Recovery and Refining Process of Gypsum from Waste Plaster Board

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ABSTRACT

This study was conducted to obtain granular crystalline gypsum that can be used as raw material for plaster boards or cements from waste plaster board. Gypsum could be preferentially disintegrated to gypsum needle in 10 μm or less size by hydration after the dehydration of crushed waste plaster board. The finer the gypsum needle, it is easier to remove coarse impurities and to recover the gypsum needle. The optimum conditions for obtain the finer gypsum size were dehydration rate of 75~85%, solid concentration at hydration of 10~15%, agitation speed of 250~400 rpm, crushing size before dehydration of 2 cm or less. Gypsum of 98.21% grade was recovered with 99.0% yield as the undersize of 325 mesh wet screening followed by the dehydration-hydration process performed at the conditions of dehydration rate of 80%, solid concentration at hydration of 15%, agitation speed of 300 rpm, crushing size before dehydration of 2 cm or less. After the recrystallization of recovered gypsum, Plate-like gypsum of 151 μm size with 99.49% grade was obtained as the oversize of 270 mesh in a wet screening.

Key words: waste plaster board, gypsum, recover, refining, hydration, dehydration, crystallization

1. Introduction

In the year 2000, 555.6 Mm² (approximately 4.86 million tons) of plaster boards were produced in Japan. The total annual volume of the discarded waste plaster boards is estimated to be around 2 million tons.[1-3] Waste plaster boards are usually discarded as the scrap of manufacturing and distribution processes. They are often found at construction and demolition sites of buildings. This volume is likely to increase explosively in the near future because the buildings built during the 1970s, when the use of plaster boards spreaded rapidly, are now to be reconstructed and renovated. In addition, the plaster boards should be disposed at controlled type landfill sites since the regulation changed in June 1999, while they could be disposed at stabilized type landfill sites before 1999. This implies that the cost for disposing of plaster board is supposed to increase due to the lack of landfill site of controlled type in Japan.

This situation stimulates many researches on the recycling and re-using of waste plaster boards.[4-6] One of the method studied is to simply apply crushing and screening to the boards for rejecting impurities which is added as ingredient to manufacture plaster boards or gypsum brick. The recovered gypsum powder is to be used as the raw material of plaster board by mixing it with general calcined gypsum or as the raw material of cement after calcinations. However, the concentration of organic matters in the recovered gypsum by the simple crushing and screening is 0.5~2.5% (mainly reliant on the size of mesh), which is too high for its use as a raw material for cement, in addition, the crystal size of recovered gypsum is 10 μm or less, while the size should be about 100 μm as a raw material for plaster board. For this reasons, the mixing rate of recovered gypsum with virgin gypsum is restricted to less than 5%. In order to increase the recycling of waste plaster board, it is necessary to ensure that recovered gypsum can be used in plaster boards (comprised 54.7% of total gypsum demand in Japan in 1999) and in cement (32.8%). Therefore, the development of technology for increasing the quality and yield of recovered gypsum is a prerequisite.

In this study a possible utilization of crystallographical characteristics of gypsum for the recycling of waste plaster board was discussed. The influence of dehydrating and hydrating conditions on the yield and grade of recovered gypsum in wet screening to remove impurities were also investigated.

2. Experiment

The leading domestic plaster board manufacturers, company A and company B, provided waste plaster board samples collected independently. Sample A was on being crushed less than 2 cm provided by company A, and sample B was powder with low paper content being obtained by crushing and dry screening of waste plaster boards, provided by company B.

Analytical tools such as PSA, XRF, XRD, TG-DTA were used: Particle size was analyzed by SYMPATEC HELOS particle size analyzer. For XRF, Philips PW-2404; RINT 2500V for XRD; and RIGAKU TG8120 for TG-DTA.

Analysis of the organic matter's content was conducted in a high temperate of 100°C, following JIS K 0102-17. However, the oxidation time was set as 2 hours to assure a more perfect oxidation of organic matter. First, the consumption volume of $KMnO_4$ was measured varying the concentration of water soluble starch and poly vinyl alcohol (PVA), and the average value of multiple experiments was used to plot calibration curve. Then, the contents of organic matter were calculated from the calibration curve by substituting consumption volume of $KMnO_4$ for the analyzed sample.

The yield of gypsum from 325 mesh wet screenings was calculated as follows:

$$Y_G = \frac{U_G}{U_G + O_G} \times 100 \tag{1}$$

Where, Y_G is yield of gypsum (%), U_G is the weight of gypsum in undersize and O_G is the weight of gypsum in oversize.

