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

Preparation of Calcium Sulfate Hemihydrate Using Stainless Refinery Sludge and Waste Sulfuric Acid

Hee Tai Eun[1], Ji Whan Ahn[1], Hwan Kim[2], Jang Su Kim[3] and Ghee Woong Sung[3]
[1] Institute of Geoscience & Mineral Resources, Taejon, 305-350, Korea
[2] School of Materials Science and Eng., Seoul national University, Seoul, 151-742, Korea
[3] Pohang Iron & Steel Co., Pohang, 790-785, Korea

In this study, calcium sulfate(gypsum) powder was obtained using waste sulfuric acid and stainless refinery sludge by-produced from chemical reagent and the iron industry, by the neutralization of waste sulfuric acid. As variables for the experiment, the mole ratio of the H_2SO_4 : $Ca(OH)_2$, the pH, the reaction temperature and time, the amount of catalyst were used. The crystal shape and microstructure of obtained powder were observed by XRD and SEM, and the thermal property was investigated by DTA.

As the NaCl is added 0~20wt% as a catalyst to the H_2SO_4-$Ca(OH)_2$ system, it can be found that the crystal shape goes through the processes as follows ; gypsum dihydrat→gypsum hemihydrate+gypsum dihydrate→gypsum hemihydrate. And gypsum hemihydrate is β-type as the result of DTA.

As waste sulfuric acid and stainless refinery sludge were used, the pH of reacted solution (which was 0.8) was rapidly raised up to 8~9 by the addition of stainless sludge and gypsum dihydrate was produced as a by-product. Therefore, it was found that stainless refinery sludge is sufficiently applicable for the neutralization of waste sulfuric acid.

Keywords : Gypsum powder, stainless refinery sludge, waste sulfuric acid, catalyzer

1. Introduction

With the facilitation of industrial activities and economic growth, discharged waste are more and more increased and becomes complicated in quality. Though these wastes are managed in various ways, they are being used for the reclamation of the foreshore and the residential land development in the end. However, it became difficult to secure waste landfills because of the reduction in the landfill around cities and the prevention of environmental pollution, and thus, the issue of its recycling are arousing people's interest[1].

Therefore, the waste of inorganic industry which is represented by slag, waste acid, waste alkali, and each kind of slurry and dust, is enormous in the discharged amount and contains various kinds of toxic substances, and its treatment and disposal are beginning to constitute a great public problem. Particularly, for the treatment of waste acid which has strong toxicity, neutralization should be accompanied. For this, a large amount of lime is mainly used and gypsum is discharged as a by-product.

In general, gypsum which has the chemical constitution of calcium sulfate has been widely known as construction material from old times, and fundamental investigations like polymorphism, crystal structure, crystal change, etc. have been made so far[2-5]. Gypsum is being used for building materials like a plaster or a boards, a reinforcing agents using a fibrous gypsum, a cement solidification retardant, a inorganic filler of paper, rubber and plastic, a casting molds of ceramics, a medical use and a soil stabilizer. In recent years, the phosphorus gypsum, the desulfurization gypsum, and the titanic gypsum are being discharged in large quantities as industrial waste. Studies to recycle them as a raw materials for the industrial use by nonhazardous treatment, and some of them are being put to practical use.

In this study, waste sulfuric acid was neutralized with stainless refinery sludge containing a large amount of CaO from iron industry, and the properties of gypsum formed during the process were investigated. Also, Gypsum was prepared using sulfuric acid of pure reagent and calcium hydroxide, and the experimental variables which have an effect on the preparation of gypsum were examined. They were applied to the formation of gypsum using waste acid and stainless refinery sludge. The changes in the crystal shape and the microstructure of gypsum which were made according to the H_2SO_4:CaO ratio, the reaction temperature, the pH, the amounts of catalyst, were found by XRD, SEM and the investigation of thermal properties.

2. Experimental Methods

2.1 Preparation of Gypsum

For the preparation of gypsum using chemical reagent, Sulfuric acid (H_2SO_4, 95%, Oriental Co.) and Calcium hydroxide ($Ca(OH)_2$, 95%, Sigma Chemical) were used as a starting materials and Sodium chloride (NaCl. 99.5%, DAEJONG Co.) was applied as a catalyst. Waste sulfuric acid and stainless refinery sludge were all from POSCO.

