Characterization and Pretreatment of Spent Petroleum Refinery Catalyst for its Biodissolution

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ABSTRACT

This research is concerned with the bioleaching of valuable metals from spent catalyst using iron oxidizing bacteria culture. For the pretreatment of spent catalyst, boiled acetone was used as the washing reagent. The pretreatment was performed with the help of a soxhlet. The acetone washed spent catalyst was analyzed by different physico-chemical method such as XRD, SEM, BET surface analyzer, DTA and ICP. The ICP analysis showed the metal content in the spent catalyst was as follows (wt %): Al-19.5, Ni–2.0, V–9.0 and Mo–1.4. XRD analyses revealed Al in a form of Al_2O_3, Ni as $Ni_{3-x}S_2$ and Mo as form of Mo_3S_4 as well as MoO_3, V as V_4O_9 and S in elemental form. DTA analysis showed the presence of coke in the spent catalyst. Bioleaching experiments were conducted using iron oxidizing bacteria cultures by varying different leaching conditions such as contact time, Fe(II) concentration, particle size, pulp densities, pH and temperature were studied in details. The leaching efficiencies of Ni and V were 86%. The leaching followed dual kinetics, i.e., initial faster followed by slower rate. The leaching rate of Ni and V werefound to be higher than that of Mo. The mutual effects of two reasons, such as hydrophobic sulfur layer over the molybdenum matrix and refractory nature, attributed to the lower Mo leaching.

Keywords:Spent catalyst, Characterization, Bacterial leaching, Leaching parameters

INTRODUCTION

Catalysts used in the hydrotreating process of different petroleum refinery industries are physically deactivated after several cycles, and further cannot be reused in the same process [1]. The deactivated catalysts are discarded as solid wastes and called as spent catalyst. Worldwide the annual generation rate of the spent catalyst is above 170,000 tons [2]. They generally contain various metallic and nonmetallic elements like aluminum (Al), vanadium (V), molybdenum(Mo), cobalt(Co), nickel(Ni), iron (Fe), sulphur (S), and carbon(C). They are included in the list of hazardous wastes by the United State Environmental Protection Agency[3]. Handling of the hazardous waste follows the stringent environmental regulations which are the actual headache for the refinery industries[4,5]. There are different ways to manage the spent catalyst [1]. One of the management policies is reclamation of metal values present in the spent catalyst using extractive metallurgy [6-11]. Bioleaching technique is one of the modern extractive metallurgy technique has potential to extract metals from different low-grade ores and solid wastes. Indeed, different types of

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natural occurring microorganisms have been evaluated for their biotechnological leaching potential [12,13].

Different genera of *Acidithiobacilli*spp., *Pseudomonas* spp., *Aspergillus* spp. and *Penicillium*spp. have shown ability to leach metals from various resources [14]. *Acidithiobacillusferrooxidans* is a bacterium of *Acidithiobacilli* spp. generally used in the bioleaching conducted at the ambient condition. This is a chemolithoautotrophic bacteriumoxidizes different components of iron and sulphur. The oxidized end products of iron and sulphur are respectively ferric iron and sulphuric acid then act indirectly as reacting species that solubilize metal sulfides and oxides during the bioleaching process. Also this bacteria can directly leach metals to some extent [15-17].

However, the mineralogy of the solid materials and their composition play the deciding factor for the utility of the bioleaching process. Since microorganisms are very specific to different metals and their concentration, the elemental composition has a major role in the application of bioleaching process. Therefore, a complete characterization of the solid material to be used in a bioleaching study is necessary prior to the implementation of bioleaching. In this article, a spent refinery catalyst was characterized in details for the purpose of bioleaching using *Acidithiobacillusferrooxidans*.

PRETREATMENT PROCESSES

Spent refinery catalyst was collected from SK Petroleum Group, South Korea.As such spent catalyst from the company was covered with a film of oils and organic pollutants. Since thisspent catalyst looks like waxy material as shown in Figure 1(a),as such catalyst received from the petroleum company cannot be used directly in our leaching purpose. Therefore a proper pretreatment is required prior to the bioleaching. For the pretreatment of such spent catalyst, any of two alternatives can be considered, such as calcinations and washing with suitable organic solvent. Since calcinations process is an energy intensive process and it exits SO_2 to the atmosphere, we preferred washing with proper organic solvent over calcinations. There is no loss of organic solvents because it can be recycled and reused easily after washing process.

