Recovery of Calcium Sulfate Hydrates from SDA Waste Sludge and Bag Filter Ashes

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Abstract—SDAWS (Spray drying absorption waste sludge) and BFA (bag filter ash), which are the wastes generated in the SDA (spray drying absorption) process, are only partially recycled as cement additives, gypsum boards, building materials, and the rest are being landfilled in managed landfills. However, wastes that have not been disposed of at the landfill are accumulated around the landfill. Therefore, it is necessary to study the recycling method for SDAWS and BFA. In this study, the effects of various parameters, pH, reaction temperature, sulfuric acid concentration (or type) on the preparation of calcium sulfate have been investigated. The major parameters influencing the crystalline phase and recovery efficiency of calcium sulfate from the SDAWS and BFA were type of sulfuric acid and Ca(OH)₂ content, respectively. There was little difference between the reagent grade sulfuric acid and the spent sulfuric acid in the preparation of calcium sulfate, only Ca(OH)₂ contained in the SDAWS and BFS affected. Also, it can be concluded that the desired crystalline phase of calcium sulfate can be obtained by controlling the concentration of sulfuric acid during the sulfidation reaction. Also, when the impurities suspended in the upper part of the reactor are removed during the sulfidation reaction, calcium sulfate having a much higher chromaticity can be produced. The characterization of the raw waste and calcium sulfate was carried out by XRD.

Keywords - Bag filter ash, Calcium sulfate, Gypsum, Spray drying absorption, Sulfuric acid, Sulfidation

I. INTRODUCTION

In the industrial field, acidic gases such as sulfur oxides and hydrogen chloride are neutralized by calcium-based absorbents such as CaCO₃, CaO and Ca(OH)₂. The dry desulfurization method is a method of spraying an alkaline powder into an exhaust gas and reacting with the sulfur oxide to remove it in the form of calcium sulfate. The sulfur oxide removal efficiency of this method is about 30-60%. The reaction product, calcium sulfate, is collected and removed together with dust in a dust collector such as a bag filter and EP (electrostatic precipitator). In the wet desulfurization method, an alkaline aqueous solution is sprayed onto an absorption tower to cool the exhaust gas temperature, and the acid gas is removed by contacting with the exhaust gas.

SDA (Spray drying absorption) is a method of absorbing acid gas by spraying alkali solution or slurry into combustion exhaust gas. The removal efficiency of sulfur oxides by the SDA method is about 70%. The dry method has excellent economic efficiency, but the removal efficiency of acid gas such as sulfur oxides is low. The wet method has high pollutant removal efficiency but has problems such as waste water treatment and corrosion of apparatus. However, SDA has the advantage of not only high removal efficiency of acid gas, but also little waste water, equipment corrosion, and white smoke [1, 2].

As shown in Fig. 1, the SDA is a method of removing harmful gases (SO₂, SO₃, HCl, HF, etc.) generated in the combustion process of various combustion facilities such as industrial boilers and incinerators by using CaO or Ca(OH)₂ slurry. When the high temperature combustion gas enters the SDA reactor, it comes into contact with the Ca(OH)₂ slurry which is finely sprayed by the atomizer installed in the reactor. The sulfur oxides contained in the flue gas react with the Ca(OH)₂ slurry to form calcium sulfate, which precipitates along with other particulate matter to the bottom of the SDA reactor, which is called SDAWS (spray drying absorption waste sludge). The exhaust gas leaving the SDA reactor contains a large amount of dust (fly ash, CaSO₄, unreacted Ca(OH)₂, etc.) should be collected in a bag filter before being discharged to the atmosphere. This dust collected in the bag filter is called BFA (bag filter ash).

SDAWS and BFA generated in the SDA process are part of general industrial wastes and are partially recycled as cement modifiers, gypsum boards, building materials, etc. However, surplus that has not been recycled has been landfilled in a managed landfill, but nowadays, large amounts are not processed and accumulated, which has a great influence on the surrounding landscape and the environment. Therefore, it is necessary to study the recycling method for SDAWS and BFA. The SDAWS and BFA discharged from the SDA process contain a large amount of unreacted Ca(OH)₂. Thus, this study is intended to be recycled as calcium sulfate by reacting with sulfuric acid.
We also aimed to derive an optimal preparing condition by experimenting on the effect of the pH, the concentration of sulfuric acid solutions (and types), and the temperature of reactions.

