

Comparison of Bioleaching of Metals from Spent Petroleum Catalyst Using *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*

Haragobinda Srichandan, Ashish Pathak, Dong Jin Kim, Seung-Won Lee

Abstract—The present investigation deals with bioleaching of spent petroleum catalyst using *At. ferrooxidans* and *At. thiooxidans*. The spent catalyst used in the present study was pretreated with acetone to remove the oily hydrocarbons. FESEM and XPS analysis indicated the presence of metals in sulfide and oxide forms in spent catalyst. Both *At. ferrooxidans* and *At. thiooxidans* were found to be highly effective in producing the acid. Bioleaching with *At. ferrooxidans* and *At. thiooxidans* led to higher recovery of metals compare to control. During bioleaching similar recoveries of metals were obtained using *At. ferrooxidans* and *At. thiooxidans*. This might be due to the presence of metals as soluble oxides and sulphides in the spent catalyst. At the end of bioleaching, about 87-90% Ni, 34% Al, 65-73% Mo and 92-97% V were leached using above bacteria. It is elucidated that bioleaching with *At. thiooxidans* is comparatively more advantageous due to lower cost of sulphur.

Keywords—Spent catalyst, *At. ferrooxidans*, Bioleaching, Metal recovery.

I. INTRODUCTION

Oil refinery industries use huge quantity of metal catalysts in order to produce desirable products from its precursors. These catalysts constitute of different metals such as, Ni, V, Co, Mo, Fe etc. The metals in the catalyst are present in the form of oxides and sulfides [1]. The catalysts are used continuously until its catalytic value approaches zero. These deactivated catalysts are now considered as waste materials and referred as spent catalyst. Due to presence of heavy metal, spent catalyst is categorized into hazardous waste. The spent catalyst therefore needs to be treated for its heavy metal content to ensure safe disposal. Conventionally, pyrometallurgical and hydrometallurgical techniques have been used to recover metal values from spent catalyst [2], [3].

Mr. Haragobinda Srichandan is a Research assistant at Mineral Resource Research Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), Gwahang-no 124, Yuseong-gu, Daejeon, 305-350, South Korea, and also a PhD student at Chungnam National University, Daejeon, 305-764, South Korea (e-mail: buna.biot@gmail.com).

Dr. Ashish Pathak is a Post Doctoral Fellow at the Mineral Resource Research Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), Gwahang-no 124, Yuseong-gu, Daejeon, 305-350, South Korea (e-mail: ashishpathak05@gmail.com).

Dr. Dong Jin Kim* is a Principal Researcher at Mineral Resource Research Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), Gwahang-no 124, Yuseong-gu, Daejeon, 305-350, South Korea (e-mail: djkim@kigam.re.kr)

Prof. Seung-Won Lee is a Professor at Nano Engineering Division, School of Engineering, Chungnam National University, Daejeon, 305-764, South Korea (e-mail: leeswon@cnu.ac.kr).

However, both these processes are energy expensive and also produce secondary pollutants. Recently, research focus has been shifted towards an alternative technique known as biohydro-metallurgical process.

Biohydro-metallurgical processes employed for recovery of metals are eco-friendly and cost effective. Biohydro-metallurgical processes are based on the metabolic activity of iron and sulfur-oxidizing microorganisms leading to the solubilization of metals. In the past, many bioleaching studies have been reported by using iron and sulphur-oxidizing microorganisms such as *Acidithiobacillus ferrooxidans* (*At. ferrooxidans*) and *Acidithiobacillus thiooxidans* (*At. thiooxidans*) [4]-[7]. Briand et al. used *At. thiooxidans* to treat a spent vanadium-phosphorous catalyst [8]. Mulak et al. investigated the effect of different parameters on the rate of nickel leaching from spent nickel oxide catalyst (NiO and Al₂O₃) [9].

