The 6th International Symposium on East Asian Resources Recycling Technology
October 23 - 25, 2001, Gyeongju (慶州), Korea
ISBN: 89-952527-0-7 93530

Recover of gypsum from waste plaster board and the refining process

YoungJun Song[1], Hiroki Yotsumoto[2]
1),2)Particle Separation Group, Research Institute for Green Technology, National Institute of Advanced Industrial Science and Technology,JAPAN

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. We could disintegrate preferentially gypsum to gypsum needle in 10㎛ or less size among the contents of waste plaster board (gypsum, paper, fiber, and inorganic material .etc.) by hydration afterwards the dehydration of crushed waste plaster board. In this case, the optimum conditions for minimizing the size of gypsum were dehydration rate of 75%~85%, hydration concentration of 10~20%, agitation speed of 250~400rpm, crushing size of 2cm or less. Gypsum of 98.21% grade was recovered with 99.0% yield from under screenings of 325mesh wet screening which followed by the dehydration-hydration process performed in the conditions of dehydration rate of 80%, hydration concentration of 15%, agitation speed of 300rpm, crushing size of 2cm or less. Subsequently, Plate-like crystalline gypsum of 151㎛ size and the grade of 99.49% with the Yield of 98.0% from the upper screenings of 270mesh wet screening carried out after the re-crystallization of the recovered gypsum needle slurry.

Introduction

In 2000, Japan's production of plaster boards amounted to 555.6Mm^2 (approximately 4.86 million tons). Waste plaster boards are usually the by-products of the manufacturing and distribution processes. They are often found at new construction sites and during the tearing down of old buildings. The total annual volume of these waste plaster boards is estimated to be around 2 million tons.[1),2),3)] This volume is likely to face explosive growth in the near future because the buildings built during the 1970s - when the use of plaster boards in construction spread - are now starting to be reconstructed and renovated. In addition, since June 1999, in accordance with the newly enacted regulations on processing of disposed materials and wastes, plaster boards are now classified as materials that need landfill of controlled type. In the past, they were considered as safety disposal materials. The key implication here is that the cost of disposing of plaster boards is likely to increase. Also, a bigger problem is lack of landfill.

Amidst this changing social atmosphere, numerous researches on recycling and re-using of waste plaster boards were conducted.[4),5),6)] One of the methods being studied is simply crushing and screening the board to remove impurities, which in turn is used as ingredient for the manufacture of plaster boards or gypsum brick. Other methods are the use of recovered gypsum powder as raw material of gypsum plaster by mixing it with general calcined gypsum or as raw material of cement after calcinations. 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%) to increase the recycling purpose of waste plaster board. However, the concentration of organic matters in recovered gypsum from simple crushing and screening method is 0.5-2.5% (mainly reliant on the size of mesh), the figure is too high for its use as a raw material for cement in addition to the size of recovered gypsum, 10㎛ or less. As a raw material for plaster board, the size of gypsum needs to be about 100㎛ . For this reasons, the mixing rate of recovered gypsum with virgin gypsum is restricted to less than 5%. Therefore, the development of technology is a prerequisite in increasing the quality of recovered gypsum and yield which will in turn lead to more recycling of waste plaster boards.

This study mainly leveraged the crystallographical characteristics of calcined gypsum and gypsum, and controlled the size of gypsum preferentially. Impurities were removed through wet screening. The influence of dehydrating condition, hydrating condition on the yield, and grade of recovered gypsum in wet screening were mainly discussed.

Experiment

The leading local plaster board manufacturers, company A and company B, provided the samples collected independently. Sample A is a crushed only waste plaster board less than 2 cm provided by company A, and sample B is the powder that has a low content of paper obtained by crushing and dry screening , provided by company B.
Analytical tools such as PSA, XRF, XRD, TG-DTA, and others were used. Particle size was

analyzed by SYMPATEC HELOS particle size analyzer. For XRF, Philips PW-2404 was used; RINT 2500V for XRD; and RIGAKU TG8120 for TG-DTA.

