Available online at www.sciencedirect.com

Journal of the European Ceramic Society 26 (2006) 777–783

www.elsevier.com/locate/jeurceramsoc

Synthesis of large plate-like gypsum dihydrate from waste gypsum board

Yoshiyuki Kojima*, Tamotsu Yasue

Department of Materials and Applied Chemistry, Faculty of Science and Engineering, Nihon University,
8, Kanda-Surugadai 1-Chome, Chiyoda-ku, Tokyo 101-8308 Japan

Abstract

This paper reports the synthesis of large plate-like gypsum (calcium sulfate) dihydrate generated from waste gypsum board via a wet process. Gypsum hemihydrate was formed by dehydrating waste gypsum board in a sodium sulfate solution at 100 °C for 1 h to form needle-like crystals. The large gypsum dihydrate was formed by lowering the temperature of the gypsum hemihydrate suspension below 80 °C. The large plate-like gypsum dihydrate was obtained by adding seed crystals to a suspension cooled at 80 °C. When 40 μm seed crystals were added at 0.5 mass%, the large plate-like gypsum dihydrate crystals obtained from waste gypsum board had average dimensions of 250 μm length × 100 μm width × 35 μm thickness.

Keywords: Large plate-like gypsum dihydrate

1. Introduction

Gypsum board consists of hardened gypsum sandwiched between two sheets of paper. Gypsum board is extremely light, with a density of approximately 1 g/cm^3, and has several useful properties, including fire-resistance, and heat and sound insulation. As a fire retardant, surface of gypsum board can rapidly reach temperatures exceeding 400 °C, causing only 2% shrinkage strain with intense cracking, hence gypsum board can help structural resistance of walls for considerable periods of time during fire exposure. Gypsum dihydrate can be converted to gypsum hemihydrate by heating at 180 °C for about 30 min. The largest use of gypsum is in the manufacture of gypsum board.

In Japan, the amount of waste gypsum board discharged annually is about 1,700,000 t, which is a cause for concern as Japanese gypsum resources are scarce and Japan is highly dependent on flue-gas gypsum or foreign imports. Hence, recycling of waste gypsum board for production of gypsum is highly desirable authors have done a series of investigation on gypsum.[1–6] Gypsum hemihydrate can be used for the manufacture of gypsum board, and is prepared by heating gypsum dihydrate. If the gypsum dihydrate particles become too small during the dehydration process (typical particle size is less than 5 μm), the gypsum hemihydrate can set too quickly and the quality of the product deteriorates. Hence, only about 10% of waste gypsum board can be regenerated for use as raw materials of gypsum board. In order to recycle greater quantities of waste gypsum board, particle size of the gypsum dihydrate needs to be much larger. To this end, a wet process is more effective than a dry process.

Large plate-like gypsum dihydrate is manufactured from waste gypsum board by a wet process utilizing the reversible reaction between gypsum dihydrate and gypsum hemihydrate. Arai[7] studied the deposition and growth of gypsum, and Yasue[1] has reported crystallographic results for producing gypsum dihydrate from waste gypsum board.

This paper reports the synthesis of large plate-like gypsum dihydrate from waste gypsum board via a wet process. The optimum process and synthetic conditions were investigated.

---

* Corresponding author. Tel.: +81 3 3259 0868; fax: +81 3 3293 7572.
E-mail address: ykojima@chem.cst.nihon-u.ac.jp (Y. Kojima).

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.06.018

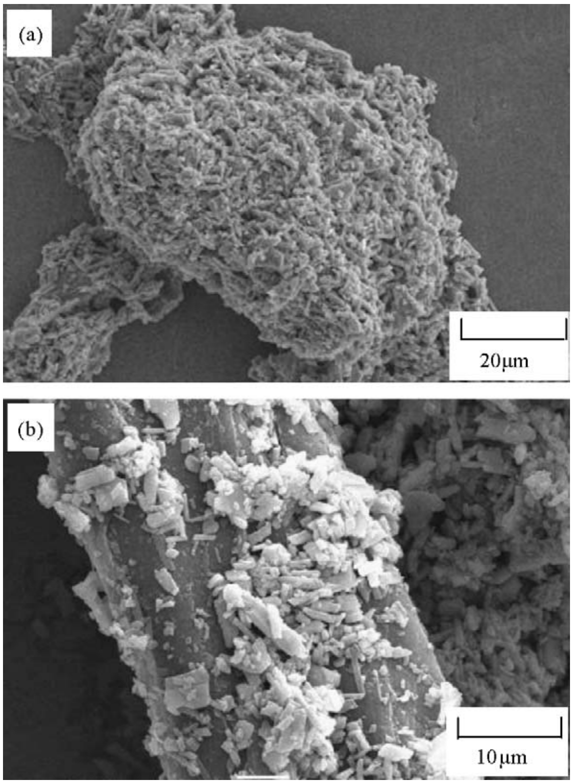

Fig. 1. Scanning electron microscopic photographs of waste gypsum board (A): (a) original and (b) magnification.