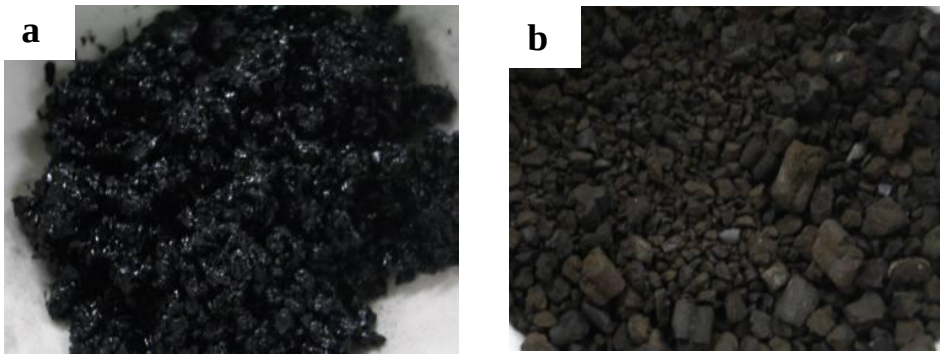

Figure 1. (a) raw spent catalyst (b) acetone washed spent catalyst.

The solvent acetone is chosen over all other organic solvents for the washing purpose. The spent catalyst was subjected to the washing in acetone using a soxhlet to remove the oil coating over them. The acetone washed spent catalyst was then dried in open air. Figure 1(b) shows the acetone washed spent catalyst. After removing the oil the clear shape of the spent catalyst was visible. The major fraction of the catalyst was cylindrical in shape, and approximately 2-3mm in length and 0.5mm in diameter. Some fraction of catalyst was also spherical in shape. The spherical shape may be due to deposition of metals like V and Ni during the hydro-treating process of the refineries. The acetone washed spent catalyst

wasground 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.

CHARACTERIZATIONS

Morphological Characterization

The morphological characterization of the acetone washed spent catalyst was conducted using Scanning Electron Microscope (JEOL, JSM-6380LA). Samples were prepared on metallic studs using carbon tape. Figure 2 shows the morphology of acetone washed spent catalyst from which we can observe a variety of cracks which helps the penetration of the lixiviant in to bulk of the catalyst particle in the course of leaching.

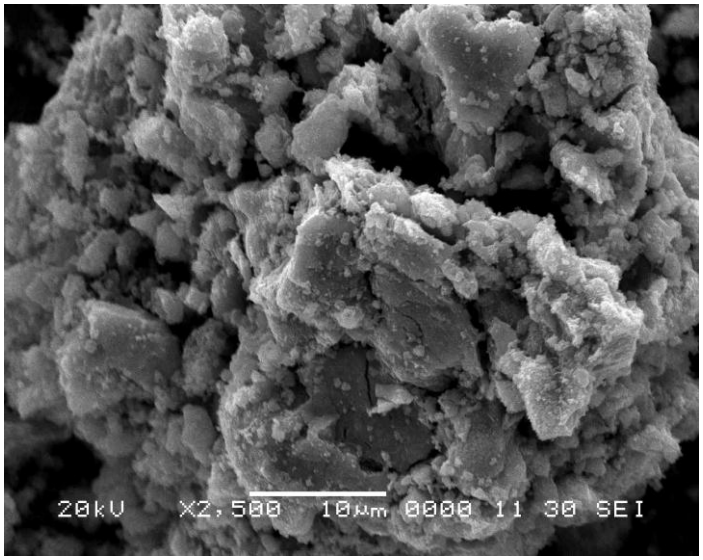

Figure 2. SEM photomicrograph of acetone washed spent catalyst.

BET Surface Area Analysis

The specific surface area and pore size of the acetone washed spent catalyst were measured using Brunauer-Emmett-Teller (BET) method using liquid Nitrogen adsorption-isotherm method (Micromeritics, Tristar 3000, Unit 1). Table 1 shows the data of surface area and pore size of the acetone washed spent catalyst.

Table 1. Specific surface area and pore size analysis data.

BET surface area	42 m^2/g
Pore size range	1.7 to 300 nm
Surface area of pores	18.65 m^2/g
Volume of pores	0.0105 cm^3/g

Particle Size Distribution

The particle size distribution of the acetone washed spent catalyst was analyzed using particle size analyzer (Malvern Mastersizer 2000, Version 2.00). Figure 3 shows the results of particle size distribution analysis for different sieve size fraction as: (a) -212+106 µm (b) -106+45 µm (c) -45 µm. From the figures it can be observeda broad size distribution for particle size -212+106 µm. However, the size distribution is low for particle size range -

106+45 and -45 µm. During sonication, the particles are dispersed to its original size which is smaller than the size we have mentioned.

