On the technology of aluminosilicate and high-alumina phosphate hardening products

A Vlasov and E Vlasova

Samara State Technical University, Molodogvardeyskaya ul., 194, Samara 443001, Russian Federation

E-mail address: alvlass@yandex.ru

Abstract. The influence of alumocalcium sludge on the physical, mechanical and thermal properties of aluminosilicate and high-alumina products of phosphate hardening intended for operation at temperatures up to 1500 °C. It was found that the use of alumocalcium sludge in the compositions of non-burning phosphate compositions helps to reduce the polymerization temperature and thus provides an earlier formation of rock-like phases that are not subject to hydration. Based on the obtained mathematical model, optimal non-burning compositions are developed that are not inferior to similar products in terms of physical, mechanical and thermal parameters, which provides an expansion of the range of applications of the raw material base.

1. Introduction

Significant progress has been made in the design and construction of heat engineering structures. However, even today, the design, construction and operation of structures operating in high temperatures have major disadvantages, which lead to a relatively rapid failure of them and to an increase in the cost of construction.

Damage to some structures of thermal units occurs due to physical and chemical processes occurring in the material, in other structures due to high temperature stresses or deformations, and in many cases from the combined influence of both factors.

The reason for the short service life of structures of thermal units is in most cases their execution from piece refractories on binders mainly of hydration hardening [1-4]. More promising is the creation of binders, which are based on other physical and chemical processes. Such binders, in particular, include compositions that harden as a result of reactions of certain materials with phosphoric acid or its acidic derivatives, i.e. binders of phosphate hardening [5-8]. However, based on the work of recent years, it is clear that the use of phosphate hardening materials leaves a large range of technical problems, which can be solved by nanotechnogenic waste from various industrial enterprises, including alumocalcium sludge - waste from non-ferrous metallurgy [9-12].

To improve the physical, mechanical and thermal properties of heat-resistant and refractory compositions, due to the General lack of natural raw materials, man-made waste from various industries is widely used, which also helps to combat environmental pollution, namely, the quantitative reduction of landfills and landfills for waste storage. It is proved that man-made waste can become a huge wealth from a heavy burden, and with a scientific approach to its processing, it can become a valuable, and sometimes even scarce raw material.
2. Materials and methods
Samara metallurgical plant (JSC «Alcoa SMZ») is one of the largest suppliers of man-made sludge raw materials. As a result of numerous studies, it was found that the slurries formed at the metallurgical plant can be used as refractory fillers, including alumocalcium slurries in the production of pressed phosphate-fireclay refractories.

The plant operates modern treatment facilities. At various installations of these structures, aluminum-alkaline sludge (alkaline etching sludge of aluminum products and parts), which has a pH > 12, is neutralized with another liquid sludge-containing waste, namely carbonate sludge, the main component of which is CaCO₃. By mixing almadellago slurry of the carbonate (i.e., by reacting the sludge with high pH) is formed aljumokalievye liquid slurry with pH = 7, which after passing the filter press (figure 1) in the form of «curd» sludge is disposed of on special polygons.

![Figure 1. Filter press installation.](image1.png)

Also, the dimensions of the alumocalcium sludge particles were tested using the Membrane-2 diffractometer at the B. p. Konstantinov St. Petersburg Institute of nuclear physics in 2010. The obtained results showed that the studied sludge can be attributed to nanoobjects of the 2nd level, since the nanoscale of the particles is less than 100 nm.

The chemical composition of the sludge is shown in figure 2.

![Figure 2. Chemical composition of alumocalcium sludge.](image2.png)

X-ray structural analysis of alumocalcium sludge showed that the main constituent minerals are calcite, quartz and hydroargillite (figure 3).
Figure 3. X-ray diffraction pattern of calcium alumina sludge.

In the tests were also used: fillers-fireclay sand (scrap), fr. 0-5 mm; mullite sand (scrap), fr. 0-5 mm; binder (sealing liquid) - orthophosphoric acid H₃PO₄ (concentration, %: 40, 50, 60, 70, 80).

In the study, using standard methods, General patterns were considered in changing the basic properties of phosphate-chamotte compositions obtained on the basis of orthophosphoric acid with the addition of nanotechnogenic raw materials – alumocalcium sludge. In this regard, at the first stage of the study, alumocalcium sludge was introduced into the charge compositions, while the charge composition consisted of 65 % fireclay sand fr. 0-5 mm and 35 % alumocalcium sludge. The resulting charge was closed in excess of 100 % orthophosphoric acid H₃PO₄ of different concentrations, which ranged from 40 to 80 %. Obtaining the required concentration was achieved using the relationship between the concentration of orthophosphoric acid and its density.

