Journal of Korean Association of Crystal Growth
Vol. 7, No. 4 (1997) 673-680

Crystal growth of gypsum by neutralization reaction of waste sulphuric acid using sludge and dust in Pohang Iron & Steel plant

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포항제철(주) 슬러지와 Dust를 이용한 폐황산 중화반응에서 얻어진 석고의 결정성장연구

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Abstract NaOH, Na_2CO_3, CaO, $Ca(OH)_2$ and $CaCO_3$ are widely used counteractives for neoutralizing the waste sulphuric acid produced during the metal surface treatment process and/or the metal refining process. To reduce the tremendous expenses for the neutralization treatment of the waste sulphuric acid, the sludge from calcination plant and the stainless refining dust in POSCO (Pohang Iron & Steel co. Ltd.) was utilized.

For the sludge, it will be effective to use calcined and then hydrated sludge in strong acid region ($pH<2$) and to use the sludge itself in weak acid region ($pH>2$). The gypsum, the by-product of this treatment, was tested to fit the industrial standard of gypsum, so it is expected that it will solve the lack of gypsum supply. For the stainless refining dust, the phase and the morphology of produced gypsum from waste sulphuric acid neutralization was compared with those from pure sulphuric acid. Because of high reactivity and reaction temperature, $CaSO_4$ non-hydrate was obtained in pure sulphuric acid. But $CaSO_4$·dihydrate was obtained in waste sulphuric acid. It is also judged to be a good material for a counteractive of the waste sulphuric acid.

요 약 금속 표면 처리 공정 및 제련 공정 중에 발생하는 폐황산의 중화처리에는 NaOH, Na_2CO_3, CaO, $Ca(OH)_2$, $CaCO_3$ 등이 널리 사용되고 있다. 그러나, 이러한 중화제의 사용시 드는 높은 처리비용으로 인해, 본 연구에서는 포항제철(주)의 소성 공장으로부터 나오는 슬러지와 스테인레스 제조 공정에서 나오는 dust의 활용을 모색하였으며, 이 때 나오는 석고부산물의 결정 및 재활용 연구를 수행하였다. 본 연구 결과, 슬러지를 중화제로 사용할 경우 강산 영역($pH<2$)에서는 소성 후 수화시킨 것을 사용한 후 약산영역($pH>2$)에서 순수한 슬러지를 사용하여 중화시키는 방법이 효과적일 것으로 판단되었으며, 이 때 생성되는 석고 부산물의 화학 분석 결과는 석고원료 품질규격에 부합됨을 확인할 수 있어 이 제조법에 의한 석고원료 공급부족현상 해결에 도움을 줄 수 있을 것으로 기대된다. 또한, 스테인레스 제조 공정에서 나오는 dust를 이용해 순수한 황산 및 폐황산의 중화 과정에서 생성되는 석고의 상 및 형상을 비교한 결과, 순수한 황산의 경우 높은 반응성과 반응온도로 인해 구형의 응집체형 석고가 생성되고, 폐황산의 경우 순수한 황산에 비해 낮은 반응성으로 인해 휘스커형 석고가 생성됨을 전자현미경 사진으로부터 확인할 수 있었다.

폐황산과 dust와의 반응에서 생성되는 부산석고의 석출과정에서는 반응용액에서의 과포화도가 매우 중요한 역할을 하는 것으로 사료된다. 과포화도에 따라 석출되는 부산석고의 결정은 과포화도가 낮은 영역에서 대형 섬유상이 생성되며 반면 높은 영역에서는 미세입자의 응집체가 생성되었다. 즉 폐황산으로 반응시에는 폐기 dust 현탁액을 조금만 넣어주어도 낮은 과포화도 영역에 주로 있으며 이 때 대형 섬유상의 휘스커 형상이 생성됨을 알 수 있었다.

1. Introduction

Recently the increasing demand for gypsum boards makes the supply of raw materials unstable. To solve this problem, by-productive gypsum generated from the reaction of waste sulphuric acid and calcium carbonate has been considered as industrial uses [1]. This study presents the by-productive gypsum synthesis focused only on gypsum dihydrate synthesis and the reactivity between sulphuric acid and lime.

The waste acid generates from many industries, such as the metal surface treatment, the non-iron metal (such as copper, zinc, aluminum, titanium, nickel and mercury) refining, the plating treatment of copper with gold, patrol purification, the production of chemicals, etc. And its neutralization is a very serious problem.

The counteractives used for neutralizing waste acids are NaOH, Na_2CO_3, CaO, $Ca(OH)_2$ and $CaCO_3$. We should consider several factors, such as its solubility, difficulty of treatment, economic efficiency and removal of water for selecting a counteractive. NaOH has a large solubility and its neutralizing speed is high as well, but it is expensive. $CaCO_3$ has low solubility, so it is used in the form of fine powder or slurry. The stricter the environmental restriction becomes, the more we should consider effects of the neutralizing treatment for the process and the cost of production.