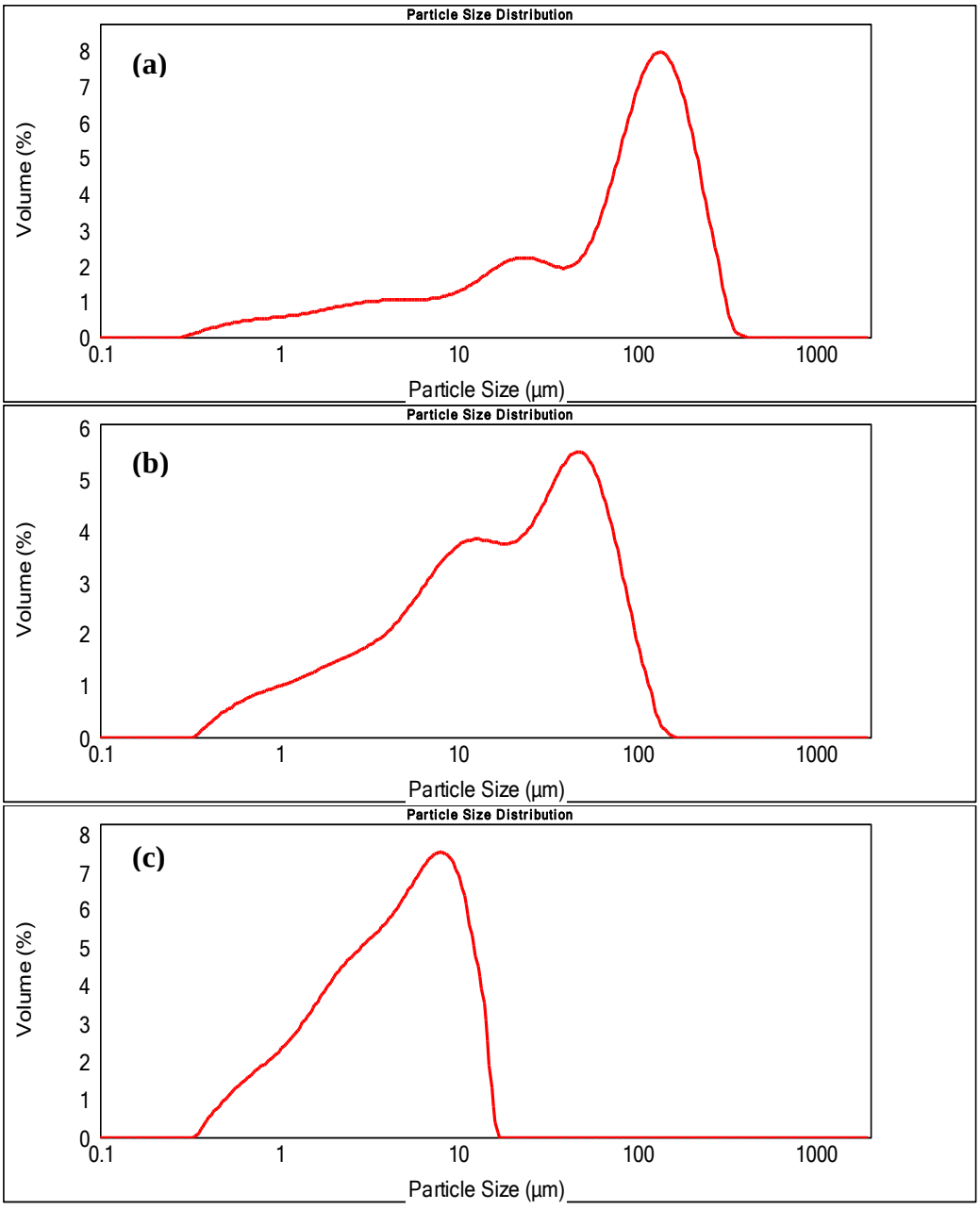

Figure 3. Particle size distribution of the acetone washed spent catalyst, (a) -212+106 µm (b) -106+45 µm (c) -45 µm.

Elemental Analysis

To evaluate the exact composition of spent catalyst, four sets of spent catalyst samples were used. Of the four samples three were pretreated spent catalyst and another one was raw spent catalyst. The three pretreatment processes were as acetone washed; calcinations at 700 ^{o}C; acetone washed followed by calcinations. Then we followed an acid digestion process to dissolve the metals present in the samples. For each set of digestion about 2 g of sample was taken and digested in 100 mL aqua regia on a hot plate for duration of 4 hrs. Then the digested liquors were filtered and analyzed in ICP-AES (JOBIN-YVON, JY 38). The typical chemical composition of the four spent catalysts samples is given in Table 2.From the table it can be observed that the mass fraction of all metals increased after the pretreatment processes

while compared to the composition of raw spent catalyst. The gain in metal fraction in the pretreated catalyst samplesmay be due to either loss of oil fraction or oxidation of sulfide to oxide. To find out this we calculated the weight loss in each process. In acetone washed process the weight loss was found to be 18 %; however the same was 33% and 35% for samples pretreated by calcinations and acetone washed followed by calcinations, respectively. The 18 % weight loss in case of acetone washed sample was due to loss of soluble organic compounds coated over the spent catalyst particle. The remaining 17% weight loss may be due to either volatile carbonic components within 700 ^{o}C or oxidation of metal sulfides to oxides in the calcinations process or both. In addition, vanadium content in the spent catalyst was higher than nickel and molybdenum showing large content of vanadium in process feed of the hydroprocessing units.