2. Experimental

2.1. Sample

Waste gypsum boards (A)–(C) were kindly donated by the Japanese gypsum board manufacturing company. The boards and lining paper were ground together and sieved through 18 mesh sieve. Table 1 shows the chemical compositions of waste gypsum board and commercial reagent grade gypsum dihydrate. The main component of the waste gypsum was $CaSO_4{\cdot}2H_2O$ with varying quantities of $CaSO_4{\cdot}1/2H_2O$, II-$CaSO_4$, lining paper, organic matter and heavy residues such as sand. The lining paper content was decreased by using 48 mesh sieves.[8] The specific surface area of all waste gypsum board was 2.3–4.0 m^2/g. Fig. 1 shows scanning electron microscopic photographs of waste gypsum board (A), showing fine crystals of gypsum dihydrate with a particle size of 3–5 μm. The gypsum dihydrate can be observed as an aggregate (a) or strongly adhered to the lining paper surface (b). The average particle size of gypsum dihydrate was the same in all waste gypsum boards.

In order to provide the same composition as that of waste gypsum board, measured amounts of lining paper removed from sample (A) and starch were added to synthetic calcium sulfate dihydrate. Twelve different dehydrating agents were used to transform gypsum dihydrate to gypsum hemihydrate; sodium nitrate ($NaNO_3$), potassium nitrate (KNO_3), magnesium nitrate ($Mg(NO_3)_2$), calcium nitrate ($Ca(NO_3)_2$), ammonium nitrate (NH_4NO_3), sodium chloride (NaCl), potassium chloride (KCl), magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$), sodium sulfate (Na_2SO_4), potassium sulfate (K_2SO_4) and ammonium sulfate ($(NH_4)_2SO_4$).

The gypsum dihydrate seed crystal was synthesized by reaction of $CaCl_2$, Na_2SO_4 and sodium citrate ($Na_3C_6H_5O_7$) in aqueous solution. All reagents were prime classes from Kanto Kagaku Co., Inc.

2.2. Experimental

Synthesis of large plate-like gypsum dihydrate from waste gypsum board was as follows. Waste gypsum board was sieved through 18 mesh sieve and added at a concentration of 0–10 mass% to the additive solutions in separate flasks, each equipped with an agitator and thermometer, to give a suspension concentration of 33 mass% (i.e. a solid/liquid mass ratio of 1/2). The suspension was stirred at 200 rpm and slowly heated (0.5 °C/min) with a heating mantle from 25 to 100 °C. The suspension was heated at 100 °C for 1–6 h. The suspension was then cooled to 80 °C (0.5 °C/min) and the preparation of gypsum dihydrate was initiated by addition (0.5–10 mass%) of plate-like or columnar gypsum dihydrate seed crystals of 10–115 μm particle size. The suspension was held at 30–80 °C for 1–6 h. The large plate-like gypsum dihydrate was isolated, washed with hot water and dried at 40 °C. In order to examine the effect of impurities in the waste gypsum board, a comparison experiment was performed where starch and lining paper were added to synthetic calcium sulfate dihydrate.

The products were characterized by X-ray diffraction, thermal analysis (TG-DTA), specific surface area measurement, laser diffraction particle size analysis and scanning electron microscope.

Table 1
Chemical compositions (unit: mass%) of waste gypsum board and synthetic calcium sulfate dihydrate

	$CaSO_4{\cdot}2H_2O$	$CaSO_4{\cdot}1/2H_2O$	II-$CaSO_4$	Lining paper	Organic matter	Heavy residue	Total
Waste gypsum board (A)	93.1	2.7	1.7	1.7	0.3	0.4	99.9
Waste gypsum board (B)	94.1	1.3	3.1	0.3	0.2	0.8	99.8
Waste gypsum board (C)	87.3	0.5	7.4	4.5	0.3	–	100.0
Synthetic gypsum dihydrate	Above 98.0						

Specific surface area (m^2/g): (A) 2.3, (B) 2.3, (C) 4.0.

