

Bioleaching of Spent Catalyst using Moderate Thermophiles with Different Pulp Densities and Varying size Fractions without Fe Supplemented Growth Medium

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Abstract—Bioleaching of spent catalyst using moderate thermophilic chemolithotrophic acidophiles in growth medium without Fe source was investigated with two different pulp densities and three different size fractions. All the experiments were conducted on shake flasks at a temperature of 65 °C. The leaching yield of Ni and Al was found to be promising with very high leaching yield of 92-96% followed by Al as 41-76%, which means both Ni and Al leaching were favored by the moderate thermophilic bioleaching compared to the mesophilic bioleaching. The acid consumption was comparatively higher for the 10% pulp density experiments. Comparatively minimal difference in the leaching yield with different size fractions and different pulp densities show no requirement of grinding and using low pulp density less than 10%. This process would rather be economical as well as eco-friendly process for future optimization of the recovery of metal values from spent catalyst.

Keywords—Bioleaching, spent catalyst, leaching yield, thermophilic

I. INTRODUCTION

THE growing demand for metals around the globe have aligned the current research on metal extraction mostly on secondary metal resources together with newer technologies promoting primary metal resources. The huge tonnage of industrial wastes generated having high metal values have prompted the industries to look forward for recycling options, where primary mineral resources are limited or exhausted. All the recycling methodologies have to be eco-friendly as well as cost-effective to be scaled up for a full scale operation for recovery of metal values. Among all the secondary metal resources, spent hydro-processing catalysts generated from oil refineries is well known to be rich in metal values like Al, V, Mo, Co, Ni and Fe. In an oil refinery the solid catalysts are used to treat the crude oil to achieve higher desired fuel products. These solid catalysts contain the metals such as Ni,

Al, Mo, V, Co etc, which are in the form of metal, metal oxides and metal sulfides [1]. With the extensive use of the solid catalyst during the processing of crude oil, this catalyst's lose their potential for its further use resulting as a waste product referred as spent catalyst [2]. Landfill of the spent catalyst is not an Environment friendly/Eco-friendly process, due to the presence of lot of metal values in the spent catalyst, which could be leached out creating harmful effects on the life process existing on the earth crust. Therefore prior to landfill its worthy to recover the metal values present in the spent catalyst, for which extensive research works has been carried out to find out a suitable method to extract the metal values. Pyro-metallurgical together with hydrometallurgical techniques has been well applied and investigated in past to recover metal values from the spent catalyst. Pyro-metallurgical processes based on high temperature (>1000 °C) stands to be an energy intensive process releasing SO₂ gas into the atmosphere [2]. However, the hydrometallurgical processes based on the principle of acid or alkali leaching resulting with highly acidic or alkaline solutions as by product would incurs a cost for its neutralization before its disposal into the environment together with limited success in the metal recovery due to its selectivity in leaching of the desired metals [3]. Various alternative methods have also been investigated using biological treatment of spent petroleum catalyst, among which both autotrophic and heterotrophic microorganisms have been used to recover metal values from them. Considering the heterotrophic microorganisms like few bacteria and fungus for metal recovery from spent catalyst also has its own limitations due to the cost involved in the growth medium, where sugar source such as sucrose incurs the biggest cost. Apart from the cost of the growth medium, another big cost would be the sterilization of the spent catalyst together with the growth medium, which is energy intensive as well as less feasible to scale up the process. However the process cost using heterotrophic microorganisms would not be economical considering the extent of metal values recovered. Another major problem would be encountered if the sterilization could be avoided i.e., the rapid growth of aerial microorganisms inhabiting the operational region resulting in the inhibition of the growth process and functioning of the desired microorganisms. Use of the autotrophic microorganisms like chemolithotrophic acidophiles and Archaeal species growing at low pH ranging from 1.0-2.0 has the advantage over the heterotrophs as no sterilization is required due to the low pH, where other aerial heterotrophs will be unable to grow without any hindrance to the bioleaching process [4-9]. Use of mesophilic acidophiles

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comprising of iron oxidizers and sulfur oxidizers has been observed to show their inability to leach optimum amount of Al, Mo and V, therefore attempts have been made in this present study to conduct bioleaching of spent catalyst with different size fraction at 5% and 10% pulp density using moderate thermophilic acidophiles comprising of iron and sulfur oxidizers. The leaching yield of Al, Ni, V and Mo from the spent catalyst was determined together with the estimation of the amount of acid required during bioleaching followed by the study of microbial population dynamics.

