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Thermal decomposition of potassium tetraborate tetrahydrate to anhydrous potassium tetraborate in a fluidized bed

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Abstract

Production of anhydrous potassium tetraborate from potassium tetraborate tetrahydrate (PTT) was investigated in a controlled fluidized bed calcinatory (FBC). Single step calcination gives a puffed product with very low bulk density and the calcination of potassium tetraborate tetrahydrate is incomplete since agglomeration starts at temperature higher than 250 °C. Effect of the temperature on the bulk density of the product obtained at the end of single step is given and compared with theoretical calculation. In order to obtain anhydrous potassium tetraborate, dehydration should be carried out at least two stages. The most important step dominating the final bulk density is the first step. Dehydration of potassium tetraborate tetrahydrate up to 85% $K_2B_4O_7$ content and temperature lower than 150 °C in the first step gives commercial available product at final stage. As a result, both puffed and denser anhydrous potassium tetraborate of 99.5% purity with bulk density around 0.4 and 0.7 g cm^{-3} has been produced by two and three stage calcinations.
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1. Introduction

A large number of borate salts such as borax, sodium perborate, boric acid and zinc borate have been used in industrial purpose. Boron minerals are hydrated borates combined with alkaline-earth and alkaline metals such as Na, K, Ca, Mg and Li. Among these potassium tetraborate tetrahydrate (PTT) ($K_2B_4O_7 \cdot 4H_2O$) is produced resulting from the controlled reaction of potassium hydroxide and boric acid in aqueous media. As it is known, potassium tetraborate is used in lubricating oil composition [1], glass article [2], disinfectant [3], treatment of contact lenses [4] and dishwashing detergent [5]. In addition to these, it can replace borax where an alkali borate is needed but sodium salt cannot be used. However, the water content of boron minerals are not appropriate in some application such as the manufacture of high quality glass, frit production, ceramic and refinement of precious metals. Thus, dehydration of hydrated boron minerals such as boric acid [6], borax [7], ulexit [8], colemanite [9] and potassium tetraborate tetrahydrate are very important.

Production methods applicable to conversion of potassium tetraborate tetrahydrate to anhydrous potassium tetraborate may be categorized into two main groups. These are: (a) melting and (b) dehydration in fluidized bed.

Anhydrous potassium tetraborate can be produced in a fixed bed or refractory-lined jacked furnace by fusing at temperature higher than the melting point of potassium tetraborate (815 °C) ranging from 1200 to 1400 °C similar to the ones utilized to production process of anhydrous borax [10]. But, in this system, the molten potassium tetraborate is highly corrosive which can only be prevented by forming a layer of solid calcined potassium tetraborate on the refractory material of the furnace. By using this process, high density of anhydrous potassium tetraborate is produced, but there are many technical difficulties in the process, such as corrosion and handling problems. The other disadvantages of this kind of method are that the product needs crushing, grinding and homogenization before being used.

Fluidized bed calcinations technique which allows uniform temperatures, high heat transfer rate between the particles and continuously controlled dehydration operation has many advantages. Production of anhydrous potassium tetraborate without melting is very attractive with respect to energy consumption and corrosion. Also, heat input of the system is lower compared

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to the former method and the post processing of the product, such as crushing and grinding is not needed. Earlier workers have obtained anhydrous form of some borates in powdered or granular form with this technique by using constant temperature and multi-stage calcinations [11–14].

The only disadvantage of fluidized bed method is that the obtained anhydrous potassium tetraborate at the end of constant temperature has a lower bulk density than one produced by melting technique. Such a puffed product, with large quantities of liquids and gas, can be loaded onto the expanded potassium tetraborate as suggested borax [15]. In addition to this, puffed potassium tetraborate having large surface area can be used for solid-gas reactions. The obtained anhydrous potassium tetraborate at constant temperature is very fragile, thus it can be easily converted to powder form by grinding. This operation increases the bulk density of anhydrous potassium tetraborate. The calcinations of potassium tetraborate tetrahydrate to anhydrous form have been carried out by stage-wise calcinations as applied borax [13–15] in order to produce anhydrous potassium tetraborate having higher bulk density.

The calcinations of potassium tetraborate to anhydrous form in solid state are necessary to know the time required to dry from one moisture content to another specified condition, in order to determine drying schedules and to establish the size of equipment. Measurements of the rate of the batch drying are relatively simple to make and provide much information not only for batch but also for continuous operation [16].

