Heat-resistant Binders Synthesis with Application of Alumina-containing and High-alumina Waste

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Abstract. The article presents various methods for producing mixed heat-resistant binders able to harden in air at normal temperature. The processes of binders synthesis based on hydraulic cements and inorganic refractory industrial waste: aluminium-chromium petrochemical waste and expanded clay dust are considered to create high-temperature heat-resistant binders and concretes based on them. Light concretes with porous aggregates are offered to obtain a highly porous refractory material of air hardening.

1. Introduction

Technical progress in construction involves the widespread use of new type materials reducing material consumption, the introduction of industrialization and construction mechanization, products and structures performance improving, by-products – industrial waste using for building materials manufacture which save the environment from pollution.

Such a problem as materials manufacture with specified physical and mechanical properties is also of great importance for lining products of thermal units operating in difficult operating conditions (high temperature, aggressive gas or liquid medium, contact of refractory lining with molten metals and alloys). Nowadays just like a century ago lining of thermal units in most cases is carried out from various piece refractory bricks and products. This option requires a lot of manual labour which does not provide the necessary quality. Weak or narrow areas of any construction are the lining seams, formed at the masonry between single-piece ceramic refractories. The initial destruction of the lining begins with the seams. Especially clearly this phenomenon is observed in the metallurgy furnaces, the ovens of the building, i.e. heating and thermal installations where the formation of a melt of metals, fluxes and other corrosive environment, penetrating the joints and refractory pores, very soon deduce the structure of the lining failure.

Recently in this regard, large-format elements of heat-resistant concrete are used for lining structures of various thermal units and industrial furnaces, the use of which in the installation process allows minimizing the presence of seams, increase durability and increase the lining durability.

Heat-resistant concrete is a special type of concrete that has the ability not to reduce the strength performance at high temperatures for a long time. Heat-resistant composites are a non-burning artificial stone building material. They are increasingly used in the lining of thermal units of many industries. The advantages of heat-resistant concrete in comparison with firing refractories are that there is no need for such an expensive, energy-intensive and time-consuming process as high-temperature firing of ceramics. From heat-resistant composites can be made monolithic, very solid construction of the lining...
of complex configuration and large dimensions, which is almost impossible to implement when using piece refractory ceramic products. The use of heat-resistant composites allows very complex design solutions of individual elements of industrial furnaces and other thermal units, which cannot be carried out using piece ceramic refractories [1]. Heat-resistant concretes are composites that consist of a bundle and a filler. A bundle is a mixture of a binder with a mineral refractory fine-milled additive, or less often – without it. Small and large aggregates are prepared mainly by crushing refractory and refractory rocks, firing ceramic products and some other man-made products, in particular, industrial wastes with high melting temperatures.

Binders suitable for the preparation of heat-resistant concrete are classified into four categories: hydraulic, air (silicate) and sulfate-chloride (periclase cement), chemical (silicate-block, phosphate and similar compounds), and organic.

Hydraulic or hydration binders are represented by disperse systems, in which the function of the dispersed phase is performed by Portland cement and its varieties: alumina, high-alumina, barium-containing, periclase aluminate, slag-alkaline cements, and the dispersed medium – water or alkaline solutions [1]. These binders include new high-refractory cements, such as aluminum zirconium, calcium and aluminum zirconium strontium [2]. Different fine ground slags from industry wastes can be binders [3].

During the hydraulic hardening of Portland cement in the form of a crystal frame of cement stone, calcium hydroxide Ca(OH)\(_2\) is formed. While cement stone heating there is dehydration of the hydrosilicates and calcium aluminate hydrates, as well as dehydration of the hydroxide Ca(OH)\(_2\), leading to free calcium oxide formation.

