Claydite dust - a unique technogenic raw material for heat-resistant concretes production

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Abstract. The article presents various methods of heat-resistant materials synthesis on the basis of aluminosilicate wastes of expanded clay production. Researches have shown that the application of physical and chemical methods in the course of studying of expanded claydite dust composition, structure and properties makes it possible to define the reason of physical and thermal parameters increase of the heat-resistant binders prepared in its composition. The article investigates the influence of refractory mineral waste of petrochemistry - aluminochromium spent catalyst IM-2201 on the processes of increasing the strength and performance indicators of binders based on expanded clay dust. The possibility of the fire resistance increase of mixed binders synthesized on the basis of expanded claydite dust and aluminochromium waste has been established. Application of phosphate and liquid glass binders in the processes of heat-resistant binders synthesis on the basis of expanded claydite dust allowed to increase their performance.

1. Introduction

Industrial furnaces and other thermal units are used in many sectors of the national economy. These are metallurgical, chemical, oil refining, machine-building industries, enterprises producing firing building materials, as well as the heat and power complex. In most cases, the lining of these units uses piece ceramic refractories: fireclay, high-alumina, magnesite and chromomagnesite, corundum and zirconium. In the process of lining manufacture in the form of brickwork, the used refractory mortars do not correspond to the chemical composition of the basic lining material. Due to this reason the mortar is not sufficiently sintered. Therefore, as a result of thermal stresses due to sharp temperature changes, the destruction of refractories occurs at the point of contact. That is, the seams in brickwork are “narrow” place in any lining. The process of destruction starts here. That's why the recent use of heat-resistant concrete (in the form of large-format elements or blocks) in industrial furnaces has made it possible to minimize the seams and increase the lining resistance and durability.

The NIIZhBa (the head institute on concrete and reinforced concrete in Moscow) researches established the fact that for heat-resistant composites manufacturing portland cement, sodium liquid glass, silicate lump, alumina and high-alumina cements, periclase cement, phosphate cements, etc. can be used as binders. [1]

Previous studies at Samara State Technical University [2] have shown that industrial waste in the form of technogenic and nanotechnogenic raw materials is, for the most part, a valuable raw material that can be used to produce various materials useful for the economy, including heat-resistant concrete, mortars, torcret and refractory packaged masses.
2. Methods and materials

Mineral natural and artificial fired ceramic materials and industrial by-products can be used as fine refractory additives (chromite ore, broken fireclay, magnesite or ordinary bricks, andesite, pumice, granulated blast furnace slag, fuel slag, fly ash, spent chromium-alumina catalyst in the petrochemical industry IM-2201, etc.) According to the grain size composition, a requirement is imposed on fine-ground additives: the passage through sieve No. 008 should be at least 70-80%. [3-4]

At the expanded clay factories, a large amount of dusty wastes are formed with various dispersion, the chemical composition of which is close to the composition of either clay raw materials or burnt gravel of a similar product. But the efficiency of dust collecting devices operating at expanded clay plants is not perfect. Expanded clay wastes penetrate into all cracks of unsealed equipment and pollute the environment. So, when examining a number of expanded clay plants in Samara, operating on clay raw materials from the Smyshlyaevskoye deposit, the formation of four types of dusty waste was revealed. When using four furnaces, the total output of dusty waste exceeds more than one hundred cubic meters per day.

The harmful effect of aluminosilicate waste, which includes expanded clay dust, on the environment is associated with the content of aluminum, silicon, iron and their compounds, sulfates. This impact is very often beyond control and numerous factors indicate that it is increasing. This situation is associated with the development of old industries, the emergence of new ones, often without a reliable environmental forecast. [5]

Varieties of expanded clay wastes and their chemical compositions are shown in table 1. The table also shows data on the hydraulic activity of various varieties of expanded clay dust in relation to CaO. The rest of the physicochemical indicators are presented in table 2.

The high hydraulic activity of expanded clay dust taken under the junction of a two-drum furnace (115 mg CaO per 1 g of expanded clay dust) suggests its use in heat-resistant compositions using Portland cement. Figure 1 shows an X-ray diffraction pattern of a sample of expanded clay dust formed at the joint in a double-drum furnace, which has a high hydraulic activity in relation to CaO. X-ray studies were carried out using a modern diffractometer "ARLXTRA".

