High-alumina slurry waste metallurgy aluminium alloys - complex modifier of heat-resistant and refractory composites

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Abstract. The effect of aluminate slimes on the thermomechanical properties of heat-resistant and refractory composites has been investigated. The optimal content of nanotechnogenic raw materials in the studied compositions was revealed. It has been established that the replacement of expensive refractory powders (alumina, chamotte) with high-alumina industrial waste in general has a positive effect on the durability of refractories. The chemical components of aluminate sludges and the principles of their action on refractory compositions in the area of critical operating temperatures are given. The decrease in the water-cement ratio allowed in mineral compositions based on hydraulic binders to form plastic structures with enhanced rheological characteristics. The mechanism of the proceeding processes in refractory materials on phosphate binder is clarified.

Introduction
In recent years, in world practice there has been a tendency to reduce energy consumption in the production of heat-resistant and fireproof materials. This is realized both in the direction of creating fundamentally new compositions, and by increasing the share of resource-saving technologies. Since technical progress in the construction of industrial furnaces is inextricably linked with the introduction of new technology, which entails new requirements for refractories. The new refractory lining materials include unburned materials and products that can be used both in monolithic form and in the form of blocks or panels.

As is known, heat-resistant and refractory materials and products, depending on their requirements, can be made using various binders. Traditional binders are hydraulic (Portland and alumina) cements, sodium liquid glass and anhydrous sodium silicates with application temperatures from 1000ºС to 1400ºС [1-3], products with different concentrations of orthophosphoric acid H₃PO₄ and aluminophosphate are also well-proven solutions modified with various additives [4-7].

To increase the physicochemical and mechanical properties of heat-resistant and refractory compositions, technogenic wastes of various industries are widely used today, which is primarily due to the general depletion of the natural resource base and, secondly, to environmental pollution due to the formation of a huge number of landfills and landfills for waste storage. It has been proven that man-made waste can become a tremendous wealth from a heavy burden, and with a scientific approach to recycling it can be transferred to the area of valuable, and sometimes even scarce, raw materials.
Main part
The expediency of using technogenic raw materials in the building complex has been proved by research, information about which can be obtained in a significant number of scientific publications [8-14]. It is worth noting a large role in the development of this area of the department "Production of building materials, products and structures" of Samara State Technical University. Specific scientific recommendations on the processing of waste of different industries into building materials are reflected in numerous scientific works of the department staff [15-20].

A definite gap in building materials science can be considered as the fact that a whole group of technogenic raw materials, which includes sludge waste, has remained outside of the attention of researchers. Of the total amount of industrial waste in Russia, sludge accounts for about 30–40%, which makes it possible to attribute them to large-scale man-made raw materials.

The Samara Metallurgical Plant (CJSC "Alkoa SMP"), the largest enterprise of the aluminum industry in Europe, can be considered one of the suppliers of technogenic slurry. As a result of numerous studies, it was found that the sludges produced at the metallurgical plant are easy to classify, since they are very stable in terms of the composition of the mineral part. The constancy of the composition of sludge waste also demonstrates their technological advantages over other man-made raw materials. Particular attention from the group of mineral sludge deserve alum alkaline (sludge alkaline etching of aluminum) and alumina calcium sludge, capable of performing the functions of both the primary and the corrective component.

Aluminum alkaline pickling sludge is a waste resulting from the etching of aluminum and its alloys with caustic alkali (Figure 1). In the process of interaction of aluminum with alkali solutions, hydrogen is released and a precipitate of tetrahydroxyaluminate is formed, all of which can be represented as the following total reaction

\[ 2\text{NaOH} + 2\text{Al} + 6\text{H}_2\text{O} = 2\text{Na}[\text{Al(OH)}_4] \downarrow + 3\text{H}_2 \uparrow. \]

Figure 1 - CJSC "ALKOA SMP": precipitate of aluminum etching baths with a solution based on sodium hydroxide

The second most important alumo-calcium sludge is formed as a result of neutralization of effluent with lime milk with the formation of a mineral sediment of complex composition, but with the advantage of oxides of calcium and aluminum.

For the most part, the components in the chemical compositions of the sludge can be attributed to aluminate (Figure 2).
Also, the particle size of aluminate slurries was tested using the Membrane-2 diffractometer on the basis of the St. Petersburg Institute of nuclear physics in 2010. The results showed that the studied slurries can be attributed to the nanoobjects of the 2nd level, because the nanosize of the particles is less than 100 nm.

