by varying concentration of Na₂CO₃ from 10 to 50 g/L while other parameters kept constant such as H₂O₂ concentration at 5% (v/v), temperature at 30°C and leaching time for 1 hr. The leaching efficiency of Ni, V and Mo are shown in Fig. 3. From Fig. 3 it can be observed that the leaching rate of V and Mo increased rapidly with increase of Na₂CO₃ concentration from 10 to 40 g/L and slowed upon further increase of Na₂CO₃ concentration. However, the leaching efficiency of Ni was less than 10% in all cases. Also at 40 g/L of Na₂CO₃ concentration, only 45 and 72% of V and Mo, respectively, were leached out. To get the remaining metal values, the all leached residues were further dissolved with 1 M H₂SO₄. The details of result in the total process; i.e. Na₂CO₃ leaching followed by acid washing was given in Table 1. Although leaching efficiency of Mo in this process was better than earlier (only acid leaching of acetone washed spent catalyst),

we could not get 100% of Mo which was our main purpose of sulfur removal of acetone washed spent catalyst. Therefore further one set of leaching experiment for CS₂ washed spent catalyst were carried out with 1 M H₂SO₄ followed by washing with 40 g/L Na₂CO₃. The method of this process is similar to the above as 1 M H₂SO₄ was used as lixiviant while other parameters kept constant as H₂O₂ concentration at 5% (v/v), temperature at 30°C and leaching time for 1 hr. The % of leaching of Ni, V and Mo was found to be 98, 96 and 42, respectively. Subsequently the leach residue was washed with 40 g/L Na₂CO₃ and the washing sample was analyzed in ICP. It was observed that 55% of Mo washed out to the leach liquor in the washing process. The results are given in Table 1. From the table we can observe that almost all Ni, V and Mo were leached out in a process of acid leaching followed by washing with alkali for CS₂ washed spent catalyst.

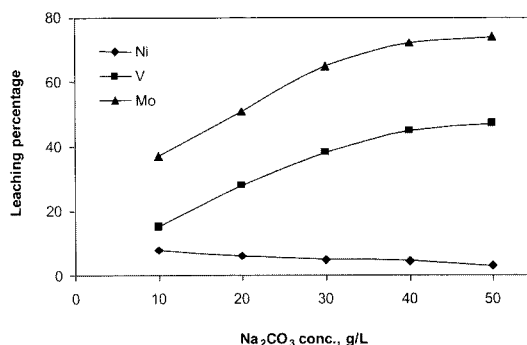


Fig. 3. Leaching of Ni, V and Mo at different concentration of Na₂CO₃ (H₂O₂: 5% (v/v), temp.: 30°C, time: 1 hr, pulp density: 10% (w/v).

Table 1. Percentage of leaching of Ni, V and Mo from CS₂ washed spent catalyst with acid and alkali. Conditions: H₂O₂, 5% (v/v); temperature, 30°C, pulp density, 10% (w/v)

Leaching conditions	Leaching with Na ₂ CO ₃ , %			Washing with 1 M H ₂ SO ₄ , %			Total metal leaching, %			
	Na ₂ CO ₃ , g/L	Ni	V	Mo	Ni	V	Mo	Ni	V	Mo
10		8	15	37	45	56	8	53	71	45
20		6	28	51	54	48	7	60	76	58
30		5	38	65	61	42	5	66	80	70
40		4.5	45	72	68	36	5	72	81	77
50		3	47	74	72	37	4	75	84	78
1 M H ₂ SO ₄	Leaching with H ₂ SO ₄ , %			Washing with 40 g/L Na ₂ CO ₃ , %			Total metal leaching, %			
		98	96	42	<1	2	55	98	98	97

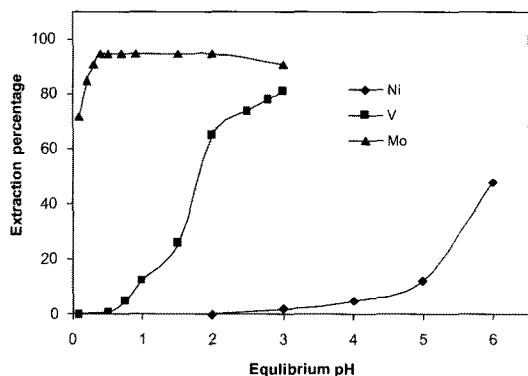


Fig. 4. Effect of equilibrium pH on extraction of Ni, V and Mo using 10% LIX-84I and A : O = 1 : 1.

