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Drying Experiment of Borate Waste and Characteristics of Dried Products

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붕산함유폐액의 건조와 건조물의 특성

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Abstract

An experiment was conducted to determine the reaction of boric acid with lime and the drying of its product using a reactor-dryer. The characteristics of dried products were observed. The major chemical species of dried products was calcium borate of $2CaO \cdot B_2O_3$. From the particle size distribution of the dried products, it was found that quick lime was better than slaked lime as an additive. The Ca/B mole ratio of reaction was determined to be 3/4 considering the cohesion and agglomeration properties of dried products. The flowability of dried products up to 8 wt% of water content was acceptable for transport process and to reduce drying time.

요 약

모의 붕산폐액을 석회와 반응시키고 반응기를 겸한 건조기에서 이를 건조시켜 얻어진 건조물의 특성을 살펴보았다. 반응과 건조후 생성된 건조물의 주된 화학종은 $2CaO \cdot B_2O_3$로 확인되었다. 건조물의 입도분포로부터 첨가제로서는 생석회가 소석회보다 우수함을 알 수 있었고, 건조물의 부착성 및 응집성을 고려하여 반응몰비(Ca/B)는 3/4인 조건으로 결정하였다. 수분함량이 8 wt% 정도까지 되도록 건조시켜도 건조물은 유동성이 있어 수송에 문제가 발생되지 않으며 건조시간의 단축도 가능하다.

1. Introduction

In nuclear power plants, the liquid radwaste containing boric acid from coolant systems is concentrated to 12 wt% boric acid and these concentrates are solidified with cement adding an additive generally. But this method only produces a low volume reduction effect, and the solidified waste of boric acid concentrates occupies around 40 wt% of the total waste in drums. Therefore, considering the capacity of waste disposal facilities and the cost of interim storage and transportation, the development of a solidification technology with high volume reduction is essential. To reduce the volume of waste, utilization of an advanced technology for borate waste treatment is needed. In serveral countries, studies on pretreatment of boric acid concentrates, separation into solid–liquid phases, and cement solidification are proceeding. The development of technologies such as drying of waste, pelletizing, and plastic solidification of dried waste has also been actively carried out [1, 2]. In the case of treating the liquid radwaste of BWR, a drying process using a vertical thin film evaporator has been performed [3]. However, when this method is applied to PWR liquid waste containing boric acid, some difficulties such as the adhesion of dried waste to the heated wall of the dryer can be expected.

In this study, boric acid concentrates are reacted with lime as an additive, and the reaction mixture is dried in a simple reactor–dryer. The experiment then attempts to discover a reaction condition without the disadvantages of adhesion and agglomeration. The chemical and physical properties of dried products are investigated. The fluid property of dried products containing a different water content and the physical properties of plastic solidified forms of them are also tested. Pilot–scale equipment is designed and installed, and the optimum operating for the drying process will be obtained.

2. Experimental

2.1. Chemical Species of Dried Products

The boric acid solution (boric acid concentration of 12 wt%) was prepared and heated up to 80℃. When this solution began to bubble, slaked lime or quick lime was added to the solution. The reaction mole ratios of lime to boric acid were varied as 2, 1, 3/4, 1/2, 1/3, and reactants were stirred for 3 hours. The reaction was performed with recycling of evaporated water. The products were then heated up to 90℃ in a reactor–dryer and were dried for 4 hours. The reactor–dryer was designed as shown in Fig. 1. The volume of this dryer was 1.5 ℓ and the material used was stainless steel. The gap between the paddle and the inside of reactor was 2~3mm. The paddle was connected to a D.C. motor and the speed of it could be controlled. The paddle was used to stir the reactants, stopped during drying, and then used for powdering the bulk of dried products. There were three caps on the top of this dryer. And these were closed during reaction and opened during drying. A heating mantle was used as a heating apparatus of reaction and drying. Dried products obtained from reaction and drying were smashed into fine powder. The chemical species of these products were certified by x–ray diffraction analysis (XRD, Geigerflex analyzer of Rigaku Denki). A sample was fixed on the analysis plate by adding alcohol and scanning was per-