3. Results and discussion

3.1. Selection of additives for promoting dehydration of gypsum dihydrate

Dehydration of gypsum dihydrate to gypsum hemihydrate in liquid phase can be understood in terms of solubility. The cross point of solubility of gypsum dihydrate and hemihydrate are at 97 ± 1 °C in pure water.[9] The hemihydrate is hardly formed, even if the dihydrate is heated in water at 100 °C (Fig. 2). Therefore, it is necessary to use either autoclaves or additives to form the hemihydrate from the dihydrate. Dehydration from dihydrate to hemihydrate was examined using waste gypsum board (C) as starting material and the 12 compounds described in Section 2.1. Using any of the potassium salts KCl, K_2SO_4 or KNO_3 resulted in the formation of a K_2SO_4–$CaSO_4$–H_2O system double salt (syngenite), as confirmed by X-ray diffraction.[10] When Na_2SO_4 or NaCl were used as additives, gypsum dihydrate was successfully dehydrated after several hours at 100 °C. The 10 other reagents failed to form the hemihydrate even after 6 h at 100 °C.

Fig. 2 shows the effect of additives and reaction time on preparation of gypsum hemihydrate, based on the results of thermal analysis (TG-DTA). The change of water of crystallization of sample retained in the pure water of 100 °C for 6 h could not be observed. However, a gypsum hemihydrate suspension was produced from a gypsum dihydrate suspension in Na_2SO_4 solution after 1 h at 100 °C and in NaCl solution after 3 h. Addition of Na_2SO_4 and NaCl were effective for the preparation of gypsum hemihydrate. Dissolution differences of the hemihydrate at 100 °C influenced the dehydration rate.

It was desirable to determine the lowest possible dehydration temperature. Fig. 3 shows the effect of additives and reaction time on preparation of gypsum hemihydrate at 85 or 90 °C. The water of crystallization slightly decreased when the waste gypsum suspension was kept in NaCl solution for 5 h at 90 °C. Gypsum hemihydrate was formed when the waste gypsum board suspension was kept in Na_2SO_4 solution for 2 h at 90 °C. However, at 85 °C, dehydration did not occur. Regarding the effect of the concentration of the additives, the results showed that dehydration was extremely slow in Na_2SO_4 solutions below 10 mass% concentration.

The above results indicate that dehydration of the waste gypsum board to form gypsum hemihydrate was effective at 100 °C using Na_2SO_4 whereas it was not using NaCl. The dimensions of the synthesized needle-like gypsum hemihydrate crystals were 15–30 μm length and 1–3 μm width.

3.2. Preparation of plate-like gypsum dihydrate by adding seed crystal

We investigated the effect of the lining paper and starch contained in waste gypsum board on particle size and crystal shape of the gypsum dihydrate formed by rehydration. The synthetic gypsum dihydrate used as starting material. The large gypsum dihydrate crystals were synthesized by cooling gypsum hemihydrate suspension, which was previously prepared by heating a waste gypsum board suspension at 100 °C for 2 h in Na_2SO_4 solution. Starch and lining paper did not influence particle size and crystal shape of gypsum dihydrate. The particle size (length) of the formed gypsum dihydrate was about 100 μm, and at that size the entanglement between lining paper and gypsum dihydrate was not observed. Therefore, though the lining paper was difficult to remove from the waste gypsum board, the removal of the paper was simplified by the increase in the particle size of gypsum dihydrate.

Fig. 4 shows the effect of temperature on the average particle size of gypsum dihydrate obtained from synthetic gypsum dihydrate. The particle size of the dihydrate was measured by a laser diffraction particle size analyzer. The average particle size of the gypsum dihydrate was a maximum, 115 μm, at 60 °C. The particle size reduced at lower temperature. The hydration of gypsum hemihydrate began to occur at below 80 °C. The decrease in average particle size of gypsum dihydrate at 70 °C was due to the existence of the unhydrated

