



# An integrated sequential biological leaching process for enhanced recovery of metals from decoked spent petroleum refinery catalyst: A comparative study



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## ABSTRACT

We report on the effectiveness of a two-stage sequential integrated bioleaching process for enhanced recovery of metals from decoked spent petroleum catalyst. Fourier transform-infrared spectra confirmed that decoking led to removal of entrained hydrocarbons and carbonaceous deposits from the raw spent catalyst. Several two-stage sequential leaching strategies (two-stage bioleaching, two-stage abiotic leaching, bioleaching followed by alkali leaching, alkali leaching followed by acid leaching, and two-stage alkali leaching) were evaluated in batch reactors. The results suggested that two-stage bioleaching (240 h) with *Acidithiobacillus thiooxidans* was the most effective strategy to recover Ni (79%) and V (90%). Whereas integrating bioleaching with alkaline leaching remarkably improved leaching yield of Mo (88%) in a shorter period of time (125 h). A mineral liberation analysis of the treated residue also confirmed that most of the Mo was leach out during second stage alkali leaching.

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## 1. Introduction

The petroleum refinery industry generates significant quantities of spent catalyst as a waste product and this has increased in recent years due to the rise in demand for petroleum products, lower quality refinery feedstock, and regulations limiting the sulfur content of fuels. At the current rate of consumption approximately 178,000 tonnes per annum of hydro-treating and 358,000 tonnes per annum of fluid cracking catalysts will be required by the petroleum industry (Menoufy and Ahmed, 2008). Spent catalysts are designated as hazardous by USEPA due to the presence of appreciable concentration of toxic metals such as Mo, Ni, and V (Rapaport, 2000). Due to strict environmental regulations for disposal, different processes have been examined to remove/recover these metals from spent refinery catalyst.

Various attempts have been made to remove these metals by conventional hydrometallurgical processes that have employed strong acid (8 M H<sub>2</sub>SO<sub>4</sub>), strong alkali (4 M NaOH), salt roasting with Na<sub>2</sub>CO<sub>3</sub> or NaCl followed by water or Na<sub>2</sub>CO<sub>3</sub> (30 g/L) leaching (Kar et al., 2005; Ognyanova et al., 2009; Park et al., 2007). Different pyrometallurgical techniques such as smelting, calcination, and anhydrous chlorination have also been used to recover metals from spent catalyst (Kar et al., 2005). Although these hydrometallurgical processes show

reasonable extraction efficiencies, the use of high strength acids and/or alkalis, which are secondary pollutants and expensive to treat in downstream processing, has restricted their large scale use. In contrast, pyrometallurgical processes suffer from high energy consumption and emit toxic gases that require downstream treatment. Because of this the use of relatively benign bio-hydrometallurgical processes to recover metals from spent petroleum catalysts is gaining attention.

Biohydrometallurgical processes involving the use of mesophilic chemoautotrophic bacteria (*Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*) and heterotrophic fungi (*Aspergillus niger*) to remove metals from spent catalyst have been reported widely (Gholami et al., 2011; Mishra et al., 2007; Pradhan et al., 2010). Studies have also been conducted to evaluate the leaching of metals from spent catalysts containing Ni, Mo, and Al using thermophilic cultures (Srichandan et al., 2012). The use of *A. thiooxidans* to treat a spent vanadium–phosphorous catalyst has also been reported (Briand et al., 1996). The effects of various parameters such as substrate concentration, pulp density, particle size, and pH on bioleaching have been examined (Kim et al., 2010; Srichandan et al., 2012). Several studies have also reported that during bioleaching, the rate of diffusion of metals from the catalyst matrix is reduced by catalyst fouling by entrained hydrocarbons, sulfide species, or carbonaceous deposits (Bharadwaj and Ting, 2013; Mulak et al., 2005). Therefore, pretreatment of spent catalyst to remove hydrocarbons and carbonaceous materials, and transform sulfide species into more leachable forms is required prior to bioleaching.