II. MATERIALS AND METHODS

A. Spent petroleum catalyst

The spent catalyst used for all bioleaching experiments was received in bulk from a petroleum refinery located in South Korea. An initial pretreatment of the spent catalyst was conducted by acetone-washing in a Soxhlet apparatus to get rid of all organic impurities sticking to the surface. This pretreatment was carried out for 20-25 days per batch to ensure maximum removal of the organic deposits on the spent catalyst. After the completion of the washing of the spent catalyst, they were filtered and dried in a hot air oven at 50°C until no change in the weight was observed. Thereafter, the dried spent catalyst was ground using mortar and pestle followed by sieving into three different size fractions viz. 45-106 µm, 106-212 µm and >212 µm respectively. The chemical composition of the spent catalyst for three different size fractions were determined using Induced couple Plasma spectroscopy (ICP-MS) (Table I) and the mineralogical analysis was carried out via Powder X-Ray Diffraction analysis (P-XRD) (Table II).

TABLE I
CHEMICAL COMPOSITION OF SPENT CATALYSTS (%)

Size fraction (µm)	S	Fe	Mo	V	Ni	Al
45-106	4.39	1.78	2.15	9.74	3.02	16.1
106-212	4.79	0.87	2.16	10.4	2.85	17.7
>212	5.30	0.64	1.93	13.5	3.03	16.6

TABLE II
MINERALOGY OF SPENT CATALYSTS

Mineral	Chemical formulae
Iron Nickel sulfide	Fe _{4.5} Ni _{4.5} S _{7.8}
Iron Molybdenum sulfide	FeMo ₂ S ₄
Vanadium sulfide	V ₂ S ₃
Molybdenite	MoO ₃
Molybdenum (IV) sulfide	Mo ₃ S ₄
Alumina	Al ₂ O ₃
Vanadium (IV) oxide	V ₄ O ₉
Nickel sulfide	Ni _{3-x} S ₂
Iron (III) oxide	Fe ₂ O ₃

B. Microorganisms

The microorganisms used for the bioleaching experiments were taken from the moderate thermophilic lab culture maintained in the laboratory. The moderate thermophilic lab culture was mixed culture of iron- and sulfur-oxidizing microorganisms obtained from a microbiology laboratory in

the USA. The growth medium used for the cultivation of the microbial culture was a modified Kelly (MK) medium comprising of 0.4 g/L (NH₄)₂SO₄, 0.04 g/L K₂HPO₄ and 0.4 g/L MgSO₄·7H₂O [10] and supplemented with 0.2 g/L of Yeast extract as a carbon source, 9 g/L of ferrous iron (Fe²⁺) and 2 mM of Sodium thiosulfate (Na₂S₂O₃). The microbial culture was grown in 250-ml Erlenmeyer conical flasks at a working volume of 100 ml in a shaking incubator at 60 °C. Regular measurements of the redox potential, pH, viable planktonic cell counts and residual Fe²⁺ iron concentrations were measured until the microbial cultures were full grown or reached stationary growth-phase.

C. Analytical and Instrumentation techniques

The analytical and instrumentation techniques used in the present investigation measured the following parameters: Redox potential, pH, viable planktonic cell count, chemical composition, and mineralogy. A platinum electrode with a Ag/AgCl reference electrode was used for measurements of the redox potential, while the pH value was measured by an Orion portable pH meter. The pH meter was calibrated regularly with a three-point calibration with the standard buffers of pH 1.68, 4.0 and 7.0. The viable microbial planktonic cell count was carried out on an improved Neubauer hemocytometer under a phase-contrast microscope (Olympus Model No BX51TF). The chemical composition of the feed, residues and leach liquor was carried out by inductively coupled plasma mass spectroscopy (ICP-MS). The mineralogical studies of the residues and feed were conducted by XRD using a RIGAKU R4-200 diffractometer equipped with a continuous scanning device using Cu Kα radiation at 40 kV and 30 mA and a sample rotation of 30 rpm. The analysis of the measured diffraction patterns were carried out in the 2θ range of 10° to 90°, while the crystalline phases were identified using the joint committee for powder diffraction standards (JCPDS) file of the instrument.

