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Foundry Core Mixtures with Orthophosphoric Acid and Different Aluminum-Containing Compounds

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The scientific and practical issues of the development of core mixtures for foundry, based on phosphate binding materials, are considered. The binder presented in this article differ from those previously known by the fact that scarce prepared metal phosphate binding components and powder solidifiers are not used to produce them. As a result, all developed binders are different forms of aluminum phosphates. It is shown that to obtain them it is possible to use combinations of orthophosphoric acid with aluminum-containing materials of different chemical nature.

The formation of high-strength phosphate binders in the interaction of phosphoric acid with aluminosilicates (for example, distan-silimanite and pyrophyllite) and sludge wastes of aluminum production has been established. They are rationally used for processes of thermal strengthening of cores in the temperature range of 200…300 °C.

The formation of binders in the interaction of orthophosphoric acid with inorganic aluminum salts are theoretically proved and practically confirmed. The article demonstrates examples of the synthesis of aluminum phosphates from its nitrate and sulfate when heated to 200...250 °C. The results are confirmed by thermodynamic calculations, as well as by X-ray phase analysis.

Prospects for the practical implementation of the developed binding materials are due to the fact that they exhibit high adhesion to refractory quartz filler and low physical and chemical activity to the melts of iron and steel. It provides high mechanical strength of cores and their satisfactory antiburning properties.

The compositions of the developed core mixtures and examples of their application for obtaining high-quality castings from iron and steel are presented.

Key words: aluminosilicate, aluminum nitrate, orthophosphoric acid, binder, core mixture, aluminum sulphate, casting.

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Introduction

Phosphates occupy a special place among the binder materials. They have a number of valuable properties due to which they are also known as heat-resistant, corrosion-resistant and heat-resistant materials [1].

Today a significant amount of information has been accumulated regarding the chemical, thermal and other properties of phosphorus compounds. In particular, core mixtures based on orthophosphoric acid, aluminophosphate and alumina-chromophosphate binders were developed for the foundry industry. These mixtures as an obligatory component include hardeners – pure oxides or complex oxide compounds, which are a scarce and expensive raw material. Therefore, such binder systems are practically not used [1, 2, 3].

Scientific and technological issues are new schemes for obtaining aluminum phosphate binders in core mixtures, precluding the use of scarce hardeners and simplifying the processes of mixing.

It should be borne in mind that one of the advantages of orthophosphoric acid is the ability to form binding compounds with many types of refractory materials: oxides, silicates, aluminum silicates [4]. However, this advantage is practically not used. In the newest scientific developments in different countries of the world, only previously known schemes for the synthesis of phosphate binders, including aluminum hydroxide, oxides of chromium, boron and some others, are being implemented

[5-11]. In the foundry industry, as in other areas of technology, the scientific issues of the synthesis of phosphate binders from materials in which aluminum is in the form of inorganic salts or similar compounds are not considered.

The object of research in the article is the formation of phosphorus salts of aluminum, which have binding properties, in the interaction of orthophosphoric acid with various aluminum-containing materials.

Inorganic aluminum compounds are an extensive group of different substances, most of which are widely used in the foundry industry, including in the composition of molding and core mixtures.

To systematize the results of theoretical and practical research, all aluminum-containing materials in our work are divided into three groups, according to the chemical-mineralogical nature. The first group includes refractory aluminosilicate compounds: clay minerals, distan-silimanite and pyrophyllite (layered aluminosilicate).

The second group combines industrial products containing aluminum. We used the by-products of the production of primary aluminum (sludge), the smelting of aluminum alloys (slag), and fine aluminum powder.

The third group includes inorganic aluminum salts. The most accessible are sulfate and nitrate, which are limitedly used as binders in antiburning coating and in ceramic shell molds for precision casting.

I. Goals of article

The aim of the study is to develop new binders for core mixtures formed by the interaction of orthophosphoric acid with inorganic aluminum compounds.

To achieve the stated goal, the following tasks were set:

1. To investigate the processes of the interaction of orthophosphoric acid with inorganic aluminum compounds.
2. To analyze the influence of the chemical nature of materials, temperature and technological factors on the formation of aluminum phosphate binders.
3. To investigate hardening modes and properties of core mixtures with developed binders.
4. To establish the optimal component composition and methods of preparation of core mixtures.
5. To conduct laboratory tests of cores on iron-carbon alloy castings.

II. Materials and Methods

To solve the problems posed, theoretical and experimental studies were carried out, which included: X-ray phase analysis (XRPA), thermodynamic calculations, mathematical planning of experiments, determination of physical and mechanical properties using traditional methods of testing mixtures, laboratory tests on castings from iron-carbon alloys.

The structure and phase composition of the binders was determined on a RIGAKU diffractometer model "Ultima IV".

Refractory filler in all mixtures was river quartz sand, corresponding to the brand $3K_5O_3025$. Concentrated (85 %) orthophosphoric acid was used.