After a pH electrode, a thermometer and a stirrer were installed in 4-neck flask, the solution of sulfuric acid with 0.3M concentration was stirred at 100 ℃ of reaction temperature at the speed of 400rpm for 10 ~ 20 minutes. At this point, the pH of the solution was around 0.7~0.8. $Ca(OH)_2$ slurry was added to the mixed solution of H_2SO_4/NaCl, about 20 minutes after NaCl had been added 0~20wt% as a catalyst. The reaction solution was separated to a solid and a liquid through filtering and the solid was dried in a 100℃ oven for 24 hours. The same method was applied to the experiment using a waste sulfuric acid solution and stainless refinery sludge.

2.2 Measurement

The crystal shape of the prepared gypsum was identified with the X-ray diffraction analyzer (X'pert, Philips Co.). The measuring conditions were CuK α, 40kV, 40mA, and the scanning angle of 10～80° [2Θ]. The thermal properties of gypsum were analyzed using the DT/TGA (SDT 1500, TA Instrument), at the increasing temperature speed of 5℃/min in the air, up to 700℃ at room temperature. The microstructures of the gypsum prepared was observed using the scanning electron microscope (JSM 6400, JEOL Co.) after the Au coating.

3. Results And Consideration

3.1 Preparation of Gypsum Using Chemical Reagent

After changing the mole ratio of H_2SO_4 : $Ca(OH)_2$ up to 1:0.4～1:1.2 and reacting it at 100℃ of reaction temperature, the main peak of gypsum hemihydrate was observed at 31.7° , 29.7° , 14.7° , 25.6° , 49.2° of 2Θ.

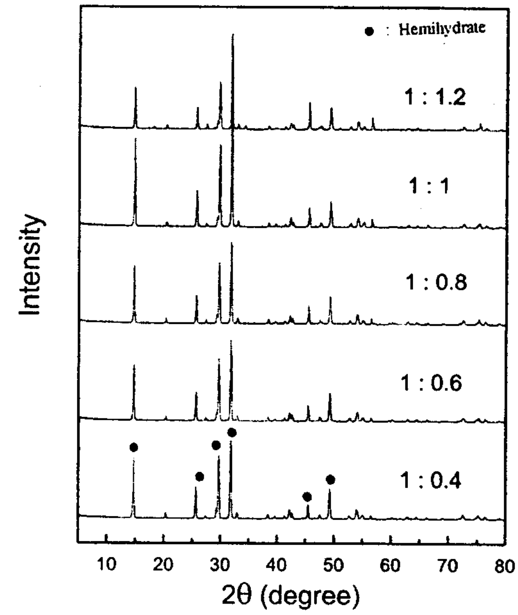
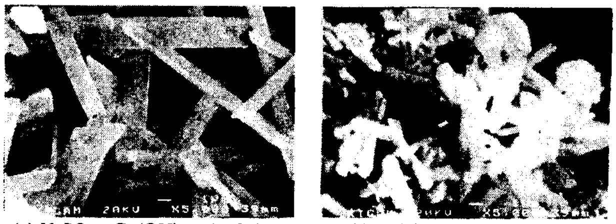


Fig. 1 XRD patterns of gypsum powders obtained from chemical reagent H_2SO_4 and $Ca(OH)_2$.

That is, it can be found that gypsum hemihydrate is produced though the mole ratio of H_2SO_4: $Ca(OH)_2$ is changed. On the other hand, according to SEM analysis (Fig. 2), fibrous gypsum with large aspect ratio was observed if the mole ratio of H_2SO_4: $Ca(OH)_2$ was lower, while the aspect ratio was reduced and plate shape gypsum was observed as that of H_2SO_4 : $Ca(OH)_2$ was raised, which is estimated to be caused by excessive CaO.



(a) H_2SO_4 : $Ca(OH)_2$ = 1 : 0.4 (b) H_2SO_4 : $Ca(OH)_2$ = 1 : 1.2

Fig. 2 SEM photographs of gypsum powders obtained from chemical reagent H_2SO_4 and $Ca(OH)_2$ with various mole ratio at 100℃.

Fig. 3 shows the result of X-ray diffraction analysis of the gypsum prepared by changing the amounts of NaCl as a catalyst, when the mole ratio of H_2SO_4 and $Ca(OH)_2$ is 1:1 in chemical reagent. If the NaCl is not added, the typical peak in gypsum dihyrate is shown when 2Θ is 11.6° , 23.4° , 20.7° , 29.1° , 29.7° . As the NaCl is added 5wt%, the peak becomes to have a perfectly different shape. 2Θ also shows such a value of gypsum hemihydrate as 14.7° , 29.7° , 31.9° 25.6° , but it is estimated that there exists some gypsum dihyrate. However, judging from the fact that the main peaks get to have the order of 29.3° , 31.9° and 14.7° since the NaCl has been added 10wt%, it is estimated that the change into perfect gypsum hemihydrate occurs.

