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Increasing the bulk density of STPP – influence of the process parameters

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The new requirements that were placed on STPP, like high bulk density, the proper relation of Form I and Form II and suitable physicochemical properties, resulted in the development of the present production methods. The paper presents the research results on increasing the bulk density of STPP by a chemical method. In the introduced method the solid sodium phosphate from spray drying and sodium orthophosphate solution, after acid neutralization, were rubbed together. Such an operation changes the physicochemical properties of the dried sodium phosphate before calcining, which results in increasing the bulk density of STPP to a level of 0.80 kg/dm3. The dependence of STPP bulk density on process parameters such as: sodium orthophosphate solution to solid sodium phosphate mass ratio, temperature of dosed sodium orthophosphate solution, as well as the calcining temperature of mixtures were analysed.

Keywords: sodium tripolyphosphate, STPP, high bulk density.

INTRODUCTION

The detergent market is one of the most competitive in the world. Despite the presence of different forms of detergent formulas like liquids, gels or tablets, washing powders are still most often used by Polish consumers.

Sodium tripolyphosphate (STPP), because of its beneficial properties, is one of the most commonly used washing powder components in the form of an active builder[1–3]. The development of production methods and inactive builders elimination from the washing formula initiate evolution to compact powders, concentrates and tablets manufacturing. Such products are more effective and are characterized by higher bulk density than the former ones, which reduces the washing costs and improves the economic and ecological parameters[4].

The STPP production consists of the following stages: phosphoric acid neutralization with soda ash or caustic soda, dehydration of the obtained mixture and its calcining. Technological solutions are based on a one-stage method, where dehydration and calcining are realized in one apparatus, or a two-stage method which separates these processes [3]. In the two-stage method the mixture of monosodium- and disodium hydrogen phosphates obtained after the neutralization process is dried in a spray drier, where partial condensation to sodium pyrophosphates occurs and solid mixtures receive a structure of "empty shells" with low density of around 0.4 kg/dm^3 [5, 10]. In the final stage the mixture of sodium orto- and pyrophosphates is calcined in a rotary kiln, where further condensation to STPP takes place. The calcining temperature relates to the parameters of final products and is on average 350–550°C. Bulk density of the final product is increased from 0.45–0.65 kg/dm^3 to nearly 0.9 kg/dm^3 during further technological operations of deep milling, hydration or compactation[5]. The milling operation increases the product bulk density to 0.85 kg/dm^3 but enlarging the fine-grain fraction reduces its possible use. Methods of granular STPP production, widely described in the literature, are based on the hydration process of STPP after calcining[6–9].

The presented solutions result in higher energy consumption, hence the modification of accessible methods of raising the bulk density of STPP is well-grounded. Such a method, in wide demand, should enable obtaining STPP with suitable and controlled quality parameters, higher concentration and reduced energy consumption.

The conducted research reveals that the bulk density of STPP can be increased by addition of water or sodium orthophosphate solution to a semi-finished product from spray drying before calcining. Such an operation results in partial dissolving of dried sodium phosphate and hydration of phosphates salts, and in effect the charge for calcining has different physicochemical characteristic, which doubles the bulk density of the product after calcining[10–12].

EXPERIMENTAL SECTION

The presented research series comprised the process of increasing bulk density by rubbing the mixture of solid sodium phosphates (SP), used also at our earlier investigations[10–12], with the solution of liquid sodium orthophosphates (LOP), both of which were semi-products from the technological plant of obtaining STPP. The P_2O_5 content of the used semi-products was respectively: 27.35% at concentrated liquid sodium orthophosphates and 51.16% at solid sodium phosphates. 15–30 g of LOP solution were added with the constant velocity 800 μl/s to 100 g of SP while rubbing the components for the constant time 120 s in a laboratory mortar. The LOP solution with the concentration of 13.36% P_2O_5 was prepared by dilution of the concentrated liquid sodium orthophosphates with water in the 1:1 mass ratio and added in the two temperatures of 30°C and 80°C. The obtained mixtures with a variable content of the LOP solution (Table 1) were then calcined in a laboratory chamber kiln at a temperature of 350°C and 550°C for 1 h.