The compressive strength of the mixtures was monitored on standard cylindrical specimens using a universal installation model US-700.

III. Experimental Results

At the preliminary stage, a qualitative analysis was conducted of the ability of aluminum-containing materials to form binding products with H_3PO_4. Each mixture contains 3 % H_3PO_4, 2.5 % water and 5 % aluminum-containing substance. Samples of the mixtures were kept in air for 24 hours and in an oven for 1 hour at a temperature of 250 °C.

Under normal conditions, only two aluminum-containing compounds showed activity towards orthophosphoric acid. This sludge and powder, which contain in its composition the particles of metallic aluminum. And the powder reacts intensively with acid, with a large heat release. And sludge, in turn, provides a very low compressive strength during cold hardening – not more than 0.2 MPa.

When heated, all aluminum-containing substances showed activity towards H_3PO_4, but to varying degrees (Fig. 1). Aluminum sulphate and nitrate, in turn, are endowed with their own binding ability: a mixture with 3 % $Al(NO_3)_3$ after thermal curing has a strength of 0.5 MPa, and a mixture with 3 % $Al_2(SO_4)_3$ – 1.5 MPa. However, the results obtained with the introduction of these salts together with H_3PO_4 are significantly higher. This effect can be explained by their chemical interaction with acid, which leads to the formation of new binders.

Aluminosilicates represent a large group of materials, in crystalline lattices of which in different combinations alternate siliceous Si-O and aluminous Al-O layers. Such materials are capable of reacting with orthophosphoric acid, primarily due to the presence of aluminum [4].

For implementation of hardening it is necessary to heat. It is known from the literature that some aluminosilicates react with an acid closer to 300 °C [1, 4]. At the same time, minerals, which have a simpler crystalline structure, are better. Clay minerals susceptible to water absorption and having a layered structure are also capable of forming binders with orthophosphoric acid, but the strength of the mixtures is low.

More detailed studies of the interaction of aluminosilicates with H_3PO_4 allowed to obtain strength indicators sufficient for making foundry cores. To do this, work was carried out to determine the optimal ratio of components, and also investigated various modes of preparation of the mixture.

Three commonly known methods of preparing mixtures have been implemented (Fig. 2):

1 – 3 % H_3PO_4 and 3% aluminosilicate were added successively to the refractory filler;

2 – H_3PO_4 and dust-like aluminosilicate were premixed with each other, maintained at 300 °C. The resulting composition in the amount of 5 % was added to

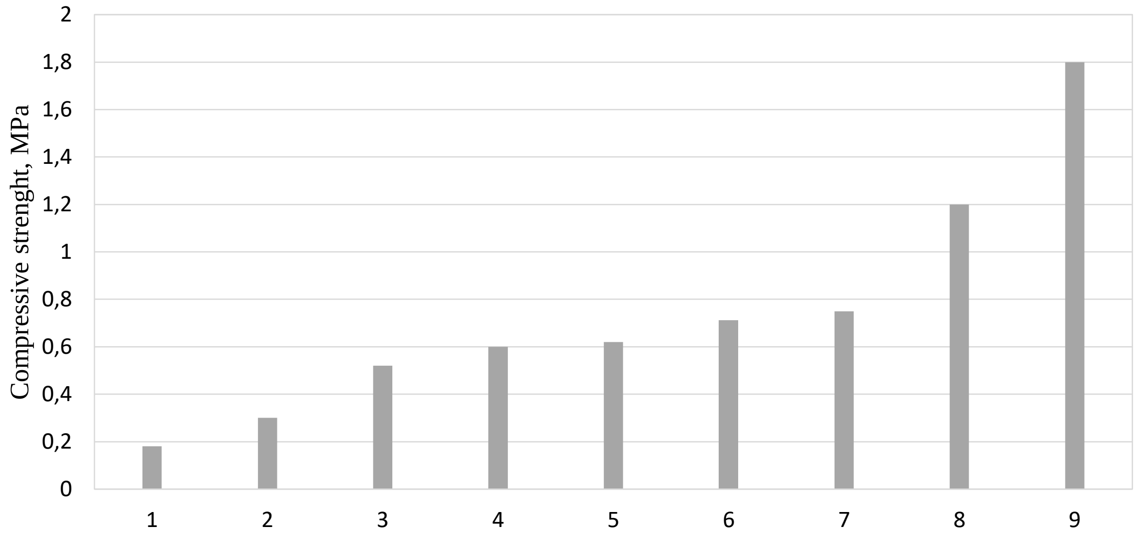


Fig. 1. Strength of mixtures with orthophosphoric acid and various aluminum-containing materials: 1 – bentonite clay; 2 – kaolin clay; 3 – aluminum slag; 4 – distan-silimanite; 5 – pyrophyllite; 6 – aluminum powder; 7 – aluminum sludge; 8 – aluminum nitrate; 9 – aluminum sulphate.