In this paper, we studied on the reactivity and neutralization characteristics of lime sludge and waste sulphuric acid, and the properties of reaction products.

2. Experimental Process

The starting materials were sludge and dust generated from the Pohang Iron & Steel Co. Ltd (POSCO, hereafter it is called POSCO). The sludge is produced from calcination plant and the dust from the by-raw material treatment process of stainless refining. Tremendous amount of waste sulphuric acid produced from POSCO by the 2-step neutralization method using the sludge and the dust from POSCO. Therefore, the sludge from calcination plant was used to elevate the value of pH up to 2 and the stainless refining dust to make the waste sulphuric acid neutral. Tables 1 and 2 presents chemical composition of the sludge from the calcination plant and that of the POSCO refining dust, respectively.

The sulphuric acid used in this experiment was the waste acid produced in the refining process of copper and zinc. For comparison, pure sulphuric acid was used after its pH was controlled to be the same as that of waste acid. Then, neutralization experiment was done using two different kinds of sludge from the POSCO and pure $CaCO_3$ (Kanto Chem. Co.,

Table 1

The chemical composition of POSCO calcination plant sludge (unit: %)

Element	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	Ig. loss	Water content
Content (%)	52.1	0.8	2.3	1.2	0.3	0.07	0.22	43.01	21.1

Table 2

The chemical composition of the by-product produced after the 1st neutralization experiment (unit: %)

Element	CaO	SO_3	Disbonded water	Bonded water	As	Cu	Fe	Pb	Zn	pH
Calcination plant sludge	31.7	42.3	15.38	16.44	0.19	0.14	0.32	0.01	0.03	6.3
Limestone	31.1	44.2	12.77	15.09	0.16	0.11	0.12	0.01	0.03	6.4

Extra-pure). Three different kinds of slurry were made with the above samples for acid neutralization. Each samples was calcined, hydrated in the water for 30 min and finally carbonated. The samples were mixed. With sulphuric acid of which the pH value was 0.1, and stirred the mixture.

3. Results and Discussion

3.1. The neutralization with calcination plant sludge and by-product properties

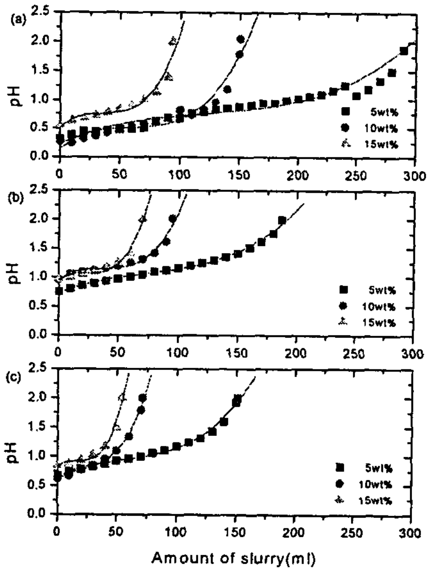

Fig. 1. Relation between pH and amount of slurry (a) slurry of the sludge from calcination plant, (b) slurry of the calcined and hydrated sludge from calcination plant, (c) slurry of pure $Ca(OH)_2$ (Sigma Chemical. co., 99 %).

3.1.1. pH change

Slurries were made from the sludge from calcination plant, the calcined and hydrated lime of the sludge, pure reagent $Ca(OH)_2$. The results of their neutralization ability are shown in Fig. 1. For the purpose of application of the 2-step neutralization, we examined the 1st step in which the pH value elevated up to 2, and found that when the pure $Ca(OH)_2$ was used the smallest amount of slurry was consumed, and also, that when the slurry of the sludge was used the largest amount was consumed. And the results obtained with the calcined and hydrated lime of the sludge was similar to that of pure reagent $Ca(OH)_2$. According to Fig. 1, pH changed very rapidly in all cases in the range of pH>1.5, because the change in pH is logarithmical. Therefore, it would be effective on neutralization to use the calcined and hydrated lime of the sludge in the pH range of <1.5 and the sludge itself after it.

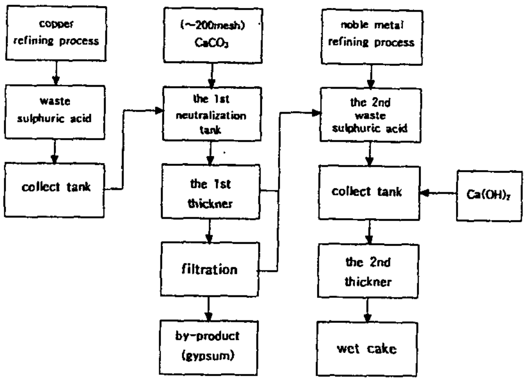

Fig. 2. The neutralization process of waste sulphuric acid.

