

## Sulfuric Acid Leaching of Valuable Metals from Spent Petrochemical Catalyst using Hydrogen Peroxide as a Reducing Agent

Kyung-Ho Park<sup>1)</sup>, Jeong-Soo Sohn<sup>1)</sup>, Jong-Seok Kim<sup>2)</sup>

1) Korea Institute of Geoscience & Mineral Resources, Korea

2) E&B Korea co., Ltd., Korea

### Abstract

The spent petrochemical catalyst used in the manufacturing process of terephthalic-acid contains valuable metals such as cobalt and manganese. To recover these metals, sulfuric acid leaching was performed with hydrogen peroxide as a reducing agent. Low extractions of Mn, Co and Fe were obtained by sulfuric acid leaching without reducing agent. With adding hydrogen peroxide as a reducing agent, the high extraction of these metals could be obtained. Different from general leaching experiment, the extraction rates of metal components were decreased with increasing reaction temperature in this case. Under the optimum condition, the extraction rates of Mn, Co and Fe were 93.0%, 87.0% and 100% respectively.

**Key words:** Spent petrochemical catalyst, Hydrogen peroxide, Reducing agent, Sulfuric acid leaching, Cobalt, Manganese

### 1. Introduction

In Korea, the amount of catalyst used for producing petrochemicals has been rapidly increasing with steady increase of investment on the petrochemical industry. Many studies have been performed to recover valuable metals from spent petrochemical catalyst which were composed of precious metals and rare earth metals like Pd, Pt and Mo<sup>1),2)</sup>. However, there is few studies on the recycling of petrochemical catalyst including Mn and Co metals.

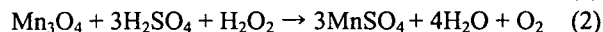
CMB(Cobalt Manganese Bromide) catalyst which is composed of Co 3%, Mn 6% and Br 15.3%, is a mixture of manganese acetate, cobalt acetate and methyl bromide and the domestic annual demands for CMB are approximately 12,000 - 15,000 M/T. This spent catalyst generated from the above process is roasted for its stabilization before recycling. After roasting, the components are changed into oxides such as manganese oxide that is not easy to leach.

To develop the recovery process of valuable metals such as cobalt and manganese from this catalyst, some experiments were carried out to investigate the leaching behaviors in the acid solution. Leaching behavior of Mn, Co and Fe in the sulfuric acid solution with and without hydrogen peroxide as a reducing agent was examined with various experimental conditions such as sulfuric acid concentration, reaction temperature, reaction time and amount of reducing agent.

### 2. Theoretical Background

Hydrogen peroxide is generally known as an oxidant but hydrogen peroxide acts as an amphoteric agent when it is coexisting with strong oxidant like manganese dioxide. Eq. (1) and (2) represent the reactions of manganese oxide with hydrogen peroxide acting as a

reducing agent. Eq. (1) represents the reduction of +4 valent manganese ion in the sulfuric acid solution. In eq. (2), hydrogen peroxide also acts a reducing agent because Mn<sub>3</sub>O<sub>4</sub> is composed of divalent and quadrivalent manganese ions like Mn<sup>+2</sup>Mn<sup>+4</sup>O<sub>4</sub>.<sup>3),4)</sup>



From these equations, theoretical amounts of hydrogen peroxide required for reducing 1 gram of manganese oxide are 0.018 and 0.006 mole of H<sub>2</sub>O<sub>2</sub>, respectively.

### 3. Experimental

The spent CMB catalyst obtained from petrochemical industry was roasted and was crushed into the fine powders of -200 mesh size. Table 1 shows the chemical compositions of the spent catalyst. Mn and Co mainly consist of this spent catalyst that also includes a small amount of Na, Fe and Al. Fig. 1 shows the XRD pattern of the spent catalyst. As shown that figure, manganese compound is composed of the oxide form such as Mn<sub>3</sub>O<sub>4</sub>.

For leaching tests, one liter of sulfuric acid solution was poured into the five-neck glass flask that was wrapped in heating mantle. After the solution temperature had been stabilized, the spent catalyst sample was added, and the solution was agitated with a teflon paddle at constant agitation speed.

