KAPITEL 1 / *CHAPTER 1*

PHYSICO-CHEMICAL FUNDAMENTALS OF SYNTHESIS OF BINDING MATERIALS FROM ORTHOPHOSPHORIC ACID AND INORGANIC SALTS OF METALS

ФІЗИКО-ХІМІЧНІ ОСНОВИ СИНТЕЗУ ЗВ’ЯЗУВАЛЬНИХ МАТЕРІАЛІВ ІЗ ОРТОФОСФОРНОЇ КИСЛОТИ ТА НЕОРГАНІЧНИХ СОЛЕЙ МЕТАЛІВ

DOI: 10.30890/2709-2313.2021-07-08-015

1.1. Modern scientific issues of creation and use of binders

Binders are used in many fields of technology, such as construction, chemical, paint and varnish, mechanical engineering and instrumentation. They have also found their purpose in the medical and food industries. At the same time, metallurgy, foundry production and production of refractories have a significant advantage in terms of specific consumption of binders [1-4].

According to official data, today it is necessary to use 7…8 tons of auxiliary (molding) materials for the production of one ton of foundry products, part of which are binders [1, 5-8]. Prospects for the development of foundry production and mechanical engineering, which in many countries of the world form the main part of the state budget and regulate economic processes, depend on their properties, quality, and environmental friendliness.

Since the early 90’s of the twentieth century, the leading place in foundry technology has been occupied by sand-resin molding and core mixtures of both cold and thermal hardening. Binders in them are urea, phenol-formaldehyde and furan resins [1, 2, 5]. In many countries around the world, the production of resin binders has been discontinued due to high environmental threats to the components (phenol, formaldehyde, furfural, etc.). Therefore, recently the search for new technical solutions based on the use of inorganic binders has become relevant.

One of the main directions in the search for new inorganic binders is the study of phosphate materials. They are a large group of compounds that can be obtained in finished form or by chemical synthesis from non-deficient and environmentally friendly components. The problems of creating phosphate binders were studied by prominent scientists: W. D. Kingery [9], D. Wygant [10], V. F. Zhuravlyov [11], M. M. Sychov [12], L. G. Sudakas [13, 14], V. A. Kopeikin [4] and others. Investigations of molding and core mixtures with binder components were carried out in the works of Yu. P. Vasin [15], E. S. Gamov [16], S. S. Zhukovsky [17], I. E. Illarionov [18, 19], S. P. Doroshenko [20].

The scientific basis for the synthesis of phosphates from oxide materials is quite clear, but not fully disclosed in some areas. This hinders the development of new types of binders, particularly for molds and cores. To date, there is no description of the laws of physicochemical processes of interaction of orthophosphoric acid with inorganic salts of sulfuric, hydrochloric, nitric, carbonic and other acids. There are no regularities in the formation of phosphates of active metals (elements of groups I and II of the periodic table), which have binding properties, there is no data on the dynamics of their transformations during heating. Information on the mutual conversions of phosphates and sodium polyphosphates and the comparison of their binding properties is fragmentary.

1.2. The aim and objectives of the study

The aim of the study is to establish the laws of physicochemical interaction of the most common inorganic metal salts with orthophosphoric acid and to study the binding properties of synthesized products.

Research objectives:

1. Qualitative analysis of the processes that occur during the interaction of orthophosphoric acid with inorganic metal salts.
2. Calculation and analysis of thermodynamic parameters of orthophosphoric acid interaction processes with inorganic metal salts at different temperatures.
3. Establishing the influence of side physicochemical processes (hydration, dehydration, hydrolysis, thermal decomposition) on the interaction of inorganic salts with orthophosphoric acid.
4. Establishment of phase and mineralogical composition of products synthesized in the studied systems.
5. Research of the binding potential of synthesized products by determining the strength of samples based on granular quartz filler.
6. Research of the dynamics of transformations of synthesized phosphate binders components when heated to 1000 °C.

1.3. Method of experiments and calculations

Binders based on a combination of inorganic metal salts and orthophosphoric acid have not yet been developed. The general chemical scheme by which this process could take place, in a simplified form can be represented as follows:

$$Me_x(AR)_y + H_3PO_4 = Me_3(PO_4)_y + H_x(AR),$$

$$\text{or } Me_x(AR)_y + H_3PO_4 = Me_3(PO_4)_y \cdot nH_2O + \text{gas}, \qquad (1)$$

where Me – metal;
AR – acid residue;
x, y – valence of acid residue and metal.

The most common acid residues are SO_4; SO_3; NO_3; Cl, as well as PO_4. Phosphates $Me_3(PO_4)_y$ or their crystal hydrate form $Me_3(PO_4)_y \cdot nH_2O$, usually have binding properties.

Acid H_3PO_4 is weaker than H_2SO_4; H_2SO_3; HCl; HBr and HNO_3, and from this point of view the passage of reactions (1) is impossible.

If an insoluble salt or gaseous product is formed in the right part of the reaction, the weak acid can displace the strong one from its salts, provided that the strong acid salt is water-soluble.

Phosphates are mostly insoluble, with the exception of sodium phosphate and, according to some data [21], sparingly soluble magnesium phosphate. Therefore, the probability of exchange reactions (1) exists. After that their thermodynamic possibility comes to the fore.

The thermodynamic possibility of interaction of orthophosphoric acid with inorganic metal salts was evaluated by the calculated values of the isobaric-isothermal potential (Gibbs energy) for each chemical reaction. The reaction potential was determined at different temperatures from 20 to 300 °C, or from 293 to 573 K.

Two formulas can be used to find the isobaric-isothermal reaction potential when the temperature rises. The first of them takes into account the dependence of heat capacity on temperature (using virial coefficients a, b, c). However, these coefficients for the vast majority of reagents (including aluminum salts) are not listed in the literature [22-24 and others]. In addition, the heating of the samples in our case is relatively insignificant, and therefore the dependence of heat capacity on temperature can be neglected. Based on this, the formula is used in the calculations:

$$\Delta G_T = \Delta H^0_{298} - T \cdot S^0_{298} + \Delta C^{\,0}_{p\,298}(T - 298) - \Delta C^{\,0}_{p\,298} \cdot T \cdot \ln\frac{T}{298}, \qquad (2)$$

where ΔG_T – change of isobaric-isothermal potential (Gibbs energy), J/mol;

ΔH^0_{298} – standard enthalpy, J/mol;

T – temperature, K;

S^0_{298} – standard entropy, J/(mol·K);

ΔC_p – heat capacity, J/(mol·K).

Based on the results of calculations, a conclusion was made about the thermodynamic probability of the studied reactions.

Cylindrical specimens (Fig. 1) with a diameter and height of 50 mm were made to assess the binding potential of the synthesized phosphate or complex materials. Such samples are a standard test for the strength of molding and core mixtures in foundry production.

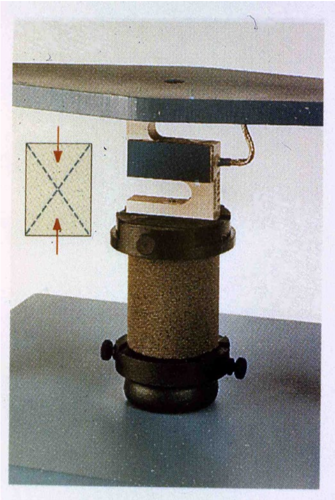


Fig. 1 – Standard cylindrical sample for compressive strength test

The mixture from which the samples were made, included a granular quartz filler, the particle size distribution of which is shown in table 1.

Table 1 – Particle size distribution of quartz sand

The size of quartz particles, mm	2.5	1.6	1.0	0.63	0.4	0.315	0.2	0.16	0.1	0.063	0.05	<0.05
Percentage, %	0.0	0.0	0.0	2.5	10.9	15.7	36.3	21.5	8.5	3.1	0.5	1.0

Samples were made from mixtures according to the following two options:

1. Granular quartz filler (92.0% by weight), orthophosphoric acid (3.0% by weight), inorganic metal salt (3.0% by weight), water (2.0% by weight) – the graphs show as "acid + name of inorganic salt".

2. Granular quartz filler (90.0% by weight), pre-prepared binder composition (5.0% by weight) and water (5.0% by weight) are shown on the graphs as "binder composition". This name refers to a dry composition prepared by pre-mixing 1 mass part of orthophosphoric acid and 5 mass parts of inorganic metal salt, followed by exposure for 1 hour at a temperature of 200 °C (473 K).

Technical orthophosphoric acid in the form of an 85% solution was used in all experiments.

The compressive strength of the samples was determined on a specialized unit "УС-700" after exposure to 24 hours at normal temperature and after drying for 1 hour at temperatures from 100 to 200 °C (from 373 to 473 K). In some cases, after the analysis of physicochemical processes, additional experiments were performed at temperatures up to 300 °C (573 K).

Strengths less than 1.0 MPa were considered unsatisfactory, as this is not enough for any practical application.

1.4. Qualitative analysis of the chemical interaction of inorganic salts with orthophosphoric acid

To conduct a qualitative study, inorganic metal salts in the amount of 5 mass parts with orthophosphoric acid in the amount of 1 mass part were mixed. The total weight of each sample was 20 g.

To the thus obtained samples were added 5 ml of water to convert them to a liquid state, and then monitored the behavior of the compositions at normal temperature for 5 hours.

Similar portions of each mixture were subjected to pre-heat treatment (150… 200 °C or 423…473 K). Then 5 ml of water was added and the behavior of each of them at normal temperature for 5 hours was studied.

The results of the observations are presented in table 2. The hardening of the compositions was determined visually as well as with a sharp object (their conditional strength was controlled with a needle with a diameter of 1 mm). If the sample remained wet or became crumbly after the water evaporated, the absence of any binding properties was recorded (0). If the sample did not fall apart, but visually did not have strength – 1. Low conditional strength was estimated at 2 points, medium strength – 3 points, high strength – 4 points. High conditional strength – the sample is almost not susceptible to abrasive effects, was rated 5 points.

Table 2 – The results of the interaction of orthophosphoric acid with inorganic metal salts

Pos. ind.	The main substance of the sample	Processes after mixing with H_3PO_4	Conditional strength of the samples after the addition of water and exposure, score	
			in the initial state	heat treated at 423…473 K
1	Li_2SO_4	without visible reaction	0	1
2	Na_2SO_3	gas evolution, pungent odor	1	4
3	$Na_2S_2O_5$	gas evolution, pungent odor	1	4
4	$Na_2S_2O_8$	gas evolution, pungent odor	0	1
5	$MgSO_4 \cdot 7H_2O$	without visible reaction	0	1
6	$Al_2(SO_4)_3 \cdot 18H_2O$	without visible reaction	0	1
7	$CoSO_4 \cdot 7H_2O$	changed the color to burgundy	0	1
8	$FeSO_4 \cdot 7H_2O$	without visible reaction	0	1
9	$MnSO_4 \cdot 5H_2O$	without visible reaction	0	2
10	KCl	without visible reaction	0	1
11	KBr	without visible reaction	0	2
12	NaCl	without visible reaction	0	3
13	$CaCl_2 \cdot 4H_2O$	heating, pungent odor	0	3
14	$MgCl_2 \cdot 6H_2O$	without visible reaction	0	1
15	$MnCl_2 \cdot 4H_2O$	pungent odor	1	4
16	$NiCl_2 \cdot 6H_2O$	gas evolution, pungent odor	0	1
17	$BaCl_2$	without visible reaction	0	1
18	$NaNO_3$	without visible reaction	0	1
19	$Ca(NO_3)_2 \cdot 4H_2O$	without visible reaction	2	5
20	$Al(NO_3)_3 \cdot 9H_2O$	without visible reaction	0	1
21	$Sr(NO_3)_2$	without visible reaction	0	1
22	$Ba(NO_3)_2$	without visible reaction	0	1
23	Li_2CO_3	active reaction	0	1
24	Na_2CO_3	active reaction	1	1
25	$NaHCO_3$	active reaction	1	1
26	$CaCO_3$	slight heating	2	1
27	$BaCO_3$	without visible reaction	1	1

1.5. Synthesis of phosphate binders using sulfuric acid salts

Sulfuric acids are stronger than orthophosphoric acid, and therefore from a chemical point of view, only those reactions are possible, as a result of which insoluble phosphates are formed. The materials used in this work are salts of various acids: sulfuric H_2SO_4, H_2SO_3, and mixed or complex salts with anions (SO_2SO_3), (S_2O_8).

Salts of sulfuric acid are subject to hydrolysis by anion. Many sulfates have stable crystal hydrate forms. These factors are taken into account when analyzing the processes in the studied systems.

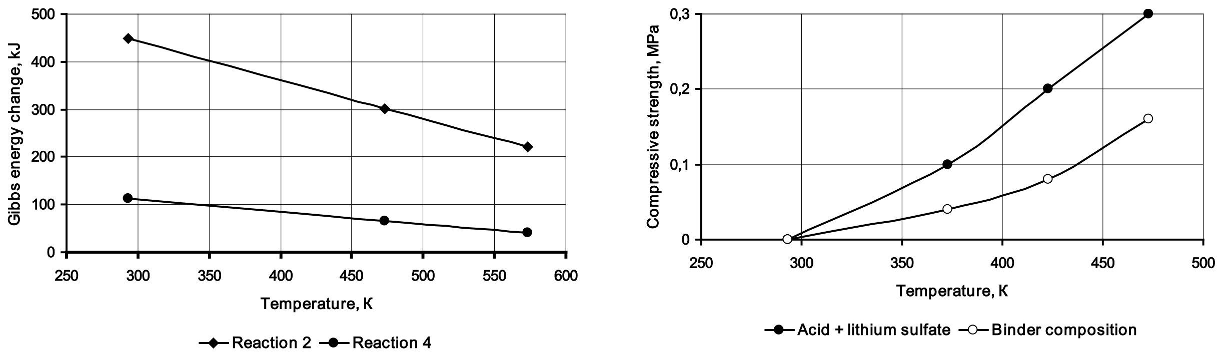
Thermodynamic calculations for chemical reactions of orthophosphoric acid interaction with a number of sulfate salts are performed and their results are analyzed.

The following reactions (2)…(4) were analyzed for **lithium sulfate Li_2SO_4**. Thermodynamic characteristics of the reactions are shown in Fig. 2 (a):

$$3\ Li_2SO_4 + 2\ H_3PO_4 \rightarrow 2\ Li_3PO_4 + 3\ H_2O \uparrow + 3\ SO_3 \uparrow \quad (2)$$

$$Li_2SO_4 + H_3PO_4 \rightarrow Li_2HPO_4 + H_2O \uparrow + SO_3 \uparrow \quad (3)$$

$$Li_2SO_4 + 2\ H_3PO_4 \rightarrow 2\ LiH_2PO_4 + H_2O \uparrow + SO_3 \uparrow \quad (4)$$



a **b**

Fig. 2 – Gibbs energy change in the range from 293 to 573 K for the reactions of interaction of lithium sulfate with orthophosphoric acid (a) and the compressive strength of samples (b)

Lithium sulfate is not prone to hydration and hydrolysis. Therefore, no other processes can occur except reactions (2)…(4). It is thermodynamically established that these reactions are impossible (Fig. 2, a), and, consequently, the phosphate binder is not formed in this system. This is also confirmed by the data of the previous experiment (see Table 2). Hardening of the mixture with this system almost does not occur (Fig. 2, b).

However, the numerical strength of the samples indicates that the binder in the mixture is still present. There are two reasons for this. First, lithium sulfate has its own binding capacity. Secondly, orthophosphoric acid interacts with quartz (filler mixture) when heated. This has been confirmed by the authors [4, 14], in particular in our publications [25-27]. However, heating up to 573 K is required for the interaction of the acid with quartz, so the formation of silicon phosphate in this case is only partial. Therefore, the strength of the investigated samples is due to lithium sulfate and partly silicon phosphate. However, the result of 0.3 MPa is obviously insufficient.

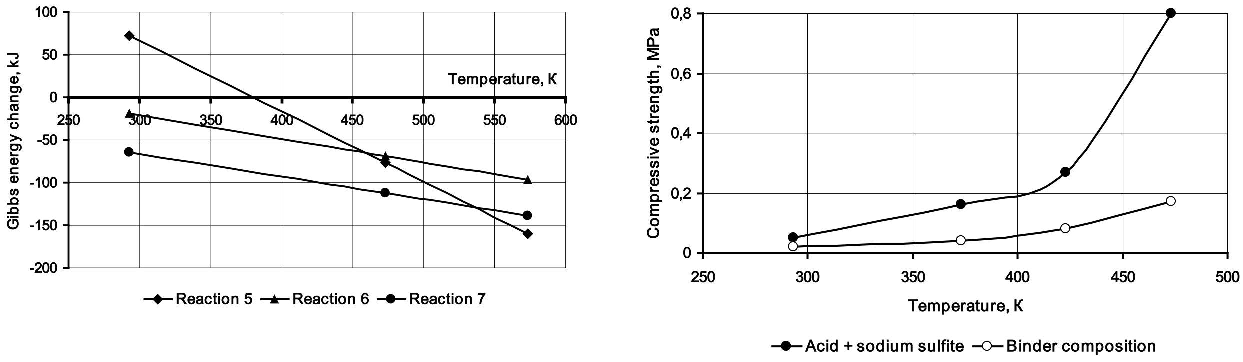
Reactions (5)...(7) were analyzed for **sodium sulfite Na_2SO_3**. The thermodynamic characteristics of these reactions are shown in Fig. 3 (a).

$$3\ Na_2SO_3 + 2\ H_3PO_4 \rightarrow 2\ Na_3PO_4 + 3\ H_2O \uparrow + 3\ SO_2 \uparrow \quad (5)$$

$$Na_2SO_3 + H_3PO_4 \rightarrow Na_2HPO_4 + H_2O \uparrow + SO_2 \uparrow \quad (6)$$

$$Na_2SO_3 + 2\ H_3PO_4 \rightarrow 2\ NaH_2PO_4 + H_2O \uparrow + SO_2 \uparrow \quad (7)$$

Sodium sulfite is a salt of sulfuric acid that is slightly stronger than orthophosphoric acid. It is thermodynamically established that the chemical reaction of sodium phosphate formation is possible at any temperature, including under normal conditions. A previous experiment (see Table 2) showed the release of gas with a pungent odor. According to official sources, it is SO_2. Thus, the main process in the system is the formation of sodium phosphate.



a **b**

Fig. 3 – Gibbs energy change in the range from 293 to 573 K for the reactions of sodium sulfite with orthophosphoric acid (a) and compressive strength of samples (b)

However, a satisfactory strength index could not be achieved (Fig. 3, b). Complete conversion of sodium sulfite to its phosphates in the first sample (acid + sodium sulfite) is possible, taking into account the mass ratios of chemical reactions (5)…(7). This should form a mixture of acidic sodium phosphates with a small amount of trisubstituted orthophosphate. These compounds provide an increase in strength in Fig. 3 (b). The effect of temperature is explained by the fact that the curing of the composition with water-soluble sodium phosphates requires the removal of moisture. In the second sample (binder composition), the maximum amount of sodium sulfite that can react is 37%, the rest remains in the original state. The strength of the samples is much lower, because they are dominated by sodium sulfite, rather than its phosphates.

