

Dehydration Behaviour of Borax Pentahydrate to Anhydrous Borax by Multi-Stage Heating in a Fluidized

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In order to optimize the anhydrous borax process in a fluidized bed calcinator, it is absolutely necessary to study the dehydration behaviour of borax pentahydrate. It was found that the basic feature of the dehydration of borax pentahydrate to anhydrous borax is concerned with the conditions employed. The bulk density and sodium borate content of the end product were determined to be a function of number of stages of temperature of the dehydration period in the fluidized bed. It was observed that bulk density also depends on the number of moles of water remaining in the borax pentahydrate structure.

High purity, low density and powdered anhydrous borax up to 99.9% can be produced by multi-stage calcination. Therefore, anhydrous borax may be produced in a convenient fluidized bed system by multi-stage heating of borax pentahydrate.

Key Words: Borax pentahydrate, dehydration, fluidized bed, bulk density

Introduction

Anhydrous borax (BA), $\text{Na}_2\text{B}_4\text{O}_7$, is an industrial product produced from borax decahydrate (BDH; $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and borax pentahydrate (BPH; $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$). It is used as a flux material in metallurgy, and in the production of high quality glasses, ceramic materials and enamels¹.

BA is preferred to other hydrated borax salts in high temperature applications, because it does not cause any foaming problems originating from dehydration of the water of crystallization.

BA has three different crystalline forms besides its amorphous form. Crystalline α , β and γ forms have melting points of 1015, 993 and 936 K respectively^{2,3}. α - $\text{Na}_2\text{B}_4\text{O}_7$ is the stable form. Since the amorphous form of BA softens gradually in the course of increasing the temperature, it causes sintering problems during the transformation of hydrated borax salt to anhydrous borax.

BDH can be transformed to BPH at temperatures around 333 K and then to borax dihydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 2\text{H}_2\text{O}$) at 389-393 K. The main problem in the calcination of BDH to BA can be understood

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by taking into account the molecular structure of borax hydrates. The borax ion present in BDH and BPH crystals is $[\text{B}_4\text{O}_5(\text{OH})_4]^{-2}$ ^{4,5}. Two of the water molecules in these crystals thus exist as hydroxyl groups and can be considered to be molecular water. The other eight molecules exist as actual crystal water. Therefore these two molecules of water are difficult to remove during the calcination and can only be removed by molecular decomposition. Thus, physical properties such as particle size distribution and bulk density of calcined borax salts can be controlled by thermal history of calcination up to two molecules of water. After this point, technological properties are somewhat difficult to control.

With present technology, BA is produced from BDH and BPH by a two-stage process. The first is dehydration and the second is fusion. Fusion is carried out at a temperature higher than the melting point of BA, ranging from 1273-1673 K at the different parts of the firebox. The reason for using high temperatures is to decrease the viscosity of the molten mass and to produce proper fluidization conditions for flow out from the firebox. The low melting point of BA causes very dangerous corrosion problems which can only be prevented by forming a layer of solid calcined borax on the refractory material of the furnace. The resulting BA from this furnace process is largely amorphous and difficult to grind¹.

Production of BA without fusion is very attractive in terms of energy consumption and corrosion. Since that kind of solid-state transformation process does not have crushing and grinding steps, it has more advantages. The main disadvantages of this process is the puffing of the particles during removal of molecular water. Puffing causes the product to have lower bulk density, higher surface area and larger quantities of void. This kind of product is likely to be subject to rehydration during storage and causes increases in transportation cost.

Despite these disadvantages, by virtue of such a puffed structure, large quantities of liquids and/or solids can be loaded onto the expanded borax, rendering such a product useful as a bulk carrier in numerous applications. For example, organics such as trichloroethylene, cyclohexanone and pentachlorophenol can be loaded at very high percentages onto the puffed borax, as can non-ionic, cationic and anionic surfactants, with the product retaining its free-flowing characteristics. This renders the puffed borax very useful in such diverse compositions as dairy cleaners, fabric softeners and bath additives⁶.

Calcination of BDH and BPH fluidized bed calciner is the best way. The advantage of fluidized bed is the uniformity of calcination temperature, and the high rate of heat transfer between the particle and hot air, which allows continuous controlled calcination.

As already shown⁷, single step dehydration gives very low values of bulk density and causes sintering problems. At constant heating rates, there is no sintering problem and the bulk density of the product can be controlled to some extent. But this procedure, which requires a very long time to obtain the desired $\text{Na}_2\text{B}_4\text{O}_7$ content, is difficult to apply in industry. Therefore, in this study, stage-wise calcination properties were investigated in a fluidized bed calciner.

Two different studies^{8,9} have reported the dehydration of BPH to BA. In these studies, they give no precise relationship between the bulk density and $\text{Na}_2\text{B}_4\text{O}_7$ content of samples for different first and final dehydration temperatures.