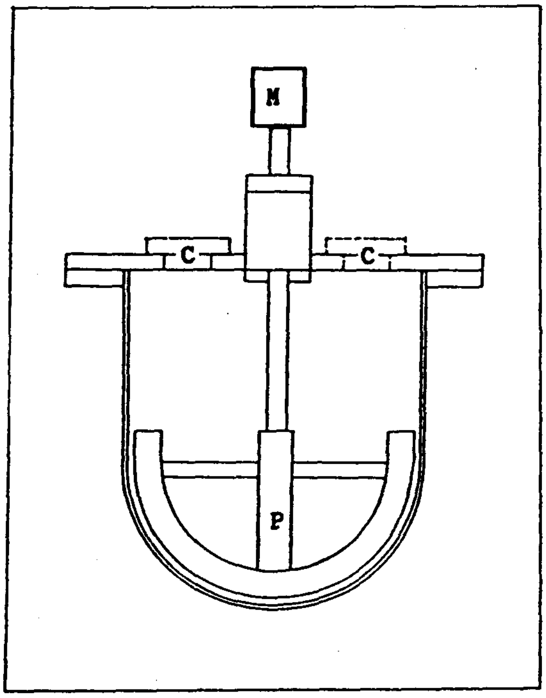

Fig. 1. The Perspective Drawing of a Reactor–Dryer.
(P : Paddle, C : Cap, M : D.C. Motor)

formed with 2θ values of 0~100. Products were determined by using a XRD data file of inorganic compounds [4].

2.2. Cohesion and Agglomeration Properties of Dried Products

When the reactant mole ratio and the type of additive were changed, the cohesion of dried products to the wall and blade of the dryer and the agglomeration of them was observed. Variations were given to the mole ratios of reactants as 1, 3/4, 2/3, 1/3 of Ca/B, and slaked lime or quick lime was used as an additive (The size distribution of reactants is shown in table 1 and 2). Reaction conditions such as time and temperature were the same as mentioned above. For powdering the bulk of dried products, products were rotated using a paddle of the dryer with a speed of 15 rpm for 5 minutes. These powdered products were then poured by means of tipping the dryer. The weights of powdered products and products adhered to the wall and blade of the dryer were measured. The separated products were sieved using twelve pieces of standard sieve and the particle size distribution of them was observed. In addition, the morphology of the dried products was obtained by SEM analyzer. The properties of dried products were analyzed by using these photomicrographs.

2.3. Water Content, Flowability and Solidification of Dried Products

To observe the effect of water on flowability of products, a boric acid solution was reacted with quick lime by Ca/B mole ratio of 3/4 in the reactor–dryer and heating mantle. These products were dried at a drying time varying from 30 minutes to two hours to measure the water content of dried products. In this experiment, the start of drying time was the time not to observe the supernatant on the surface of products. Dried products containing water were put in a polyethylene bottle to prevent the evaporation of water. The products were overturned or shaked a little, and than the extent of flowability was observed by eye.

Dried products by the reaction and drying of boric acid solution and quick lime (Ca/B mole ratio=3/4) were produced, and products containing 4%, 8%, 12%, 16% of water were prepared by adding water to completely dried products. These products were mixed with unsaturated polyester diluted by styrene as a solidifying agent (dilution ratio is 1/10), and then this mixture was cured. In each case, the mixing ratio of completely dried products and solidifying agent was one by weight. The specific gravity and volume change of solidified forms were calculated by using weight, height and diameter of waste forms. The compressive strength measurement was performed with a universal tester of Shimadzu UEA–200A.

3. Results and Discussion

3.1. Chemical Species of Dried Products

From each experiment of reaction and drying, white and fine powder was obtained. XRD patterns of dried products are shown in Fig. 2.

