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Recovery and Recycling of Valuable Metals from Fine Industrial Waste Materials

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Recycling metals from fine industrial waste streams is important since natural resources could be conserved, as well as environmental problems due to the waste disposal could be alleviated. Metal producers and manufacturing facilities are generating off-gas, which contains a large amount of dust. Therefore, dust collection systems, such as baghouse and cyclones, are installed to control the emission of air pollutants. Dust, collected from various facilities, contained metal values; however, most fine wastes are currently landfilled due to the lack of an economically feasible metal recovery process. In this study, valuable metals from fine wastes were recovered by hydrometallurgical and pyrometallurgical processes from oil fly ash and aluminum smelter baghouse dust.

Keywords : Waste recycling, Oil fly ash, Aluminum dust, Extractive metallurgy

1 INTRODUCTION

Recycling metals from industrial waste streams is growing attention since metal recovery from secondary sources could conserve natural resources. Moreover, environmental problems due to the waste disposal also could be alleviated by removing volatile and toxic materials from the wastes. Dust, collected from various facilities, usually contains metal values; however, most fine wastes are currently landfilled [1].

In this study, recovery of valuable metals from fine wastes was investigated by hydrometallurgical and pyrometallurgical processes. Two fine waste materials, oil fly ash and aluminum smelter baghouse dust, were used to recover vanadium and aluminum, respectively. The chemical composition of wastes is different depending on the industry where they came from. Therefore, these waste streams were analyzed with the inductively coupled plasma atomic emission spectroscopy (ICP-AES). Oil fly ash and aluminum smelter baghouse dust showed a relatively large amount of vanadium and aluminum, respectively. For these reasons, this study mainly focuses on the recovery of vanadium and aluminum from these waste streams. Aluminum smelter baghouse dust was treated by alkaline leaching followed by $Al(OH)_3$ precipitation to extract aluminum selectively, and vanadium extraction from oil fly ash was investigated by carbon burning and salt-roasting followed by hot water leaching.

2 Experimental Procedures

2.1 Materials

2.1.1 Oil fly ash: Fly ash, also known as flue-ash, is a dust-like material, which came from the combustion of coal or oil. Fly ash is a fine particle, so it could rise with the flue gas. In general, most fly ash is captured by flue gas cleaning systems, such as mechanical separators and electrostatic precipitators. These residues contained potentially hazardous elements; therefore, disposal of the waste might cause significant economic and environmental problems [2]. The oil-fired power plant generates fly ash after its operation, and it contains a huge amount of unburned carbon and a low concentration of vanadium. For this reason, removing carbon from the waste could produce more vanadium concentrated sample after the process. The concentration of vanadium in the oil fly ash is low; however, extraction of vanadium can be economically feasible after carbon removal step to concentrate vanadium in the sample [3-6].

2.1.2 Aluminum smelter dust: Aluminum smelter baghouse dust, which is generated by shredding or smelting operation from secondary aluminum production facilities, was used for the aluminum recovery [7-8]. Typically, dust from aluminum industry, which size is larger than 20 mesh has a large amount of aluminum; however, an undersized fraction (smaller than 20 mesh) is landfilled due to its low aluminum content. Therefore, disposal of aluminum containing dust could be an issue due to its flammable and leachable nature from the landfill site. In EU countries, baghouse dust from aluminum production facilities is already designated as a hazardous waste; therefore, a proper recovery process for the aluminum was investigated in this research.

2.2 Initial characterization

2.2.1 Chemical composition: Inductively coupled plasma (ICP) spectroscopy is an analytical techniqueto measure the elemental content of a sample quantitatively. For the ICP analysis, a solid sample should be dissolved in a liquid. In this research, lithium borate fusion method was used to make the ICP sample since the borate fusion process helped to dissolve minor refractory minerals [9]. 0.1 g of fine waste samples were fused with 1 g of lithium

Table 1 Chemical composition of waste streams (wt.%)

Element	Oil fly ash	Al SBD		
	as-received	<45μm	45~150μm	150~250μm
Al	0	13.0	15.0	20.3
Ca	0	2.3	1.0	1.1
Cu	0	0.2	0.2	0.5
Fe	1.9	2.5	2.5	2.8
Mg	0	1.0	0.8	0.8
Ni	0.4	0	0	0
Si	0	5.2	8.6	10.4
V	2.2	0	0	0
Zn	0	0.4	0.3	0.4
Ti	0	0.2	0.2	0.4

borate mixture in a graphite crucible at 1000°C for 1 h. After the borate fusion process, the melt was digested in 25% nitric acid. In general, dilution of ICP sample was required to meet a detection limit of the equipment, therefore 2 % of the nitric acid was used for the dilution.