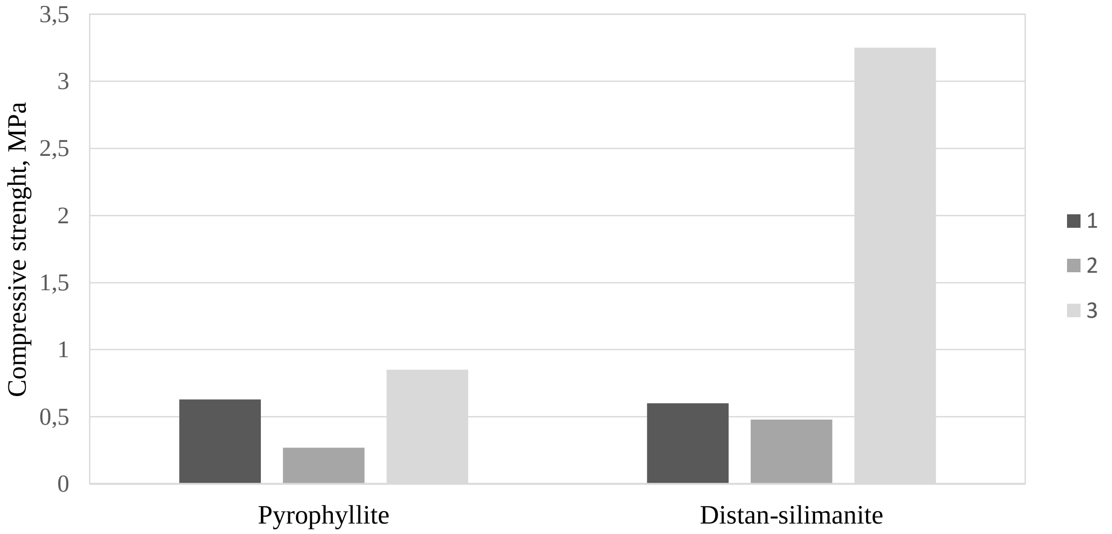


Fig. 2. Strength of mixtures in different ways of introducing aluminosilicates: 1 – a mixture with a separate input of components; 2 – a mixture with a binder composition; 3 – a mixture with a binder solution (suspension).

a refractory filler;

3 – H_3PO_4 and dust-like aluminosilicate were premixed with each other. The resulting suspension of 5% was added to a refractory filler.

Samples of mixtures were strengthened for 1 hour at 300 °C.

The best result is achieved in the mixture, which includes a suspension of H_3PO_4 and 10…30 % of the dust-like distain-sillimanite. The strength is 2.8…3.2 MPa, which is sufficient for foundry cores [12].

Industrial aluminum-containing products – sludge, slag, and aluminum powder – interact in different ways with H_3PO_4. Slag consists mainly of aluminum oxide, which is less active with respect to acid, therefore it was not possible to obtain a high-strength binder. Powder is a fine (extremely dust-like) fraction of metallic aluminum particles. It is intense, with significant heat dissipation, interacts with acid under normal conditions. This complicates the process of mixing.

Sludge is a set of particles of various sizes (from dust-like to 2.5 mm) of the following chemical composition: SiO_2 – 5.6…14.8 %; MgO – 2.4 %; Fe_2O_3 – 6.7…11.1 %; Al_2O_3 – 48.5 %; chloride ions – 0.15 %; $\Sigma(Na_2O+K_2O)$ – 1.75 %; P_2O_5 < 0.1 %; P – 0.15 %; S – 0.12 %; C – 0.5 %; loss during calcination – 8.32 %; metallic aluminum particles – 25.2 %. Despite the presence of metal particles, the sludge practically does not form a cold-hardening mixture with H_3PO_4 but is capable of interacting with it when heated.

The content of active oxides is of decisive importance in the hardening of such phosphate systems

The sludge contains a sufficient amount of such compounds. The hardening of the composition is due to the formation of phosphates of metals such as Mg, Fe, possibly also Na. Thus, the interaction of aluminum sludge with acid forms a complex binder, which is a mixture of phosphates of the active elements.

Strengthening the mixture provides the ratio of sludge to acid 1:1 by weight. In this case, 5…6 % of these components are sufficient (Fig. 3,a). The optimum temperature of hardening is 200…220 °C (Fig. 3,b), while achieving a compressive strength of 2.0...2.4 MPa.

Inorganic aluminum salts have not previously been used to synthesis aluminophosphate binders.

The thermodynamic conditions of chemical reactions of aluminum nitrate and aluminum sulphate with phosphoric acid are analyzed. Calculations of the change in the free energy (Fig. 4) were carried out for reactions (1) and (2) under the condition of their implementation at 20 °C (293 K) and at 200 °C (473 K).

$$2Al(NO_3)_3 + 2H_3PO_4 = 2AlPO_4 + 3H_2O + 3N_2O_5 \qquad (1)$$

$$Al_2(SO_4)_3 + 2H_3PO_4 = 2\ AlPO_4 + 3H_2O + 3SO_3 \qquad (2)$$

Both salts cannot interact with acid under normal conditions. However, heating the compositions reduces the change in free energy, and at a temperature of about 250 °C the reaction of aluminum nitrate with H_3PO_4 becomes possible.