Samples for testing were made by semi-dry pressing from masses containing 12 % solution of orthophosphoric acid solution, a certain amount of moistened powdery mass consisting of fireclay sand and alumocalcium sludge was poured into the mold. The resulting mixture consists of solid particles of various shapes and sizes. Then the mass in the mold was compressed from opposite sides with two punches. Stepwise pressing was used to equalize the pressure and remove air from the pressed mass. After the end of pressing, the resulting product was pushed out of the mold and placed in a muffle furnace for heat treatment. The samples were heat-treated at three control temperature points: 400 °C, 800 °C and 1200 °C. After heat treatment, the samples were cooled and tested for compressive strength using a hydraulic press.

3. Results and discussions

As a result of the conducted experiments with compositions consisting of fireclay sand and alumocalcium sludge and closed with orthophosphoric acid of different concentrations, positive results were obtained on changes in physical and mechanical properties. Figure 4 shows the dependence of the compressive strength of fireclay-phosphate refractory compositions on the acid concentration and pressing pressure.

Figure 4. Dependence of the compressive strength of chamotte-phosphate refractory compositions depending on acid concentration and pressing pressure:
1 – sample pressing pressure 50 kgf/cm²;
2 – sample pressing pressure 100 kgf/cm²;
3 – sample pressing pressure 150 kgf/cm²;
4 – sample pressing pressure 200 kgf/cm²;
5 – the pressing pressure of a sample of 250 kgf/cm².
The graph shows the spread of experimental data. Compositions 3 and 4 are the best. The compressive strength of samples from fireclay-phosphate refractory compositions of these compositions after heat treatment at 400 °C is 37.8 MPa and 36.1 MPa, respectively. The constructed separate curves of the dependence of the strength of fireclay-phosphate refractory compositions on the concentration of acid and pressing pressure do not give an answer about the optimal parameters.

In order to reduce the number of experiments and determine the optimal values of the selected parameters, mathematical processing of experimental values was performed, for this purpose, factors with a variable component were included in the mathematical planning plan of the experiment – the pressing pressure taken in the range from 50 kgf/cm² to 205 kgf/cm² and the concentration of orthophosphoric acid in the range from 40 % to 80 % (table 1).

Table 1. Natural factors, their values and variation intervals.

| Factor levels and their range of variation | Names and values of factors |
|-------------------------------------------|-----------------------------|
|                                           | the pressing pressure of acid concentration |
| Top level (+2)                            | 5                           | 80                          |
| Top level (+1)                            | 4                           | 70                          |
| Basic (zero) level                        | 3                           | 60                          |
| Lower level (-1)                          | 2                           | 50                          |
| Lower level (-2)                          | 1                           | 40                          |
| The range of variation in                 | 1                           | 10                          |
| Unit                                      | ton                         | %                           |
| Identification of factors                 | $x_1$                       | $x_2$                       |

Also, for the two-factor experiment, a planning matrix was calculated, where the arithmetic mean values of the compressive strength after heating up to 400 °C were calculated.

In the regression analysis program «STATISTICA 10.0», a second-order regression equation was obtained from two factors. The regression equation of the «$y$» function, after calculating the coefficients found using the student's t-test, takes the following form:

$$R_{\text{com.}}^{400} = -25.9851 + 12.548x_1 + 1.3217x_2 - 2.07x_1^2 + 0.0157x_1x_2 - 0.0113x_2^2$$

The chosen mathematical model adequately describes the system under study with a confidence probability of 0.95. Using the obtained regression equation, the response surface isolines were constructed using the computational and graphical program «STATISTIKA» (figure 5).

The 3D isolines made it possible to accurately determine the optimal range of changes in parameters (pressing pressure and orthophosphoric acid concentration), providing maximum properties. At the same time, the optimal value of the pressing pressure was 160 kgf/cm² (3.2 t), and the acid concentration was 62 % (1.442 g/cm³).

The study of a series of compositions based on phosphoric acid showed that already during heat treatment at 400 °C, the hardening of the structure of products occurs, and the mathematical model revealed optimal variable parameters that positively affect the physical and mechanical properties. To confirm the influence of alumocalcium sludge on the main properties of chamotte-phosphate compositions, the composition without additives (№1) and compositions with different amounts of alumocalcium sludge (№2 and №3) from 35 % to 65 % were studied (table 2).
Figure 5. Response surface Isolines with optimal parameter range (3D surface for variable parameters).

Table 2. Influence of the amount of alumocalcium sludge and heat treatment on the physical and mechanical properties of chamotte-phosphate compositions.