Sodium pyrosulfite $Na_2S_2O_5$ is a mixed salt of sulfuric acids (H_2SO_4, H_2SO_3). It is less stable and emits SO_2 gas when heated to 338 K, melts at 423 K and decomposes completely at 575 K [28]. There are no reliable data on the thermodynamic characteristics of sodium pyrosulfite, so no analysis of its chemical reactions with orthophosphoric acid was performed.

According to the previous experiment (see Table 2), the evolution of gas in the process of mixing this salt with acid indicates the passage of a chemical reaction, which results in the formation of one of the sodium phosphates. Significant hardening of the samples (Fig. 4), compared with the samples of the second sample, in which there is a significant amount of residual sodium pyrosulfite, confirms the formation of sodium phosphates.

Similar processes, according to sample observations (see Table 2), occur in the system with **sodium persulfate $Na_2S_2O_8$**. It is a salt of sulfuric acid, but less stable and prone to decomposition. However, the decomposition apparently occurs only partially (before the formation of ordinary sodium sulphate Na_2SO_4). Since data on the thermodynamic parameters of sodium persulfate are also not available, it is not possible to analyze the Gibbs energy change for its reactions with acid. Indirect evidence of the formation of sodium phosphates in this system are the results obtained in Fig. 5.

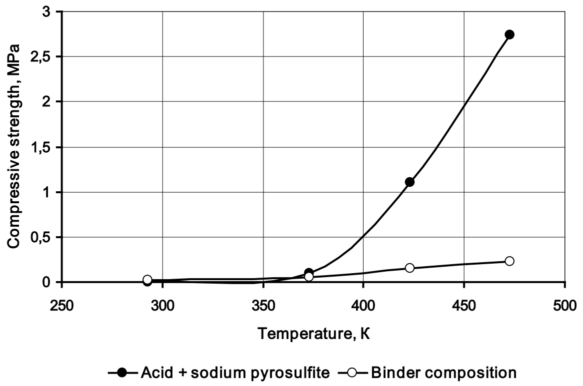


Fig. 4 – Dependence of compressive strength of samples of a mixture with orthophosphoric acid and sodium pyrosulfite on temperature

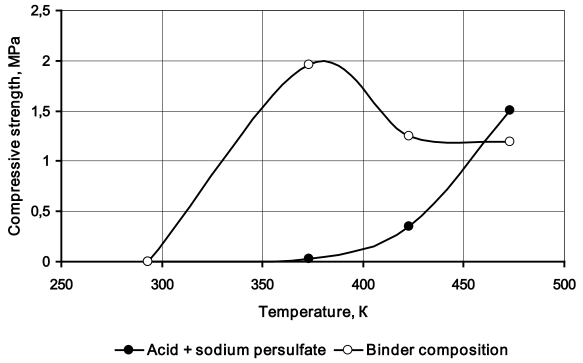


Fig. 5 – Dependence of the compressive strength of samples of a mixture with orthophosphoric acid and sodium persulfate on temperature

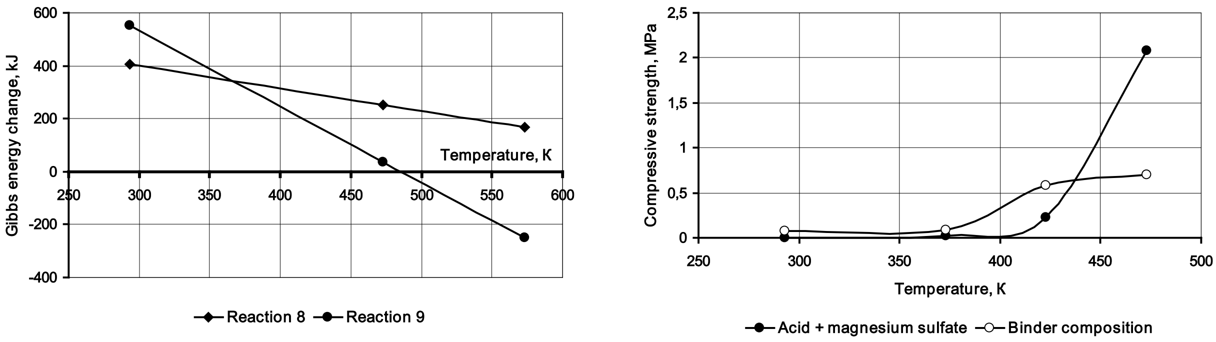
The process of phosphate formation occurs at a temperature of about 473 K, because this temperature compared to others provides a significant strengthening of the samples. The second sample consists of a binder composition treated at 473 K. It obviously contains water-soluble sodium phosphates. Hardening of the sample is due to the removal of moisture at a temperature of 373…423 K.

Reactions (8) and (9) were analyzed for **magnesium sulfate $MgSO_4$**. Thermodynamic characteristics of the reactions are shown in Fig. 6 (a).

$$3\ MgSO_4 + 2\ H_3PO_4 \rightarrow Mg_3(PO_4)_2 + 3\ H_2O + 3\ SO_3 \uparrow \quad (8)$$

$$3\ [MgSO_4 \cdot 7H_2O] + 2\ H_3PO_4 \rightarrow Mg_3(PO_4)_2 + 24\ H_2O + 3\ SO_3 \uparrow (9)$$

Magnesium sulfate is a salt of a strong acid. Crystalline heptahydrate magnesium sulfate was used in the research. At a temperature of 473 K and more, as shown in the graphs in Fig. 6 (a), it must interact with orthophosphoric acid by reaction (9). Since this salt is not subject to hydrolysis and has a high thermal stability (decomposition temperature 1410 K) [28], this system really should form a phosphate binder component. These conclusions are confirmed by the properties of the samples of the mixture. The figures are very low up to a temperature of 473 K. The samples have a strength of 2.1 MPa when it is reached (Fig. 6, b).



a **b**

Fig. 6 – Gibbs energy change in the range from 293 to 573 K for the reactions of interaction of magnesium sulfate with orthophosphoric acid (a) and compressive strength of samples (b)

The mass ratio of components for chemical reaction (9) and reactions of formation of acidic magnesium phosphates is analyzed, since the probability of their formation is also high:

$$MgSO_4 \cdot 7H_2O + H_3PO_4 \rightarrow MgHPO_4 + 8\ H_2O + SO_3 \uparrow \qquad (10)$$

$$MgSO_4 \cdot 7H_2O + 2\ H_3PO_4 \rightarrow Mg(H_2PO_4)_2 + 8\ H_2O + SO_3 \uparrow \qquad (11)$$

The mass ratio of magnesium sulfate to acid in reaction (9) is 3.2:1, in reaction (10) – 2.15:1, in reaction (11) – 1.05:1. Thus, in the first sample, the ratio is closest to the formation of monosubstituted magnesium phosphate $Mg(H_2PO_4)_2$. According to researchers [10-14], acidic phosphates of metals have a much higher binding potential.

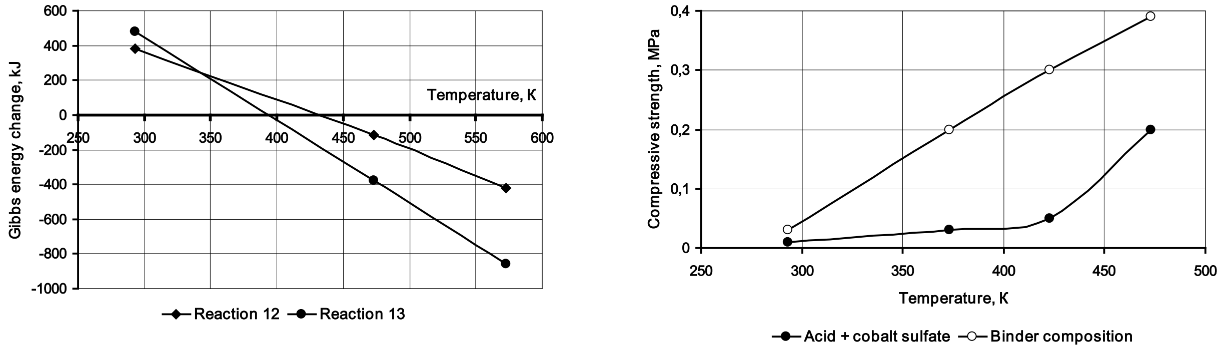
The mixture with the binder composition does not provide sufficient strength. First, this is due to the fact that it has already undergone a partial conversion of magnesium sulfate to phosphate. Magnesium phosphate is poorly soluble in water and therefore does not form adhesive bonds when mixed with quartz filler. Second, the estimated amount of magnesium sulfate that reacted is not more than 64%, and the rest is residual magnesium sulfate. The calculation also shows that trisubstituted magnesium phosphate is formed in this sample. Its binding potential is much lower, which leads to a much lower value of strength (Fig. 6, b).

Comparison of thermodynamic data (Fig. 6, a) and the results of control of the strength of samples (Fig. 6, b) lead to a fundamental scientific conclusion: **It has been established that the replacement of a strong acid salt with its crystal hydrate analogue can be a theoretical basis for the synthesis of a phosphate binder.**

Reactions (12)…(13) were analyzed for **cobalt sulfate $CoSO_4$**. Thermodynamic characteristics of the reactions are shown in Fig. 7 (a).

$$3\ CoSO_4 + 2\ H_3PO_4 \rightarrow Co_3(PO_4)_2 + 3\ H_2O \uparrow + 3\ SO_3 \uparrow \qquad (12)$$

$$3\ [CoSO_4 \cdot 7H_2O] + 2H_3PO_4 \rightarrow Co_3(PO_4)_2 + 24H_2O\uparrow + 3SO_3\uparrow \qquad (13)$$



a **b**

Fig. 7 – Gibbs energy change in the range from 293 to 573 K for the reactions of interaction of cobalt sulfate with orthophosphoric acid (a) and compressive strength of samples (b)

Cobalt sulfate is a much less stable chemical compound than the sulfates previously discussed. Heptahydrate cobalt sulfate at 314…316 K turns into hexahydrate, at 344 K – into monohydrate and in the range of 523…693 K completely loses crystal hydrate water [29]. In addition, cobalt sulfate is prone to cation hydrolysis. This can result in the formation of cobalt hydroxide, which is also able to react with acid.

The thermodynamic possibility of reactions has been proven with any form of cobalt sulfate. According to the graphs in Fig. 7 (a), the interaction can begin as early as 373…423 K. As a result, insoluble in water cobalt phosphates can be formed – anhydrous, octagonal (there is up to 413 K) dihydrate (there is up to 873 K). These phosphates are purple, and this is the color of the sample of the binder and samples of the core mixture.

Additionally, the chemical reactions of formation of cobalt acid phosphates were analyzed and it was established that for reaction (13) the ratio of cobalt sulfate to acid should be 3.65 : 1, for reaction (14) – 2.45 : 1, for reaction (15) – 1.21 : 1.

$$CoSO_4 \cdot 7H_2O + H_3PO_4 \rightarrow CoHPO_4 + 8H_2O\uparrow + SO_3\uparrow \qquad (14)$$

$$CoSO_4 \cdot 7H_2O + 2H_3PO_4 \rightarrow Co(H_2PO_4)_2 + 8H_2O\uparrow + SO_3\uparrow \qquad (15)$$

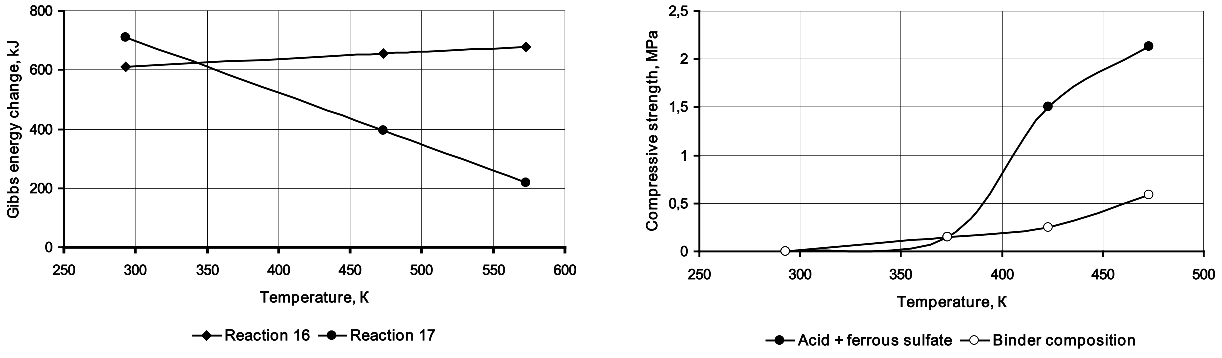
After analyzing the chemical reactions of heptahydrate cobalt sulfate with orthophosphoric acid, it was found that in the first sample (acid + cobalt sulfate) the conversion of sulfate to cobalt phosphate can be completed, and in the second sample (binder composition) only 73% of sulfate can react. Acidic phosphates are formed, so they have increased binding capacity. However, the overall strength remains low.

Reactions (16)…(17) were analyzed for **ferrous sulfate $FeSO_4$**. The thermodynamic characteristics of these reactions are shown in Fig. 8 (a).

$$3\ FeSO_4 + 2\ H_3PO_4 \rightarrow Fe_3(PO_4)_2 + 3\ H_2O\uparrow + 3\ SO_3\uparrow \qquad (16)$$

$$3\ [FeSO_4 \cdot 7\ H_2O] + 2\ H_3PO_4 \rightarrow Fe_3(PO_4)_2 + 24\ H_2O\uparrow + 3\ SO_3\uparrow \qquad (17)$$

Ferrous sulfate is used in crystal hydrate heptahydrate form. Thermodynamic analysis showed that none of the reactions of formation of iron phosphate from its sulfate is possible. Even significant heating (573 K or more) will not contribute to the formation of the binder component in this system. However, ferrous sulfate can be hydrolyzed by the cation to form hydroxosulfate $[Fe(OH)]_2SO_4$ or even hydroxide $Fe(OH)_2$ [28]. In a mixture containing water, this process is possible. Iron hydroxide, in turn, can react with orthophosphoric acid to form iron phosphate.



a **b**

Fig. 8 – Gibbs energy change in the range from 293 to 573 K for the reactions of interaction of ferrous sulfate with orthophosphoric acid (a) and compressive strength of samples (b)

It is obvious that in the temperature range of 423…473 K such a chemical process of interaction of the formed iron hydroxide with acid takes place, which ultimately provides high strength (Fig. 8, b). The calculation of the mass ratios of the components, taking into account the reaction of hydrolysis of ferrous sulfate (18) and subsequent formation of phosphates (19)…(21), showed that in the first sample (acid + ferrous sulfate) in excess acid (less than 80% acid reacts), and in the second sample (binder composition) there is an excess of iron sulfate (no more than 72% of it reacts).

$$FeSO_4 \cdot 7\,H_2O \rightarrow Fe(OH)_2 + H_2\,SO_4 \uparrow + 5\,H_2O \qquad (18)$$

$$3\,Fe(OH)_2 + 2\,H_3PO_4 \rightarrow Fe_3(PO_4)_2 + 6\,H_2O \qquad (19)$$

$$Fe(OH)_2 + H_3PO_4 \rightarrow FeHPO_4 + 2\,H_2O \qquad (20)$$

$$Fe(OH)_2 + 2\,H_3PO_4 \rightarrow Fe(H_2PO_4)_2 + 2\,H_2O \qquad (21)$$

The relatively low strength of the pre-prepared binder composition is due to the fact that all ferrous phosphates are insoluble in water and do not provide the formation of adhesive bonds with the quartz filler. In addition, trisubstituted iron phosphate has a lower binding potential compared to acidic phosphates, the formation of which is typical for the first mixture, the strength of which is much higher (Fig. 8, b).