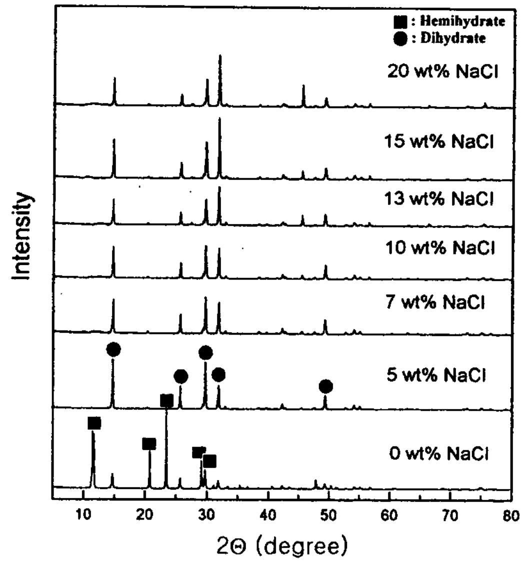


Fig. 3 XRD patterns of gypsum powders obtained from chemical reagent H_2SO_4 and $Ca(OH)_2$ at various amounts of NaCl.

In general, Gypsum hemihydrate has polymorphism of α and β. α-type gypsum hemihydrate is identified by the exothermic peak directly after the dehydration of gypsum hemihydrate, by the differential thermal analysis, β-type gypsum hemihyrate is distinguished by the exothermic peak around 330～340℃.

Fig. 4 shows the result of thermal analysis of the gypsum prepared by changing the amount of NaCl as a catalyst, when the mole ratio of H_2SO_4 and $Ca(OH)_2$ is 1:1 in chemical reagent. As the result of differential thermal analysis, if the NaCl is not added, two distinct endothermic peaks are observed around 100~150℃, which is assumed to be a typical result of the thermal analysis of gypsum dihydrate. Judging from the high endothermic peak around 150℃ and the exothermic peak around 340℃ with the addition of NaCl, it can be viewed that it goes forward into gypsum hemihydrate. Furthermore, it can be found that β-type gypsum hemihydrate is formed, judging from the fact that the exothermic peak cannot be observed any more immediately after the dehydration at 150℃. And, it is estimated that the endothermic peak at 640℃ shows the transfer of anhydrous gypsum by dehydration.

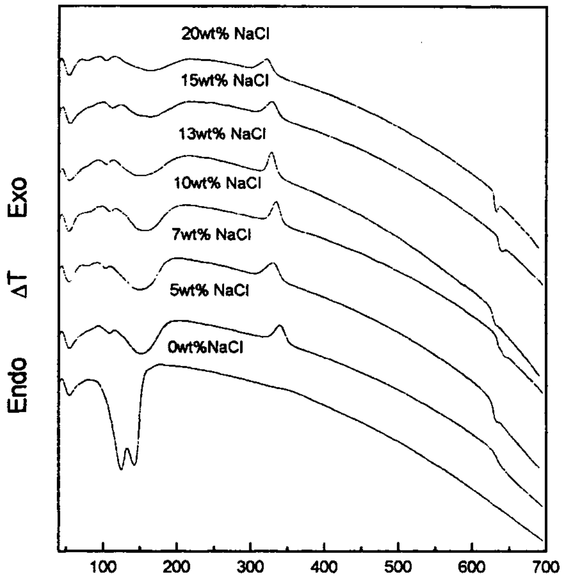
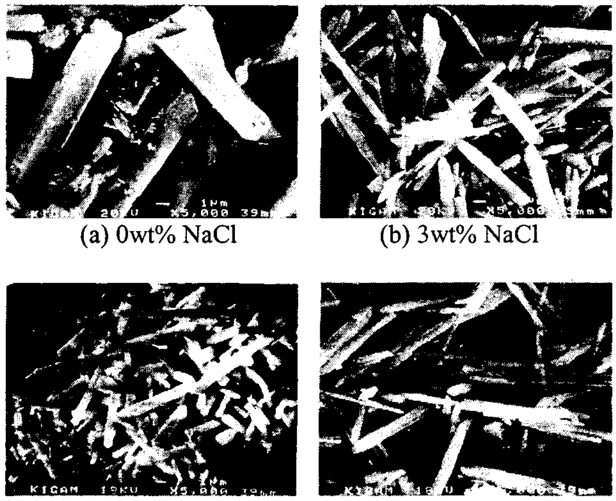


Fig. 4 DTA curves of gypsum powders obtained from chemical reagent H_2SO_4 and $Ca(OH)_2$ at various amounts of NaCl.