The bioleaching of metals from ores depends upon the bacterial oxidation of Fe²⁺ and sulfur into Fe³⁺ and H₂SO₄, respectively. *At. ferrooxidans* is capable of oxidizing both Fe²⁺ and sulfur species whereas *At. thiooxidans* can oxidize only sulfur during bioleaching. Many investigations have been performed for metal recovery from petroleum refinery spent catalyst using Fe/S oxidizing bacteria. However, not much work has been reported on evaluation of comparative efficiency of *At. ferrooxidans* and *At. thiooxidans* in solubilization of metals from spent catalyst.

In the present study, a comparative evaluation of bioleaching using *At. ferrooxidans* and *At. thiooxidans* has been reported. The experiments were conducted using acetone washed spent catalyst in 2.5 L stirred tank batch reactor.

II. MATERIALS AND METHODS

A. Spent Petroleum Catalyst

The spent catalyst used in bioleaching experiments was received from the Petroleum Refinery Company located in South Korea. The raw spent catalyst was coated with oily matter and therefore was pretreated with acetone in a Soxhlet apparatus followed by drying in a hot air oven. The acetone washed dried spent catalyst was ground using vibrating cup mill (FRITISH, Germany, No. 094000/01109). This acetone washed dried powder sample was used as a feed material in all experiments. The particle size distribution was determined by using Malvern Mastersizer (HYDRO 2000 MU). The particle size ranged from 1 to 200 μm.

Thermo-gravimetric analysis was carried out using a TG-DTA analyzer (SHIMADZU, Model DTG-60H) with air as a carrier gas. The sulphur and carbon analysis was performed using LECO (CS-600) analyzer. Mineralogical phases were determined using X-ray photoelectron spectroscopy (XPS Thermo scientific model-Sigma probe) at a beam voltage of 15 kV and beam current of 6.7mA. For XPS analysis, a monochromatic AlK α (1486.7eV) X-ray radiation was allowed to fall at 30° on powdered sample placed on the carbon tape. The emitted electron from sample was detected by analyzer placed at an angle of 40°. The surface topography of acetone washed spent catalyst was examined using Field Emission Scanning Electron Microscope (FESEM) model Magellan 400 and is shown in Fig. 1. FESEM result confirmed the presence of Ni, Al, Mo, O, S and V in the spent catalyst

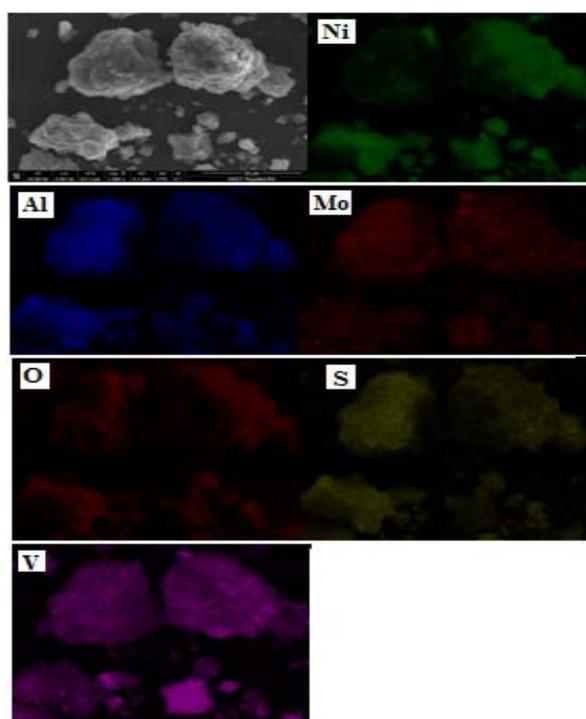


Fig. 1 FESEM images of acetone washed spent catalyst

The chemical composition of the acetone washed spent catalyst was determined by Induced Couple Plasma Spectroscopy (OES) (PerkinElmer's Optima 8300). The concentration of Ni, Al, Mo, V, and S is presented in Table I.