Comparison of thermodynamic data from Fig. 8 (a) and the results of the strength control of the samples (Fig. 8, b) lead to another fundamental conclusion: **It has been established that salts of strong acids and transition metals can interact with orthophosphoric acid in a stepwise scheme – hydrolysis by cation with subsequent formation of phosphates, which is the scientific basis for the synthesis of phosphate binders.**

Reactions (22)...(23) were analyzed for **manganese sulfate $MnSO_4$**. Thermodynamic characteristics of the reactions are shown in Fig. 9 (a).

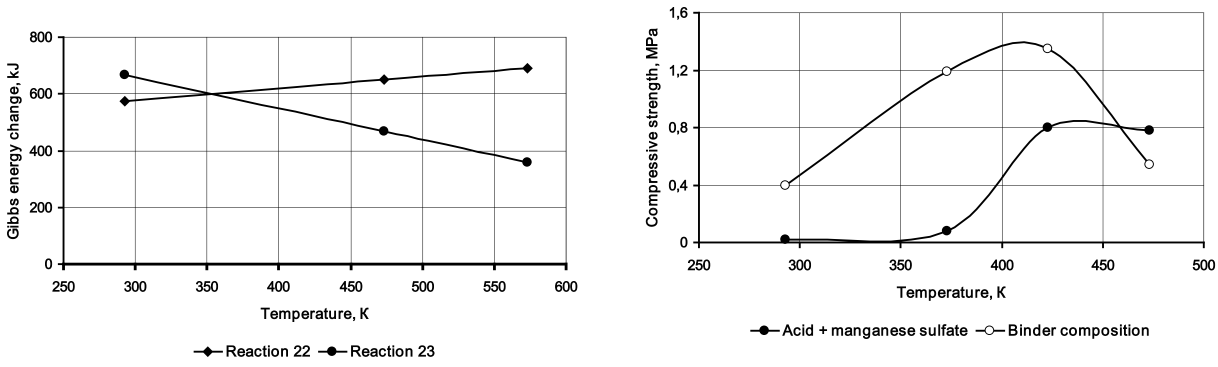
$$3\,MnSO_4 + 2\,H_3PO_4 \rightarrow Mn_3(PO_4)_2 + 3\,H_2O \uparrow + 3\,SO_3 \uparrow \qquad (22)$$

$$3\ [MnSO_4 \cdot 5\ H_2O] + 2\ H_3PO_4 \rightarrow Mn_3(PO_4)_2 + 18H_2O \uparrow + 3SO_3 \uparrow \qquad (23)$$

Manganese sulfate is used in the crystal hydrate pentahydrate form. This salt also cannot thermodynamically react with orthophosphoric acid. However, it, like ferrous sulfate, is hydrolyzed to form $Mn(OH)_2$ hydroxide by the reaction:

$$MnSO_4 \cdot 5\ H_2O \rightarrow Mn(OH)_2 + H_2\ SO_4 \uparrow + 3\ H_2O \qquad (24)$$

Manganese hydroxide, in turn, is able to interact with orthophosphoric acid and form phosphates. Manganese phosphates are water-soluble (especially monosubstituted $Mn(H_2PO_4)_2$). In addition, they are more prone to hydration. This is indicated by the fact that in the previous experiment (see Table 2) the sample with manganese sulfate has a higher conditional strength than the sample with ferrous sulfate.



a **b**

Fig. 9 – Gibbs energy change in the range from 293 to 573 K for the reactions of interaction of manganese sulfate with orthophosphoric acid (a) and compressive strength of samples (b)

Mixtures with a binder composition have better strength than with individual components (Fig. 9, b). After aging in the oven, the composition changed its color from pink, inherent in manganese sulfate, to light gray. Apparently, acidic manganese phosphates have formed here, which have a high binding potential. However, the recalculation of the mass ratios for the hydrolysis reactions and the subsequent formation of phosphates (25)…(27) indicates that no more than 62% of manganese sulfate will react.

$$3\ Mn(OH)_2 + 2\ H_3PO_4 \rightarrow Mn_3(PO_4)_2 + 6\ H_2O \qquad (25)$$

$$Mn(OH)_2 + H_3PO_4 \rightarrow MnHPO_4 + 2\ H_2O \qquad (26)$$

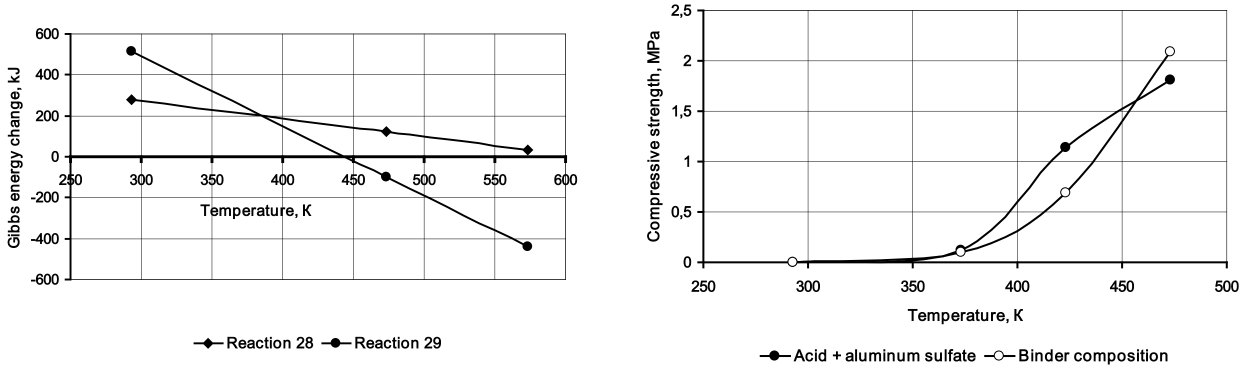
$$Mn(OH)_2 + 2\ H_3PO_4 \rightarrow Mn(H_2PO_4)_2 + 2\ H_2O \qquad (27)$$

A significant amount of manganese sulfate remains in the sample, which obviously has a better binding capacity than phosphate, and therefore provided a higher strength index. This is indicated by the fact that the strength of the mixtures with the first sample is less. According to the calculation of mass ratios in this case, manganese phosphate is completely formed.

The following reactions (28)…(29) were analyzed for **aluminum sulfate $Al_2(SO_4)_3$**. Thermodynamic characteristics of the reactions are shown in Fig. 10 (a).

$$Al_2(SO_4)_3 + 2\ H_3PO_4 \rightarrow 2\ AlPO_4 + 3\ H_2O \uparrow + 3\ SO_3 \uparrow \qquad (28)$$

$$Al_2(SO_4)_3 \cdot 18H_2O + 2\ H_3PO_4 \rightarrow 2\ AlPO_4 + 21\ H_2O \uparrow + 3\ SO_3 \uparrow \qquad (29)$$



a **b**

Fig. 10 – Gibbs energy change in the range from 293 to 573 K for the reactions of interaction of aluminum sulfate with orthophosphoric acid (a) and compressive strength of samples (b)

Aluminum sulfate is used in the form of eighteenhydrous crystal hydrate. It was found that, as for other sulfate materials, the crystal hydrate is more active, and this activity depends on the number of moles of water. Anhydrous aluminum sulfate cannot react with orthophosphoric acid in the considered temperature range. Eighteenhydrous sulfate is able to interact when heated in the range of 423…473 K. In addition, aluminum sulfate is prone to hydrolysis by cation, which results in the formation of hydroxide $Al(OH)_3$. Such hydroxide at a temperature of about 373 K can react with acid. This is the basis for the preparation of well-known aluminum-phosphate and other complex binder components [3, 4, 14, 30, 31].

In the temperature range 423…473 K the samples of the mixture are harden. Regardless of the method of preparation, approximately the same result is achieved. From the analysis of Fig. 10 (b), it should be assumed that the strength of the mixtures can be determined by both sulfate and phosphate of aluminum, because the strength of mixtures with both samples gives the same results.

X-ray phase analysis was performed to determine the composition of the products of interaction between the components. The object of the research is a composition of 10 mass parts of aluminum sulfate $Al_2(SO_4)_3 \cdot 18H_2O$ and 1 mass part of orthophosphoric acid. After mixing, the sample was kept in an oven at 473 K for 1 hour. The diffractogram of the composition is shown in Fig. 11.

A number of new phases have been identified in the composition. In particular, the actual aluminum sulfate $Al_2(SO_4)_3 \cdot 16.4H_2O$ was identified, which differs from the original sulfate $Al_2(SO_4)_3 \cdot 18H_2O$ by the number of moles of crystal hydrate water. Two types of phosphates and aluminum hydroxide were also found. Therefore, the role of the binder component here is obviously performed by both aluminum phosphates and its sulfate, which predominates in the sample.

Based on the obtained results, the analysis of the kinetics of transformations that led to the formation of the specified phase composition was performed.

At the first stage there was a partial decomposition of crystal hydrate aluminum sulfate. In article [32] all forms of existence of crystal hydrates of this salt are investigated and it is shown that 16.4-hydrous sulfate really exists, and separation of 18 moles of crystal hydrate water occurs gradually in a wide range of temperatures – from 356.5 K to 713 K.

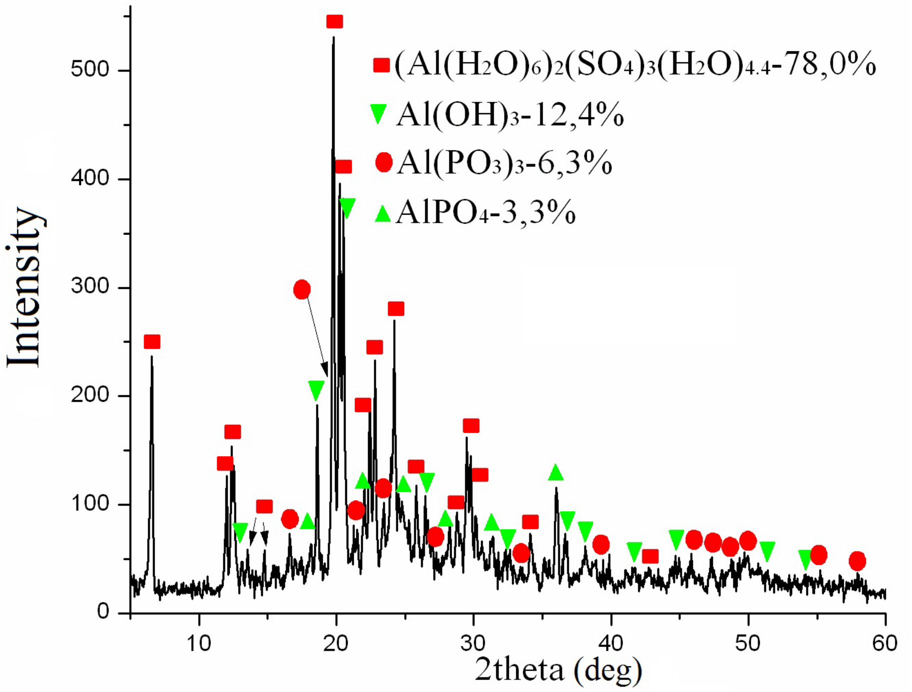


Fig. 11 – X-ray phase analysis of the composition of eighteenhydrous aluminum sulfate (10 mass parts) with orthophosphoric acid (1 mass part) after heat treatment at 473 K

In our case, the chemical reaction is as follows:

$$2Al_2(SO_4)_3\cdot 18H_2O \rightarrow Al_2(SO_4)_3\cdot 16{,}4H_2O + 2Al(OH)_3 + 3SO_3 + 1{,}6H_2O \qquad (30)$$

Using the molar masses of the components, it can be calculated that the decomposition of 1332 mass parts of 18-hydrous sulfate produces 637 mass parts of 16.4-hydrous sulfate and 210 mass parts of aluminum hydroxide.

Thus, it is scientifically established that **in the systems of sulfates of transition metals with orthophosphoric acid the formation of intermediate phases (hydroxides) is possible not by hydrolysis reactions, but due to partial thermal compounds that form phosphates at relatively low (423…473 K) temperatures.**

Aluminum sulfate does not interact with orthophosphoric acid, as established thermodynamically. However, the hydroxide can interact with it at a temperature of 363…383 K. The binders in the test sample are formed by reactions:

$$Al(OH)_3 + H_3PO_4 \rightarrow AlPO_4 + 3H_2O \qquad (31)$$

$$Al(OH)_3 + 3H_3PO_4 \rightarrow Al(PO_3)_3 + 6H_2O \qquad (32)$$

In the sample, the mass ratio of aluminum sulfate to acid is 10 : 1. Returning to the reaction (30), we find that we have 1332 mass parts of 18-hydrous sulfate account for 133 mass parts of acid, and taking into account its concentration – 112 mass parts of H_3PO_4. To complete the reaction (31) on 105 mass parts of hydroxide, 98 mass parts of H_3PO_4 are required. Therefore, the maximum amount of hydroxide that could react: $105\cdot\frac{112}{98}=120$ mass parts. At the same time there were 210 – 120 = 90 mass parts of hydroxide. Also by this reaction, the amount of aluminum orthophosphate formed from 120 mass parts of aluminum hydroxide: $122 \cdot \frac{120}{105} = 140$ mass parts.

After transformations (30) and (31), the sample must contain 637 mass parts (or 73.5%) of 16.4-hydrous aluminum sulphate, 90 mass parts (or 10.4%) of aluminum hydroxide, 140 mass parts (or 16.1%) of aluminum orthophosphate.

In fact, two different phosphates were formed in the sample, so the reaction (32) should be analyzed. For its full implementation, 105 mass parts of hydroxide require 297 mass parts of acid, and taking into account its concentration – 350 mass parts of H_3PO_4, and we have only 133 mass parts of H_3PO_4. Therefore, only a part of the hydroxide could react: $105 \cdot \frac{133}{350} = 40$ mass parts. This left 210 – 40 = 170 mass parts of aluminum hydroxide. Also by this reaction instead of 264 mass parts of aluminum metaphosphate, formed from 40 mass parts of hydroxide: $264 \cdot \frac{40}{105} = 100$ mass parts of aluminum metaphosphate $Al(PO_3)_3$.

After transformations (30) and (32), the sample must contain 637 mass parts (or 70.2%) of 16.4-hydrous aluminum sulphate, 170 mass parts (or 18.7%) of aluminum hydroxide, 100 mass parts (or 11.0%) of aluminum metaphosphate.

The calculated composition of the sample is very close to that determined by phase analysis, so the analyzed chemical processes (30)-(32) fully reflect the formation of the binder in this system. Since the binder contains two types of inorganic salts, it should be assigned to a new class – phosphosulfate binder.

In order to study the dynamics of transformations of this binder component during heating, a differential thermogravimetric analysis of the same sample was performed (Fig. 12).

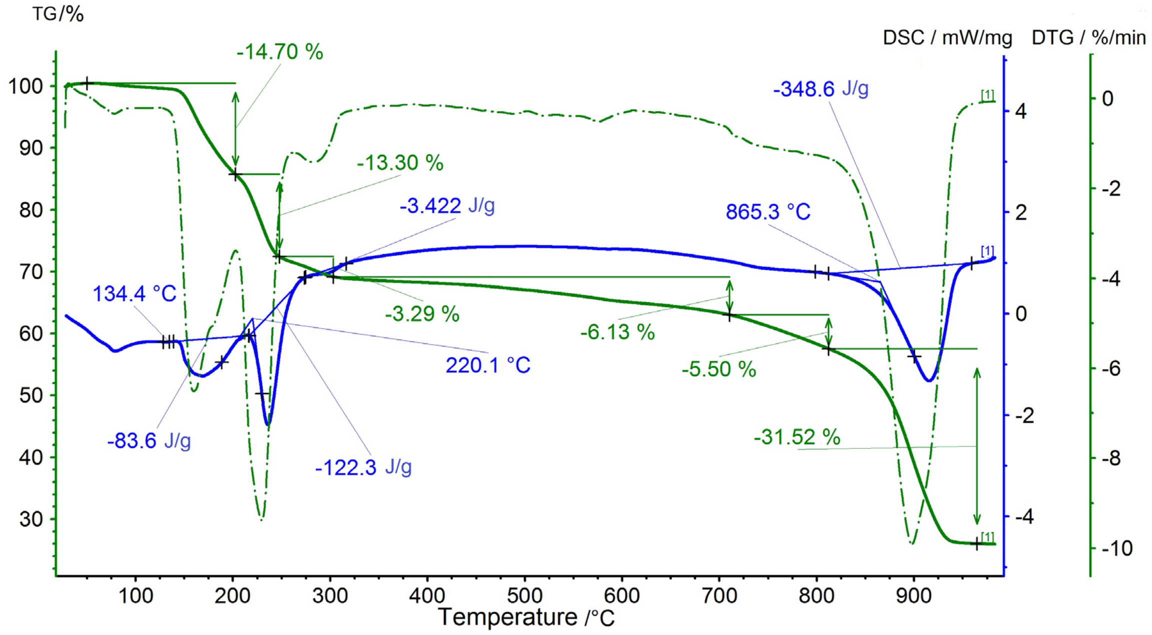


Fig. 12 – Differential thermogravimetric analysis of the composition of aluminum sulfate (10 mass parts) with orthophosphoric acid (1 mass part) after exposure at heat treatment of 473 K

Aluminum crystalline sulfate is gradually losing moles of bound water. This process is two- or even three-stage (the graph shows two large endothermic effects and one effect with a small intensity of about 300 °C). In general, the process is expressed by the equation:

$$Al_2(SO_4)_3 \cdot 16{,}4H_2O \rightarrow Al_2(SO_4)_3 + 16{,}4H_2O\uparrow \qquad (33)$$

According to the molar ratios of the components, we see that 637 mass parts of crystal hydrate sulfate forms 342 mass parts of anhydrous sulfate and 297 mass parts of H_2O. Given the phase composition of the investigated sample, in our case 780 mass parts of crystal hydrate aluminum sulfate forms 417 mass parts of anhydrous sulfate and 363 mass parts of H_2O. The release of H_2O from the total mass of the sample is 36.3%, and the total weight loss in Fig. 12 in the range up to 300 °C 14.7% + 13.3% + 3.3% = 31.3%, which is close to the calculated data.