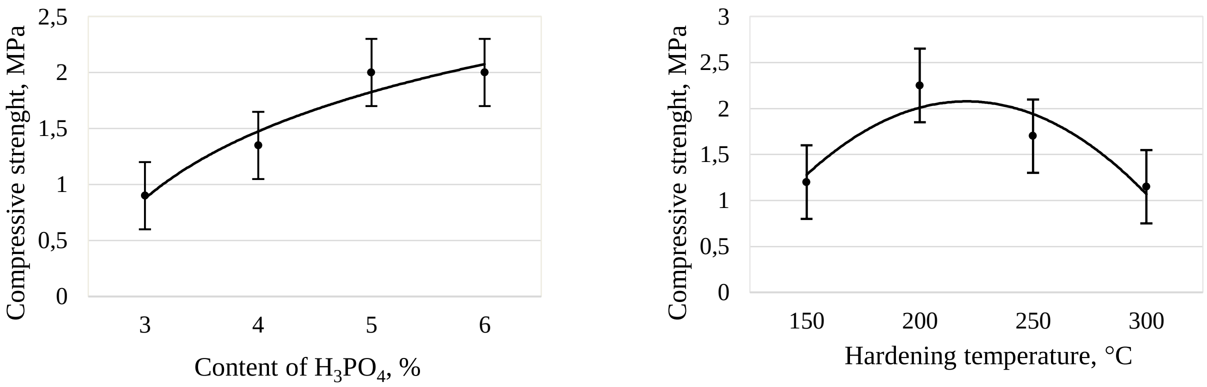
The XRPA of this composition (Fig. 5), hardened at 250 °C, shows that the only compound in the sample is aluminum phosphate (berlinite), which is the product of a chemical reaction (1). Thus, in the system studied, a phosphate binder from an inorganic aluminum salt was successfully synthesized.

Three methods of making mixtures with both inorganic aluminum salts have been implemented, as in experiments with aluminosilicates (Fig. 2).

Aluminum nitrate in the solution of H_3PO_4gives the mixture a strength 2 times higher than with a separate introduction of components (Fig. 6). The lack of strength with a thermally treated $Al(NO_3)_3$composition is due to the fact that, in this composition, aluminum nitrate was completely reacted with H_3PO_4 to form orthophosphate Al by reaction (1). It is an insoluble compound, and in the mixture in the presence of water it does not form adhesive bonds with the filler.

In the solution, $Al(NO_3)_3$ remains in its original form, and only when heated reacts with acid (directly in the samples of the mixture). Since the solution precociously coats the filler grain and forms an adhesion bond, then with the further formation of orthophosphate Al there is already a second stage of strengthening the mixture – guiding cohesive bonds.

Sulphate Al in the binder composition and in the binder solution provides increased strength (Fig. 6). From a thermodynamic point of view, its interaction with H_3PO_4 is impossible. As can be seen from Fig. 4, an increase in temperature only slightly affects the change in reaction energy. The fact of the hardening of this system is also not explained by XRPA and other analyzes.



a **b**

Fig. 3. Dependence of the strength of mixtures with aluminum sludge (5%) on the content of H_3PO_4 (a) and on the hardening temperature (b).

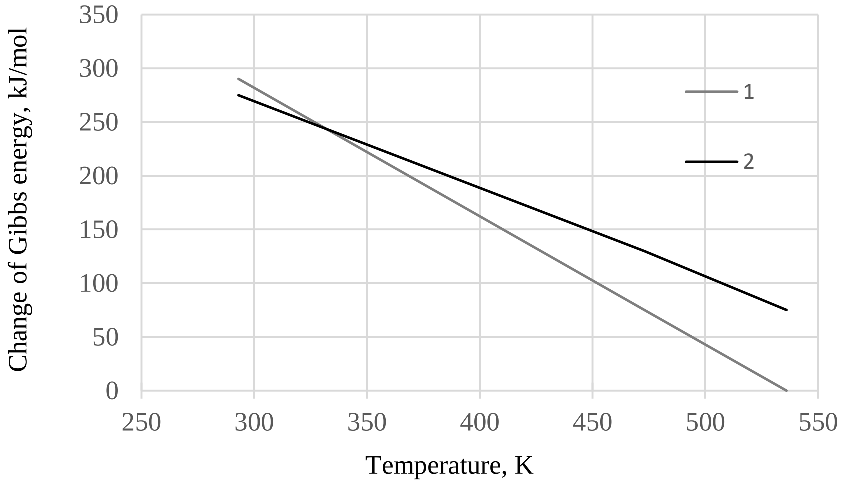


Fig. 4. Gibbs energy change for reactions (1) and (2).

