

Recovery of Calcium Carbonate and Calcium Sulfate from Waste Gypsum

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Abstract— This study was carried out to recover calcium sulfate and calcium carbonate from the waste desulfurization gypsum which is buried as industrial general wastes. The availability of waste sulfuric acid was also studied to reduce the cost of wastewater treatment in recovering calcium sulfate. Calcium sulfate was synthesized through sulfidation reaction and the recovery rate of calcium sulfate was compared according to experimental conditions. XRD analysis was performed for the crystal phase analysis. After the sulfidation reaction, CO₂ gas was injected into the filtrate, and calcium carbonate was recovered using carbonation reaction. The recovered calcium carbonate was analyzed by XRD and SEM. In this study, the effects of various parameters, pH, reaction temperature, sulfuric acid type on the preparation of calcium sulfate have been investigated. There was little difference between the reagent grade sulfuric acid and the spent sulfuric acid in the preparation of calcium sulfate

Keywords - Calcium carbonate, Calcium sulfate, Carbonation, Gypsum, Sulfidation, Waste Gypsum

I. INTRODUCTION

Waste desulfurization gypsum (WDG), which is a general industrial waste, is produced in Korea in an annual amount of more than 4 million tons, and is partially recycled for cement additives, gypsum board, and agricultural use [1]. The WDG that has not been recycled is either landfilled or left near the plant [1].

Gypsum generally refers to CaSO₄·2H₂O. When heat is applied to CaSO₄·2H₂O, it becomes gypsum hemihydrate (CaSO₄·1/2H₂O), and anhydrous gypsum (CaSO₄) through the dehydration reaction. In addition, when water is added to the gypsum hemihydrate and anhydrous gypsum, the rehydration process is carried out to obtain a gypsum hydrate (CaSO₄·2H₂O). The gypsum can be divided into three major types, namely, gypsum hydrate, gypsum hemihydrate, and anhydrous gypsum. The gypsum produced in watery condition is low in reactivity and does not cause any serious problems when it mixed with aggregate. However, it can be changed to gypsum hemihydrate in the process of handling aggregate. So far, there have been few studies on the effect of gypsum hemihydrate on concrete and aggregate [2].

Gypsum hemihydrate is increasingly used for medical purposes, but alpha-hemihydrate gypsum containing a large amount of impurities is difficult to use for medical use [3].

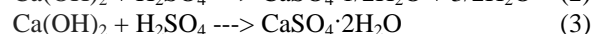
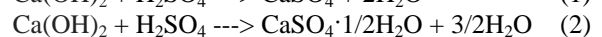
Calcium carbonate is classified into precipitated calcium carbonate (PCC) produced by chemical precipitation reaction and ground calcium carbonate (GCC) produced by crushing and directly crushing limestone. The GCC is not uniform in particle size or shape, but PCC is very regular in particle size and shape. Calcium carbonate is widely used in various industries such as paints, paper, thinners, fillers, cosmetics, insecticides, pharmaceuticals, and plastics. In particular, the demand for PCC is gradually increasing [4]. Calcium carbonate is classified into calcite, aragonite and vaterite depending on crystal structure, and each of them is dimorphism. Calcite is the most thermodynamically stable state with hexagonal crystals and the vaterite is the most unstable and has spherical or rugby-ball-like crystals and is easily transformed into calcite or aragonite [5]. At present, aragonite is a material undergoing much research and is converted to calcite at over 440 °C and is characterized by needle-like crystals and high aspect ratio. Aragonite is regarded as a new functioning inorganic particle capable of changing the mechanical and optical properties of rubber, plastic, paint, and varnish [6].

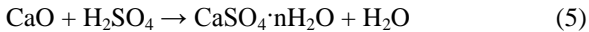
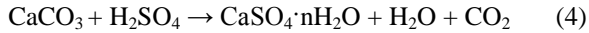
In the first step, CaO contained in WDG is recovered as calcium sulfate by reacting with sulfuric acid (reagent grade sulfuric acid and waste sulfuric acid). And the next step is developing a new technique for producing calcium carbonate by reacting carbon dioxide with unreacted calcium component remaining in the solution. We also investigate the parameters and optimum conditions affecting the synthesis of PCC and calcium sulfate.

