



## A kinetic study on hydrochloric acid leaching of nickel from Ni–Al<sub>2</sub>O<sub>3</sub> spent catalyst

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### ABSTRACT

Hydrochloric acid leaching of nickel from spent Ni–Al<sub>2</sub>O<sub>3</sub> catalyst (12.7% Ni, 39.2% Al and 0.68% Fe) has been investigated at a range of conditions by varying particle size (50–180 μm), acid concentration (0.025–2 M), pulp density (0.2–0.4%, w/v) and temperature (293–353 K). Nickel was selectively leached from the catalyst, irrespective of the different conditions. Under the most suitable conditions (1 M HCl, 323 K, stirring at 500 rpm, 50–71 μm particle size), the extent of leaching of Ni and Al after 2 h was 99.9% and 1%, respectively. The XRD pattern of the spent catalyst corresponded to crystalline α-Al<sub>2</sub>O<sub>3</sub> along with elemental Ni. The peak due to elemental Ni was absent in the residue sample produced at the optimum leaching conditions, confirming the complete dissolution of Ni from the spent catalyst. The leaching results were well fitted with the shrinking core model with apparent activation energy of 17 kJ/mol in the temperature range of 293–353 K indicating a diffusion controlled reaction.

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### 1. Introduction

Nickel, in the form of metal, oxide or sulfide, has wide applications in catalysts used in the petroleum industry and several other commercial processes such as: (i) hydrogenation, hydrodesulphurization, hydrorefining including fat hardening process (Ni–Mo/Al<sub>2</sub>O<sub>3</sub>, NiO/Al<sub>2</sub>O<sub>3</sub>, Raney nickel alloy), (ii) refinery hydro-cracking (NiS, WS<sub>3</sub>/SiO<sub>2</sub>Al<sub>2</sub>O<sub>3</sub>), and (iii) methanation of carbon dioxide from hydrogen and ammonia synthesis gases (NiO/Al<sub>2</sub>O<sub>3</sub>, NiSiO<sub>2</sub>) [1]. Nickel metal is found to be the active ingredient in most commercial catalysts and its content varies from 10 to 25% (w/w) according to operating conditions and type of process [2]. The spent petroleum catalysts for desulfurization of the various fractions, during the refining of petroleum products from the crude [3,4] are considered as a major secondary source of nickel. After several cycles, these catalysts gradually lose the activity as a result of the accumulation of S, C, V, Fe, Mo, Si, As and P on the catalytic surface [5]. Due to the presence of soluble organic and inorganic compounds, the spent catalysts are harmful to the environment. They are classified as hazardous materials restricting the use in landfills and direct disposal [6,7].

Recycling of these secondary resources, namely spent catalysts, in order to lower their production costs, reduce waste

and prevent the environmental pollution has become a necessity. Moreover, the spent catalysts are regarded as one of the best potential sources of metals such as Ni, Mo, V, Co and Al [8]. The increasing demand of the nickel metal has also necessitated its extraction from the secondary resources. The final wastes obtained after recovery of the metal values from the spent waste catalyst are found to be less toxic than the original form [6,12]. Therefore, much attention is being given toward the development of comprehensive utilization schemes by various processes for metal extraction from spent hydro-processing catalysts to avoid pollution in land disposal and to minimize the landfill space [3,9–11].

Hydrometallurgical flow sheets for the recovery of metal values from the spent catalysts are considered as environmental-friendly and attribute to low energy consumption, low gas emissions, low waste generations and complete recovery of metals [12]. The processing of spent catalyst can be conducted by indirect or direct methods. In indirect methods, the spent catalysts are subjected to a pretreatment (oxidation, roasting or baking) process in the presence of solid, liquid or gaseous oxidant to liberate the valuable metal oxides from sulfide based spent catalysts, followed by water/acid treatment depending on the requirements [4,13]. These pretreatment operations, considered as intermediate stages, are time consuming and may lead to unfavorable economics. In contrast, the direct method involves the use of mineral acids or alkali as lixiviants for the leaching of metals from spent catalysts. Overall leaching efficiency from direct method was found to be

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satisfactory in the case of spent catalysts which consist of metals or metal oxides [12].

A number of acidic reagents, such as HCl, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> have been used as the lixiviant to leach metal values in spent catalysts [8,10,13–15]. Despite the high efficiency, the leaching with these reagents can consume high energy if operated at high temperatures over long reaction times [12]. Moreover, the leaching of the spent catalysts with mineral acids such as H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> is less selective as they extract large quantities of Al along with Mo, Ni or Co. This causes complications on the downstream separation and purification operations and lengthens the flowsheet.

The recovery of valuable metals from spent catalysts using HCl, developed by Chaudhary et al. [12], seems to be an attractive and promising option. The use of HCl is advantageous due to its selectivity and favorable economics. It has also been recognized as an effective lixiviant for the dissolution of base metal values from various sulfidic, oxidic and metallic resources [16]. However, kinetic studies on leaching of metals from spent catalysts using HCl is limited [15,17] compared to the studies using other acidic/alkaline reagents. This paper investigates the kinetics of nickel leaching from spent catalyst (Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) with HCl by varying the process parameters such as leaching time, stirring speed, acid concentration, temperature and particle size at a low pulp density.

