Synthesis of air-curing phosphate binders and heat-resistant composites based on them

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Abstract. The article discusses methods for synthesizing phosphate binders hardening in air at normal temperature. Mixed binders are offered to obtain heat-resistant composites. They have the ability to acquire stripping strength in air conditions. It is concluded that the proposed binders should be synthesized from powdered industrial waste or from pure oxides, providing a reasonable ratio of their activity degree.

1. Introduction
Nowadays, in lining constructions of most thermal devices and high-temperature installations both large block parts made of heat-resistant concrete and monolithic compositions in the form of solutions, mortars and other masses are used. This improvement of refractory lining technology allows increasing chemical resistance and durability of linings in general. The use of heat-resistant concretes in monolithic and precast variants in lining constructions of thermo technical plants allowed designers to create quite rational solutions for manufacturing of separate complex elements of thermal units, which cannot be created on piece refractories [1].

Heat-resistant concretes necessarily include such binders as portland cement with refractory additives, alumina cement, silicate liquid glass and its semi-finished products in the form of silicate blocks, as well as phosphate compositions in the form of mixtures of powdered refractory fillers with orthophosphoric acid or liquid phosphate bonds.

Very scarce refractory components prepared on the basis of special ceramics (chamotte, mullite, magnesite, etc.) are used as fine aggregates and fillers in the composition of heat-resistant concrete. Technological production process of refractory fine aggregate and fillers is connected with such energy-consuming operations as hard ceramics crushing and grinding. In this connection, the use of local industrial refractory wastes and other technogenic raw materials in the composition of heat-resistant concrete is a very urgent task [2].

Multiple research and industrial tests have shown that the use of phosphate cements in the composition of heat-resistant concrete allows the development of very advanced refractory lining materials with improved physical, thermal and operational parameters [3].

Most phosphate compositions and heat-resistant concrete based on them require heat treatment up to 500-600°C for their curing. The curing process of plastic phosphate compositions can be controlled by adjusting the ratio between the components of the finely dispersed component and the chemical activity of the mixing liquid.
Recently, phosphate cements, which are chemical binders and allowing to create materials and products with high physical and mechanical properties, have become widely used in heat-resistant concrete technology [3].

It is possible to control the process of hardening of plastic phosphate cement masses by regulating the activity of the thin-walled component (e.g. increasing the fineness of grinding, heating temperature, ultrasound processing, etc.) and the activity of the mixing liquid (changing the acid concentration, quantity, the introduction of substances that accelerate or slow down the setting processes in air conditions).

2. Theoretical foundations for the synthesis of phosphate compositions

Powdered oxides of many metals and H₃PO₄ - orthophosphoric acid forming hydrophosphates of various degrees of substitution as a result of the reaction are used for the phosphate cements synthesis. Studying the processes of reactions of various powder components with H₃PO₄ of various concentrations, Kinzheri [4] noted that during hardening of phosphate compositions the heat formation as a result of an exothermic reaction is a very important factor.

Therefore, according to Hess’s law, the heat effects of the MeₓOᵧₕ - H₃PO₄ reactions were calculated in order to determine the required amount of heat for the formation of phosphate masses under normal air conditions [5].

The heat effect of any chemical reaction “Q” is equal to the sum of the heat formation of the interacting substances of this reaction. When calculating the heat effect of reactions, the numerical values of the heat formation were taken from the reference book [6]. To perform the calculations, the assumption was applied that, as a result of the interaction of oxides with H₃PO₄, intermediate phosphates are formed. To reveal the influence of thermal effects on the hardening process of phosphate masses, the reduced reaction effect was taken, determined by the formula:

\[ Q_{\text{given}} = \frac{Q}{M} \]

where – heat of reaction, found according to Hess’s law, cal/g;  
\( Q_{\text{given}} \) – conditional thermal effect of the reaction, cal/g;  
\( M \) – gram-mole of oxide.

According to the values of the conditional thermal effect formed as a result of the interaction of powdery oxide with orthophosphoric acid, the hardening masses were divided into three groups based on the heat received:

1- group – phosphate compositions, curing at heat treatment (200 °C and more);  \( Q_{\text{given}} \leq 30 \text{ cal/g} \)  
2- group – phosphate compositions, curing in normal air conditions (\( t = 20°C \));  \( 30 > Q_{\text{given}} > -200 \text{cal/g} \)  
3- group – phosphate compositions, which do not form monolith at the oxide reaction with H₃PO₄;  \( Q_{\text{given}} < -200 \text{cal/g} \).