TABLE I
CHEMICAL ANALYSIS OF ACETONE WASHED SPENT CATALYST

Elemental composition (%)					
Ni	Al	Mo	V	C	S
3.31	20.56	2.58	11.40	1.48	4.55

B. Microorganism and Growth Condition

Pure strains of *At. ferrooxidans* and *At. thiooxidans* were obtained from the Korea Research Institute of Bioscience and Biotechnology (KRIBB) culture center. *At. ferrooxidans* was

grown in IEM medium composed of three components solution A, B and C. Medium for batch culture was prepared by adding to distilled water: ferrous sulfate heptahydrate solution A (1.0mL L⁻¹); macronutrient solution B (20mL L⁻¹) and micronutrient solution C (1.0mL L⁻¹) [10]. The 20g L⁻¹ Fe₂SO₄·7H₂O (4 g L⁻¹ Fe²⁺) and 10 g L⁻¹ S⁰ were added to the medium as bacterial energy sources. The final pH was adjusted to 1.68. *At. thiooxidans* was grown in iron free 9K medium supplemented with 10g L⁻¹ S⁰ as an energy source at pH 3.5. After achieving complete growth, the bacterial cells were passed through a membrane filter (0.45 μ m) and the cells were inoculated in respective batch reactors for further experiment.

C. Bioleaching Experiments

Experiments were carried out in stirred tank batch reactors (2.5L) using *At. ferrooxidans* and *At. thiooxidans* separately. All the experiments were performed in a controlled environmental conditions such as initial pH-1.4 \pm 0.05, stirring speed-250rpm, working volume-1L. Prior to the bioleaching with *At. ferrooxidans*, the bacterial cells were suspended in fresh IEM medium supplemented with 4g L⁻¹ Fe²⁺ and 10g L⁻¹ elemental S⁰ at pH 1.68. When all Fe²⁺ converted to Fe³⁺ and pH decreased to 1.4, acetone washed spent catalyst was added to this medium (10 g L⁻¹). Similarly, *At. thiooxidans* were suspended in iron free 9K medium by providing 10g L⁻¹ S⁰. When pH of the medium decreased to 1.4, acetone washed spent catalyst was added to this reactor (10g L⁻¹). All the experiments were continued till 120h. One control experiment was also performed without addition of bacterial cells under similar conditions. To the above reactors, continuous air was supplied at a flow rate of 1 LPM to ensure homogenous mixing of the bioleaching pulp.

Samples were withdrawn at every 20h for analysis of Fe, Ni, Al, Mo and V. pH measurements were conducted using an Orion portable pH meter whereas redox potential was measured using a platinum electrode fitted with a Ag/AgCl reference electrode. At the end of experiments, bioleach pulp was filtered by passing through Whatman filter paper No. 1 to separate liquid and solids. The liquid solution was analyzed by ICP-OES for the elements Fe, Ni, Al, Mo, V. The leaching yields of the desired element was calculated based on both the elemental content of the feed and leach liquor as per the formula given below.

$$\text{Leaching yield (\%)} = \left[\frac{M(l)}{M(f)} \right] \times 100$$

where, M(l) is the metal (Ni, V, Mo, Al) content in the leach liquor and M(f) is the metal (Ni, V, Mo, Al) content in the feed catalyst.

III. RESULTS AND DISCUSSION

A. Characterization Of Spent Catalyst

TG/DTA profile of the raw and acetone washed spent catalyst is illustrated in Fig. 2. The temperature difference i.e. the peaks in the DTA plot are associated with phase transitions

or thermal events such as desorption, combustion etc. The plot for the raw catalyst is more complex than for the acetone washed sample. Initially there was loss of volatile hydrocarbons. As the temperature increases, the DTA plot has a peak at approx. 285°C, likely due to the oxidation of hydrocarbons. This peak was absent in acetone washed sample. As the temperature increases further, the DTA plot has another peak at approx 364°C likely due to the oxidation of the carbonaceous material. This peak also occurred in acetone washed sample at approx. 374°C.