2.2.2 Heating value: Heating values of as-received wastes were measured to determine the feasibility of energy recovery from the wastes. Oxygen bomb calorimeter, which uses a pressurized oxygen bomb to ignite and burn the sample, measured the amount of heat release during the tests. The calorimeter automatically calculated the gross heat of combustion based on the sample weight and the temperature change after the sample ignition. Less than 1 g of sample was weighed in a crucible. Then the sample was connected to an ignition thread for the test. 30 atm of oxygen gas was filled into the pressurized bomb, and it was located into the 2 L of DI water chamber. Finally, the specimen was ignited through the ignition threads, and the calorimeter calculated the released heat from the sample [10].

3 Results and discussion

3.1 Chemical composition

Two waste materials, such as oil fly ash and aluminum smelter baghouse dust, were analyzed with ICP-AES, and the result is shown in Table 1. For the aluminum smelter baghouse dust, the sample was further classified by its size due to its wide size distribution, and the composition change was observed at different size range. Based on Table 1, oil fly ash contained about 2.2% of vanadium, 1.9% of iron, and 0.4% of nickel. The overall metal contents in the sample were about 4.5% total since the waste was mostly composed of carbon.

In the aluminum smelter baghouse dust, aluminum content was about 13 to 20%, and it was increased with its size. Aluminum smelter baghouse dust also contained calcium, copper, iron, magnesium, and silicon as impurities. Based on the chemical composition, we focused on the recovery of vanadium and aluminum from these two wastes using mineral processing as well as extractive metallurgical techniques.

3.2 Heating value of waste materials

Heat recovery from waste materials could be a possible way to reuse the wastes. Summary of heating values of the waste materials is shown in Figure 1. Oil fly ash, which had a huge amount of carbon, shows a heating value of 25,900 kJ/kg, and this value is equivalent to the heating value of bituminous coal. On the other hand, aluminum smelter baghouse dust had heating values about 5,000～7,500 kJ/kg. The main factor affecting the heating value is the carbon and hydrogen contents of a sample, and moisture of a sample could reduce the heating value of a sample. According to the World Bank technical guidance report, heating values of wastes should be higher than 7 MJ/kg for fuel sources [11]. Based on this criterion, heat recovery from the oil fly ash could be economically feasible, since it shows a relatively high heating value. However, other toperating parameters and environmental issues should be carefully considered to ensure the feasibility of heat recovery.

3.3 Aluminum recovery from Al SBD

Hydrometallurgical processes, leaching and precipitation, were used to recover aluminum recovery from the aluminum smelter baghouse dust. The main advantage of the hydrometallurgical process is its selectivity. In general, leaching with a proper chemical can selectively dissolve a target metal out of gangue [12]. For selective aluminum dissolution, sodium hydroxide was used since the Bayer process already uses it during digestion step. As shown in Figure 2, sodium hydroxide selectively dissolved aluminum and zinc from the waste. In the aluminum smelter baghouse dust, it contained about 13 wt.% of aluminum and 0.4 wt.% of zinc based on the ICP analysis (-45 μm size). For this reason, the actual amount of zinc in the leach solution was relatively small compared to the aluminum due to its low content in