As is well known, a common disadvantage of refractory and heat-resistant composites on traditional binders is the reduction of their strength properties in the range of operating temperatures (800÷1000°C). This behavior is naturally and to a greater extent associated with the phenomenon of dehydration of tumors of heat-resistant cement stone and the resulting internal stresses between the aggregate and cement stone due to the difference in temperature deformations. The use of such chemical binders as liquid glass, phosphate ligaments virtually eliminate the negative effects mentioned above, but their use in the compositions of heat-resistant composites greatly complicates the technological the process of mixing concrete masses in a large volume and in general makes the final products much more expensive. The behavior of heat-resistant concretes on various binders is presented in Figure 3.

In this work, great attention is paid to the processes of modification of heat-resistant compositions with the use of hydraulic cements. The main task in the research was to find the optimal amount of aluminate sludge in the compositions of heat-resistant compositions.

Experiments have shown that the introduction of nanoparticles of sludge alkaline etching of aluminum in the amount of 10% in heat-resistant compositions based on Portland cement and alumina cement is optimal, because positively influenced such physicothermal and mechanical parameters as
refractoriness, heat resistance, reduction in water binding ratio, increase in compressive strength (table 1).

**Table 1 - Control and modified compositions of heat-resistant compositions based on hydraulic binders and their properties**

| No. of composition | Type of main hydraulic cement and quantity | Water / cement ratio, % | Compressive strength after normal-humidity hardening, MPa | Fire resistance, °С | Thermal resistance, (water heat changes) |
|--------------------|------------------------------------------|-------------------------|----------------------------------------------------------|---------------------|----------------------------------------|
| 1                  | Portland cement PC 500-D0 + chamotte (ground) | 28,2                    | 23,3                                                      | 1220                | 12                                     |
| 2                  | Portland cement PC 500-D0 + 10% sludge + chamotte | 24,1                    | 31,4                                                      | 1380                | 20                                     |
| 3                  | Aluminous cement AC-40                   | 28,0                    | 40,5                                                      | 1450                | 20                                     |
| 4                  | Aluminous cement AC-40 + 10% sludge       | 23,3                    | 48,4                                                      | 1555                | 25                                     |

Analysis of the results of table 1 shows that in the compositions where it was introduced, the addition of aluminum alkaline pickling sludge refractoriness increases, due to the increased content of Al$_2$O$_3$ in them. The fact of a decrease in the water-cement ratio in the compositions of heat-resistant compositions with a 10% sludge additive indicates the formation of a plastic structure with increased mobility and water-holding capacity. If we consider that the sludge nanoparticles have a dimension less than 100 nm, which is 1000 times smaller than the size of the cement grains, this explains the formation of plastic mass as a result of the active formation of a cluster structure. This type of structure contributes to a sharp increase in the mobility of plastic mortar and concrete compositions on modified binders, which makes it possible in general to consider aluminate slimes to be strong plasticizers.

As a result of the modification of hydraulic binders by sludge alkaline etching of aluminum on their basis, compositions of concrete with a temperature of operation up to 1450ºС were developed. At the same time, it is worth noting that the fireclay bricks (class B) and mullite refractories MLS-62 were used as aggregates. The selection of the compositions of mullite and chamotte concrete was made experimentally, taking into account the condition for obtaining compositions with a maximum average density. The process of making concrete samples consisted in molding them on a vibrating plate, after which they hardened for 3 days in normal-humidity conditions (NHC). The removal of prototypes produced 24 hours after their formation.

Subsequently, after NHC and heat treatment of chamotte and mullite concrete samples, their physicomechanical and thermal characteristics were determined.

In our experiments, large-tonnage technogenic raw materials in the form of aluminate slimes were also used in the technology of producing pieceless refractory refractory materials on phosphate binders using semi-dry pressing with a specific pressure of not more than 200 kg/cm$^2$, which does not require special firing and cooling modes, as well as special equipment.

The initial components of the refractory compositions under investigation were represented by fillers, fillers and mixing fluid. In addition to aluminate sludges, another production waste in the form of a spent IM-2201 catalyst was used as the main filler ($S$ units. = 7800 cm$^2$/g). The mineralogical composition of the fillers is mainly represented: $\alpha$-Al$_2$O$_3$ (corundum), $\gamma$-Al$_2$O$_3$ (technical alumina),
Al(OH)$_3$. In the experiments, orthophosphoric acid $\text{H}_3\text{PO}_4$ of 50% concentration was adopted in the experiments.

In the course of the research, the basic properties of refractory materials on phosphate binders were studied (Table 2).