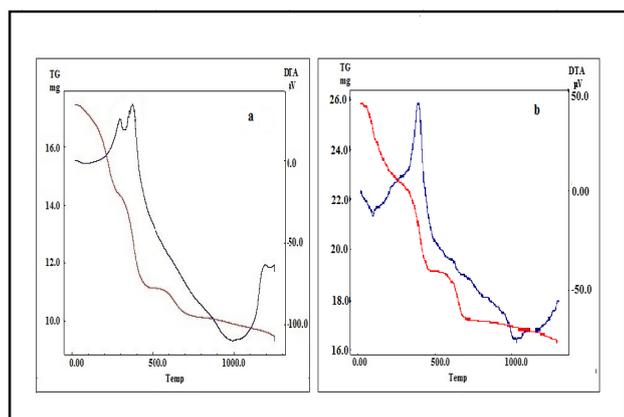


Fig. 2 TG/DTA curve for (a) raw and (b) acetone washed spent catalyst

It is to be noted that the two oxidation peaks for the raw catalyst overlap. Compared to the two peaks (at 285°C and 364°C) in raw spent catalyst, only one peak (at 374°C) was observed in acetone washed spent catalyst. This might be due to removal of hydrocarbon during pretreatment of spent catalyst with acetone.

XPS analysis of Ni, Al, Mo, V and C is presented in Fig. 3. In raw and acetone washed spent catalyst, the presence of all above seven elements was confirmed. Ni2p spectra confirmed the presence of Ni as oxide (Ni₂O₃ with binding energy of 857 eV), where Al2p spectra confirmed the presence of Al as oxides (α -Al₂O₃ with 74 eV, γ -Al₂O₃ with 74 eV and Al₂O₃ with 74.5 eV). Mo3d spectra confirmed the presence of Mo as sulfide and oxides (MoS₂ with 229.5 eV, MoO₂ with 229 eV and MoO₃ with 232.5 eV). V2p spectra confirmed the presence of V as oxides with 515.5-517.5 eV and C1s spectra confirmed the presence of C with 285 eV.

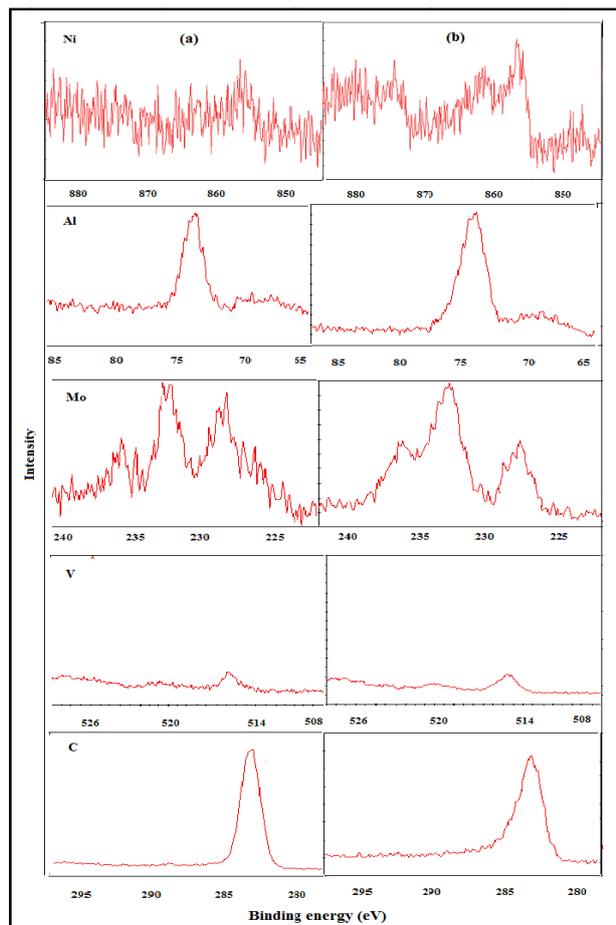


Fig. 3 Mineralogical phases analysis of (a) raw and (b) acetone washed spent catalyst by XPS

B. Change in pH

Fig. 4 represents the change in pH during bioleaching and control. Initially, rise in pH was observed in control and bioleaching experiments. After 20h, a gradual increase in pH was observed in reactor operated with *At. thiooxidans* whereas pH started to decrease in reactor operated with *At. ferrooxidans*. A rapid increase in pH was observed in first 20 h during control experiment. After 20h, pH remained constant till the end (2.2). At the end of 120h, the final pH of the bioleaching experiments conducted with *At. ferrooxidans* and *At. thiooxidans* was 1.3 and 1.8, respectively. The low pH values achieved during bioleaching as compared to control were due to the potentiality of the microorganism to produce acid. The same was not possible in control due to the absence of bacterial activity. The initial increase in pH during bioleaching and control was due to the acid consumption by metal oxides present in the spent catalyst. The dissolution of the metal oxides in the spent catalyst is usually an acid consuming process and can be represented as per (1):



where Me represents the metal such as Ni, Al, Mo, V, Fe etc.