II. EXPERIMENT

A. Materials

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) [7].





The samples used in this experiment were WDG, which is generated in the process of dry removal of SO₂ from petro coke combustion in a circulating fluidized bed combustor (CFBC) of refinery. The ratio of fly ash to bottom ash in the CFBC desulfurization process is about 7:3. However, they were mixed and discharged without separation; the composition was greatly different according to the discharge position and operating conditions. In order to observe the changes in composition of the WDG by season, boiler type, calcium carbonate characteristics and operating variables, we analyzed 7 times and the average composition of the samples is shown in Fig. 1. As shown in Fig. 1, the mean (standard deviation) of CaO, CaSO₄, CaCO₃ and SiO₂ were 32.9% (9.0), 53.3% (11.9), 11.5% (6.5), and 4.6% (3.3), respectively.

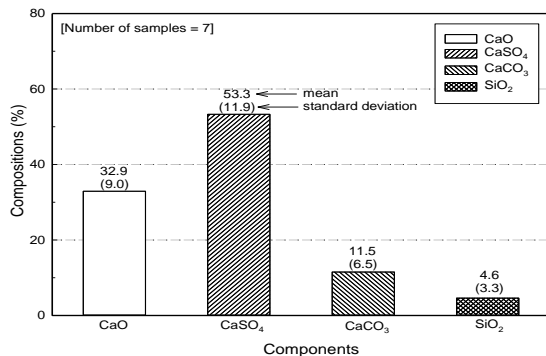


Fig. 1. Chemical compositions of the WDG.

Prior to the experiment, impurities were removed by sieving. Table 1 shows the mass fraction of the WDG generated from the desulfurization process. The mass fraction of 850 ~ 180 μm particles was 15.01%, the mass fraction of 180 ~ 63 μm particles was 45.05%, and the ratio of particles smaller than 63 μm was 38.01%, respectively.

Table 1.
Mass fraction of waste desulfurization gypsum

Particle size (μm)	Weight (g)	Ratio (%)	Particle size (μm)	Weight (g)	Ratio (%)
850>	34.81	0.36	355~300	218.86	2.26
850~600	10.22	0.11	300~212	700.37	7.24
600~500	59.47	0.62	212~180	307.25	3.18
500~425	119.45	1.24	180~63	4354.73	45.05
425~355	186.62	1.93	63<	3674.58	38.01

Fig. 2 shows the XRD diagram of the WDG for three particle sizes. As can be seen in the Fig. 5, the major components are CaSO₄ and CaO and some CaCO₃ is present in all particle sizes.

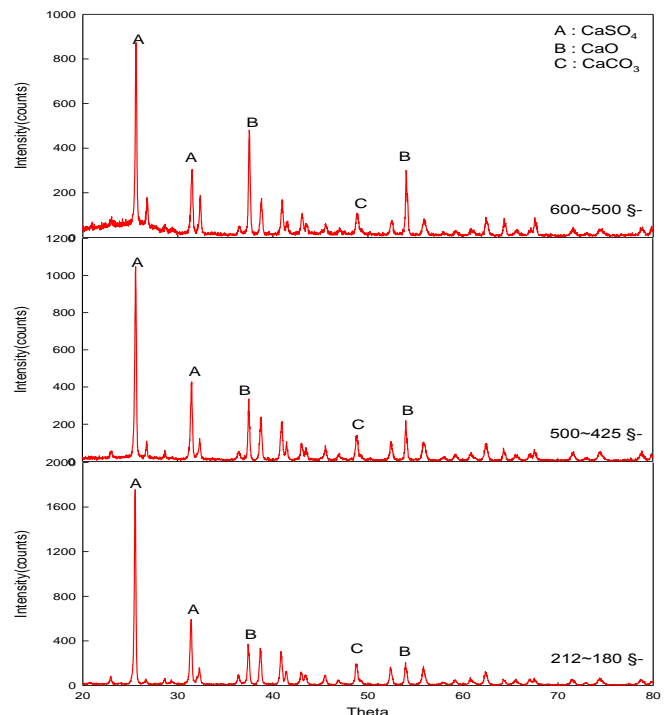


Fig. 2. XRD diagram of the WDG with particle size.