Significant endothermic effect at a temperature of 865 °C is associated with thermal destruction of aluminum sulfate:

$$Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3SO_3\uparrow \qquad (34)$$

According to [33], this process should take place at a temperature of 580 °C. In our case, the binder is complex – phosphosulfate. Aluminum phosphate acts as a mineralizer, which significantly increases the decomposition temperature of the sulfate component.

According to the material balance of reaction (34) from 102 mass parts of aluminum sulfate should be formed 102 mass parts of aluminum oxide and should be released 240 mass parts of SO_3. In our sample, 417 mass parts of sulfate form 124 mass parts of Al_2O_3 and 293 mass parts of SO_3. The weight loss for the removal of the gaseous product is 29.3%, according to the DTG curve – 31.5%, this confirms the reaction (34).

Therefore, this system has been fully investigated and it has been established that binder is formed not by direct interaction of aluminum sulfate with acid, but due to the formation of aluminum hydroxide. It is a by-product of the partial decomposition of sulfate when heated.

Decomposition during heating of the binder component (aluminum sulfate) will lead to a significant decrease in strength at temperatures above 800 °C. The researched system is not suitable for use in refractory concretes, furnace linings and similar areas. However, the unique property of losing strength after heating makes it promising for molds and cores, because after pouring and crystallization of the metal should reduce the strength (ideally to zero) in order to reduce the work of removing castings from molds and cores from castings.

1.6. Synthesis of phosphate binders using salts of halogen acids

Halogen acids are stronger than orthophosphoric acid. This makes it impossible to chemically react this acid with halogen salts at normal temperature. However, thermodynamic calculations confirmed the possibility of phosphate formation when heated.

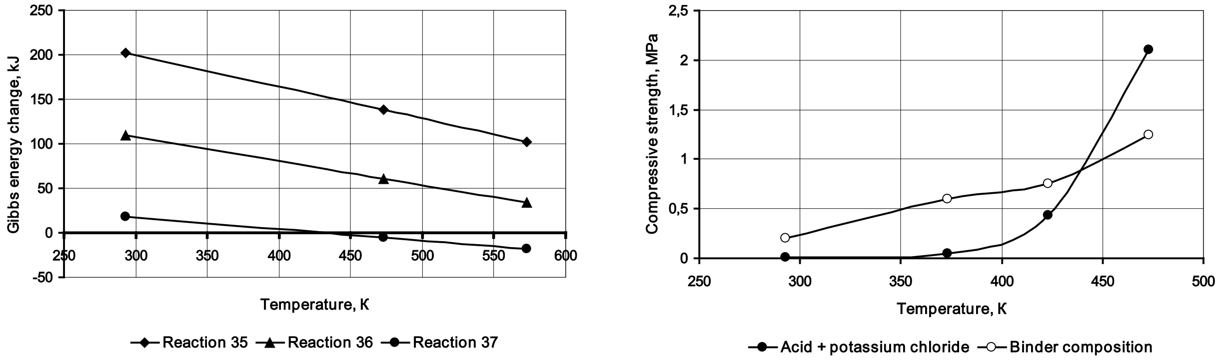
Reactions (35)…(37) were analyzed for **potassium chloride KCl**.

Thermodynamic analysis of reactions is shown in Fig. 13 (a).

$$3\ KCl + H_3PO_4 \rightarrow K_3PO_4 + 3\ HCl\uparrow \qquad (35)$$

$$2\ KCl + H_3PO_4 \rightarrow K_2HPO_4 + 2\ HCl\uparrow \qquad (36)$$

$$KCl + H_3PO_4 \rightarrow KH_2PO_4 + HCl\uparrow \qquad (37)$$



a **b**

Fig. 13 – Gibbs energy change in the range from 293 to 573 K for the reactions of interaction of potassium chloride with orthophosphoric acid (a) and compressive strength of samples (b)

The most probable from a thermodynamic point of view is the formation of monosubstituted potassium orthophosphate by reaction (37), which can occur starting from a temperature of 473 K. Potassium chloride is not prone to hydrolysis, so we do not consider this possibility. Only direct chemical interaction in this system is possible. Analysis of the mass ratios of the reagents showed that in the first sample (acid + potassium chloride) due to excess acid should be formed acid phosphates by reactions (36) and (37). In the second sample (binder composition) with an excess of potassium chloride, the formation of phosphates is incomplete, and a maximum of 39% of the total amount of KCl reacts.

It has been experimentally confirmed that samples with H_3PO_4 and potassium chloride at a temperature of 473 K have high mechanical properties (Fig. 13, b). In the second sample, the strength is about twice as low due to excess potassium chloride, although it also reaches a minimum sufficient level of 1 MPa. Analysis of the data in Fig. 13 (a) showed that a temperature of 473 K is obviously sufficient for the formation of monosubstituted potassium phosphate. This temperature is not enough for the synthesis of other types of potassium phosphates. This position is confirmed by the results obtained in an additional experiment. The strength of the samples in the experiment was determined at temperatures exceeding 473 K (Fig. 14). The highest strength of the samples is observed in the temperature range 513…543 K.

Thus, a scientific conclusion is formulated: **In the system of potassium chloride and a number of other halogen salts (as confirmed below) with orthophosphoric acid, phosphate synthesis occurs by simple metabolic reactions, the possibility of which is determined solely by thermodynamic factor and heating temperature.** This result has not previously been achieved in orthophosphoric acid systems with compounds of group I metals due to their very high chemical activity.

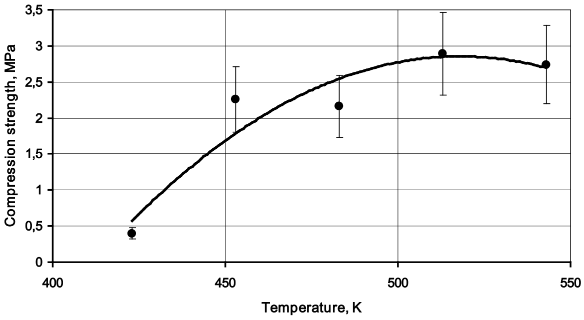


Fig. 14 – The effect of temperature on the compressive strength of samples of a mixture with potassium chloride

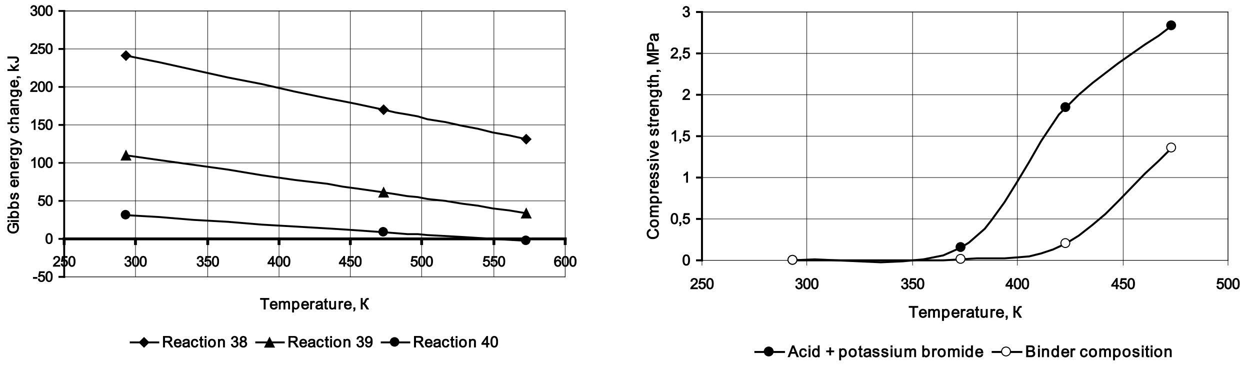
Reactions (38)…(40) were analyzed for **potassium bromide KBr**. Thermodynamic analysis of reactions is shown in Fig. 15 (a).

$$3\ KBr + H_3PO_4 \rightarrow K_3PO_4 + 3\ HBr \uparrow \quad (38)$$

$$2\ KBr + H_3PO_4 \rightarrow K_2HPO_4 + 2\ HBr \uparrow \quad (39)$$

$$KBr + H_3PO_4 \rightarrow KH_2PO_4 + HBr \uparrow \quad (40)$$

Potassium bromide in combination with acid behaves like potassium chloride. Thermodynamically, the formation of monosubstituted potassium phosphate is most likely. However, taking into account the mass ratios, it was found that in the first sample (acid + potassium bromide) there is an excess of acid, which should lead to the formation of acidic potassium phosphates by reactions (39) and (40). In the second sample (binder composition), taking into account the excess potassium bromide, 62% of this salt may react and 38% remains.



a **b**

Fig. 15 – Gibbs energy change in the range from 293 to 573 K for the reactions of interaction of potassium bromide with orthophosphoric acid (a) and compressive strength of samples (b)

The interaction of potassium bromide with orthophosphoric acid leads to a significant strengthening of the samples of the mixture (Fig. 15, b). This is a confirmation of the implementation in the system of synthesis of phosphate binder component. The difference in the strength of the samples is explained by a more complete reaction and the formation of acid phosphates in the first sample and also the presence of residual potassium bromide and the formation of trisubstituted potassium phosphate in the second sample.

From the graphs in Fig. 15 it is also obvious that the formation of potassium phosphates occurs in the temperature range above 473 K, which is confirmed by additional research. Determined the strength of samples that were made at higher temperatures (Fig. 16). Thus, the conclusion about the chemical nature of the formation of the binder in this system due to exchange reactions was confirmed.

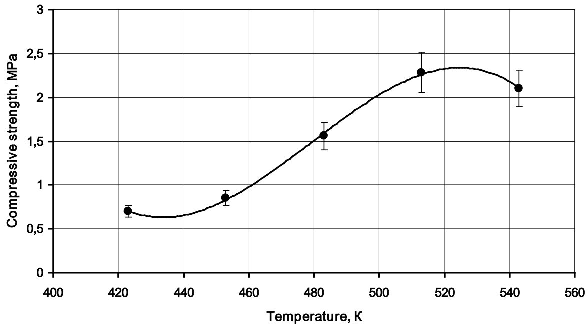


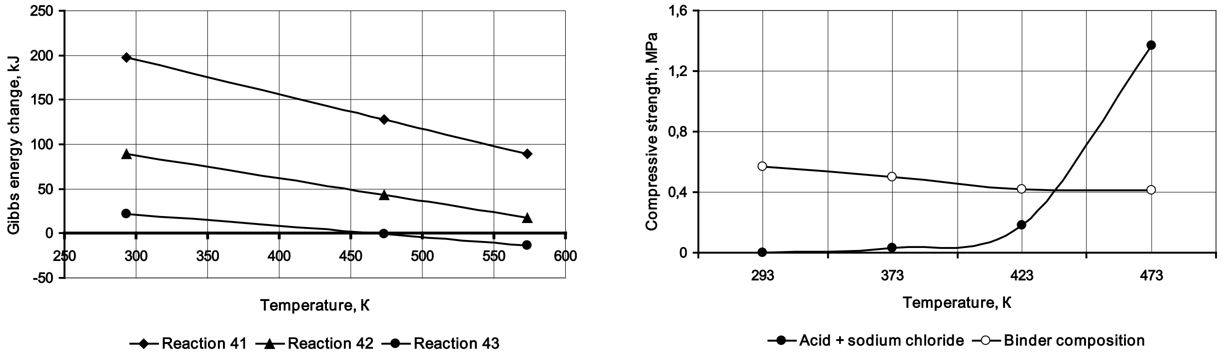
Fig. 16 – The effect of temperature on the compressive strength of samples of a mixture with potassium bromide

Chemical reactions (41)…(43) were analyzed for **sodium chloride NaCl**. Thermodynamic characteristics of the reactions are shown in Fig. 17 (a).

$$3NaCl + H_3PO_4 = Na_3PO_4 + 3HCl\uparrow \quad (41)$$

$$2NaCl + H_3PO_4 = Na_2HPO_4 + 2HCl\uparrow \quad (42)$$

$$NaCl + H_3PO_4 = NaH_2PO_4 + HCl\uparrow \quad (43)$$



a **b**

Fig. 17 – Gibbs energy change in the range from 293 to 573 K for the reactions of interaction of sodium chloride with orthophosphoric acid (a) and compressive strength of samples (b)

Reaction (43) is possible when heated to 473 K, for reactions (41) and (42) requires a higher temperature. The synthesis of sodium phosphates in this system is also possible. Their formation is indicated by the results of determining the strength of the samples (Fig. 17, b). In the first sample (acid + sodium chloride), according to the calculated mass ratios, the formation of all three sodium phosphates is possible. In the second sample (binder composition), the maximum amount of sodium chloride that can react is 30%. The low percentage of conversion of sodium chloride to phosphates leads to low strength of the samples.

Also, according to Fig. 17, it is obvious that temperatures above 473 K leads to intensification of phosphate synthesis reactions. Confirmation of this fact was obtained after conducting research in this temperature range (Fig. 18). The maximum strength corresponds to a temperature of 573 K.

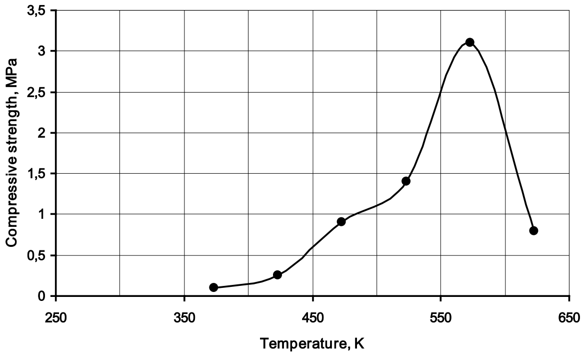


Fig. 18 – The effect of temperature on the compressive strength of samples of a mixture with sodium chloride

The formation of sodium phosphates in the system "sodium chloride – orthophosphoric acid" was confirmed by X-ray phase analysis (Fig. 19). It was found that none of the reactions (41)…(43) occurs.

Instead of sodium orthophosphates, sodium trimetaphosphate was formed. A chemical reaction led to its formation:

$$3NaCl + 3H_3PO_4 = Na_3P_3O_9 + 3HCl\uparrow + 3H_2O\uparrow \qquad (44)$$

The formation of sodium trimetaphosphate is due to the fact that it occurs in the temperature range 523…573 K. It is known that at temperatures below 488 K the most stable is orthophosphoric acid H_3PO_4, from 488 to 573 K – pyrophosphoric acid $H_4P_2O_7$, and at 573 K and more – metaphosphoric acid HPO_3 [14]. Therefore, in a sample kept at 573 K, the formation of sodium metaphosphate is absolutely logical.

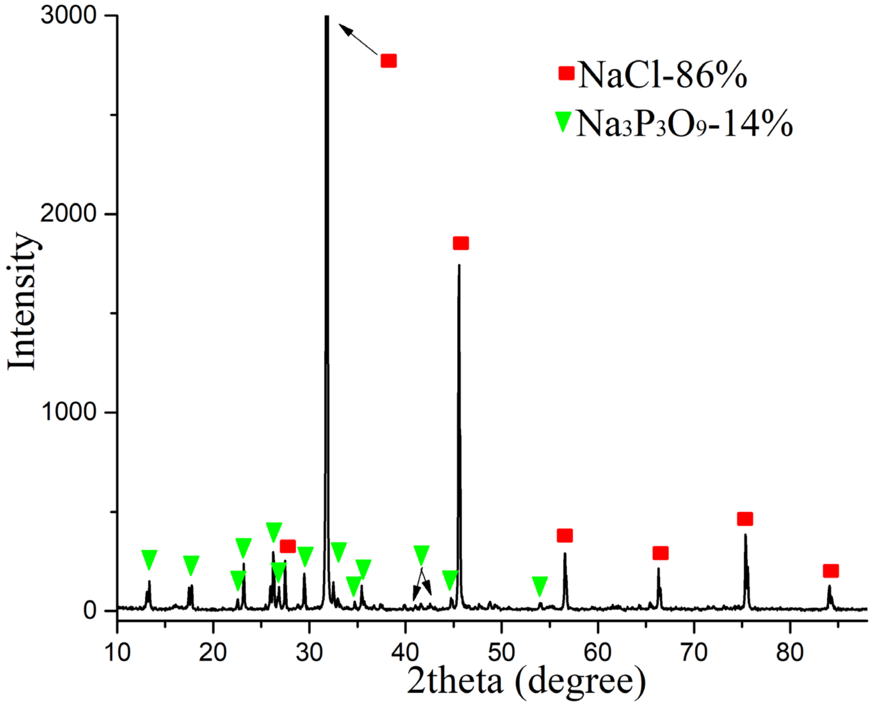


Fig. 19 – X-ray phase analysis of the composition of sodium chloride (8 mass parts) and orthophosphoric acid (3 mass parts) after exposure to 573 K

To pass reaction (44), the mass ratio of sodium chloride to acid should be 176 : 294, and taking into account the acid concentration – 176 : 346. In the experimental sample, the ratio is 8 : 3, or 176 : 66. Therefore, a significant portion of sodium chloride, which is in excess, does not react and remains in its original form. It is estimated that $176\cdot\frac{66}{346}=33$ mass parts of chloride should react. 143 mass parts of chloride (or 70%) should remain, and $309\cdot\frac{66}{346}=60$ mass parts (or 30%) of sodium trimetaphosphate should be formed. This calculated composition completely coincides with the result of the phase analysis.