The difference of the pH value can be explained on the basis of oxidizing capacity of bacteria. *At. ferrooxidans* and *At. thiooxidans* have the ability to oxidize elemental sulfur into H_2SO_4 which results in decrease in pH. The acid produced by the bacteria compensated the acid consumed by metal oxides during bioleaching experiments. On the other hand, in control experiment, the acid consumed by spent catalyst was not compensated due to the absence of bacterial activity resulting in high pH. In the present investigation (Fig. 4), *At. ferrooxidans* was found to be highly effective in producing acid as compared to *At. thiooxidans*.

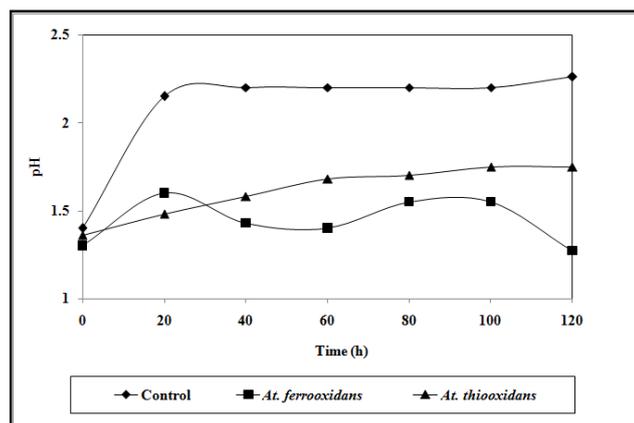
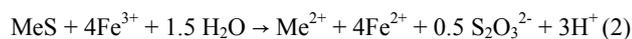


Fig. 4 The pH evolution profile during bioleaching and control

Spent catalyst was found to contain metals in oxide form (Fig. 3). Some of the metals were also present in sulfidic forms. The metal sulfides can be categorized into two types, acid soluble and acid insoluble. The acid insoluble metal sulfides followed the thiosulphate pathway as in the case of pyrite (FeS_2) and molybdenite (MoS_2) whereas acid soluble sulfides follow the polysulphide pathway [11]. The solubilization of acid insoluble metal sulfides is depends on the action of Fe^{3+} . The spent catalyst contains iron and molybdenum sulfides which are oxidized by the Fe^{3+} ion generated by *At. ferrooxidans* as shown in (2):



The sulphur intermediates formed ($\text{S}_2\text{O}_3^{2-}$ or S^0) are oxidized by the bacterium to form sulphate ions and H^+ ions compensating the part of acid consumption (3) and (4).



The acid insoluble metal sulfides could not be solubilized by *At. thiooxidans* due to its sulfur specific oxidizing activity. The acid soluble metal sulfides were solubilized by both *At. ferrooxidans* and *At. thiooxidans*.

C. Bioleaching Yield

Figs. 5 (a) and (b) represent the leaching profile of metals during bioleaching with *At. ferrooxidans* and *At. thiooxidans*, respectively. During bioleaching with *At. ferrooxidans* (Fig. 5 (a)), recovery of Ni and V was found to be higher as compared to Mo and Al. Similar leaching profile was also obtained during bioleaching with *At. thiooxidans* (Fig. 5 (b)). Recovery of Ni, Mo and V was significantly higher during bioleaching with *At. ferrooxidans* and *At. thiooxidans* as compared to control.

