

## Chemical prosperity of various chemical gypsums from viewpoint of particle morphology

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**Abstract.** Dissolution rate of various chemical gypsums in the water was investigated by using batch experiment. The rate of the dissolution of the gypsum had good agreement for explanation of dissolution of plate particle. The rate constants of the experimental formula were different with particle morphology of the gypsums. When morphology of the particle was sheet-like, the dissolution rate was 10 times larger than that of block-shaped particle. From the result of observation of dissolution phenomena of the in the water, it was found that dissolution of the gypsum was preceded on long axis. From these results, particle morphology is seen to be an important parameter for using chemical gypsums.

### 1. Introduction

Chemical gypsum is calcium sulfate dihydrate ( $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ ) produced from various chemical industries such as phosphate, fluoride and titanium production, and the fuel gas desulfurization (FGD) process in coal-fired power plant. Many amounts of these chemical gypsums are used for plasterboard in wall of the building. After demolition of the building, many amounts of waste plasterboards are generated and disposed to landfill. In Japan, recycling of the waste plasterboard is strongly demanded because of lack of landfill capacity. By production of phosphate from phosphate rock, five tons of waste gypsum are generated by production of one ton of phosphoric acid. Therefore, reuse of the gypsum (phosphogypsum) is one of the important issues for phosphate industries <sup>[1]</sup>. For another chemical industry, reuse of the byproduct gypsum is important on the viewpoint of ecological and economical aspects.

Major application of recycling of the waste gypsum is ground stabilizer for soft ground and/or construction sludge <sup>[2, 3]</sup>. The application is considered that gypsum has hydraulic property and makes hardening soil or sludge. This property is caused by “calcium sulfate”. Gypsum has various particle shapes, and particle and chemical property may be different. It was reported that particle size of the



gypsum is able to increase by addition of sodium sulfate <sup>[4]</sup>, and sodium tripolyphosphate <sup>[5]</sup>. Variation of particle shape is affect to powder property such as fluidity. In case of gypsum, dissolution rate and adhesion property of water molecule are different by crystal orientation <sup>[6, 7]</sup>.

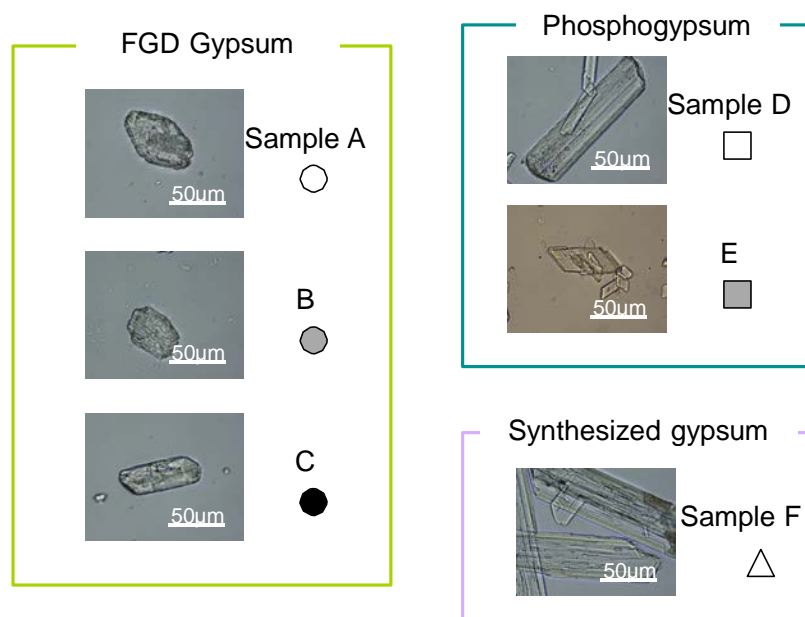
In this study, dissolving property of various chemical gypsums was investigated. From results of the experiment, it was appeared that dissolving rate of the chemical gypsum was controlled by specific crystal face.

## 2. Experimental

### 2.1. Materials and chemicals

Chemical gypsums used in this study were byproduct from phosphate production and the FGD process. In comparison, synthesized gypsum from conventional precipitation process was also used. Two point five grams of the gypsum was mixed with 1 L of the pure water. The water purified by Mill-Q water purifier (Mill-Q Academic, Merck-Millipore).

Particle shape of the gypsums was observed by optical microscope (ECLIPSE LV100D, Nikon, Japan). Figure 1 shows particle shape of the chemical gypsums used in this study. FDG gypsums (samples A and B) were block-like shape, and phosphogypsums were plate-like shape.