Differential thermogravimetric analysis of this sample is presented in Fig. 20. The thermogram shows two endothermic effects of different intensity. The mass of the sample in the range up to 800 °C is practically unchanged.

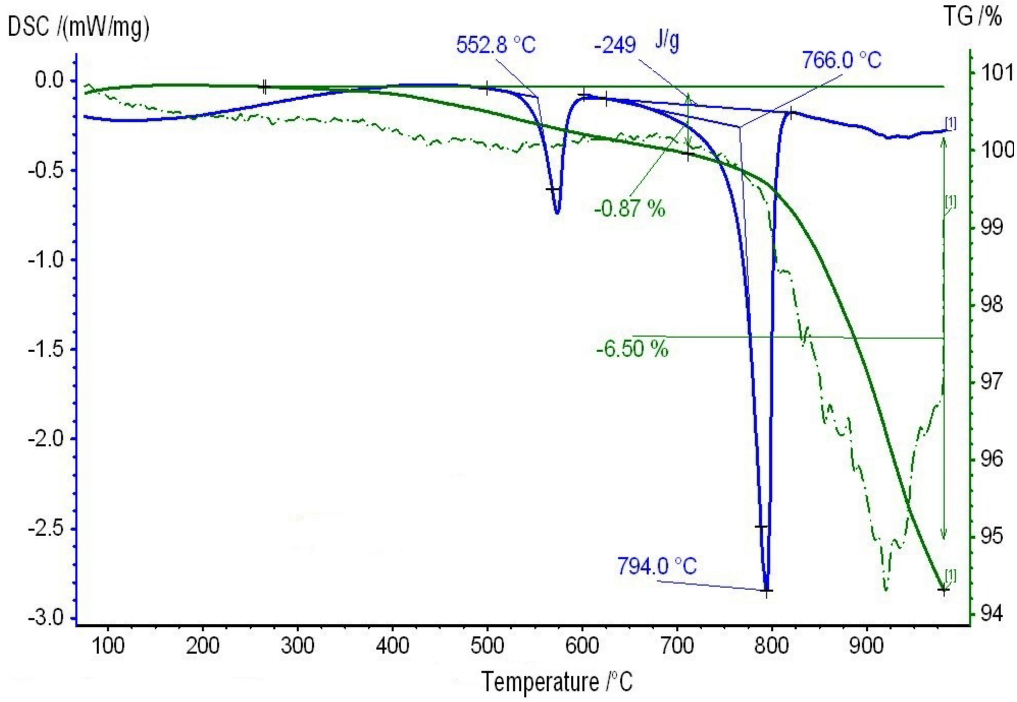


Fig. 20 – Differential thermogravimetric analysis of the composition of sodium chloride (8 mass parts) and orthophosphoric acid (3 mass parts) after exposure in the oven at a temperature of 573 K

The endothermic effect at 553 °C corresponds to the melting of sodium trimetaphosphate. The endothermic effect at 794 °C is associated with the melting of residual sodium chloride.

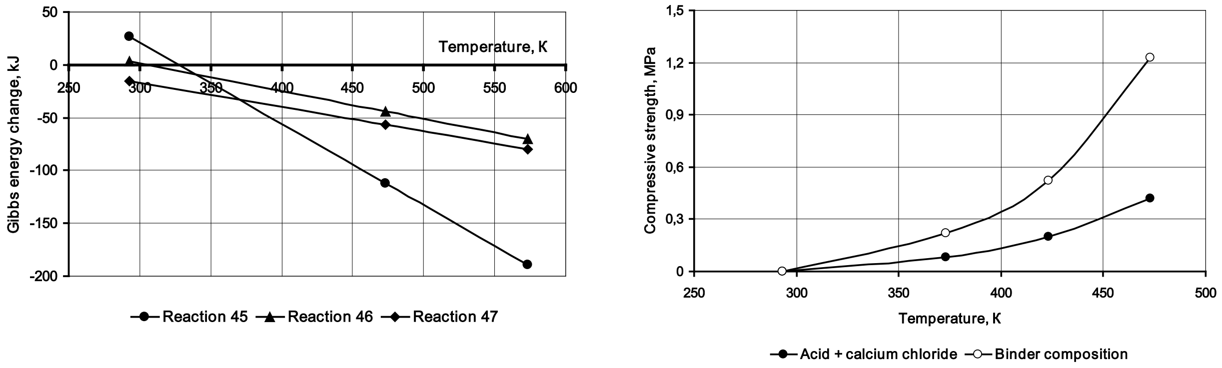
The researched system has low thermal stability. It has low-melting phases. However, this can be useful for some fields of application. For example, in foundry cores, the liquid phase formed by the melting of sodium phosphates can help protect the surface of cast parts from scorching, and the water solubility of sodium phosphates will ensure easy removal of cores from the internal cavities of cast parts.

The following reactions (45)…(47) were analyzed for **calcium chloride $CaCl_2$**. Thermodynamic characteristics of the reactions are shown in Fig. 21 (a).

$$3\ CaCl_2 + 2\ H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6\ HCl\uparrow \qquad (45)$$

$$CaCl_2 + H_3PO_4 \rightarrow CaHPO_4 + 2\ HCl\uparrow \qquad (46)$$

$$CaCl_2 + 2\ H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + 2\ HCl\uparrow \qquad (47)$$



a **b**

Fig. 21 – Gibbs energy change in the range from 293 to 573 K for the reactions of interaction of calcium chloride with orthophosphoric acid (a) and compressive strength of samples (b)

Thermodynamically, the reaction of the interaction of calcium chloride with orthophosphoric acid is possible even without heating. Table 2 shows that during the mixing of these reagents there is an active interaction with the release of gaseous substances that have a pungent odor. This confirms the passage of the reaction between them.

The mass ratios of the components in the studied samples are such that in the first (acid + calcium chloride) a mixture of acidic calcium phosphates should be formed. In the second sample (binder composition) due to excess calcium chloride, it reacted no more than 48%. The higher strength of the samples with the second test (Fig. 21, b) is due to the presence of residual calcium chloride, which obviously has a better binding capacity than the formed calcium phosphates. However, the overall strength in this system is low, so for practical use it can't be recommended.

The following reactions (48)…(49) were analyzed for **magnesium chloride $MgCl_2$**. Thermodynamic characteristics of the reactions are shown in Fig. 22 (a).

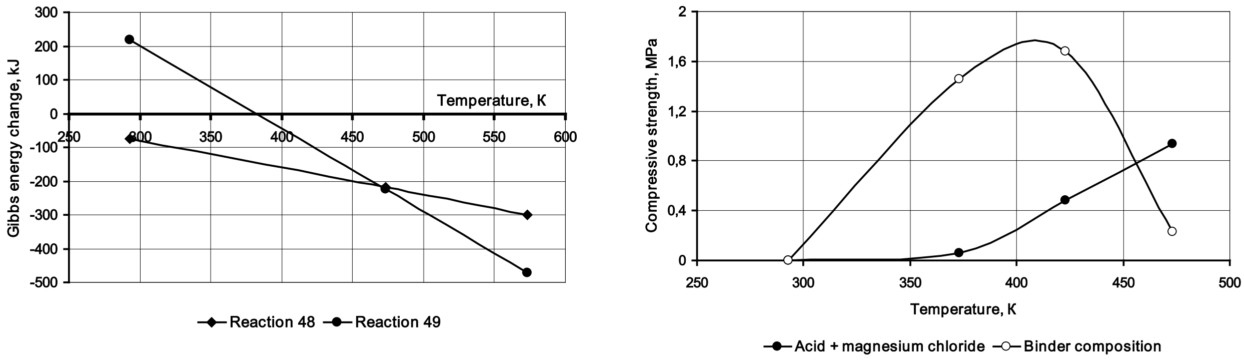
The experiment used a crystal hydrate form – hexahydrous magnesium chloride. The analysis of transformations in this system confirmed the previously formulated scientific position that crystal hydrate salts are more active against orthophosphoric acid than conventional ones. The reaction of anhydrous chloride with acid requires heating above 423 K, and the crystal hydrate can interact when heated below 373 K (Fig. 22, a). It is possible to form not only trisubstituted, but also two acidic magnesium phosphates by chemical reactions:

$$MgCl_2\cdot 6\ H_2O + H_3PO_4 \rightarrow MgHPO_4 + 6\ H_2O\uparrow + 2\ HCl\uparrow \qquad (50)$$

$$MgCl_2\cdot 6\ H_2O + 2\ H_3PO_4 \rightarrow Mg(H_2PO_4)_2 + 6\ H_2O\uparrow + 2\ HCl\uparrow \qquad (51)$$

$$3\ MgCl_2 + 2\ H_3PO_4 \rightarrow Mg_3(PO_4)_2 + 6\ HCl\uparrow \qquad (48)$$

$$3\ [MgCl_2\cdot 6\ H_2O] + 2\ H_3PO_4 \rightarrow Mg_3(PO_4)_2 + 18\ H_2O\uparrow + 6\ HCl\uparrow \qquad (49)$$



a b

Fig. 22 – Gibbs energy change in the range from 293 to 573 K for the reactions of interaction of magnesium chloride with orthophosphoric acid (a) and compressive strength of samples (b)

The calculation of mass ratios for reactions (49), (50), (51) showed that in the first sample (acid + magnesium chloride) it is closest to the formation of monosubstituted phosphate or a mixture of acidic magnesium phosphates. These phosphates provide hardening of the sample after heating to 423…473 K and increasing strength, as shown in Fig. 22 (b). Such a temperature (instead of 323…373 K, as determined by the analysis of graphs in Fig. 22, a) is obviously required to intensify the removal of the reaction product H_2O.

In the second sample (binder composition), a maximum of 52% of magnesium chloride reacted, and the rest remains in its original form. After 389.7 K, magnesium chloride crystal hydrate loses chemically bound water [28, 29], which gives it binding properties. Upon further heating, the strength of the samples decreases. Thus, the binder in this system is represented by two compounds – magnesium phosphate and magnesium chloride crystalline. The magnesium chloride, in view of the data obtained in Fig. 22 (b), has a better binding capacity and can therefore be used as a stand-alone binding component. However, for use in compositions operating at temperatures above 423 K, it will be advisable to describe here the process of synthesis of magnesium phosphate, with adjustment of the mass ratio of components.

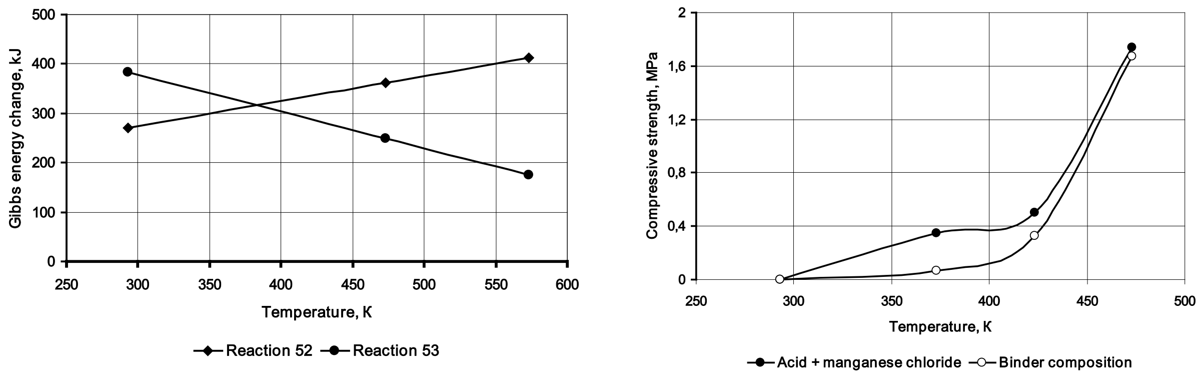
The chemical reactions (52)…(53) were analyzed for **manganese chloride $MnCl_2$**. Thermodynamic characteristics of the reactions are shown in Fig. 23 (a).

$$3\ MnCl_2 + 2\ H_3PO_4 \rightarrow Mn_3(PO_4)_2 + 6\ HCl\uparrow \tag{52}$$

$$3\ [MnCl_2 \cdot 4\ H_2O] + 2\ H_3PO_4 \rightarrow Mn_3(PO_4)_2 + 12\ H_2O + 6\ HCl\uparrow \tag{53}$$

Thermodynamic impossibility was established for both reactions. However, qualitative analysis of the composition (see Table 2) showed a fairly intense interaction with the release of gas, which has a pungent odor. Turning to the accumulated information about manganese chloride, we see that it is prone to active hydrolysis, especially during dehydration. Since manganese chloride tetrahydrate is used in the work, the transformation in the system should be explained by a two-stage process. In the first stage, the reaction is hydrolyzed:

$$MnCl_2 \cdot 4\ H_2O \rightarrow Mn(OH)_2 + 2\ HCl\uparrow + 2\ H_2O \tag{54}$$



a **b**

Fig. 23 – Gibbs energy change in the range from 293 to 573 K for the reactions of interaction of manganese chloride with orthophosphoric acid (a) and compressive strength of samples (b)

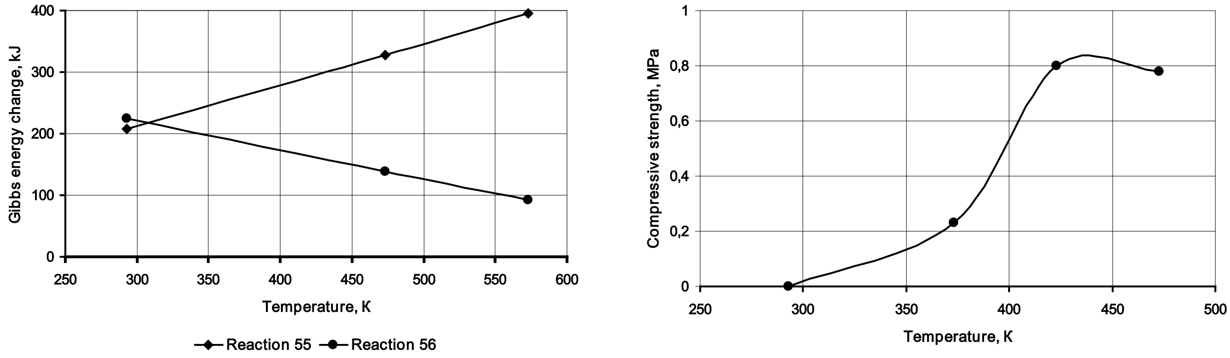
As a result of this process, a gas with a pungent odor is released. Subsequently, manganese hydroxide reacts with orthophosphoric acid in one of the above reactions (25), (26), (27).

The calculation of the mass ratios of reactions (25), (26), (27) and (54) showed that in the first sample (acid + manganese chloride) transformations can occur in full with the formation of acidic manganese phosphates. A significant increase in strength in the range of 423…473 K (Fig. 23, b) can be explained by intensive removal of by-products, especially H_2O. In the second sample (binder composition), a maximum of 50% manganese chloride may react, with the remaining in its original form or as a hydroxide. The strength of the sample provides the formed manganese phosphate, the absolute estimated amount of which is approximately the same as in the first sample. Therefore, the strength is at the same level.

The reactions (55), (56) were analyzed for **nickel chloride $NiCl_2$**. Thermodynamic characteristics of the reactions are shown in Fig. 24 (a).

$$NiCl_2 + 2\ H_3PO_4 \rightarrow Ni_3(PO_4)_2 + 6\ HCl \uparrow \qquad (55)$$

$$3\ [NiCl_2 \cdot 6\ H_2O] + 2\ H_3PO_4 \rightarrow Ni_3(PO_4)_2 + 18H_2O \uparrow + 6\ HCl \uparrow \qquad (56)$$



a **b**

Fig. 24 – Gibbs energy change in the range from 293 to 573 K for the reactions of interaction of nickel chloride with orthophosphoric acid (a) and compressive strength of samples (b)

Thermodynamic impossibility was established for both reactions. However, qualitative analysis of the composition (see Table 2) showed a fairly intense interaction with the release of gas, which has a pungent odor. The nature of the curves in Fig. 24 (b), and the results of the observation of the sample lead to similar conclusions about the interaction of manganese and nickel chlorides with orthophosphoric acid. The first transformation in a system with nickel chloride is hydrolysis by reaction:

$$NiCl_2 \cdot 6\,H_2O \rightarrow Ni(OH)_2 + 2\,HCl\uparrow + 4\,H_2O \qquad (57)$$

Reaction (57) explains the reason for the release of the gaseous product.