Dehydration temperature was fixed at 160°C and dehydration rate was calculated as follows:

$$D = \frac{W_{45} - W_n}{W_{45} \times G \times I} \times 100 \tag{2}$$

Where D is dehydration rate (%), W_{45} is the weight of sample dried in 45°C for 24 hours, W_n is the weight after dehydration, G is the theoretical rate of crystalline water within gypsum (0.209), I is content of gypsum contained in the samples.

Solid concentration at hydration was calculated based on the weight of samples before the dehydration, and hydration temperature was set as room temperature (16~21°C) with hydration time, 30 minutes, and a 1×5-cm impeller with two blades (twist of 15°) was used for agitation.

The composition of waste plaster boards was analyzed according to the analysis flow shown in Fig. 1. A 10 g sample crushed to less than 1 cm size was weighed with the accuracy of 0.1 mg. The content of hygroscopic water was calculated from the weight loss during drying for 24 hours at 45°C. Then the sample was completely dehydrated for 2 hours at 250°C, and was soaked into 5 *l* distilled water to dissolve the calcium sulfate contained in the sample. The solution was separated from the insoluble one by filtration. Gypsum content was calculated from the smaller value of between Ca^{2+} content measured by back titration method of oxalate with $KMnO_4$, and SO_4^{2-} content measured by the analytical method for sulfuric acid described in JIS R 9101. The contents of soluble
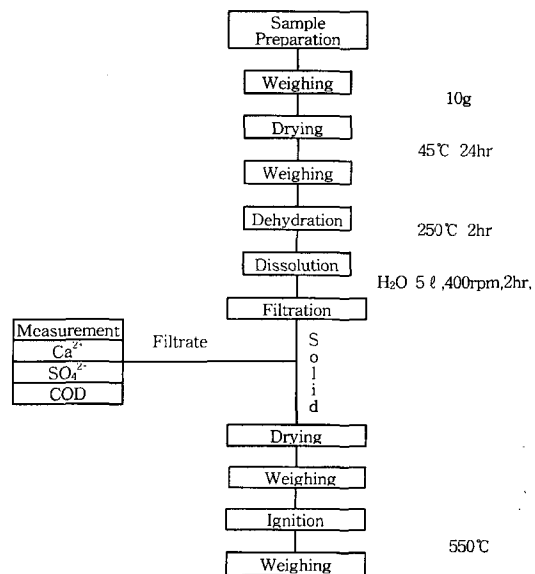

Fig. 1. Flowsheet of rational analysis of waste plaster board

organic materials were measured with JIS K 0102-17 method. Insoluble materials from the dissolution reaction mentioned above were washed and dried, and then weighed and ignited for over 2 hours under 550°C of oxidation condition. In this ignition, the contents of the insoluble inorganic materials were calculated from the weight of ash and those of insoluble organic materials were considered as ignition loss.

3. Results and Discussion

The constitution of sample A and B analyzed with the flow in Fig. 1 is shown in Table 1. From the results,

it is shown that Sample A contains a large amount of insoluble organic materials (mainly paper) and hygroscopic water and a low content of gypsum(about 90%). Sample B contains a relatively large amount of insoluble inorganic materials (3.7%). The contents of total organic materials in both samples were relatively high at 1.1% or more. This means it would be difficult to use the samples, without some treatment, as raw material for cements or plaster boards.

Figs. 2, 3, and 4 show the SEM image, size distribution, XRD and XRF for the materials contained in the waste plaster boards. The results of the Iodostarch reaction conducted to confirm the water

Table 1. Major constituent of waste plaster board.