D. Bioleaching experiments

Six different batch bioleaching experiments for the spent catalyst using moderate thermophiles on three different size fractions (45-106 µm, 106-212 µm and >212 µm) and two different pulp densities (5% and 10%) in a 250-ml Erlenmeyer flasks on an orbital shaking incubator maintained at a temperature of 60 °C. To ensure homogenous mixing of the bioleaching pulp the rotation speed of the shaker incubator was maintained at 180 rpm. The working volume for all the experiments was 100 ml, which comprised of 90 ml of the growth medium and 10 ml of the full-grown microbial culture. The growth medium used in all six experiments was Modified Kelly (MK) medium without Fe supplement. Two different pulp densities of 5% and 10% (w/v) were taken for the three different size fractions of the spent catalyst. The aim of these experiments was to investigate the bioleaching efficiency based on the leaching yield of the elements of interest in a growth medium without Fe supplement at two different pulp densities and three different size fractions to optimize the best leaching condition with respect to cheaper growth medium, best size fraction and best pulp density. All the six bioleaching experiments were carried out in a pH controlled condition at pH value of 1.8 by adding 2M H₂SO₄ as per the requirement.

The bioleaching profile was determined from the redox potential profile obtained from the measurements carried out on regular basis. The microbial population studies conducted by counting the viable planktonic cells regularly ensured the presence of the optimum level of the microorganisms in the bioleaching experiments. All the bioleaching experiments were carried out until the pH and redox potential were stabilized. The bioleaching pulp was harvested after completion of each experiment and filtered followed by thorough washing of the filter-cake with a measured volume of deionized water acidified to pH 1.8 with H₂SO₄ to avoid precipitation of metal ions from the solution. The amount of wash water added was measured and taken into account for the calculation of leaching yield based on the leach liquor analysis. The bioleach residue obtained after filtration and thorough washing was hot air oven dried at 50 °C for 4-5 days until no change in weight was observed. The chemical composition bioleach residue and bioleach liquor were analyzed by ICP-MS as shown in Table III and IV.

TABLE III
CHEMICAL COMPOSITION OF BIOLEACH RESIDUES (%)

Size fraction (μm)	Pulp Density (%)	S	Fe	Mo	V	Ni	Al
45-106	5	3.37	4.73	2.75	14.6	0.21	13.1
	10	3.33	2.76	2.76	15.2	0.24	10.7
106-212	5	3.02	3.31	2.45	15.3	0.21	12.6
	10	3.98	1.69	2.76	15.2	0.24	11.6
>212	5	4.7	2.77	2.61	18.5	0.27	10.2
	10	5.07	1.36	2.43	17.9	0.34	9.64

TABLE IV
CHEMICAL COMPOSITION OF BIOLEACH LIQUOR (g/L)

Size fraction (μm)	Pulp Density (%)	SO ₄ ²⁻	Fe	Mo	V	Ni	Al
45-106	5	28.31	0.05	0.14	0.21	1.10	4.08
	10	46.50	0.14	0.29	0.59	1.58	6.82
106-212	5	29.34	0.05	0.27	0.36	1.20	4.44
	10	42.30	0.08	0.26	0.68	1.33	6.26
>212	5	32.57	0.03	0.21	0.35	1.32	4.99
	10	40.80	0.06	0.22	0.71	1.40	6.12

The leaching yield of the desired elements of interest was calculated based on both the elemental composition of the bioleach residue and bioleach liquor with respect to the feed. However, a very good mass balance was obtained from the leaching yield calculated with respect to residue and leach liquor analysis. The percentage of the leaching yield obtained from the feed and residue analysis was calculated by formula given below.

$$\text{Leaching yield (\%)} = \left[1 - \frac{M(r)}{M(f)} \right] \times 100$$

Where, M(r) is the metal (Ni, V, Mo, Al) content in the bioleach residue and M(f) is the metal (Ni, V, Mo, Al) content in the feed.