The phase composition of the SP, mixtures, as well as products was identified with the X-ray diffraction method (Philips X'Pert diffractometer), the thermal process course was observed during the thermal analysis (2960 Simultaneous DTA-DTG TA Instruments). Both the sieve analysis and bulk density analysis of the SP and products were carried out according to a standard method[14, 15]. The bulk density analysis was marked for constant specified grain composition: 10% fraction above 1.00 mm; 20% fraction between 0.85–1.00 mm; 5% – 0.60–0.85 mm; 58% – 0.25–0.60 mm and 7% fraction lower than 0.25 mm[16].

Table 1. The characteristic of the mixtures before calcining

NO.	LOP to SP MASS RATIO [g/g]	LOP SOLUTION TEMPERATURE [°C]	H_20 CONTENT [%]	PHASE COMPOSITION OF MIXTURES BEFORE CALCINING
1	0.15	30	8.09	$Na_2HPO_4{\cdot}2H_2O$, $Na_4P_2O_7$, $Na_5P_3O_{10}$ (II)
2	0.20	30	10.16	$Na_2HPO_4{\cdot}2H_2O$, $Na_4P_2O_7$, $Na_5P_3O_{10}$ (II)
3	0.25	30	11.22	$Na_2HPO_4{\cdot}2H_2O$, $Na_2HPO_4{\cdot}7H_2O$, $Na_4P_2O_7$, $Na_5P_3O_{10}$ (II)
4	0.30	30	12.64	$Na_2HPO_4{\cdot}2H_2O$, $Na_4P_2O_7$, $Na_5P_3O_{10}$ (II), Na_2HPO_4, Na_3PO_4
5	0.15	80	8.02	$Na_2HPO_4{\cdot}2H_2O$, $Na_5P_3O_{10}$ (II), Na_2HPO_4, $Na_4P_2O_7$
6	0.20	80	9.36	$Na_2HPO_4{\cdot}2H_2O$, $Na_5P_3O_{10}$ (II), NaH_2PO_4, $Na_4P_2O_7$, Na_2HPO_4
7	0.25	80	11.32	$Na_2HPO_4{\cdot}2H_2O$, $Na_2HPO_4{\cdot}7H_2O$ $Na_5P_3O_{10}$ (II), $Na_4P_2O_7$,
8	0.30	80	11.73	$Na_2HPO_4{\cdot}2H_2O$, $Na_2HPO_4{\cdot}7H_2O$, $Na_4P_2O_7$, $Na_5P_3O_{10}$ (II), Na_3PO_4

In the mixtures before calcining the moisture content was additionally analyzed (moisture analyzer HG63 Mettler Toledo)[13].

RESULTS

The SP is characterized by low bulk density of 0.423 kg/dm^3 on average and its basic crystalline phase, shown in Figure 1, is double salt of sodium dihydrogen phosphate and disodium hydrogen phosphate accompanied by disodium hydrogen phosphate, tetrasodium pyrophosphates and form II of sodium tripolyphosphate (which may appear because of the local preheating of the mixture during spray drying). The addition of the LOP solution to the SP results in double salt decomposition and hydration of disodium hydrogen phosphate. At the highest liquid to solid mass ratio 0.30 trisodium phosphate also appears in the mixtures before calcining (Table 1).

The thermal process course of the SP (Figure 2) and the mixture with the addition of 15 g and 30 g of the LOP solution (Figures 3 and 4, respectively) indicates that the phase transformation was similar. At temperatures up to 90°C moisture was eliminated and decomposition of $Na_2HPO_4{\cdot}7H_2O$ took place. Up to 140°C the chemically bound water is removed. The range of 190–295°C indicates the condensation of orthophosphate forms into pyrophosphates and the beginning of the STPP formation. At a temperature higher than 450°C a low-temperature form II of STPP transforms into a high-temperature form I.

As a result of calcining all the mixtures at a temperature of 350°C, the low-temperature form II of STPP was received as the main phase. The calcining product was accompanied only by sodium pyrophosphate in the case of mixtures with liquid to solid mass ratio 0.15–0.20 and additionally sodium dihydrogen phosphate and tetrasodium pyrophosphates in the case of mixtures with liquid to solid mass ratio 0.25–0.30. STPP in form I was obtained at 550°C independently of the liquid phase content (Figure1).

