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# Kinetics and statistical behavior of metals dissolution from spent petroleum catalyst using acidophilic iron oxidizing bacteria

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ABSTRACT

Bioleaching of spent catalyst were carried out using *Acidithiobacillus* type of microorganisms. Various leaching parameters like contact time, Fe(II) concentration, particle size, pulp densities, pH and temperature were studied in details. All the four metal ions like Ni, V, Mo and Al 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 and Al. The thermodynamic parameters like $\Delta G$, $\Delta H$ and $\Delta S$ for all metals were calculated. The leaching kinetics followed first order rate. Rates of dissolution of Al, V and Ni increased, and Mo decreased with increase of Fe(II) addition whereas that of all metals decreased with increase of pulp density and particle size. Leaching kinetics of Al, Mo, V increased with decrease of pH. Variation of initial pH of the leaching medium showed an inadequate effect on Ni dissolution. The rate determining step found to be pore diffusion controlled. The correlation between observed and theoretical values of leaching efficiency for different parameters was evaluated using Multi-Linear Regression Analyses which showed the significance of the leaching. A total of 5 factors were evaluated by data reduction technique using Principal Component Analysis.


## 1. Introduction

In the petroleum refinery industry, crude oils are purified to transportation fuels by application of hydrotreating process [1]. Various solid catalysts are used in petroleum industries to improve this process efficiency [2]. The catalyst materials contain chemicals containing metal, metal oxides, metal sulfides etc. which helps in treating the crude to different fractions to produce full range of transportation fuels with desired specifications [3]. The used catalysts have a definite self-life and with time they lose their activity. The deactivated catalysts are reactivated and reused. But after few cycles of activation–deactivation, the catalysts lose their activity in totality and in that case they are discarded. The solid waste catalyst contains appreciable amounts of metals like Mo, V, Ni, Co etc. Therefore, the catalysts are considered as hazardous materials and these cannot be discarded as such [4]. For the treatment of waste catalyst, any of two alternatives can be considered such as preservation in a proper way so that it would not contaminate the environment and recovery of metal values. The later is chosen as prospective alternative because the metal values can be recovered and subsequently can be reused.

There are number of processes developed to recover the metal values from waste catalyst like pyro, hydro and combination of the two. In the pyrometallurgical process, the waste material was treated at high temperature (>1000 °C) in presence of reductant and fluxes [5,6]. The valuable metals like Mo, V, Ni, Co etc. were recovered as alloys where the base materials like alumina, silica etc. were reported in the slag phase. The slag in some cases was used as abrasive materials [7]. In hydrometallurgical process, a number of lixiviants were used for dissolution process such as acids and alkali [8,9]. In the combination process, the waste material was roasted either alone or in presence of acid or alkali. The roasted mass was subjected to leaching process by addition of suitable lixiviant such as acid or alkali [10,11]. Due to several drawbacks of the conventional techniques described above, biotechnological leaching processes have been developed as a potential alternative. Different acidophilic microorganisms are used to recover metal values from various resources including waste petroleum catalyst [12–14]. Bacteria can produce various metabolites which are capable of extracting metal values from waste materials. In order to exploit the intrinsic capabilities of some microorganisms to extract metal values from various resources, more efforts need to be examined [15].

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In the present communication, bioleaching studies were carried out to extract metal values from the spent refinery catalyst using an iron oxidizing bacteria culture. Since there are several important parameters such as pH, nutrient availability, temperature, pulp density, metal toxicity etc., which profoundly affect the bioleaching kinetics, a detailed studies were carried out to determine the effects of these entire parameters vis-à-vis individual leaching kinetics of the constituents. Further rate determining steps were also evaluated. Statistical analyses were also carried out which would help during the scaling up operation.

## 2. Experimental

All chemical and water used in the present investigation were of analytical grade (AR) and distilled respectively.