This system is similar to "H_3PO_4 – manganese chloride", so the determination of the strength of the samples was performed on only one sample (acid + nickel chloride). Heating to 423…473 K promotes the formation of nickel phosphates, which act as a binder in this mixture. The formation of these phosphates occurs by chemical reactions:

$$3\,Ni(OH)_2 + 2\,H_3PO_4 \rightarrow Ni_3(PO_4)_2 + 6\,H_2O \qquad (58)$$

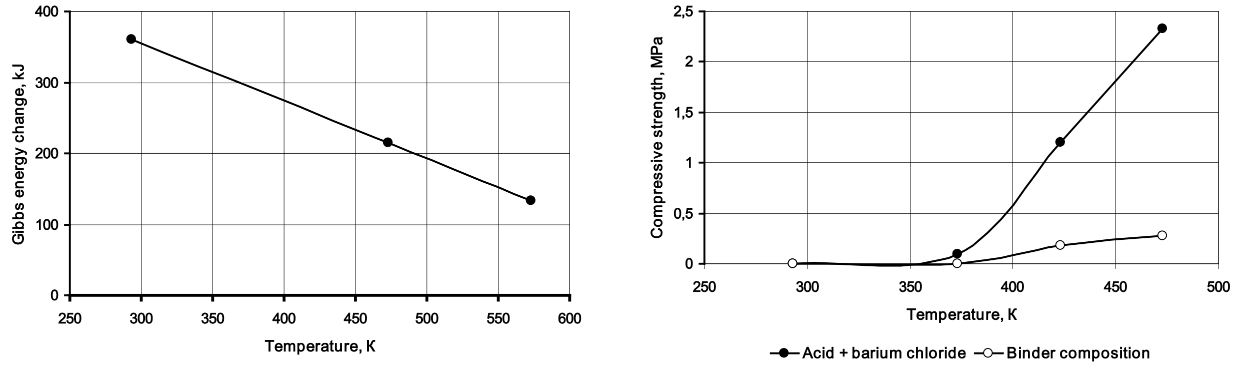
$$Ni(OH)_2 + H_3PO_4 \rightarrow NiHPO_4 + 2\,H_2O \qquad (59)$$

$$Ni(OH)_2 + 2\,H_3PO_4 \rightarrow Ni(H_2PO_4)_2 + 2\,H_2O \qquad (60)$$

Analysis of the mass ratios of the components by reactions (57)…(60) shows that monosubstituted nickel phosphate should be formed in the sample by reaction (60), which determines the achievement of a certain level of strength (see Fig. 24, b). However, the binding capacity of nickel phosphates is obviously lower than that of elements of group I phosphates and phosphates of iron, manganese, magnesium, and aluminum. Therefore, they can’t be considered perspective binders.

There are no data on the thermodynamic properties of acidic barium phosphates, so the analysis of the interaction of orthophosphoric acid with **barium chloride $BaCl_2$** was performed by only one chemical reaction (61). Thermodynamic analysis of the reaction is shown in Fig. 25 (a).

$$3\,BaCl_2 + 2\,H_3PO_4 \rightarrow Ba_3(PO_4)_2 + 6\,HCl\uparrow \qquad (61)$$



a **b**

Fig. 25 – Gibbs energy change in the range from 293 to 573 K for the reactions of interaction of barium chloride with orthophosphoric acid (a) and compressive strength of samples (b)

The value of Gibbs energy in the studied temperature range remains positive. Barium chloride is not hydrolyzed [28, 29], and therefore the formation of phosphates in this system seems completely impossible.

However, the interaction in this system, according to Fig. 25 (b), when heated above 423 K occurs. The result of this interaction is the achievement of high strength – more than 2 MPa. There is no explanation for this fact yet, but the formation of barium phosphates cannot be denied. Assuming that the chemical interaction did occur, the second sample (binder composition) contains residual barium chloride and barium phosphates, which are insoluble. Both of these salts do not have binding properties. This explains the low strength of the mixture with the second sample. This system has binding potential and requires further research.

1.7. Synthesis of phosphate binders using nitric acid salts

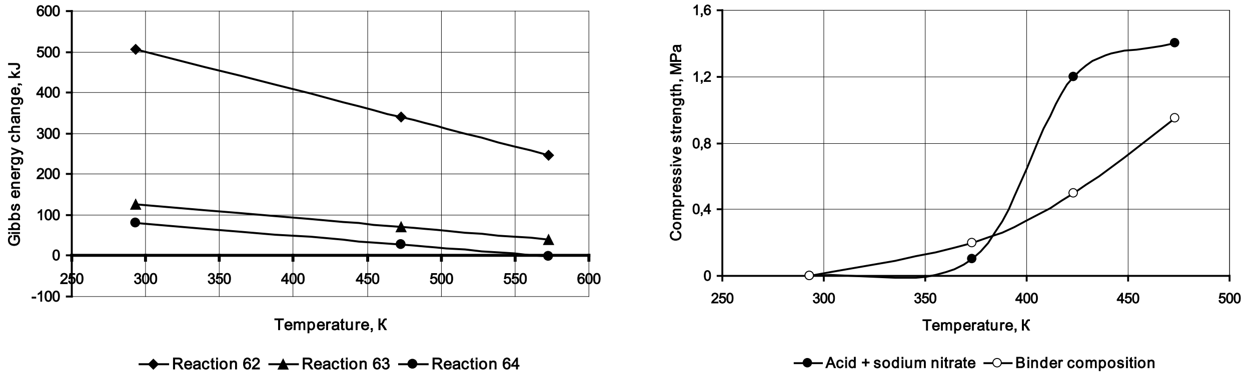
Nitric acid is stronger than orthophosphoric acid, so at normal temperatures most of its salts should not enter into chemical reactions. However, some nitrates undergo slight physicochemical transformation when slightly heated, which allows phosphates to be obtained from by-products.

The following reactions (62), (63), (64) were analyzed for **sodium nitrate $NaNO_3$**. The thermodynamic characteristics of the reactions are shown in Fig. 26 (a).

$$6\ NaNO_3 + 2\ H_3PO_4 \rightarrow 2\ Na_3PO_4 + 3\ H_2O \uparrow + 3\ N_2O_5 \uparrow \tag{62}$$

$$2\ NaNO_3 + H_3PO_4 \rightarrow Na_2HPO_4 + H_2O \uparrow + N_2O_5 \uparrow \tag{63}$$

$$2\ NaNO_3 + 2\ H_3PO_4 \rightarrow 2\ NaH_2PO_4 + H_2O \uparrow + N_2O_5 \uparrow \tag{64}$$



a **b**

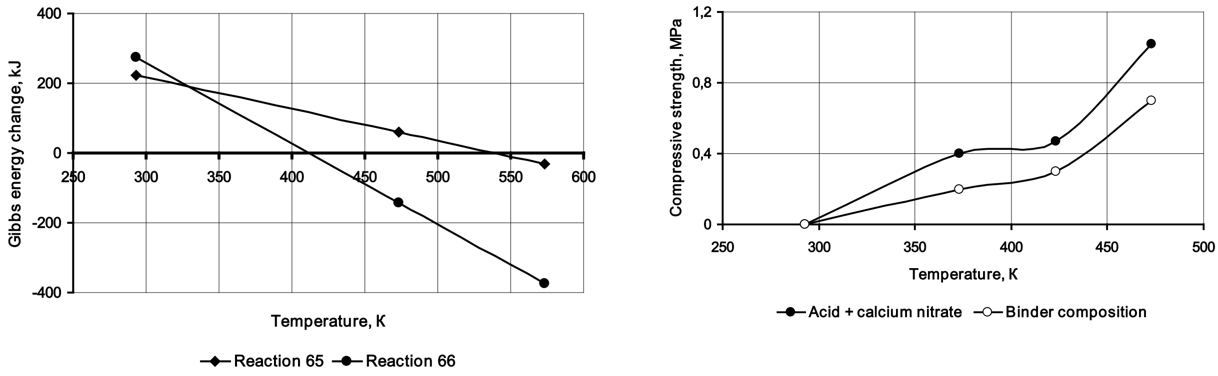
Fig. 26 – Gibbs energy change in the range from 293 to 573 K for the reactions of interaction of sodium nitrate with orthophosphoric acid (a) and compressive strength of samples (b)

Sodium nitrate is characterized by high chemical and thermal resistance. Therefore, in the whole range of research temperatures it remains unchanged, and the strength of the samples in Fig. 26 (b), is determined mainly by sodium nitrate. As a water-soluble salt, it provides hardening of the samples at 423…473 K due to water removal. The binder composition is mainly sodium nitrate, because chemical reactions do not occur in the formation of sodium phosphates and in the second sample (Fig. 26, b) we observe its own binding potential. Thus, the synthesis of phosphate binder component in the system of orthophosphoric acid and sodium nitrate is impossible.

The reactions (65), (66) were analyzed for **calcium nitrate $Ca(NO_3)_2$**. The thermodynamic characteristics of the reactions are shown in Fig. 27 (a).

$$3\ Ca(NO_3)_2 + 2\ H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 3\ H_2O\uparrow + 3\ N_2O_5\uparrow \qquad (65)$$

$$3\ [Ca(NO_3)_2 \cdot 4H_2O] + 2H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 15H_2O\uparrow + 3N_2O_5\uparrow \qquad (66)$$



a **b**

Fig. 27 – Gibbs energy change in the range from 293 to 573 K for the reactions of interaction of calcium nitrate with orthophosphoric acid (a) and compressive strength of samples (b)

Tetrahydrate calcium nitrate was used in the experiment. It was found that, as for other inorganic salts, calcium nitrate is more active, as can be seen from the graph in Fig. 27 (a), and when heated to 423…473 K can theoretically form calcium phosphates. It is also theoretically possible to form acidic phosphates by reactions:

$$Ca(NO_3)_2 \cdot 4H_2O + H_3PO_4 \rightarrow CaHPO_4 + 5H_2O\uparrow + N_2O_5\uparrow \qquad (67)$$

$$Ca(NO_3)_2 \cdot 4H_2O + 2H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + 5H_2O\uparrow + N_2O_5\uparrow \qquad (68)$$

However, it is known that calcium nitrate at a temperature of 405 K (even before the possible reaction with H_3PO_4) loses chemically bound water [28, 29], and to interact with anhydrous nitrate acid requires heating above 523 K, as shown in Fig. 27 (a). Therefore, the strength of the mixture with both individual components and the binder composition is provided not by phosphate but by calcium nitrate, and the strength results are almost the same and low (Fig. 27, b). Therefore, the synthesis of the phosphate binder in this system also does not occur.

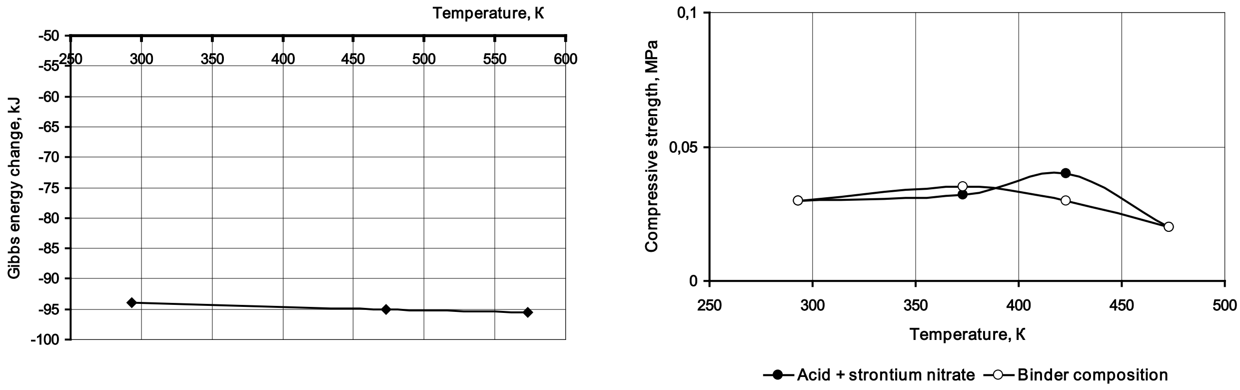
For **strontium nitrate $Sr(NO_3)_2$** the following reactions were analyzed:

$$3\ Sr(NO_3)_2 + 2H_3PO_4 \rightarrow Sr_3(PO_4)_2 + 3\ N_2O_5\uparrow + 3\ H_2O\uparrow \qquad (69)$$

$$Sr(NO_3)_2 + H_3PO_4 \rightarrow SrHPO_4 + N_2O_5\uparrow + H_2O\uparrow \qquad (70)$$

$$Sr(NO_3)_2 + 2H_3PO_4 \rightarrow Sr(H_2PO_4)_2 + N_2O_5\uparrow + H_2O\uparrow \qquad (71)$$

Fig. 28 shows as an example only the graph for reaction (69), because the change in free energy for these reactions is much less than zero. All reactions are possible under normal conditions.



a **b**

Fig. 28 – Gibbs energy change in the range from 293 to 573 K for the reactions of interaction of strontium nitrate with orthophosphoric acid (a) and compressive strength of samples (b)

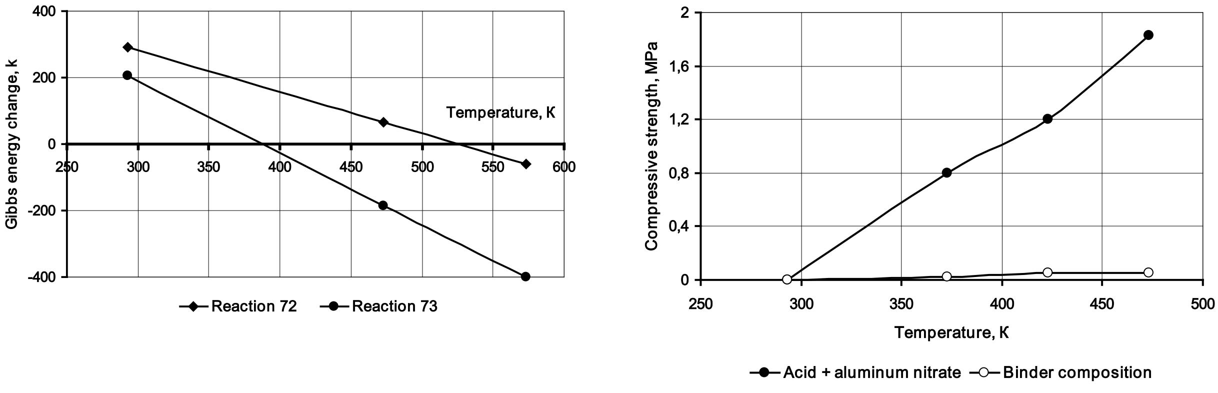
Chemical interaction in this system leads to the formation of strontium phosphates. The calculation of the mass ratios of the components for reactions (69)…(71) shows that in the first sample (acid + strontium nitrate) monosubstituted phosphate is mainly formed. In the second sample (binder composition) trisubstituted phosphate is formed, while no more than 55% of strontium nitrate can enter into reaction (69). It was found that strontium phosphates are completely devoid of binding capacity, because the samples do not have sufficient strength (Fig. 28, b).

Research has led to another scientific conclusion: **Guaranteed phosphate formation does not always ensure the strength of the system, as a number of phosphorus salts are devoid of binding capacity.**

Reactions (72), (73) were analyzed for **aluminum nitrate $Al(NO_3)_3$**. The thermodynamic characteristics of the reactions are shown in Fig. 29 (a).

$$2\,Al(NO_3)_3 + 2\,H_3PO_4 \rightarrow 2\,AlPO_4 + 3\,H_2O\uparrow + 3\,N_2O_5\uparrow \qquad (72)$$

$$2\,[Al(NO_3)_3 \cdot 6H_2O] + 2\,H_3PO_4 \rightarrow 2AlPO_4 + 15H_2O\uparrow + 3\,N_2O_5\uparrow \qquad (73)$$



a **b**

Fig. 29 – Gibbs energy change in the range from 293 to 573 K for the reactions of interaction of aluminum nitrate with orthophosphoric acid (a) and compressive strength of samples (b)

Aluminum nonahydrate $Al(NO_3)_3 \cdot 9H_2O$ was used in the experiments. When heated slightly above the melting point (346.6 K), it loses first one and then two more water molecules, turning into hexahydrate $Al(NO_3)_3 \cdot 6H_2O$, so the reaction (73) was subjected to thermodynamic analysis. It was found that for interaction with orthophosphoric acid of anhydrous aluminum nitrate it is necessary to heat about 523 K, for hexahydrous – more than 373 K (see Fig. 29, a).

In the composition, hydrolysis processes are also possible with the formation of aluminum hydroxynitrate $Al(OH)_2(NO_3)$ or aluminum hydroxide $Al(OH)_3$:

$$2\ Al(NO_3)_3 \cdot 6H_2O \rightarrow 2\ Al(OH)_3 + 3\ N_2O_5 + 3\ H_2O \qquad (74)$$

Thermal decomposition of anhydrous aluminum nitrate at 473 K leads to the formation of amorphous aluminum oxide [34]. Therefore, reaction (72) is also impossible, because before its beginning, aluminum nitrate decomposes by the reaction:

$$4\ Al(NO_3)_3 \rightarrow 2\ Al_2O_3 + 12\ NO_2\uparrow + 3\ O_2\uparrow \qquad (75)$$

The interaction of alumina with orthophosphoric acid requires a temperature of about 573 K [4, 13, 14], so in our experiment the formation of phosphate binder occurs through the hydrolysis of aluminum nitrate by reaction (74) with subsequent interaction of aluminum hydroxide with orthophosphoric acid. The formation of the binder begins at 373 K, and further heating contributes to the intensification of processes and increase the strength of the samples (Fig. 29, b).

The mass ratios were calculated for the reactions:

$$Al(OH)_3 + H_3PO_4 \rightarrow AlPO_4 + 3H_2O \qquad (76)$$

$$2\ Al(OH)_3 + 3\ H_3PO_4 \rightarrow Al_2(HPO_4)_3 + 6H_2O \qquad (77)$$

$$Al(OH)_3 + 3\ H_3PO_4 \rightarrow Al(H_2PO_4)_3 + 3H_2O \qquad (78)$$

It is taken into account that aluminum hydroxide was formed by reaction (74). It has been established that in the first sample (acid + aluminum nitrate) with equal mass fractions of aluminum nitrate and orthophosphoric acid, monosubstituted aluminum phosphate should be formed. In the second sample (binder composition) no more than 65% of aluminum nitrate can react, and the reaction produces tri-substituted aluminum phosphate. This explains the significant difference in the strength of the samples (see Fig. 29, b). Insoluble aluminum phosphate cannot be used as a ready-to-use binder. The combination of aluminum nitrate with orthophosphoric acid leads to the synthesis of aluminum phosphates directly in the mixture during heating and provides high strength samples.

