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STUDY OF THERMAL DEHYDRATION OF SODIUM ORTHOPHOSPHATE MONOSUBSTITUTED

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Проведено дослідження процесу високо-температурної дегідратації натрій ортофосфату однозаміщеного. Встановлено хімічну схему і температурні діапазони утворення поліфосфатів змінного складу. Одержані експериментальні залежності складу поліфосфатних продуктів дегідратації від часу ізотермічної обробки натрій ортофосфату однозаміщеного. Показана можливість направлено синтезу сумішей поліфосфатів з прогнозованим кількісним складом

Ключові слова: полімерні фосфати, високотемпературна дегідратація, натрій ортофосфат однозаміщений, хімічна схема

Проведено исследование процесса высокотемпературной дегидратации натрий ортофосфата однозамещенного. Установлены химическая схема и температурные диапазоны образования полифосфатов переменного состава. Получены экспериментальные зависимости состава полифосфатных продуктов дегидратации от времени изотермической обработки натрий ортофосфата однозамещенного. Показана возможность направленного синтеза смесей полифосфатов с прогнозируемым количественным составом

Ключевые слова: полимерные фосфаты, высокотемпературная дегидратация, натрий ортофосфат однозамещенный, химическая схема

1. Introduction

Condensed phosphates of alkali metals have been widely applied in different sectors of industry, such as food, cosmetic, pharmaceutical, chemical, construction, etc.

Depending on the conditions of application and the requirements put forward to the properties, individual polyphosphates and mixtures of variable composition are utilized. Ammonium polyphosphate is used as a fertilizer and a fire retardant. Polyphosphates of calcium, potassium, and ammonium improve the taste qualities of food products. Among the polyphosphates of alkali metals, the most commonly used are sodium polyphosphates, which possess considerable restructuring properties and rather high solubility in water.

Sodium polyphosphates are actively used in water pre-treatment and anticorrosive protection of the conduits of circulating water supply. The inhibition of corrosion by polyphosphates makes it possible to substantially increase the period of operation of heating and cooling systems and in power engineering. The use of sodium phosphates in the polymeric form is promising in modern processes of the hot working of metals by pressure. By applying the molten

phosphates as components of technological lubricants, it is possible to substantially intensify the processes of the hot working of metals, as well as improve ecological conditions of labor. Polyphosphate mixtures contribute to reduction in the deformation forces; substantially increase the lifecycle of tools and productivity of the presses of rolling mills.

Thus, the development of technologies for obtaining the inorganic polymeric phosphates with the assigned composition and predicted physical-chemical properties is a relevant task of contemporary chemical science.

2. Literature review and problem statement

The basic properties that determine commercial use of polyphosphates are cheapness, ecological safety and biodegradability. Polyphosphates bind into complexes the cations of different metals. The possibility to form hydrogenous bonds predetermines the capability of polyphosphates to retain significant amount of water [1].

Polyphosphates are used as fertilizers [2], non-halogen, highly effective and nontoxic inorganic fireproofing com-

bound [3, 4]. Ammonium polyphosphate is an additive, applied for improving the quality of food products [5], it protects bacteria from the oxidizing stress and stabilizes the protein structure [6]. Polyphosphates are widely employed in the production that processes minerals as dispersants and rheological modifiers [7].

Phosphates and polyphosphates are applied in the field of treatment of the surface of metals. Steel structures being the most common construction material possess low anticorrosive durability. In this regard, a steel surface requires additional protection. Depending on the operating conditions and requirements to the physical-mechanical properties of surface of steel constructions, galvanic [8, 9], varnish-and-paint or conversion coatings are used. It is well known that the modification of composition of the paint and varnish coatings with anticorrosive pigments may improve the resistance of protective coatings to exfoliation. Polyphosphates of zinc and aluminum are the promising reagents, which can be utilized for this purpose [10, 11]. Conversion coatings based on phosphates ensure high protective properties [12, 13]. Polymeric phosphates are applied in the production of technological greases, used in the processes of metal working at high temperatures [14, 15].

As can be seen from the scientific literature data, polyphosphates have a rather extensive scope of application. Depending on the requirements put forward to the properties of polyphosphates, compounds with different structure and variable length of the polymer chain are used. The synthesis of polyphosphates of the assigned structure in each particular case requires a specific technique and selection of optimum conditions for conducting the process.