The main crystalline phases in this sample of expanded clay dust are: quartz, aluminum oxide, hematite, cristobalite.

| Table 1. Chemical compositions of clay production waste (Samara). |
|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| №  | SiO₂ | Al₂O₃ | Fe₂O₃ | FeO | CaO | MgO | R₂O | TiO₂ | SO₃ | Loss on ignition | Activity in mg relative to CaO |
|----|------|------|------|-----|-----|-----|-----|------|-----|-----------------|-----------------------------|
| 1  | 60.96 | 17.54 | 4.10  | 0.64 | 2.38 | 2.2  | 2.98 | 0.66  | 0.07 | 10.16           | 75                           |
| 2  | 64.56 | 14.31 | 5.49  | 0.72 | 2.81 | 2.19 | 3.01 | 0.68  | 0.22 | 6.01            | 115                          |
| 3  | 53.94 | 14.96 | 7.44  | 1.34 | 2.96 | 3.70 | 4.32 | 0.40  | 0.37 | 10.56           | 88                           |
| 4  | 64.72 | 13.81 | 5.05  | 1.11 | 2.66 | 2.27 | 4.11 | 0.63  | 0.43 | 5.16            | 84.5                         |

Note: No. 1-dust from cyclones of a two-drum furnace;
No. 2-dust formed at the joint in a two-drum furnace;
No. 3-dust from the dust-collecting chamber of a two-drum furnace;
No. 4-dust from the single-drum furnace's dust-collecting chamber;

| Table 2. Physical and mechanical properties of expanded clay dust (1-4). |
|-------------------------|-------------------------|-------------------------|
| Indicator                              | Value                 |
| Bulk density, (kg / m³)                | 750÷770               |
| Fineness of grinding (pass h / c 0.14 %) | 65÷70                |
| Fire resistance, (°C)                  | 1230÷1250             |

The nature of the x-ray shows the predominance of the amorphous component before the crystal phase. This circumstance explains the high hydraulic activity of expanded clay dust. One of the rational
applications of expanded clay dust is its participation in the processes of synthesizing a heat-resistant binder based on Portland cement.

During the research, the following materials were used to obtain binders: alumochromic waste -spent catalyst IM-2201 of the NovoKuibyshev petrochemical plant (Samara region), expanded clay dust - spillage from the two-drum furnace of the Samara expanded clay plant. The fillers of these concretes were class a firecracker bricks: firecracker crushed stone and firecracker sand obtained by crushing refractory scrap from a clay plant. The selection of concrete compositions was carried out experimentally, based on the conditions for obtaining mixtures with the maximum density.

3. Results and discussion

The analysis of physical and mechanical parameters of heat-resistant binders and concretes shows that it is possible to synthesize refractory composites with application temperatures up to 1100-1200 °C on the basis of clay production waste. Such heat-resistant binders can be obtained not only by using hydraulic cements, but also by using sodium liquid glass, silicate blocks and phosphate binders.

However, the use of phosphate binders for the synthesis of the binder allowed increasing the fire resistance of the heat-resistant composition based on expanded clay dust to 1300-1350 °C.

Orthophosphoric acid and alumochromophosphate binder were taken as phosphate binders. Metal phosphates are known to have high melting points [6]. Therefore, the course of reactions of the "oxide-phosphate binder" type allowed a number of low-melting substances in clay dust to be converted into refractory ones.

It is also possible to increase physical and thermal characteristics of heat-resistant composites (binders and concretes) based on expanded clay dust by synthesizing fine-ground refractory components of binders with the addition of alumochromium waste (spent petrochemicals catalyst IM-2201) and using liquid-glass or phosphate binders. Figure 2 shows graphical curves of changes in the fire resistance of mixed binders based on clay dust and alumina waste using sodium liquid glass.