The sieve analysis of the SP indicates that the dominant fraction (51.96%) was of 0.25–0.6 mm. There were 23.68%

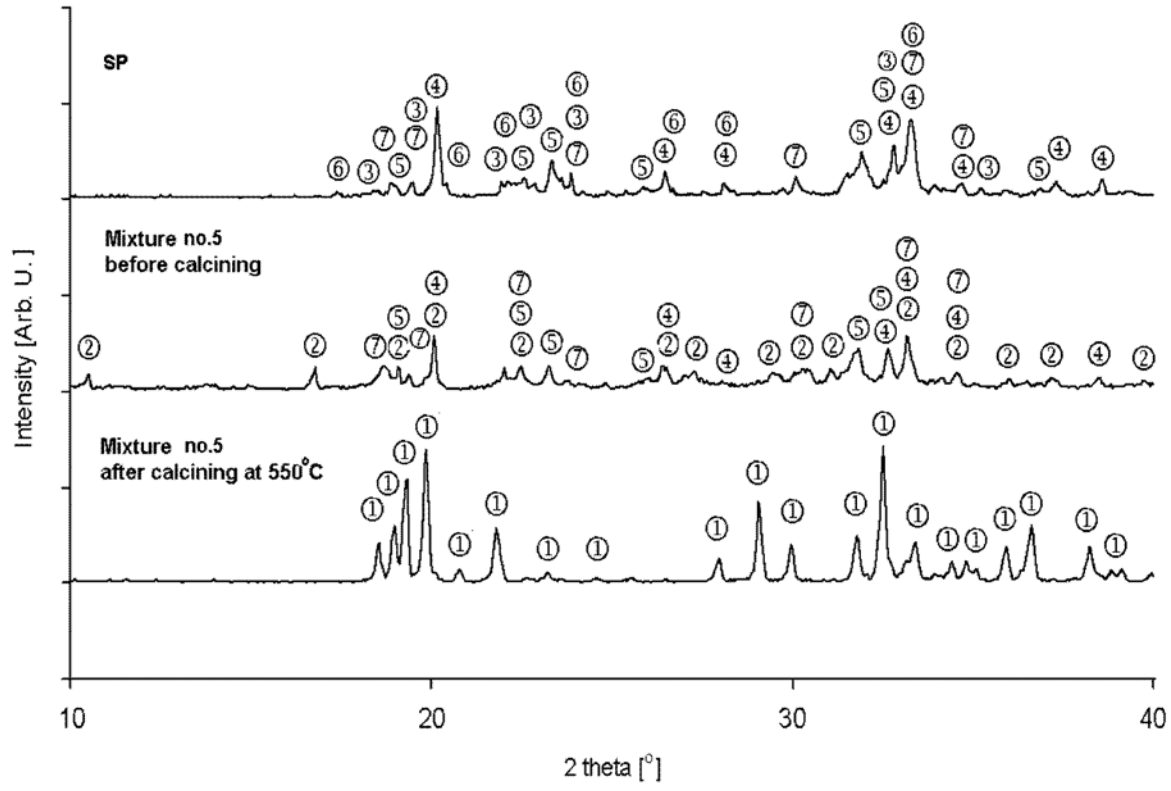

Figure 1. XRD patterns of solid sodium phosphates (SP) and mixture 5 before calcining and after calcining at 550°C. ① – $Na_5P_3O_{10}$ (I), ② - $Na_2HPO_4{\cdot}2H_2O$, ③ – NaH_2PO_4, ④ – $Na_4P_2O_7$, ⑤ – Na_2HPO_4, ⑥ – $NaH_2PO_4{\cdot}Na_2HPO_4$, ⑦ - $Na_5P_3O_{10}$ (II).