Fig. 5 shows the result of SEM analysis of the gypsum prepared by changing the amount of NaCl as a catalyst, when the mole ratio of H_2SO_4 and $Ca(OH)_2$ is 1:1 in chemical reagent. If the NaCl is not added, the fibrous gypsum with 2~4 of a aspect ratio is observed and it shows smooth surface. If the NaCl is added 5wt%, the fine fibrous gypsum with 1㎛ of diameter is prepared, whose aspect ratio is within the range of 5~20 or so. If the diameter is over 1㎛ and the aspect ratio is over 20, it is designated the whisker. It can be known that if the NaCl is added about 5wt%, the whisker gypsum is made. The whisker gypsum was observed even when the amount of NaCl is increased 10 and 20wt%. It is reported that the reason why gypsum grows into a particular fibrous shape as the amount of NaCl increases like this, is that Cl^- ions in the solution play the role of making gypsum grow toward a specific direction[3].



(a) 0wt% NaCl (b) 3wt% NaCl

(c) 10wt% NaCl (d) 20wt% NaCl

Fig. 5 SEM photographs of gypsum powders obtained from chemical reagent H_2SO_4 and $Ca(OH)_2$ with various NaCl contents at 100℃.

3.2 Preparation of Gypsum Using Waste Sulfuric Acid And Stainless Refinery Sludge

Waste sulfuric acid and stainless refinery sludge which come from the iron industry contain various kinds of toxic materials. Lime was mainly used for the neutralization of waste sulfuric acid to date. In this study, however, the neutralization of waste sulfuric acid and the properties of gypsum accompanied by it were examined using stainless refinery sludge where CaO is included in great quantities.

Table 1 and 2 respectively show the result of chemical analysis of waste sulfuric acid and stainless refinery sludge from the iron industry. As the result of the XRF analysis of stainless refinery sludge, it is found that CaO, SiO_2, MgO and Al_2O_3 is included 55%, 26%, 5.6% and 4.4%, respectively, and a high CaO content will contribute to the neutralization of waste sulfuric acid.

The neutralizing effect by the addition of stainless refinery sludge to waste sulfuric acid was estimated by observing the change in the pH of the reacted solution. The pH of waste sulfuric acid was around 0.7 or 0.8. If the stainless refinery sludge was added at an mole ratio without the addition of NaCl, the solution shows sudden reaction within 5 minutes after stainless refinery sludge was added. The pH of the solution was rapidly raised up to 8.0 or so, and after 10 minutes, the pH was little changed. After 30 minutes, it was thought that the reaction was completed, judging from the fact that the pH was no more changed. Meanwhile, if the NaCl is added as a catalyst,

The pH of the solution is reduced from 0.8 to 0.3~0.2 according to the added amount. By the addition of stainless refinery sludge, the pH of the solution is also rapidly raised, and after 30 minutes, it shows no more change.

Table 1 XRF result of stainless refining sludge in POSCO. (wt.%)

Elements	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	ZnO	TiO_2	PbO	CuO	Cr_2O_3	Total	LOI	Cl (ppm)
Amount	26.0	4.36	1.77	55.0	5.61	0.11	0.04	0.04	0.07	0.47	-	0.002	1.93	108.12	4.33	95.82

Table 2 ICP result of waste sulfuric acid solution (ppm)

Elements	B	Cr	Fe	Mg	Zn	Hg
Amount	70	35	50000	50	40	200

Fig. 6 shows the result of X-ray diffraction analysis when waste sulfuric acid and stainless refinery sludge are used and the NaCl is added 0 and 15wt% as a catalyst. If a catalyst is not added, the characteristic peak of gypsum dihydrate is clearly observed, while a quite different peak from that of gypsum dihydrate is observed if the NaCl is added 15wt%. It is estimated that's because the addition of NaCl facilitated the change into gypsum hemihydrate.