B. Experimental Apparatus and Methods

The experimental setup used in this study is shown in Fig. 3. 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 reaction. CO₂ was injected from the cylinder to the bottom of the reactor using an MFC controller (Lokas Automation, GMATE 2000) and a sparger was used to uniformly distribute the injected CO₂ to the reactor. Temperature changes (0~100 °C ± 0.2 °C) were continuously measured and a pH meter (Ecomet, P15) was used to measure pH change during CO₂ injection. The reactor used Pyrex material with a capacity of 500 ml.

At the end of the experiment, the product was filtered to recover calcium sulfate and precipitated calcium carbonate, and dried for about 12 hours in a drying oven maintained at 110 °C to analyze the crystal phase, recovery efficiency, and physical properties.

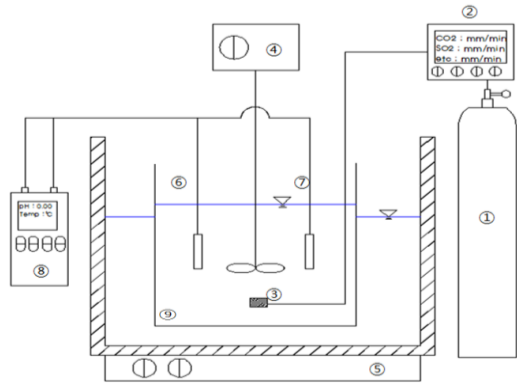


Fig. 3. Schematic diagram of the experimental setup.

(1: CO₂ gas, 2: MFC Controller, 3: Bubbler, 4: Stirrer, 5: Water bath, 6: pH electrode, 7: Thermometer, 8: pH meter, 9: Reactor)

The experimental procedure is shown in Fig. 4, calcium sulfate was recovered through sulfation reaction, and calcium carbonate was recovered through sequential carbonation reaction. Prior to the experiment, the coarse particles contained in the WDG were removed by sieving and a sample with a particle size distribution of a certain size was selected and used in the experiment. Table 2 shows the experimental parameters such as sulfuric acid type, pH, and reaction temperature.

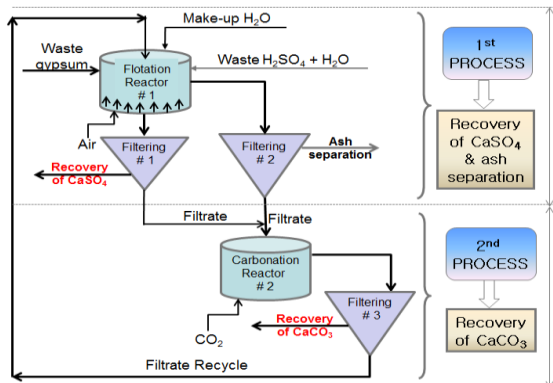


Fig. 4. Process chart of the experimental procedure.

Table 2.
Experimental conditions

Variables	Conditions
H ₂ SO ₄	Reagent grade & waste H ₂ SO ₄
Reaction temperature (°C)	30, 50, 60, 70
pH	6, 7, 8
Flow rate of CO ₂ gas (ml/min)	30, 50, 100
Stirring rate (rpm)	250, 500

Sieved WDG and sulfuric acid solution were injected into a 500 ml Pyrex reactor and stirred at 250 rpm. When the pH reached 7 (or 8), the experiment was terminated. At the end of the experiment, the experimental running time was about 1 hour and 30 minutes, depending on the concentrations of ash and sulfuric acid. The filter cake obtained by filtration after the termination of the sulfidation reaction was dried to recover calcium sulfate.

