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Future trends for the use of nanotechnogenic slurry waste in the production of special building materials

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Abstract. The article provides information about the main directions of the use of nanotechnogenic slurry waste, i.e. the industrial waste of Samara enterprises in the production of special building materials, namely, heat-resistant binders and concretes on their basis. It is found that nanotechnogenic wastes exert a polyfunctional impact in heat- resistant compositions (binders, mortars, concretes). High – alumina slurries are a plasticizer in heat-resistant composites on hydraulic cements. They are also a major component in the production of high- alumina binders and in the process of synthesizing phosphate binders which make it possible to obtain high-quality heat-resistant composites (mortars, coatings, concretes, impregnations).

1 Introduction

Currently, the volume of modern construction associated with the production and application of special building materials with the improved performance, expansion of the raw material base by the use of a variety of man-made materials, etc. is rapidly increasing. Organization of the production of highly heat-resistant composites is inseparably connected with the creation of competitive home materials. It is necessary to strive to reduce resource and energy intensity of production, labor costs, to optimize capital investments in the special construction of industrial furnaces and other thermal units. The decrease in the volume of imported refractory products in the Russian Federation will allow creating additional workplaces at enterprises of the country, and the production of domestic equipment will increase the level of no fired material output, i.e. heat-resistant concretes needed as a lining material for many industries. Manufacturing refractory products according to international requirements will increase the interest of foreign firms to Russian producers, which will facilitate the exchange of experience and technical information, strengthening of business ties and positive dynamics in the investment strategy.

Modern technologies for binders and materials on their basis are aimed at using both natural and man-made debris. This fact is due to the acute need to recycle the large-tonnage industrial and slurry- concrete waste that will significantly improve the environment within

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towns and cities. One of the progressive directions for special concretes is the development of nanotechnologies to apply nanotechnogenic raw materials in manufacturing heat-resistant composites: mortars, concretes, gunning bodies, coatings, impregnations, etc. Technical and technological interest for using nanotechnogenic waste in the production of special concretes is due to the high possibility for fundamental changes in properties with the aim of obtaining materials with desired physical and technical parameters.

2 Research

For over 50 years (since 1956) the department "Production of building materials, products and constructions" of Samara State Technical University and Institute of Architecture and Civil Engineering [1-11] has been actively carrying out research on rational application of multiple, large-tonnage and slurry nanotechnogenic wastes in the production of materials for general construction work and special purposes [6].

Slurry wastes are produced during the chemical interaction of metal products to be processed in alkaline environment or during formation of spent catalysts [11]. Depending on the business type where slurry wastes are formed, they are x-ray amorphous or crystalline. For example, the rapid oxidation of metal powders used as catalysts in the technology of the synthetic rubber production leads to the formation of fine Nano products. Nano disperse sediments resulting from complex chemical processes associated with the non-ferrous metal working (electroplating, machining of aluminum parts in alkaline solutions at metallurgical enterprises, etc.) are of significant interest

The major part of resulting calcium-aluminum and alkaline-aluminum sludge are the hydroxides of aluminum and other metals, as well as hydroxides of calcium and magnesium which are formed after the waste water neutralization with lime [4]. It is found that slurries have a high adhesive strength and in mixtures with different binders they are inorganic nano disperse additives that increase plasticity, the ability to actively interact with various acids, segregation resistance, etc. [11].

In various construction compositions of special purpose nanotechnogenic sludge perform the following functions [9]:

- The formation of a set-up mineralogical composition in composite binders not only for general construction work, but also for special purposes;
- The performing functions of the plasticizer in composites based on hydraulic cements (Portland and aluminous);
- The activation of the cement grain surface energy in compositions with binders that enhance their activity;
- The formation of mortars which are not subjected to sedimentation during their interaction with acids.

One of the most important results of sludge participation in the formation of structure, physic-chemical and mechanical properties of construction materials is a significant increase in durability [9].

High-alumina industrial wastes represent a great interest to be used in heat-resistant concretes instead of the expensive technical and refractory raw materials.

Heat-resistant concretes and mortars is a modern refractory lining material. Unlike a piece ceramic refractory heat-resistant concretes can be applied in construction technologies and repairing linings of industrial furnaces in monolithic and precast options in large volumes.