Although many studies have been done on the dehydration of alkali borates [6–14,17] we have not found any studies on the dehydration of potassium tetraborate tetrahydrate in fluidized bed. Thus, the main aim of the present work is oriented toward determining the optimum calcination temperature to prevent puffing and sintering and decomposition of potassium tetraborate tetrahydrate to anhydrous form in fluidized bed dryer. Therefore, the bulk density, B_2O_3 content, sieve analysis of the product obtained at the end of constant and stage-wise calcinations have been investigated under thermal decomposition condition.

2. Experimental

Calcination experiments of potassium tetraborate tetrahydrate were carried out using the system shown in Fig. 1. In order to observe the process visually, a heat resistance glass column (30 mm-ID, 600 mm high) has been used. The distribution plate was made of 3 mm thick stainless steel containing 39 holes each 0.1 mm in diameter. The other surface of the glasses column was insulated with 50 mm thick ceramic wool. Fluidization air was fed through a pressure regulator, a calibrated rotameter and an electrical heater unit controlled by a PID type temperature controlling system. The temperature of fluidization air (inlet air) was measured and controlled by means of NiCr–Ni thermocouple, which was fixed at the bottom of the distribution plate. The moisture content of fluidization air was measured by a humidity meter placed before hating unit. During constant temperature experiments, 15 g potassium tetraborate tetrahydrate particles were fed at the top of fluidized bed calcinatory (FBC), which
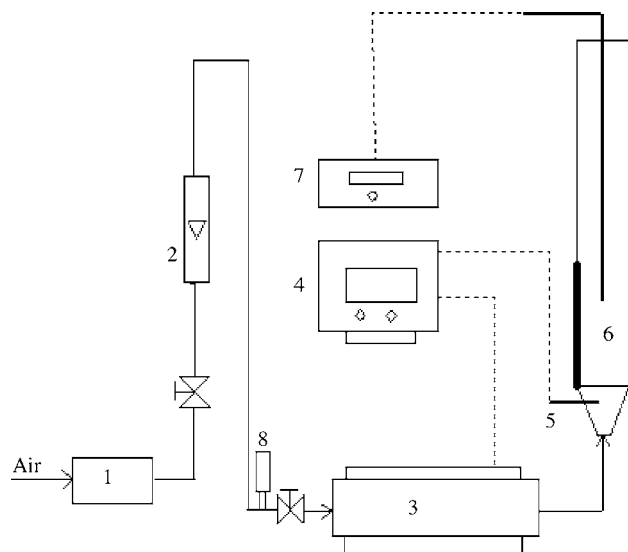

Fig. 1. Experimental set-up: (1) pressure regulator; (2) rotameter; (3) heating furnace; (4) temperature controller; (5) thermocouple; (6) fluidized bed; (7) bed temperature; (8) humiditymeter.

had been at thermal equilibrium at the experimental temperature. During all the experiments the flow rate of fluidization air was kept constant at $400 \, l \, h^{-1}$. At predetermined time intervals, samples were withdrawn out using a vacuum sampling tube.

Titrimetric method was used to determine the $K_2B_4O_7$ and B_2O_3 [18] content of samples. Bulk density was measured by a standard method [19]. At a stage-wise calcination, experiments were conducted similar to the constant temperature except that the second and third step temperature of FBC was changed and after reaching pre-determined temperature the experiment was started. The particles size of potassium tetraborate tetrahydrate used in the experiments was chosen in the range of 500–710, 400–500 and 315–450 μm.