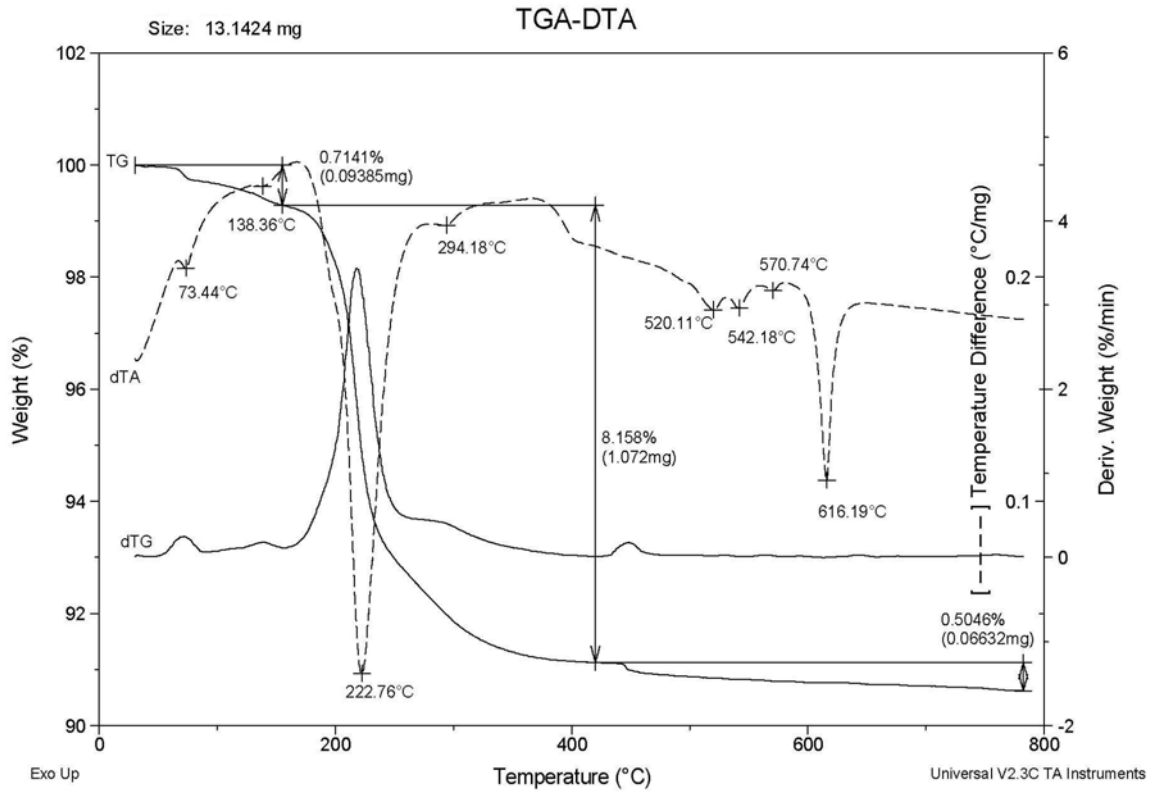

Figure 2. Thermal analysis of the dried sodium phosphates (SP)