Most of the metals during bioleaching were leached in first 20h. About 80-85% Ni, 20-26% Al, 53-60% Mo and 82-86% V was leached in first 20 h followed by a slow increment till 40h. After 40h, leaching remained constant till the end. Overall, higher recovery of Ni and V was obtained compared to Mo and Al during bioleaching with both *At. ferrooxidans* and *At. thiooxidans*. The higher recovery of Ni and V as compared to Mo and Al can be explained from Eh-pH diagram which was plotted using the metal ion concentrations in bioleach liquor (Figure not shown here). As per the Eh-pH diagram, Ni and V are highly soluble in the Eh and pH range of the present investigation. Under these conditions, Ni and V exists as soluble $\text{Ni}_2\text{OH}^{+3}$ and VO_2^{2+} , respectively and resulted in higher yield. Low Mo recovery in both bioleaching experiments was due to its existence as insoluble $\text{MoO}_3 \cdot \text{H}_2\text{O}$. The Eh-pH diagram for Al suggested its existence as soluble $\text{Al}(\text{OH})_4^{-1}$ in the leaching solution. On the contrary, low Al was recovered, which might be due to the fact that the Al was not leached out significantly from the Al_2O_3 matrix. The spent catalyst used in the present study was made up of aluminium matrix in the form of Al_2O_3 . Al_2O_3 poses the properties such as high hardness, high melting point (2,072°C), boiling point (2,977°C) and insolubility in water making it a suitable candidate as supporting material and hence expected as a cause for low dissolution during bioleaching. Lower solubilization of Al was also observed in earlier bioleaching study conducted with spent catalyst [12]. The higher leaching yields of Ni and V in the present study is in agreement with a study performed with acetone washed spent catalyst [3], [5]. Bioleaching with *At. ferrooxidans* resulted in solubilization of 90% Ni, 34% Al, 65% Mo and 97% V as compared to 87% Ni, 34% Al, 73% Mo and 92% V with *At. thiooxidans*. Compared to bioleaching, control experiment resulted in low metals recovery (50% Ni, 19% Al, 60% Mo and 40% V). It was expected that *At. ferrooxidans* will result in high leaching yield due to the presence of two oxidants Fe^{3+} and H_2SO_4 . However, similar metals recoveries were obtained during bioleaching with *At. ferrooxidans* and *At. thiooxidans*. It was probably due to the presence of all metal sulfides in acid soluble form. Due to acid soluble metal sulfides, H_2SO_4 alone was sufficient for metal dissolution. *At. thiooxidans* resulted in similar recovery by using only one energy source (S^0) and hence considered more economical as compared to *At. ferrooxidans* for possible scale up.

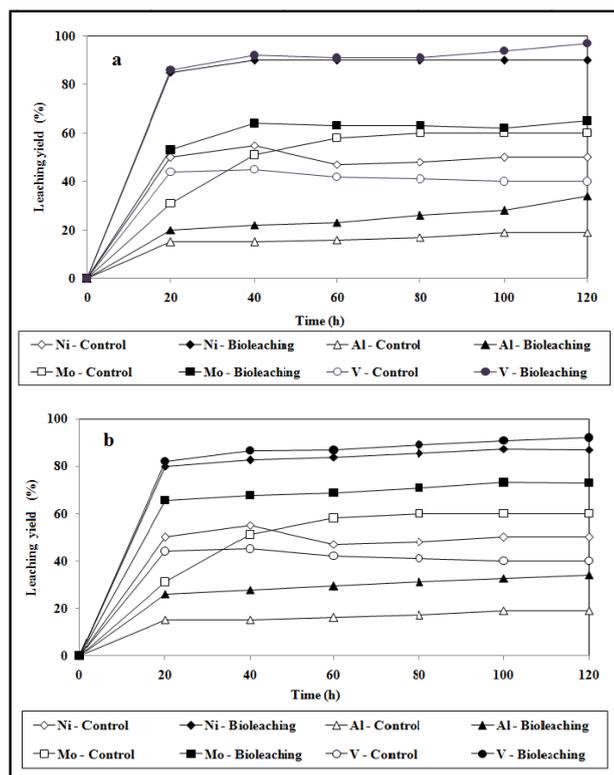


Fig. 5 Leaching yield of metals during bioleaching with (a) *At. ferrooxidans* and (b) *At. thiooxidans*