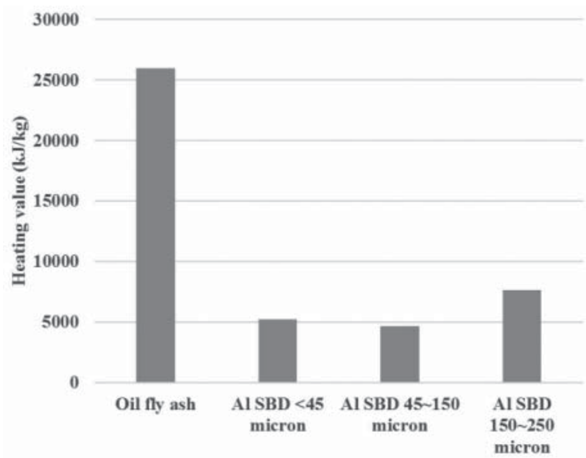

Figure 1 Heating values of waste samples

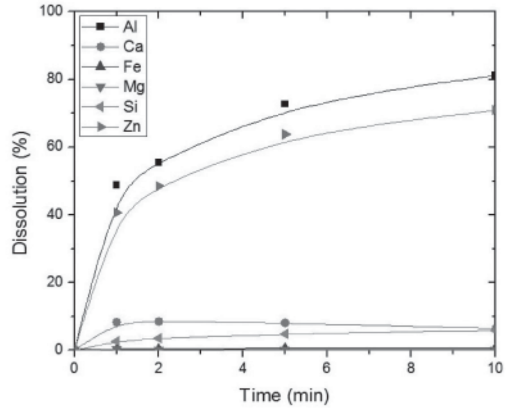

Figure 2 Dissolution of major elements from Al SBD

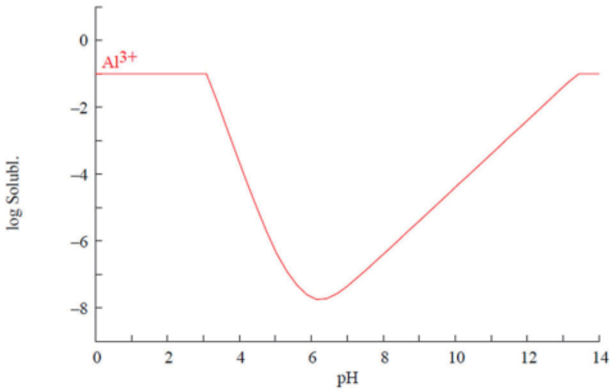

Figure 3 Aluminum solubility at different pH conditions

the starting material. Solution purification and concentration steps are usually required before metal recovery step since impurities in the solution affect the purity of final product. However, aluminum was selectively concentrated in the leach solution, and it does not require further solution treatments for metal recovery.

Metal recovery from leach solution is the final stage of hydrometallurgical processes. In general, metal recovery is achieved by several different methods including crystallization, ionic precipitation, reduction with gas, cementation, and electrowinning of metal. In this research, crystallization method was considered for aluminum recovery as $Al(OH)_3$. Crystallization is the simplest method to recover metals from an aqueous solution as metal compounds. The crystallization process mainly utilizes the solubility of metal compounds at different temperature and pressure. As the temperature and pressure were changed, the amount of metal salt in a solution could exceed the solubility limit, and metal salt crystallized in the solution by nucleation and growth. Therefore, thermodynamic modeling of $Al(OH)_3$ precipitation was conducted with the MEDUSA chemical equilibrium software. Since the crystallization process utilizes the solubility of metal compounds, pH vs. log [solubility] diagram was obtained, as shown in Figure 3. The minimum solubility of aluminum could be observed around pH 6, therefore an optimum pH value for the $Al(OH)_3$ precipitation was around pH 6 to obtain the maximum amount of precipitate from the leach solution.

$Al(OH)_3$ precipitation tests were conducted by adding 1 M of nitric acid to control the pH of the solution. Initial pH of the leach solution was about 12.6, and it was decreased to 10.5 for the precipitation. As shown in Figure 4 (b), white-colored precipitates were obtained from the leach solution after 30 min of precipitation tests.

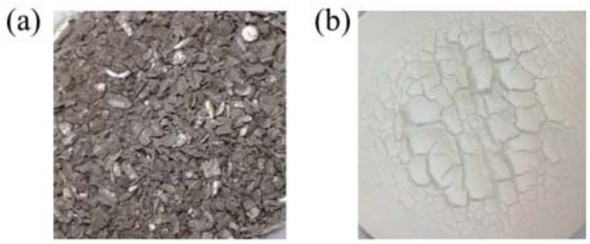

Figure 4 Sample images of aluminum smelter baghouse dust (a) as-received, (b) filtered precipitates