Free CaO in contact with water or water vapor is hydrated with a significant volume increase leading to concrete cracking. Therefore, Portland cement in the compositions of heat-resistant composites is used, as a rule, in a mixture with finely ground refractory additives of high-alumina or aluminosilicate species. While burning free oxide CaO reacts with the alumina Al\(_2\)O\(_3\) and silica SiO\(_2\) that are present in the refractory fine supplements. In this case, stable and resistant to hydration and heating compounds are formed in the form of aluminates and calcium silicates in the following reactions:

\[
\begin{align*}
\text{nCaO + mAl}_2\text{O}_3 & \rightarrow \text{nCaO} \cdot \text{mAl}_2\text{O}_3 \\
\text{nCaO + mSiO}_2 & \rightarrow \text{nCaO} \cdot \text{mSiO}_2
\end{align*}
\]

When hardening alumina and high-alumina cements free hydroxide Ca(OH)\(_2\) is not formed. In this regard, there is no need to use fine-milled refractory additives in the composition of heat-resistant concrete.

Air heat-resistant binders include the so called silicate compositions in which the dispersed phase are various fine-milled refractory powders – cements and the dispersed medium – soluble alkaline silicates (sodium liquid glass), ethyl silicates, and other solutions containing silicic acid sols. Silicate binders based on sodium liquid glass are used in a composition with chemical hardeners, sodium silicate Na\(_2\)SiF\(_6\), silicates and calcium aluminates (Portland cement, alumina cement, ferrochrome slag, electrothermophosphoric slags, nepheline sludge), and other industrial wastes.

Chemical heat-resistant binders include silicate-block which is a vitreous alloy of alkaline silicates, most often sodium silicate with modulus \(m = 2.8 – 3.3\). Therefore, in its composition silicate-block contains at least 22-28 % of Na\(_2\)O and 70-76 % of SiO\(_2\). For the use in the composition of heat-resistant binder silicate lump is ground in a composition with refractory ceramic fillers to the fineness of the grinding in terms of the specific surface area of 2500-3000 cm\(^2\)/g. Then the resulting fine-milled silicate-sodium heat-resistant binders are mixed with water. While further drying of concrete products, which is carried out at temperatures of 150-200 °C, the structure of the material forms a fluid glass, which hardens all particles in a single conglomerate.

Phosphate cements and binders are also widespread as chemical binders in heat-resistant composites. This is a disperse system in which the disperse phase are various refractory fine powders and the dispersion medium is H\(_3\)PO\(_4\) phosphoric acid or aqueous solutions of phosphates of metals. Usually, as
phosphate binders, liquid compounds are used in the form of aluminium phosphate, magnesium phosphate, calcium phosphate ligaments, and similar compounds, as well as compositions in the form of high-temperature finely dispersed metal oxides with \( \text{H}_3\text{PO}_4 \).

Aggregates of heat-resistant concrete are natural, artificial, and inorganic materials of a certain grain composition, non-destructive when heated to the maximum permissible temperature of heat-resistant concrete. Fillers for heat-resistant composites should not only be stable at high temperatures, but also have a uniform temperature expansion. For this reason, rocks containing free quartz (quartz sands, crushed granite or sandstone) are not suitable for heat-resistant composites, although the mineral quartz melts at a very high temperature (1713 °C). The reason is the fact that when heated, the phenomenon of polymorphism occurs, i.e. the transformation of quartz, accompanied by its volume increase.

Fireclay refractory was widely used as a filler for heat-resistant concrete. Lump fireclay obtained by refractory clay roasting, fights and scrap refractory products are usually used. They are not contaminated with impurities. On the basis of fireclay filler it is possible to obtain heat-resistant composites with an operating temperature of 900-1300 °C.

Aggregates from natural chromite ore, the periclase refractory prices, as well as high-alumina (nullite, mullerovter, corundum and nullite-alumina bricks and products) are used for heat-resistant composites operating at higher application temperature (1400-1700 °C). Fillers can also be prepared from of carbon ferrochrome production slag, chrome alumina and titanium alumina slag, as well as the slag of aluminothermic production. For the thermal insulation of thermal units space lightweight heat-resistant concrete with an average density of 500-700 kg/m³ operating temperature up to 1200 °C and above is used. For the preparation of light heat-resistant composites, porous fillers that resist the action of high temperatures (from 700 to 1000 °C) it is recommended to use expanded clay gravel and agloporite, perlite obtained by volcanic glasses, obsidians, and vermiculite firing obtained by water-containing, micas firing with a low content of alkalis, which reduce fire resistance. Volcanic tuff, slag, ash, porous igneous rocks are also suitable for light heat-resistant composites.