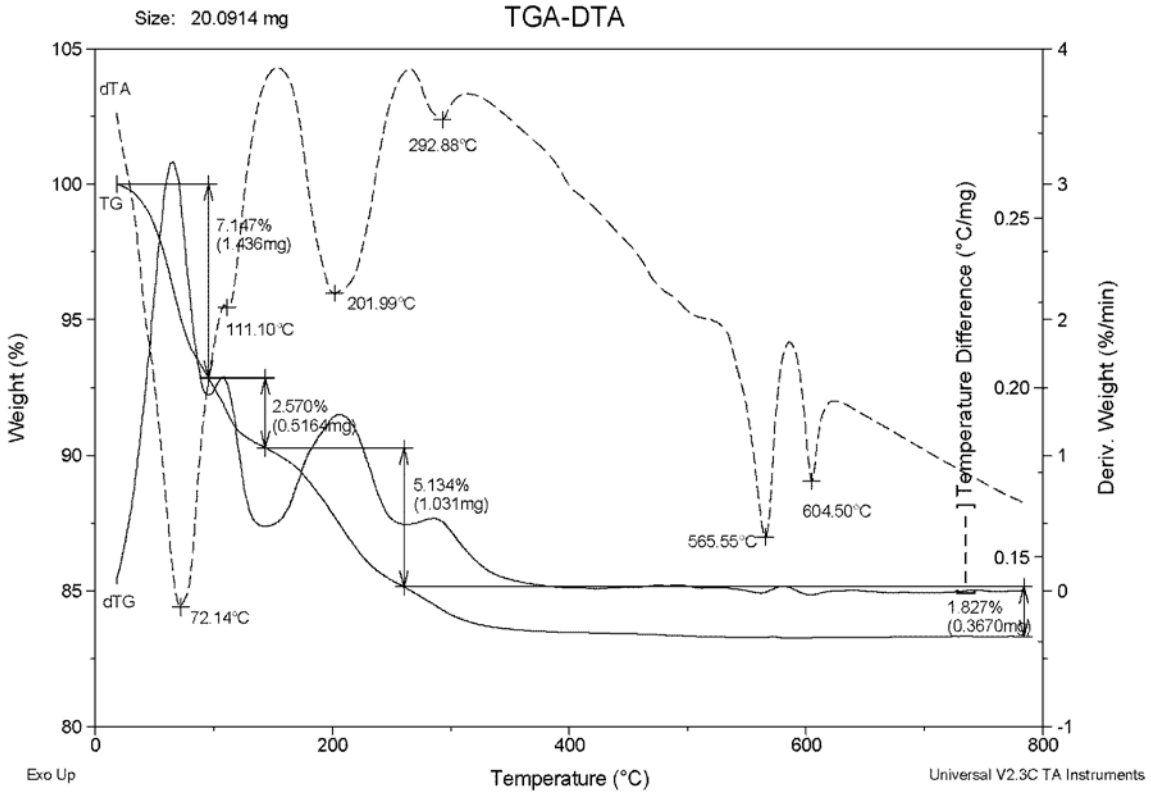

Figure 3. Thermal analysis of the mixture of dried sodium phosphates (SP) and the solution of liquid sodium orthophosphates (LOP) at the mass ratio 0.15 [g/g] – mixture 5

grains above 1.00 mm and 13.82% grains between 0.6–0.85 mm. The grained fraction smaller than 0.25 mm and the fraction between 0.85–1.00 mm had the lowest share, amounting to 5.67% and 4.87%, respectively. The material is even-grained, the different granularity coefficient is on average 2.27, and the grains equivalent diameter 0.55 mm. Calcining the SP at a temperature of 350°C results in decreasing the quantity of the following fractions: above 1.00 mm, 0.85–1.00 mm and 0.25–0.6 mm, and increasing the quantity of the grains between 0.6–0.85 and those smaller than 0.25 mm. The different granularity coefficient is on average 2.30 and the grains equivalent diameter 0.32 mm. A higher SP calcining temperature (550°C) increases only the fine-grain fraction up to 16.21%. The