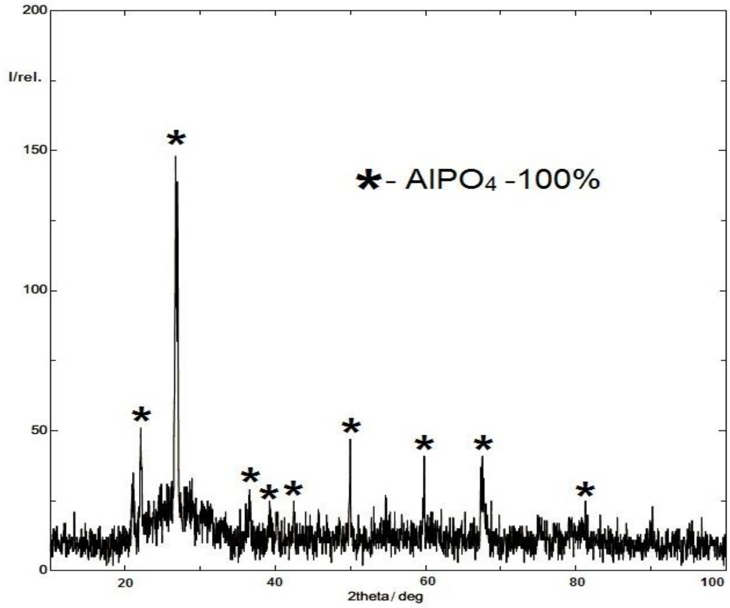


Fig. 5. X-ray phase analysis of the composition of aluminum nitrate (5 mass parts) with orthophosphoric acid (3 mass parts).

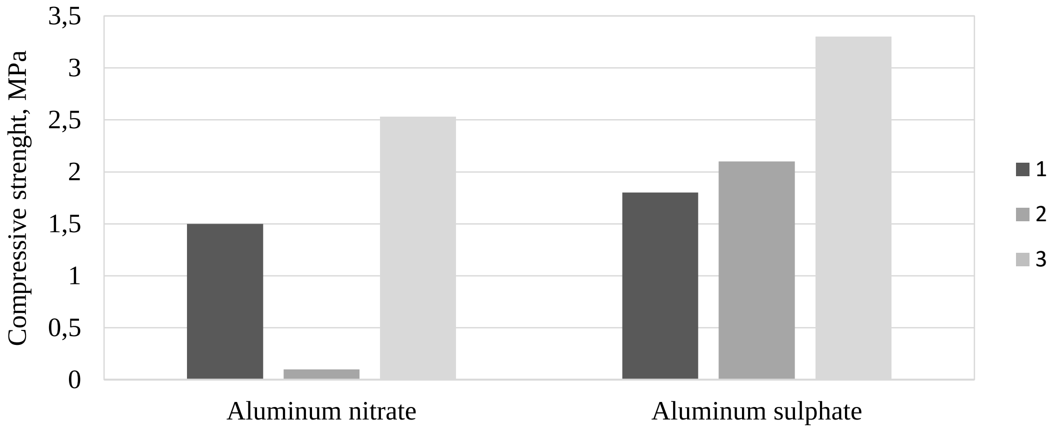


Fig. 6. Compressive strength of mixtures in different ways of introducing components: 1 – a mixture with a separate input of components; 2 – a mixture with a binder composition; 3 – a mixture with a binder solution.

Aluminum sulphate often contains several moles of crystalline water. Accordingly, the chemical and thermodynamic conditions of its interaction withH_3PO_4can be different:

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

$$Al_2(SO_4)_3{\cdot}6H_2O+2H_3PO_4 \rightarrow 2AlPO_4+9H_2O\uparrow+3SO_3\uparrow \quad (4)$$

$$Al_2(SO_4)_3{\cdot}18H_2O+2H_3PO_4\rightarrow 2AlPO_4+21H_2O\uparrow+3SO_3\uparrow \quad (5)$$

In our research, 18-water aluminum sulphate was used. Thermodynamic calculation (Fig. 7) confirms the possibility of its reaction with an acid. Obviously, this fact is the cause of the hardening of the mixture.

Since the premixing of sulphate with acid provides higher strength of the mixtures (Fig. 6), then this method was chosen for the composing of a core mixture with this binder system.

Thus, the finished mixture does not contain an orthophosphoric acid as a separate component.

To prepare the binding compositions, the starting materials were 85% orthophosphoric acid and 18-water aluminum sulphate. These components in different mass ratios (from 3 parts by weight to 20 parts by weight on one mass part of H_3PO_4) was mixed in a laboratory vessel. After premixing they was placed in a heating oven, where they were kept at a temperature of 200 °C for 1 hour. Subsequently, batches were taken from the furnace, cooled in the air and if they have lumps or sintered conglomerate particles were crushed in a laboratory mortar. Obtained compositions were sieved through a 0,2 mm sieve cell, followed by used to prepare mixtures.

The composition of the mixture included: quartz sand, binder composition (5 %), water (5 %). Strengthening of samples was carried out for 1 hour in the furnace at 200 °C. The results of the determination of strength are shown in Fig. 8.