3. Result and discussion

In the first step of the experimental work, TG and DTG analysis of the potassium tetraborate tetrahydrate were performed under nitrogen atmosphere at $5 \, °C \, min^{-1}$ heating rate as shown in Fig. 2. From Fig. 2, total weight-loss was calculated
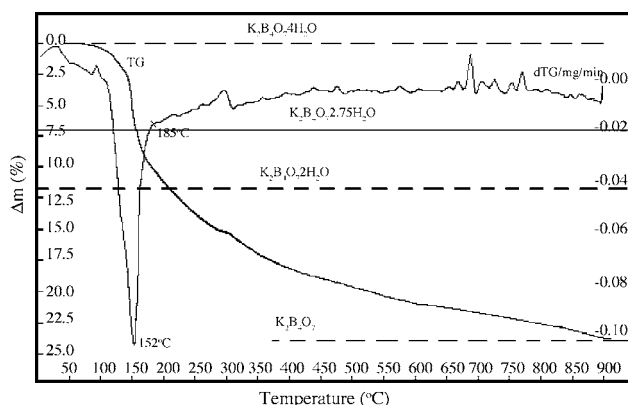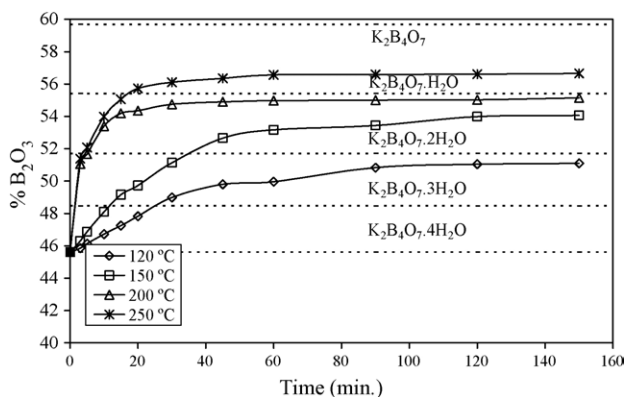

Fig. 2. TG/DTG curves for potassium tetraborate.

Fig. 3. Effect of calcination temperature on the dehydration of potassium tetraborate with the initial particle size of 500–710 μm.

Fig. 4. Variation of bulk density of product at different temperature.

as 23.59% which corresponds to the removal of 4 mol of water in the temperature range of 100–900 °C. Simultaneous TG-DTG curves show that the highest water-loss in samples was observed between 100 and 200 °C. The remaining 2 mol of structural water was lost gradually up to about 900 °C. Marezio et al. [20] claimed that the structural formula of potassium tetraborate tetrahydrate can be best represented as $K_2[B_4O_5(OH_4)]\cdot 2H_2O$ which means that 2 mol of water are in molecular structure and the remaining consist of hydroxyl groups. Many hydrated alkaline borates showed step-wise dehydration from one hydrated step to another one or to anhydrous borate [21–25]. In the present work, the dehydration step was observed with the separations of 2 mol of crystal water. This means that the thermal decomposition of potassium tetraborate tetrahydrate realizes in two different step named dehydration and decomposition. It is not known which step controls the final physical properties of the anhydrous potassium tetraborate. Therefore, the dehydration step and final decomposition step should be checked experimentally in the fluidized bed calcinator with respect to bulk density and sieve analysis.

At the beginning of the experimental work of FBC a series of pre-experimental have been done in order to observe the potassium tetraborate tetrahydrate behavior at the different initial fluidization air temperature. Fig. 3 shows the $\%B_2O_3$ content of the samples at different bed temperatures as a function of time. As seen from this figure the higher the bed temperature, the higher dehydration rate and the shorter the dehydration time will be to reach any specified water content. Potassium tetraborate monohydrate can almost be obtained at 250 °C in 20 min (Fig. 3). On the other hand, one step calcinations process of potassium tetraborate tetrahydrate cannot be run over 250 °C, since sintering effect was started. At temperature higher than 250 °C, during the dehydration, it is determined that the formation of water vapor on the surface of potassium tetraborate particles will quickly accelerate the sintering phenomena and particles strongly adhere to each other a result of this fluidization will be cut off. The effect of dehydration temperature on bulk density and $\%K_2B_4O_7$ levels for the samples taken from the fluidized bed at the end of run is given in Fig. 4. In this figure theoretical values of bulk density are also shown for comparison in order to see any shape changing. Theoretical bulk density is calcu-
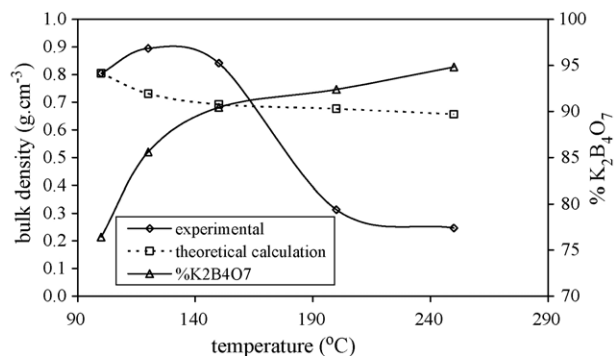
lated from the original bulk density of the potassium tetraborate tetrahydrate assuming that particles keep their dimension and shape during calcinations. In this calculation water loss determined experimentally is taken into account. Experimental bulk density values are higher than theoretical values at temperature up to approximately 170 °C which is corresponding to 2 mol of water whereas it becomes lower than theoretical at temperature higher then 170 °C which is corresponding to structural decomposition. This behavior can be explained by two different but competitive physical phenomena, one is shrinking and the other is puffing. At low temperature, rate of water loss is slow and particles have a tendency of turning to denser monohydrate structure without puffing and therefore they shrink. At higher temperature that 170 °C, fast transformation of tetrahydrate to dihydrate due to realizing of water vapor cause the particles to puff. These two phenomena should be taken into account in order to obtain commercially desired bulk density for the product. As seen in Fig. 4 the bulk densities of calcined product are higher than initial bulk density values at temperature range between 120 and 150 °C. From the point of dehydration, temperature of bed should be as high as possible. Therefore, taking into account puffing and shrinking, optimum dehydration temperature is found around 150 °C, in the case of using step-wise calcinations.