To establish the fact of phosphate binder synthesis in this system, X-ray phase analysis was performed. The results of the analysis are shown in Fig. 30.

Only the products of the interaction were identified in the composition: complex aluminum phosphate (92.8%), aluminum orthophosphate in the form of berlinite (6.2%) and residual nitrogen-containing phase (0.9%). Aluminum nitrate was not detected in the sample, so it completely decomposed and reacted with the acid.

Complex aluminum phosphate is a combination of orthophosphate $AlPO_4$ and hydrophosphate $Al(H_2PO_4)_3$. Six moles of crystal hydrate water remained from aluminum nitrate hexahydrate.

The graph of differential thermogravimetric analysis (Fig. 31) has a number of thermal effects: at 148 °C, 222 °C, 386 °C and 490 °C. The first two effects are associated with the decomposition of crystal hydrates, and the last two – with the decomposition of nitrogen-containing phase and conversion of acid phosphate aluminum on trisubstituted (berlinite). In the future, the binding component consists of one phase – $AlPO_4$. The phase is stable at high temperatures, so when heated above 500 °C there are no transformations.

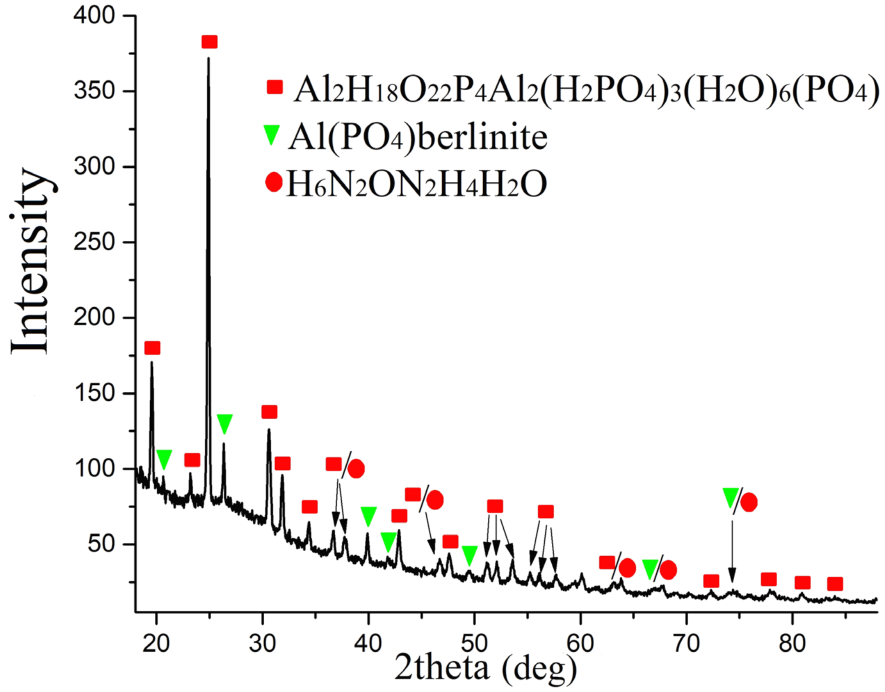


Fig. 30 – X-ray phase analysis of the composition of aluminum nitrate (5 mass parts) with orthophosphoric acid (3 mass parts) after treatment at 473 K

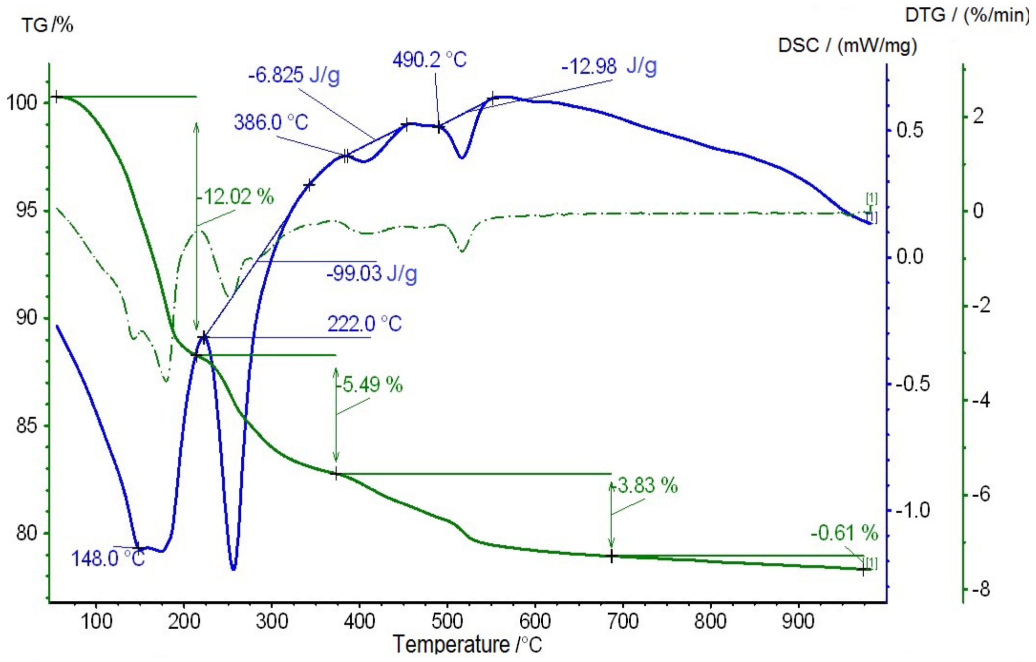
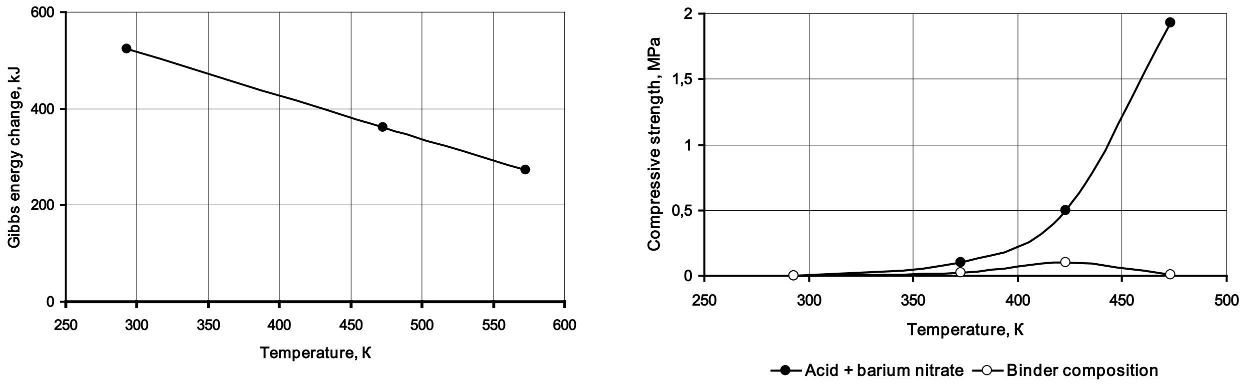


Fig. 31 – Differential thermogravimetric analysis of the composition of aluminum nitrate (5 mass parts) with orthophosphoric acid (3 mass parts) after heat treatment at 473 K

The analysis of chemical reactions of **barium nitrate $Ba(NO_3)_2$** is not fully carried out because there are no data on the thermodynamic characteristics of acidic barium phosphates. Therefore, the change in free energy was determined only for the following reaction:

$$3\ Ba(NO_3)_2 + 2\ H_3PO_4 \rightarrow Ba_3(PO_4)_2 + 3\ N_2O_5 \uparrow + 3\ H_2O \uparrow \qquad (79)$$

The results of thermodynamic analysis (Fig. 32, a) indicate the impossibility of this chemical reaction. However, the results of determining the strength of the samples (Fig. 32, b) confirm the assumption of the formation of a phosphate binder, because after heating to 473 K the samples have high strength. Apart from reaction (79), there is no other mechanism of interaction in the system, because barium nitrate is not subject to hydrolysis or thermal decomposition. Therefore, this question remains open.



a **b**

Fig. 32 – Gibbs energy change in the range from 293 to 573 K for the reaction of barium nitrate with orthophosphoric acid (a) and compressive strength of samples (b)

In the second sample (binder composition), no more than 68% of barium nitrate may react by mass ratio of components. The strength of the samples of this sample is close to zero, because barium nitrate has no binding properties and barium phosphates are insoluble. However, there are no confirmed data on the formation of barium phosphates today.

1.8. Synthesis of phosphate binders using carbonates

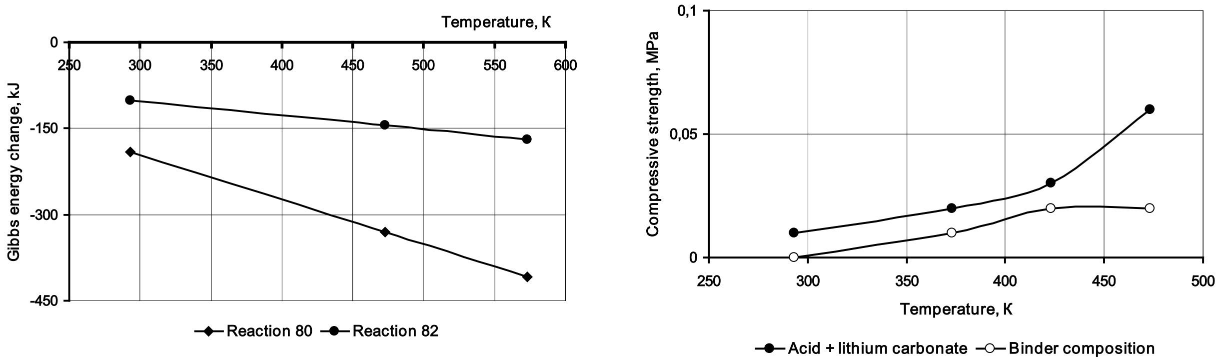
Carbonates are salts of weak carbonic acid. Therefore, their reactions with orthophosphoric acid according to chemical ideas can occur under normal conditions.

Reactions (80), (81), (82) were analyzed for lithium carbonate Li_2CO_3. The thermodynamic characteristics of the reactions are shown in Fig. 33 (a):

$$3\ Li_2CO_3 + 2\ H_3PO_4 \rightarrow 2\ Li_3PO_4 + H_2O \uparrow + CO_2 \uparrow \qquad (80)$$

$$Li_2CO_3 + H_3PO_4 \rightarrow Li_2HPO_4 + H_2O \uparrow + CO_2 \uparrow \qquad (81)$$

$$Li_2CO_3 + 2H_3PO_4 \rightarrow 2LiH_2PO_4 + H_2O \uparrow + CO_2 \uparrow \qquad (82)$$



a **b**

Fig. 33 – Gibbs energy change in the range from 293 to 573 K for the reaction of interactions of lithium carbonate with orthophosphoric acid (a) and compressive strength of samples (b)

In the system with lithium carbonate, lithium phosphates are formed at normal temperature. This is established by thermodynamic analysis in Fig. 33 (a). The mass ratios of lithium carbonate to acid are as follows: for reaction (82) – 0.95 : 1, for reaction (83) – 0.65 : 1, for reaction (84) – 0.3 : 1. Therefore, in the first sample (acid + lithium carbonate) trisubstituted lithium orthophosphate is formed. It is practically devoid of binding capacity, and therefore is expressed in unsatisfactory strength of the samples (Fig. 33, b).

The amount of lithium carbonate that could react with the acid is not more than 20% in the mixture with the binder composition. The strength of the samples is even lower.

The results confirm once again that not all phosphates have binding capacity.

The reactions (83), (84), (85) were analyzed for **calcium carbonate $CaCO_3$**. Thermodynamic characteristics of the reactions are shown in Fig. 34 (a).

$$3\ CaCO_3 + 2\ H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 3\ H_2O\uparrow + 3\ CO_2\uparrow \tag{83}$$

$$CaCO_3 + H_3PO_4 \rightarrow CaHPO_4 + H_2O\uparrow + CO_2\uparrow \tag{84}$$

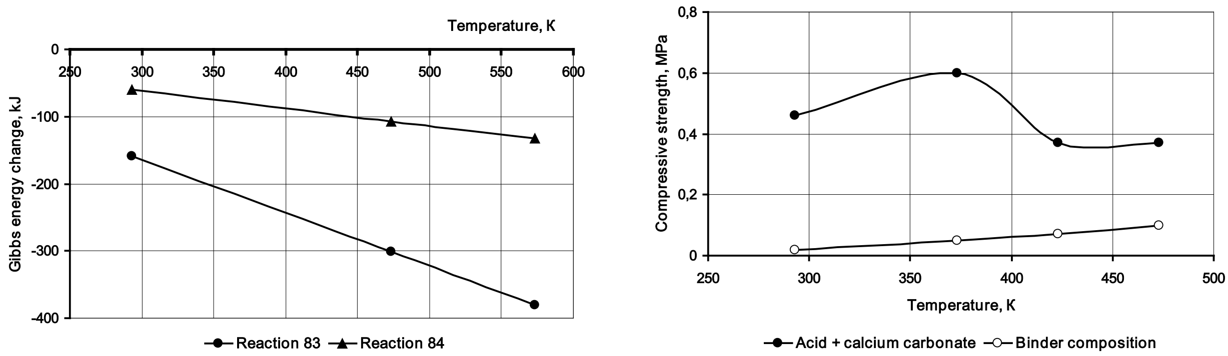
$$CaCO_3 + 2\ H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + H_2O\uparrow + CO_2\uparrow \tag{85}$$

It is established that all reactions can occur at normal temperature. Since they are accompanied by a certain exothermic effect, which was found during the qualitative analysis (see Table 2), the removal of the by-product (H_2O) is possible without heating. Therefore, the samples have approximately the same strength regardless of temperature (Fig. 34, b).

The formation of insoluble calcium phosphates and their lower relative amounts are the reasons for the low strength of the samples with the second sample (binder composition). The calculation of the mass ratios for reactions (83)…(85) shows that in the first sample a mixture of all three calcium phosphates should be formed, and in the second – 26% of the initial amount of calcium carbonate can react.

For **barium carbonate $BaCO_3$**, there are no data on the thermodynamic properties of its acidic phosphates, analyzed only one chemical reaction:

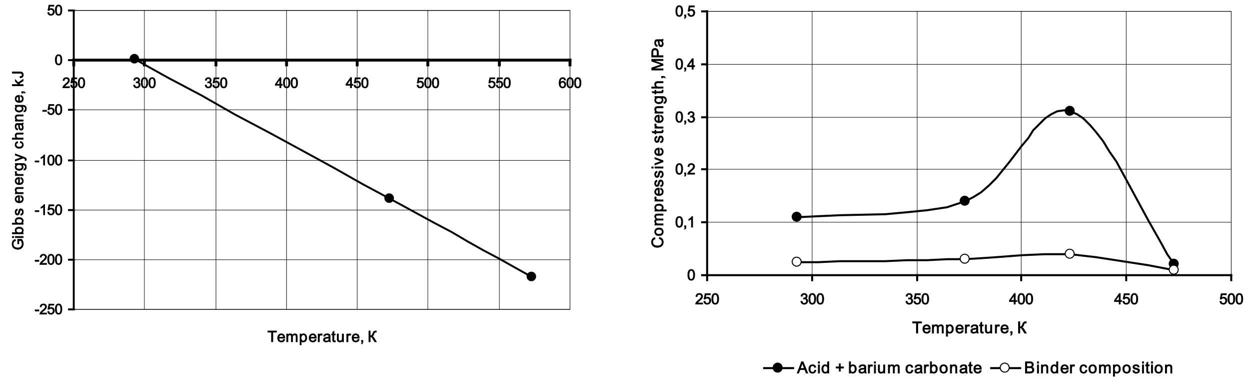
$$3\ BaCO_3 + 2\ H_3PO_4 \rightarrow Ba_3(PO_4)_2 + 3\ CO_2\uparrow + 3\ H_2O\uparrow \tag{86}$$



a b

Fig. 34 – Gibbs energy change in the range from 293 to 573 K for the reaction of interactions of calcium carbonate with orthophosphoric acid (a) and compressive strength of samples (b)

As can be seen from the graph of changes in free energy (Fig. 35, a), the reaction is possible both under normal conditions and when heated. Barium phosphate strengthens the mixture after heating to 423…473 K (Fig. 35, b), but as in the case of calcium carbonate, the insolubility of barium carbonate leads to a slowdown in its chemical interaction with the acid. The insolubility of barium phosphates does not allow to achieve a sufficiently high value of strength. In the first sample (acid + barium carbonate), taking into account the ratio of reagents, should be formed monosubstituted barium phosphate. In the second sample (binder composition), trisubstituted barium phosphate should be formed by reaction (86). No more than 51% of the initial amount of barium carbonate may react.



a b

Fig. 35 – Gibbs energy change in the range from 293 to 573 K for the reaction of interactions of barium carbonate with orthophosphoric acid (a) and compressive strength of samples (b)

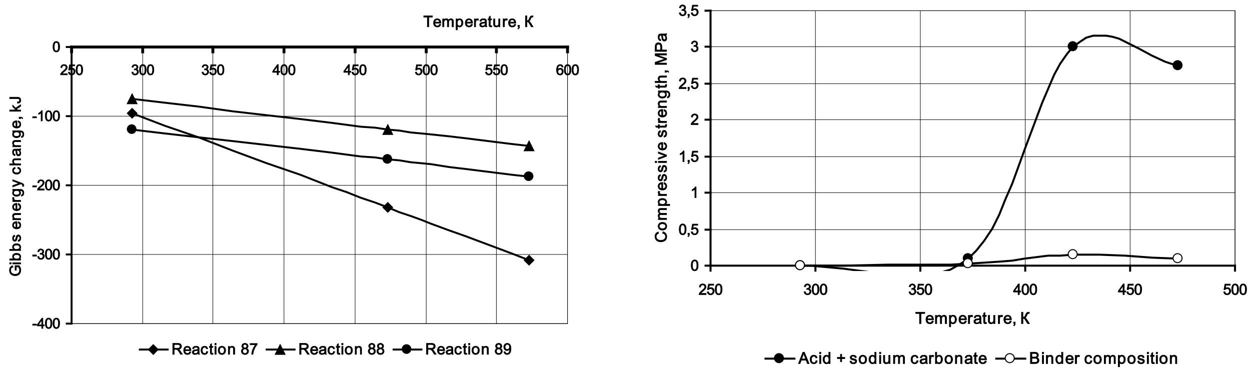
A comparison of the results of determining the strength of samples in systems with barium chloride (Fig. 25, b), barium nitrate (Fig. 32, b) and barium carbonate (Fig. 35, b) leads to the conclusion that the synthesis of barium phosphates from its carbonate is not effective.