III. RESULTS AND DISCUSSION

A. Characterization of the spent catalyst

The characterization of the spent catalyst with different size

fractions was carried out based on the results obtained from the chemical analysis conducted by ICP-MS (Table I) and the mineralogical analysis carried out by XRD (Table II). The chemical composition of the spent catalyst from different size fractions varied with some degrees of variation, but nothing spectacular or remarkable variation was observed with the change in size fraction (Table I). However the minor differences in the chemical composition cannot be avoided as it makes bigger influence on the leaching yield, hence it is important to not underestimate the chemical analysis of the spent catalyst with different size fractions. The interesting phenomenon observed in the mineralogical analysis is that the mineralogy of the spent catalyst remained unchanged despite of different size fractions (Table II).

B. pH evolution with time and the amount of acid consumption during bioleaching

As all the bioleaching experiments were conducted in a pH control condition with a pH value of 1.8, the amount of 2M H₂SO₄ consumed was plotted with the initial and final pH as shown in Fig. 1 and finally the cumulative addition of 2M H₂SO₄ was calculated in terms of concentrated sulfuric acid required per ton of spent catalyst.

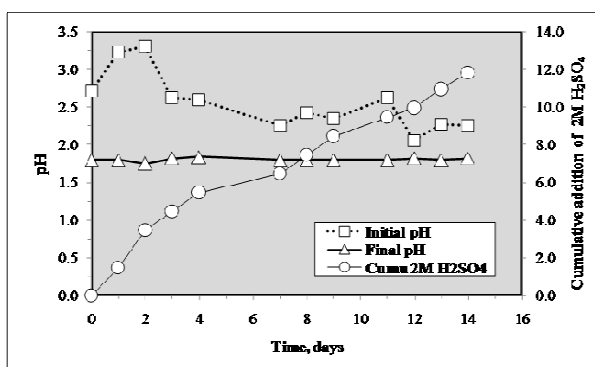
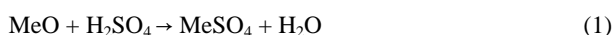
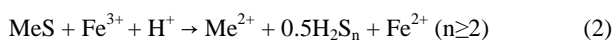


Fig. 1 An example of the pH evolution in the bioleaching experiment on a size fraction of 45-106 microns and 5% pulp density

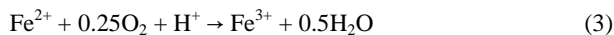
An increase in pH level above 1.8 was observed in all of the experiments during the initial period of the bioleaching due to the alkaline nature of the spent catalyst and the acid-consuming metal oxides present in it. The dissolution of the metal oxides in the spent catalyst is usually an acid consuming process, which led to an increase in pH value above 1.8 resulting in a higher consumption of acid during the initial days of the experiment compared to the later part (Eq. 1).



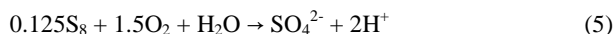
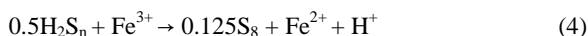
The acid insoluble metal sulfides such as pyrite (FeS₂), molybdenite (MoS₂) and tungstenite (WS₂), whichever present in the spent catalyst will be oxidized by the Fe³⁺ ion coming from the Fe³⁺ ion rich microbial inoculum (Eq. 2).



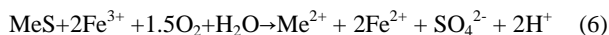
The Fe^{3+} ion mediated oxidation of the metal sulfides via reduced the Fe^{3+} ions to Fe^{2+} ion (Eq. 2) and further this Fe^{2+} ion in the bioleaching solution is oxidized to Fe^{3+} ion (Eq. 3) by the help of iron oxidizing microorganisms releasing back more Fe^{3+} into the solution until complete oxidation of the metal sulphides is obtained.



The acid soluble metal sulfides, such as nickel sulfides will follow the polysulfide mechanism (Eqs. 2, 3, 4 and 5).



However the overall reaction would be as follows



However the sulfur oxidation process is well known to be an acid-producing process compensating the acid requirements during bioleaching. As shown in Fig. 1 as an example of the pH evolution during the bioleaching process in one of the experiment, similar profiles were obtained for all the experiments and the acid requirements during the bioleaching of the spent catalyst for all the experiments with 5% and 10% pulp density with different size fractions of spent catalysts is described in Table V.