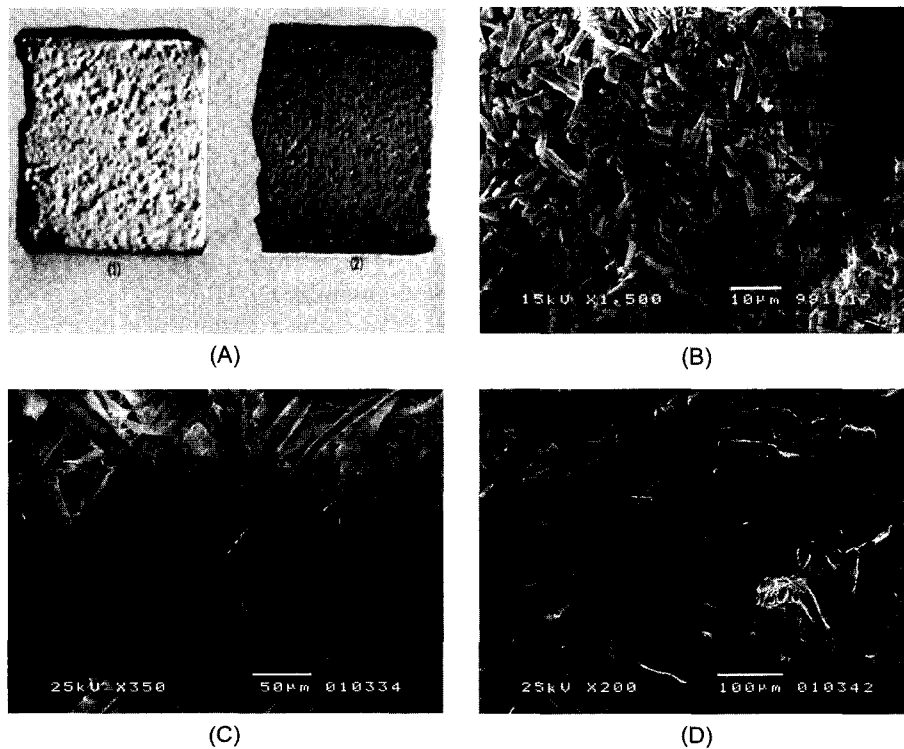| Constituent / Sample	Gypsum(%)	Organic impurity (%)		Inorganic impurity(%)	Hygroscopic water (%)	The Rest (%)
		insoluble	soluble			
Sample A	90.1	5.3	0.2	0.5	3.8	0.1
Sample B	93.8	0.9	0.2	3.7	1.1	0.3

(A)

(B)

(C)

(D)

Fig. 2. Photograph of waste plaster board and Scanning Electron Micrographs of the constituent parts (A)Waste plaster board slices of before (1) and after (2) iodostarch reaction (B) Gypsum (C) insoluble organic impurity (D) inorganic impurity

board, a material generally used as an adhesive for plaster boards, is shown on Fig. 2(A). It is shown that water soluble starch tends to distribute mainly on the upper and lower surfaces of plaster boards within 2 mm. However, some portions even penetrate to the inner side. This result means that complete removal of water-soluble starch by peeling off only paper in the upper and lower surfaces of the board is impossible.

Gypsum particles in waste plaster board exist in dense aggregation of 10 μm or less size needle (See Fig. 2(B)).

The majority of insoluble organic materials was corrugated paper made of 500 μm or longer fiber. The isolated fiber (from paper or not) has the length of 100 μm or more (Fig. 2(C)). Unlike gypsum particles and insoluble organic materials, the particle size and composition of inorganic materials showed
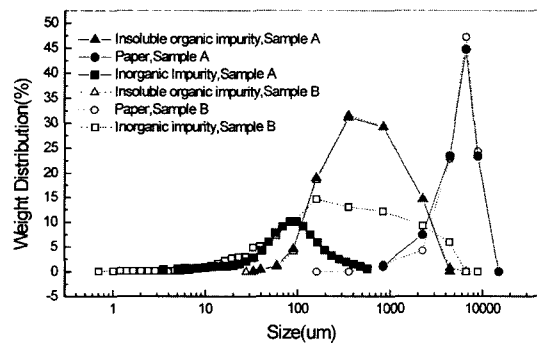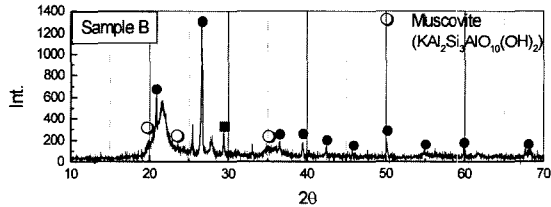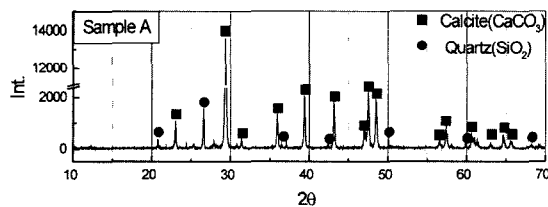
different results in samples A and B. Inorganic impurities in sample A were 30~300 μm particles, mostly based on massive $CaCO_3$, and in sample B, 50~5000 μm particles, mainly composed of massive SiO_2 (Fig. 2-D).