II. THEORETICAL CONSIDERATION

A. Sulfidation Reaction

The basic equations for the reaction of calcium compounds with sulfuric acid for the preparation of calcium sulfate are shown in equations (1) to (5) [2].

\[
\begin{align*}
\text{Ca(OH)}_2 + \text{H}_2\text{SO}_4 &\rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O} \quad (1) \\
\text{Ca(OH)}_2 + 2\text{H}_2\text{SO}_4 &\rightarrow \text{CaSO}_4\cdot\text{H}_2\text{O} + 3\text{H}_2\text{O} \quad (2) \\
\text{Ca(OH)}_2 + 2\text{H}_2\text{SO}_4 &\rightarrow \text{CaSO}_4\cdot\text{H}_2\text{O} + 3\text{H}_2\text{O} \quad (3) \\
\text{CaCO}_3 + \text{H}_2\text{SO}_4 &\rightarrow \text{CaSO}_4\cdot\text{nH}_2\text{O} + \text{H}_2\text{O} + \text{CO}_2 \quad (4) \\
\text{CaO} + \text{H}_2\text{SO}_4 &\rightarrow \text{CaSO}_4\cdot\text{nH}_2\text{O} + \text{H}_2\text{O} \quad (5)
\end{align*}
\]

B. Gypsum

Gypsum generally refers to \(\text{CaSO}_4\cdot2\text{H}_2\text{O}\). When heat is applied to \(\text{CaSO}_4\cdot2\text{H}_2\text{O}\), it becomes plaster of Paris (\(\text{CaSO}_4\cdot\text{H}_2\text{O}\)) through the dehydration reaction as shown in equations (6) to (7). In addition, when water is added to the plaster of Paris, the rehydration process is carried out to obtain a gypsum dihydrate or gypsum hemihydrate as shown in equations (8) to (9) [3].

\[
\begin{align*}
\text{CaSO}_4\cdot2\text{H}_2\text{O} + \text{Heat} &\rightleftharpoons \text{CaSO}_4\cdot\text{H}_2\text{O} + 3\text{H}_2\text{O} \quad (6) \\
\text{CaSO}_4\cdot\text{H}_2\text{O} + \text{Heat} &\rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O} \quad (7)
\end{align*}
\]

The gypsum can be divided into three major types, namely, gypsum dihydrate, gypsum hemihydrate, and anhydrous gypsum.

As shown in Table 1, when the gypsum is specifically divided, the gypsum hemihydrate is classified into \(\alpha\)-type and \(\beta\)-type, and anhydrous gypsum is distinguished from type I to III [3]. The gypsum hemihydrate and anhydrous gypsum can be divided into soluble gypsum hydrated by atmospheric or ambient moisture and insoluble gypsum that does not hydrate.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Dihydrate</th>
<th>Hemihydrate</th>
<th>Anhydrite III</th>
<th>Anhydrite II</th>
<th>Anhydrite I</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF*</td>
<td>(\text{CaSO}_4\cdot2\text{H}_2\text{O})</td>
<td>(\text{CaSO}_4\cdot\text{H}_2\text{O})</td>
<td>(\text{CaSO}_4)</td>
<td>(\text{CaSO}_4)</td>
<td>(\text{CaSO}_4)</td>
</tr>
<tr>
<td>M.W*</td>
<td>172.17</td>
<td>145.15</td>
<td>136.14</td>
<td>136.14</td>
<td>136.14</td>
</tr>
<tr>
<td>S.G*</td>
<td>2.32</td>
<td>2.76</td>
<td>2.59</td>
<td>2.48</td>
<td>2.96</td>
</tr>
</tbody>
</table>

* C.F: Chemical Formula, M.W: Molecular weight, S.G: Specific gravity

Fig. 3 is the differential thermal analysis (DTA) curve of the gypsum [4]. It is affected by the type of gypsum, crystal state, impurities or additives depending on the heating temperature. Fig. 4 shows the solubility curve of the calcium sulfate compound proposed by Kelly [6]. As can be seen from the Fig. 4, it can be seen that the difference in solubility is significant depending on the type of gypsum.
III. EXPERIMENT

A. Materials

SDAWS (spray drying absorption waste sludge) and BFA (bag filter ash) were used for the experiments. The chemical composition of SDAWS and BFA is shown in Fig. 5. The contents of Ca(OH)₂ in SDAWS and BFA were about 70.0% and 72.5%, respectively, and those of CaSO₄ and CaCO₃ were 6.3% and 15.4%, and 3.4% and 1.2%, respectively. And the remaining unburned and other impurities accounted for 19.3% and 10.9%, respectively.