TABLE V
ACID REQUIREMENT PER TON SPENT CATALYST

Size fraction	Pulp density	Kg Conc. H_2SO_4 / ton spent catalyst
45-106	5%	528
	10%	707
106-212	5%	553
	10%	683
>212	5%	655
	10%	757

Comparative analysis of the acid requirement shows higher acid requirement ranging from 683-757 kg/ton spent catalyst in the experiments with 10% pulp density, while the acid requirement ranges from 528-655 kg/ton spent catalyst in the experiment with 5% pulp density. The reason for higher acid consumption in the experiment with 10% pulp density is due to the high content of oxides with higher pulp density.

C. Redox potential profile

The redox potential profiles in Fig. 2, 3 and 4 states the comparative analysis of the experiments with 5% and 10% pulp density for different size fractions. The redox potential profile states the oxidation-reduction reaction occurring during the bioleaching process, where the $\text{Fe}^{2+}/\text{Fe}^{3+}$ is considered to be the prominent redox couple. The redox potential starts

decreasing with the decrease in the Fe^{3+} ion concentration when the Fe^{3+} ion oxidize the sulfide minerals present in the spent catalyst resulting in formation of Fe^{2+} ion.

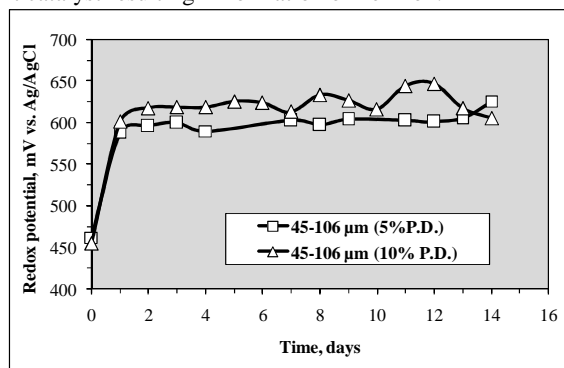


Fig. 2 Comparative Redox potential profile in the experiments with 5% and 10% P.D. at a size fraction of 45-106 μm

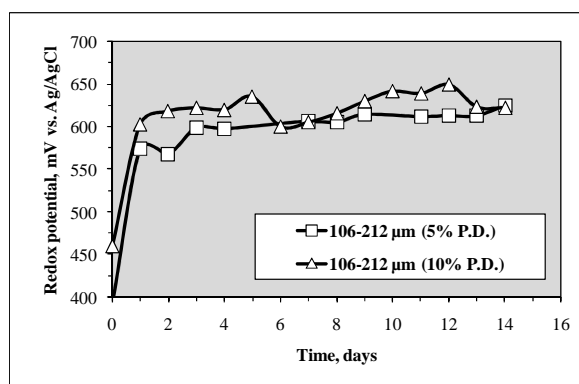


Fig. 3 Comparative Redox potential profile in the experiments with 5% and 10% P.D. at a size fraction of 106-212 μm

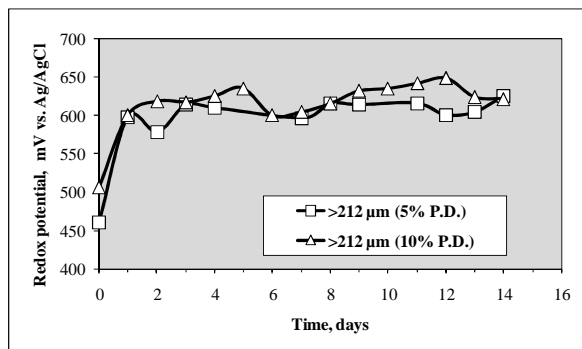


Fig. 4 Comparative Redox potential profile in the experiments with 5% and 10% P.D. at a size fraction of >212 μm

Later this Fe^{2+} ion produced is oxidized by the iron oxidizing microorganisms to form Fe^{3+} ion resulting in an increase in the redox potential. However, in the present context together with $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple, there exist many other redox pairs such as V, Mo and Ni rather having smaller influence on the redox potential. Comparatively higher redox potential value was observed for the experiment with 10%

pulp density at a value of 650 mV compared to 625 mV in the experiments with 5% pulp density with all size fractions. These redox potential profiles are mostly used to study the microbial activity showing faster lag phase and a longer stationary phase, which seems to take longer time for stabilizing the redox couple with slight variation until the end of the experiment.