Fig. 5 and Fig. 6 show the summaries[7] of studies thus far made on dehydration or hydration of gypsum. That is, Fig. 5 shows the phase transition of gypsum in various condition and Fig. 6 shows the DTA curves of calcium sulfate hydrate. In this study, gypsum in crushed waste plaster board is dehydrated in air with the process of ①→②→③ (Fig. 5) and is disintegrated into fine needle by hydration of ❸→(2). This fine gypsum needle can be easily recovered by general classification method, e.g., wet screening. For more
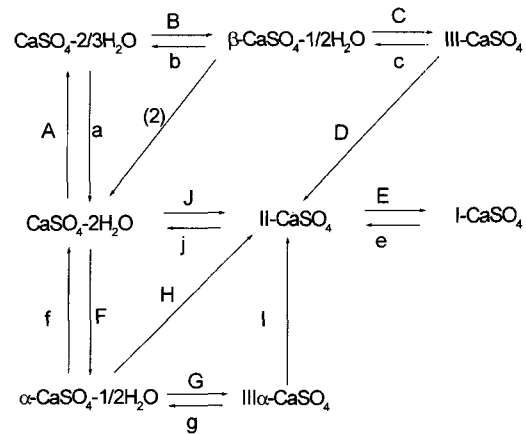

Fig. 3. Particle size distribution of impurities contained in crushed waste plaster board.

Fig. 5. Phase transition of gypsum in various conditions.

Chemical composition   (Unit : %)

Content \ Sample	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	S
Sample A	33.03	7.87	1.22	0.92	0.66	0.19	0.06	0.09
Sample B	2.06	66.02	6.65	1.86	0.77	0.45	0.74	0.25

Fig. 4. X-Ray Diffraction pattern and chemical composition of inorganic impurities contained in waste plaster board.
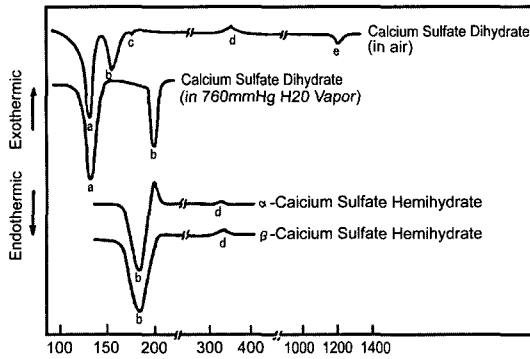
Fig. 6. DTA curves of calcium sulfate hydrates.
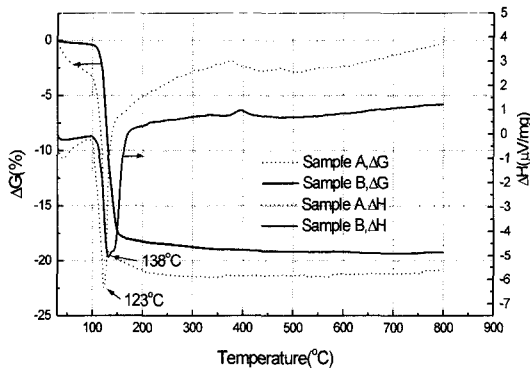
Fig. 7. TG-DTA curves of waste plaster board.

(a) before dehydration

(b) after hydration

Fig. 8. Scanning electron micrographs of recovered gypsum before and after dehydration-hydration reaction.
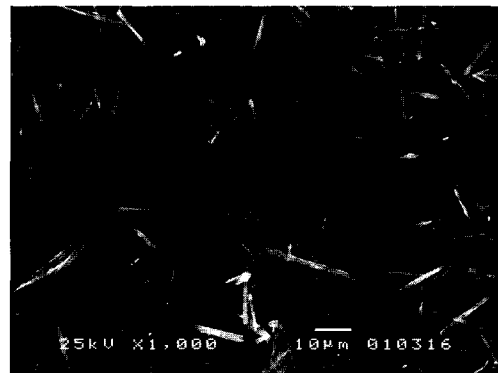
refining of recovered gypsum, the fine gypsum needle was dehydrated again within water (⑥) and re-crystallized to more granular particle through hydration.

On the TG-DTA curve (see Fig. 7), sample A and sample B showed a typical dehydration pattern of gypsum that have an endothermic peak at 120°C~140°C. Sample A has more weight loss and is more endothermic than sample B mainly because of the influence of hygroscopic water.