Analysis of the organic matter's content was conducted in a high temperate environment of 100 ℃ , using 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 according to the concentration of water- soluble starch and polyvinyl alcohol (PVA), and the average value 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 screening was calculated as follows:

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

Where, Y_G is yield of gypsum (%), U_G is gypsum in under screenings (g) and O_G is gypsum in upper screenings (g).

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

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

Where D is dehydration rate (%), W_{45} is weight of sample dried in 45 ℃ for 24 hours (g), W_n is weight after dehydration (g), G is theoretical rate of crystalline water within gypsum (0.209), I: partial rate of gypsum within samples.

Hydration concentration was calculated based on the weight of samples before the dehydration, and hydration temperature was set for room temperature (16～21 ℃) with hydration time set for 30 minutes, and a 1×5-cm impeller with two wings (twist of 15 ℃) was used.

The composition of waste plaster boards is analyzed based on JIS specifications and processed according to the analysis flow shown in Fig.1. A 10g sample crushed to less than 1 cm is accurately weighed up to 0.1 mg. The content of hygroscopic water was calculated from the weight loss during drying for 24 hours at 45 ℃. Then the sample was completely dehydrated for 2 hours under 250 ℃, and the calcium sulfate contained in the sample was dissolved with 5ℓ distilled water. The soluble material 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 in JIS R 9101. The contents of soluble organic material were measured with JIS K 0102-17 method. Insoluble materials from the above-mentioned dissolution reaction were washed and dried, and then weighed and heated for over 2 hours under 550 ℃ of oxidation condition. In this ignition, the contents of the insoluble inorganic material were calculated from the weight of ash and the insoluble organic material were considered as ignition loss.

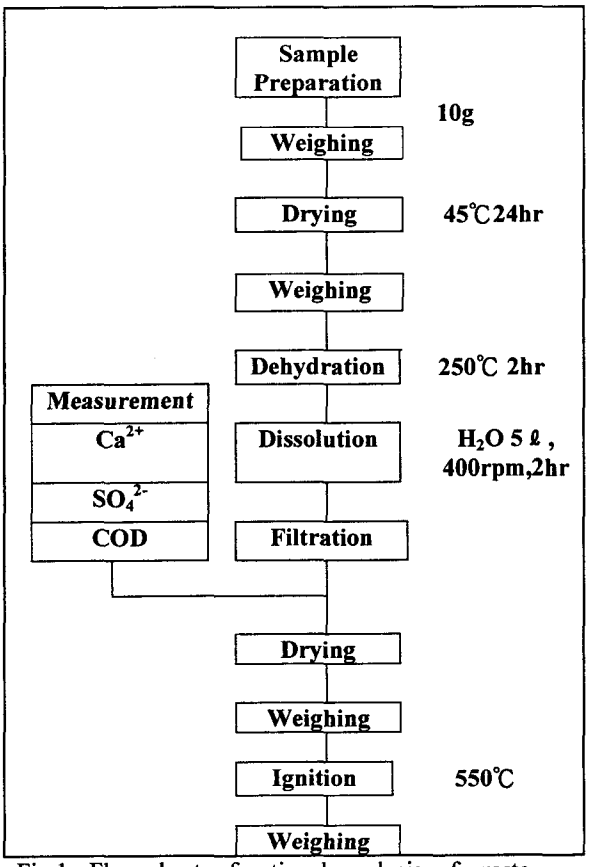


Fig.1. Flow-sheet of rational analysis of waste plaster board

Results and Discussion

Constituent contents of sample A and sample B were analyzed (see Fig. 1 for the process and Table 1 for the results). From the results, we can see that Sample A contains many insoluble organic materials, composed mainly of paper, hygroscopic water, and show a low content of gypsum, about 90%. Sample B contained relatively many insoluble inorganic materials, at 3.7%. The contents of total organic materials, including paper, in both samples were relatively high at 1.1% or

more. This means it would be difficult to use as is the samples as raw material for cements or plaster boards.