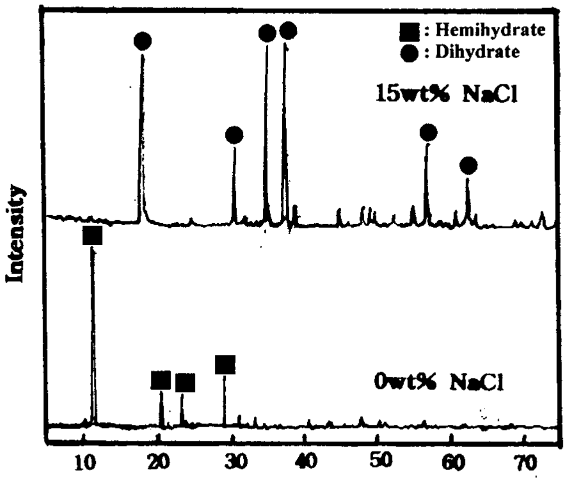


Fig. 6 XRD patterns of gypsum powders obtained from waste sulfuric acid and stainless refining sludge.

To decide whether the prepared gypsum hemihydrate is α or β, the differential thermal analysis is made, and its result is shown in Fig. 7. Judging from a weak endothermic peak around 200℃ and a strong exothermic peak around 310℃, it can be known that the gypsum prepared with waste sulfuric acid and stainless refinery sludge is also β-type gypsum hemihydrate.

Therefore, in this study, the change in the crystal shape of gypsum as well as the recycling of waste resources could be made, by using not lime but stainless refinery sludge to neutralize waste sulfuric acid. This by-produced gypsum was estimated to be sufficiently applicable for the cement industry and as soil stabilizer.

4. Conclusions

In this study, gypsum was prepared using chemical reagent, waste sulfuric acid and stainless refinery sludge, and the change in the shape of gypsum was induced by the addition of NaCl as a catalyst.

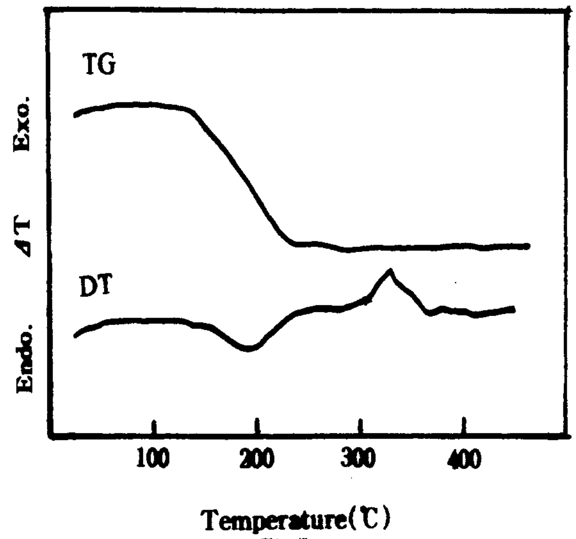


Fig. 7 DT/TGA curves of gypsum powders obtained from waste sulfuric acid and stainless refining sludge.

The results are as follows

1. If pure reagent is used, Gypsum hemihydrate is prepared irrespective of the change in the mole ratio of H_2SO_4 and $Ca(OH)_2$. As the amount of $Ca(OH)_2$ increases, particles become to have irregular size.

2. As the NaCl is added 0~20wt% as a catalyst to the H_2SO_4-$Ca(OH)_2$ of chemical reagent, the crystal shape of gypsum goes through the process as follows ; gypsum dihydrate o gypsum hemihydrate + gypsum dihydrate o gypsum hemihydrate, and as the result of differential thermal analysis, gypsum hemihydrate was identified as β-type.

3. If waste sulfuric acid and stainless refinery sludge are used, the pH of the reacted solution is rapidly raised by the addition of stainless refinery sludge from 0.8 to 8~9. Therefore, it can be found that stainless refinery sludge is sufficiently applicable for the neutralization of waste sulfuric acid.

4. Gypsum dihydrate is by-produced by the reaction of waste sulfuric acid and stainless refinery sludge, and is changed into β-type gypsum hemihydrate if the NaCl is added 15wt% as a catalyst.

References

[1] S. AOKI, *Gypsum & Lime,* 206, 51 (1987).

[2] Y. KUDOU and A. YAMAZAKI, G*ypsum & Lime*, 241, 35 (1992).

[3] T. YASUE, Y. KOJIMA, Y. KISHIMOTO and Y. ARAI, *Gypsum & Lime*, 239, 12 (1992).

[4] M. J. Ridge. Roy. *Aust. Chem. Ind*., 39, 55 (1972).

[5] Y. ARAI, *Gypsum & Lime*, 167, 9 (1980).