Recovery of cobalt and molybdenum from consumed catalyst using hydrochloric acid

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Abstract. Cobalt and molybdenum are valuable metals whose presence in nature is very limited. The consumed catalyst, which is abundantly available in the petroleum refinery industry, is a potential source of those metals. A hydrometallurgical process using acid as a leaching agent is usually used to extract and separate the metals more effectively. This method is considered capable of yielding recovery of a higher percentage of metal. In this study, hydrochloric acid solutions at various concentrations of 1.0, 1.5 and 2 M were used. The consumed catalyst was obtained from Pertamina Refinery Unit IV, Cilacap, Indonesia. Leaching experiment was carried out for 300 minutes and sampling was undertaken at 1, 3, 5, 15, 30, 90 and 300 minutes. The particle size and agitation speed were fixed at 200 mesh and 400 rpm. Samples of consumed catalyst were analyzed using EDXRF before the leaching process. Samples of solution were analyzed using ICP-EOS. Experimental results have shown that the recovery of cobalt and molybdenum increases with the increase of either concentration of hydrochloric acid or temperature. The highest recoveries in cobalt and molybdenum were 34.66% and 5.03%, respectively, obtained at a concentration of hydrochloric acid of 2 M and temperature 60°C.

1. Introduction
Valuable metals are metals that have a very important role in various industrial fields, such as the petrochemical industry, petroleum, steel and so on. Valuable metals are usually obtained from the minerals industry through exploration. Indonesia has the potential for quite large mineral reserves, but minerals are natural resources that cannot be renewed, while the demand for valuable metals globally continues to increase every year. The alternative and effective solution to tackle the demand for valuable metals is by processing metals from end-of-life products or better known as urban mining [1]. Consumed catalysts or used catalysts are an example of end-of-life products that can be obtained from various wastes in the chemical industry and the oil industry. The catalyst consists of non-metal and metal materials. The heavy metal content still present in consumed catalysts allows it to be classified as hazardous waste since it poisons and pollutes the humans and environment respectively. Usually, the consumed catalysts are collected and resold. To be used as a reference for processing consumed catalysts should be as raw materials to obtain the desired valuable metals [2].
To recover valuable metals from consumed catalysts, a pyrometallurgical or hydrometallurgical process is usually used to extract and separate metals more effectively, depending on the presence and composition of the constituents in the material [3]. Currently, the leaching method has been widely used to extract metals from a material. This method is considered capable of producing a higher percentage of metal. In general, acids are used as leaching agents or solvents for extraction [4].

Leaching valuable metals are influenced by various parameters including the type of reagent used, solution concentration, solution pH, extraction temperature, extraction time and stirring speed. This has led to several types of research to determine the effect of each parameter on leaching efficiency. The choice of acid will greatly affect the leaching results [5]. The final results of this study are expected to improve the welfare of the Indonesian people by sustainably utilizing Indonesia's mineral resources.

2. Materials and Method
Consumed catalyst which was obtained from Pertamina Refinery Unit IV, Cilacap, Indonesia, was milled and sieved to yield 200 mesh particles (< 0.0074 mm). EDXRF analysis was performed to determine the elemental composition of metals in consumed catalysts. The instrument used for analysis was EDXRF (Shimadzu edx-8000 fluorescence spectrometer).

| Element | % (wt.) |
|---------|---------|
| Mo      | 67.603  |
| Al      | 18.591  |
| Co      | 11.114  |
| As      | 0.993   |
| Si      | 0.774   |
| Fe      | 0.564   |
| Cu      | 0.138   |
| K       | 0.091   |
| Ca      | 0.065   |
| Se      | 0.043   |
| Zn      | 0.023   |

As shown from Table 1, the consumed catalyst had a cobalt content of 11.114% and a molybdenum content of 67.603%. The reagent used for the leaching process was a hydrochloric acid solution. In this study, hydrochloric acid with concentrations of 1 M, 1.5 M and 2 M was used. The leaching process was carried out in a three-neck flask. The solid-liquid ratio was 200 g/L obtained by dissolving 60 g of sample solids into 300 ml of hydrochloric acid solution. The temperature was varied at 30, 40 and 60°C, with a stirring speed of 400 rpm. The setting of the experimental apparatus can be shown in Fig. 1. Samples of product solution were taken at 1, 3, 5, 15, 30, 90 and 300 minutes. The product samples were analyzed using ICP-OES (Optima 8300 type device by Perkin Elmer, USA) to determine cobalt and molybdenum concentration in product solutions.
3. Results and discussion

3.1 Effect of reagent concentration on recovery results

The result on the effect of hydrochloric acid concentration on cobalt and molybdenum on various concentrations and recovery is shown in Figure 2 and Figure 3. The temperature of experiment was set at an optimum temperature of 60°C [6].