**Table 1** Chemical compositions of spent petrochemical catalyst

Element	Mn	Co	Na	Fe	Al
wt. (%)	27.86	16.12	4.21	3.54	3.19
Element	K	Mg	Zn	Ni	Cu
wt. (%)	0.45	0.44	0.13	0.11	0.058

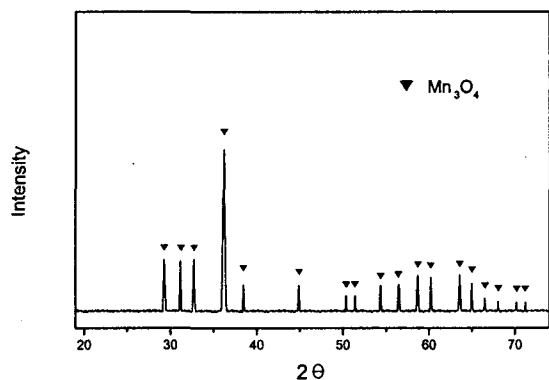


Fig. 1 XRD pattern of the spent petrochemical (CMB)catalyst.

For analyzing, 10ml of solution was sampled at fixed interval during leaching experiment. After filtering the sample solutions, these were analyzed by AAS and ICP instrument for checking the amount of Mn, Co and Fe.

## 4. Results and Discussion

### 4.1 Effects of Lixiviants

In order to investigate the effects of the various lixiviants, leaching tests were carried out with different acid solutions without reducing agent. Fig. 2 shows the extraction percentages of Fe, Mn and Co at 10g/L pulp density, 25°C in the sulfuric acid solution. For manganese and cobalt, there are little effects of acid concentration with 21% extractions. But it was shown that the extraction of iron was increased from 42.9% to 74.3% as the sulfuric acid concentration was increased from 0.5 to 2.0N.

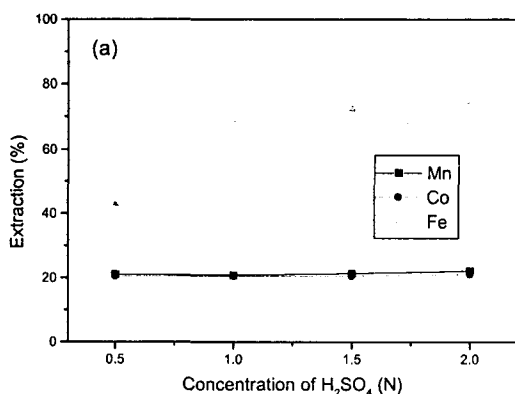


Fig. 2 Effect of H<sub>2</sub>SO<sub>4</sub> concentrations on extraction of the valuable metals without reducing agent. (10g/L S/L, 25°C, 300rpm, 1 hr)

Fig. 3 shows the extractions of Fe, Mn and Co at 10g/L pulp density, 25°C in the hydrochloric acid solution. Different from the results of sulfuric acid solution, the extractions of Mn and Co were increased with increasing

acid concentration. On the other hands, 100% of Fe was extracted with the use of 2.0N HCl.

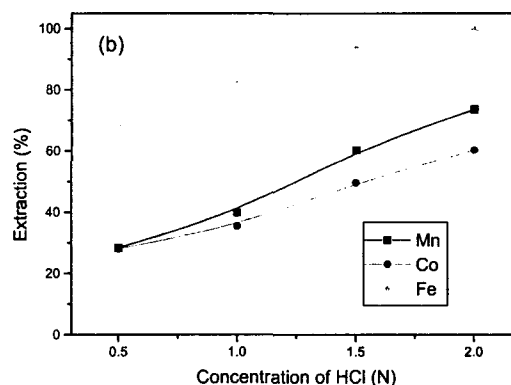


Fig. 3 Effect of HCl concentrations on extraction of the valuable metals without reducing agent. (10g/L S/L, 25°C, 300rpm, 1 hr)

Fig. 4 also shows the extraction of Fe, Mn and Co in the nitric acid solution at 10g/L pulp density, 25°C. In this case, leaching behavior of Mn, Co is similar to that of sulfuric acid leaching. But extraction percentage of iron was decreased with the increase of acid concentration.