**Figure 1.** Particle shape of the chemical gypsums used in this study.

### 2.2. Dissolution of the gypsums

Mixture of water and the gypsum stirred by baffled mixer (MBF-250-ME, ELENA, Japan). Small amount (about 2-3 mL) of the mixture was sampled every 10 seconds. The sampled mixtures were filtered by 0.45 µm of membrane filter. Calcium and sulfur concentration were analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES, 720ES, Agilent-Varian).

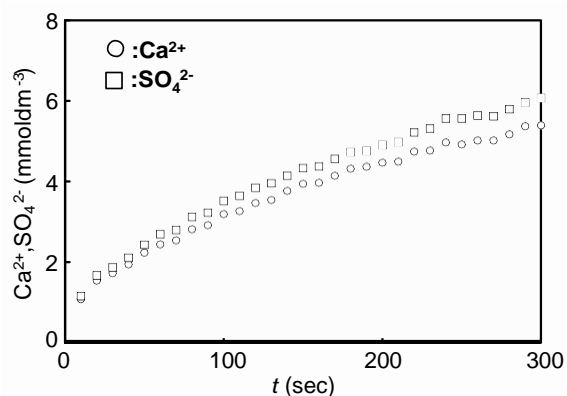
### 2.3. Observation of dissolution of the gypsums

The optical microscope was used for observation dissolving phenomena of the gypsums in the water.

### 3. Results and discussions

#### 3.1. Dissolution rate of the chemical gypsums

Dissolution rate of the various chemical gypsums in the water was investigated by using batch mixer. Mixture of the gypsum and water collected every 10 seconds and filtered. Calcium and sulfur concentrations were analyzed by ICP-AES. Figure 2 shows change in concentrations of calcium and sulfate (calculated by concentration of sulfur) ions in the water after added gypsum (sample A).

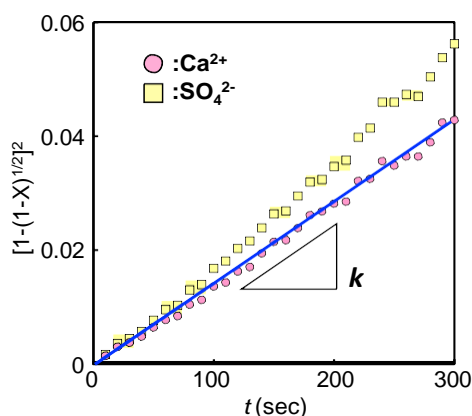


**Figure 2.** Change in concentration of calcium and sulfate ions in the water after added gypsum.

To characterize dissolving rate of the gypsum, model equation for dissolving plate-shaped particle in water was applied. The model equation is equation (1) [8].

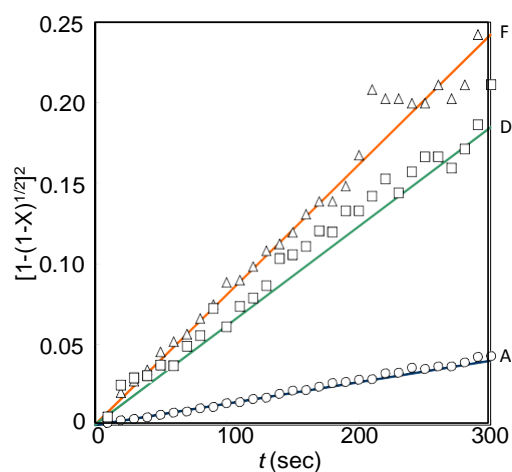
$$kt = [1 - (1-X)^{1/2}]^2 \quad (1)$$

X of the equation indicate fraction of the dissolving ions ( $X = 0$  to  $1$ ),  $t$  is time and  $k$  is apparent rate constant. By using equation (1), result of Figure 2 was standardized to liner relationship like Figure 3. The  $k$  value was calculated by change in calcium concentration in the figure.