3.3. Solvent extraction studies

Solvent extraction experiments were carried out for a synthetic solution with a composition according to the leach liquor obtained by using 1 M H₂SO₄ as a lixiviant. The typical composition of the solution was as: Ni, 2 g/L; V, 9 g/L; Mo, 0.6 g/L. The pH of the solution was maintained at 0.62 by adding H₂SO₄, according to the final pH of the leaching experiment.

Extractions of Ni, V and Mo from the synthetic solution according to the composition of leach liquor were carried out with 10% (v/v) LIX-84I in kerosene at an aqueous to organic (A:O) phase ratio 1:1 for equilibrium pH. Extraction isotherm curves for each metal were developed by using pure individual metal ion solution. The pH ranges for Mo, V and Ni were 0.1-3.0, 0.1-3.0 and 2.0-6.0, respectively. The results are shown in Fig. 4. It was observed that Mo extraction efficiency is higher than V at low pH. The extraction efficiency of V increased with increase of equilibrium pH. At equilibrium pH more than 2.0, the solvent extracted both V and Mo. Up to equilibrium pH 3.0, there was a negligible extraction Ni. Therefore, LIX-84I extractant was selected for treating the leach liquor. From Fig. 4, it can be concluded that Mo and V can be co-extracted at higher pH or individually extracted at low and high pH, respectively. We have selected separation at low pH to achieve good separation factor and also because the obtained leach liquor has a low pH at 0.62.

A Mo extraction isotherm curve was developed by plotting log D versus equilibrium pH up to 0.5 and is

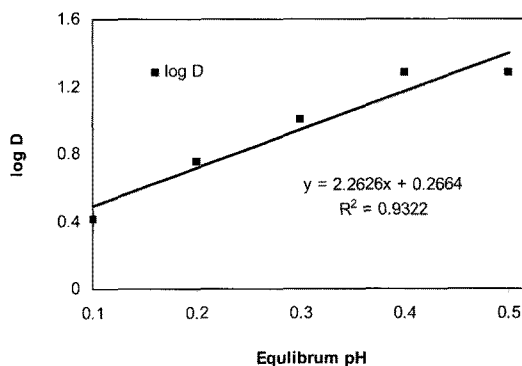
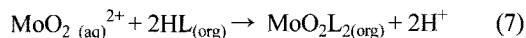


Fig. 5. Extraction isotherm of Mo at equilibrium pH using 10% LIX-84I and A : O = 1 : 1.

shown in Fig. 5. The curve showed good linearity and the slope was calculated to be 2.26. In order to explain slope analyses, the following equilibrium equation is proposed:



and the corresponding relation is

$$\log D = \log K + 2 \log [\text{H}^+] + 2 \log [\text{HL}]_{(\text{org})} \quad (8)$$

where, D and K are distribution ratio and equilibrium constant, respectively. Thus MoO₂L₂ was the extracted species.

After establishing the stoichiometry of the reaction an Mo extraction isotherm curve was established by varying the A:O ratio from 1:10 to 10:1 while other parameters, such as total volume 24 mL, pH at 0.5, LIX-84I extractant with 10% (v/v) in kerosene, and Mo concentration 0.6 g/L, kept constant. To find out the A:O ratio and number of phases, a McCabe-Thiele plot was drawn for Mo extraction isotherm¹⁷⁾ and is shown in Fig. 6. By putting an operating line at A:O ratio of 5:2, 98% of Mo can be extracted from the leach liquor in a 2 stage process. The co-extraction of V was very marginal with a value of 80 mg/L in above condition. Stripping studies were carried out by using three different solutions such as; NH₄OH (20%), NH₄OH (20%) + (NH₄)₂CO₃ (2M) and 10% H₂SO₄. It was observed that 20% NH₄OH showed better efficiency when compared to the other two stripping reagent at A:O ratio 5:2. From stripping studies 99% Mo was stripped by 20% NH₄OH at A:O ratio 5:2.