After the sulfidation reaction, the filtrate placed in the reactor. When the temperature reached a predetermined temperature, the mixture was stirred at 250 rpm (or 500 rpm) while injecting CO₂ through MFC. The pH of the carbonation reaction was set at 6, 7, and 8. After the carbonation reaction, the PCC was collected by filtration. The precipitate was washed 3~4 times with ethanol to remove ionic components remaining in the PCC and then filtered. The synthesized sample was dried in a drying oven at 105 °C or higher for 24 hours. The recovery of calcium sulfate and PCC was analyzed by measuring the weight difference before and after the experiment. XRD (X-Ray Diffraction) was used to confirm the crystal phase of the synthesized sample, and the shape and particle size were confirmed by SEM (Scanning Electron Microscope).

III. RESULT AND DISCUSSIONS

A. Calcium Sulfate Preparation

Effect of Sulfuric Acid

In order to investigate the recovery efficiency of calcium sulfate, sulfidation was performed by mixing H₂SO₄ with WDG at a temperature of 30 °C. When the pH reached 7, the experiment was terminated.

This experiment was performed 4 times and the average recovery rate is shown in Fig. 5. The average recovery efficiency (range) of calcium sulfate was 92.98% (91.95~94.25%) when reacted with WDG and reagent grade H_2SO_4 . When reacted with waste H_2SO_4 the average recovery efficiency (range) was 93.93% (92.32 ~ 96.10%).

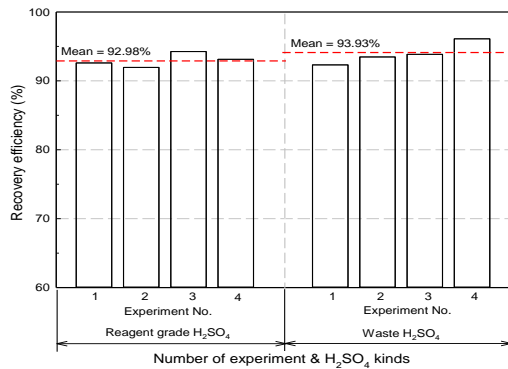


Fig. 5. Recovery of calcium sulfate by sulfidation of WDG.

Fig. 6 shows the XRD curve of calcium sulfate produced during the sulfation reaction by reacting sulfuric acid with WDG. When WDG was reacted with reagent grade sulfuric acid and waste sulfuric acid at a reaction temperature of $30^\circ C$, the anhydrous gypsum was the main component and some of the gypsum dehydrate was produced.

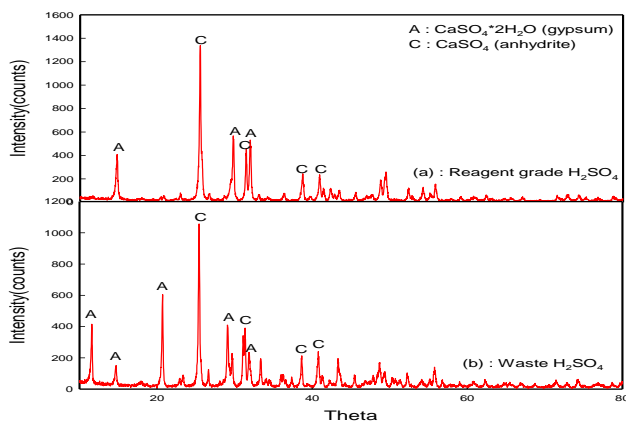


Fig. 6. XRD diagram of calcium sulfate after sulfidation.

Fig. 7 shows the appearance of calcium sulfate produced during the sulfidation reaction of WDG according to the type of sulfuric acid at a reaction temperature of $30^\circ C$. The chromaticity of calcium sulfate produced after the sulfation reaction was improved more than that of the pre-reacted sample, and the color improvement was more effective when reagent grade sulfuric acid was used than waste sulfuric acid.

