Ways to improve physical and thermal performance of refractory lining materials

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Abstract. Refractory lining materials, which include ceramic refractories and nonfired heat-resistant concretes, have a very short lifespan during the turnaround time measured in years and sometimes months. Therefore, increasing the service life of thermal generating units by 1.5-2 times will bring significant economic benefits. The main factor that determines the durability of refractory lining materials is the thermal resistance. It is possible to increase the thermal resistance by improving such physical and mechanical properties as strength and density. As for the ceramic refractory performance improvement, such technological methods as their structural and chemical modification by phosphate binder impregnation, as well as introduction of phosphate components into the ceramic batches during the molding process increase, in particular, their thermal stability. The use of aluminous and high-alumina cements contributes to a significant increase of not only strength, but also physical and thermal performance of heat-resistant concretes with different fillers. Switching to the use of chemical binders in the compositions of heat-resistant concretes (liquid glass with effective hardeners; silicate-block and phosphate binders) enables to develop high-heat resistant materials which do not soften in a wide range of heating temperatures from 400 °C to 1600 °C. The positive results on increasing the thermal resistance of heat-resistant composites can be obtained by reinforcing them with high temperature fibers.

1 Introduction

Traditional ceramic refractories including fired ceramic concretes, as well as nonfired heat-resistant concretes with different binders belong to refractory lining materials. Piece ceramic refractories made by the traditional ceramic technology (molding → drying → firing) have various chemical and mineralogical compositions affecting ultimately their physical and thermal operation factors (strength properties, deformation temperature under the load, heat and chemical resistance, etc. For example, the thermal resistance of piece refractories, i.e. the main property that determines their durability, varies from 10 water thermal cycles for fireclay refractories to 100 for corundum ceramics. And the limit of the compressive strength ranges from 15 to 100 MPa, respectively.

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However, lining constructions made of piece ceramic refractories have a large number of joints which are the “neck stage” between piece refractories in the brick masonry, where the entire lining failure begins.

Since the amount of refractory lining works increases annually, heat-resistant concretes have been used recently to reduce the number of these joints.

Heat-resistant concretes are modern refractory lining materials made with the use of the known hydraulic binders (Portland cement, alumina cements) and special chemical binders (liquid glass, silicate – block, phosphates). Crushed heavy and light piece refractories, as well as artificial fired porous aggregates (expanded clay gravel, haydite, perlite, vermiculite, etc.) serve as aggregates for heat-resistant concretes. On the basis of binders listed above it is also possible to produce heat-resistant cellular concretes.

Heat – resistant concretes, as well as conventional ones can be used in the manufacture of thermal unit linings in precast and monolithic variants. These variants of heat-resistant concrete use during refractory lining works enable to obtain thermal unit linings with minimum joints. Reducing the number of joints in lining constructions leads not only to the improvement of their properties and durability, but also to the saving of material resources, because it reduces the number of routine, average and general repairs required in practice of works with refractories. According to the information provided above, the development of ways to improve physical and thermal performance of refractory lining materials, including the thermal stability, is regarded as a priority [1÷3].

2 Materials and methods

The Portland cement is one of the widely used kinds of binders for chemically bonded refractory composites. The Portland cement as a hydraulic binder contains 75-80% of the highly basic calcium silicate, 5-15% of the highly basic calcium aluminate and 10-20% of the tetracalcium aluminoferrite. The major feature of the Portland cement as a binder for making heat-resistant composites is the formation of significant quantities of the calcium hydroxide Ca(OH)_2 (up to 15% by weight) in the cement stone as a result of hardening. During drying and the first heating at a temperature of about 500°C calcium hydroxide decomposes into calcium oxide and water. Re-slaking of the newly formed calcium oxide with the water vapor contained in the air, leads to the destruction of the cement stone and concrete respectively, due to the formation of Ca(OH)_2 from CaO . To prevent this process, agents capable of binding the calcium oxide to more heat stable compounds are added to the Portland cement. For this purpose traditional fine-ground refractory additives are used: granular blast-furnace slag, alumina-chromium waste in the form of the dead petrochemical catalyst, chamotte, cordierite, volcanic ash, fly ash, alumina cement and other substances capable of reacting with the calcium oxide CaO . Positive results, in particular the strength increase, are provided by the addition of the sodium tripolyphosphate after its introduction into the Portland cement binders, as well as classical plasticizers of C-3 type or nanotechnogenic high-alumina sludge-waste of non-ferrous metallurgy [3-5].