Thus, the mixed polyphosphate $\text{Na}_4\text{Mg}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ was obtained by authors of [16] by the stepwise heating of a mixture of magnesium oxide, soda and ammonium orthophosphate monosubstituted to 900°C with the subsequent cooling of reaction mixture under assigned temperature mode. By using the method of solid-phase recovery, there was received the new compound $\text{Pb}_{12}[\text{Li}_2(\text{P}_2\text{O}_7)_2(\text{P}_4\text{O}_{13})_2]$ (P_4O_{13}), containing in its structure several polyphosphate groups [17]. In [18], a method of spontaneous crystallization was applied to synthesize polyphosphate, which contains two different polyphosphate anions. Centrally symmetrical and asymmetrical polyphosphate structures were synthesized by the high-temperature melting by authors of article [19]. The compound $\text{Cs}_6\text{Mg}_6(\text{PO}_3)_{18}$ was synthesized from CsF , MgF_2 and $\text{NH}_4\text{H}_2\text{PO}_4$ through the solid-phase interaction of reagents. Under the analogous conditions, the polyphosphate compound $\text{Cs}_2\text{MgZn}_2(\text{P}_2\text{O}_7)_2$ was obtained from a mixture of CsF , MgF_2 , ZnO and $\text{NH}_4\text{H}_2\text{PO}_4$. The basic method of obtaining the condensed sodium phosphates in the crystalline and powder-like state is the thermal dehydration of acid orthophosphates. Thus, the high-temperature treatment of sodium orthophosphate monosubstituted monohydrate was applied in [20] to synthesize polyphosphates with a variable length of the polymer chain. The synthesis was carried out at 700°C and 775°C and duration of thermal treatment from 30 minutes to 9 hours. In the process of high-temperature dehydration, depending on the temperature and duration of the process, various forms of polymeric phosphates are created.

It should be noted that composition of the mixture of polyphosphates, obtained at high-temperature dehydration of sodium orthophosphate monosubstituted, essentially defines the properties of technological lubricants. In particular, when rolling the pipes in automatic mills, it is expedient to use as a phosphate component of lubricants salt systems based on the pyro-, tripoly and metaphosphates of alkali metals [14, 15]. In this regard, it is a promising task from the point of view of obtaining technological lubricants with the assigned properties to predict the synthesis of a mixture of polyphosphates. The literary sources lack the systems research into qualitative ratios of the components of this mixture, synthesized from orthophosphates. Therefore, it appears very important to establish the experimental dependences of the composition of polymeric phosphates on the temperature regimes of dehydration and duration of the process of high-temperature treatment of sodium orthophosphate monosubstituted.

3. The aim and tasks of research

The aim of present work is to establish special features of thermal dehydration of sodium orthophosphate monosubstituted with the formation of polymeric phosphates of variable composition. This will make it possible to purposefully control the process of the synthesis of polyphosphates, ensuring the controlled qualitative ratio of the obtained products.

To accomplish the set aim, the following tasks were to be solved:

- to explore the effect of temperature of dehydration of sodium orthophosphate monosubstituted on the composition of the obtained polymeric phosphates and to establish the chemical scheme of conversion;
- to examine the effect of temperature and duration of the process on the composition of salt mixtures of polymeric phosphates, which are formed at different temperature regimes of conducting the dehydration of sodium orthophosphate monosubstituted.

4. Materials and methods for examining the high-temperature dehydration of sodium orthophosphate monosubstituted

Obtaining the polymeric phosphates from sodium orthophosphate monosubstituted was carried out on the laboratory installation whose schematic is shown in Fig. 1.

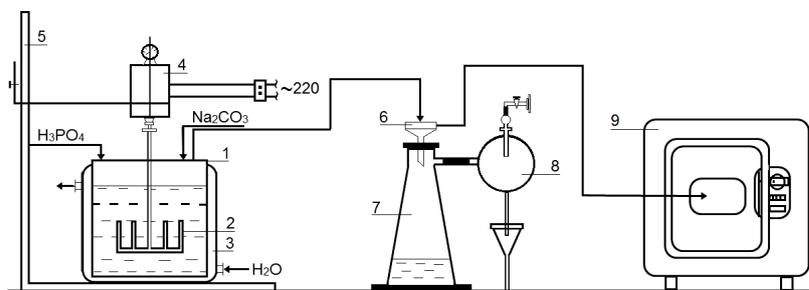


Fig. 1. Schematic of laboratory installation for obtaining the polymeric phosphates from sodium orthophosphate monosubstituted: 1 – reactor-crystallizer; 2 – mixer; 3 – jacket; 4 – electric drive; 5 – support; 6 – Buechner funnel; 7 – Bunsen flask; 8 – water-jet pump; 9 – muffle furnace