Table 2. Composition of both raw and pretreated spent catalyst (in g/kg).

Sample specification	Al	V	Ni	Mo	S
Raw spent catalyst	142	78	17	12	106
Acetone washed	195	90	20	13.8	115
Calcinations at 700 ^{o}C	204	98	22	14	21
Acetone washed + Calcinations at 700 ^{o}C	208	101	22	14	18

SEM-EDX Analysis

The Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) analysis of acetone washed spent catalyst was conducted usingScanning Electron Microscope (JEOL, JSM-6380LA). The sample was sputter-coated with gold after spreading thesample on metallic studs with carbon tape prior to observation under the SEM. Figures 4& 5 show the SEM-EDX analysis of the acetone washed spent catalyst. From the figures it can be observed that except Al, Ni, V, Mo, S and O, small amount Si present in the spent catalyst. So the raw catalyst may contain mullite($2Al_2O_3$ SiO_2)as supporting material for Ni and Mo.

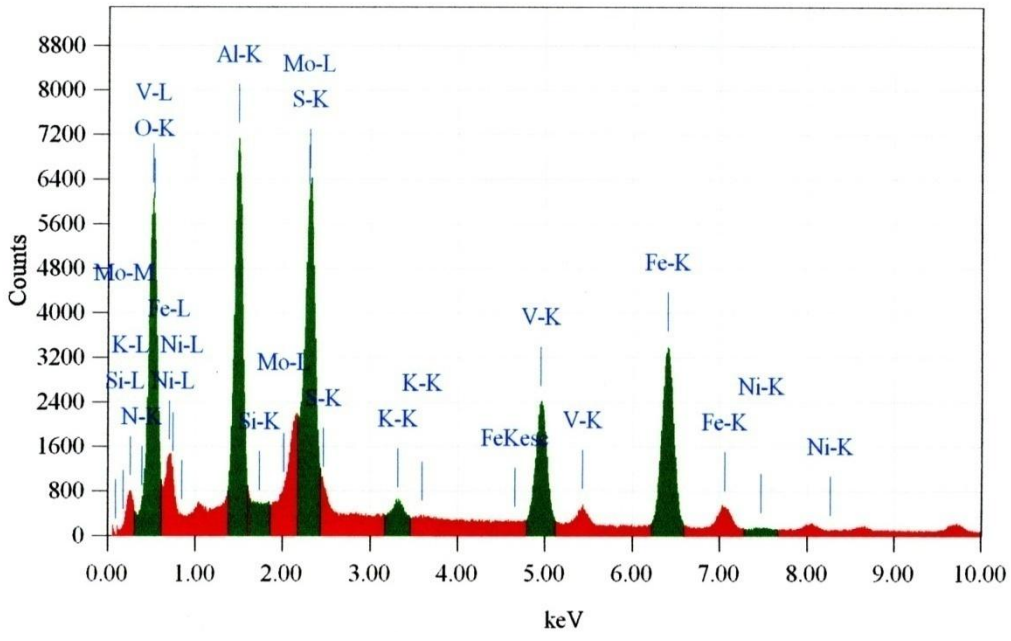

Figure 4. EDX analysis of acetone washed spent catalyst.