Various heating units or high-temperature furnaces operate in the variety of sectors of the national economy. Such industries as metallurgy, chemistry, power industry, petro chemistry, oil refining and others use in their technologies thousands of heating units and installations in which heat-resistant lining materials take up one-sided heating at temperature from 350°C to 1800°C. Chamotte, mullite, mullite silica and alumina refractors are known to be used among piece ceramic ones with the increase of their service life. Comparisons of the chemical composition of refractory ceramics' show that with the Al_2O_3 percentage increase their physical and mechanical properties improve.

It is known that the high-temperature stability of thermal unit linings manufactured with the use of refractory ceramics is very low [5]. Depending on the chemical composition of the refractory ceramics used and the type of the aggressive environment in the thermal unit, the lining original life ranges from several months to two years. The use of masonry mortars which differ in the chemical composition from the main lining material promotes the reduction of the brick lining durability. As a result, the mortar does not sinter during the first and subsequent heating of the thermal unit. This fact leads to the formation of thermal stresses due to the rapid temperature change and, consequently, the destruction of ceramic refractory materials in places of their contact with the mortar. Thus, the seams in the lining masonry are a "bottleneck" from which the corrosion process of refractory's starts.

Lining materials made of heat-resistant concretes are free from this effect. Heat-resistant concretes represent the composition of the binder with refractory aggregates. Nowadays, there is a great variety of heat-resistant concretes. Along with hydraulic binders (Portland, calcium aluminate and high alumina cements) chemicals are widely used, namely, alkali silicate and phosphate binders.

Among hydraulic binders only Portland cement in compositions of heat-resistant concretes requires the presence of the finely ground fire additive. It is connected with harmful effects of the hydroxide Ca $(OH)_2$. Many of finely ground refractory additives, such as SiO_2 and Al_2O bind a free CaO to be compounds which do not decompose at high temperatures by the following reactions:

$$nCaO + mSiO_2 \rightarrow nCaO \cdot mSiO_2 \quad (1)$$

$$nCaO + mAl_2O_3 \rightarrow nCaO \cdot mAl_2O_3 \quad (2)$$

Physical and mechanical parameters of heat-resistant cement bricks (fire resistance, strength after heating, temperature resistance, etc.) range widely depending on the use of refractory finely ground additives (chamotte, fireclay, chromites, etc.). Studies have shown that the growth of oxides Al_2O_3 and Cr_2O_3 in the additive contributes to the formation of heat-resistant binders based on Portland cement with high operational performance [12].

However, the use of aluminous and high-alumina cements as the refractory binder does not require the use of fine refractory additives. As a result of the aluminous and high-alumina cement mineral hydration highly stable hydro aluminates of $nCaO\ mAl_2O_3\ pH_2O$ type are formed and dehydrate after heating. It is reflected on the decrease in the heat-resistant composite strength after heating them at temperatures of 800 ÷ 1000°C. Therefore, heat-resistant compositions with aluminous and high-alumina cements need only to increase the initial strength by reducing the water-cement factor.

As studies have shown [13,14], hardened compositions based on alkali silicate and phosphate binders have very high physical and mechanical parameters of heat-resistant composites.

Alkali silicate heat-resistant composites are synthesized with soluble sodium silicate in the solid state entitled silicate-block, and the use of the syrupy alkali silicate. Application of sodium water glass in the composition of the heat resistant binder requires the introduction of the fine ground fireproof additive and chemical hardener, e.g. a traditional sodium flu silicate Na_2SiF_6 [13]. Further, sodium flu silicate as a water glass hardener has been replaced by such products with calcium silicates or aluminates as phosphate slag and aluminous cement. This fact has made it possible to considerably increase physical and mechanical parameters of heat-resistant alkali silicate composites [13].

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If a silicate block, i.e. a solid vitreous semi liquid glass is used in the synthetic process of heat-resistant binders, a very important technological conversion is needed, that is the mixed grinding of the silicate block with refractory ceramics in a predetermined ratio. To gain the strength of heat-resistant composites with hydrated binders, a dry heat treatment of products at temperatures from 160 to 180°C is required [15]. However, in our opinion, the best way to improve composites of alkali-silicate hardening is their modification by special high-alumina nano additives aimed at the reduction of liquid-solid and water-solid ratio.