Obtaining the polymeric phosphates was accomplished in several stages – the synthesis of sodium orthophosphate monosubstituted and its thermal treatment. Sodium orthophosphate was obtained in the cylindrical reactor – crystallizer 1, equipped with jacket 3 and stirring device 2. In the reactor we loaded the calculated quantity of 85 % of thermal phosphoric acid and, at the enabled mixer 2, we neutralized it with soda ash to pH=3.5–4.0. The exothermic process of neutralizing the phosphoric acid was accompanied by the creation of supersaturation due to the progress of irreversible chemical reaction of forming the crystals of sodium orthophosphate from the solution. The pulp of sodium orthophosphate was cooled in the reactor-crystallizer to the temperature of 25–30 °C, by feeding the cooling water to jacket 3, with subsequent separation of crystals on Buechner funnel 6. Drying the obtained sample of sodium orthophosphate was performed in the muffle furnace SNOL (Lithuania) 9 with the accuracy of temperature registration ± 2 °C at temperature 25–30 °C to a constant mass. The obtained product met the standard “pure for analysis” in line with GOST 245-76. We experimentally established that the crystalline hydrate of sodium orthophosphate monosubstituted contained 1.3 molecules of H₂O, which can be linked to the crystallization mono- and dihydrates from the solution of the mixture. The thermal treatment of sodium orthophosphate was carried out in muffle furnace 9 at different temperatures.

The thermograms were recorded on the derivatograph Q-1500 D (Hungary), Paulik system, in the air atmosphere in the range of temperatures 20–1000 °C at the heating rate of the sample NaH₂PO₄·1.3H₂O equal to 0.17 to K/s.

The radiographs were recorded on the diffractometer DRON 3.0 (Russia) using the Cu_{K α} -emission. The interplanar spacing on the radiographs of dehydration products was compared to the data in the catalog of ASTM (American Society for Testing and Materials).

Quantitative composition of the dehydration products was established by the method of eluent ion exchange chromatography, which is the most effective for the separation of various forms of phosphates. The chromatographic separation of phosphates was conducted employing the following procedure. As a chromatographic column we used a glass column of diameter 15 mm and length 90 mm, and as an ion-exchange resin – the anionite IF-23 (Ukraine). Determining a mass fraction of P₂O₅ in the samples was conducted according to GOST 20291-80, with the help of the photoelectric colorimeter FEK-56M (Russia) at wavelength 440 nm.

The selection of optimum conditions for conducting the chromatography of the mixture of phosphates was carried out experimentally. It is established that the relationship (or ion-exchange potential) of phosphates to the resin IF-23 (Ukraine) increases with an increase in the polarizability of anions, which is characteristic for the highly alkaline ion exchangers.

We examined a dependence of the washing-out rate of ions of ortho-, pyro-, tripoly-, and metaphosphate from the ion-exchange column on the eluent pH. Fig. 2 shows the curves of elution of standard solutions of ions (optical density characterizes the ion concentration in separate portions of eluent) depending on the concentration and volume of eluent.

Results of the studies testify to the fact that the maximum separation of the mixture of ortho-, pyro-, tripoly- and metaphosphates can be reached at the eluent pH 5.6–5.8 (Fig. 2, curve 2). It is necessary to sequentially increase the eluent concentration from 0.1 mol/l to 0.4 mol/l (Fig. 2). The

passage rate of eluent through the column must not exceed 2 ml per 1 minute.