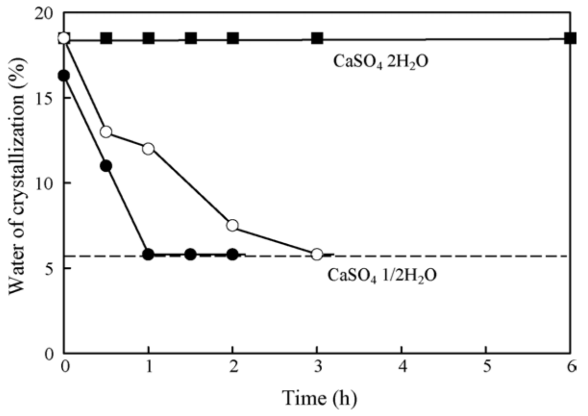

Fig. 2. Effect of additives and time on preparation of gypsum hemihydrate from waste gypsum board at 100 °C. Additives: (●) Na_2SO_4; (○) NaCl; (■) No addition.

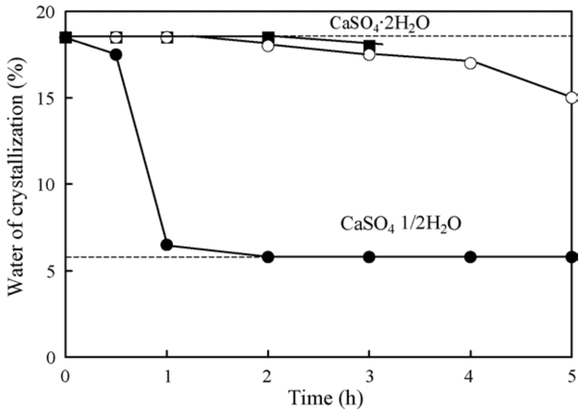

Fig. 3. Effect of additives and time on preparation of gypsum hemihydrate from waste gypsum board at 85 or 90 °C. Additives: (●) Na_2SO_4 (90 °C); (■) Na_2SO_4 (85 °C); (○) NaCl (90 °C).

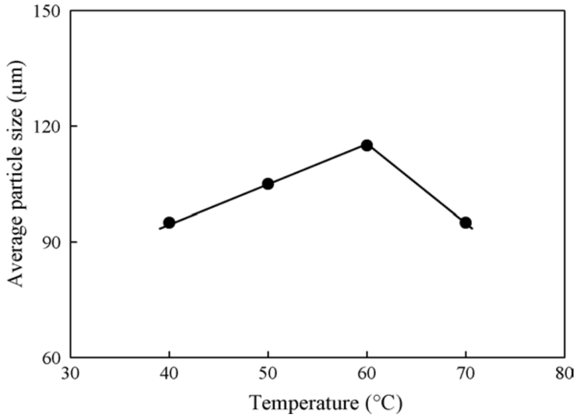

Fig. 4. Effect of temperature on average particle size of gypsum dihydrate obtained from synthetic gypsum dihydrate.

gypsum hemihydrate. Thus, large crystals of gypsum dihydrate were obtained by hydration of the gypsum hemihydrate to the dihydrate by cooling and then by maintaining the suspension at 60 °C.

The effect of seed crystal addition was investigated in order to synthesize gypsum dihydrate crystals with greater thickness. Seed crystals with three different particle sizes were synthesized by the $CaCl_2$–Na_2SO_4–$Na_3C_6H_5O_7$ system solution reaction. Fig. 5 shows scanning electron microscopic photographs of the three different seed crystals of gypsum dihydrate. The crystal shapes of gypsum dihydrate seed crystals (a) and (b) were mixtures of plate-like and prismatic crystals. The crystal shape of seed crystal (c) was plate-like. The X-ray diffraction peak strength of the (0 2 0) plane near $2\theta = 11°$ rose with the increase in particle size. (0 2 0)/(1 2 1) planes peak strength ratio of seed crystal (c) was biggest in these. The average particle sizes of seed crystals (a)–(c) were about 10, 40 and 115 μm, respectively.

These seed crystals were added at 80 °C during the cooling of the gypsum hemihydrate suspension, since gypsum hemihydrate hydrated to gypsum dihydrate at 80 °C. Fig. 6 shows the effect of particle size and the amount of seed crystal addition on particle size of gypsum dihydrate. When seed crystals (a) (particle size: 10 μm) or (c) (particle size: 115 μm) were added as accelerators of crystal growth, the particle size of the gypsum dihydrate decreased with increased amounts of additive. On the other hand, particle sizes of gypsum dihydrate prepared by adding seed crystals (b) (particle size: 40 μm) of 0.5–1.0 mass% increased slightly compared with no addition, and was about 120 μm. The crystal shape was plate-like. In the surface of large seed crystal, there are small numbers of kink and step necessary for the crystal growth. Conversely, in the case in which 10 μm seed crystals were added, the particle size of formed gypsum dihydrate decreased since formation of the crystal nucleus was rapidly increasing.