The results from above tests show that hydrochloric acid was a good lixiviant for high extractions of valuable metals. But in this process, sulfuric acid is used as lixiviant because of its low cost and manufacturing facility for metal sulfate.

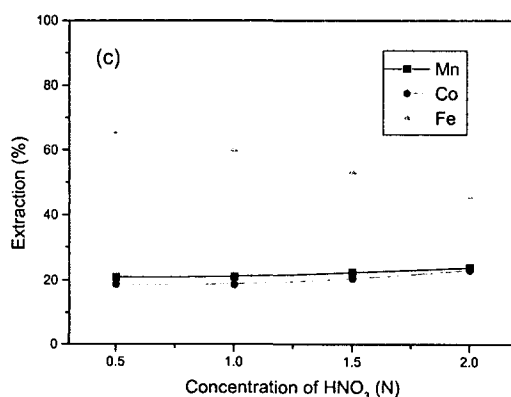


Fig. 4 Effect of HNO<sub>3</sub> concentrations on extraction of valuable metals without reducing agent. (10g/L S/L, 25°C, 300rpm, 1 hr)

### 4.2 Effect of Reaction Time

Fig. 5 shows the extraction percentages of metals in 0.5N H<sub>2</sub>SO<sub>4</sub> without adding reducing agent at 10g/L pulp density, 25°C. The extractions of metals were increased suddenly to 15 minutes, and increased slowly after 15 minutes with reaction time. However, the extractions of

Mn, Co and Fe after reaction time of 3 hours were only 31%, 25% and 60% respectively.

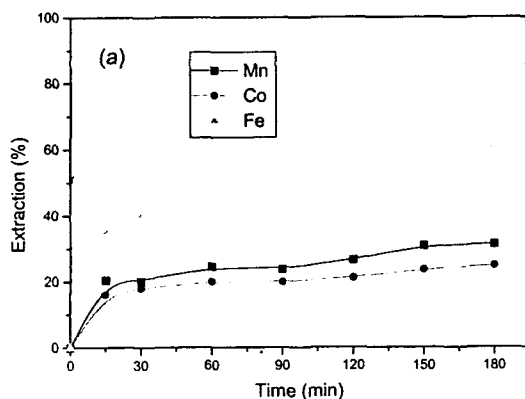


Fig. 5 Effects of reaction time on valuable metals without reducing agent (10g/L S/L, 0.5N H<sub>2</sub>SO<sub>4</sub>, 25 °C, 300rpm).

Fig. 6 shows the extractions of metals in 0.5N H<sub>2</sub>SO<sub>4</sub> with adding reducing agent of 0.036 M H<sub>2</sub>O<sub>2</sub> at 10g/L pulp density, 25 °C. Apart from Fig.3(a), the leaching reaction was very fast and instantaneous. It was found that extractions of Mn, Co and Fe were 93.4%, 87.7% and 100% respectively within reaction time of 30 min. It was confirmed that hydrogen peroxide as a reducing agent enhanced the extractions of metals from the catalyst.

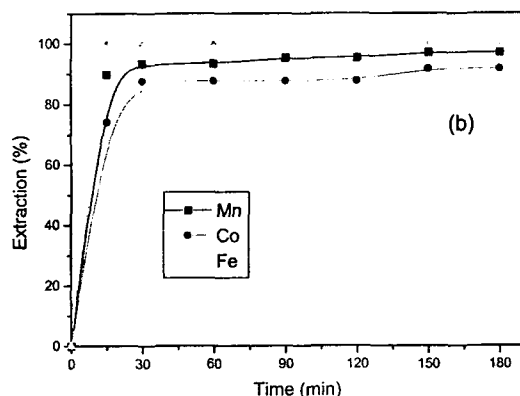


Fig. 6 Effects of reaction time on valuable metals with reducing agent (10g/L S/L, 0.5N H<sub>2</sub>SO<sub>4</sub>, 0.36mol/L H<sub>2</sub>O<sub>2</sub>, 25 °C, 300rpm).