The strength of the mixtures increases to 2.0 MPa at the content of aluminum sulphate 10 mass parts (Fig. 8), which is the optimal composition of the dry binder.

The mixtures with this binder composition have high strength values that reach 3.0 MPa (Fig. 9), which is sufficient for making foundry cores. The optimum temperature for strengthening the cores with this binder composition – 200 °C.

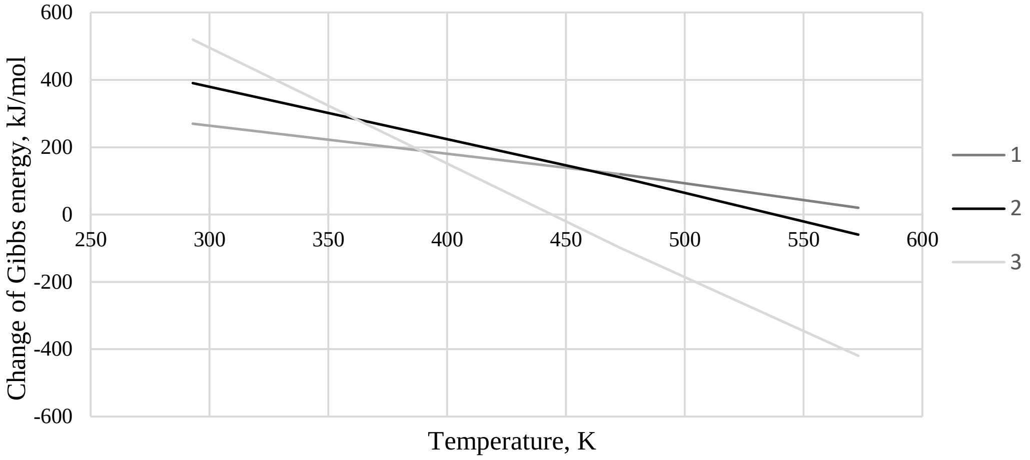


Fig. 7. Gibbs energy change for reactions of interaction of aluminum sulphate with orthophosphoric acid: 1 – anhydrous sulphate; 2 – 6-water sulphate; 3 – 18-water sulphate

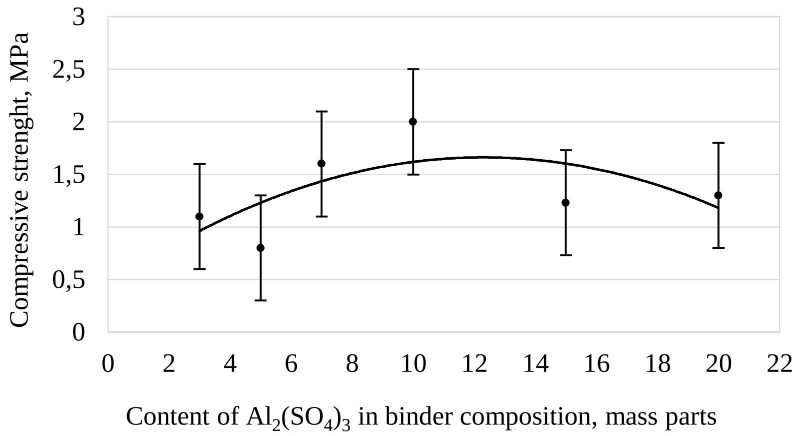


Fig. 8. Dependence of the strength on the content of aluminum sulphate in the binder composition.