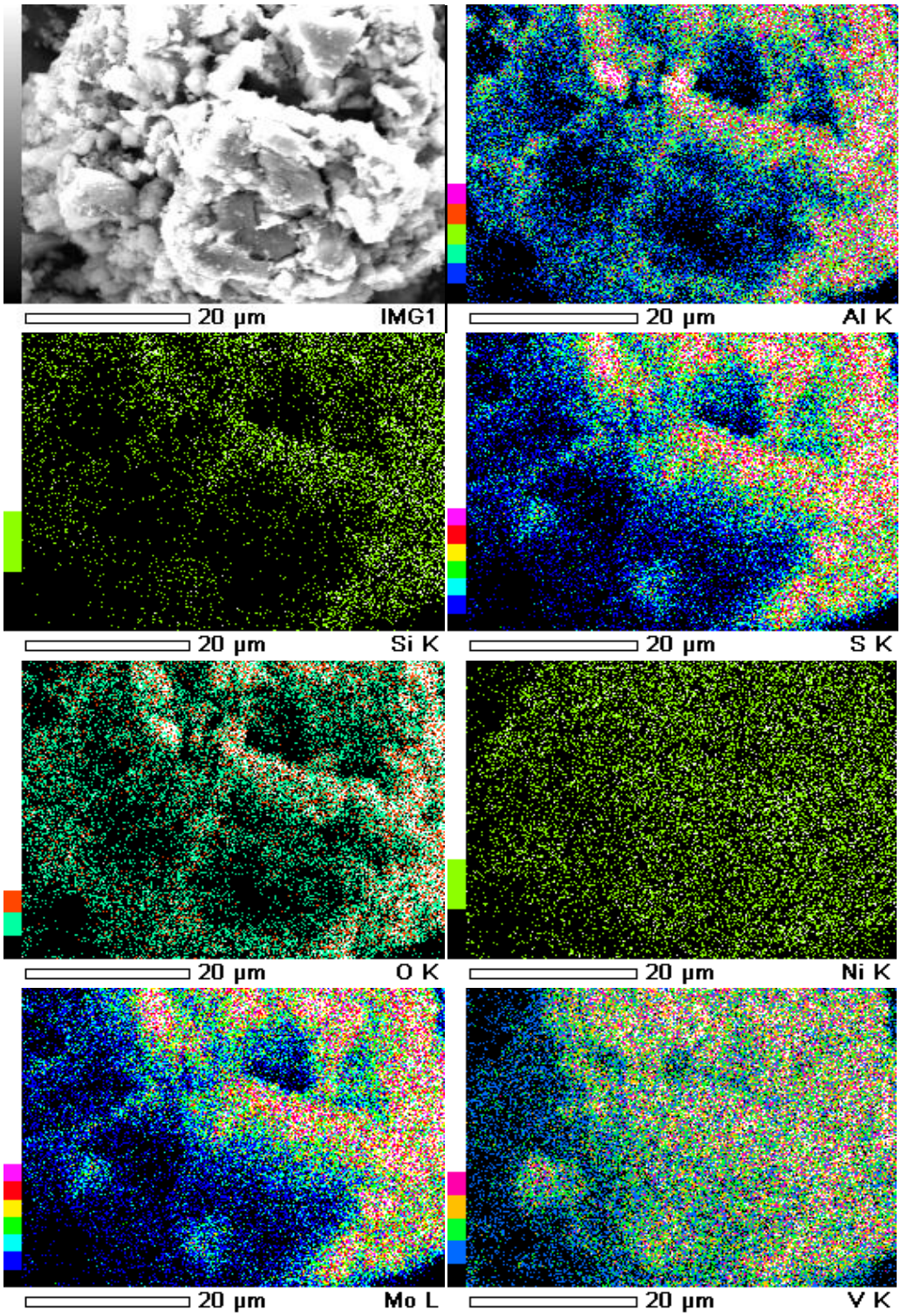

Figure 5. SEM-EDX of acetone washed spent catalyst.

XRD Analysis

The XRD analysis of acetone washed spent catalyst was conducted using X-Ray Diffractometer (RIGAKU, R4-200). The intensity of the peaks of the XRD was very low concluding the spent catalyst was amorphous in nature (Figure 6). Therefore the

compositions of spent catalyst were listed in a tabular form (Table 3). The XRD analyses showed Al in a form of γ-Al_2O_3, Ni as $Ni_{3-x}S_2$ and Mo as form of Mo_3S_4 as well as MoO_3, V as V_4O_9 and S in elemental form. No phases could be identified related to C. So the C may be in the form of hydrocarbon or oxides.

Table 3. XRD phases of the spent catalyst and their respective'd' values.

XRD Phases	"d" values (Major peaks)			Card No (JCPDS)
Sulfur	4.04	3.23	2.90	23-0562
ε-MoO_3	3.92	3.60	3.39	09-0209
Mo_3S_4	6.46	1.94	2.63	27-0319
γ-Al_2O_3	4.24	8.04	7.21	31-0026
V_4O_9	4.12	3.22	3.18	23-0720
$Ni_{3-x}S_2$	2.96	1.82	4.13	14-0358