Furthermore, it is well known that the transformation of $\text{BDH}(\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O})$ to $\text{BPH}(\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O})$ is easily realized at 333.8 K in aqueous media, since both BDH and BPH contain the same polyion $[\text{B}_4\text{O}_5(\text{OH})_4]^{-2}$. But in the solid phase calcination temperature of BPH¹⁰ is different from that of BDH which was studied by Waclawska¹¹. Thus, the dehydration behaviour of BPH in a fluidized bed is very important for industrial uses. The best way to follow the calcination of BPH is to measure the $\text{Na}_2\text{B}_4\text{O}_7$

content and bulk density value of the product.

The experiments

The experimental system is shown in Figure 1. In order to see the fluidization properties during the calcination, a heat resistance glass column 600 mm long with a 40 mm inner diameter was used. The smoothness of fluidization was provided a stainless steel distribution plate with holes at a certain angle and direction. The fluidization air was heated by a temperature controlled furnace and then fed into the fluidized bed at a rate determined by fluidization. The outer surface of the column was insulated by 40 mm thick ceramic wool. The temperature of fluidization air was measured by Ni-Cr thermocouples.

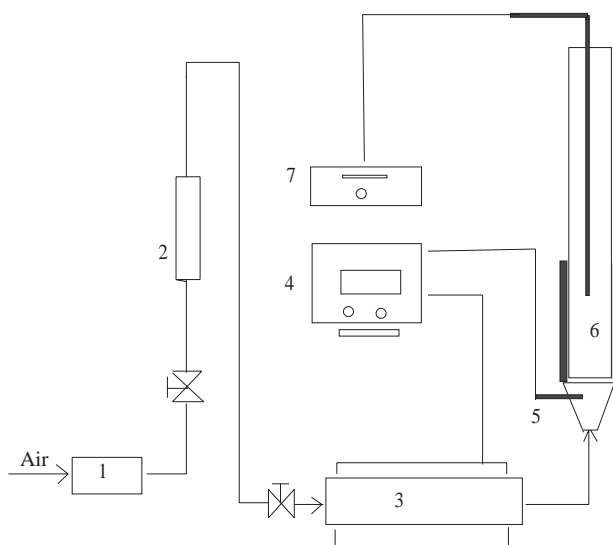


Figure 1. Experimental Set-up (1) pressure regulator; (2) rotameter; (3) heating furnace; (4) temperature controller; (5) thermocouple; (6) fluidized bed; (7) temperature measurement.

Closely sized BPH crystals were used in the experiments, obtained by sieving the technical grade BPH between 500-600 μm sieves. The titrimetric method was used to determine the borax content of samples¹². Bulk density was measured by a standard method¹³. The original $\text{Na}_2\text{B}_4\text{O}_7$ content of the sample was determined to be 69.95% and bulk density to be $0.911 \text{ g}\cdot\text{cm}^{-3}$. Samples were fed into the fluidized bed calciner (FBC) heated to the predetermined temperature. During the experiments, samples were taken out by vacuum tube in order to determine the $\text{Na}_2\text{B}_4\text{O}_7$ content and bulk density.

Results and Discussion

In previous work⁷, it was determined that BPH reached the trihydrate state at 398 K in 30 minutes. At higher temperatures, thermal decomposition because of the release of molecular water causes a sharp decrease in bulk density. Therefore 398 K was considered the critical temperature in step-wise calcination, this and temperature was chosen for the first step.

Two series of experiments were carried out. In the first group, precalcined BPH at 398 K for 30 minutes was calcined at 573 K for up to 180 minutes. Samples were taken out at certain times and analyzed. The results are given in Table 1.

Table 1. The result of two-step calcination

Step	Time (min)	Temperature (K)	% Na ₂ B ₄ O ₇	Bulk Density (g.cm ⁻³)
1	30	398	79.9	0.85
2	10	573	91.69	
	20	//	93.07	
	30	//	93.34	
	40	//	93.65	
	50	//	93.95	
	60	//	93.95	
	75	//	93.94	
	90	//	94.15	
	120	//	94.56	
	150	//	95.11	
	180	//	95.93	0.1399

In this two-step calcination and at 573 K final temperature, a product containing approximately 95% of Na₂B₄O₇ with a bulk density around 0.14 is produced. Hypothetic borax monohydrate (Na₂B₄O₇H₂O) and hemihydrate (Na₂B₄O₇·0,5 H₂O) contain 91.78% and 95.72% Na₂B₄O₇, respectively. As can be seen from Table 1, the monohydrate level can be produced in 10 minutes and then the rate of dehydration becomes very slow. This shows that the thermal energy given to the system is not enough for reaching the final decomposition state at 573 K in 3 hours.