The maximum operating temperature for the widely used fireclay refractory concrete on the Portland cement does not exceed 1200°C. When using a heat-resistant concrete on the Portland cement as a fine-ground refractory additive and fillers of more highly refractory materials, such as chromomagnesite or periclase products, its operation temperature rises to 1600°C [3].

Aluminate binders, including alumina and high-alumina cements, consist of low-basic calcium aluminates. The total content of the aluminum oxide in the aluminous cement is not more than 50%, and in the high-alumina cement is not less than 17%. These cements are quick-hardening and very active, i.e. high-strength binders. During mixing with water alumina cements do not form the calcium hydroxide Ca(OH)_2 and other compounds that

reduce the performance of heat-resistant composites. The cement stone based on the alumina cement is highly refractory in comparison with the Portland cement due to the increased content of the aluminum oxide Al_2O_3 [6]. The heat-resistant concrete on aluminous cement has higher performance characteristics than concrete on the Portland cement. This type of the heat-resistant concrete was tested at temperatures of 1300-1400°C in neutral and weakly reducing environments. However, when working with this type of the heat-resistant concrete on the installation site, the ambient temperature must be taken into account.

The heat-resistant concrete on the high-alumina cement and high-alumina aggregate (e.g., a white electrofused corundum) can be used not only in oxidizing, but also reducing environments at an ambient temperature of not more than 1700°C. After heating to a temperature above 800°C, the strength of concretes on the high-alumina cement decreases. However, their residual strength is higher than that of concretes on the Portland and alumina cements and averages 40-45% of the grade value [2; 6].

The dense concrete on the high-alumina cement and corundum can have a grade of 600 and 650 and a residual strength of 25-30 MPa when the average density of the normally compacted concrete mix is 2900-3100 kg/m³.

This type of concrete is sufficiently stable both in oxidizing and reducing environments and it is resistant to abrasive particles.

It is also possible to increase physical and thermal characteristics of heat-resistant composites (concretes, solutions, shotcrete masses) by using liquid-glass and phosphate binders.

3 Experiments and results

The liquid glass used in heat-resistant concrete compositions is an aqueous solution of the sodium silicate of 1,3-1,5 g/sm³ density. The ratio of silica to the sodium oxide is usually 2-3.5. The hardening of the liquid glass and concretes on its basis is the result of their dehydration or action of hardening initiators. The solidification of materials by drying is possible only if they contain a large number of pores and the exposed surface of the concrete. In dense concretes one can observe a rapid formation of a vapor- tight surface film of the liquid glass which prevents drying and hardening of deep sections of the concrete. In this regard, the solidification of liquid-glass materials by introducing chemical hardeners which ensure the volume curing is more promising. The sodium silicofluoride, self-separating slag of ferrochromium production, nepheline sludge, Portland cement, aluminous cement and nepheline flame retardant can be used as hardeners [7].

The melting point of sodium and potassium silicates is relatively low (about 900⁰ C) and the liquid glass in the composition of the lining material is a fluxing agent, but in the combination with aluminosilicates, corundum, magnesite and other compounds with high refractory properties, it allows obtaining concretes and protective coatings that withstand the temperature of about 1600°C [8; 9].

Concretes and solutions based on the liquid glass retain for a long time the ductility under the load which is much less than their strength limit. The reduction and complete elimination of this defect is achieved by using high-temperature drying (at the temperature above 120°C).

The heat resistant concrete on the liquid glass and fireclay filler is used at the temperature of not more than 1300°C. This type of concrete properly resists the action of acidic media, provided that the sodium silicofluoride is used as a hardener for the liquid glass. Therefore, concretes on the liquid glass with the sodium silicofluoride can be used for linings of thermal units in acidic corrosive media.

The concrete on the liquid glass can be placed both by vibrating and by shotcreting. When replacing the sodium silicofluoride with the self-separating ferrochrome slag with the fine-ground aluminosilicate powder, physical and mechanical properties of the concrete are improved. And along with this its residual strength increases by about 10% and before the first heating at the operating temperature it becomes less sensitive to moisture.