The crystal used in this study prepared by dissolving the powder particles of potassium tetraborate tetrahydrate at 70 °C in a batch crystallizer with stirrer. Then the saturated solution at 70 °C cooled slowly up to 30 °C in the presence of seed crystals. By this way, the obtained crystal with the size 510–710 μm used in experimental study and microscope photographs of potassium tetraborate tetrahydrate in pure, calcined at 250 °C (120 min) and in other experiment calcined at 150 °C (20 min), 300 °C (20 min) and 400 °C (30 min) are given in Fig. 5, respectively. As can be seen in Fig. 5(a) the main crystal habit of potassium tetraborate tetrahydrate appears to be composed of two and three inter growing individuals, know as a twin and triplet. A typical example of this behavior is sodium perborate tetrahydrate which can form a twin and triplet formations are seen in the size range of approximately 50–300 μm. [26]. The other example showing this behavior is orthorhombic potassium sulphate which can form a twin looking almost with a hexagonal pyramid [27].

Potassium tetraborate tetrahydrate calcined at 250 °C (Fig. 5(b)) is puffed and result of this the bulk density decreased from 0.81 to 0.22 g cm^{-3}. In same figure (Fig. 5(c)), the
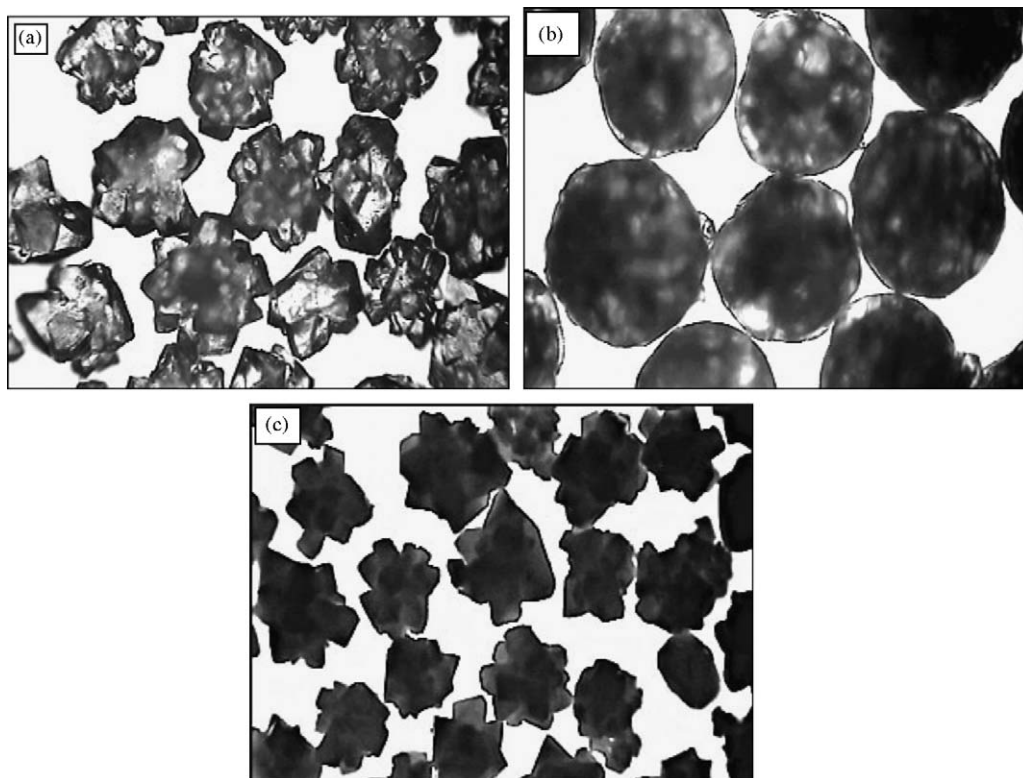
Fig. 5. Microscopic photographs of potassium tetraborate with the initial particle size of 500–710 μm (a) initial crystal; (b) puffed particles calcinated at 250 °C; (c) shrinking particle calcinated at 150 °C (20 min), 300 °C (20 min) and 400 °C (30 min).