Scanning electron microscopic photographs of plate-like gypsum dihydrate are shown in Fig. 7. For addition of seed crystals of 40 μm at 0.5 and 1.0 mass%, there was no difference in particle size by a laser diffraction particle size

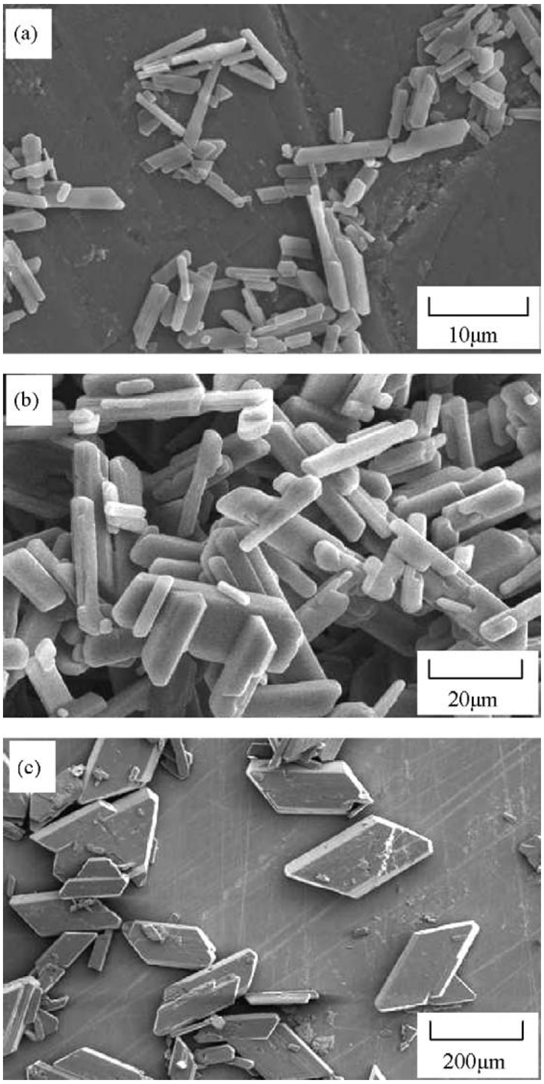

Fig. 5. Scanning electron microscopic photographs of three different seed crystals of gypsum dihydrate. Average particle size (μm): (a) 10; (b) 40; (c) 115.

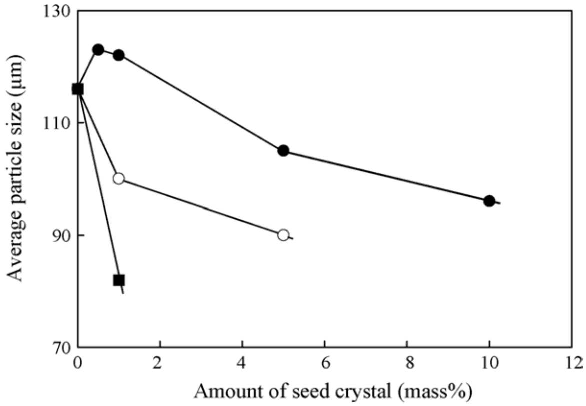

Fig. 6. Effect of particle size and amount of seed crystal addition on particle size of gypsum dihydrate. Average particle size of seed crystal (μm): (■) 10; (●) 40; (○) 115.