This is because the unreacted ash suspended in the upper layer during the reaction was removed.

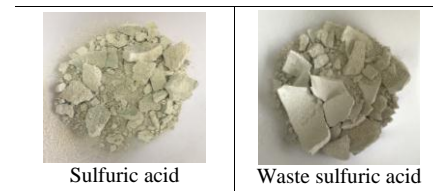


Fig. 7. Photos of calcium sulfate produced after sulfidation.

Effect of Reaction Temperature

Experiments were conducted to investigate the formation of calcium sulfate, the crystal phase, and the recovery rate depending on the reaction temperature at $30^\circ C$, $50^\circ C$, $60^\circ C$, and $70^\circ C$. The XRD curves of the calcium sulfate produced after the sulfidation reaction is shown in Fig. 8. The anhydrous gypsum was the major product and some of the gypsum dehydrate was present at $30^\circ C$, $60^\circ C$, and $70^\circ C$. However, at $50^\circ C$, the main product was gypsum dehydrate and some of the anhydrous gypsum appeared.

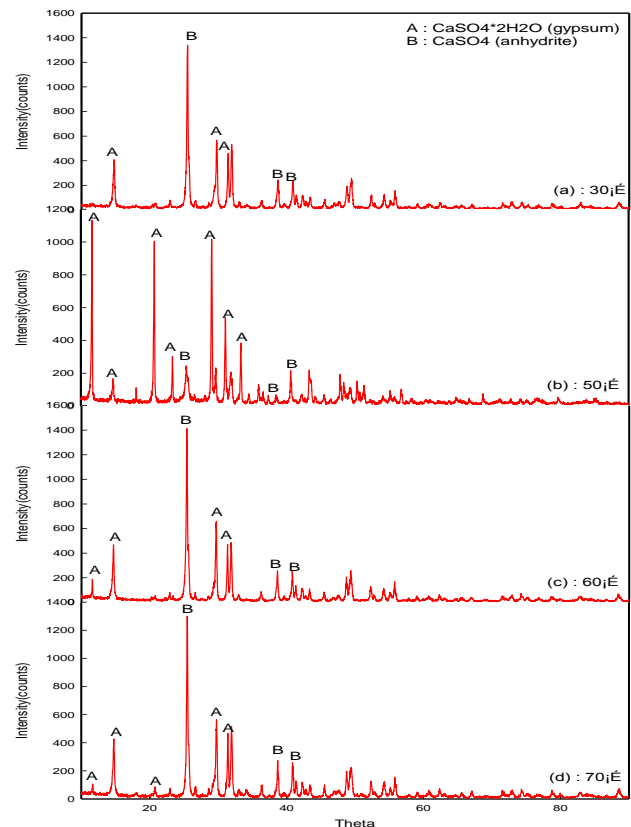


Fig. 8. XRD diagram of calcium sulfate after sulfidation of the WDG with reagent grade sulfuric acid according to reaction temperature.

B. Calcium Carbonate Preparation

As shown in Fig. 3, after calcium sulfate was prepared by the sulfidation reaction of WDS with sulfuric acid (first step), CO₂ was injected into the solution for the recovery of the calcium component remaining in the solution to prepare the PCC (second step). Experiments were conducted mainly on the effects of temperature and pH on the preparation of the PCC.

Effect of reaction temperature

In order to investigate the effect of reaction temperature on the formation of the PCC, the crystalline phase and recovery rate of the PCC were investigated while changing the reaction temperature to 30°C, 50°C, 60°C, and 70°C. The change in pH with temperature before carbonation was investigated and is shown in Fig. 8. As the reaction temperature increased from 30°C to 70°C, the pH before carbonation decreased from 11.79 to 10.59 (Fig. 9). Because of the heat generated by the neutralization reaction, the water is dissociated and the pH is lowered by Le Chatelier's law due to the endothermic reaction as the temperature increases. It is considered that the increase of temperature affects the pH of the aqueous solution of calcium hydroxide, and also affects the pH and recovery efficiency in the synthesis of calcium carbonate. In this experiment, the carbonation was terminated when the pH reached 8 by injecting 50 ml/min of CO₂, and the recovery efficiency and crystalline phase according to each temperature were confirmed.