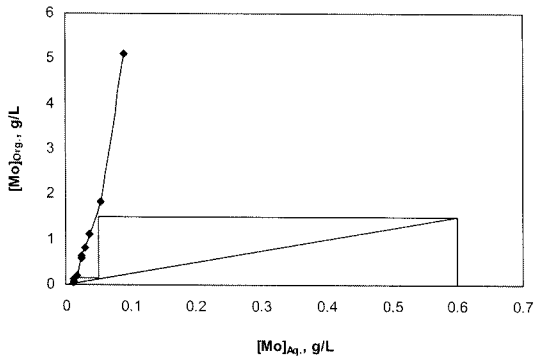


Fig. 6. McCabe-Thiele plot for extraction isotherm of Mo with 10% LIX-84I (pH : 0.5, A : O; 1 : 10 ~ 10 : 1, Mo conc., 0.6 g/L).

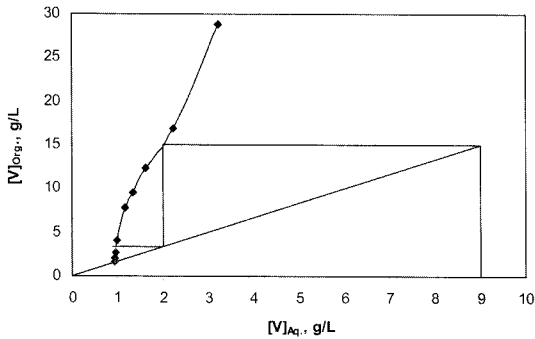


Fig. 7. McCabe-Thiele plot for extraction isotherm of V with 40% LIX-84I (pH : 2.0, A : O; 1 : 5 ~ 5 : 1, V conc., 9 g/L).

After extraction of Mo by LIX-84I (10%) the pH of the raffinate increased to 2.0 by addition of NaOH. During pH adjustment, there was no loss of V or Ni. Extraction isotherm studies were carried out on Mo-barren leach liquor after pH adjustment using 40% LIX-84I solution by varying the A:O ratio from 1:5 to 5:1 while other parameters, such as total volume 24 mL, pH at 2.0, LIX-84I extractant with 40% (v/v) in kerosene, and V concentration 9 g/L, kept constant. The McCabe-Thiele plot for the V extraction is shown in Fig. 7. It was observed that 82% of V can be extracted at A:O ratio of 5:3 in a 2 stage process. Stripping studies were carried out using various stripping agents: NH_4OH (20%), $(\text{NH}_4)_2\text{CO}_3$ (2M), and NH_4OH (20%) + $(\text{NH}_4)_2\text{CO}_3$ (2M). Among the three, the combination of NH_4OH (20%) and $(\text{NH}_4)_2\text{CO}_3$ (2M) showed a better stripping efficiency than other

two reagents at A:O ratio 5:3. More than 99% of V from the loaded organic was stripped out using the combination of NH_4OH (20%) and $(\text{NH}_4)_2\text{CO}_3$ (2M) at A:O ratio 5:3.

4. Conclusion

Recovery of Ni, V and Mo from spent refinery catalyst was conducted through a leaching followed by solvent extraction process. 1 M sulphuric acid (1 M H_2SO_4) could leach out more than 95% of Ni and V whereas Mo leaching was limited to 30% only within 1 hr of leaching time. The activation energies of the leaching reactions were calculated, and it showed the dissolution process follows a diffusion control mechanism. The leaching experiments were conducted with sulfur free spent refinery catalyst. For sulfur free spent refinery catalyst, leaching with 1 M sulphuric acid followed by sodium carbonate washing showed better leaching with almost 100% leaching of Ni, Mo and V when compared to a leaching process with sodium carbonate followed by sulphuric acid washing. Solvent extraction and stripping were carried out for a leach liquor containing Ni, 2 g/L; V, 9 g/L, Mo, 0.6 g/L. More than 98% of Mo was extracted from the leach liquor at A:O ratio of 5:2 in a 2 stage process. In addition 99% Mo was stripped from the loaded organic by 20% NH_4OH . Similarly 82% of V was extracted at A:O ratio of 5:3 in a 2 stage process. Unlike single stripping reagent for Mo, a mixture of NH_4OH (20%) and $(\text{NH}_4)_2\text{CO}_3$ (2M) stripped more than 99% of V from the loaded organic.

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