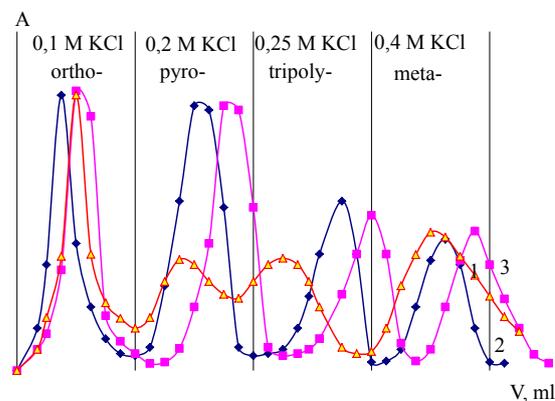


Fig. 2. Elution curves of the mixture of ortho-, pyro-, tripoly- and metaphosphates at pH: 1 – 9; 2 – 5.7; 3 – 4

It was established that when using the neutral or weak-alkaline solutions of eluent, it is not possible to reach the complete separation of ortho-, pyro- and tripolyphosphates (Fig. 2, curve 1). The reason for this is the increased value of the coefficient of anion confinement at such pH. The use of eluent solutions with pH lower than 4 (Fig. 2, curve 3) leads to an increase in the volume of eluent that must be used for the complete washing out of the analyzed ions, which considerably increases the duration of analysis.

Metrological characteristics of determining the ortho-, tri- and metaphosphates by the method of ion exchange chromatography are given in Table 1.

Table 1

Results of determining the ortho-, pyro-, meta- and tripolyphosphates by the method of ion exchange chromatography in the model solutions ($n=5$, $P=0.95$)

Defined anion	Introduced, mg	Found ($\bar{x} \pm \delta$), mg	Sr*
orthophosphate	5.00	5.04 \pm 0.12	0.02
pyrophosphate	5.00	4.97 \pm 0.28	0.05
tripolyphosphate	5.00	5.04 \pm 0.18	0.03
metaphosphate	5.00	5.05 \pm 0.10	0.02

Note: * n – the number of measurements; P – confidence probability; Sr – relative standard deviation

The low values of relative standard deviation of the analytically determined amount of anion from the true values testify to sufficient sensitivity of the procedure and reproducibility of the results.

5. Results of examining the thermal dehydration of crystalline hydrate of sodium orthophosphate monosubstituted

The process of high-temperature dehydration of sodium orthophosphate is described by complicated chemical reactions. It is experimentally established that the isothermal

treatment of sodium orthophosphate at a temperature lower than 180 °C is accompanied only by removal of crystallization water from the sample, which agrees well with the results of thermogravimetric studies [15].

Fig. 3 shows that a number of endoeffects is observed at a temperature lower than 130 °C. In this case, obviously, there occurs the removal of the physically sorbed moisture from the sample, the melting of mono sodium phosphate (MSP) crystalline hydrate in the crystallization water and the loss of the crystallization water.

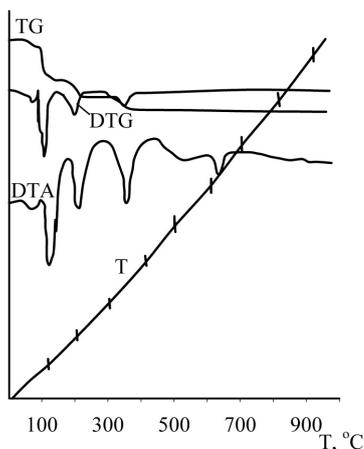


Fig. 3. Derivatogram of crystalline hydrate of sodium orthophosphate monosubstituted at heating rate of the sample 10 deg/s

It was experimentally established that the obtained model of MSP contains crystallization water in the amount of 1.3 molecules of H₂O.

The radiographs of the model sample, thermostatically controlled at t=130 °C (Fig. 4), registered the maxima at d_{HKL}=6.65, 3.83, 3.35 and 3.20 Å. The latter relate to the interplanar spacing of the waterless sodium orthophosphate monosubstituted NaH₂PO₄.