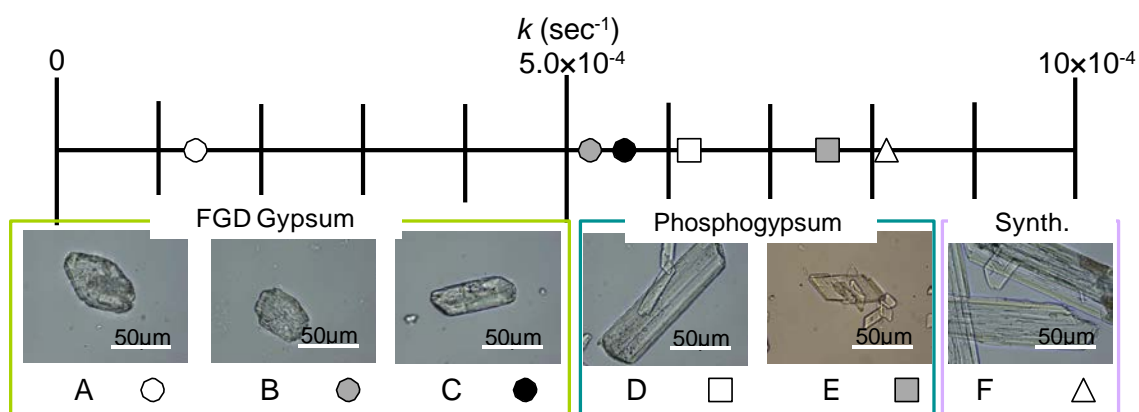


**Figure 3.** Standardized of change in concentration of by equation (1).

By using this standardization, result of samples were shown in Figure 4. The figure shows results of samples A, D and F. The figure shows dissolving rate of the gypsum was quite different of each samples. Figure 5 shows variation of the apparent rate constants of all samples. The figure also shows particle shape of the samples. From the figure, the  $k$  value was smaller in case of particle shape was block-liked.



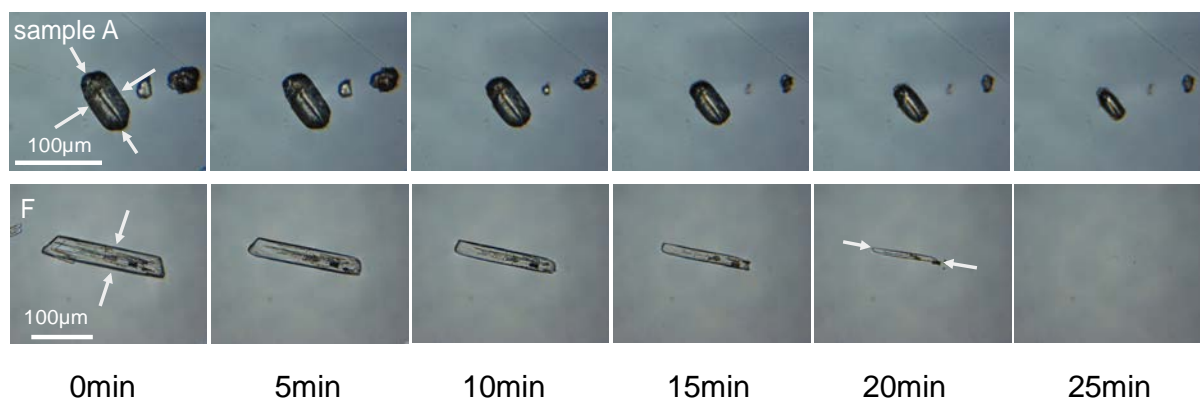
**Figure 4.** Dissolving rate calculation of all samples.



**Figure 5.** Variation of the  $k$  values.

### 3.2. Dissolution phenomena of the chemical gypsums

To discuss difference of the  $k$  values in the chemical gypsums, dissolution phenomena of the gypsums in the water were observed by using optical microscope. Change of shape of the particle was observed every 5 minutes. Sample A and F were selected because of difference of the  $k$  value. Figure 6 shows change of particle shape after immersion of the gypsums into water.



**Figure 6.** Dissolution of gypsum particle.

Dissolving rate of the sample F was larger than it of sample A. In case of the sample F, dissolving was started on minor axis and particle shape changed to slim. After that, dissolving was observed on major axis of the gypsum particle. On the other hand, dissolving of sample A was isotropic.

Particle morphology of sample F seems to be typical shape of gypsum crystal. Flat face of the particle was (010). Dissolving rate of (010) face is smaller than another face such as (110) and (111) <sup>[9]</sup>. From this results, orientation of crystal seems to be predominant to dissolving rate.

#### 4. Summary

In this study, dissolution rate of various chemical gypsums in the water was investigated by using batch experiment. Obtained results were as follows;

- 1) The rate of the dissolution of the gypsum had good agreement for explanation of dissolution of plate particle.
- 2) The rate constants of the experimental formula were different with particle morphology of the gypsums.
- 3) When morphology of the particle was sheet-liked, the dissolution rate was 10 times larger than it of block-shaped particle.
- 4) From result of observation of dissolution phenomena of the in the water, it was found that dissolution of the gypsum was preceded on long axis. Especially, crystal orientation of (010) face is one of the important factors of controlling dissolving rate.

From these results, particle morphology seems to be important parameter for using chemical gypsums.

Gypsum is used in another applications. Tsunami disaster on Higashi-Nippon earthquake made salt-affected soil in large area. Addition of gypsum is one of the solutions to remediate the salt-affected soil by ion exchange between sodium and calcium ions from the gypsum <sup>[10]</sup>. In case of usage of gypsum for remediation of the salt-affected soil, supply of calcium ion from gypsum is one of the important properties. For usage of the chemical gypsum for various applications, understanding and controlling of particle shape of the chemical gypsum seems to be important aspects.

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