Analysis of curves shows that such an important technological parameter of heat-resistant binders as refractoriness can be easily regulated using high-temperature fine-ground additive in the form of alumochromium waste. The setting time of binders remains normal and, depending on the applied hardeners of liquid glass (sodium silicofluoride, alumina cement, the following values: the beginning - 45 minutes, the end of setting - 1 hour - 25 minutes). These parameters are provided by hardeners of liquid glass binders: sodium silicofluoride, introduced in an amount of 10% of the mass of liquid glass and alumina cement the content of which is one third of the mass of the fine-ground component.
The tests results of mixed heat-resistant binders with the use of expanded clay dust and liquid glass (figure 2; table 3) showed that the replacement of sodium silicofluoride as a fusible substance with such a high-temperature compound as alumina cement significantly increased the initial strength indicators and performance. The fire resistance of the mixed heat-resistant binders exceeded 1450 °C, which makes it possible to obtain concretes based on them with an application temperature of 1300-1350 °C.

![Figure 2](image-url)  
*Figure 2. Fire resistance changes of mixed liquid-glass binders based on expanded clay dust:  
1 – hardener - sodium silicofluoride,  
2 – hardener - alumina cement*
Figure 3 shows the curves of changes in the fire resistance of mixed binders based on expanded clay dust and alumochromium waste with the use of phosphate binders.

Analysis of curves shows that the use of phosphate binders (H₃PO₄; alumochromophosphate binder) as a mixer of binders based on expanded clay dust allows to increase their fire resistance in a wide range, which is an important factor in the operation of these compositions. The setting time of phosphate-cured binders is slightly longer in comparison with liquid-glass binders, but still remains acceptable for the lining technology.

The heat-resistant concrete on phosphate composite binder with the use of claydite dust is presented in table 4. As shown by the test results of blended binders with the use of claydite dust replacement of liquid glass on phosphate mixers (H₃PO₄; alumochromophosphate binder) has improved performance of heat-resistant concrete and increased the operating temperature to 1400 ºC.

Due to the fact that concrete mixtures based on orthophosphoric acid (H₃PO₄) slowly hardened in air and required heat treatment for acceleration, we developed a composition of a refractory filling mass. Expanded clay dust, as shown by experiments in its composition, contains a clay component, which ensures the plasticity of the filling mass. The samples of a given mass on orthophosphoric acid, which can be immediately removed from the mold, were made by filling.

The composition of the filling mass was as follows:
- expanded clay dust from the cyclone - 453 kg/m³;
- fireclay sand - 1301 kg/m³;
- orthophosphoric acid ρ = 1.52 g/ m³ - 190 kg/m³.

The strength indicators of this refractory filling mass, which were determined after high-temperature firing (1300 ºC), fluctuated within 37 ÷ 40 MPa.
The heat-resistant binder obtained in this way based on expanded clay dust and phosphate mixer was the basis for obtaining repair filling masses used directly to extend the service life of the lining of thermal units at factories where these wastes are generated. [7]

Table 4. Physical and thermal properties of heat-resistant concrete on phosphate binders with the use of claydite dust.

| №  | Concrete composition, kg/m³ | Average density in dry state, kg/ m³ | The limit of compressive strength MPa after heating, (°С) | Thermal resistance, water heat changes |
|----|-----------------------------|-------------------------------------|-------------------------------------------------|--------------------------------------|
| 1  | Expanded clay dust - 180    |                                     | 2100 5,5 28,6 33,2 30,5 25                     |
|    | Alumochromium waste - 260   |                                     |                                                 |
|    | Fireclay crushed stone - 650|                                     |                                                 |
|    | Fireclay sand - 750         |                                     |                                                 |
|    | Phosphoric acid (70% concentration) - 360 | |                                                 |
| 2  | Expanded clay dust - 160    |                                     | 2120 7,5 31,7 35,4 34,2 (1400) 28              |
|    | Alumochromium waste - 280   |                                     |                                                 |
|    | Fireclay crushed stone - 650|                                     |                                                 |
|    | Fireclay sand - 750         |                                     |                                                 |
|    | AChFS (ρ = 1.52 g/cm³) - 380|                                     |                                                 |

4. Conclusions
Thus, the use of such chemical binders as liquid glass and phosphate binders allowed to create a wide range of heat-resistant concretes with relatively high physical and thermal characteristics on the basis of clay production waste. The resulting increased performance characteristics of heat-resistant concretes allow to be used for refractory lining works in many thermal units, including in contact with aggressive media, as well as in enterprises with refractory inorganic waste.

References
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