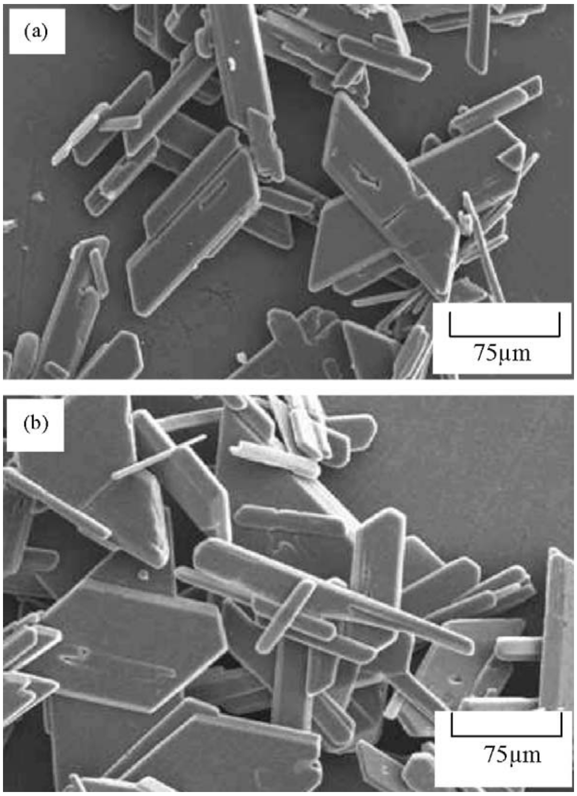

Fig. 7. Scanning electron microscopic photographs of large plate-like gypsum dihydrate obtained from synthetic gypsum dihydrate. Amount of seed crystal (mass%): (a) 0.5 and (b) 1.0.

analyzer. However, the product obtained by adding seed crystals of 1.0 mass% included needle-like crystals with a big aspect ratio. By adding 0.5 mass% of seed crystal (b), thickness of the dihydrate increased to about 30 μm.

We investigated the effect of aging time on the particle size of gypsum dihydrate. The particle size of gypsum dihydrate obtained by aging the suspension for 5 min at 60 °C was about 90 μm, and the particle size increased after 2 h for crystal growth by dissolution of the small crystals. The aging time at 60 °C was for 2 h as a synthetic condition.

Thus, the particle size of the gypsum dihydrate varied with the particle size and quantity of seed crystal, and the largest sized plate-like gypsum dihydrate was produced by adding 40 μm seed crystals at 0.5 mass%.

3.3. Characteristics of large plate-like gypsum dihydrate prepared from waste gypsum board

The characteristics of large plate-like gypsum dihydrate prepared from waste gypsum board via a wet process were investigated. A comparison was performed using identical conditions for synthetic gypsum dihydrate as a raw material.

Fig. 8 shows scanning electron microscopic photographs of large plate-like gypsum dihydrate obtained from waste gypsum boards (A) and (B). The large plate-like gypsum dihydrate crystals obtained from waste gypsum board (A) were, on average, 250 μm length × 100 μm width × 35 μm thickness, and those obtained from waste gypsum board (B) were 200 μm length × 100 μm width × 25 μm thickness. Fig. 9 shows the X-ray diffraction patterns of waste gypsum board (A) and large plate-like gypsum dihydrate, which formed using waste gypsum board (A). The peak of waste gypsum board expanded 10 times. The particle size

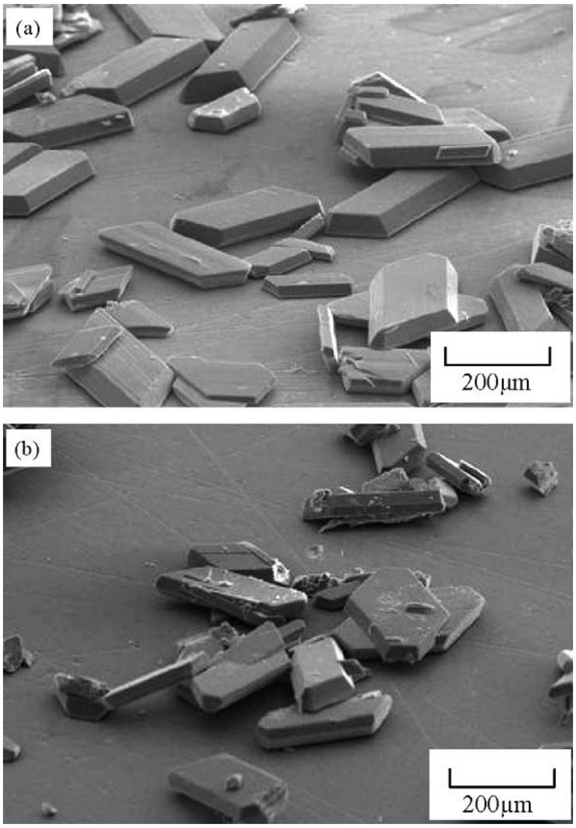

Fig. 8. Scanning electron microscopic photographs of large plate-like gypsum dihydrate obtained from waste gypsum board. Waste gypsum board: (a), (A) and (b), (B).