B. Experimental Apparatus and Methods

The experimental setup used in this study is shown in Fig. 7.
A water bath (Hanbaek Scientific, HB-205WS) was used to adjust the reaction temperature constantly. An agitator (MTops, MS-3040D) was used to maintain uniform mixing and uniform reaction. Continuous temperature changes (0 to 50 °C, ± 0.2 °C) were measured, and pH changes were continuously measured using a pH meter (Ecomet, P15). The reactor used Pyrex material with a capacity of 500 ml. At the end of the experiment, calcium sulfate was separated by filtration and dried in a drying oven at 110 °C for about 12 hours. And the crystalline phase, recovery efficiency, and physical properties were analyzed. Table 2 shows the experimental parameters such as sulfuric acid type (RG-H2SO4, Reagent Grade H2SO4, LIC-W-H2SO4, Waste H2SO4 with Low concentration and containing Inorganic Contaminants, and HOS-W-H2SO4, Waste H2SO4 with High concentration and containing Organic Solvent), pH, and reaction temperature.

Sieved samples (2 kinds) and sulfuric acid solution (3 kinds) were injected into a 500 ml Pyrex reactor and stirred at 250 (or 250) rpm. When the pH reached 7 (or 8), the end point of the sulfidation reaction was set. At the end of the experiment, the experimental time was about 1 hour and 30 minutes, depending on the type of sample and the concentration of sulfuric acid.

![Fig. 7. Schematic diagram of the experimental setup.](image)

**Table 2. Experimental conditions**

<table>
<thead>
<tr>
<th>Variables</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>SDAWS, BFA</td>
</tr>
<tr>
<td>H2SO4</td>
<td>RG-H2SO4, LIC-W-H2SO4, HOS-W-H2SO4</td>
</tr>
<tr>
<td>Reaction Temp. (°C)</td>
<td>30, 50, 60, 70</td>
</tr>
</tbody>
</table>

IV. RESULT AND DISCUSSIONS

A. Sample Size Distribution

Fig. 8 shows the particle size distribution of SDAWS and BFA.

![Fig. 8. Mass fraction of SDAWS and BFA.](image)

B. Recovery Efficiency

Fig. 9 is the measurement of the recovery efficiency of calcium sulfate by reacting reagent grade sulfuric acid and waste sulfuric acid with SDAWS and BFA. The experiment was terminated when the pH reached about 7-8 at a reaction temperature of 30°C. The experiment was carried out four times and the average recovery efficiency was measured. When SDAWS was reacted with reagent grade and waste sulfuric acid, the average recovery efficiency (standard deviation, range) of calcium sulfate was 76.47% (10.3, 72.0–82.8%) and 75.85% (5.92, 70.8–80.8%), respectively. The mean recovery efficiency (standard deviation, range) of calcium sulfate was 84.77% (9.05, 72 – 91.3%) when reacted with reagent grade sulfuric acid in the case of BFA. When waste sulfuric acid was used, the average recovery efficiency (standard deviation, range) of calcium sulfate was 80.92% (5.91, 69.7 – 71.9%).

In terms of the recovery efficiency of calcium sulfate, there is no difference between reagent grade sulfuric acid and waste sulfuric acid (about 0.62% for SDAWS and about 3.85% for BFA). Only the content of Ca(OH)2 in SDAWS and BFA seem to have affected.
From these experimental results, it is considered that the recycling of waste sulfuric acid as a SO$_4^{2-}$ ion donor is possible for the production of calcium sulfate.

![Graph showing recovery efficiency](image)

**Fig. 9. Recovery of calcium sulfate by sulfurization of SDAWA and BFA.**

### C. Crystalline phase of calcium sulfate

In this experiment, three kinds of sulfuric acid were used in the production of calcium sulfate using waste containing Ca(OH)$_2$. Also, we confirmed the effect of sulfuric acid concentration and impurities on the crystalline phase of calcium sulfate and the possibility of recycling of spent sulfuric acid.