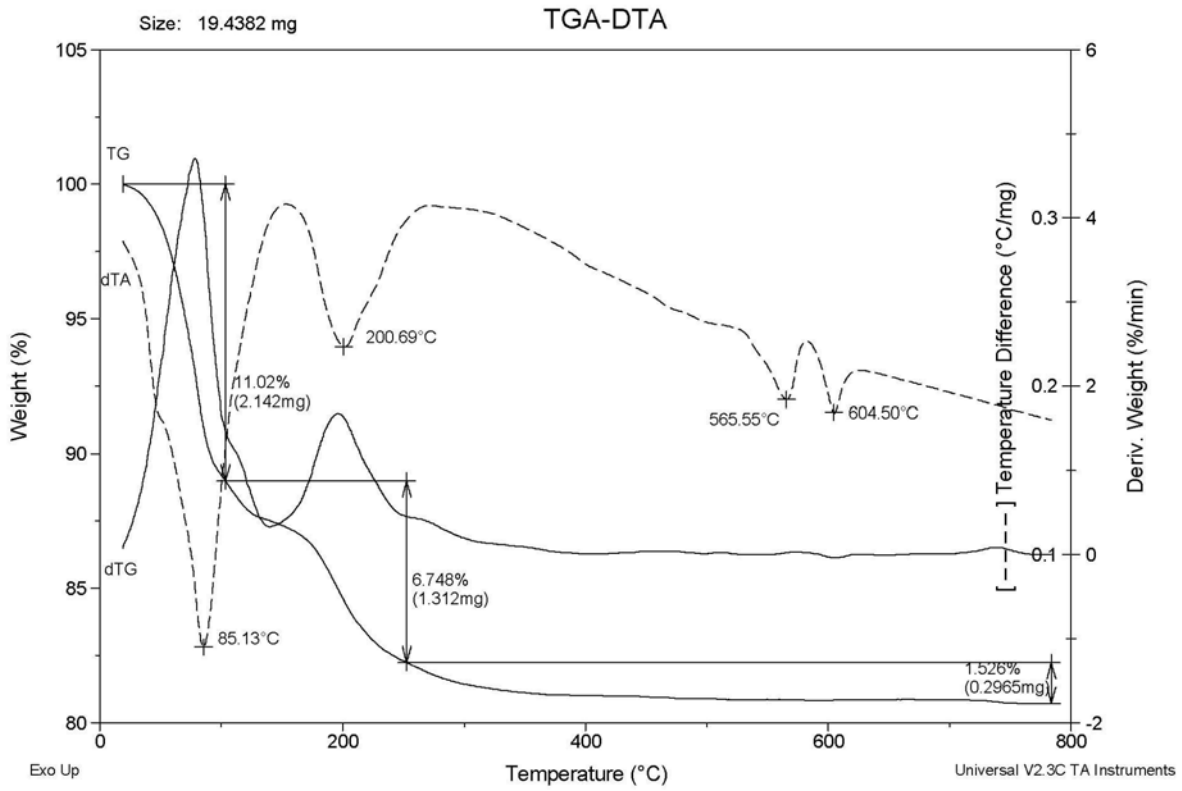

Figure 4. Thermal analysis of the mixture of dried sodium phosphates (SP) and the solution of liquid sodium orthophosphates (LOP) at the mass ratio 0.30 [g/g] – mixture 8

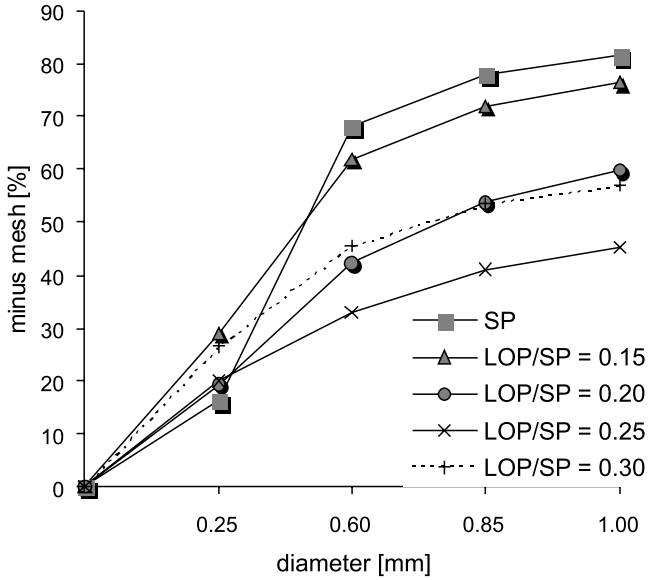

Figure 5. The curves of minus mesh of a STPP products after calcining mixtures 1 to 4 at temperature 550°C in comparison to SP