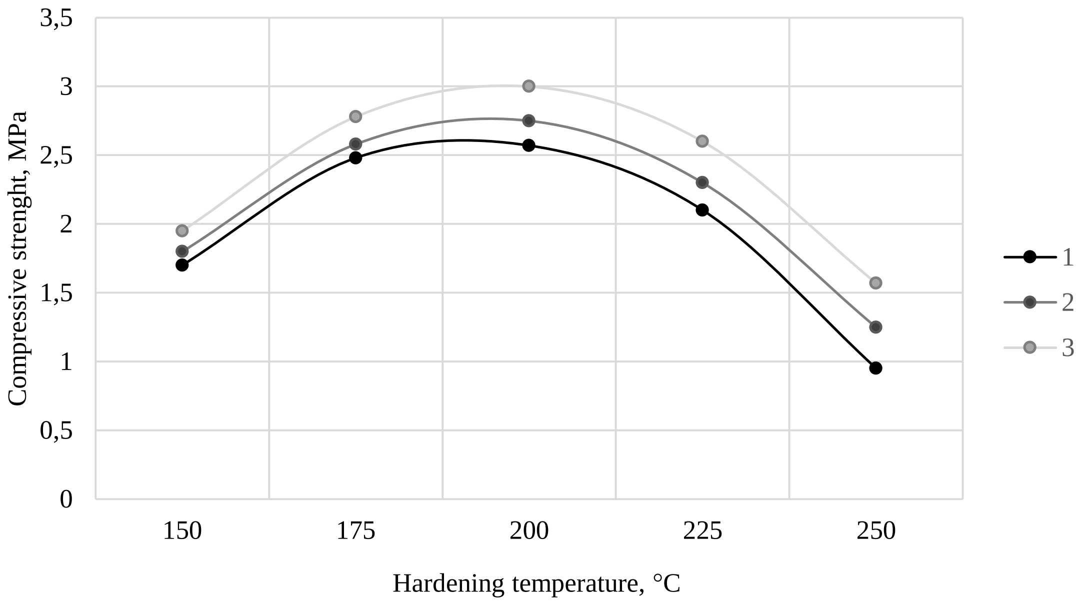


Fig. 9. Dependence of the strength of the mixtures on the temperature and amount of binder composition: 1 - 3 % of the binder composition; 2 - 5 % of the binder composition; 3 - 7 % of the binder composition.

Orthophosphoric acid is not added into the mixture as a component, therefore, all the liquid phase in it is represented by water, and it is given a decisive role in dispersing the binding composition over the surfaces of sand grains and creating adhesive bonds. It has been established that less than 5 % of water is insufficient for the implementation of this process. It is expressed, that with increasing the number of the binder composition in the mixture does not increase its strength (Fig. 10, curves

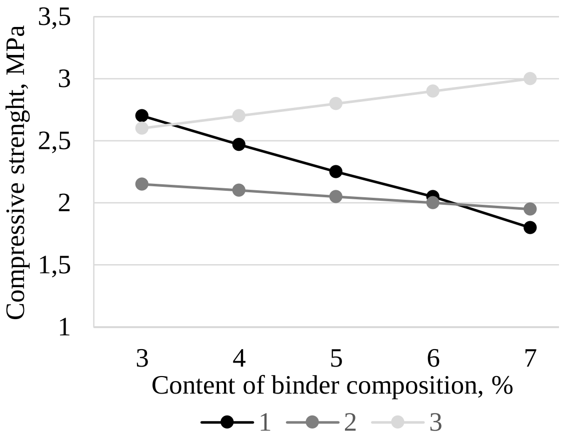


Fig. 10. The dependence of the strength of the mixtures on the amount of water and binder composition: 1 - 3 % water in the mixture; 2 - 5 % water in the mixture; 3- 7 % water in the mixture.

1, 2). At 7 % of water in the mixture there is a traditional growth of the strength with an increase in the percentage of the binding composition (Fig. 10, curve 3).

As a result of research, component composition of core mixtures has been determined (Table 1).

The high thermal resistance of aluminum phosphates is known for a long time. Their low activity to iron-carbon melts determine the area of use of mixtures. It is most expedient to apply them to steel and cast iron castings.

Specific areas of use of the investigated mixtures can be cores and molds, which are made by heating. From the developed mixtures were made as separate cores, as well as whole shell molds.

From the mixture № 1 (Table 1), a shell mold was made according to the hot equipment. The size of the cavity of the form is: diameter – 80 mm, height – 15 mm. The form was poured with heat-resistant steel (0.3 % C; 25 % Cr; 2 % Al; 0.15 % Ti) at a temperature of 1560 °C. This steel contains a high percentage of chromium, which can result in a burning-on in the case of physical and chemical interaction of steel with the material of the mold. Burning-on and other surface defects were not detected.

From the mixture № 2 (Table 1), cores were made to produce cylindrical castings with a wall thickness of 4 mm. The mold with a vertical parting was made in two flasks and designed to produce eight castings: 5 castings with an internal diameter of 22 mm and three castings with

a

b

Fig. 11. Casting from heat-resistant steel, made in shell mold (a) and block of castings, obtained using cores from the developed mixture (b).

an internal diameter of 16 mm (Fig. 11). The mold is made of raw sand-clay mixture, casting was carried out with grey cast iron at 1450 °C.

The cores are of sufficiently high strength to carry out operations for removing them from core box and setting in mold. The cores don't have frames, they have not been exposed to antiburning coating before pouring the mold. The castings have no defects caused by interaction with the components of the foundry mold. Cores are knocked out without much effort, the inner surface of the castings is devoid of burning-on and surface defects.

Table 1

Composition and properties of mixtures with orthophosphoric acid and inorganic salts of aluminum

№ mixture	Component content, mass %					The temperature of the strengthening, °C	Compressive strength, MPa
	H_3PO_4	binder composition with $Al_2(SO_4)_3 \cdot 18H_2O$	$Al(NO_3)_3$	water	quartz sand		
1	3…4	–	3…4	1…2	rest	180	1.2…1.5
2	–	5…7	–	5…7	rest	200	2.5…3.0

Conclusions

1. The possibility of synthesis binders directly in the composition of core mixtures when the reaction of concentrated orthophosphoric acid with a number of aluminum-containing materials was theoretically and experimentally confirmed. It is shown that the conditions of interaction are determined by the type of chemical bond of aluminum in these materials.