IV. CONCLUSION

Bioleaching experiments were separately conducted with *At. ferrooxidans* and *At. thiooxidans*. FESEM and XPS analysis concluded that the metals in spent catalyst were present as both sulfide and oxides. Both *At. ferrooxidans* and *At. thiooxidans* were highly effective in producing acid as well as in leaching of metals in comparison with control. Experiment with *At. ferrooxidans* resulted in leaching of 90% Ni, 34% Al, 65% Mo and 97% V as compared to 87% Ni, 34% Al, 73% Mo and 92% V with *At. thiooxidans*. Application of *At. thiooxidans* led to similar solubilization of metals as achieved with *At. ferrooxidans*. The results of the study indicate that bioleaching is an effective technique for recovery of metals from spent catalyst.

ACKNOWLEDGEMENT

The authors are grateful to the research support extended by the Global R&D Center's Program of the National Research Foundation of Korea (NRF), which was funded by the Ministry of Science, ICT and Future Planning.

REFERENCES

- [1] M. Marafi, A. Stanislaus, "Options and process for spent catalyst handling and utilization" J. Hazard. Mater. Vol. 101, p.123-132, 2003.
- [2] M. Marafi, A. Stanislaus, "Spent catalyst waste management: A review Part I-Developments in hydroprocessing catalyst waste reduction and use" Res. Conserv. Recyc. Vol. 52, p.859-873, 2008.

- [3] D. Pradhan, D. Mishra, D. J. Kim, J.G. Ahan, G.R. Chaudhury, "Bioleaching kinetics and multivariate analysis of spent petroleum catalyst dissolution using two acidophiles" J. Haz. Mater. Vol.175, p. 267-273, 2010.
- [4] R. M. Gholami, S. M. Borghei, S. M. Mousavi, "Bacterial leaching of a spent Mo-Co-Ni refinery catalyst using *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*" Hydrometallurgy. Vol.106, p.26-31, 2011.
- [5] D. Pradhan, D. J. Kim, J. G. Ahn, G. R. Chaudhury, S. W. Lee, "Kinetics and statistical behavior of metals dissolution from spent petroleum catalyst using acidophilic iron oxidizing bacteria" J. Indust. Engg. Chem. Vol.16, p.866-871, 2010.
- [6] D. Mishra, D. J. Kim, D. E. Ralph, J. G. Ahn, Y. H. Rhee, "Bioleaching of spent hydro-processing catalyst using acidophilic bacteria and its kinetics aspect" J. Hazard. Mat. Vol.152, p.1082-1091, 2008.
- [7] D. Mishra, D. J. Kim, D. E. Ralph, J. G. Ahn, Y. H. Rhee, "Bioleaching of vanadium rich spent refinery catalysts using sulfur oxidizing lithotrophs" Hydrometallurgy. Vol. 88, p.202-209, 2007.
- [8] L. Briand, H. Thomas, E. Donati, "Vanadium (V) reduction in *Thiobacillus thiooxidans* cultures on elemental sulfur" Biotechnology letters. Vol. 18, p. 505-508, 1996.
- [9] W. Mulak, B. Miazga, A. Szymczycha, "Kinetics of nickel leaching from spent catalyst in sulphuric acid solution" Int. J. Miner. Process. Vol. 77, p.231- 235, 2005.
- [10] K.R. Blight, D.E. Ralph, D.E., 2004. Effect of ionic strength on iron oxidation with batch cultures of chemolithotrophic bacteria. Hydrometallurgy 73, 325- 334.
- [11] T. Rohwerder, T. Gehrke, K. Kinzler, W. Sand, "Bioleaching review part A: progress in bioleaching: fundamentals and mechanisms of bacterial metal sulfide oxidation" Appl Microbial Biotechnol. Vol 63, p. 239-248, 2003.
- [12] A. Bharadwaj, Y. P. Ting, "Bioleaching of spent hydrotreating catalyst by acidophilic thermophile *Acidianus brierleyi*: Leaching mechanism and effect of decocking" Bioresource Technol. Vol 130, p. 673-680, 2013.