In the other group of experiments, the number of calcination steps is increased. Table 2 gives the experimental results. It can be seen that the conversion of BPH to BA is not related to the number of stages of calcination, since the conversion of BPH is nearly the same at the same temperature and calcination time. These results also show that the temperature profile during the calcination has a limited effect on the bulk density. Bulk density is primarily a function of the Na₂B₄O₇ content of the calcine. Figure 2 shows the variation in bulk density with Na₂B₄O₇ content, obtained from these experiments. Variations in theoretical bulk density may be calculated from the initial bulk density, assuming that particles keep their original sizes and shapes during the dehydration. The values calculated are shown in Figure 2. The water per mol of Na₂B₄O₇ is shown on upper axis of Figure 2.

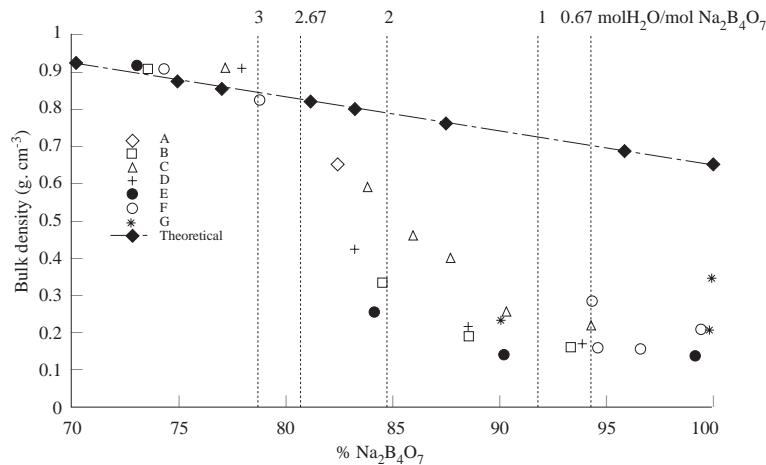
**Figure 2.** The changes in bulk density with % Na₂B₄O₇ contents

Table 2. Multi stage heating with different calcination times and temperatures

Experiments		Temperature (K)									
		398	423	448	473	523	573	723	898	923	948
	Waiting time (min)	30	10				30	10			
A	% Na ₂ B ₄ O ₇	74.30	82.48				94.56	96.60			
	Bulk Density (g.cm ⁻³)	0.842	0.606				0.145	0.145			
	Waiting time (min)	20	10			10	30				
B	% Na ₂ B ₄ O ₇	70.52	84.50			88.47	93.29				
	Bulk Density (g.cm ⁻³)	0.857	0.307			0.171	0.146				
	Waiting time (min)	30	10	10	10	10	30				
C	% Na ₂ B ₄ O ₇	77.16	83.82	86.01	87.62	90.27	94.33				
	Bulk Density (g.cm ⁻³)	0.854	0.550	0.430	0.370	0.230	0.201				
	Waiting time (min)	30	10			10	30				
D	% Na ₂ B ₄ O ₇	77.96	83.22			88.44	93.85				
	Bulk Density (g.cm ⁻³)	0.867	0.389			0.196	0.156				
	Waiting time (min)		5		10		20			10	
E	% Na ₂ B ₄ O ₇		73.08		84.15		90.21			99.21	
	Bulk Density (g.cm ⁻³)		0.864		0.235		0.129			0.112	
	Waiting time (min)	30	10				30	40			
F	% Na ₂ B ₄ O ₇	74.25	78.76				94.36	99.47			
	Bulk Density (g.cm ⁻³)	0.850	0.800				0.266	0.187			
	Waiting time (min)	30					30		30		
G	% Na ₂ B ₄ O ₇	72.89					90.02		99.74		
	Bulk Density (g.cm ⁻³)	0.877					0.213		0.186		

In order to understand the effect of thermal shock applied to the particles between the steps, in the last experiment (Experiment G), particles were heated at 5 K/min from one step to another. Since no appreciable difference was observed, it was concluded that thermal forces are insignificant.

The interesting features of Figure 2 are given below:

a) Experimental bulk densities are almost the same as the theoretical ones up to around the trihydrate state. Therefore, puffing has no effect in this region.

b) Very quick changes in bulk densities begin from somewhere between the $\text{Na}_2\text{B}_4\text{O}_7 \cdot 3\text{H}_2\text{O}$ and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 2,67\text{H}_2\text{O}$ structures. This clearly shows that puffing has an effect before the dihydrate step.

c) Minimum bulk densities are always obtained at less than the monohydrate step. Minimum points are obtained around at the structure of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 0,67\text{H}_2\text{O}$.

d) Variations in bulk densities are reversed after the minimum point and then the sintering effect increases it. Approaching the anhydrous form by increasing the temperature enhances the sintering effect.

e) Temperature steps and calcination times in multi-stage calcination have an effect on the bulk densities. But the shapes of the bulk density variations are similar.