3.4 Vanadium recovery from oil fly ash

Vanadium recovery from oil fly ash was conducted by several steps, such as carbon burning, salt-roasting, and water leaching. Fly ash from previously burned heavy oil contained a large amount of unburned carbon. Therefore, carbon burning from the oil fly ash was considered the first step to obtain a vanadium-enriched product. As shown in Figure 5, vanadium-enriched product, which contained about 19 wt.% of vanadium, could be obtained after carbon burning. Then vanadium in the sample was selectively dissolved in an aqueous solution by salt roasting followed by leaching. During salt-roasting, sodium carbonate reacted with vanadium pentoxide to produce a water-soluble vanadium compound. Then vanadium from the roasted product could be selectively dissolved by water at an elevated temperature. In this research, the effect of the salt-roasting process on the vanadium extraction was compared in Figure 5. Without the salt-roasting process, vanadium extraction from the vanadium-enriched product was below 5%; however, after the salt-roasting process, about 90% of vanadium could be dissolved into water. In addition, water did not dissolve other impurities, such as iron and nickel, from the vanadium-enriched product. Therefore, the solution could be used for the metal recovery without solution purification step [13]. After leaching, ammonium sulfate was added to the solution to precipitate vanadium as ammonium vanadate, and the final product is shown in Figure 6 (b).

4 Conclusions

Recovery of valuable metals from fine industrial wastes was investigated by pyrometallurgical and hydrometallurgical processes. Based on the ICP analysis, oil fly ash contained about

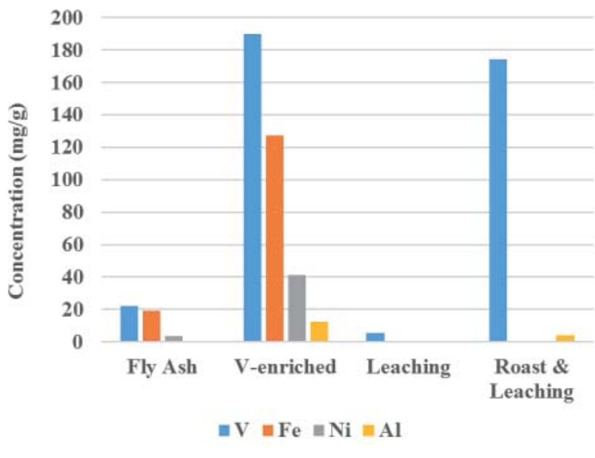

Figure 5 Concentration change of major elements at different steps

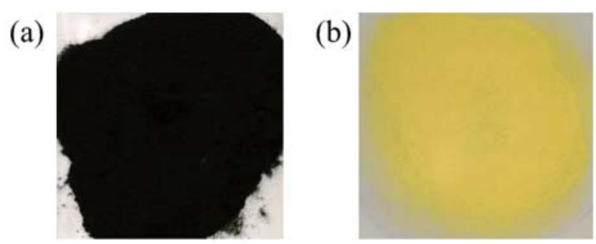

Figure 6 Sample images of oil fly ash (a) as-received, (b) filtered precipitates

2.2% of vanadium, and aluminum smelter baghouse dust contained about 13～20% of aluminum, depending on the particle size. This research focused on the recovery of vanadium and aluminum. Before the metal recovery experiments, heating values of as-received samples were measured and the oil fly ash showed a heating value of 25,900 kJ/kg, which is equivalent to the heating value of bituminous coal.

For aluminum recovery, the waste was treated by sodium hydroxide leaching followed by $Al(OH)_3$ precipitation to extract aluminum selectively. During sodium hydroxide leaching, aluminum was selectively dissolved in the leach solution. The percentage of aluminum dissolution was about 80% after 20 min of leaching, and the leach solution contained aluminum predominantly due to the selective leaching characteristic. Then, $Al(OH)_3$ precipitation was conducted by pH adjustment. After 30 min of $Al(OH)_3$ precipitation, white-colored precipitates were obtained from the leach solution.

For vanadium recovery, several recycling steps, including carbon burning, salt-roasting, and leaching, were investigated to extract vanadium. Carbon burning was conducted to concentrate vanadium in the ash. Then, the sample was mixed with sodium carbonate, and it was subsequently roasted at high temperature to produce water-soluble vanadium compound. Water-soluble sodium vanadate was dissolved in water at an elevated temperature. To precipitate vanadium from the leach solution, ammonium sulfate was added to the leach solution, and yellow-colored precipitates were obtained from the leach solution.

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