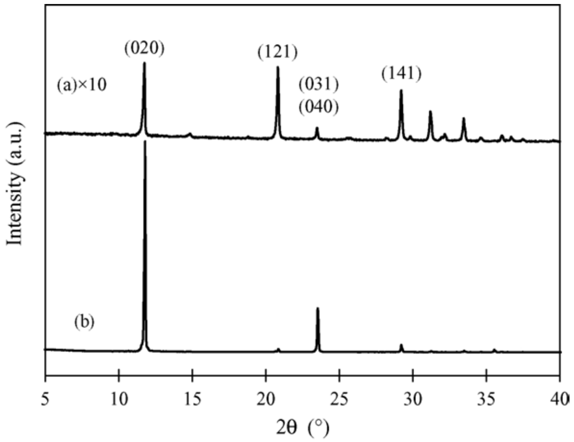

Fig. 9. X-ray diffraction patterns of waste gypsum board (A) and large plate-like gypsum dihydrate, which formed using waste gypsum board (A). (a) Waste gypsum dihydrate (A) and (b) Large plate-like gypsum dihydrate.

of gypsum dihydrate, which is included in the waste gypsum board is small, and therefore, the peak intensity was low. The peak intensity of (0 2 0) plane and (1 2 1) plane was almost same. On the other hand, the peak intensity of large plate-like gypsum dihydrate was about 30 times of waste gypsum board (A). The (0 2 0) plane developed on the large plate-like gypsum dihydrate crystal, and (1 2 1) plane which showed in the thickness direction was not almost observed near $2\theta = 20^\circ$.

The peak strength of the (0 2 0) plane of large plate-like gypsum dihydrate crystals synthesized from waste gypsum board (A) was slightly higher than those of waste gypsum board (B). The viscosity of gypsum hemihydrate suspension (A) was higher than that of (B). The small organic component was also regarded as a cause of interference in the crystal growth. Therefore, it is believed that the thickness of the gypsum dihydrate synthesized from waste gypsum board (A) was greater.

The purity of large plate-like gypsum dihydrate obtained from the waste gypsum board increased to 96.1 mass%, because the quantity of lining paper and organic matter was decreased. The large plate-like gypsum dihydrate contained 0.08 mass% Na^+ ion. Na^+ ion is not desirable, because it reduces adhesion of gypsum board and lining paper. The content of Na^+ ion hardly lowered, even if the washing was sufficiently carried out.

Particle disintegration in water of gypsum hemihydrate obtained by heating gypsum dihydrate was examined. Particle disintegration in water is not a desirable characteristic for gypsum hemihydrate, and its adverse effects are reflected by its rheological properties (viscosity, moisture content), setting time and in the strength of hardened body.[11,12] Gypsum dihydrate was heated at 130 °C for 6–10 h in a thermohygrostat, and the obtained III-anhydrous gypsum was stored in a desiccator. Then, gypsum hemihydrate was obtained by placing the III-anhydrous gypsum for 4 h in a thermohygrostat maintained at 20 °C and 60% humidity. For example, the increases in Blaine specific surface area after water stirring of gypsum hemihydrate obtained from natural gypsum and flue-gas gypsum were 31 and 24%, respectively. That of large plate-like gypsum dihydrate obtained from waste gypsum boards (A) and (B) were 25 and 13%, respectively. Particle disintegration in water hardly was observed. Particle disintegration in water of large plate-like gypsum dihydrate was slightly smaller than natural gypsum or flue-gas gypsum.

The water-carrying capacities of gypsum hemihydrate obtained from large plate-like gypsum dihydrate (A) and (B) were 89.5 and 91.4%, respectively. However, the water-carrying capacity of gypsum hemihydrate (A) and (B) which was crushed for 10 min with a magnetic ball mill decreased to 63.4 and 61.0%, respectively. For (A) and (B) after crushing, the bulk densities were 1.16 and 1.29 g/cm^3, respectively, and the compressive strengths were 139 and 138 kgf/cm^2, respectively. These values are similar to those of gypsum hemihydrate obtained from natural gypsum. Regarding the setting times for gypsum hemihydrate obtained from large plate-like gypsum dihydrate (A) and (B), the initial setting times were 7.1 and 12.2 min, respectively, and the final setting times were 20.5 and 25.0 min, respectively. Again, these values are similar to those of gypsum hemihydrate obtained from natural gypsum or flue-gas gypsum.