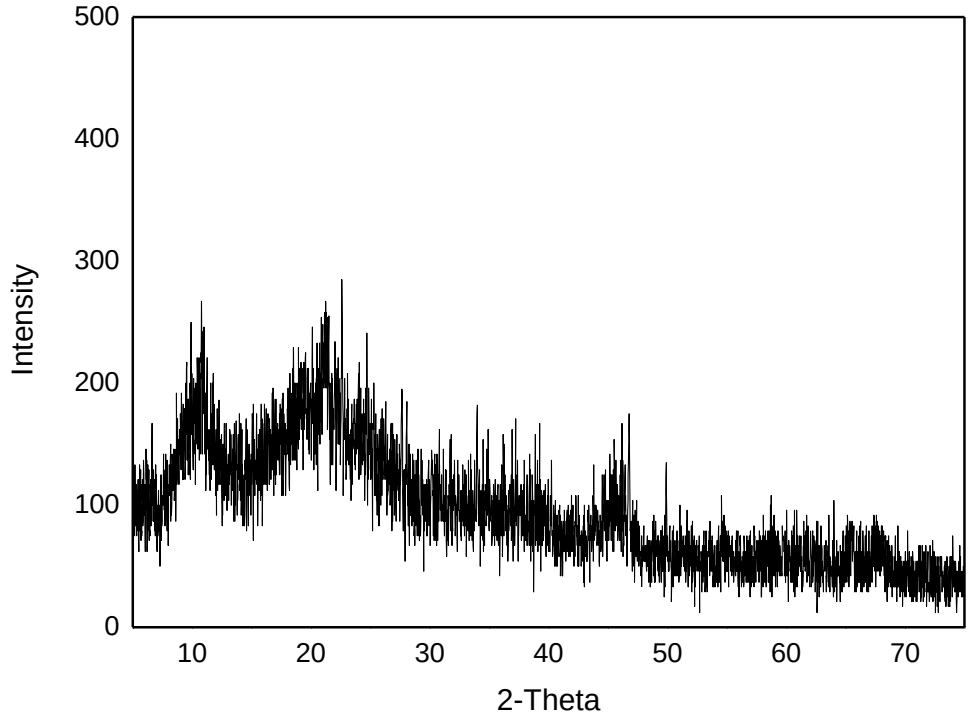

Figure 6. XRD pattern of acetone washed spent catalyst.

DTA Analysis

The Thermo Gravimetric Analysis/Differential Scanning Calorimetry (TG–DTA/DSC) analyses of spent catalyst were conducted with a temperature range from 20 to 700 °C with a linear heating rate of 10 °C/min using TG-DTA instrument (SHIMADZU). Figure 7 shows the TG-DTA result of the spent catalyst. The DTA profile displays clearly exothermic peaks at 284 ^oC and 408 ^oC. The peak at 284 ^oC may be due to loss of hydrocarbon present in the spent catalyst. The peak at 408 ^oC may be due to transformation of sulfides to oxides of Ni and Mo.

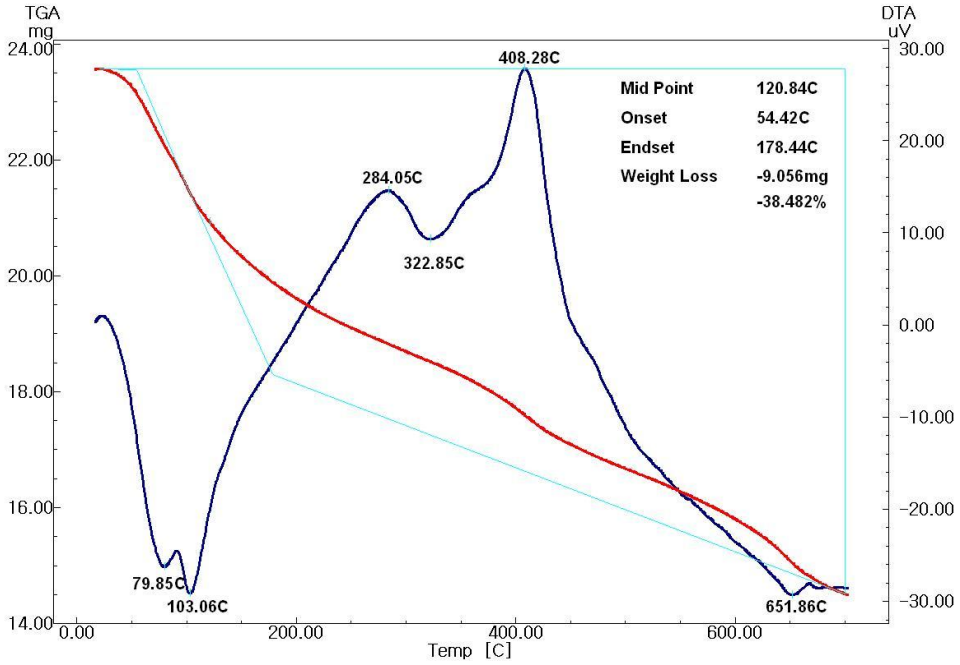

Figure 7. TG-DTA of acetone washed spent catalyst.