Phosphate binders include both liquid water-soluble ones containing P_2O_5 bonds (e.g. alum chrome-phosphate and alumoboronphosphate bonds produced by the chemical industry) and phosphate cements formed by mixing fine ground super refractory oxides of metals or carbonatesc (Al_2O_3; Cr_2O_3; $CaCO_3$; $MgCO_3$) with a phosphoric acid H_3PO_4 of different concentrations [14; 16]. The hardening of heat-resistant composites with the use of phosphate binders is carried out by chemical reactions with the formation of refractory phosphate metals. Therefore, the resulting heat-resistant composites (concretes, mortars, coatings) have higher physical and mechanical parameters (heat stability, compressive strength, deformation of temperature under load, chemical resistance.)

The study of alum chrome-phosphate and alumoboronphosphate formation processes and phosphate cements with the use of H_3PO_4 makes it clear that most of the technical products can be replaced with the industrial waste of similar chemical, mineralogical and granulometric compositions. Such replacement allows not only to reduce the cost of compositions on the whole, but also to improve some technological processes in their production.

The most versatile nanotechnogenic component suitable to be used in the processes of perfection of heat-resistant composites on hydraulic cements and chemical binders is a nana disperse product, namely, a chrome-alumina petrochemical waste, i.e. a dead catalyst IM-2201. In the Samara region it is formed at the Novokyibyshevsk petrochemical plant and in Togliatti at the synthetic rubber plant.

Physical-chemical studies of the chrome-alumina waste showed that it is a nanodispersed powder with a specific surface area of more than 7800 cm^2/g and fire resistance of more than 2000 °C. High fire resistance of the chrome-alumina waste IM-2101 is due to its peculiar chemical composition (Al_2O_3 in the form of corundum is in the range of 72÷75%, and the content of the chromium oxide is 13÷15%).

Mixed high refractory binders containing nanotechnogenic waste, e.g. the alum-alkali sludge, have also been examined to increase the operational performance of many heat-resistant composites. Alum-alkali sludge or sludge of alkali etching of aluminum is a coproduct for manufacturing parts from aluminum-magnesium alloys produced at the Samara metallurgical plant. The as-wasted alum-alkali sludge is of the creamy consistency. Studies have shown that the particle size of the sludge consisting of hydrargillite ($Al(OH)_3$) is 20-80 nm [17].The presence of such nanoparticles in the sludge allows you to use it as a mineral plasticizer in heat-resistant composites based on Portland and alumina cements, water glass and silicate-sodium composite binders. The presence of the nano dispersed sludge in heat-resistant composites with binders mentioned above made it possible to considerably increase their physical and thermal parameters.

Chemical and mineralogical compositions of alum alkali sludge were taken into account in the design of aluminate cement raw mixes, for high-alumina cements in particular. Designing compositions of raw mixtures we were guided by recommendations given in the work [18]. The composition calculated according to the basicity factor representing the following mass relation $M_o = CaO / Al_2O_3$ was taken to be initial.

Chemical composition of the alum-alkali sludge is given in Table 1.

Table 1. Chemical composition of high-alumina alum-alkali sludge.

Content, mass %							
Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	R_2O	loss on ignition	∑
44.1	0.8	1.4	6.6	0.58	10.73	35.31	10.32

Under factory conditions the sludge of the aluminum alkali dip from the Samara metallurgical plant was used as an alumina-containing component and a lime-containing one was a slaked lime Ca $(OH)_2$ from the local enterprise.The basicity factor was variable from $M_o = 0.275 – 0.55$, because recommendations [18] state that if the value is $M_o = 0.55$, it is possible to obtain clinker of a monoaluminate composition, and when $M_o = 0.275$, the ceramic of a dealuminated composition is formed.

Production tests have resulted in a high alumina cement satisfying GOST 969-91 and having the following physical-mechanical parameters:

- specific surface area, cm^2/g - 3000;
- normal consistency, % - 27.7;
- setting time, hour-minutes
  - beginning - 1-00
  - end - 1-20;
- compression strength in 3 days, MPa - 45.0 – 55.0;
- fire-resistance, °C - 1750 – 1800.