The above results show that the characteristics of large plate-like gypsum obtained from waste gypsum board are the same as for natural gypsum and flue-gas gypsum, which are used to produce the board at present.

4. Conclusion

We investigated the synthesis of large plate-like gypsum dihydrate obtained from waste gypsum board via a wet process utilizing the reversible reaction between gypsum dihydrate and gypsum hemihydrate. Na_2SO_4 was effective as an additive for promoting dehydration from gypsum dihydrate to gypsum hemihydrate. The needle-like gypsum hemihydrate was obtained by heating a waste gypsum board suspension of 33 mass% at 100 °C for 1 h. Large gypsum dihydrate crystals were prepared by cooling the gypsum hemihydrate suspension. The optimal growth conditions involved maintaining the suspension at 60 °C for 2 h. The particle size of the obtained gypsum dihydrate was about 115 μm. In addition, large plate-like gypsum dihydrate was obtained by adding seed crystals to a suspension cooled at 80 °C. When 40 μm seed crystals were added at 0.5 mass%, the large plate-like gypsum dihydrate crystals obtained from waste gypsum board had average dimensions of 250 μm length × 100 μm width × 35 μm thickness. The characteristics of gypsum dihydrate obtained by this process were similar to those of natural gypsum and flue-gas gypsum, which are used as the raw materials of gypsum board.

References

1. Yasue, T., Challenge to recycle society by resources recycling of waste gypsum materials. *J. Soc. Inorg. Mater. Jpn.*, 2000, **7**, 492–502.
2. Arai, Y., Yasue, T. and Kojima, Y., Direct preparation of hardened gypsum body from the hemihydrate formed by the exothermic reaction of sulfuric acid and calcium carbonate. *J. Soc. Inorg. Mater. Jpn. (Gypsum & Lime)*, 1986, **203**, 7–14.
3. Yasue, T., Kojima, Y., Kishimoto, Y. and Arai, Y., Preparation of α-gypsum hemihydrate and control of its crystal shape under atmospheric pressure. *J. Soc. Inorg. Mater. Jpn. (Gypsum & Lime)*, 1992, **239**, 12–20.
4. Yasue, T., Kojima, Y., Inoue, H. and Arai, Y., Preparation of gypsum hemihydrate fiber incorporating strontium ion and the decrease of its solubility. *J. Soc. Inorg. Mater. Jpn. (Gypsum & Lime)*, 1990, **228**, 18–26.
5. Kojima, Y., Funada, S. and Yasue, T., Production of gypsum hardened body contained active carbon from waste gypsum board and its adsorption property. *J. Soc. Inorg. Mater. Jpn.*, 2004, **11**, 212–218.
6. Kojima, Y., Yasue, T. and Arai, Y., Preparation of gypsum block from waste gypsum board. *J. Soc. Inorg. Mater. Jpn.*, 2000, **7**, 460–466.
7. Arai, Y., From advancing researches on calcium salt in recent 50 years. *J. Soc. Inorg. Mater. Jpn.*, 2000, **7**, 363–384.

8. Kojima, Y., Yasue, T. and Arai, Y., Preparation of hardened gypsum body from waste gypsum board. *J. Soc. Inorg. Mater. Jpn. (Muki-Materiaru)*, 1997, **4**, 415–422.
9. Knacke, O. and Gans, W., The thermodynamic of the system calcium sulfate-water. *Z. Phys. Chem.*, 1977, **104**, 41–48.
10. Arai, Y. and Yasue, T., Crystal structure for double salts of gypsum. *J. Soc. Inorg. Mater. Jpn. (Gypsum & Lime)*, 1980, **164**, 27–35.
11. Setoyama, K. and Takahashi, S., Disintegration of calcium sulfate hemihydrate particles in water. *J. Soc. Inorg. Mater. Jpn. (Gypsum & Lime)*, 1978, **153**, 11–15.
12. Setoyama, K. and Takahashi, S., Particle disintegration in water of calcium sulfate hemihydrate prepared from chemical gypsum. *J. Soc. Inorg. Mater. Jpn. (Gypsum & Lime)*, 1983, **187**, 67–70.