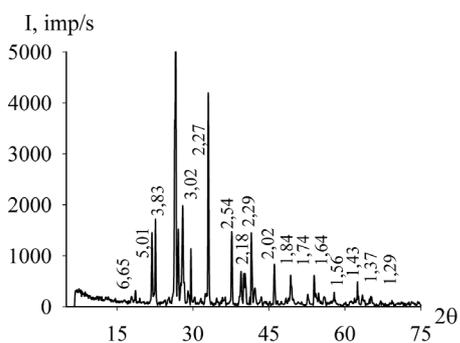


Fig. 4. Radiograph of the sample NaH₂PO₄·1.3H₂O, treated at temperature 130 °C

Dehydration in the temperature interval of 130–220 °C is accompanied by the endoeffect, which corresponds to 188 °C. In this case, there occurs the splitting of 0.5 mole of water and formation of the sodium dihydropyrophosphate Na₂H₂P₂O₇. This is confirmed by data, received when conducting the X-ray phase studies (Fig. 5). The radiograph of the model sample, treated at 220 °C, displays the maxima at d_{HKL}=2.92, 3.07, 3.42 Å.

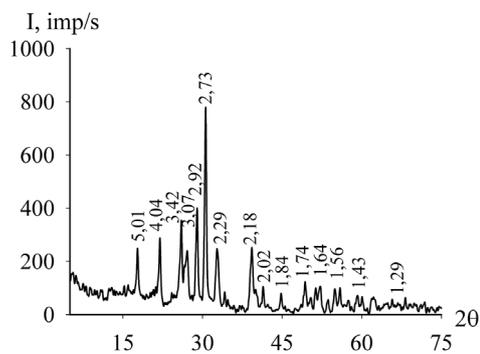


Fig. 5. Radiograph of the sample NaH₂PO₄·1.3H₂O, treated at temperature 220 °C

The thermochemical transformations, which take place in the range of temperatures from 300 °C to 420 °C, are accompanied by the absorption of heat at 342 °C, by the removal of 0.5 moles of water and by the formation of Na₃P₃O₉. Essential inhibition of dehydration is caused by the emergence of a dense film at the surface of the product, which hampers dehydration. The formation of Na₃P₃O₉ is confirmed by the existence of maxima in the radiograph of the sample (Fig. 6) at d_{HKL}=6.70, 3.42, 3.85 and 3.07 Å.

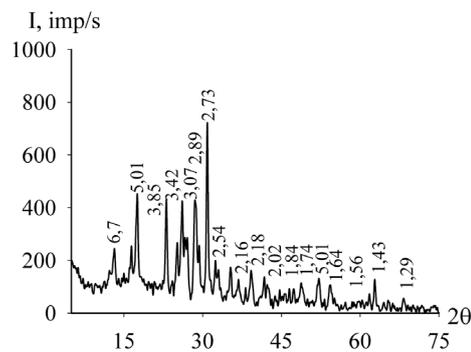


Fig. 6. Radiograph of the sample NaH₂PO₄·1.3H₂O, treated at temperature 420 °C

The transformation of sodium trimetaphosphate into hexametaphosphate proceeds with a change in the temperature from 450 °C to 650 °C. At 650 °C, hexametaphosphate of amorphous structure forms, which is indicated by the absence of lines of the crystalline phases against the background of halo on the radiograph (Fig. 7).

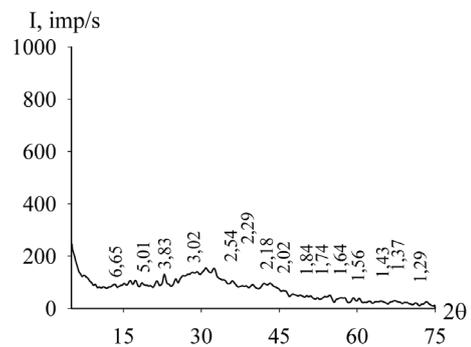


Fig. 7. Radiograph of the sample NaH₂PO₄·1.3H₂O, treated at temperature 650 °C

Thus, the thermal treatment of $\text{NaH}_2\text{PO}_4 \cdot 1.3\text{H}_2\text{O}$ in the range of temperatures 200–650 °C is accompanied by the formation of polymeric phosphates of different structure.

6. Discussion of results of examining the thermal dehydration of crystalline hydrate of sodium orthophosphate monosubstituted

A composition of the products of high-temperature dehydration depends on both the temperature and the duration of process. The quantitative composition of dehydration products, which corresponds to the specific time of thermal treatment, was determined by the method of eluent ion exchange chromatography.

Fig. 8 shows a time dependence of the percentage of various forms of polymeric phosphates (ω , % by weight), obtained from MSP at temperature 220 °C.