2. Thermodynamic calculations are substantiated and experimentally proved that as a result of the interaction of orthophosphoric acid with nitrate aluminum at a temperature of 200...250 °C, a binder is formed which has the form of the orthophosphate of aluminum and allows to achieve the compressive strength of the mixture in the range of 2.3...2.8 MPa.

3. It has been experimentally established that when the interaction of the orthophosphoric acid with aluminum sulphate at 200 °C, a reaction product is formed which has a binding potential and can be used as a binder in core mixtures. The optimal composition of the binder should be 10 mass parts of $Al_2(SO_4)_3 \cdot 18H_2O$ per 1 mass part of H_3PO_4, which provides the highest level of properties of the mixture.

4. Developed binders have high refractoriness and low physical and chemical activity to iron-carbon melt, which allows them to be used in core mixtures for the production of castings of steel and cast iron at various temperatures of pouring, which is confirmed experimentally. Castings, obtained using the cores of the developed mixtures, do not have burning-on and other surface defects, and the roughness of cast surfaces is in the range of 12.5...50.0 microns.

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[1] L.G. Sudacas, Phosphate binding systems (RIA «Kvintet», St. Petersburg, 2008).
[2] S.P. Doroshenko, V.P. Avdokushyn, K. Rusin, I. Matsechek, Molding materials and mixtures (Vyshcha shkola, Kyiv, 1990).
[3] A.N. Boldin, N.I. Davydov, S.S. Zhukovsky, T.N. Kiryukhina, N.N. Kuzmin, S.D. Teplyakov and A.I. Yakovlev, Foundry molding materials. Forming, core mixtures and coatings: a Handbook (Mashinostroyeniye, Moscow, 2006).
[4] V.A. Kopeikin, V.S. Klementieva and B.L. Krasnyy, Refractory phosphate binders (Metallurgiya, Moscow, 1986).
[5] Zhang Youshou, Liu Dong, Xia Lu, Ren Yanzhen, Cai Peng, Zhou Lei, Patent China No. 108907069 (30 November 2018).
[6] Yang Yang, Patent China No. 106734858 (31 May 2017).
[7] S. Alferyev, V. Polyakov, Patent USA No. 2014175323 (26 June 2014).
[8] Kim Jai Ha, Hur Yang Wook, Son Sung Han, Joo Kyoung, Patent Korea No. 20090058977 (10 June 2009).
[9] Xia Lu, Ren Yanzhen, Zhang Qian, Zhang Youshou, Liu Dong, Zhou Lei, Patent China No. 108405794 (17 August 2018).
[10] Jung Yeon Gil, Kim Eun Hee, Woo Ta Kwan, Lee Je Hyun, Patent Korea No. 20180017400 (21 February 2018).
[11] Jing Jinlong, Chen Xuegeng, Patent China No. 104815943 (5 August 2015).
[12] R.V. Lyutyy, D.V. Keush, Ye.A. Anisimova, Patent Ukraine No. 99789 (25 June 2015).

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Дослідження процесів зміцнення стрижневих сумішей з ортофосфорною кислотою і алюмовмісними матеріалами різного класу

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Розглянуто наукові та практичні питання розробки стрижневих сумішей для ливарного виробництва, заснованих на зв’язувальних матеріалах фосфатного класу. Зв’язувальні матеріали, які представлені в цій статті, відрізняються від раніше відомих тим, що для їх отримання не використовуються дефіцитні компоненти і порошкові затверджувачі. Замість цього використовуються комбінації ортофосфорної кислоти з алюмовмісними матеріалами різної хімічної природи.

Встановлено утворення високоміцних фосфатних зв’язувальних компонентів при взаємодії ортофосфорної кислоти з алюмосилікатами (на прикладі дистен-силіманіту і пірофіліту) і шламовими відходами виробництва алюмінію. Їх раціонально застосовувати для процесів теплового зміцнення ливарних стрижнів в інтервалі температур 200...300 °С.

Теоретично доведено і практично підтверджено утворення зв'язувальних компонентів при взаємодії ортофосфорної кислоти з неорганічними солями алюмінію. У статті продемонстровані приклади синтезу фосфатів алюмінію з його нітрату і сульфату при нагріванні до 200...250 °C. Результати підтверджені термодинамічними розрахунками, а також рентгенофазовим аналізом.

Перспективи практичного впровадження розроблених зв'язувальних матеріалів обумовлені тим, що вони проявляють високу адгезію до вогнетривкому кварцового наповнювача і низьку фізико-хімічну активність до металевих розплавів чавуну і сталі. Це забезпечує високу механічну міцність ливарних стрижнів і їх задовільні протипригарні властивості.

Представлено склади розроблених стрижневих сумішей і приклади їх застосування для отримання якісних виливків з чавуну і сталі.

Ключові слова: алюмосилікати, нітрат алюмінію, ортофосфорна кислота, зв'язувальний компонент, стрижнева суміш, сульфат алюмінію, виливок.