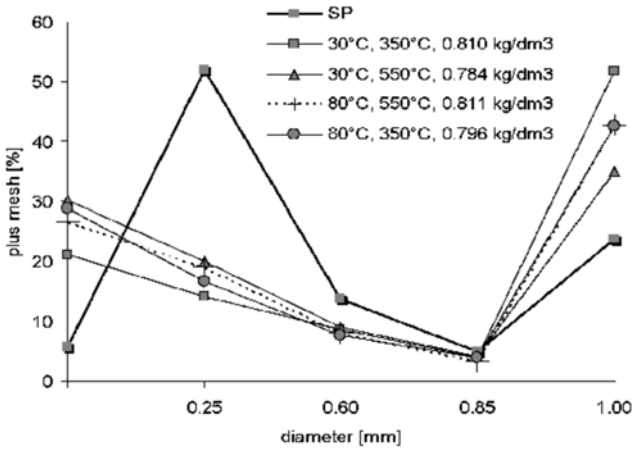

Figure 6. The curves of plus mesh of a STPP products with the highest bulk density in comparison to SP

different granularity coefficient rises to 3.82 and the grains equivalent diameter to 0.47 mm on average. The addition of the LOP solution changes the physicochemical properties of the dried sodium phosphate before calcining. With the added amount of the LOP solution, mixtures consistency changes its form from a loose material to paste. As a consequence, the product received after calcining of the mixtures 1–8 was of different grains. An average different granularity coefficient increased from 6.32 (mixtures 1 and 5 with the lowest addition of the LOP solution) to 11.39 (mixtures 4 and 8). The changes in grain size distribution observed in the calcining products are characterized by cumulative minus mesh curves (Figure 5) and plus mesh curves for the mixtures with the highest bulk density (Figure 6) .

The bulk density of the calcining products strongly depends upon the amounts of the LOP solution added to the prepared mixtures. Moreover, the LOP solution temperature and the calcining temperature of mixtures also influence the bulk density of STPP products (Figures 7 and 8). With the increase in the liquid to solid phase mass ratio from 0.15 to 0.30 the bulk density of the products rises from 31% to 92% in comparison to the SP. Lesser influence is noticed for the temperature of the LOP solution added to mixtures before calcining. With dosing 15 g of the solution at a temperature of 80°C, the bulk density of STPP obtained after calcining at 550°C is 10% higher than in the case of using the same solution at a temperature of 30°C. A higher calcining temperature of mixtures

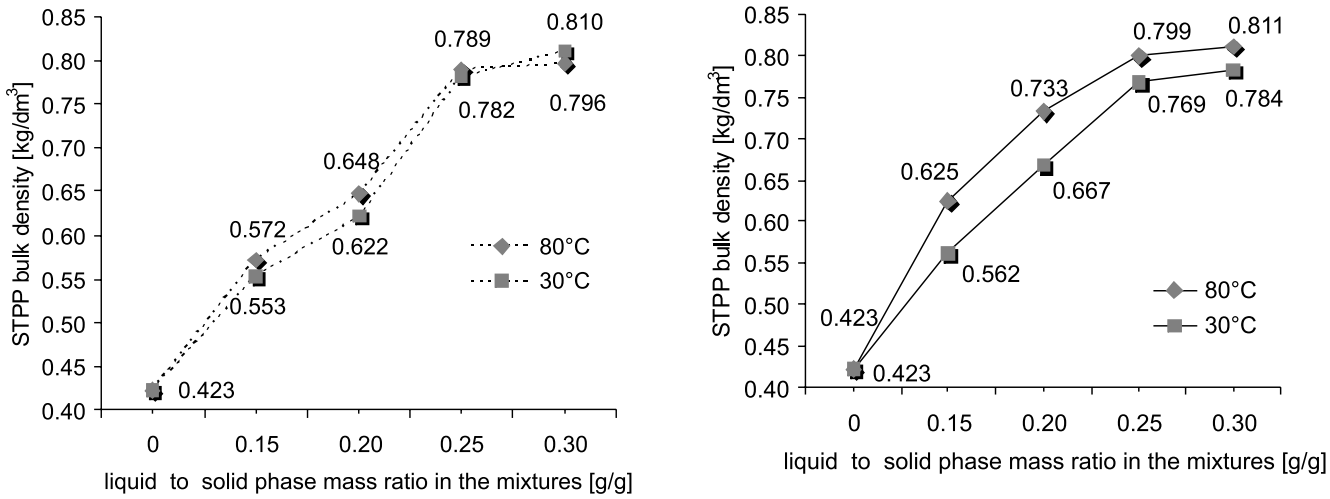

Figure 7. The influence of the mass ratio of the LOP solution to SP and the solution temperature on bulk density of STPP obtained after calcining at : a). 350°C, b). 550°C