In analyzing the XRD patterns of dried products, there were some difficulties in certification of each peak because of too many peaks and low intensity of peak. Expectable products were searched using XRD data files of inorganic compound in computer software. And products were determined by comparing the XRD patterns of products with that of pure inorganics.

Regardless of the change of the reaction mole ratio, the chemical species of major products were $2CaO \cdot B_2O_3 \cdot H_2O$ and its anhydrate, $2CaO \cdot B_2O_3$. Comparing the reaction of slaked lime with that of

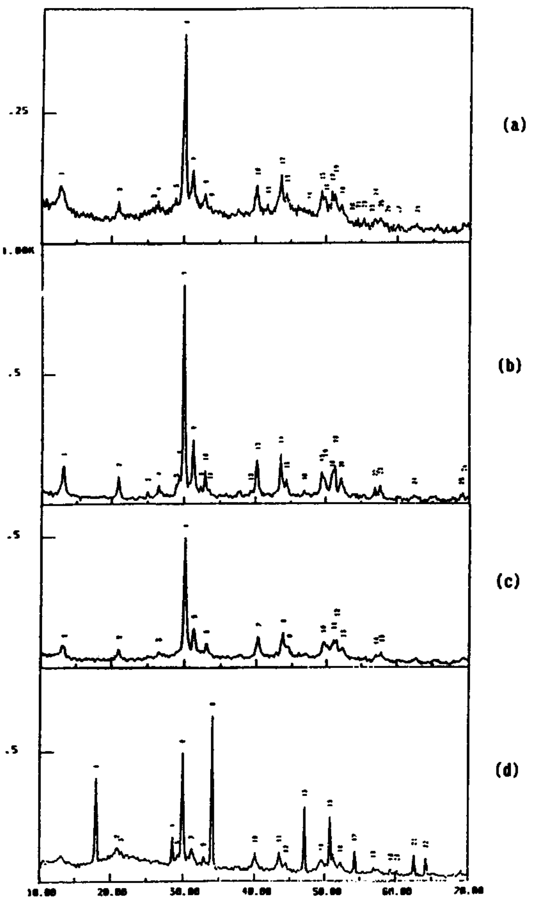

Fig. 2. XRD Patterns of Dried Products:

a. reaction mole ratio of slaked lime and boric acid =1:2

b. reaction mole ratio of slaked lime and boric acid =1:1

c. reaction mole ratio of quick lime and boric acid= 3:4

d. reaction mole ratio of quick lime and boric acid= 2:1

quick lime, major products were the same. When the amount of lime is small (Ca/B=1/2), it is expected that a major product is $CaO{\cdot}B_2O_3$ by stochiometric chemical reaction. In case the amount of lime is large (Ca/B=2), the production of $4CaO{\cdot}B_2O_3$ is presumed. But it was found that $2CaO{\cdot}B_2O_3$ was a major compound, and this was the product of Ca/B ratio of one. It could be explained that $2CaO{\cdot}B_2O_3$ is the most stable chemical species among all calcium borates.

When the mole ratio of Ca/B was 1/2, a by-product was produced and it was confirmed to be $CaO{\cdot}B_2O_3$. In that case where the mole ratio of Ca/B was 1/3, the production of $CaO{\cdot}3B_2O_3$ was certified and boric acid of the reactant was not found regardless of excess amount. It is shown that the XRD patterns of dried products in the event of reaction mole ratio of 1/3, 1/2 and 3/4 have side-peaks and represent low intensity. These results could be explained from the fact that the crystal form of dried powder was not good, and products were a mixture of several compounds. When the mole ratio of reactants (Ca/B) was two, the excess calcium remained as a form of $Ca(OH)_2$, and calcium borate of $2CaO{\cdot}B_2O_3$ was also produced. In every reaction, the production of calcium carbonate was certified as a by-product. It is caused by the reaction of lime with carbon dioxide in the solution.