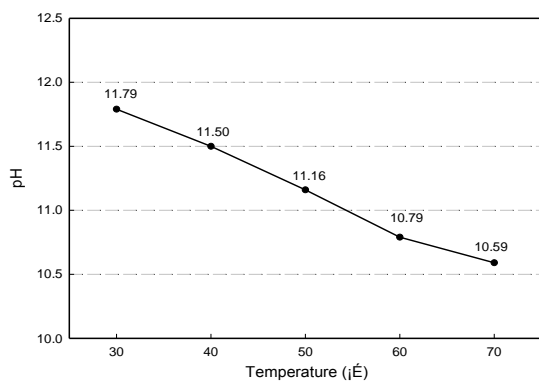


Fig. 9. pH change with temperature before carbonation reaction.

Fig. 10 shows the crystalline phase of the PCC produced after the carbonation reaction with varying reaction temperature. Calcium carbonate produced at the reaction temperature of 30°C appeared as hexagonal crystals with a size of about 5 μm and a small amount of acicular shape.

However, it was confirmed that aragonite CaCO₃ was formed in the form of acicular calcium carbonate at the reaction temperature of 70°C. From this, the crystalline phase gradually changed from hexagonal to acicular as the reaction temperature increased. This means that as the reaction temperature increases, the transition from calcite to aragonite occurs.

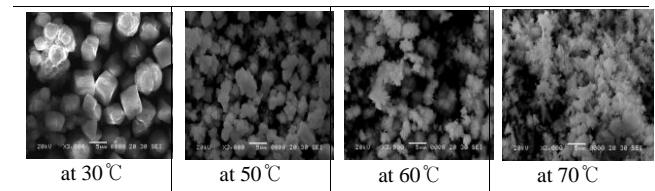


Fig. 10. SEM images of CaCO₃ prepared using the WDG at pH 8.

Fig. 11 shows the crystalline phase of calcium sulfate produced by reacting WDG with reagent grade H₂SO₄. As can be seen in Fig. 10, the crystalline phase was CaCO₃ at all temperatures. As can be seen in the SEM image of Fig. 11, it is consistent with previous studies that aragonite is produced in increasing the reaction temperature [8].

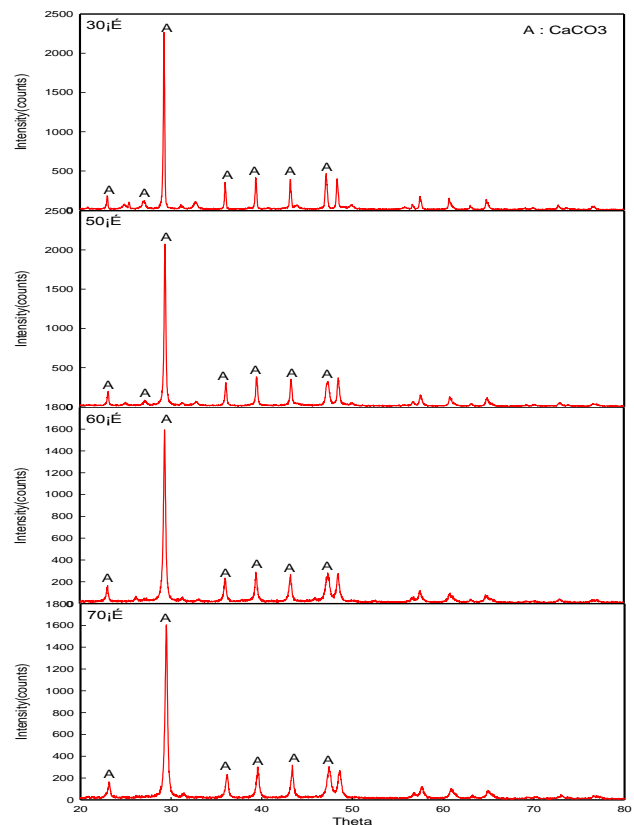


Fig. 11. XRD diagram of CaCO₃ prepared by using the WDG according to reaction temperature.