① Dehydration in air of 50°C or more temperature, DTA endothermic curve shows it in 140~160°C ❶ Hydration in moisture or water ② Dehydration in air of 76°C or more temperature, DTA endothermic curve shows it in 150~185°C ❷ Hydration in moisture (2) Hydration in water ③ Dehydration in air of 130°C or more temperature, DTA endothermic curve shows it in 180~215°C ❸ Hydration in moisture or water ④ Phase Transition in air of 250°C or more temperature, DTA exothermic curve shows it at 330°C ⑤ ❺ Phase transition in air at 1180°C ⑥ Dehydration in water of

97°C or more temperature ❻ Hydration in water ⑦ Dehydration in air of 130°C or more temperature, DTA endothermic curve shows it in 180~215°C ❼ Hydration in moisture or water ⑧ Phase transition in water of 97°C or more temperature ⑨ Phase transition in air of 180°C or more temperature, DTA exothermic curve shows it in 190~220°C Dehydration in water of 41°C or more temperature ❿ Hydration in water

a: $CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot 1/2H_2O$
b: $CaSO_4 \cdot 1/2H_2O \rightarrow III\text{-}CaSO_4 \cdot nH_2O$
c: $III\text{-}CaSO_4 \cdot nH_2O \rightarrow III\text{-}CaSO_4$
d: $III\text{-}CaSO_4 \rightarrow II\text{-}CaSO_4$
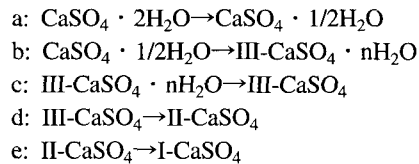e: $II\text{-}CaSO_4 \rightarrow I\text{-}CaSO_4$

Fig. 8 and Fig. 9 show respectively the changes of shape and size distribution before and after the dehydration-hydration reaction. This figures show that the 85.69 μm (mean size) massive gypsum agglomerates
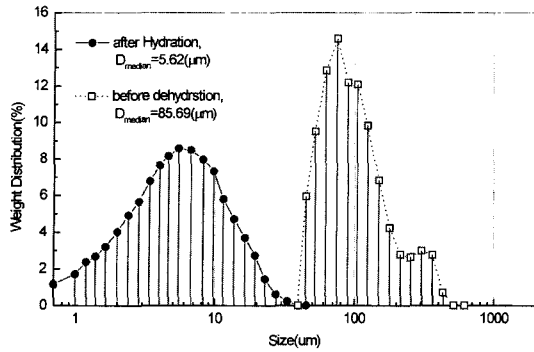
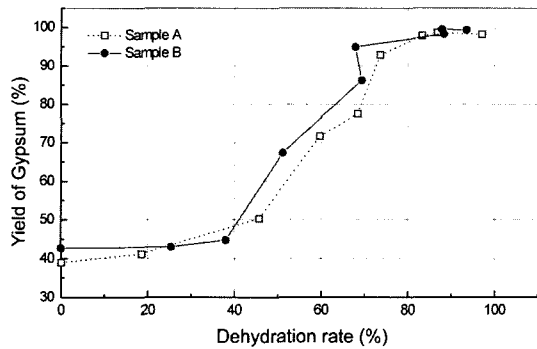Fig. 9. Particle size distribution of recoverd gypsum before and after dehydration-hydration reaction.

Fig. 11. Effect of hydration pulp density on the yield of gypsum in 325 mesh wet screening after dehydration-hydration reaction.

Fig. 10. Relationship between dehydration rate and the yield of gypsum in 325 mesh wet screening after dehydration-hydration reaction

Fig. 12. Effect of agitation during the hydration on the yield of gypsum in 325 mesh wet screening after dehydration-hydration reaction.

have converted into 5.62 μm isolated gypsum needle during the hydration after dehydration.

Also the influence of the conditions of the dehydration-hydration reaction on the yield of gypsum recovered from under screenings of 325 mesh wet screening was investigated. The standard condition for this investigation was set as follows: dehydration rate of 80%, dehydration temperature of 160°C, hydration time of 30 minutes, solid concentration at hydration of 10%, agitation speed of 300 rpm, crushing size of 2 cm. Figs. 10~14 show the results of each experiment.