Such structural and energy parameters of solids as ionic density and the energy of a single bond have a great influence on the course of chemical reactions. [7] In this regard, it becomes possible to examine the hardening process of phosphate compositions and derive a new indicator determining the activity of powdered metal oxides [2].

Ionic density (\( P \)), determining the process of ion packing as a result of crystallization of the solid framework of substances, is calculated by the formula of prof. A.A. Novopashin [7]:

\[ P = \frac{2.52 \cdot \rho_{i}}{M \cdot \sum n_{i} \cdot r_{i}^{3}} \]

where  
\( \rho_{i} \) – true oxide density, g/cm³;  
\( M \) – molecular weight;  
\( n_{i} \) – the number of ions of a given type in a molecule;  
\( r_{i} \) – ion radius in tenths of a nanometer.
The process of chemical interaction of solid metal oxides with $\text{H}_3\text{PO}_4$ completely depends on the packing density of the ions composing these oxides. However, the structure of a solid will be the more stable, the higher the value of the energy of a single bond between cations and anions. Thus, the ability of solid metal oxides to interact with $\text{H}_3\text{PO}_4$ and form compositions hardening with it can be estimated through their activity and presented as a dependence

$$K_a = f(P_i \cdot \varepsilon)$$  \hspace{1cm} (3)

where $K_a$ – activity coefficient of oxides;

$P_i$ – ionic density of oxides;

$\varepsilon$ – the energy of a single bond between oxide cations with oxygen; kcal / mol, taken from Sun's experimental data [7].

It becomes possible to calculate the activity coefficient $K_a$ of oxides by the formula:

$$K_a = \frac{44}{P_i \cdot \varepsilon}$$  \hspace{1cm} (4)

where $P_i$ – ionic density of oxide;

$\varepsilon$ – energy of a single bond between oxide cations with oxygen, kcal / mol [7].

44 – product value $P_i \cdot \varepsilon$ for phosphorus anhydride $\text{P}_2\text{O}_5$.

The results of mathematical calculations allowed classifying metal oxides by the following scheme:

$K_a > 2.42$ – I group - phosphate compositions of the hardening structure do not form;

$0.85 < K_a < 2.41$ – II group - phosphate compositions hardening under normal air conditions ($t = 20^\circ\text{C}$);

$K_a < 0.85$ – III Group - phosphate compositions are formed during heat treatment (200$^\circ\text{C}$ and above).

Such classification allowed forming a new pattern of formation of solid structures in plastic phosphate compositions taking into account the modifying state of powdered oxide. This modified state of solid oxide allows fixing its ionic density. In this connection, it was found that the minimum amount of heat required to create air-curing phosphate compositions is 70 cal per 1 gram of solid oxide.

Therefore, it is possible to mix powdered metal oxides with each other, forming mixtures in which the total heat release will approach 70 cal per 1 g of total mass. Naturally, the beginning of mass setting will be due to the heat generated by the reaction of active oxide with $\text{H}_3\text{PO}_4$. Phosphate composition in this case acquires initial strength, which is required for dismantling, transportation and individual elements assembly. Final structural formation of cement stone with stable phosphate component is observed during further heat treatment, which can be carried out during the first heating of the thermal unit due to the chemical reaction of the inactive part of the thin-walled additive with $\text{H}_3\text{PO}_4$.

As a result, it was found that using the obtained dependence of the effect of $K_a$ of powdered oxides on the process of the appearance of hardening masses in phosphate masses, it is possible to synthesize cements with normal setting times.

It is obvious that the basis for the selection of raw components to obtain a normally solidifying phosphate plastic masses is the activity factor of $K_a$ oxides. It allows to search for raw materials components, which are a natural mixture of oxides in the composition of industrial waste.

In the group of oxides having binder properties under normal conditions, there are the following mixtures $\text{Fe}_2\text{O}_3 - \text{H}_3\text{PO}_4$ and $\text{FeO} - \text{H}_3\text{PO}_4$. Among iron-containing industrial waste, the maximum amount of iron oxides is contained in the waste heaps of sulphuric acid production - pyrite cinder, formed after firing of raw materials in the form of pyrite.

The main components of pyrite cinders are oxides of ferrous and ferric iron. Their maximum content exceeds 70%. However, the chemical composition of pyrite cinders also includes such oxides as $\text{SiO}_2$; $\text{CaO}$; $\text{MgO}$ and $\text{Al}_2\text{O}_3$.