Two types of sodium carbonates are common in different fields of technology (**ordinary Na_2CO_3** and **acidic $NaHCO_3$**), so the reactions of both of these salts with orthophosphoric acid are subjected to thermodynamic analysis:

$$3Na_2CO_3 + 2H_3PO_4 \rightarrow 2Na_3PO_4 + 3CO_2\uparrow + 3H_2O\uparrow \quad (87)$$
$$Na_2CO_3 + H_3PO_4 \rightarrow Na_2HPO_4 + CO_2\uparrow + H_2O\uparrow \quad (88)$$
$$Na_2CO_3 + 2H_3PO_4 \rightarrow 2NaH_2PO_4 + CO_2\uparrow + H_2O\uparrow \quad (89)$$

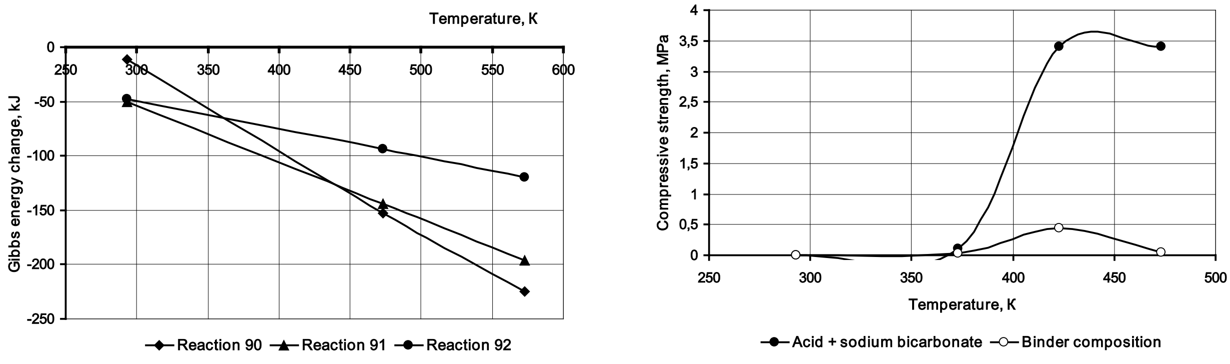
$$3NaHCO_3 + H_3PO_4 \rightarrow Na_3PO_4 + 3CO_2\uparrow + 3H_2O\uparrow \quad (90)$$
$$2NaHCO_3 + H_3PO_4 \rightarrow Na_2HPO_4 + 2CO_2\uparrow + 2H_2O\uparrow \quad (91)$$
$$NaHCO_3 + H_3PO_4 \rightarrow NaH_2PO_4 + CO_2\uparrow + H_2O\uparrow \quad (92)$$

The change in free energy for reactions (87)…(89) is shown in Fig. 36 (a), and for reactions (90)…(92) – in Fig. 37 (a). The strength of the samples using these salts is shown in Fig. 36 (b) and Fig. 37 (b).



a b

Fig. 36 – Gibbs energy change in the range from 293 to 573 K for the reaction of interactions of sodium carbonate with orthophosphoric acid (a) and compressive strength of samples (b)



a b

Fig. 37 – Gibbs energy change in the range from 293 to 573 K for the reaction of interactions of sodium hydrogen carbonate with orthophosphoric acid (a) and compressive strength of samples (b)

As expected, the chemical interaction of the components and its results are almost identical. Both forms of sodium carbonate react with orthophosphoric acid at normal temperature, but the presence of H_2O as a reaction product requires heating to ensure solidification of the samples. Analysis of the mass ratios for reactions (87)…(89) shows that in the first sample (acid + sodium carbonate) a mixture of sodium phosphates should be formed. In the second sample (binder composition), no more than 28% of sodium carbonate may react, and the resulting product is trisubstituted sodium phosphate.

A similar analysis of reactions (90)…(92) showed that in the first sample (acid + sodium bicarbonate) the binder is represented mainly by acidic sodium phosphates. In the second sample (binder composition) almost 44% of sodium hydrogen carbonate can react, which provided higher strength of the samples – 0.44 MPa in Fig. 37 (b) against 0.15 MPa in Fig. 36 (b).

Theoretical conclusions made during the analysis of chemical transformations were confirmed by X-ray phase analysis of the composition of sodium carbonate with orthophosphoric acid (Fig. 38).

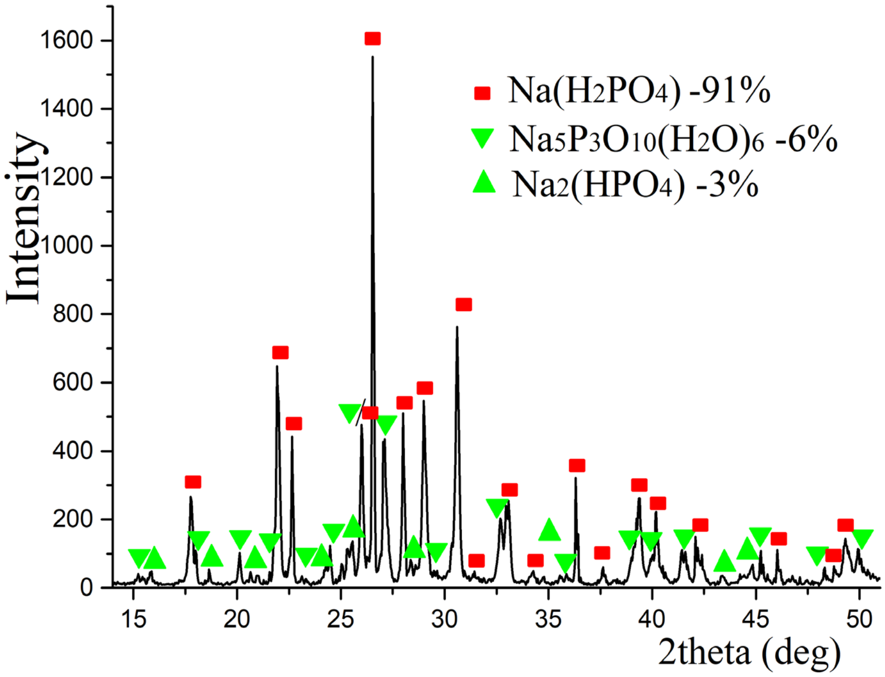


Fig. 38 – X-ray phase analysis of the composition of sodium carbonate (1 mass part) with orthophosphoric acid (1.5 mass parts) after heat treatment at 423 K

The sample revealed 91% monosubstituted phosphate NaH_2PO_4 and 3% disubstituted sodium phosphate Na_2HPO_4. Also identified 6% of the crystal hydrate sodium tripolyphosphate $Na_5P_3O_{10} \cdot 6H_2O$, which was formed by the reaction:

$$5Na_2CO_3 + 6H_3PO_4 \rightarrow 2\ Na_5P_3O_{10} \cdot 6H_2O + 5CO_2\uparrow \qquad (93)$$

3 mol of H_2O are not enough for the formation of $Na_5P_3O_{10} \cdot 6H_2O$ in this reaction. The formation of this compound is logical given the water added to the mixture and the 15% content of H_2O in the orthophosphoric acid solution.

There are a number of transformations in the investigated sample during heating of the formed binder. They were detected by differential thermal analysis (Fig. 39).

The first endothermic effect, observed at 169 °C, was associated with dehydration of sodium hexahydrous tripolyphosphate. After dehydration, the sample consists of 92.5% dihydrogen phosphate, 4.5% anhydrous tripolyphosphate and 3% sodium hydrogen phosphate.

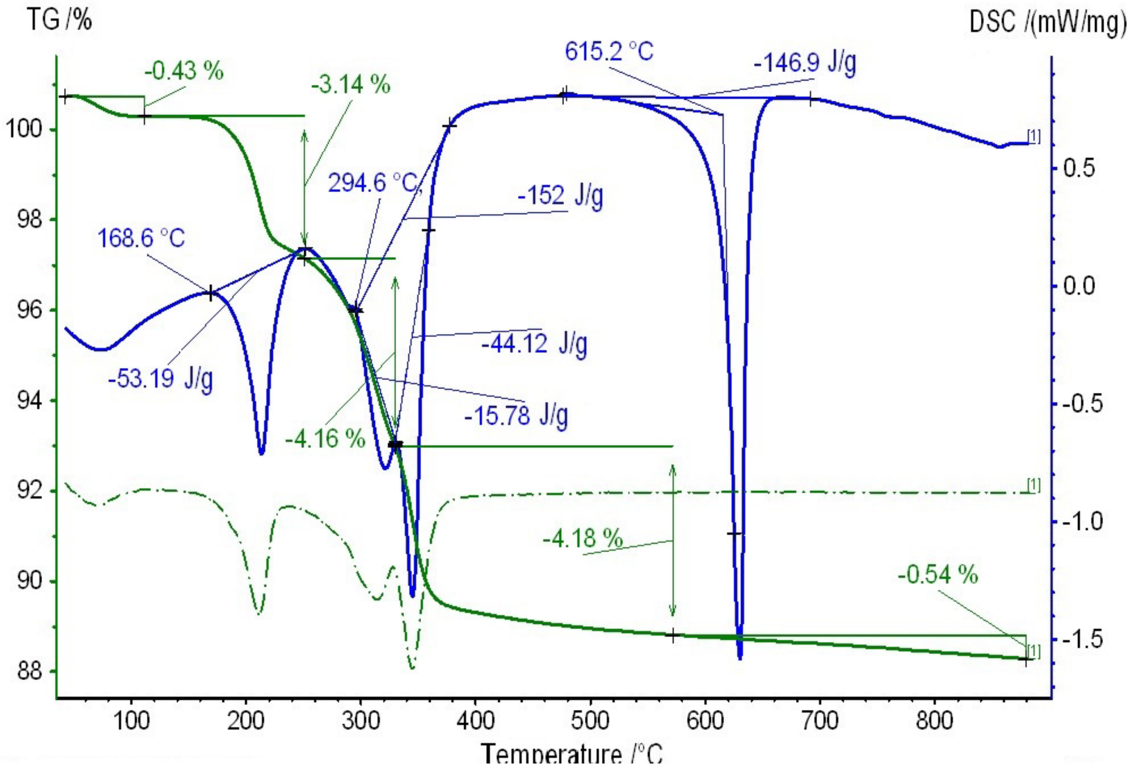


Fig. 39 – Differential thermogravimetric analysis of the composition of sodium carbonate (1 mass part) with orthophosphoric acid (1.5 mass parts) after heat treatment at 423 K

The double endothermic effect, which begins at 295 °C, corresponds to the conversion of acidic sodium phosphates. According to data [35-37], acidic sodium phosphates after decomposition are converted mainly into metaphosphate. Here are the following reactions:

$$NaH_2PO_4 \rightarrow NaPO_3 + H_2O \qquad (94)$$

$$2\ Na_2HPO_4 \rightarrow NaPO_3 + Na_3PO_4 + H_2O \qquad (95)$$

The weight loss by reaction (94) is 15%, which is 13.6% of the initial weight of the sample. By reaction (95), the weight loss is 6% and 0.2%, respectively. The total weight loss is estimated at about 14%, according to the experiment (see Fig. 39) – about 13%.

As a result of reaction (94) 1 mass part of sodium dihydrogen phosphate gives 0.85 mass parts of sodium metaphosphate. Accordingly, 92.5 mass parts of dihydrogen phosphate contained in the sample give 78.6 mass parts of metaphosphate.

As a result of reaction (95) 1 mass part of sodium hydrogen phosphate gives 0.36 mass parts of metaphosphate and 0.58 mass parts of orthophosphate. Then 3 mass parts of hydrophosphate contained in the sample give 1.1 mass parts of metaphosphate and 1.7 mass parts of orthophosphate.

After these transformations, the sample contains 79.7 mass parts of metaphosphate (92.8%), 1.7 mass parts of orthophosphate (2.0%) and 4.5 mass parts of sodium tripolyphosphate (5.2%).

The greatest thermal effect is observed at a temperature of 615 °C. It corresponds to the melting of sodium metaphosphate $NaPO_3$, which is observed by various researchers in the temperature range from 480 to 620 °C. The thermal melting effect of this compound [38] is 17.3 kJ/mol, or 168 J/g. Given that in the sample of 92.8% sodium metaphosphate, the thermal effect should be 156 J/g. The thermal analysis curve revealed 147 J/g, which is within the error and clearly indicates a correct interpretation of the transformation.

The presence of a low-melting component limits the scope of the synthesized sodium phosphate binder component. However, there is a positive property: the water solubility of sodium metaphosphate. For example, such a set of properties can be useful for making foundry molds and cores.

These data open the possibility of synthesis of high-strength sodium phosphate binder in the process of direct interaction of orthophosphoric acid with sodium carbonate when heated to 423 K.

Conclusions

Theoretical and practical research of processes in orthophosphoric acid systems with different groups of inorganic metal salts allow us to formulate the most important conclusions:

1. In a number of orthophosphoric acid systems with inorganic metal salts formed by stronger acids, direct synthesis of phosphates by exchange reactions upon heating is possible. The results are confirmed by the negative values of the free energy of the reactions, the strength of the samples with the formed phosphates and the data of the phase analysis. This effect was observed for KCl, KBr and NaCl.

2. Replacement of anhydrous metal salts with crystal hydrates contributes to the intensification of chemical interactions with orthophosphoric acid. This is due to a significant decrease in the value of free energy of direct interaction reactions, which is confirmed for $MgSO_4 \cdot 7H_2O$, $CoSO_4 \cdot 7H_2O$, $CaCl_2 \cdot 4H_2O$, $MgCl_2 \cdot 6H_2O$.

3. In orthophosphoric acid systems with crystal hydrate sulfates of transition metals, the interaction occurs when heated due to a two-stage process. In the first stage, a part of the crystal hydrate water is cleaved off to form a by-product, a hydroxide, which reacts directly with an orthophosphoric acid, leading to the formation of phosphates. This scheme is confirmed for the system with $Al_2(SO_4)_3 \cdot 18H_2O$. Similar transformations obviously occur in systems with $FeSO_4 \cdot 7H_2O$ and $MnSO_4 \cdot 5H_2O$.

4. Phosphate synthesis in a number of orthophosphoric acid systems with salts of weaker acids or complex salts (Na_2CO_3, $NaHCO_3$, Li_2CO_3, $CaCO_3$, $BaCO_3$, Na_2SO_3, $Na_2S_2O_5$, $Na_2S_2O_8$) occurs at normal temperature, which is confirmed by both thermodynamic analysis and experimental analysis. However, for curing of all compositions it is necessary to heat above 373 K to remove the by-product of the reactions – H_2O.

5. Orthophosphoric acid does not chemically react with some inorganic salts ($NaNO_3$, Li_2SO_4, $Ca(NO_3)_2$, $MnCl_2$) in the studied temperature range. Phosphate synthesis does not occur in such systems. Reactions with these salts are thermodynamically impossible. Also, these salts are not subject to hydrolysis or other

transformations that lead to the formation of intermediates.

6. Not all metal phosphates have been shown to have binding properties. For example, with the guaranteed formation of phosphates in orthophosphoric acid systems with $NiCl_2 \cdot 6H_2O$, $Sr(NO_3)_2$, Li_2CO_3 low strength values are observed. This does not allow us to recommend these binding systems for technical use.

7. Phosphate synthesis in systems with sulfate or chloride salts Na_2SO_3, $Na_2S_2O_5$, $Na_2S_2O_8$, $CaCl_2$, $NiCl_2$, $MnCl_2$ is accompanied by the release of gaseous products with a pungent odor, which limits the possibility of direct synthesis of these phosphates in refractory compositions or other compositions. Priority is given to the use of ready-made (pre-synthesized) phosphates from $Na_2S_2O_8$ or $MnCl_2$, compounds. They can provide reversible hardening of mixtures in combination with water.

8. For the first time, the schemes of synthesis of phosphates of metals investigated in our work can be realized for refractory concretes, for inorganic compositions which are strengthened at insignificant heating, and also molding and core mixtures in foundry production. Depending on the inorganic metal salt used, the synthesized phosphates are endowed with a different set of properties: thermal and chemical resistance, hygroscopicity, water solubility, reusability.