The results of the Iodostarch reaction conducted to confirm the water soluble starch ' s state of distribution in waste plaster board, a material generally used as an adhesive for plaster boards, are shown on Fig.2. Photo A of Fig.2 indicates that the 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 also existed in dense aggregation within the about 10㎛ needle (Fig.2-B). The paper, the majorities in insoluble organic materials, was corrugated paper, made of 500㎛ or more fiber. And the isolated fiber(from paper or not) has the length of 100㎛ or more (Fig.2-C). Unlike gypsum particles and insoluble organic materials, the particle size and composition of inorganic materials showed different results in sample A and sample B. Inorganic impurities in sample A were 30～300㎛ particles, mostly based on massive $CaCO_3$, and in sample B, 50～5000㎛ particles, mainly composed of massive SiO_2 (Fig.2-D).

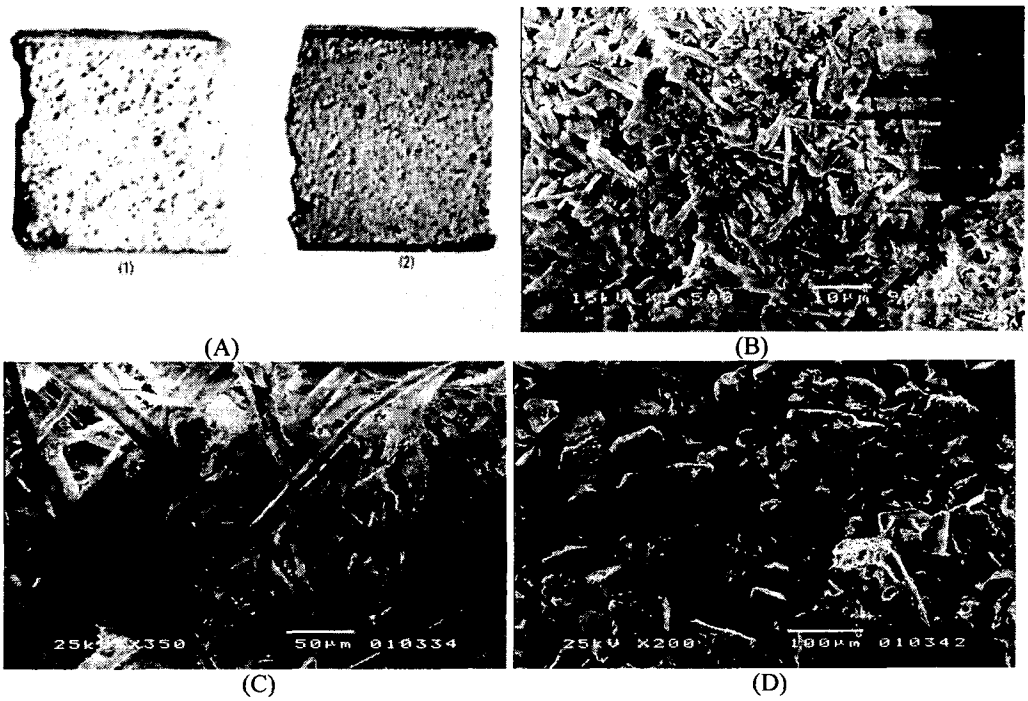


Fig.2. Photograph of waste plaster board and Scanning Electron Micrographs of the constituent parts
(A) Waste plaster board slices of before(1) and after(2) Iodostarch reaction
(B)Gypsum agglomerate (C)Insoluble organic impurity (D) Insoluble inorganic impurity

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

In this study, gypsum in crushed waste plaster board was dehydrated in air with the progress of ①→ ②→ ③ (Fig.3) and disintegrated in fine gypsum needle by hydration of ❸→ (2). This fine gypsum needle can be easily recovered by general fractionation method, e.g., wet screening. For more

refining of recovered gypsum, the fine gypsum needle was dehydrated again within water (⑥) and re-crystallized to more granular particle through hydration ❻.