Figure 2. Effect of HCl concentration on the amount of yielded (a). Cobalt, and (b). Molybdenum, at 60°C.
Figure 3. Effect of HCl concentration on recovery of (a). Cobalt, and (b). Molybdenum, at 60°C.

As shown from Figure 2 and Figure 3, the percentage of leaching increases by the increase of HCl concentration from 1 M to 2 M. The maximum recovery of cobalt and molybdenum was 34.66% and 5.03% respectively at a 2 M concentration. The more hydrochloric acid in the solution was, the higher the intensity of contact between Cl ions with catalyst particles was resulting in a higher amount of cobalt and molybdenum ions that bound to Co and Mo [7]. The greater amount of Cl- resulted in more recovery of cobalt and molybdenum [8].

The cobalt metal content in consumed catalysts was usually in the form of Cobalt (II) oxide (CoO) and Cobalt (III) oxide (Co₂O₃). The reaction of the metal content in the depleted catalyst depends on the type of acid used in the leaching process. The reaction of cobalt oxide with hydrochloric acid is as follows [9]:

\[ \text{CoO} + 2\text{HCl} \rightarrow \text{CoCl}_2 + \text{H}_2\text{O} \]  

Molybdenum metal in consumed catalysts was extracted in the form of MoO₃. The reaction that occurs in molybdenum during leaching process using hydrochloric acid is as follows [9]:

\[ \text{MoO}_3 + 2\text{HCl} \rightarrow \text{MoO}_2\text{Cl}_2 + \text{H}_2\text{O} \]  

The efficiency of Mo leaching with the solutions of hydrochloric acid (in the range of concentrations studied) reached a maximum of 5.03% [Figure 3 (b)]. The leaching agents were more effective for Co leading to the dissolution of 34.66% of this metal [Figure 3 (a)]. An increase in acid concentration (between 1 and 2 M) did not affect significantly the amount of the leached Mo, while it increased the amount of Co leached [10]. According to the Eh-pH diagram, cobalt and molybdenum is present as the Co²⁺ ion and MoO₂H²⁻ in acidic solutions [11]. Furthermore, the solubility of a solute, means that the dissolved substance will dissolve easily and increase recovery [12]. The solubility of Co in this condition is \( K_{sp} = 1.48 \times 10^{-3} \) and the solubility of Mo in this condition is \( K_{sp} = 5.24 \times 10^{-4} \). So that the recovery value of Co is greater than that of Mo.
3.2 Effect of operating temperature on recovery results
The profile of the effect of temperature on the percentage of leaching is shown in Figure 4. For temperature variations, the temperatures used were 30°C, 40°C and 60°C with the concentration of hydrochloric acid using the optimum value of 2 M, and the time variable using 5 hours.

As shown in Figure 4, the leaching percentage increased from 30°C to 60°C. Maximum leaching of cobalt and molybdenum were 34.66% and 5.03% respectively at 60°C. As shown in Figure 4, the recovery increases as the temperature rises. Leaching cobalt and molybdenum from spent catalysts occurs by a combination of diffusion and complex reactions. The increase in temperature rises the kinetic energy molecules/ions, especially Cl⁻ [13]. This results in a more intensive collision and accelerates reactions of cobalt-chloride and molybdenum-chloride. In addition, the increase in kinetic energy also increases molecular movement thereby accelerating diffusion in the leaching process [14]. The rate of recovery of cobalt and molybdenum at each temperature is quite high in the initial minutes of the leaching process. The increase in the recovery is not significant after 90 minutes. This trend is mainly found in high-temperature leaching at 60°C. Initially, the amount of reactants is still large and the system is still far from equilibrium so that the increase in the value of recovery occurs quickly [15]. The longer the leaching process, the amount of reactants is getting smaller and the system is getting closer to the equilibrium condition so that it slows down the rate of reactions and the recovery value remains almost constant. The use of high temperatures increases the leaching rate which speeds up in achieving equilibrium [16].

The observed anomaly for the molybdenum leaching data in Figure 4 (b) shows the amount of Mo leached at various temperature variations and 2 M acid concentration showed that the effect of temperature was not significant on molybdenum recovery. The three reaction temperatures show the same trend. However, the Mo recovery tends to coincide with each other. This indicates that the temperature variation has no significant effect on the Mo leaching recovery.

4. Conclusion
Experimental results showed that the recovery of cobalt and molybdenum increased with either concentration of hydrochloric acid or temperature. The highest recovery in cobalt and molybdenum was 34.66% and 5.03%, respectively, obtained at a concentration of hydrochloric acid of 2 M and temperature 60°C.

Figure 4. Effect of temperature on recovery of (a). Cobalt, and (b). Molybdenum at HCl concentration of 2 M.
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