One of the main advantages of the heat-resistant concrete on the liquid glass is that it unlike concrete on hydraulic binders does not practically reduce the strength when heated. In certain cases, for example, when the ferrochrome slag or aluminous cement are used as liquid glass hardeners and when a finely ground aluminosilicate additive is introduced into the concrete mix; the heat-resistant concrete after heating it to 800°C increases its mechanical strength. The result is that its residual strength becomes higher than the grade one.

It is possible to consider the heat-resistant concrete on the silicate-block, i.e. on the same sodium metasilicate, but in the form of a dry fine powder, to be an analogue to the heat-resistant concrete on the liquid glass. The approximate composition of the heat – resistant concrete on the silicate –block is as follows, % by weight: silicate- block 6.0; technical barium chloride 0.6; finely ground fireclay additive 34.4; fireclay sand 30; crushed fireclay 30; water of mixing 300 liters per 1m³ of the concrete mix. The concrete mix is prepared in fixed-drum concrete mixers by mixing dry components during 1,0-1,5 min and placed by vibration. The concrete takes 4-6 hours to harden at 100-150°C [8; 9].

The basic physical and technical properties of the heat-resistant concrete on the silicate –block are: the usage temperature limit- 1200°C-1600°C; grade strength- 20-30 MPa; residual strength- 100%; average density- 1900 kg/m³; high-temperature strength-23 water-based thermal cycles (water is 800°C). The linear shrinkage after heating to 1200°C does not exceed 0.5%. The characteristic feature of this type of concrete is the increased high-temperature strength under acidic gases.

The heat-resistant concrete on the silicate-block differs from other types of heat-resistant concretes by the increased strength and thermal stability. In addition, the silicate-block is cheaper than the liquid glass and its consumption per 1m³ of the concrete mix calculated on the dried basis is approximately 20% less. However, the heat-resistant concrete on the silicate-block can only be effectively used for the manufacture of blocks and individual elements.

Heat-resistant compositions on phosphate cements and binders have very high physical and thermal parameters. Phosphate cements are formed during the reaction of the orthophosphoric acid with metal oxides or metallic mineral materials (including ashes, slags, natural and artificial silicates, etc.). Depending on the activity of the material used against the phosphoric acid, the binding properties of the resulting cements prove themselves at normal, elevated or high temperatures. At the temperature of about 200°C the hardening phosphate compositions can be prepared on the basis of magnesium and zinc oxides, titanium, aluminum and zirconium hydroxides previously passivated at 1100-1200°C. Binding properties of phosphate cements based on oxides of titanium, aluminum, zirconium, chromium and a number of other metals appear only when heated to 200-500°C [10;11].

The settling time of the cold hardening phosphate compositions can be controlled by changing the specific surface of the solid component (e.g. to change its grinding fineness and the reaction activity of grain surface either by thermal or chemical treatment, or pre-neutralizing of the liquid component.

Industrial water solutions of aluminum phosphate or aluminophosphate are the most common liquid phosphate binders. The density of the aluminophosphate binder is about 1,5r/sm³. Aluminum chromophosphates have approximately the same density and are a sticky liquid of green color. In addition, partially or completely dehydrated powders of

aluminophosphate and aluminochromophosphate are sometimes used. Binding properties of partially dehydrated powders and water solutions appear at the same temperatures and those of completely dehydrated ones at elevated and high temperatures.

Solidification of liquid phosphate binders occurs due to their drying and subsequent polymerization and condensation or introduction of hardening initiators reacting with the acid group present in the composition of binders. Here hardly soluble compounds are formed.

The strength increase of phosphate binders together with that of the heating temperature is their characteristic feature. In the production of wear-resistant, highly plastic and corrosion-resistant coatings (slag-resistant included), the mechanical characteristics of materials based on them are taken into account.

The heat-resistant concrete with an alumochromophosphate binder (AChPhB) and zircon aggregate can be used at temperature of not more than 1500°C. The characteristic feature of this type of concrete is its basic and weakly acidic slag repellency. Therefore, it can be effectively used to line the bottom of boiler furnaces with the liquid ash removal, non-ferrous melting furnaces and other thermal units.