On the TG-DTA curve (Fig. 4), sample A and sample B showed a typical dehydration pattern of gypsum that had an endothermic peak at 120℃ ~ 140℃. Sample A had more weight loss and was more endothermic than sample B mainly because of the influence of hygroscopic water. On the other hand, the first and second endothermic peaks are overlapping influenced by impurities and heating condition.

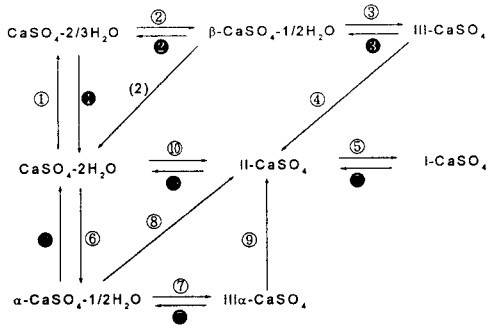


Fig.3. Phase Transition of Gypsum in Various Conditions.

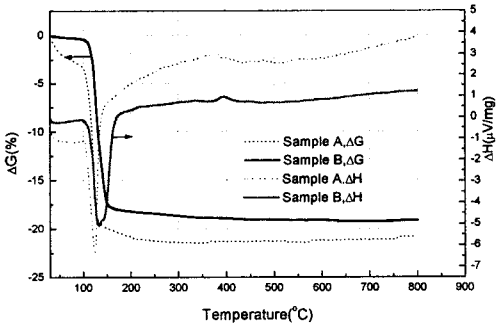
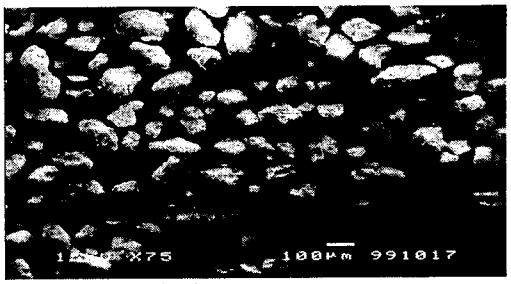
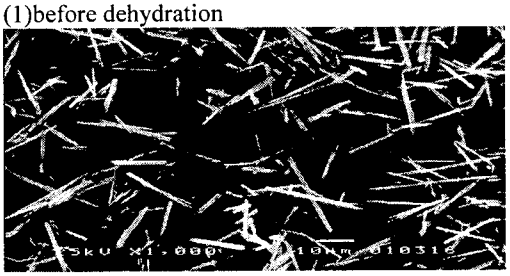


Fig.4. TG-DTA curves of crushed waste plaster board.

Figs.5 and 6 show respectively the changes of shape and size distribution before and after the dehydration-hydration reaction. This figures show that the 85.69㎛ (mean size) massive gypsum agglomerates had converted into 5.62㎛ isolated gypsum needle during the dehydration after dehydration.



(1)before dehydration



(2)after hydration

Fig.5.Scanning Electron Micrographs of recovered gypsum before and after Dehydration-Hydration Reaction.

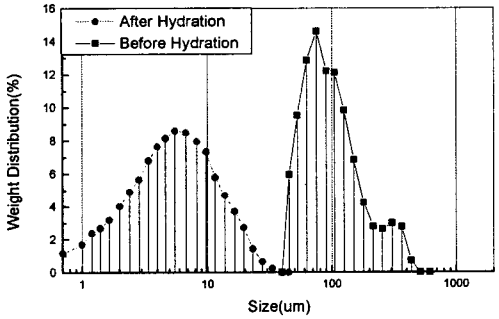


Fig.6.Particle Size Distribution of recovered gypsum before and after Dehydration-Hydration Reaction.

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℃, hydration time of 30 minutes, hydration concentration of 10%, agitation speed of 300 rpm, crushing size of 2 cm. Figs.7 ~ 10 show the results of each experiment.