potassium tetraborate tetrahydrate particles calcined by stage-wise procedure at 150 °C during 20 min, at 300 °C during 20 min and at 400 °C during 30 min are shrinking and thus, the bulk density values increased to 0.741 while it is expected around 0.620 theoretically.

Fig. 6 shows the effect of particle size on the drying rate. The experiments were all performed at the same gas velocity and bed temperature of 150 °C. As seen in this figure with increasing the mean particles diameter from 382.5 to 605 μm produced a light increase in the drying rate. The proportion of gas in the bubble phase in the bulk of the bed must have been considerably greater with the small particles than with the large particles. As a result of this, all the gas is equally effective in contacting the particles in the entry zone of the bed.
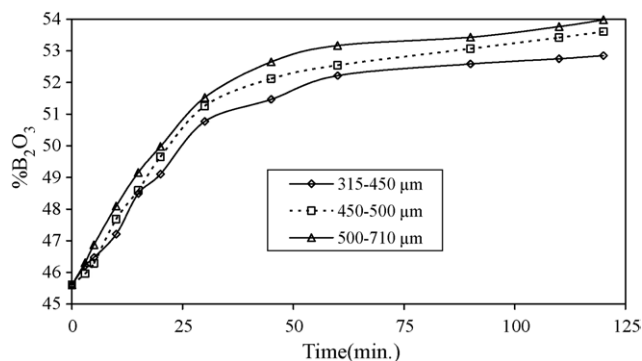

Fig. 6. Changes of calcinations with particle size.

As can be seen in Figs. 2 and 4, at higher temperature than 170 °C, thermal decomposition because of liberate of molecular water cause a sharp decrease in bulk density. Therefore, the temperature between 120 and 170 °C was considered the critical temperature in step-wise calcinations and this temperature range was chosen for the first step. The results of step-wise calcinations of potassium tetraborate tetrahydrate to anhydrous form are illustrated in Table 1. In the first two experiments, calcinations were carried out for 20 and 40 min at 150 °C and then for 30 min at 400 °C. Bulk density of last product of first two experiments calcinated at 400 °C was found as 0.502 and 0.491 g cm^{-3} which were higher than the values obtained in constant temperature experiments realized at 200 and 250 °C (Fig. 4), but lower than the expected values at this stage assuming that shrinking dominates the bulk density.

In the third and forth experiment the first step of calcinations of potassium tetraborate tetrahydrate was carried out 45 and 20 min at 130 and 170 °C and second stage of calcinations was realized, 30 min at 400 °C, 90 min at 375 °C, respectively. As seen in these experiments, the bulk density decreases with respect to first two experiments. This phenomenon can be explained by using TG/DTG curves shown in Fig. 2. As can be seen in TG curve the maximum liberation speed of crystal water of potassium tetraborate which is corresponding to the water content of 2.75 H_2O realize at the temperature higher than 152 °C. Thus, in the first step of calcinations, temperature and water content of potassium tetraborate tetrahydrate must be lower than 152 °C and 2.75 mol H_2O/mol $K_2B_4O_7$, respectively. In the fifth and sixth experiments, the effect of particle size on