| №  | Charge composition                                                                 | Average density $\rho$, g/cm$^3$ (numerator), compressive strength $R_{\text{com.}}$, MPa (denominator) of samples after heat treatment to temperature, ($^\circ$C) |
|----|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1  | - Fireclay sand (150 g)                                                            | 1.67 / 17.8                                                                                                                                  1.71 / 20.5                                                                                                                                  1.7 / 21.2 |
|    | - $\text{H}_3\text{PO}_4$, $\rho = 1.42$ g/cm$^3$, the concentration of the acid is 60 % |                                                                                                                                                    1.42 / 31.2                                                                                                                                  1.7 / 31.2 |
|    | - Alumocalcium sludge (50 g)                                                        |                                                                                                                                                        1.42 / 31.2                                                                                                                                  1.7 / 31.2 |
| 2  | - Fireclay sand (100 g)                                                            | 2.11 / 36.8                                                                                                                                  2.12 / 39.6                                                                                                                                  1.97 / 41.4 |
|    | - $\text{H}_3\text{PO}_4$, $\rho = 1.42$ g/cm$^3$, the concentration of the acid is 60 % |                                                                                                                                                    1.42 / 31.2                                                                                                                                  1.7 / 31.2 |
|    | - Alumocalcium sludge (100 g)                                                       |                                                                                                                                                        1.42 / 31.2                                                                                                                                  1.7 / 31.2 |
| 3  | - Fireclay sand (50 g)                                                             | 1.67 / 27.3                                                                                                                                  1.68 / 29.1                                                                                                                                  1.66 / 31.2 |
|    | - $\text{H}_3\text{PO}_4$, $\rho = 1.42$ g/cm$^3$, the concentration of the acid is 60 % |                                                                                                                                                    1.42 / 31.2                                                                                                                                  1.7 / 31.2 |

As can be seen from table 2, after heating to 800 °C and 1200 °C, all experimental samples show an increase in the compressive strength. At the same time, it is worth noting that the sample №2 initially selected for research has the best physical and mechanical properties, and in the sample №3, where the amount of sludge was brought to 65 %, there is an increased fire shrinkage and the content of the stopper up to 17 %. In the course of research, it was found that at an acid concentration of less than 60 %, not all components of the alumocalcium sludge react, which is clearly visible in freshly formed samples in the form of white grains that did not react with the acid. At a concentration of more than 60 %, a strong clumping is observed during mixing of the charge, which leads to an inhomogeneous distribution of sludge particles in the sample body and, accordingly, to a decrease in the compressive strength.
Similar studies were conducted with another aggregate, where fireclay sand was replaced with mullite. The initial components for the series of these compositions were: alumocalcium sludge; mullite sand; orthophosphoric acid with an optimal concentration of 60% as a charge stopper.

The study of changes in compressive strength was also carried out in a wide temperature range from 400 °C to 1200 °C. To confirm the similarity of the results of physical and mechanical properties, a cycle of experiments was carried out during heat treatment at 400 °C. The data for the compressive strength is shown in figure 6.

**Figure 6.** Dependence of the compressive strength of mullite-phosphate refractory compositions from acid concentration and pressing pressure.

Much attention was paid to the mode of heat treatment of phosphate compositions (figure 7).

**Figure 7.** The Mode of heat treatment of samples.

Thus, it can be assumed that the regulation of the strength properties of pressed products is possible by optimizing the pressing pressure and regulating the fractional composition of mixtures, as well as by introducing the optimal amount of stopper.
4. Conclusions
As a result of research, it was found that the use of fireclay and mullite fillers in phosphate compositions based on acid of 60% concentration allowed to obtain products with increased physical, mechanical and thermal parameters.

In the future study, instead of orthophosphoric acid, it is planned to use acidic water-soluble phosphate bundles (alumophosphate, alumocalcium phosphate, and alumochromophosphate bundles) obtained by partial neutralization of H₃PO₄ with aluminum, calcium, and chromium oxides.

References
[1] Kuznetsova T V 1988 Aluminous cement (Moscow: Stroiizdat) p 272
[2] Butt Yu M 1974 Portland Cement (Moscow: Stroiizdat) p 328
[3] Bazhenov Yu M 2006 Modified high-quality concretes (Moscow: Publishing House Assoc. construction universities) p 368
[4] Karklit A K 1974 The refractories of the high alumina raw materials (Moscow: Metallurgy) p 152
[5] Abyzov V A 2016 Energy-efficient technology of phosphate binders, adhesives and cellular concrete Science of SUSU (Electronic resource) materials of the 68th scientific conference Sections of technical Sciences pp 17-20.
[6] Sudakas L G 2008 Phosphate Knitting Systems (St. Petersburg: RIA Quintet) p 260
[7] Latypova L I 2012 Heat resistant phosphatic materials on the basis of high-alumina waste products Bulletin of SUSU Series Construction and architecture 15 (38) pp 69-71
[8] Sychev M M 1986 Inorganic adhesives (L.: Chemistry) p 152
[9] Khlystov A I 2013 The use of mineral sludge waste in the processes of synthesizing liquid phosphate ligaments Bulletin of SUSU Series Construction and architecture 13 (2) pp 43–46
[10] Chumachenko N G 2011 The use of high-alumina slimes in technological processes for the production of unburned refractories and clinker ceramic materials Refractories and technical ceramics 7-8 pp 47-50
[11] Korenkova S F 2004 Basics and concepts of utilization of chemical precipitation of industrial waste in the construction industry (Samara: Samarsk. state arch. building. Univ) p 203
[12] Khlystov A I 2017 Heat-resistant concretes based on industrial waste in the Samara region monography (Samara: ASI SamGTU) p 171