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A recent bioleaching study reported that decoking of spent petroleum refinery catalyst can lead to a significant increase in the leaching yield of Mo compared to a coked sample (Bharadwaj and Ting, 2013). However, this study was conducted at 70 °C using thermophilic bacteria that require significant energy to heat the leaching solution; hence, the process was considered to be too expensive.

It has also been reported that Mo yield during bioleaching is generally low in a single-stage treatment step due to the limited solubility of Mo oxoanions in a weakly acidic solution, the refractory nature of MoS<sub>2</sub>, the formation of a product layer on the Mo species, or a combined effect of all of the above (Kim et al., 2010; Mishra et al., 2007; Pradhan et al., 2010). Because of this, an additional treatment step is required to successfully extract the remaining Mo present in the treated spent catalyst. Our previous investigation suggested that a two-stage sequential reactor employing bioleaching followed by alkaline leaching significantly improved the yield of Mo from spent catalyst (Pradhan et al., 2013). However, that study was conducted using *A. ferrooxidans* as a leaching microorganism in the first stage and acetone-washed spent catalyst as a feed material. *A. thiooxidans*, another acidophile, is also capable of leaching metals from spent refinery catalyst using sulfur as an energy source. This can be advantageous due to the low cost of sulfur compared to sulfuric acid. This study, therefore, reports on two-stage sequential reactor studies using decoked spent petroleum catalyst and employing mesophilic sulfur-oxidizing microorganisms (*A. thiooxidans*) as a means to develop an efficient process for the leaching of metals from spent refinery catalyst. The use of a two-stage sequential process for decoked spent catalyst and involving bioleaching–bioleaching or bioleaching followed by chemical leaching has not been previously reported.

In the present study, several two-stage sequential leaching strategies were tested in order to test their effectiveness in achieving high metal leaching yield from the decoked spent catalyst. These were (1) bioleaching followed by bioleaching, (2) bioleaching followed by alkali leaching, (3) alkali leaching followed by acid leaching, and (4) alkali leaching followed by alkali leaching.

## 2. Materials and methods

### 2.1. Pretreatment and characterization of spent catalyst

The spent catalyst was procured from a petroleum refinery company located in South Korea. The raw spent catalyst was oily and had carbonaceous deposits. It was decoked by heating in a furnace at 500 °C for 5 h then ground in a vibrating cup mill (FRITSH). This powdered decoked spent catalyst was used as the feed material in all leaching experiments.

The carbon content of the spent catalyst was determined with a LECO CS-600 analyzer. The carbon content of the decoked spent catalyst (1.48%) was significantly less than that of coked (raw) spent catalyst (22.80%). The particle size distribution of the spent catalyst samples was determined using the laser diffraction method with a British Malvern Mastersizer 2000. The particle size range of the feed decoked sample was 0.025–125 μm. The d(0.1), d(0.5) and d(0.9) were 2.352 μm, 41.583 μm and 97.375 μm, respectively.

The X-ray diffractogram (XRD) of the decoked spent catalyst was obtained using Cu Kα radiation from an X-ray diffractometer (Smartlab, Rigaku, Japan) operated in Bragg–Brentano geometry with counting time of 3 s and steps of 0.01° in 2θ. The identified mineral phases of the decoked spent catalyst are presented in Table 1. The chemical composition of the decoked spent catalyst was determined by induced couple plasma optical emission spectroscopy using a standard method (APHA, 2005). The decoked spent catalyst contained (w/w) 3.97% Ni, 22.06% Al, 2.82% Mo, and 14.30% V. The pH measurements during the leaching experiments were performed by an electrometric method (Orion portable pH meter), whereas the redox potential was measured using a platinum electrode with a Ag/AgCl reference electrode (APHA,