**Reaction of SDAWS and BFA with RG-H$_2$SO$_4$**

Fig. 10 shows the crystalline phase of calcium sulfate produced by reacting SDAWS and BFA with RG-H$_2$SO$_4$. In both SDAWS and BFA samples, the main crystalline phase of calcium sulfate was CaSO$_4$.

![XRD patterns](image)

**Fig. 10. XRD patterns of calcium sulfate obtained in the reaction of SDAWS and BFA with RG-H$_2$SO$_4$.**

**Reaction of SDAWS and BFA with LIC-W-H$_2$SO$_4$**

Fig. 11 shows the crystalline phase of calcium sulfate produced by reacting SDAWS and BFA with LIC-W-H$_2$SO$_4$. As shown in Fig. 11, the major crystalline phase of calcium sulfate was Ca(OH)$_2$ and some CaSO$_4$·1/2H$_2$O and CaSO$_4$·2H$_2$O were detected. This is because the concentration of LIC-W-H$_2$SO$_4$ is relatively low the concentration of sulfuric acid and also contains inorganic pollutants.

**Reaction of SDAWS and BFA with HOS-W-H$_2$SO$_4$**

Fig. 12 shows the crystalline phase of calcium sulfate produced by reacting SDAWS and BFA with HOS-W-H$_2$SO$_4$. 
As shown in Fig. 12, the major crystal phase of calcium sulfate was CaSO₄·1/2H₂O and some CaSO₄ was detected. This is because the concentration of HOS-W-H₂SO₄ is relatively high and the concentration of sulfuric acid and organic solvent is included.

As can be seen from the above results, it is judged that the determination of the crystalline phase of calcium sulfate is influenced not by the kind of solid waste but by the concentration of sulfuric acid and impurities participating in the sulfidation reaction. From this, it can be concluded that the desired crystalline phase of calcium sulfate can be obtained by controlling the concentration of sulfuric acid during the sulfidation reaction.

Fig. 11. XRD of calcium sulfate obtained in the reaction of SDAWS and BFA with LIC-W-H₂SO₄.

Fig. 12. XRD patterns of calcium sulfate obtained in the reaction of SDAWS and BFA with HOS-W-H₂SO₄.

Fig. 13 shows the effect of reaction temperature on the crystalline phase of calcium sulfate in the reaction of BFA with HOS-W-H₂SO₄. As shown in Fig. 13, the crystalline phase of calcium sulfate shifts from CaSO₄·2H₂O to CaSO₄·1/2H₂O as the reaction temperature increases from 30℃ to 70℃. It can be seen from previous studies that the crystal phase varies depending on the reaction temperature and conditions [5].
Table 3 is a photos of BFA raw sample and calcium sulfate prepared by sulfidation reaction of BFA. Table 3(a) shows the raw BFA collected in the filter, gray due to ash. Table 3(b) is a photograph showing calcium sulfate prepared by reacting BFA with HOS-W-H₂SO₄. This was produced by filtration without separating ash floating in the upper layer of the reactor after the sulfidation reaction. Compared this photo with raw BFA, there was no significant difference in chromaticity.

The calcium sulfate shown in Table 3(c) was prepared by separating ash floating in the upper part of the reactor after completion of the reaction and then filtering. This calcium sulfate showed a much better chromaticity than that of Table 3(b). As a result, it is considered that the chromaticity of calcium sulfate can be greatly improved by removing the impurities rising to the upper part of the reactor during the sulfidation reaction.

V. CONCLUSIONS

The experimental results for the preparation of calcium sulfate to recover the calcium component from the waste generated by SDA process are summarized below. It was possible to prepare the calcium sulfate by recycling the waste discharged from the SDA process and spent sulfuric acid. The recycling of waste sulfuric acid as a SO₄²⁻ ion donor is possible for the production of calcium sulfate. The desired crystal phase of calcium sulfate can be obtained by controlling the concentration of sulfuric acid during the sulfidation reaction. The crystal phase of calcium sulfate changes depending on the reaction temperature and conditions. The chromaticity of calcium sulfate can be greatly improved by removing the impurities rising to the upper part of the reactor during the sulfidation reaction.
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REFERENCES