As regards the pretreatment of boric acid concentrates, the volume reduction effect grows by decreasing the mole ratio of lime. From the above results, a proper reaction mole ratio is assumed to be below one of Ca/B. This condition was thought to be satisfactory considering the reactivity of boric acid with lime.

3.2. Cohesion and Agglomeration Properties of Dried Products

The weight distribution of dried powder adhered to the dryer and separated products is shown in tables 1 and 2. Table 1 shows the results of reaction with slaked lime, and table 2 shows the results of reaction with quick lime.

According to the decrement of calcium ratio as reactants, the weight of dried products adhered to the wall and blade of dryer tended to increase, so that it could be inferred as a cause in the increase

Table 1. The Weight Distribution of the Dried Products by the Reaction of Slaked Lime and Boric Acid.

reaction mole ratio	Ca/B =1 : 1	Ca/B =3 : 4	Ca/B =2 : 3	Ca/B =1 : 3	reactant (slaked lime)
size(mesh)	distribution(%)				
above 12	2.3	1.8	3.8	15.5	
12~ 20	3.6	7.3	3.2	5.5	
20~ 40	3.9	5.5	3.9	4.5	
40~ 50	2.1	2.5	2.6	2.7	
50~ 70	2.0	2.5	2.6	1.8	
70~100	2.1	2.5	2.6	2.7	2.1
100~140	2.6	2.5	3.9	4.5	2.0
140~170	1.5	1.8	3.2	7.3	1.8
170~200	1.5	1.8	3.8	9.1	1.5
200~230	1.3	1.2	3.8	6.4	1.0
230~270	2.2	1.8	4.5	5.4	3.1
270~325	15.9	6.7	9.6	7.3	13.2
below 325	44.1	42.8	37.8	9.1	75.3
*adhered products	14.9	19.3	14.7	18.2	

* The weight percentage of dried products adhered in the wall and blade of a dryer

Table 2. The Weight Distribution of the Dried Products by the Reaction of Quick Lime and Boric Acid.

reaction mole ratio	Ca/B =1 : 1	Ca/B =3 : 4	Ca/B =2 : 3	Ca/B =1 : 3	reactant (guick lime)
size(mesh)	distribution(%)				
above 12	1.0	0.3	0.6	11.9	
12~ 20	1.1	0.6	0.7	5.5	
20~ 40	0.8	0.6	0.7	2.7	
40~ 50	0.5	0.6	0.6	1.8	
50~ 70	0.5	0.6	0.6	2.7	
70~100	6.2	6.6	5.9	9.1	
100~140	14.5	13.7	13.0	15.1	9.8
140~170	8.8	8.4	9.1	10.0	9.3
170~200	6.2	7.2	8.5	7.3	6.7
200~230	3.6	5.4	5.2	3.7	4.6
230~270	3.6	4.8	5.9	2.7	3.6
270~325	7.8	11.4	10.4	3.7	7.2
below 325	33.2	24.5	15.0	3.7	58.8
*adhered products	12.2	15.3	23.8	20.1	

* The weight percentage of dried products adhered in the wall and blade of a dryer

of cohesion of the dried products. When the size distribution of the dried products was compared with that of reactants (slake lime or quick lime), the dried products obtained from the reaction of slaked lime had a similar distribution to slaked lime as a reactant. On the other hand, in the case of the reaction with quick lime, the particles of 70 ~100 mesh in size were a large portion, but the particles of this size did not exist in the reactants. For example, when the quick lime of 100~120 mesh was used as a reactant, the particle size distribution of dried products showed 28% for 70 ~80 mesh, 56% for 80~100 mesh, 7% for 100 ~120 mesh, only 4% for below 120 mesh, and 5% for above 70 mesh. It could be seen that the size of dried products resulting from reaction and drying was larger than that of quick lime itself. And it was assumed that the reaction proceeds into the internal portion of the particle with diffusion of water and boric acid. Because the particle size of quick lime can be controlled by pulverizing, quick lime as a reactant has an advantage.