### 2.1. Preparation of spent catalyst

Spent petroleum catalyst was collected from Korean Petroleum Company. The as such spent catalyst was covered with a film of oil. Therefore, it was subjected to wash in acetone using a soxhlet to remove the oil. The metal content in the waste analyzed by ICP-AES (Jobin-Yvon JY 38) and the obtained values were as follows (metal, wt.%): Al-19.5; Ni-2.0; V-9.0; Mo-1.4; Fe-0.3. The physico-chemical characterizations were done using XRD (Rigaku, R4-200) and SEM-EDX (JEOL, JSM-6380LA). The acetone washed material was used as a base material in all the leaching studies.

### 2.2. Microorganisms

The *Acidithiobacillus* type microorganisms were isolated from local mining effluent water [16]. The isolated bacteria were activated by repeated subculturing technique. Regularly bacterial activities were monitored by iron oxidation rate (IOR).

### 2.3. Bioleaching

Bioleaching experiments were carried out by shake flasks where the shaking was done at a rate of 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 $\sim 10^8$ cells/mL. Such high bacterial count was due to use of centrifuged biomass. Periodically samples were collected for different physico-chemical parameters like pH, Eh and metal ions concentration. For leaching studies, following leaching conditions were maintained unless specified otherwise: temperature, 35 °C; pulp density (PD), 10% (w/v); particle size (PS), 106 μm; pH 2.0; initial Fe(II) concentration, 10 g/L.

### 2.4. Statistical interpretation

The leaching data were subjected to multivariate statistical analyses to evaluate the inference of various leaching parameters on the leaching rates of different metal ions. Multivariate statistical approaches such as Principal Component Analysis (PCA) and Multi-Linear Regression Analysis (MLRA) were used to determine the significance of specific parameters among the datasets. In PCA, eigen values were used to determine the percentage as well as cumulative percentage of variances. A varimax rotation of different varifactors with factor loading was calculated using eigen values greater than 1 and sorted by the results having values greater than 0.6 to have $p < 0.01$ (99% confidence level). MLRA was conducted using the step-wise forward integration method. Both PCA and MLRA were carried out using SPSS-10 software package.

**Table 1**
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 |
| $Al_2O_3$ | 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 |
| η-$Fe_2O_3$ | 3.60 | 4.36 | 6.01 | 21-0920 |

## 3. Results and discussion

### 3.1. Characterization of raw material

The XRD analyses of the material showed 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 $MoO_3$ and S in elemental form as shown in Table 1. No phases could be identified related to C and P. The C and P may be in the hydrocarbon and oxides form respectively. The SEM-EDX analysis showed exclusive elemental sulfur layer over Mo matrix (data not shown).

### 3.2. Effect of contact time

Leaching studies were carried out for 15 days to find out the effect of the same on the leaching kinetics. The results are shown in Fig. 1. 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 and Al all other elements are prone to aqueous dissolution as percentage dissolution was high. It was further observed all the elements like Mo, V, Ni and Al 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. 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 [17]. The intra-particle diffusion may be either diffusion inside the reactive matrix or through product layer formed during the course of dissolution or both. The slower and faster leaching rates for

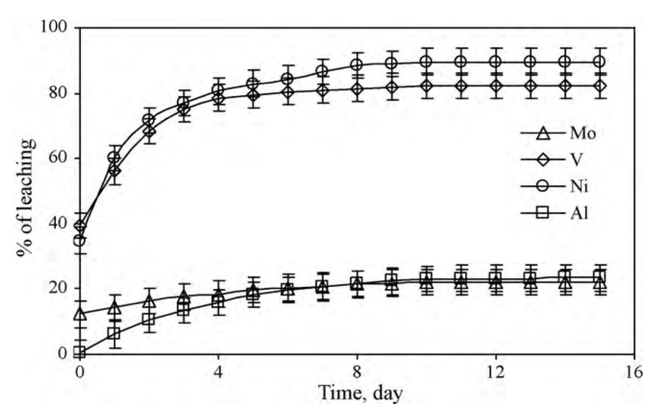


**Fig. 1.** Effect of contact time on the leaching efficiency. (conditions: pulp density, 10% (w/v); temperature, 35 °C; particle size, 106 μm; pH 2.0; initial Fe(II) concentration, 10 g/L).