For light heat-resistant composites with an operating temperature of 1500 - 1700 °C, porous corundum granules and phosphosite-phosphate refractory filler are used as a filler. Phosphosit is formed from mixtures aluminium chromium phosphate binder and fine refractory fillers, for example, alumina or alumino-silicate. The masses consisting of a mixture of a finely ground refractory filler and a phosphate solvent are granulated in any of the known methods, the obtained granules are quickly heated to 300 °C. At the same time, due to the release of water vapor, a porous structure similar to the structure of expanded clay gravel is formed [3-4].

Aggregates are classified into small and large ones. Fine aggregate consists of grains the size of which is from 0.14 to 5 mm, but the content of dust particles (fraction smaller than 0.14 mm) should not exceed 20 % (by weight). Granulometric composition of aggregates, as it is known, has a great influence not only on the properties of conventional concrete, but also on the properties of heat-resistant concrete (heat resistance, application temperature, fire shrinkage, etc.). Therefore, it is necessary to use fractionated aggregates, which provide the possibility of selecting the optimal composition of a mixture of small and large aggregates with the densest packaging.

2. Results and discussions

Natural mineral and artificial glazed ceramic materials as well as associated products industry (chromite ore, pieces of fireclay, magnesite or ordinary bricks, andesite, pumice, granulated blast furnace slag, fuel and slag, fly ash, aluminium chromium dead catalyst from the petrochemical industry IM-2201, etc.) can be applied as a finely ground refractory additives [5]. The following requirement is made to thin-ground additives relating the grain structure: pass through a sieve No. 008 should be no less than 70-80 %.

To improve physical and thermal performance of heat-resistant composites of hydraulic hardening, to increase their effectiveness mixed high-refractory binders with the use of fine aluminium chromium
waste IM-2201 and aluminosilicate clay dust were studied. The chemical composition of fine fillers and some of their physical and mechanical properties are given in tables 1 and 2.

Table 1. Chemical composition of fine-milled additives for heat-resistant concrete.

| Sample                | Al₂O₃ | TiO₂ | Fe₂O₃ | SiO₂ | Cr₂O₃ | CaO | MgO | SO₃ | R₂O | Loss on ignition |
|-----------------------|-------|------|-------|------|-------|-----|-----|-----|-----|-----------------|
| Dead catalyst IM-2201 | 73.4  | 0.1  | 0.86  | 6.0  | 13.2  | 1.86| 0.8 | 0.9 | 0.84 | 0.66            |
| Expanded clay dust    | 14.31 | 0.68 | 6.21  | 64.56| -     | 2.81| 2.19| 0.22| 3.01 | 6.01            |

Table 2. Physical and mechanical properties of fine-milled additives.

| Indicators            | Measure unit | Aluminium chromium waste IM-2201 | Expanded clay dust |
|-----------------------|--------------|----------------------------------|--------------------|
| Bulk density          | kg/m³        | 1190                             | 765                |
| True density          | g/cm³        | 4.3                              | 2.65               |
| Specific surface      | cm²/g        | 5500                             | 2910               |
| Refractoriness        | ºC           | 2050                             | 1250               |

To obtain a mixed high-refractory binder dead catalyst IM-2201 was used as alumina-containing component and expanded clay dust was used as the aluminosilicate component. Portland CEM I 32.5 and high alumina cement GC-40 are hydraulic cements. When introducing the binders into the composition with dead IM-2201 catalyst or expanded clay dust, mixed binders are formed having different properties in comparison with pure hydraulic cement. The refractoriness of mixed binders increases almost directly in proportion to the amount of alumina-containing waste introduced into the composition. The setting time of mixed binders is extended though even with the introduction of 60-80% alumina-containing or aluminosilicate dust from IM-2201 waste, the ability of the heat-resistant binder to set in air conditions and gain strength is retained.