For chemical compounds, which include many inorganic industrial wastes, the activity coefficient is recommended to be determined by the formula:
The refractoriness of synthesized phosphate cements, aluminophosphates and zirconophosphates, which are capable of non-refractoriness for temperatures. The strength necessates significant increases after the introduction of alumina product or zircon in the compositions of synthesized phosphate cements. To synthesize mixed alumina-iron-phosphate cement, alumina-chromium waste of petrochemistry was used as an alumina-containing component - a spent catalyst IM-2201 and technical alumina. Zircon concentrate KC-1 of the Volnogorsk deposit was used for zircon - iron phosphate cement. When the above raw materials are mixed in a mass of pyrite cinders with orthophosphoric acid, mixed plastic cement masses are formed, which have properties different from the masses on pure iron phosphate.

The refractoriness of the synthesized aluminum iron phosphate and zircon iron phosphate significantly increases after the introduction of alumina-containing raw materials and zircon into phosphate cements. The setting times of the synthesized phosphate cements increase, but even with 80-90% of the alumino-chromium waste IM-2201 of spent catalyst or zircon, the process of air curing of phosphate cements is observed.

The test results of the synthesized phosphate cements indicate that at an early age (1 day) they acquire the strength necessary for dismantling, transportation and installation of concrete elements prepared on their basis. This circumstance is explained by the formation of refractory compounds, such as aluminophosphates and zirconophosphates, which are capable of non-hardening when heated at high temperatures.

The results of samples testing of mixed cements in determining the refractoriness indicate that with an increase in the amount of a high-alumina product or zircon in the compositions of synthesized cements, their operating temperature increases: 1500 °C for aluminum iron phosphate and 1600 °C for zircon iron phosphate. Such an indicator of the durability of phosphate compositions as heat resistance is 30 or more water thermal cycles. Such indicators of heat-resistant compositions developed on the basis of waste are typical for many phosphate materials. Using the developed phosphate cements, the compositions of heavy heat-resistant concrete were selected. The test results shown in table 1 demonstrate that concrete mixtures based on chamotte and mullite aggregate harden under normal air conditions and being one day old they have strength indicators sufficient for dismantling and transporting products. In this regard, it becomes possible to transfer the heat treatment of concrete...
products directly to a heating unit, in which any temperature conditions can be created during drying and first heating.

In heat-resistant concretes of all the developed compositions, the compressive strength after heating up to temperatures of 1400-1600 °C does not decrease and remains constant. The deformation temperatures of refractory concretes under load are also very high, i.e., the ability of concretes to non-harden when heated is retained due to the newly synthesized cements.

3. Results and discussions
Experimental data indicate a very high physical and thermal performance of the selected concrete. A great advantage of concretes is their ability to harden and increase strength in air conditions at a temperature of 20 °C, which affects the construction of large-sized elements and allows the use the concrete mixture in a monolithic version.

| Concrete composition, (kg/m³) | Average density in a dry state, (kg/m³) | Compressive strength, MPa, after hardening and heating to temperature (°C) | Heat resistance, water heat cycle |
|--------------------------------|----------------------------------------|--------------------------------|---------------------------------|
| Alumina-iron-phosphate concrete cinder – 90 | | | |
| Aluminum chromium waste – 350 | 2082 | 2.1 | 44.7 | 45.2 | 28 |
| Chamotte crushed stone (fraction 5-10mm) – 750 | | | |
| Chamotte sand – 650 | | | |
| $\text{H}_3\text{PO}_4$ – 260 | | | |
| Zircon-iron phosphate concrete cinder – 90 | | | |
| Zircon KC 1 – 350 | 2124 | 2.2 | 48.1 | 50.8 | 32 |
| Mullite crushed stone (fraction 5-10mm) – 780 | | | |
| Mullite sand – 680 | | | |
| $\text{H}_3\text{PO}_4$ – 250 | | | |

The article also investigated nanotechnologie raw materials taken from the sludge of industrial waste of non-ferrous metallurgy. At the Samara metallurgical plant, sludge waste is formed in the form of secondary products, which are nanotechnogenic raw materials. Thus, the sludge of alkaline etching of aluminum is formed when processing aluminum-magnesium alloys with NaOH solution. The resulting high-plastic sludge (with pH level equals to 12.6) is mixed with carbonate sludge (chemical water treatment sludge) to neutralize the aluminum-alkaline sludge. As a result of this technology, alumocalcium sludge is formed at the plant treatment facilities, the chemical composition of which is shown in table 2.