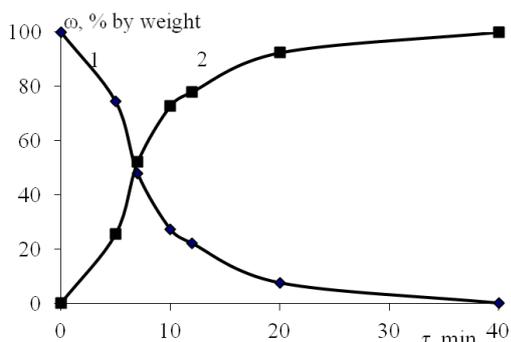


Fig. 8. Time dependences of the distribution of phosphate forms at t=220 °C: 1 – $\text{NaH}_2\text{PO}_4 \cdot 1.3\text{H}_2\text{O}$; 2 – $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$

It was experimentally established that at 220 °C the process of isothermal dehydration of sodium orthophosphate monosubstituted proceeds with high selectivity and the formation of only sodium dihydropyrophosphate ($\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$). Fig. 8 shows that during the first 10 minutes, the content of $\text{NaH}_2\text{PO}_4 \cdot 1.3\text{H}_2\text{O}$ sharply decreases, while the content of $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ grows by the exponential dependence. Subsequently, an increase in the content of $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ and reduction in the amount of $\text{NaH}_2\text{PO}_4 \cdot 1.3\text{H}_2\text{O}$ proceed at lower speed, which is, apparently, related to an increase in the diffusion resistance to the removal of water through a layer of the reaction product.

Complete transformation of sodium orthophosphate monosubstituted into dihydropyrophosphate at 220 °C finishes in 40 minutes. Thus, with the variation of time of conducting the process, it is possible to obtain a mixture of polymeric phosphates with the required content of $\text{NaH}_2\text{PO}_4 \cdot 1.3\text{H}_2\text{O}$ and $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$.

The dehydration of MSP at 420 °C (Fig. 9) is characterized by the more complicated chemistry of the process.

Isothermal dehydration of MSP at 420 °C is accompanied by the progress of three simultaneous reactions:

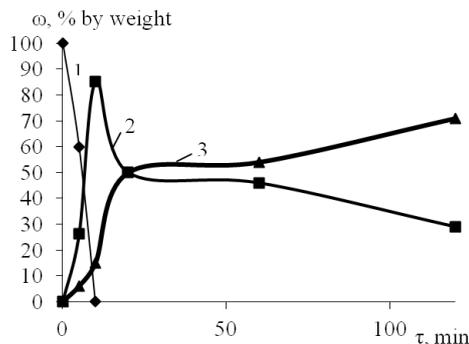
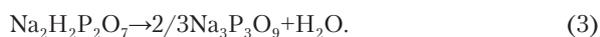
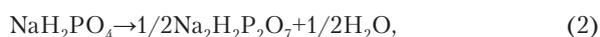


Fig. 9. Time dependences of the distribution of phosphate forms at t=420 °C: 1 – NaH_2PO_4 ; 2 – $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$; 3 – $\text{Na}_3\text{P}_3\text{O}_9$

A complete removal of the crystallization moisture from NaH_2PO_4 and the formation of $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ finish in the first 10 minutes. The formation of $\text{Na}_3\text{P}_3\text{O}_9$ has three clearly expressed regions:

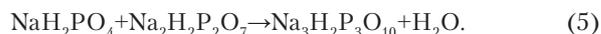
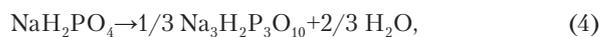
- 1) induction period (0–10 min);
- 2) the region of rapid growth of the content of $\text{Na}_3\text{P}_3\text{O}_9$ in the salt system (10–20 min);
- 3) the region of a slow change in the content of $\text{Na}_3\text{P}_3\text{O}_9$ in the salt system (20–120 min).

Induction period, characteristic for the initial period of dehydration, is explained by the predominant progress of the reactions of dehydration of $\text{NaH}_2\text{PO}_4 \cdot 1.3\text{H}_2\text{O}$ and the formation of $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$. The period of rapid growth in the content of $\text{Na}_3\text{P}_3\text{O}_9$ in the salt system is characteristic of the course of reaction (3) in the kinetic region. The region of a slow increase in the content of $\text{Na}_3\text{P}_3\text{O}_9$ is related to the transition of the process of dehydration into the region of diffusion with a limiting stage, which corresponds to the removal of water through a layer of the reaction product.