3.1.2. *By-product properties*

The 1st and 2nd neutralization treatment were done on the waste sulphuric acid produced from copper and noble metal refining process. The treatment process is given in Fig. 2. The by-product produced from neutralization treatment with both natural limestone and calci-nation was gypsum which fits in with the usable standard of gypsum ($CaO<40$ %, $SO_3<38$ %).

The industrial hydrated lime is a widely used counteractive for the 2nd neutralization treatment, so the sludge calined in 1200℃ during 2 hrs and hydrated in water during 30 min was used. For the by-product, the contents of minor element is important, and the result of the chemical composition analysis is shown in Table 3. The contents of As, Cu, Zn are a bit high, but the results are similar to those of industiral powders. So, it is expected that the sludge replaces the expensive industrial powder.

3.2. *The neutralization with stainless re-fining dust and by-product properties*

3.2.1. *pH change*

The calcium carbonate produced by calcining, hydrating and carbonating POSCO refining dust was made slurry and added as the counteractive of the waste and pure sulphuric acid. There reactivity is shown in Fig. 3. In every case, the pure sulphuric acid was neutralized when 40 ml of the slurry was added, and the reaction was completed when 100 ml was added.

3.2.2. *By-product properties*

The studies on the solubility and the phase diagram of $CaSO_4$-H_2SO_4-H_2O system were reported [2-3], but the phase diagram would not be used as a reference for the pratical application because they didn't study the reaction time. The particle shape of $CaSO_4 \cdot 0.5H_2O$ depends on the supersaturation during precipitation reaction. The solubility of $CaCO_3$ in acid region is so high that the supersaturation is very high comparing with that of $CaSO_4 \cdot 0.5H_2O$. It was reported that in the low supersaturation region, large whisker-type $CaSO_4 \cdot 0.5H_2O$ was obtained, and that in the high supersaturation region, agglomeration-type $CaSO_4 \cdot 0.5H_2O$ of small particles was obtained [4-5]. From Fig.

Table 3
The chemical composition of the minor elements of by-product produced after the 2st neutralization experiment (unit: %)

Element	Cu	Cd	Zn	Fe	As	Hg	Pb	Zn	pH
Calcination plant sludge	0.4	0.1	1.9	0.1	1.8	0.1	7.4	0.03	6.3
Hydrated lime	0.3	0.1	1.5	0.1	1.0	0.1	11.4	0.03	6.4

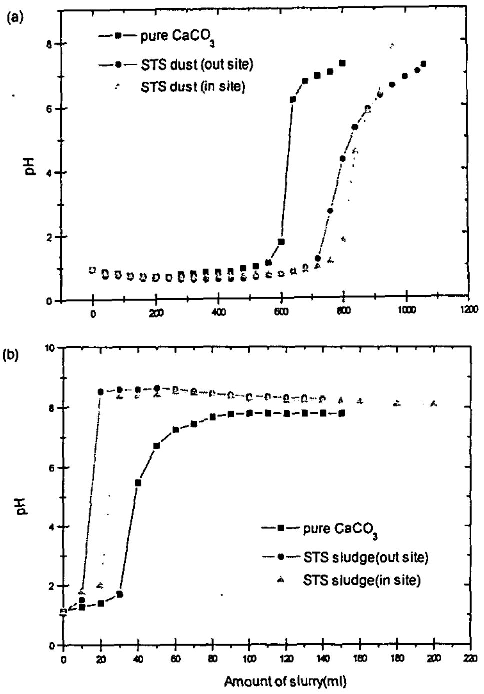

Fig. 3. Reation between pH and amount of slurry on formation of gypsum in sulphuric acidm (a) waste sulphuric acid, (b) pure sulphuric acid.

3(a), in case of pure sulphuric acid, large amount of slurry was needed to neutralize the acid, and it means that high supersaturation region was kept so long. By this reason, agglomeration-type $CaSO_4 \cdot 0.5H_2O$ like Fig. 4(a)~(c) was obtained. In case of waste sulphuric acid, a little amount of slurry neutralized it, and it means that low supersaturation region wasn't kept long. So large whisker-type $CaSO_4 \cdot 0.5H_2O$ was obtained like Fig. 4 (d)~(f) As shown in Fig. 5, the powder from the reaction with pure H_2SO_4 is an agglomerate of $CaSO_4$ non-hydrate, and the powder from the reaction with the

