Leaching behavior of lanthanum, nickel and iron from spent catalyst using inorganic acids

W Astuti¹, N M Prilitasari¹, Y Iskandar², D Bratakusuma² and H T B M Petrus³

¹Research Division for Mineral Technology, Indonesian Institute of Sciences (LIPI)
Jl. Ir. Sutami Km. 15, Tanjung Bintang, Lampung Selatan, Indonesia
²PT. Pertamina Tbk, UP Balongan, West Java, Indonesia
³Department of Chemical Engineering, Gadjah Mada University
Jl. Grafika No. 2, Yogyakarta, Indonesia

Email : widi004@lipi.go.id

Abstract. Highly technological applications of rare earth metals (REs) and scarcity of supply have become an incentive to recover the REs from various resources, which include high grade and low grade ores, as well as recycled waste materials. Spent hydrocracking catalyst contain lanthanum and a variety of valuable metals such as nickel and iron. This study investigated the recovery of lanthanum, nickel and iron from spent hydrocracking catalyst by leaching using various inorganic acid (sulfuric acid, hydrochloric acid, and nitric acid). The effect of acid concentration, type of acid and leaching temperature was conducted to study the leaching behavior of each valuable metal from spent-catalyst. It has been shown that it is possible to recover more than 90% of lanthanum, however the leaching efficiency of nickel and iron in this process was very low. It can be concluded that the leaching process is selective for lanthanum recovery from hydrocracking spent-catalyst.

1. Introduction
The growing demand for metals particularly rare earth metals (REs) around the world have aligned the current research on metal extraction mostly on secondary metal resources together with the newest 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 metal 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 valuable metal. Among all the secondary metal resources, spent hydrocracking catalysts generated from oil refineries is well known to be rich in valuable metals including rare earth metals like La, Al, V, Mo, Co, Ni and Fe etc, which are in the form of metal, metal oxides and metal sulfides. In an oil refinery the solid catalysts are used to treat the crude oil to achieve higher desired fuel products [1]. With the extensive use of the solid catalyst during the processing of crude oil, this catalyst loses its potential for its further use resulting as a waste product referred as spent catalyst [2].

Spent catalysts can be classified as hazardous materials [3]. Due to their toxic nature, the disposal of spent catalysts can pollute the environment since heavy metals are leached out. Landfill of the spent catalyst is not an environment friendly or eco-friendly process which could be leached out creating harmful effects on the life process existing on the earth crust [1]. To avoid pollution in
land disposal as well as to minimize landfill space, the spent catalysts are subjected to metal extraction by various solubilization processes and reused in variety of applications [1, 4, 5]. Therefore prior to landfill it is 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. Pyrometallurgical together with hydrometallurgical techniques has been well applied and investigated in past to recover metal values from the spent catalyst [2].

In this study the hydrometallurgical method was investigated to extract valuable metals especially lanthanum, nickel and iron from the spent hydrocracking catalyst originated from PT. Pertamina Tbk that is public oil and gas company in Indonesia. Chemical leaching tests were performed using solutions of sulphuric acid, nitric acid, as well as hydrochloric acid in some leaching parameters to study the leaching efficiency and leaching behavior of lanthanum, nickel and iron.

2. Materials and Methods

2.1. Material
Spent hydrocracking catalyst was collected from oil and gas company in Indonesia (PT. Pertamina Tbk). The sample was mineralogically and chemically characterized by X-ray fluorescence (XRF) and X-ray diffraction (XRD). Table 1 shows the chemical composition of spent catalyst. It can be seen from Table 1 that spent catalyst contains significant value of lanthanum and nickel content. The XRD pattern of spent catalyst that was presented in Fig. 1 shows that spent catalyst contains nickel alumosilicate (zeolite) and nickel hydrogen tecto-alumisilicate (ZSM-5) in its mineral fraction.

Table 1. Chemical composition of spent catalyst by X-ray Fluoroscence (XRF).

| Element | La  | Fe  | Ni  | Si  | Al  | Ti  |
|---------|-----|-----|-----|-----|-----|-----|
| Wt %    | 9.73| 1.77| 8.22| 17.11| 15.72| 1.11|

![Figure 1. X-ray diffraction (XRD) pattern of raw spent-catalyst.](image)

2.2. Leaching of the metals
Considering the high metal yields and the economic prospects for selective recovery of valuable metals, sulfuric acid, nitric acid, and hydrochloric acid were considered as a lixiviant. Leaching study
was carried out in a glass reactor over a hot plate. A known amount of the spent catalyst was transferred to the leach solution containing the desired concentration of the acids maintained at a present temperature. The slurry was stirred with a magnetic needle at 500 rpm for the entire duration of the leaching. In order to examine the progress of leaching, samples were withdrawn at different time intervals and were analyzed for the metals of interest. At the end of the leaching, the slurry was filtered over the Whatman filter paper (42 No), the residue was washed with distilled water and dried overnight at 353 K in an electric oven. The leaching efficiency was calculated by analyzing the metals in the filtrate after necessary dilution and acidification. Satisfactory mass balance was obtained for each set of experiment. All the solutions generated in the leaching were analyzed by AAS (Atomic Absorption Spectrometer). Residue samples were characterized by XRF and XRD.