As for the use of expanded clay dust in the composition with Portland cement, the milled aluminosilicate additive practically does not increase the refractoriness. However, the increased hydraulic activity of this additive (115 mg of CaO per 1g of clay dust) contributes to the increase in the strength characteristics of the mixed heat-resistant binder with the refractoriness of 1250-1280ºC. As it should to be expected, the daily mixed binder gains the strength sufficient to dismantle concrete products made on their basis. The results of the binder testing after heat treatment and heating are shown in tables 3 and 4.

Table 3. Compositions and properties of heat-resistant concrete on Portland cement with fine-milled high-alumina additive IM-2201 and with aluminium chromium expended clay dust

| Binder consumption, kg/m³ | Fine coarse aggregate, kg/m³ | Concrete type / average density when dry | Residual strength of concrete, % after firing at 800°C | Concrete application temperature, ºC |
|---------------------------|-------------------------------|-----------------------------------------|--------------------------------------------------------|--------------------------------------|
| Portland cement + IM-2201 |                               |                                         |                                                        |                                      |
| 200+200                   | Fireclay 1400                | 250/2200                                | 30                                                     | 1300                                 |
| 200+200                   | Chromomagnesite 1800         | 300/2400                                | 30                                                     | 1500                                 |
| 150+250                   | (Portland cement + expended clay dust) | Fireclay 1300 | 200/2100                               | 38                                                     | 1200                                 |
As can be seen from tables 3 and 4, the compressive strength of mixed binders decreases first and then increases sharply. This is due to the refractory aluminosilicates and aluminates formation, which are able to maintain their strength at high temperatures.

Analysis of the results of determining the deformation temperature under load shows that with the content increase of the high-alumina component IM-2201 in the compositions of mixed binders and their application temperature increases. In this way, it was possible to create air-hardening binders with an application temperature of 1200 and 1450°C on Portland cement and binders with an application temperature of 1600°C on alumina cement. The temperature resistance of the binder exceeds 20 thermal cycles, i.e., close to the thermal stability of the conventional phosphate binders. Of aluminium chromium waste introduction into the composition of the mixed binder as Portland cement and alumina cement allowed to increase the initial strength characteristics that had a positive impact on the parameters determining heat-resistant composites lifetime.

**Table 4. Thermo-mechanical properties of mixed refractory binders with the use of supplements of aluminium chromium IM-2201 and aluminosilicate expanded clay dust.**

| Binder composition, % | Compressive strength, MPa after heating to temperature, °C | Deformation temperature under load, HP | Temperature resistance, water thermal cyclings, 40% |
|-----------------------|-----------------------------------------------------------|--------------------------------------|-----------------------------------------------|
|                       | 500 800 1000 1200 1400                                   | 40%                                  | 40%                                           |
| IM waste-2201-50       |                                                           |                                      |                                               |
| aluminium chromium -50 |                                                           |                                      |                                               |
| Water-30 (over 100%)   | 29 23 27.5 33 37                                         | 1460 1550 1610                        | 28                                            |
| IM waste -2201-50      |                                                           |                                      |                                               |
| Portland cement -50    |                                                           |                                      |                                               |
| Water-30 (over 100%)   | 23.4 12.4 14.6 27                                         | 1170 1290 1340                       | 20                                            |
| Expanded clay dust – 40|                                                           |                                      |                                               |
| Portland cement 60     |                                                           |                                      |                                               |
| Water-36 (over 100%)   | 20.1 10.2 10.0 14.7                                       | 1150 1210 1250                       | 18                                            |

Thermal properties of heat-resistant concrete of synthesized binders are shown in table 5.