**Table 2 - Properties of test samples on phosphate binder**

| №   | The composition of the charge | Fraction size, mm | Acid consumption, ml | Deformation temperature under load, °С | Thermal resistance, water heat changes |
|-----|--------------------------------|-------------------|---------------------|----------------------------------------|--------------------------------------|
|     |                                |                   |                     | S.S.  | 4%     | 40%     |                     |
| 1   | Chamotte                         | 0,08              | -                   | 1275  | 1320   | 1380   | 14                   |
|     | Chamotte sand                    | 0,16-3            | -                   | 1360  | 1410   | 1460   | 20                   |
|     | $\text{H}_3\text{PO}_4$         | -                 | 22                  | 1400  | 1490   | 1520   | 24                   |
|     | Calcium sludge                   | 0,08              | -                   | 1420  | 1540   | 1600   | 30                   |
| 2   | Chamotte sand                    | 0,16-3            | -                   | 1360  | 1410   | 1460   | 20                   |
|     | $\text{H}_3\text{PO}_4$         | -                 | 20                  | 1400  | 1490   | 1520   | 24                   |
|     | Calcium sludge                   | 0,08              | -                   | 1420  | 1540   | 1600   | 30                   |
| 3   | HM-2201                          | 0,08              | -                   | 1400  | 1490   | 1520   | 24                   |
|     | Chamotte sand                    | 0,16-3            | -                   | 1420  | 1540   | 1600   | 30                   |
|     | $\text{H}_3\text{PO}_4$         | -                 | 25                  | 1400  | 1490   | 1520   | 24                   |
|     | Calcium sludge                   | 0,08              | -                   | 1420  | 1540   | 1600   | 30                   |
|     | Aluminum alkaline pickling sludge | 0,08            | -                   | 1420  | 1540   | 1600   | 30                   |

The control composition adopted under No. 1 without the addition of technogenic raw materials. In the remaining three compositions numbered 2, 3, 4, industrial waste was taken as fillers. All samples were made by the method of semi-dry pressing at a specific pressure of 150 kg/cm$^2$ from masses of shut-in with phosphoric acid of 50% concentration. Acid consumption in the compositions ranged from 20 to 25 ml (10-12% by weight of dry matter). As can be seen from table 2, thanks to the use of technogenic raw materials, it was possible to increase the temperature of deformation under load. Along with the temperature of deformation under load, heat resistance is also one of the most important factors determining the durability and temperature of service of refractories. So the increase in heat resistance by 2 times is a positive circumstance for the above factors.

To clarify the mechanism of the processes occurring in refractory materials on the phosphate binder, X-ray phase analysis of samples №3 and №4 with the best thermomechanical parameters was carried out. X-ray phase analysis was carried out on the device DRON-3. Radiographs were taken after heating to 400°C. As radiographs (Figure 4) show, at this temperature, a gradual transition of aluminum metaphosphate Al($\text{PO}_3$)$_3$ to basic phosphate (AlPO$_4$ — 4,0463; 4,045) of low-temperature quartz-type form begins.
As can be seen at a temperature of 400ºC, stable forms of aluminum phosphate AlPO$_4$ begin to form, which provides samples with the possibility of long-term storage in air without destruction. Insufficient exposure of the samples at a temperature of 400ºC leads to the formation of an unstable hygroscopic ligament due to the incomplete conversion of pyrophosphoric acid H$_4$P$_2$O$_7$ to aluminum phosphate. However, it should be noted that to obtain the necessary strength in unburned high-alumina refractories, not only heat treatment at a temperature of 400ºC is necessary, but during the temperature rise, heating should be done slowly with exposures at 110 and 220ºC in order to allow water to evaporate without damage to the structure of the samples.

In the future, for all the tested compositions, the limit of compressive strength ($R_{pr}$) was determined after heating to temperatures of 800ºC, 1000ºC, 1200ºC, 1400ºC (Figure 5).
Conclusion

In the future, in order to obtain air-hardening phosphate composites with even higher strength and refractory properties, the orthophosphoric acid used in the experiments will be replaced with the water-soluble aluminophosphate and alu-calcium phosphate ligaments developed at the department.

At the same time, it is necessary to note the fact that the synthesis of these phosphate ligaments was carried out on the basis of nanotechnogenic raw materials in the form of the same aluminite slimes.

Summarizing the results of laboratory experiments, we can draw the following conclusions:

• aluminite slimes introduced into the composition of refractory mineral compositions have a strong plasticizing effect;
• the degree of use of technogenic raw materials in refractory modified compositions reaches from 10% to 50%;
• the use of industrial wastes in various binders made it possible to obtain heat-resistant and refractory composites with enhanced thermomechanical parameters;
• developed refractory compounds can be used in the lining of most thermal units.

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