| Table 2. Chemical composition of calcium alumina sludge |
|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| Content, mass (%) | | | | |
| $\text{SiO}_2$ | 8.16 | 0.8 | 14.6 | 26.32 | 8.24 | 1.58 | 1.36 | 38.88 | 99.94 |

Physical and chemical studies conducted with aluminum-calcium, aluminum-alkaline and carbonate slurries have shown the presence of a large amount of the mineral-calcite CaCO₃ in the raw material.
The size of sludge particles, as shown by the studies [8], is 40-80 nm. This fact can be attributed to a slurry waste of Samara metallurgical plant to nanotechnologia raw materials.

Based on the sludge, liquid phosphate binders were synthesized by applying H₃PO₄ of a certain concentration. When these slurries come into contact with liquid orthophosphoric acid, an active chemical reaction occurs as a result of which almost all the solid substance is dissolved without a residue due to its nanoscale (while the resulting ligaments do not form a precipitate during long-term storage).

Using this technology, liquid phosphate binders are formed, namely, aluminum phosphate, calcium phosphate and aluminum-calcium phosphate binders due to the use of aluminum-alkaline, carbonate, and aluminum-quartz slurries, respectively.

Synthesized liquid phosphate binders due to their high chemical activity proved to be very effective mixing liquids in the development of air-hardening compositions of heat-resistant compositions: solutions, concretes and impregnating-coating masses.

Thus, the main factor determining the possibility of using oxides to produce phosphate binders is the thermal effect of the reaction Me₃Oₓ – H₃PO₄ (powdered metal oxide - orthophosphoric acid).

The activity coefficient of powdered oxides, calculated from their structural and energy parameters, is the basis for synthesizing compositions of phosphate cements that harden under normal conditions. According to this coefficient, metal oxides are distributed into III groups according to their degree of activity; thus, when interacting with H₃PO₄, the values of the oxide activity coefficient and the thermal effect found when interacting with H₃PO₄ allow for a very reliable synthesis of various phosphate cements to obtain concretes and solutions with the desired properties.

4. Conclusions

Heat-resistant heavy concrete based on iron-phosphate cement has high physical and mechanical properties. The operating temperature of such heat-resistant concrete with a fireclay component reaches 1200°C. The use of pyrite cinder in a mixture with high-alumina fine-ground powders and ground zircon made it possible to synthesize alumina-phosphate and zircon-phosphate cements and heat-resistant concretes that harden in air conditions (t = 20°C). Increased strength indicators of heat-resistant concrete are formed during drying and the first heating of the heat unit. Concrete elements of linings form a stable phosphate bond in their structure after such heat treatment. As a result, the physical and thermal performance indicators are significantly increased. This circumstance significantly increases the feasibility of using heat-resistant concrete of phosphate hardening instead of piece refractories in the linings of thermal units. Moreover, phosphate compositions (concretes and solutions) have increased chemical resistance, i.e. they are not wetted in aluminium solutions and flux salts.

The use of acidic water-soluble alumophosphate binders, in particular alumocalcium phosphate, as a mixer of heat-resistant mortar and concrete mixtures, also allowed obtaining the effect of air-curing in phosphate composites.

References

[1] Krayukhin V. I 2014 Heat-resistant concrete. Compositions. Exploitation. Restoration of basic properties after long-term operation (Saratov) p 348
[2] Khlystov A I 2004 Increasing the efficiency and improving the quality of refractory lining materials (Samara) p 134
[3] Sudakas L H 2008 Phosphate binders (St Petersburg) p 260
[4] Sychev M M 1986 Inorganic adhesives (Leningrad : Chemistry) p 152
[5] Beskov S D 1962 Techno-chemical calculations (Moscow) p 468
[6] Karapetyants M Kh, Karapetyants M L 1968 Basic thermodynamic constants of inorganic and organic substances (Moscow Chemistry) p 395
[7] Novopashin A A 1973 Mineral part of the Volga shale (Kuibyshev) p 120
[8] Khlystov A I, Sokolova S V, Konnov M V 2012 Directed structural chemical modification is one of the ways to improve the physical and thermal characteristics of aluminosilicate and high-alumina refractories Refractories and technical ceramics 11. pp 35-39.