From Fig.10, it can be seen that there are virtually no changes in the yield of gypsum when the dehydration rate is less than 40%. However, when the rate is greater than that, the yield increases as the rate of dehydration increased. When the dehydration rate of 75%, the yield reaches to a peak of 98%. In the case of low yield, we can observe many gypsum agglomerates from the
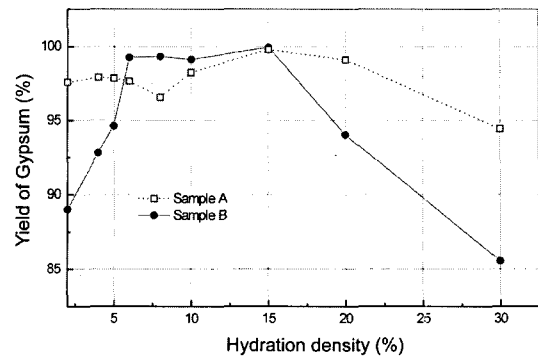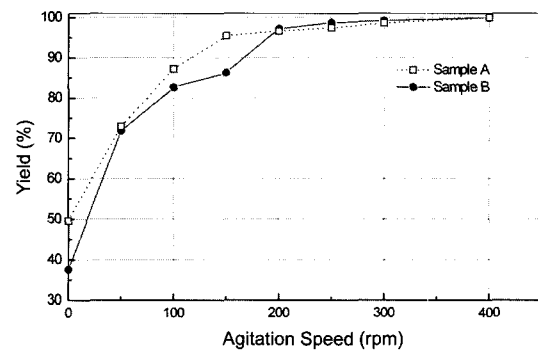
upper screenings of 325 mesh, on SEM observation (Fig.14-A). This result implies that unless gypsum in the crushed waste plaster board dehydrated up to hemihydrate gypsum or anhydrous gypsum state, the yield will decrease because the disintegration by hydration is not completely accomplished.

Fig. 11 shows that the yield of gypsum is stable as 97~100% in the solid concentration at hydration of less than 15%. However, the yield started to decrease at 20% concentration and even decreased significantly less than 95%, at 30% concentration. Many massive aggregates of gypsum needles (Fig. 14-B) are also observed in the oversize of 325-mesh wet screening after hydration at 20% or more concentration.

Fig. 12. shows the effect of agitation during hydration on the yield of gypsum in 325 mesh wet screening after dehydration-hydration reaction. The
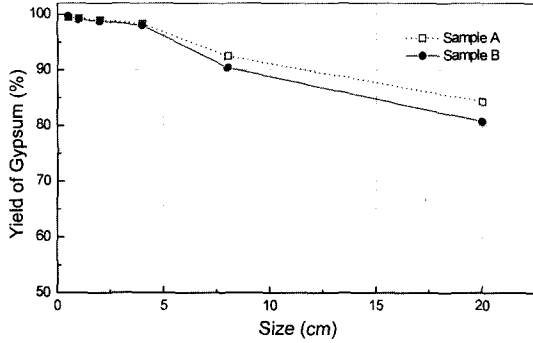
Fig. 13. Effect of Crushed board size on the yield of gypsum in 325 mesh wet screening after dehydration-hydration reaction.

yield of gypsum is 98% or more at an agitation speed of 250 rpm or more. The polycrystalline gypsum grown up radially (Fig. 14-C) is also observed in the oversize of 325 mesh wet screening carried out after hydration in the agitation speed of below 250 rpm. From these figures, it can be seen that 250 rpm or more agitation speed is needed to obtain fine gypsum particle through sufficient homogenization.

Fig. 13 shows the effect of crushing size of board on the yield of gypsum in 325-mesh wet screening after dehydration-hydration reaction. For this experiment, 12.5 mm thick of plaster board were cut into regular squares. The result shows yield of gypsum turn from bad to worse as the cutting size grow bigger by degrees. Many polycrystalline gypsum (Fig. 14-D) are observed in the oversize when cutting size is larger than 4cm. These particle were often seen on the inner surface of the paper (Fig. 14-E).

The phenomena above can be explained as follows: In the disintegration process consists of three steps, dissolution of dehydrated gypsum, dispersion and the re-crystallization of gypsum, the dissolution and dispersion are disturbed by the un-uniform hydration occurring in the inner side of a dehydrated gypsum agglomerate, where space is limited and free water is lacking. In cases when that agglomerate is too big, then the gypsum grows into radial polycrystalline.