BIOLEACHING STUDY

The water sample collected from an effluent pond at the Dalsung mine in south Korea was cultured in 9K media at pH of 1.8.The morphological characterization of the fully grown culture was done using a phase-contrast microscope (Olympus BX51 make). The fully grown culture was filtered and the filtrate was centrifuged for 20 minutes at 10,000 rpm and 20 ^{o}C using a refrigerated centrifuge (Mega21R) [18]. The pelletized biomass at the bottom of centrifuge tube was collected and subcultured in freshly prepared 9K media. The subculturing process was done repeatedly in order to increase the iron oxidation rate. All leaching studies were conducted using the active bacterial culture.All leaching experiments were conducted in 250 mL Erlenmeyer flasks containing 90 mL media and 10 mL inoculum in each. A centrifugal shaker-cum-incubator was used with the speed fixed at 180 rpm. Bacteria were inoculated into the leaching media followed by the addition of required amount of pretreated spent petroleum catalyst. The volume of inoculum was fixed at 10 %(v/v) having cell concentration of ~10^{8} cells/mL. Such high bacterial count was due to use of centrifuged biomass. Periodically, samples were collected to determine different physico-chemical parameters like pH, Eh and metal ion concentrations. The metal content in leach liquor was analyzed by ICP-AES. For leaching studies, following leaching conditions were maintained unless specified otherwise: temperature, 35 ^{o}C; pulp density (PD, 10%(w/v); particle size (PS), -106+45µm; pH, 2.0; initial Fe(II) concentration, 10 g/L.

Leaching studies were carried out for 15 days to find out the effect of the reaction time on the leaching kinetics. The results are shown in Figure8. It was observed that in all the cases the extent of leaching for metal values like V and Ni were appreciable indicating environmental leachate problem associated with the storage of the spent catalyst in open area. It further indicates that except Mo all other elements are prone to aqueous dissolution as percentage dissolution was high. The percentage of leaching of all metals like Mo, V and Ni appears to be parabolic in nature, with the initial rate being faster, followed by a decrease in leaching (Figure8). In other word the metals leaching followed dual leaching rate, i.e., initial faster followed by slower rate. The faster rate was limited to initial 4 days followed by slower

rate which lasted for about next 7 days and after that the leaching rate was almost negligible in all the cases. Therefore, all other leaching studies were carried for a total period of 10 days. In initial 4 days of experiment more than 70% of Ni and V were dissolved and with increasing the incubation time to 10 days 85% of these metals were leached out. The dual leaching rate may be due to different leaching mechanism in the entire dissolution process. The leaching would take place when the attacking species diffuse from the bulk solution to the solid surface and then dissolved species need to be diffused out to mix the bulk solution. The initial faster and slower rate may be due to surface and intra-particle diffusion respectively [19]. The intra-particle diffusion may be either diffusion inside the reactive matrix or through product layer formed during the course of dissolution or both.

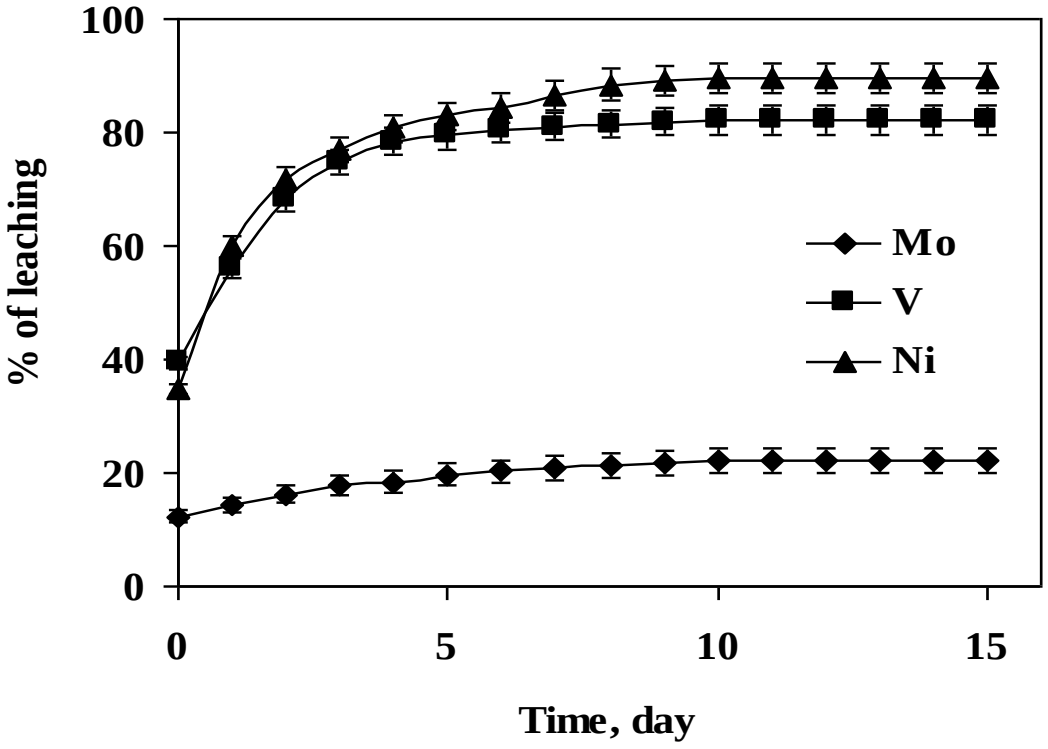

Figure 8. Effect of contact time on the leaching efficiency. (Conditions: pulp density, 10%(w/v); temperature, 35 ^{o}C; particle size, -106+45 μm; pH, 2.0; initial Fe(II) concentration, 10 g/L)