## 2. Experimental

### 2.1. Materials and apparatus

The Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst was procured from a Korean refinery plant. The metal contents of the spent catalyst were determined by ICP-AES (JOBIN-YVON JY 38) after complete digestion with concentrated HF. The samples obtained in the leaching tests were also analyzed to determine the metal ion concentration by ICP-AES. The sulfur and carbon contents of the original spent catalyst were determined by using LECO SD-432 Analyzer following the standard procedure. The XRD spectra of spent catalyst as well as some of the leach residues were recorded by using a Rigaku RU-200 spectrometer (Rigaku RTC-300, Co., Japan). Leaching tests were carried out using a three necked 500 ml round bottom flask. Heating and stirring were provided by a temperature controlled mantle heater (accuracy  $\pm 1$  °C) and an externally placed variable speed stirrer motor, respectively.

### 2.2. Leaching procedure and conditions

The lixiviant was heated with stirring at 500 rpm. After attainment of desired leaching temperature the spent catalyst sample of the appropriate particle size range was charged into the flask containing 500 ml of the HCl solution. The effect of changing one of the five parameters: (i) pulp density, (ii) rotation speed, (iii) acid strength, (iv) temperature and (v) particle size range was investigated. Table 1 summarizes the different conditions used in the present study, where one of the parameters was changed in the

**Table 2**  
Chemical analysis of original spent catalyst.

Element	Si	Ni	Al	Fe	Zn	Co	Ca	Mg	Mn	C	S	K	Na	
%		0.1	12.75	39.2	0.68	0.21	0.012	2.28	0.1	0.039	0.7	0.005	0.36	0.12

described range while other parameters were maintained constant. The effect of stirring speed was tested at 200–600 rpm. The average particle size of the spent catalyst was –100 mesh (–147  $\mu$ m) in most of the experiments, except when the effect of particle size was studied in the range of –50 to –250 mesh (50–180  $\mu$ m). The acid concentration was 1 M HCl, except when the effect of acid strength was studied at the concentration range of 0.025–2.0 M. The pulp density was maintained low at 0.2% or 0.4% solids (w/v).

### 2.3. Treatment of samples

Slurry samples of 5 ml were withdrawn at regular time intervals, filtered, diluted and analyzed for metal content by ICP-AES. At the end of leaching tests, the slurry was filtered under vacuum, followed by in situ washing of the residues with de-ionized water. The washed residues were dried in an oven at 100 °C overnight, weighed and analyzed for their metal content after digestion. Extent of leaching was calculated on the basis of both solution and solid assays. Some of the leaching tests were repeated in order to ascertain the reproducibility of the experimental results.

## 3. Results and discussions

### 3.1. Characterization of spent catalyst and leach residues

The supplied spent catalyst sample was free from oil and grease materials and the total water soluble fraction was found to be less than 1%. The chemical assay of the sample is shown in Table 2. The original spent catalyst comprises of elemental nickel and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as revealed by the XRD pattern in Fig. 1. The XRD pattern of the leach residue obtained using the experimental conditions: temperature 323 K, particle size 50–71  $\mu$ m, pulp density 0.2% (w/v), HCl concentration 1 M and stirring speed 500 rpm after 120 min, is shown in Fig. 2. The absence of a characteristic peak of crystalline elemental nickel in the leach residue indicates the complete dissolution of nickel metal from the original spent catalyst. Thermodynamic data from the HSC 6.1 database [18] predicts large equilibrium constants for the acid dissolution of both Ni and Al<sub>2</sub>O<sub>3</sub> according to the reactions listed in Table 3 at the temperature range 293–353 K. However, the fact that Al<sub>2</sub>O<sub>3</sub> remains largely unreacted in the leach residue in Fig. 2 indicates slow reaction kinetics of Al<sub>2</sub>O<sub>3</sub>. The low dissolution of alumina can also be attributed to the nature of alumina ( $\alpha$ -alumina) of original spent catalyst (Fig. 1). The solubility of  $\alpha$ -alumina is much lower compared to  $\gamma$ -alumina [12].

**Table 1**  
Summary of leaching conditions.

Figure	Particle size range ( $\mu$ m)	Pulp density % (w/v)	Temperature (K)	HCl concentration (M)	Stirring rate (min <sup>-1</sup> )
3	–147	0.2, 0.4	323	1	500
4	–147	0.2	323	1	200, 300, 400, 500, 600
5	–147	0.2	323	0.025, 0.05, 0.1, 0.5, 1, 2	500
6	–147	0.2	293, 313, 323, 333, 353	1	500
7	50–71, 71–120, 125–150, 150–180	0.2	323	1	500

Total reaction time 180 min in all cases.

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