**Table 5. Thermal properties of concrete.**

| №  | Concrete type                                 | Coefficient of thermal conductivity, W/m·K | The coefficient of thermal expansion 10⁻⁶/°C |
|----|----------------------------------------------|---------------------------------------------|---------------------------------------------|
|    |                                             | After drying at 100°C | After heating at 1000°C | Within (20-800°C) | After re-heating |
| 1  | Heavy refractory concrete on alumina cement | 2.63                          | 2.45                          | 6.8              | 5.7             |
| 2  | Expanded clay with Portland cement binder +  | 0.245                         | 0.235                         | 6.8              | 5.8             |
|    | expanded clay dust                          |                                             |                                             |                  |                |

As it can be seen from table 5, the thermal conductivity of lightweight concrete has low values, which makes it possible to apply them as highly effective thermal insulation linings of thermal units instead of piece lightweight refractories. After heating up to 1000°C, their thermal conductivity decreases slightly, this is associated with an increase in the samples porosity.
The coefficients of thermal expansion (CTE) of the studied compounds after re-heating are reduced (table 3). This is due to the fact that at the first heating in the concrete, in particular in the binder, the physico-chemical processes caused by the loss of physically bound water by crystallization of amorphous new formation, polymorphic transformations have already taken place. In General, the CTE of heat-resistant concrete has a significant effect on the thermal stability of the developed concrete compositions and their service in the linings.

The heat-resistant concretes properties on mixed highly refractory binders involving Portland cement, alumina cement, and alumina-containing and aluminosilicate waste are presented in table 6. Thus, the obtained data indicate high physical, mechanical, and thermal properties of the developed concretes. There is no need in heat treatment, which allows to produce large-sized products and parts, as well as to use concrete in monolithic structures of various configurations.

| №  | Concrete composition, kg/m³ | Average dry density kg/m³ | The limit of compressive strength after curing and heating, MPa | Deformation temperature under load °C | Apparent porosity % | Temperature resistance water thermal cycling |
|----|----------------------------|--------------------------|---------------------------------------------------------------|---------------------------------------|---------------------|---------------------------------------------|
| 1. | Portland cement -200 aluminium chromium waste-200 Fireclay rubble -650 Fireclay sand -700 Water - 180 | 2000 | 18.4 | 27.5 | 32 | 1280 | 1370 | 1410 | 22 | 35 |
| 2. | Alumina cement-220 aluminium chromium waste -220 Fireclay rubble -650 Fireclay sand-700 Water 200 | 2200 | 26.2 (3 days) | 32.4 | 45.2 | 1390 | 1480 | 1530 | 12.5 | 37 |
| 3. | Expanded clay aggregate (200) -200 Vermiculite (M150) -90 Portland cement -80 Water -80 | 450 | 2.1 (1000°C) | 4.8 | 4.5 | 910 | 950 | 1050 | 75 | 18 (air) |

3. Conclusions
The properties of light and heavy heat-resistant concrete show significant superiority over piece fireclay refractories. Heat-resistant binders synthesized on the basis of hydraulic cements turned out to be
reactive components, which positively affected the physical and thermal properties of high-temperature materials.

Such man-made materials like aluminium chromium petrochemical waste – dead catalyst IM-2201 expanded clay dust from the cyclones, the waste from industrial enterprises of building materials were also used as the fine components of heat-resistant binders.

Studies have found that the formation of the structure of high-temperature materials – heat-resistant concrete begins with the synthesis of special binders. It was found that the introduction of a high-temperature fine-milled component – dead catalyst IM-2201 in a composition with hydraulic binders increases the physical and thermal parameters of mixed heat-resistant binders. It is revealed that the properties of heat-resistant binders are fully regulated by such parameters of refractory fine-milled additives as the chemical composition and grinding fineness.

References
[1] A. I. Khlystov, Heat-resistant concretes based on industrial waste in the Samara region, Samara State Technical University, 2016.
[2] V. V. Babkov, Yu. M. Bazhenov, and A. A. Bykov Cements, Concretes, mortars and dry mixes, Part I: Reference, Edited by P. G. Komokhov St Petersburg ed: Professional, 2007.
[3] A. I. Khlystov, Improving the efficiency and quality of refractory lining materials, SGASU, Samara, 2004.
[4] B. L. Krasnyy, Refractory building materials based on phosphate binders, Dissertation of doctor of technical sciences, 2003
[5] A. I. Khlystov, V. A. Shirokov, and E. A. Chernova, Problems of air setting phosphatic binding and heat-resistant materials, based on them. XXV Polish – Russian – Slovak Seminar “Theoretical Foundation of Civil Engineering” Procedia Engineering 153, pp. 271 – 276, 2016