Table 1
Multi-step calcination of potassium tetraborate

Initial particle size ((μm)/experiment number)	Calculated parameters	First step temp. (°C)			Second step temp. (°C)		Third step temp. (°C)
		130	150	170	300	375	400
500–710 (1)	Calcination time (min)		20				30
	Bulk density (g cm^{-3})						0.502
	Mol H_2O/mol $K_2B_4O_7$		2.402				0.104
	%B_2O_3		50.354				59.215
500–710 (2)	Calcination time (min)		40				30
	Bulk density (g cm^{-3})						0.491
	Mol H_2O/mol $K_2B_4O_7$		1.886				0.008
	%B_2O_3		52.104				59.652
500–710 (3)	Calcination time (min)			20			30
	Bulk density (g cm^{-3})						0.204
	Mol H_2O/mol $K_2B_4O_7$			1.839			0.083
	%B_2O_3			52.270			59.311
500–710 (4)	Calcination time (min)	45				90	
	Bulk density (g cm^{-3})					0.425	
	Mol H_2O/mol $K_2B_4O_7$	2.793				0.028	
	%B_2O_3	49.105				59.56	
450–500 (5)	Calcination time (min)		120		30		
	Bulk density (g cm^{-3})		0.837		0.605		
	Mol H_2O/mol $K_2B_4O_7$		1.466		0.096		
	%B_2O_3		53.623		59.25		
315–450 (6)	Calcination time (min)		120		30		
	Bulk density (g cm^{-3})		0.775		0.424		
	Mol H_2O/mol $K_2B_4O_7$		1.677		0.115		
	%B_2O_3		52.851		59.167		
500–710 (7)	Calcination time (min)		20		20		30
	Bulk density (g cm^{-3})						0.741
	Mol H_2O/mol $K_2B_4O_7$		2.211				0.086
	%B_2O_3		50.986				59.297

Table 2
Changes in sieve fraction with experiment condition

Particle size (μm)	%Fraction/experiment number						
	1	2	3	4	5	6	7
+850	–	3.566	43.684	13.062	0.545	1.024	1.024
+710	6.296	10.751	44.357	24.766	0.451	0.284	0.284
+500	93.105	85.134	11.230	57.475	12.286	15.871	15.871
+450	0.315	–	–	2.951	47.097	24.317	24.317
+315	0.285	0.548	0.730	1.436	39.621	58.155	58.155
+200	–	–	–	0.309	–	0.348	0.348

the calcinations of PTT have been investigated and obtained result similar to 500–710 μm particle size. The seventh experiment, the calcinations of PTT have been carried out in three stages with condition of 20 min at 150 °C, 20 min at 300 °C and 30 min, at 400 °C. The last product obtained at the end of seventh experiment has the bulk density value of 0.741 g cm^{-3} which is higher than expected theoretical value of 0.664 g cm^{-3}.

As a result of all these, the shrinking of PTT not only depends on at dehydration step, but also it is affected by decomposition step. Sieve analysis of last product obtained at the experiments given in Table 1, are illustrated in Table 2. The chosen particle size range of PTT before calcinations for experiment number of 2, 3 and 4 was 500–710 μm and the particle size almost 1–10,

5–10 and 9–10 part of calcines were increased to +710 μm as shown in Table 2, respectively. Thus, it can be said that puffing is more effective in cause size increment with respect to shrinking and fragmentation of puffed particles. But, in the experiment number 7, 8–10 parts of calcines was decreased to −500 μm as seen in Table 2, since shrinking is more effective in size decrement with respect to puffing.

4. Conclusion

In this study, the dehydration of potassium tetraborate tetrahydrate is presented and attempts are focused on the conditions of calcinations of potassium tetraborate in fluidized bed

calcinatory. The main problem in this process is the changes in the physical properties of calcines due to heating conditions. The changes in the structure of potassium tetraborate tetrahydrate affect the particle size and bulk density value of dehydrated product. The following conclusion may be with drawn from the results obtained during calcinations of PTT in a fluidized bed calcinatory:

1- Single step calcinations carried out at temperature higher than 170 °C gives a calcinated product with low bulk density. The calcinations of PTT with single stage cannot be carried out at the temperature higher than 250 °C since agglomeration is started.
2- The bulk density of calcined product is increased at temperature lower than 170 °C, since PTT particles are shrinking.
3- During the multi stage calcinations, temperature and water content of PTT in the first step calcination should be lower than 152 °C and 2.75 mol H_2O/mol $K_2B_4O_7$, respectively. The second calcination step of these particles give similar results with respect to bulk density, particle size and B_2O_3 content when it is carried out at higher different temperature The product obtained at the end of this two stage calcination is commercially available in respect to physical and chemical properties.
4- High bulk density product with higher bulk density than in theoretical value of anhydrous potassium tetraborate is obtained with three step calcinations. Therefore, the second stage temperature of calcinations has an important role on the final bulk density of anhydrous PT.

Acknowledgements

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