The particle size distributions of dried products are shown in Table 1 and 2. As the amount of calcium decreased, the amount of particles having the size of over 20 mesh increased, and those fine particles having the size of below 270 mesh tended to diminish. Therefore, the agglomeration of dried products was found to increase by decreasing the mole ratio of calcium. In the case of the reaction with slaked lime, the fine particles of below 325 mesh and the large particles of above 50 mesh occupied a larger portion of the total products. However, particles having a size of 70~170 mesh made up the largest amount in the reaction with quick lime.

In comparing the weight distribution of dried powder, it could be seen that the cohesive and agglomerate properties of dried products tended to decrease according to the increment of calcium ratio as reactants. The high reaction mole ratio of lime contributes to the ease of the drying process operation, but this is not desirable for the volume reduction. It was concluded that the reaction mole ratio of 3/4 (Ca/B) was proper and quick lime was better than slaked lime as an additive.

A photomicrograph of the dried products by the reaction of slaked lime and boric acid (Ca/B mole ratio=3/4) appears in Fig. 3 using an SEM analyzer. Fig. 4 shows a microscopic picture of the dried products formed by the reaction of quick lime and boric acid. It can be seen that these products were grown in spherical form and have a porous structure. It was observed that the spherical form of Fig. 4 was bigger than that of Fig. 3. These results were similar to the size distribution of dried products.

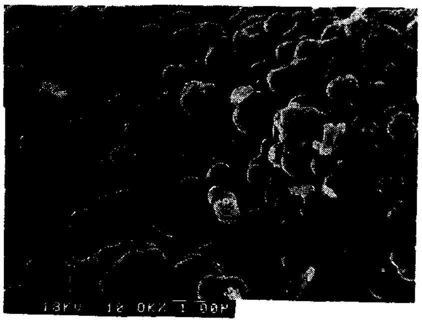

Fig. 3. A Photomicrograph of the Dried Products by the Reaction of Slaked Lime and Boric Acid(Ca/B=3/4).

Fig. 4. A Photomicrograph of the Dried Products by the Reaction of Quick Lime and Boric Acid(Ca/B=3/4).

3.3. Water Content, Flowability and Solidification of Dried Products

In order to develop a method by which drying time could be reduced and the heat efficiency of the drying process be enlarged, the water content and flowability of dried products were tested by changing the drying time. The characteristics of the plastic solidified forms of these dried products were also investigated.

Table 3 is the result of the measurement of water content and flowability of dried products according to variation in drying time. Despite the fact that the drying time was the same, the water content of the dried products obtained by stirring was smaller than that of the products obtained without stirring. Stirring was also very effective in the case of a drying time of one hour. The water content tended to show a sudden decrease with an increase in the drying time. When the water content was below 8.3%, the dried products became flowable with a consistency of fine powder and the dried product of water content above 8.3% demonstrated the property of agglomeration. The water content of about 8% in dried products was a proper limit.

Fig. 5 shows properties of waste forms solidifying the dried products of 0~16% water content with unsaturated polyester. According to the increment of the water content of dried products, the volume of the solidified forms was increased and the increment ratio was similar to that of water content. But the compressive strength and specific gravity of the waste forms were decreased by increasing water content. It was found that the value of compressive strength had a tendency to sudden decrement. The volume increment and the strength decrement could be explained by the fact that water exists among the fine particles and might interfere with the permeation of hydrophobic styrene or unsaturated polyester among the particles.