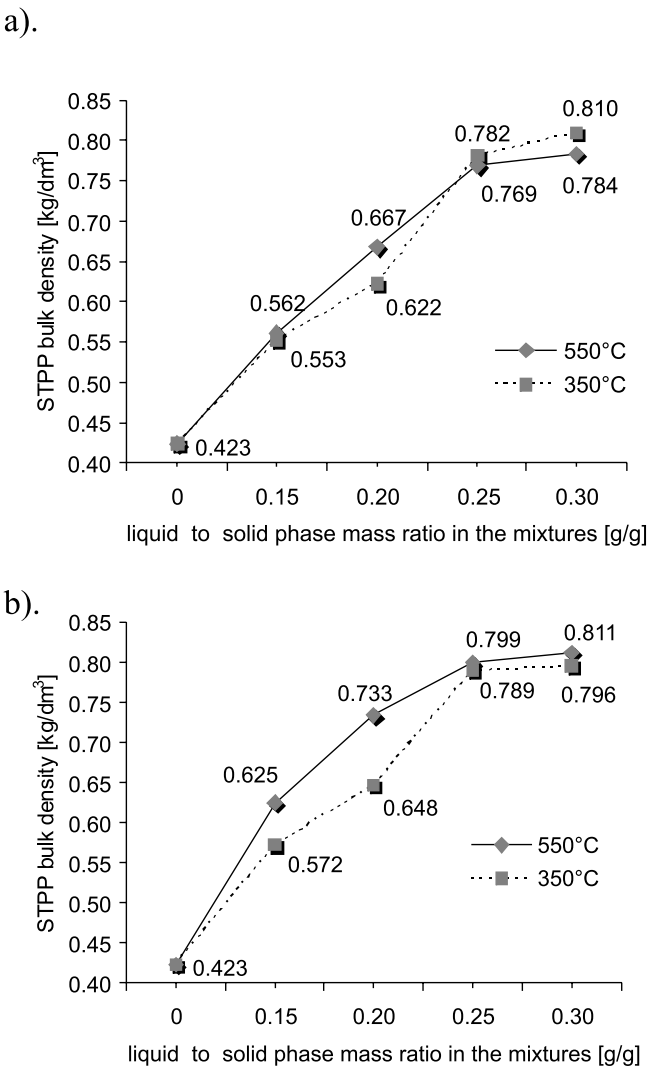

Figure 8. The influence of the mass ratio of the LOP solution to SP and the calcining temperature on bulk density of the obtained STPP when the LOP solution was dose at temperature : a). 30°C, b). 80°C

increases the bulk density of the obtained STPP only by up to 13% in the case of mass ratio 0.20 and the solution temperature 80°C.

The highest increase in bulk density was noticed for a mixture prepared by rubbing 100 g of the SP with 30 g of the LOP solution dosed at a temperature of 80°C and calcined at 550°C. The obtained form I of STPP reached the bulk density of 0.811 kg/dm^3.

CONCLUSION

It was found that there is a possibility of increasing the bulk density of the STPP by the chemical method. In the introduced method the solid sodium phosphate from spray drying and sodium orthophosphate solution, after acid neutralization, can be rubbed together at a proper mass ratio. Such an operation changes the physicochemical properties of the dried sodium phosphate before calcining, which results in increasing the bulk density of STPP to over 0.80 kg/dm^3.

The bulk density of the calcining products strongly depends upon the amounts of the liquid orthophosphates solution added to the prepared mixtures. The bulk density of the products rises 92% in comparison to the SP when the 0.30 liquid to solid phase mass ratio was applied. Other analysed parameters like temperature of dosed sodium orthophosphate solution and calcining temperature of mixtures have lesser influence on bulk density of the obtained STPP.

This method allows producing the granular STPP phase I with the bulk density 0.811 kg/dm^3 when 100 g of the SP is rubbed with 30 g of the LOP solution dosed at a temperature of 80°C and than calcined at 550°C. The process parameters optimisation is an object of our further research.

Acknowledgement

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