3. Result and Discussion

3.1. Effect of initial acid concentration
Concentration of leaching reagents is one of significant parameters in leaching process. The effect of initial acid concentration of three leaching reagents (nitric acid, sulfuric acid, and hydrochloric acid) on the leaching efficiencies of nickel and iron was investigated in the leaching conditions of leaching temperature (30 oC), leaching period (8 hours), stirring speed (500 rpm), pulp density (10% w/v), and particle size (< 75 μm). The results, shown in Fig. 2 and Fig. 3, indicate that acid concentration did not have appreciable effect on the recovery of iron and nickel. This result can be explained more using XRD analysis of leaching residue that will be demonstrated in further section.

![Figure 2](image_url)

**Figure 2.** Effect of initial acid concentration on the recovery of iron using various acid types (leaching temperature: 30°C, leaching period: 8 hours).
Figure 3. Effect of initial acid concentration on the recovery of nickel using various acid types (leaching temperature: 30°C, leaching period: 8 hours).

3.2. Effect of leaching temperature

Leaching temperature was also the significant parameter on the leaching efficiency. The effect of leaching temperature on the recovery of nickel and iron from spent hydrocracking catalyst was conducted using three leaching reagents (nitric acid, sulfuric acid, and hydrochloric acid) with 4 M of acid concentration, 8 hours of leaching period, 500 rpm of stirring speed, 10% w/v of pulp density, and < 75 μm of particle size. Fig. 4 and 5 show the effect of leaching temperature on the iron and nickel recovery from spent hydrocracking catalyst. It can be seen from those figures that temperature influenced significantly on the leaching efficiency of iron and nickel. The iron and nickel recoveries increase along with the increase of leaching temperature. The maximum iron and nickel recovery resulted from this experiment were around 33% and 19% respectively at 90°C.
3.3. Effect of leaching reagents
Leaching reagents also have influence on the leaching efficiency. In this study, three leaching reagents (nitric acid, sulfuric acid, and hydrochloric acid) were compared to get the best leaching reagent that produce the highest leaching recovery of metals. The leaching tests were carried out using 4 M of acid concentration, 8 hours of leaching period, 90 °C of leaching temperature, 10% w/v of pulp density,
<75 μm of particle size, and 500 rpm of stirring speed. The recovery of lanthanum was also analyzed using XRF analysis from solid residue of leaching. Fig. 6 depicted the effect of leaching reagents on the recovery of lanthanum, iron, dan nickel. From Fig. 6, it can be concluded that all leaching reagents used have similar effect on the recovery of lanthanum, iron, and nickel.

![Figure 6. Effect of leaching reagents on the recovery of lanthanum, nickel and iron (initial acid concentration: 4 M, leaching period: 8 hours, leaching temperature: 90°C).](image)

| Leaching Reagent | Lanthanum Recovery | Nickel Recovery | Iron Recovery |
|------------------|--------------------|----------------|--------------|
| Nitric Acid      | 90.9836            | 14.9521        | 30.0913      |
| Sulfuric Acid    | 90.9836            | 19.0664        | 20.6986      |
| Hydrochloric Acid| 94.2623            | 17.8515        | 33.7974      |

3.4. Leaching behavior of metals
Leaching behavior of metals was also investigated from the XRD pattern of solid residue after leaching. Figure 7 showed the XRD pattern of solid residue after leaching using sulfuric acid, hydrochloric acid, and nitric acid with 4 M of acid concentration, 8 hours of leaching period, 90 °C of leaching temperature, 10% w/v of pulp density, <75 μm of particle size, and 500 rpm of stirring speed. From this figure, it can be seen that XRD pattern of solid residue is as similar as the XRD pattern of raw material (Fig. 1). This result showed that nickel content in raw material was not leached effectively. It was also fitted with the result from the leaching recovery of nickel. This phenomena occured is because of the inertness of nickel form in the raw material as nickel aluminosilicate.
Figure 7. X-ray diffraction pattern of solid residue after leaching from (a) Sulfuric acid reagent; (b) Hydrochloric acid reagent; (c) Nitric acid reagent.

4. Conclusion
It is possible to recover more than 90% of lanthanum, however the leaching efficiency of nickel and iron in this process was very low. The leaching process is selective for lanthanum recovery from hydrocracking spent-catalyst.

References
[1] Marafi M and Stanislaus A 2003 J. Hazard. Mater 101 123 – 32
[2] Marafi M and Stanislaus A 2008 Conserv. Recycling 52 5859 – 73
[3] Loehr RC, Rogers LA and Erickson DC 1993 Water Res. 27 1127 – 38
[4] Furimsky E 1996 Catalysis Today 30 223 – 86
[5] Angelidis TN, Toukanidis E, Marinou E, Stalidis GA 1995 Resources, Conservation and Recycling 13 269 – 82