And Fig. 5 shows that the volume ratio of a solidified form was increased to 7.5% and compressive strength was decreased to 33% through increasing the water content to 8%. Therefore, the reduction of drying time must be determined by considering not only the fluid property of dried

Table 3. The Water Content and Flowability of Dried Products to Drying Time.

sample number	drying time (hour)	stirring yes/no	weight before drying(g)	weight after drying(g)	water content (%)	flowability
1	2	yes	10.0159	9.9991	0.17	flowable
2	2	no	10.4140	10.3910	0.22	〃
3	1.5	yes	10.0882	10.0502	0.38	〃
4	1.5	no	10.3009	10.1502	1.46	〃
5	1	yes	10.1209	10.0102	1.09	〃
6	1	no	10.1019	9.2623	8.31	〃
7	0.75	yes	9.9696	9.0831	8.89	agglomerate , flowable
8	0.75	no	10.4048	8.9258	14.21	not flowable
9	0.67	yes	10.0460	8.4317	16.07	〃
10	0.5	no	9.8960	7.7778	21.40	〃

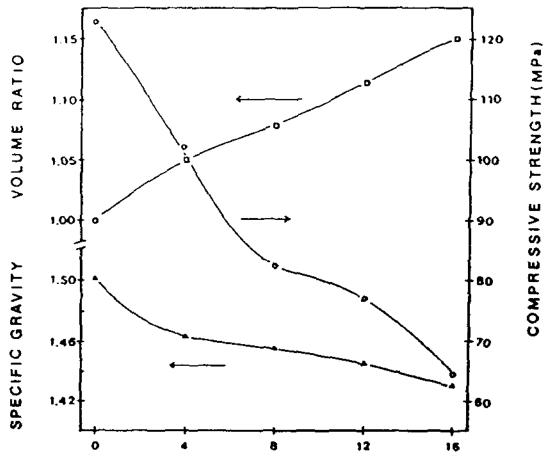

Fig. 5. The Physical Properties of Polymerized Forms of Dried Products to Water Content.

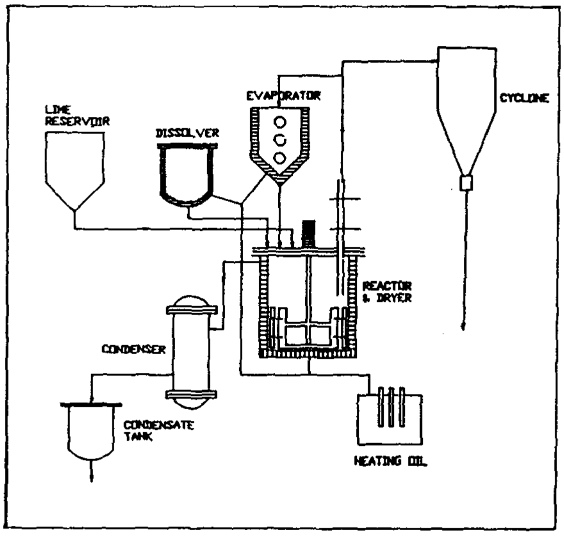

Fig. 6. A Schematic Diagram of Pilot-Scale Drying Process.

products but also the physical properties of the waste forms.

3.4. Drying Process of Borate Waste

The diagram of the drying process of borate waste is as described in Fig. 6. The Figure includes the following process : quick lime was reacted by adding a boric acid solution, products were then dried in a reactor–dryer, and the dried products were transported and stored in a cyclone. Pilot-scale equipment for the drying process was constructed. An operational experiment of drying and transportation was then performed [5, 6].

4. Conclusions

Characteristic tests of dried products, which were obtained from the reaction of boric acid with lime and the drying of the products by a reactor–dryer, were performed. From the results of these experiments, the following conclusions could be made.

1. The major product after reaction and drying was $2CaO{\cdot}B_2O_3$ regardless of the reaction mole ratio of boric acid and lime, or the type of additive.
2. Considering the increase of cohesion and agglomeration properties of dried products according to the decrement of mole ratio of lime, Ca/B reaction mole ratio of 3/4 was proper. From the results of the size distribution of dried products, it was found that quick lime was better than slaked lime as an additive.
3. When the water content of dried products was increased, the specific gravity and compressive strength of the plastic solidified forms of these dried products tended to decrease. The dried products having the water content of below 8% demonstrated a flowable property.
4. Optimum operational conditions for the drying process of borate waste will be obtained in the future. And fundamental and operational experiments of the plastic solidification of dried products will be performed.

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