Thus, at temperature 420 °C, there forms a salt mixture, which contains $\text{Na}_3\text{P}_3\text{O}_9$, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ and NaH_2PO_4 . The ratio of components changes depending on the time of thermal treatment of the reaction mixture. The obtained salt systems could be used as phosphate components when rolling the pipes in automatic mills.

Fig. 10 shows a time dependence of the percentage of various forms of polymeric phosphates, obtained from MSP at temperature 650 °C. The process of formation of $\text{Na}_6\text{P}_6\text{O}_{18}$ is superimposed with side reactions, which proceed with the formation of $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ and $\text{Na}_3\text{H}_2\text{P}_3\text{O}_{10}$ (sodium tripolyphosphate). In the first 2.5 min. the content of $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ in the sample reaches a maximum and it is lowered over time to 8%, which is associated with its transition into $\text{Na}_3\text{P}_3\text{O}_9$ and $\text{Na}_3\text{H}_2\text{P}_3\text{O}_{10}$.

Sodium tripolyphosphate forms in the course of two parallel reactions:



The formation of $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ proceeds by reaction (2).

High-temperature dehydration of $\text{NaH}_2\text{PO}_4 \cdot 1.3\text{H}_2\text{O}$ proceeds predominantly with the formation of $\text{Na}_6\text{P}_6\text{O}_{18}$ by reaction:



A composition of the salt system obtained at 650 °C during 10–30 minutes remains unchanged: 76 % $\text{Na}_6\text{P}_6\text{O}_{18}$, 8 % $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, 8 % $\text{Na}_3\text{H}_2\text{P}_3\text{O}_{10}$, 8 % NaH_2PO_4 .

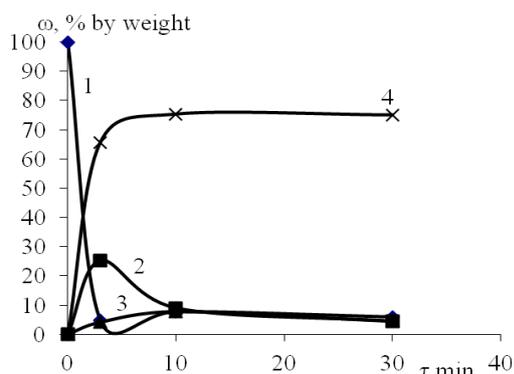


Fig. 10. Time dependences of the distribution of phosphate forms at $t=630$ °C: 1 – NaH_2PO_4 ; 2 – $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$; 3 – $\text{Na}_3\text{H}_2\text{P}_3\text{O}_{10}$; 4 – $\text{Na}_6\text{P}_6\text{O}_{18}$

Such salt systems might be used as the basic phosphate component of technological lubricants for the hot rolling of pipes in the reeler machines.

7. Conclusions

1. We examined the process of thermal dehydration of crystalline hydrate of sodium orthophosphate monosubstituted under nonisothermic and isothermal conditions and determined the composition of reaction products. We established the temperature intervals, which correspond to the thermal-chemical transformations of polyphosphates and proposed the chemical scheme of the progress of thermal dehydration of crystalline hydrate of sodium orthophosphate monosubstituted in the temperature interval of 200–630 °C.

2. It is shown that as a result of thermal treatment of $\text{NaH}_2\text{PO}_4 \cdot 1.3\text{H}_2\text{O}$ at temperature 220 °C, only $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ forms. Under the temperature regime of treating $\text{NaH}_2\text{PO}_4 \cdot 1.3\text{H}_2\text{O}$ of 420 °C, there proceed the reactions of formation of $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ and $\text{Na}_3\text{P}_3\text{O}_9$. At temperature 630 °C, sodium orthophosphate monosubstituted undergoes the transformations, which lead to the formation of polyphosphates $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, $\text{Na}_3\text{H}_2\text{P}_3\text{O}_{10}$ and $\text{Na}_6\text{P}_6\text{O}_{18}$. It is established that depending on the temperature and duration of isothermal process, it is possible to obtain the mixtures with the specific ratio of polyphosphates that form under these conditions. This provides the possibility of conducting the directed synthesis of the mixtures of polymeric phosphates with the required operational properties.

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