The slower and faster leaching rates for different metal values are shown in Table 4. It was further observed that the leaching rates of V and Ni were much higher than Mo. The XRD analyses of the acetone washed spent catalyst showed that a part of Mo and Ni were present as sulfides and the rest in oxide form. The SEM-EDX studies showed the presence of sulfur layer over the Mo-matrix (Figures4&5). The sulfur layer may be forming a diffusion barrier since it is hydrophobic in nature [17,20], thus preventing the attacking species to react with Mo matrix and thereby retarding the reaction rate. It was further reported that sulfides of Mo to be refractory[21]. Therefore, the slow Mo dissolution kinetics may be due to refractoriness as well as formation of diffusion barrier by sulfur layer.

Table 4. Rate of dissolution for the faster and slower leaching at different leaching parameters.

Parameters	Faster (%/day)			Slower (%/day)		
	Ni	V	Mo	Ni	V	Mo
Fe(II), g/L						
0	5.81	4.44	0.98	0.71	0.88	0.28
5	9.31	8.26	1.34	1.42	0.51	0.39
10	10.8	9.69	1.55	1.41	0.51	0.49
15	10.1	9.06	1.11	1.26	0.52	0.32
20	9.71	8.05	0.81	1.44	0.42	0.29
25	9.19	6.83	0.52	1.04	0.66	0.14
Pulp density, % (w/v)						
5	11.3	10.4	1.9	1.27	0.64	0.52
10	10.8	9.69	1.55	1.41	0.51	0.49
15	10.3	8.84	1.51	1.64	0.33	0.49
20	9.94	7.83	1.21	1.35	0.35	0.51
25	9.92	7.41	0.99	1.43	0.33	0.46
pH						
3	8.85	4.04	0.58	1.21	0.91	0.06
2.5	9.69	5.78	1.08	1.43	0.45	0.21
2.25	10.6	7.92	1.31	1.34	0.86	0.42
2	10.8	9.69	1.55	1.41	0.51	0.49
1.75	10.5	8.89	0.99	1.38	0.32	0.48
1.5	9.7	7.36	2.39	0.77	0.65	0.54
Temperature, ^{o}C						
10	6.74	4.21	0.22	0.76	0.54	0.29
15	7.17	4.74	0.52	0.85	0.42	0.18
20	8.14	5.63	0.69	0.92	0.45	0.33
25	9.05	6.41	1.01	1.32	0.83	0.52
30	10.2	8.46	1.27	1.34	0.44	0.52
35	10.8	9.69	1.55	1.41	0.51	0.49
Particle size, μm						
-212+106	9.52	6.56	1.05	0.74	0.94	0.37
-106+45	10.8	9.69	1.55	1.41	0.51	0.49
-45	11.8	10.26	1.74	0.59	0.91	0.55

CONCLUSIONS

In this article a details studies on characterization of spent catalyst and bioleaching of Ni, V and Mo from spent $NiMo/Al_2O_3$ catalyst using iron oxidizing bacteria culture are presented. Spent catalyst for this study was collected from SK Petroleum Group, South Korea. The raw spent catalyst was washed with boiled acetone to remove the oil coating. The acetone washed spent catalyst was further analyzed by different physico-chemical characterization such as, SEM, BET surface analysis, XRD, DTA and ICP. The metal content in the acetone washed spent catalyst was analyzed by ICP and the obtained values were as follows (wt %): Al-19.5, Ni–2.0, V–9.0 and Mo–1.4.XRD analyses revealed Al in a form of Al_2O_3, Ni as $Ni_{3-x}S_2$ and Mo as form of Mo_3S_4 as well as MoO_3, V as V_4O_9 and S in elemental form. DTA analysis showed the presence of coke in the spent catalyst.Bioleaching of spent catalyst were carried out using the iron oxidizing bacteria culture. Various leaching

parameters like contact time, Fe(II) concentration, particle size, pulp densities, pH and temperature were studied in details. All the three metal ions like Ni, V and Mo followed dual kinetics, i.e., initial faster followed by slower rate. The leaching kinetics of Ni and V observed to be higher compared to that of Mo.The lower leaching rate of Mo than Ni and V were due to the mutual effects of the hydrophobic sulfur layer over the molybdenum matrix and refractory nature.

ACKNOWLEDGEMENT

The authors are grateful to Prof. (Dr.) ManojranjanNayak, President, Siksha 'O' Anusandhan University, for providing infrastructure and encouragement throughout.

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