Effect of pH

In order to investigate the effect of pH on the recovery of calcium carbonate, the experiment was carried out while changing the pH at the end of the carbonation reaction to 6 and 8. In general, it is very important to confirm the proper pH because the PCC is known to dissolve once the pH of the carbonation reaction is lowered. The recovery efficiency of the PCC to the reaction temperature was examined at a CO₂ injection rate of 50 ml/min and a stirring rate of 250 rpm.

Fig. 12 represents the recovery rates of the PCC by reaction temperature and pH. At pH 8, the recovery efficiency of PCC was 31.1% at 30 °C and 56.1% at 50 °C, but no significant difference as the temperature increased. At pH 6, the recovery efficiency of PCC was 47.4% at 30 °C, but decreased with increasing temperature, reaching 30% at 70 °C. As can be seen in Figure 11, the lower the pH at the end of the experiment, the lower the recovery efficiency of the PCC, which was consistent with previous studies [8].

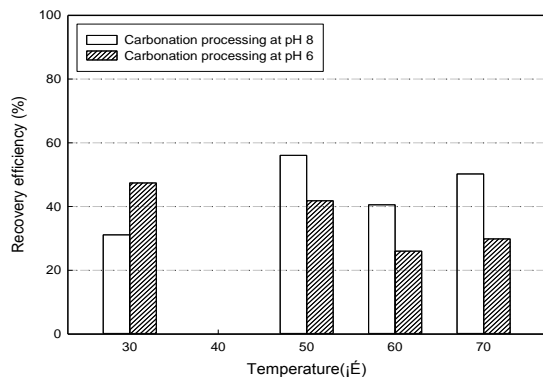


Fig. 12. Effects of temperature on the recovery efficiency of CaCO₃.

Fig. 13 shows SEM images of precipitated calcium carbonate prepared according to reaction temperature and pH at the end of carbonation reaction. As shown in Fig. 12, calcium carbonate prepared at pH 6 exhibited a hexagonal calcite shape of about 7 μm at 30 °C, but turned into acicular type at an increase of reaction temperature, and aragonite type CaCO₃ was generated.

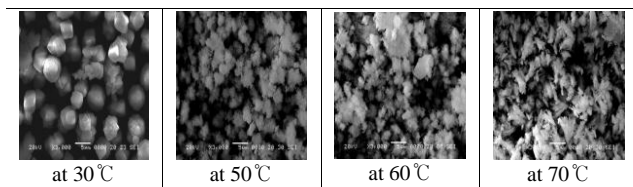


Fig. 13. SEM images of CaCO₃ prepared using the WDG at pH 6.

IV. CONCLUSIONS

The experimental results for the preparation of calcium sulfate and calcium carbonate to recover the calcium component from the waste desulfurization gypsum (WDG) are summarized below.

1. The major constituents of the WDG were CaO, CaSO₄, CaCO₃, and SiO₂, and mean concentrations were 32.9%, 53.3%, 11.5%, and 4.6%, respectively.
2. The average recovery efficiencies of calcium sulfate through the reaction of the WDG and two kinds of sulfuric acid (reagent grade & waste H₂SO₄) were more than 90%.
3. Calcium sulfate produced at 30 °C, 60 °C, and 70 °C was mainly anhydrous gypsum, but gypsum dehydrate (CaSO₄·2H₂O) reacted at 50 °C.
4. The crystalline phase gradually changed from hexagonal (calcite CaCO₃) to acicular (aragonite CaCO₃) as the reaction temperature increased.
5. The lower the pH at the end of the experiment, the lower the recovery rate of precipitated calcium carbonate.

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