The study of the chemical composition of the sludge of the aluminum alkali dip showed that it is possible to use it for the formation of phosphate binders, i.e. effective additives to heat-resistant composites. In our studies such technical products as $Al(OH)_3$ and Al_2O_3 have been replaced by the nanotechnogenic raw material, namely, the sludge of the aluminum alkali dip. The contact of the sludge with a phosphoric acid results in a chemical reaction with heat release between mineral fillers of nanotechnogenic raw materials containing H_3PO_4. The resulting liquid is an acidic alum phosphate binder consisting of acidic alum phosphates of Al $(H_2PO_4)_3$ and Al_2 $(HPO_4)_3$ type. It is possible to obtain an alum phosphate water-soluble binder of almost any density from 1.13 to 1.66 r/sm^3.

It is also possible to obtain aggregates for heat-resistant concretes from the refractory scrap resulting from the dismantling of old industrial furnace and other thermal units. After crushing the refractory spent lining in the form of bricks and its further classification, it is possible to obtain course and fine aggregates for heat-resistant concretes.

Compositions of heat-resistant binders and composites with high physical-mechanical parameters based on them have been developed on the basis of the synthesized alum phosphate binder, chrome-alumina waste hydraulic cements and alkali silicate binders with the use of refractory chamotte and mullite aggregates. Their compositions and properties are shown in Tables 2-4.

Table 2. Physical-thermal properties of binders with the use of industrial waste.

Binder mixture, %	**Compression strength, MPa after heating to temperature, °C**				**Heat-resistance, water-thermal cycling**
	400	**800**	**1200**	**1400**	
Chrome-alumina waste – 45 Portland-cement – 45 Sludge– 10 Water – 30 (above100%)	23.5	14.6	27.2	32.8 (1300°C)	22
Chrome-alumina waste – 45 Aluminate cement – 45 Sludge – 10 Water – 30 (above 100%)	29.6	23.9	33.3	37.1	26

These physical and mechanical parameters of heat-resistant binders will make it possible to obtain concretes with chamotte or mullite aggregates and working temperature respectively of 1300 ÷ 1500°C.

Table 3. Compositions and properties of heat-resistant alkali silicate binders modified by high-alumina sludge.

Binder mixture, kg/m^3	**Liquid-solid ratio, l/s**	**Compression strength, MPa after 3 days of air hardening**	**Fire-resistance of the modified binder,°C**
Chrome-alumina waste – 1350 Sodium flu silicate – 65 Alkali silicate – 650	0.46	28.8	1545
Chrome-alumina waste – 1215 Sludge – 135 Sodium flu silicate – 62 Alkali silicate – 606	0.43	32.9	1565
Chrome-alumina waste – 945 Aluminate cement – 315 Sludge – 140 Alkali silicate – 615	0.44	39.8	1620

Test results of samples of modified binders (Table 3) have shown, that the replacement of the sodium flu silicate on the alumina cement has considerably increased not only the initial mechanical performance, but also operational, i/e/ in the working process. Refractory properties of modified heat-resistant alkali silicate binders have exceeded 1600°C and it allows obtaining composites with the working temperature of 1400 - 1550°C.

Table 4. Physical – thermal properties of heat-resistant concretes on chemical binders.

Concrete mixture, kg/ m^3	**Dry specific gravity, kg/m^3**	**Compression strength, MPa after hardening and heating to temperature, °C**			
		20 (7 days)	**800**	**1200**	**1400**
Waste IM-2201 – 440 Crushed stone SHA – 750	2010	6.6	44.2	46.0	45.4

SandSHA – 650 APHC – 260					
Waste IM-2201 – 440 Crushed stone MLS 62-780 Sand MLS – 62-680 APHC – 2600	2100	7.9	47.6	50.4	50.7

3 Conclusion

The use of the synthesized alum phosphate binder to bound carbonate-containing wastes (dolomite screenings from crushing) in compositions with the chrome-alumina waste gave the possibility to obtain phosphate aerated concretes with an average density from 400 to 800 kg/m^3 and a working temperature up to 1500°C. These physical and thermal parameters of heat-resistant aerated concretes may be used as a high-performance monolithic heat insulation of lining in industrial furnaces and other thermal units. Synthesized on high-alumina slurry-like wastes an alum phosphate binder proved to be quite suitable in the compositions of phosphate aerated concretes on the basis of carbonate raw materials instead of expensive chrome-alumina and alumoboronphosphate binders.

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