From these results, the following optimum conditions for disintegrating of gypsum are recommended: crushing size of board under 2 cm, dehydration rate of 75% or more, solid concentration at hydration of 5~15%, and
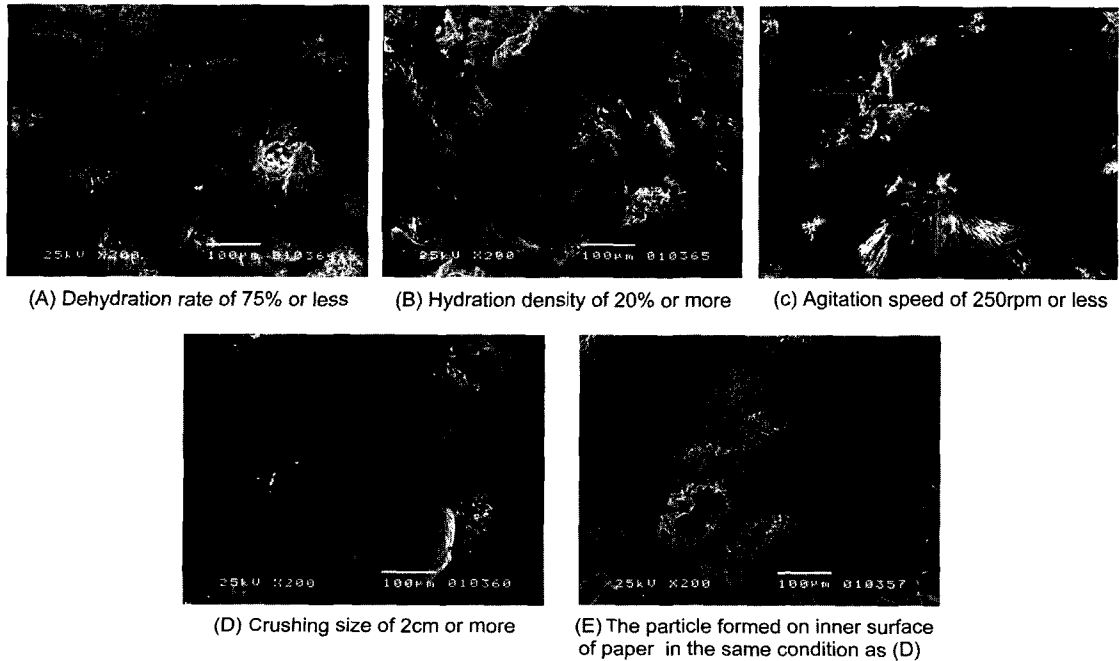

(A) Dehydration rate of 75% or less   (B) Hydration density of 20% or more   (c) Agitation speed of 250rpm or less

(D) Crushing size of 2cm or more   (E) The particle formed on inner surface of paper in the same condition as (D)

Fig. 14. Typical shapes of granular gypsum of 45 μm or more size formed from various dehydration-hydration condition.

Table 2. Result of 325 mesh wet screening after dehydration-hydration of waste plaster board on optimum condition.

Constituent \ Sample	Content of 45 μm under size					Yield of gypsum(%)
	Gypsum (%)	Organic impurity (%)		Inorganic impurity (%)	Etc. (%)	
		Insoluble	Soluble			
Sample A	98.98	0.07	0.18	0.39	0.38	98.7
Sample B	98.21	0.06	0.16	0.19	1.38	99.0

agitation speed of 250 rpm or more. A series of final test for the whole process of disintegrating and screening was conducted, based on these optimum conditions; crushing size of board under 2 cm, dehydration rate of 80%, solid concentration at hydration of 15%, and agitation speed of 300 rpm.

Table 2 shows the separation results; A yield of gypsum from sample A is 98.7%, with a grade of 98.98% and that of sample B is 99%, with a grade of 98.21%. However, the recovered gypsum has a size of about 10 μm and contains a lot of organic material. This means that the recovered gypsum cannot be used as raw material for cement or plaster board without some treatment. Therefore, the authors tried to make growth the gypsum crystal and then remove the organic material by screening.

In the general method for crystallization of gypsum, gypsum crystal is grown by controlling the reaction conditions, e.g., pressure, temperature, additives, etc.. In some process, many additives are used and it makes the process costly. However, in this study, Na_2SO_4 is used in atmospheric pressure as the only additive for

the simplification and possible cost reduction of process (see Fig. 15).

During the dehydration process, the viscosity of slurry drastically increased within 15-30 minutes after the temperature of slurry reached 95~98°C, and then the viscosity returned to its original state in 30~60 minutes. This rapid increase of viscosity is attributed to the gelation caused by the dissolution and disintegration of dehydrated gypsum. From TG-DTA for each product in the process, it was found that the dehydration of gypsum to gypsum-hemihydrates had finished in 30 minutes after reaching 95~98°C. After this 60 minutes dehydration, no changes were witnessed on the exterior of the slurry during the 2-hour dehydration and subsequent cooling procedure (1 hour) and crystallization (3 hours). For the following 3-4 hours, the color of the slurry gradually changed from white to dark brown, and after 4 hours, the trace of white, the slurry's original color, was no longer seen. This implies that the small quantities of dark brown impurity become visible due to the increase of transmissivity according to the crystal growth of gypsum.