From Fig.7, it can be seen that there were virtually no changes in yield of gypsum when the dehydration rate was less than 40%. However, when the rate was greater than that, the yield

increased explosively as the rate of dehydration increased. When the dehydration rate reached 75%, the yield increased to a peak of 98%. The upper screenings, in the case of low yield, contained many gypsum agglomerates. This result means 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.8 shows that when hydration concentration was less than 15%, the yield of gypsum was stable at 97 ~ 100%. However, the yield started to decrease at 20% concentration and even decreased significantly to 95%, at 30% concentration. Many massive particles of gypsum needles were also observed on the surface of gypsum agglomerate, from upper screenings of 325-mesh wet screening after hydration in 20% or more concentration.

Fig.8 shows the effect of agitation during hydration on the yield of gypsum in 325 mesh wet screening after dehydration-hydration reaction. The yield of gypsum was 98% or more at an agitation speed of 250 rpm or more. The polycrystalline gypsum grown up radially was also observed in the agitation speed below 250 rpm. In this condition, the yield of gypsum decreased. 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.10 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 plaster board were cut in regular squares. The yield of gypsum turned from bad to worse as the cutting size grew bigger by degrees. In the case of samples which were 4 cm or more, many polycrystalline gypsums were also observed from the upper screenings. These particle were often seen on the inner surface of the paper. This occurrence can be explained, thus: in the disintegration system that has a mechanism of Dissolution of dehydrated gypsum-Dispersion-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, hydration concentration of 5 ~ 20%, and agitation speed of 250 rpm or more.

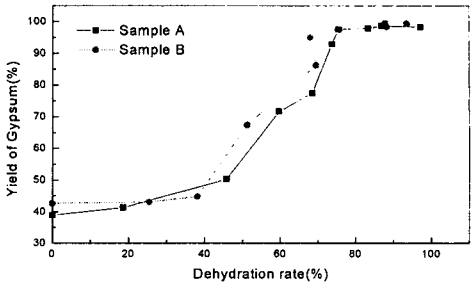


Fig.7. Relationship between dehydrtion rate and yield ofgypsum in 45μm under size

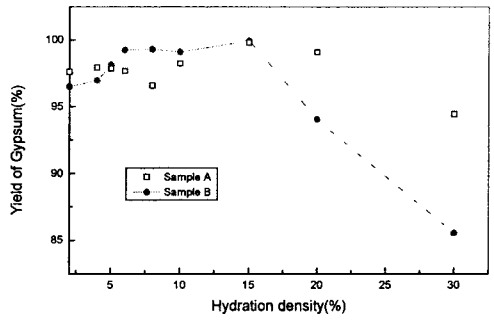


Fig.8. Effect of hydration density on yield of gypsum in 325 mesh wet screening after dehydretion-hydration reaction

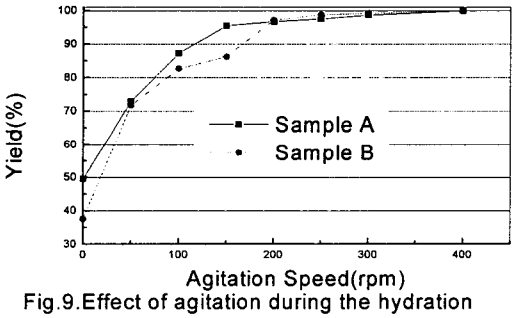


Fig.9.Effect of agitation during the hydration on the yield of gypsum

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%, hydration concentration of 15%, and agitation speed of 300 rpm. Table 2 shows the separation results; A yield of gypsum from sample A was 98.7%, with a grade of 98.98% and that of sample B was 99%, with a grade of 98.21%.