D. Microbial planktonic cell population dynamics

Microbial viable planktonic cell population dynamics studies conducted on all the bioleaching experimental shake flasks stated only the viable cells in the solution, even though this population may not be the real representation of the microbial population accelerating the bioleaching process. The planktonic viable cells only shows the viable cells free from the spent catalysts giving an overall impression of the active cells working in the bioleaching system. Some studies state the fall in microbial population just after the addition of the feed material i.e., spent catalysts into the shake flasks compared to the population present in the inoculums, due to the shock encountered by the quick fall in the redox potential and a new environment together with new solution chemistry in the initial days of all experiments [11]. A similar trend in the microbial populations was observed with the inoculum populations of 2.5×10^8 cells/mL decreasing to almost $3.0\text{--}3.5 \times 10^6$ cells/mL in the initial 1-6 days of the experiments, but after the redox potential approached 600 mV or above, the microbial cells were revived, indicating that some of them may have been redox sensitive (Figure 5 and 6).

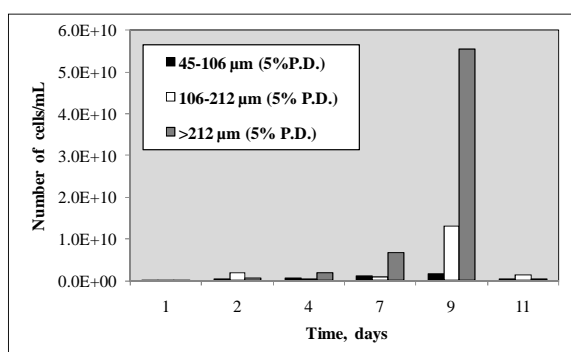


Fig. 5 Viable planktonic cell population dynamics in bioleaching experiments with 5% P.D. for three different size fractions

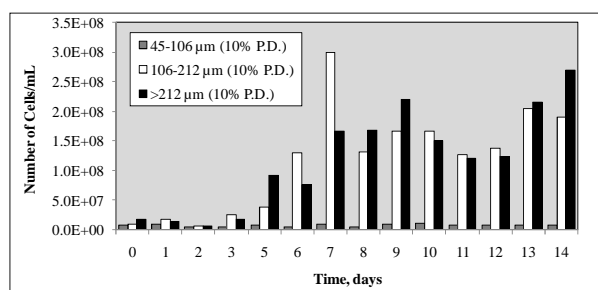


Fig. 6 Viable planktonic cell population dynamics in bioleaching experiments with 10% P.D. for three different size fractions

The important thing observed in the present study was the experiments with 10% pulp density were found to have 10 times less number of cells compared to the experiments with 5% pulp density toward the final 8-10 days of the experiment. The reason for less cell population observed in case of 10% pulp density could be due to the high elemental composition of Ni, Mo, V and Al in all the experiments with different size fractions as the feed content was higher compared to 5% pulp density. The other interesting observation made was that the experiments with the smallest size fraction (45-106 μm) had a comparatively lower microbial population compared to bigger size fractions and was probably due to the thick slurry formed leading to low gas transfer especially when carried out in a shake flask but can be avoided when carried in air sparged bioreactors. The overall microbial population dynamics study shows the sensitivity of the moderate thermophiles to elevated concentrations of the metal ions and the negative influence of a shake flasks experiment motivating further studies to be carried out in bioreactors.

E. Leaching yields

The leaching yields obtained for selected elements, such as Mo, V, Ni and Al, from the present bioleaching experiments were calculated based on the feed and residue analysis together with feed and leach liquor analysis and very good mass balance was obtained to ensure the accuracy of the experiments. The leaching yields obtained feed and residue analysis from all the experiments is plotted in the histogram shown in Fig. 7, 8 and 9 respectively. The leaching yield of Ni is found to be very prominent with a recovery ranging from 92% to 96% in all the experiments. However the leaching yield of Ni was invariably unchanged despite of increasing pulp densities, which means both the 5% and 10% pulp density experiments with each size fraction, did not have much variation in the leaching yield. The interesting phenomenon observed was that the Ni recovery for the highest size fraction (>212 μm) ranged between 92-93%, which was 2-3% less than the recovery obtained (i.e., 95-96%) from the two different smaller size fractions viz. 45-106 μm and 106-212 μm. The reason for slightly lower recovery could be due to the less liberation of minerals at >212 μm size fraction or could be developed by conducting experiments in more controlled conditions.