#### 4.3 Effect of Reducing Agent

Fig. 7 shows the extractions of metals in 0.5N H<sub>2</sub>SO<sub>4</sub> with the various concentration of H<sub>2</sub>O<sub>2</sub> at 10g/L pulp density, 25 °C. The extraction of manganese was increased from 25% to 93% with the increase of concentration of H<sub>2</sub>O<sub>2</sub> from zero to 0.036 M. The leaching behavior of cobalt is similar to that of manganese. Cobalt extraction at 0.018 mole/l H<sub>2</sub>O<sub>2</sub> reached to 83% and the rate was increased to 87.7% at 0.036 M H<sub>2</sub>O<sub>2</sub>. In the case of iron, the extraction was differed from 30.1% at 0.009 M H<sub>2</sub>O<sub>2</sub>

to 100 % at 0.036 M H<sub>2</sub>O<sub>2</sub>. The amount of 0.027 M H<sub>2</sub>O<sub>2</sub> was enough for extracting valuable metals from 10 gram of catalyst.

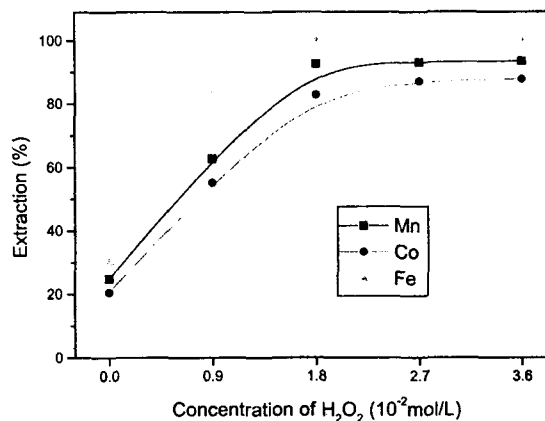


Fig. 7 Effects of H<sub>2</sub>O<sub>2</sub> concentration on valuable metals (10g/L, 0.5N H<sub>2</sub>SO<sub>4</sub>, 25 °C, 300rpm, 30 min.)

#### 4.4 Effect of Sulfuric Acid Concentration

Fig. 8 shows the effect of sulfuric acid concentration on the leaching of valuable metals at the condition of 10g/L pulp density, 0.027 M H<sub>2</sub>O<sub>2</sub>, 25 °C, 30 min of reaction time. From the figure, the extractions of metals are quickly increased with the increase of acid concentration up to the concentration of 0.3 N H<sub>2</sub>SO<sub>4</sub>. Above 0.4 N H<sub>2</sub>SO<sub>4</sub>, the extractions of metals are almost constant. In the case of iron, the extraction percentage is very low under the concentration of 0.3 N H<sub>2</sub>SO<sub>4</sub>. It means that some of dissolved iron is precipitated to Fe(OH)<sub>3</sub> in the dilute acid solution. Leaching of the catalyst is very effective at the condition of 0.5 N H<sub>2</sub>SO<sub>4</sub>, 10g/L pulp density, 0.027 M H<sub>2</sub>O<sub>2</sub>, 25 °C, 30 min of reaction time and the extractions of Mn, Co and Fe were 95%, 87% and 100% respectively.

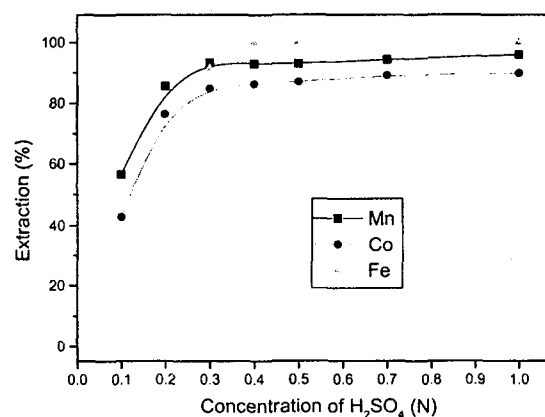
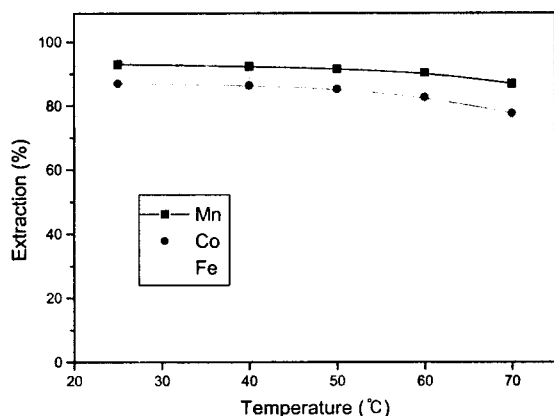