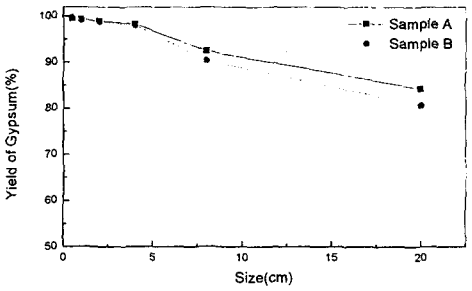


Fig.10.Effect of Crushed board size on the Yield of gypsum

However, the recovered gypsum had a size of about 10㎛ and contained about 0.2% 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 grow 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.. Especially, many additives are used and it makes the process costly. However, in this study, Na_2SO_4 is the only additive used in atmospheric pressure, considering simplification and cost of process. During the process, within 15-30 minutes after the temperature of slurry reached 95 ~ 98 ℃, the dehydrating temperature, the slurry's viscosity increased drastically with gelation. And then the viscosity returned to its original state in 30-60 minutes. The origin of gelation has deduced that it is caused by 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 finished in 30 minutes after reaching 95 ~ 98 ℃. After this 60 minutes reaction, 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, slurry's original color, was no longer seen. This could mean that the small quantities of dark brown impurity became visible due to the increase of transmissivity according to the crystal growth of gypsum.

Fig. 11 shows the changes in particle size distribution of recovered gypsum slurry before and after the crystallization process, and that the 5.6㎛ gypsum was grown to about 150㎛. Fig. 12 and Table 3 show the results of 270-mesh wet screening and shape of recovered gypsum, respectively. As the results indicate, about 150㎛ crystalline gypsum with 98.4% yield and 99.54% grade can be obtained by crystallization and screening process.

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

Constituent / Sample	Content of 45㎛ 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	0.19	99.0

Table 3. Results of 270 mesh wet screening after re-crystallization process

Constituent / Sample	Content of 53㎛ 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

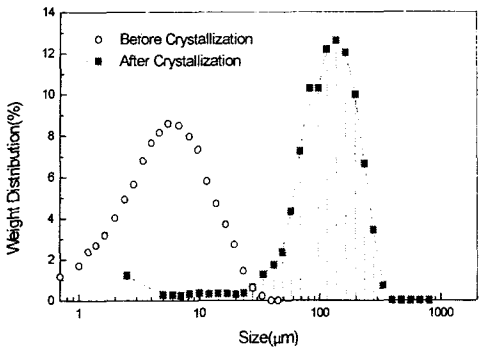


Fig.11. Particle size distribution of recovered gypsum before and after re-crystallization process

Fig.12. Scanning Electron Micrographs of re-crystallized gypsum

Conclusion

It can be said that high-grade gypsum that scarcely has limit in uses can be recovered with high efficiency from waste plaster board using a combination of dehydration-hydration-screening process and recrystallization-screening process.

We could recover gypsum with the yield of 98.7 ~99.0% and the grade of 98.2 ~99.0% from waste plaster board by the 325 mesh wet screening follows dehydration-hydration proceeded in the optimum condition; crushing size of board under 2 cm, dehydration rate of 80%, hydration concentration of 15%, and agitation speed of 300 rpm.

Subsequently, plate-like crystalline gypsum of 151 ㎛ was obtained with a grade of 99.49% and a yield of 98.0% from 270-mesh wet upper screenings, resulted after re-crystallization of the recovered gypsum needle slurry.

References

1)Shin-ichiro Ohishi, Reusing Study of Plaster-board Waste from Construction Site, Inorganic Materials, Vol.1, No.252, 364-369, 1994

2)Mitsuhiro Ohta, The Present Situation of Gypsum Board Waste Recycling, Inorganic Materials, Vol.4, Sep.464-468,1997

3)Tamotsu Yasue, Challenge to recycle society by resources recycling of waste gypsum material, Journal of the Society of Inorganic Materials, Japan, No.7, 492-502, 2000

4)Tadao Koizumi, Recycling Waste Gypsum Board, Gypsum & Lime , No.234, 435-438, 1991

5)Yoshiyuki Kojima, Tamotsu Yasue, Yasuo Arai, Preparation of Hardened Gypsum Body from Waste Gypsum Board, Inorganic Materials, Vol.4, Sep.415-422,1997

6) Yoshiyuki Kojima, Tamotsu Yasue, Yasuo Arai, Preparation of Gypsum Block from Waste Gypsum Board, Journal of the Society of Inorganic Materials, Japan, No.7, 460-466, 2000

7)Society of Inorganic Materials of Japan, Hand book of Cements, Gypsum and Lime, Gihoudou Publishing Company, 141-143, 1996