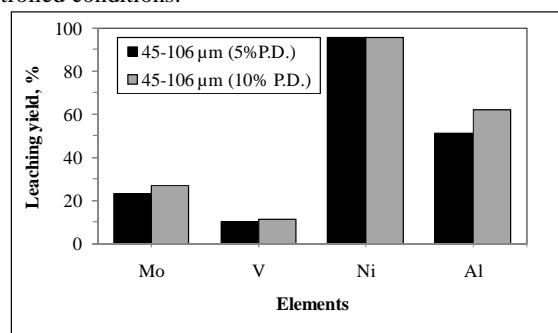


Fig. 7 Comparative leaching yield between 5% and 10% P.D. at a size fraction of 45-106 μm

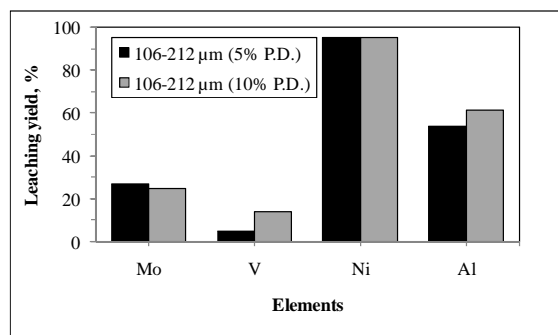


Fig. 8 Comparative leaching yield between 5% and 10% P.D. at a size fraction of 106-212 µm

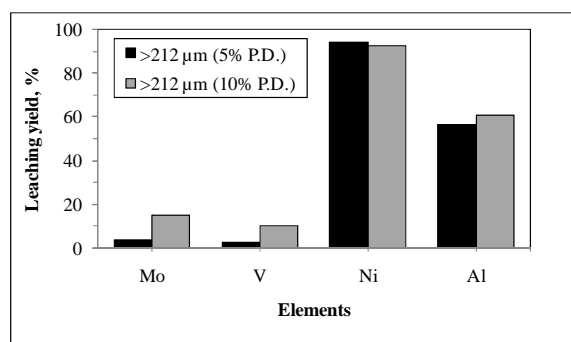


Fig. 9 Comparative leaching yield between 5% and 10% P.D. at a size fraction of ≥212 µm

The leaching yield of Mo for the two smaller size fractions was similar at a range of 25-27% despite of the difference in the pulp density, but resulted with comparatively lower recovery ranging from 4-15%. The liberation of the minerals at smaller size fractions could be the reason for the higher recovery of the Mo. The very low recovery Mo compared to Ni is due to the difficulty of Mo mineral phase dissolution in the bioleaching condition, which does not permeate Mo leaching easily in acidic conditions compared to alkaline leaching. However the leaching yield of Al was found to be quite promising with a recovery percentage of 41-76% compared to the results obtained in the previous mesophilic bioleaching works conducted in past, which suggests the elevated temperature of 65 °C favored the dissolution of Al from the spent catalyst in the bioleaching system. The leaching yield profile did not follow the leaching metals profile found for Ni and Mo, instead it was just opposite to the results obtained for Ni and Mo, which means higher size fractions resulted with higher leaching yield of Al. In case of the V, the leaching yield was remarkably low compared to all other elements with a leaching yield ranging from 5-10%, as its well known that V is difficult to be leached in acidic medium as well as ferric ion mediated leaching system. So it would be wiser to step up the process with a second step leaching of the bioleach residues obtained with a high temperature alkaline leaching for shorter duration of time. The oxidation percentage of Fe and S was calculated based on the feed and residue analysis and was found to have very high S oxidation (97-98%) compared to Fe (19-44%) (Table VI).