All these behaviours of BPH can only be explained by two different but competitive physical phenomena: shrinking and puffing.

It is given that¹⁴ pentahydrate dehydrates reversibly to an amorphous dihydrate on heating at 413 K in air. At temperatures lower than 413 K particles have a tendency to turn into a dihydrate structure and therefore they shrink. At temperatures higher than 413 K the fast transformation of BPH to dihydrate causes puffing due to fragmentation and abrasion of the puffed particles during the dehydration. To see these two physical phenomena, three different experiments were performed. Table 3 shows the effect of low temperature on bulk density during long term dehydration. It is observed that the bulk density values of calcines are higher than the theoretical ones at below 413 K. This result shows that the shrinking of BDH to BPH continues up to the dihydrate step. In addition, in Table 3, the conversion of BPH comes to approximately the same level at 413 K and bulk density quickly decreases to $0.43 \text{ g}\cdot\text{cm}^{-3}$, which is less than the theoretical value. This is due to the BPH dissolving in its own water of dehydration and the solution erupting through the partially dehydrated crystal surface, causing the bulk density decrease⁶. This is the phase transformation step of BPH to borax dihydrate. To see the effect of these two phenomena on the surface structure of crystals, electron microscopic pictures of two different calcined crystals are shown in Figure 3. This figure shows that the surface of high bulk density crystals which were dehydrated at 400 K are smooth compared with that of dehydrate at 413 K. It can be seen in the same figure that the crystals dehydrated at 413K were puffed at this temperature. A competitive shrinking and puffing mechanism was observed for the other hydrated salt, which can be found elsewhere^{15,16}.

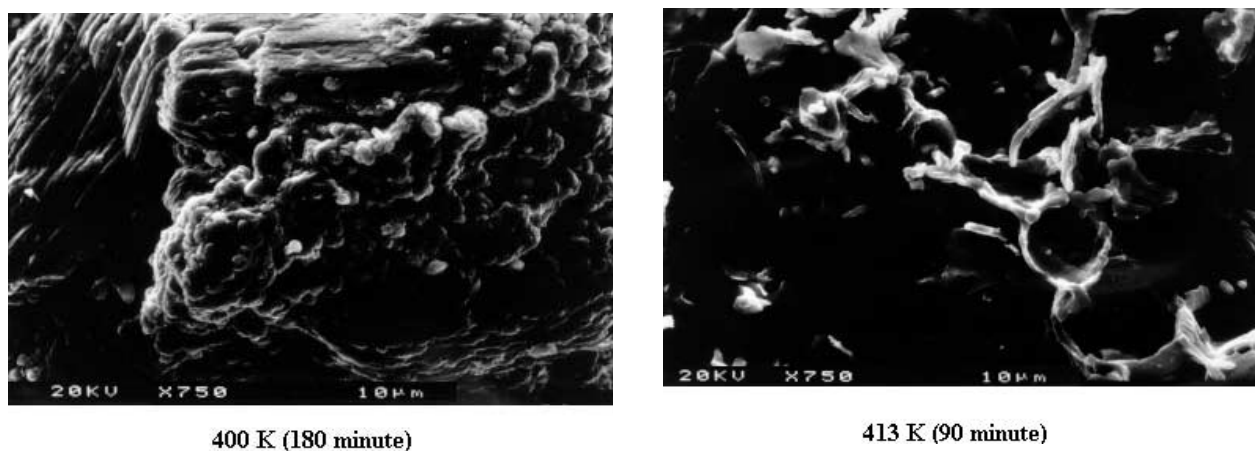


Figure 3. Electron microscopic pictures of different crystals at low temperature

Table 3. The effect of low temperature on bulk density

Time (min)	Temperature (K)	% Na ₂ B ₄ O ₇	Remaining mols of Water	Bulk density (g.cm ⁻³)
180	400	84.82	2.06	0.888
120	408	84.63	2.03	0.857
90	413	85.34	1.98	0.430

Conclusion

In this study, BPH dehydration in a fluidized bed and experimental results are presented and attempts are focused on the conditions of calcination of BPH in the fluidized bed calcinator. BPH can be easily transformed into anhydrous borax in a fluidized bed. The main problem in this process is the change in the physical properties of calcines due to the heating conditions. The changes in the structure of BPH affect the particle size and bulk density value of the dehydrated borax. The most important changes in the particle structure are observed in cases involving water between 3 and 1 moles. In addition, the change in the particle occurs at least from 4.75 to 3 moles. After the monohydrate stage, the bulk density remains very nearly constant. Thus calcination was carried out by a different step-wise calcination process which is more easily achieved in the technique area possible. By this method, the period of calcination is shortened and the quality of product is controlled despite the low heating rate and constant rate calcination. This method is still being developed to obtain a product of high bulk density.

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