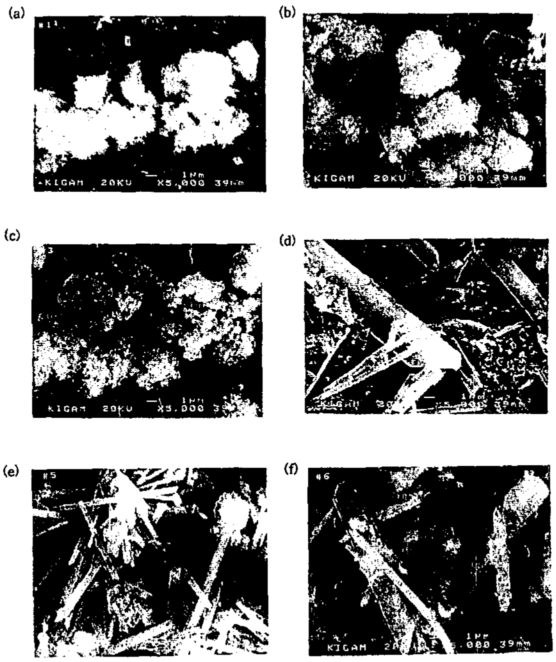

Fig. 4. Scanning electron micrographs of the gypsum formed from the reaction of $CaCO_3$ and H_2SO_4. (a), (b), (c):in pure H_2SO_4, (d), (e), (f):waste H_2SO_4, (a), (d): pure $CaCO_3$, (b), (e):STS sludge (out site), (c), (f):STS sludge (in site).

waste sulphuric acid is 'whisker-like crystal of $CaSO_4 \cdot 1/2\ H_2O$. The kind of the counteractive didn't have any effects on the morphology. The reasons why morphological change occured were that the reactivity of waste sulphuric acid is smaller than that of pure sulphuric acid, and that the reaction temperature didn't rise so much. -the reaction is exothermic. So, the dehydration of gypsum is not complete in the waste sulphuric acid. The XRD results from Figs. 5 and 6 shows that the peaks were from almost gypsum except minor $CaCO_3$. Thus, it was judged

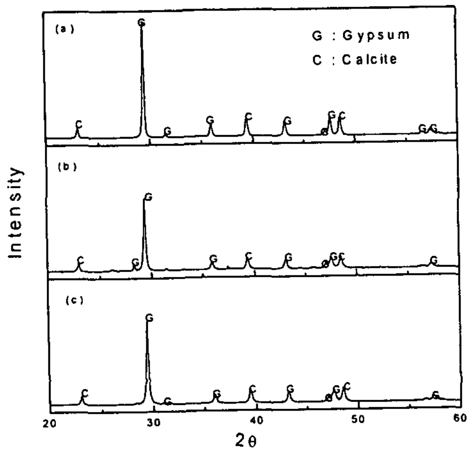

Fig. 5. X-ray diffraction of formed gypsum in pure H_2SO_4 (a) pure $CaCO_3$ (b) STS sludge (out site) (c) STS sludge (in site).

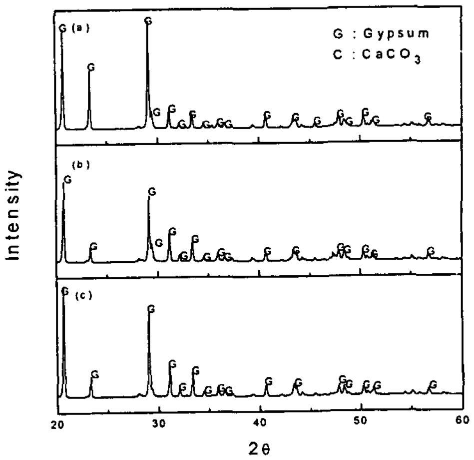

Fig. 6. X-ray diffraction of formed gypsum in waste H_2SO_4 (a) pure $CaCO_3$ (b) STS sludge (out site) (c) STS sludge (in site).

to manufacture $CaSO_4 \cdot 1/2$ hydrate in industrial condition using waste sulphuric acid and stainless refining acid. From our investigation, it was possible to synthesize $CaSO_4 \cdot 1/2\ H_2O$ and to neutralize the waste sulphuric acid using stainless refining dust.

Conclusions

The reactivity of the waste acid and the stainless refining dust and the synthesis of gypsum using this reaction were investigated. Both the sludge from the calcination plant and the stainless refining dust was tested to be good materials for neutralize treatment of waste sulphuric acid, and the quality of gypsum as by-product to fit the industrial standards. The particle shape of $CaSO_4 \cdot 0.5H_2O$ depends on the supersaturation during precipitation reaction. The solubility of $CaCO_3$ in acid region is so high that the supersaturation is very high comparing with that of $CaSO_4 \cdot 0.5H_2O$. In the low supersaturation region, large whisker-type $CaSO_4 \cdot 0.5H_2O$ was obtained and that in the high supersaturation region, agglomeration-type $CaSO_4 \cdot 0.5H_2O$ of small particle was obtained. When waste sulphuric acid was neutralized, low supersaturation region was kept long. So large whisker-type $CaSO_4 \cdot 0.5H_2O$ was formed.

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