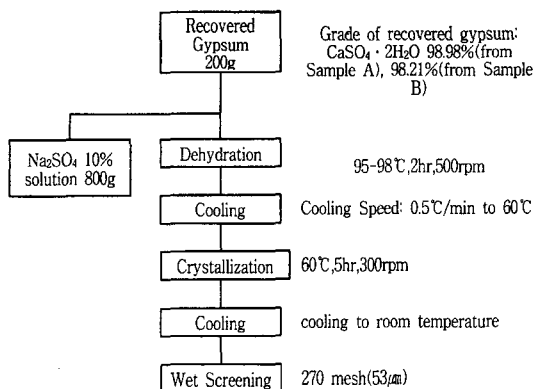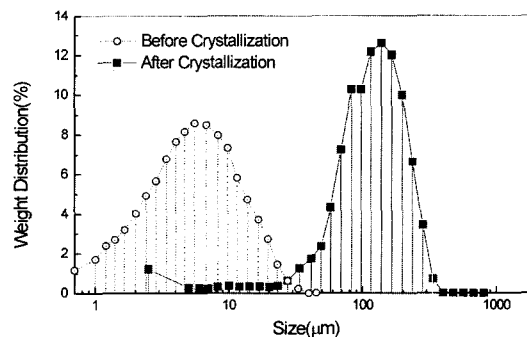Fig. 16 shows the changes in particle size distribution

Fig. 15. Flowsheet of $CaSO_4 \cdot 2H_2O$ Crystallization process

Fig. 16. Particle size distribution of recovered gypsum slurry before and after recrystallization process.

Table 3. Result of 270 mesh wet screening after recrystallization process

Constituent / Sample	Content of 53 μm over size					Yield of gypsum (%)
	Gypsum (%)	Organic impurity (%)		Inorganic impurity (%)	Etc. (%)	
		insoluble	soluble			
Sample A	99.54	0.01	0.02	0.08	0.35	98.4
Sample B	99.49	0.01	0.02	0.12	0.36	98.0

Fig. 17. Scanning electron micrographs of recrystallized gypsum.

of recovered gypsum slurry before and after the crystallization process. It is seen that the 5.6 μm gypsum grows to about 150 μm. Table 3 and Fig. 17 show the results of 270 mesh wet screening and the shape of recovered gypsum, respectively. As the results indicate, about 150 μm crystalline gypsum with 98.4% yield and 99.54% grade can be obtained by crystallization and screening process.

4. Conclusion

In order to develop a possible recycling process for waste plaster board, the recovery and purification of gypsum from waste plaster board was investigated. Gypsum contained in waste plaster board was preferentially disintegrated to gypsum needle in 10 mm or less size by hydration after dehydration. This gypsum needle could be separated from impurities by wet screening. The optimum conditions for obtain the finer gypsum size were dehydration rate of 75~85%,

solid concentration at hydration of 10~15%, agitation speed of 250~400 rpm, crushing size before dehydration of 2 cm or less.

Gypsum of 98.21% grade was recovered with 99.0% yield as the undersize of 325 mesh wet screening followed by the dehydration-hydration process with dehydration rate of 80%, solid concentration at hydration of 15%, agitation speed of 300 rpm, crushing size before dehydration of 2 cm or less.

Through the crystallization & screening process, Plate-like gypsum of 151 mm size was obtained as the oversize of 270 mesh in a wet screening with 99.49% grade and 98.0% yield. This gypsum can be used freely as a ingredient for plaster board or cement.

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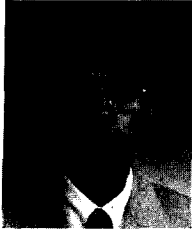
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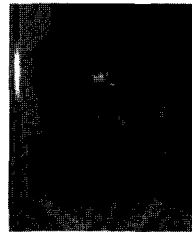
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신간 소개

비즈니스와 연구를 위한 99가지 상식과 지식

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폐플라스틱과 관련된 비즈니스와 연구를 위한 사람들의 필독서!! "무엇이 문제이고 어떻게 해야 하는가"를 저자의 경험 등을 바탕으로 해서 독자들과의 대화형태로 저술한 폐플라스틱의 처리와 재활용을 위한 지침서