TABLE VI
PERCENTAGE OF IRON AND SULFUR OXIDATION

Size fraction (µm)	Pulp density	Fe	S
45-106	5%	21	98
	10%	41	98
106-212	5%	20	98
	10%	44	98
>212	5%	19	97
	10%	40	97

The reason behind high S-oxidation could be due to the highly active and populated S-oxidizing microorganisms, whereas the Fe-oxidizing microorganisms must have been suppressed due to its lower population with scarcity of ferrous iron as its growth medium to sustain. On the contrary it is less important to have high Fe oxidation in this case as the main aim of this experiment was to recover elements like Ni, V, Mo and Al. However the high S-oxidation might have supported the acid requirement for the dissolution of the oxidic minerals present in the spent catalyst. The trends for leaching yields of the elements of interest in the present investigation can be represented as Ni>Al>Mo>V, and further investigation is needed to optimizing the conditions and to add other steps for improved recovery of all the metal values from the spent catalyst before land filling.

IV. CONCLUSION

The present study conducted for the bioleaching of spent catalyst using moderate thermophilic microorganisms comprising of Fe and S oxidizers at 5% and 10% pulp density on 3 different size fractions viz. 45-106 µm, 106-212 µm and >212 µm resulted with very high leaching yields of Ni and Al followed by lower recovery of Mo and V. The higher pulp density was worth to be tested as there were not big differences between the two pulp densities (5% and 10%) tested and indicates that the further scale of the process in bioreactor would be promising to achieve improved leaching yield as bioreactors are well known to have relatively better controlled conditions with sufficient agitation, air sparging and well maintained temperature compared to shake flask studies. This process would be much more economical as no Fe source was added to the bioleaching solution except the inoculums which was very low, indirectly reducing the operation cost due to Fe supplemented bioleaching systems. This process would also render the possibilities to leach the aluminum more effectively due to the elevated temperature moderate thermophilic bioleaching compared to mesophilic bioleaching. Another key aspect observed was the size fraction, which states there is very minimal difference in leaching yield between all size fractions stating grinding of spent catalyst may not be required and could save the cost for grinding for future optimization studies.

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REFERENCES

- [1] M. Marafi, and A. Stanislaus "Options and processes for spent catalyst handling and utilization" J. Hazard. Mater. Vol. 101, p. 123–132, 2003.
- [2] M. Marafi, and A. Stanislaus "Spent catalyst waste management: A review Part I—Developments in hydroprocessing catalyst waste reduction and use. Conserv. Recycling. Vol. 52, p.859-873, 2008.
- [3] D. Pradhan, D. Mishra, D.J. Kim, J.G. Ahn, G.R. Chaudhury, and S.W. Lee "Bioleaching kinetics and multivariate analysis of spent petroleum catalyst dissolution using two acidophiles. J. Hazard. Mater. Vol. 175, p. 267–273, 2010.
- [4] V. Bosio, M. Viera, and E. Donati "Integrated bacterial process for the treatment of a spent catalyst" J. Hazard. Mater. Vol. 154, p. 804–810, 2008.
- [5] R.M. Gholami, S.M. Borghei, and 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.
- [6] D. Mishra, D.J. Kim, D.E. Ralph, J.G. Ahn, and Y.H. Rhee "Bioleaching of vanadium rich spent refinery catalysts using sulfur oxidizing lithotrophs" Hydrometallurgy. Vol. 88, p. 202–209, 2007.
- [7] D. Mishra, J.G. Ahn, D.J. Kim, G.R. Chaudhury, D.E. Ralph "Dissolution kinetics of spent petroleum catalyst using sulfur oxidizing acidophilic microorganisms" J. Hazard. Mater. Vol. 167, p. 1231–1236, 2009.
- [8] F. Beolchinea, V. Fontia, F. Ferell, and F. Veglio "Metal recovery from spent refinery catalysts by means of biotechnological strategies" J. Hazard. Mater. Vol. 178, p. 529–534, 2010.
- [9] D.J. Kim, D. Pradhan, J.G. Ahn, and S.W. Lee "Enhancement of metals dissolution from spent refinery catalysts using adapted bacteria culture-Effects of pH and Fe(II)" Hydrometallurgy. Vol. 103, p. 136-143, 2010.
- [10] G. da Silva, M.R. Lastra, and J.R. Budden "Electrochemical passivation of sphalerite during bacterial oxidation in the presence of galena" Miner. Eng. Vol. 16, p. 199-203, 2003.
- [11] C.S. Gahan, J.E. Sundkvist, and Å. Sandström "A study on the toxic effects of chloride on the biooxidation efficiency of pyrite" J. Hazard. Mater. Vol. 172, p. 1273-1281, 2009.