**Table 1**  
Mineralogical composition of the decoked spent catalyst.

Code	Phase name	Chemical formula	IB card number
1	Aluminum oxide	Al <sub>2</sub> O <sub>3</sub>	01-075-0921
2	alpha-Aluminum oxide (corundum)	α-Al <sub>2</sub> O <sub>3</sub>	01-071-1684
3	kappa-Aluminum oxide	κ-Al <sub>2</sub> O <sub>3</sub>	00-052-0803
4	theta-Aluminum oxide	θ-Al <sub>2.427</sub> O <sub>3.64</sub>	01-079-1559
5	alpha-Aluminum sulfide	α-Al <sub>3</sub> S <sub>2</sub>	01-081-1810
6	Bunsenite	NiO	00-044-1159
7	Millerite	NiS	01-086-2281
8	Heazlewoodite	Ni <sub>3</sub> S <sub>2</sub>	00-044-1418
9	Vanadium sulfide	V <sub>5</sub> S <sub>8</sub>	01-079-1639
10	Karelianite	V <sub>2</sub> O <sub>3</sub>	01-071-0576
11	Shcherbinaite	V <sub>2</sub> O <sub>5</sub>	01-085-0601
12	beta-Divanadiumpentaoxide	β-V <sub>2</sub> O <sub>3</sub>	01-073-9431
13	gamma-Vanadium oxide	γ-V <sub>2</sub> O <sub>3</sub>	01-085-2422
14	Tugarinovite	MoO <sub>2</sub>	00-032-0671
15	eta-Tetramolybdenumundecaoxide	η-Mo <sub>4</sub> O <sub>11</sub>	01-086-1269
16	gamma-Tetramolybdenumundecaoxide	γ-Mo <sub>4</sub> O <sub>11</sub>	01-084-0687
17	Molybdenite	MoS <sub>2</sub>	00-037-1492
18	Molybdate	MoO <sub>3</sub>	01-074-7912

2005). The redox potential values obtained were converted into Eh values (+200 mV) with respect to standard hydrogen electrode. Both the pH and redox potential meters were calibrated regularly prior to analysis.

### 2.2. Fourier transform infrared spectroscopy analysis (FT-IR)

The FT-IR technique was used to characterize the organic functional groups of the raw and decoked spent catalyst. We provide a detailed surface characterization emphasizing the type and changes in different organic functional groups during the decoking process such as aromatic carbon, unsaturated hydrocarbons (C=C), and substitution of aromatic rings in the spent catalyst. Infrared spectra were recorded by co-adding 124 scans at a resolution of 2 cm<sup>-1</sup> with a Nicolet 6700 FT-IR spectrometer (Thermo Scientific, Rockford, IL, USA) with a spectral range from 7000 to 225 cm<sup>-1</sup> and resolution of 0.09 cm<sup>-1</sup>.

### 2.3. Mineral liberation analysis (MLA)

Elemental mapping of the decoked and treated samples was carried out with a mineral liberation analyzer (MLA650F, FEI, Hillsboro, OR, USA). Very stable back scattered electron signals from the scanning electron microscope SEM were used to generate quality images. The ground samples were set in epoxy resin in a round mold to form a hardened block, a cross section of which was polished and coated with carbon before being presented to the analyzer.

### 2.4. Microorganisms and growth conditions

*A. thiooxidans* was obtained from KRRIB, South Korea. The batch culture was grown in 0 K medium containing 3.0 g/L (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.5 g/L MgSO<sub>4</sub>, 0.1 g/L KCl, 0.5 g/L K<sub>2</sub>HPO<sub>4</sub>, and 0.01 g/L Ca(NO<sub>3</sub>)<sub>2</sub> supplemented with 1% (w/v) of elemental sulfur at pH 2.0, 250 rpm and 35 °C. The 0 K medium was modified media of 9 K medium (Silverman and Lundgren, 1959) without 9 g of Fe<sup>2+</sup>. A continuous supply of air was provided at a flow rate of 1 L/min. The pH of the growth medium decreased to about 1.0 as a result of elemental sulfur (S<sup>0</sup>) oxidation to sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) by *A. thiooxidans*. The bacterial culture was then allowed to pass through a Whatman No. 1 filter to remove the suspended sulfur particles. The filtrate containing the cells was filtered through a membrane filter, and the filtered cells were used for further sub-culturing.

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