Fig. 8 Effects of H<sub>2</sub>SO<sub>4</sub> concentration on valuable metals (10g/L S/L, 0.027mol/L H<sub>2</sub>O<sub>2</sub>, 25 °C, 30min, 300rpm).

#### 4.5 Effect of Reaction Temperature

Fig. 9 shows the effect of reaction temperature on the leaching of valuable metals at the condition of 10g/L pulp density, 0.027 M H<sub>2</sub>O<sub>2</sub>, 0.5 N H<sub>2</sub>SO<sub>4</sub>, 30 min of reaction time. The extractions of manganese and cobalt were



**Fig. 9** Effect of the temperature on the extractions of valuable metals.  
(10g/L S/L, 0.5N H<sub>2</sub>SO<sub>4</sub>, 0.027mol/L H<sub>2</sub>O<sub>2</sub>, 300rpm)

slightly decreased from 93% to 87% and from 87% to 77% respectively with the increase of temperature from 25°C to 70°C, But iron extraction was steeply decreased 100% to 41% with increase of temperature from 25 °C to 70 °C. This results is originated from the destruction of H<sub>2</sub>O<sub>2</sub> in the hot reaction solution<sup>3),4)</sup>.

## 5. Conclusions

The sulfuric acid leaching of Co, Mn and Fe from the spent petrochemical (CMB) catalyst was performed using hydrogen peroxide as a reducing agent. The important results are as follows.

1. The spent catalyst is composed of 27.86% Mn, 16.12% Co, 3.54% Fe and also manganese exist as Mn<sub>3</sub>O<sub>4</sub>.
2. The extractions of metals were significantly enhanced by hydrogen peroxide as a reducing agent. When H<sub>2</sub>O<sub>2</sub> concentration is varied from 0 to 0.036 M, cobalt and manganese extraction were increased from 20 % to 88 % and from 25% to 93% respectively.
3. The leaching of valuable metals was quickly reacted in 30 min. and their extractions were decreased with increasing reaction temperature.
4. The optimum leaching condition was 0.5N H<sub>2</sub>SO<sub>4</sub>, 0.027M H<sub>2</sub>O<sub>2</sub>, 25°C, and 30min at 10g/L pulp density, and the extractions of Mn, Co and Fe were 93.0%, 87.0%, 100% respectively.

## 6. References

1. "Development of Recycling Technology for Recovering Precious Metals from Spent Catalyst", KIGAM Report, 1995
2. J.H.Kim, G.S.Seo, J.G.Yang, J.S.Kim, "Recovery of Molybdenum from the Desulfurizing Spent Catalyst",

- J. of Korean Inst. of Resources Recycling, 7(2), 9-15(1998)
3. M. Kawahara, T. Mitsuo, "Dilute Sulfuric Acid Leaching of Manganese Nodules using Hydrogen Peroxide as a Reductant", J of The Mining and Materials Processing Institute of Japan, 108(5), 396-401(1992).
4. J. Shibata, T. Watari, M. Niinae, "sulfuric Acid Leaching of Cobalt-Rich Ferromanganese Crust using Sodium Sulfite and Hydrogen Peroxide as Reducing Agents", Resource Processing (in Japan), 45(2), 59-63(1998).
5. J. Shibata, T. Watari, M. Niinae, "Hydrochloric Acid Leaching of Cobalt-Rich Ferromanganese Crust using Hydrogen Peroxide and Sodium Sulfite as Reducing Agents", J of The Mining and Materials Processing Institute of Japan, 115(1), 29-34(1999).