Unlike heat-resistant concretes on orthophosphoric acid, concretes on the alumochromophosphoric binder are more technologically advanced, since it is unnecessary to perform heat-treatment to provide the structural strength to constructions manufactured from them. They can harden at a normal temperature above 15°C if certain chemical additives are introduced into the concrete mix as a hardener initiator and they do not impair the operation properties of the concrete (i.e. they do not lead to corrosion of the reinforcement, the concrete strength decrease when heated, etc.) One of such additives is the waste of the dead chromia-alumina catalyst IM-2201, which initiates hardening of AChPhS and simultaneously acts as a fine-ground additive. The concrete on the alumochromophosphate binder finally gains strength during the process of drying and the first heating of the structure made of it, thus it can be used to form larger blocks and shields, as well as during monolithic concreting and semi-dry shotcreting of structure lining where the boiler is installed [10; 11].

4 Discussion

The use of alumina-containing components in concretes and concrete grouts promotes the increase of the chemical resistance of refractory composites.

It is also possible to increase the strength characteristics of heat-resistant composites by producing individual products from refractory ramming mixtures. Earlier, ramming mixtures were used only for relining in thermal units.

The ramming mixtures in contrast to the developed heat-resistant concretes for manufacturing articles and relining have a number of specific differences due to the technological features of their compaction during the molding of individual blocks and maintenance work in furnaces and other thermal units. The consolidation of ramming mixtures (monolithic concretes) during these works is carried out only by the method of tamping which results in the reduction of the amount of the grouting fluid necessary for the high-quality placing of the concrete mix.

To improve the technological parameters necessary for the high-quality compaction of refractory ramming mixtures, refractory clay or kaolin are introduced into their composition. Considering the fact that these components are scarce and costly (practically most of the deposits of refractory clays and kaolins are concentrated on the territory of Ukraine). We have made an attempt to replace plastic components with some wastes from the ceramsite industry.

At a number of sintering plants both in the Samara region and the Russian Federation, where double-drum rotary kilns are used for the production of the claydite, a coproduct in the form of the ceramsite dust falls out from the firing unit at the junction of two drums. It was found that this coproduct is about 20-30% clay bond along with fired components.

However, the use of phosphate binders (orthophosphoric acid or liquid alumochromophosphate binder) as grouting fluids of refractory ramming mixtures with the ceramsite dust, allowed, as a result of chemical reactions between active liquid phosphates and components (oxides) of mineral fillers (including dust), obtaining high –temperature compounds in the form of the of ferric phosphate FePO_4 ; aluminum phosphate AlPO_4 ; calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ and others.

The optimum compositions of monolithic heat-resistant concretes (repair ramming mixtures) are as follows: Composition 1: clay-containing ceramsite dust -10%; aluminum chromium waste. IM 2201-30%; corundum fine ($\text{fr}<1.25$) aggregate -20%; high-alumina sand -40%. The grouting fluid is the orthophosphoric acid or an acidic alumochromophosphate binder (Liquid/Solid ratio= 0.15-0.2).

Composition 2: clay-containing ceramsite dust -10%; zircon concentrate CZ - 1 -35%; corundum fine ($\text{fr}< 1.25$) aggregate -20% ; high-alumina or fireclay sand -40%.

Grouting fluids and ramming mixture consistency are as in composition 1.

Such compositions of ramming mixtures are recommended to be used for the manufacture of both large-sized blocks and small piece critical products required for the installation and repair of thermal unit linings. In the case of manufacturing individual blocks, parts and products with the use of ramming mixtures the method of the immediate stripping is quite acceptable.

These heat-resistant composites obtain the grade strength directly in the thermal unit after the first lining heating to the operating temperature.

For the further growth of strength and other physical and thermal parameters of heat-resistant phosphate hardening composites it is recommended to treat products or carry out the structural and chemical modification by impregnation with the solution of the liquid alumophosphate binder.

The same technology can be used to improve physical and thermal parameters of fireclay and high-alumina refractories [3].

The major physical and thermal characteristics of the developed refractory ramming mixtures suitable for the production of individual products and blocks, as well as for thermal unit relining are given in Table 1.

Table1. Physical and thermal characteristics of ramming mixtures on phosphate binders

Properties	Unit of measure	Characteristics	
		Composition 1	Composition 2
Average density after thermal treatment(200 °C)	kg/m^3	2550 – 2600	2650 – 2700
		2600 – 2650	2700 – 2750
Compressive strength after drying at 200 °C	MPa	41 – 47	48 – 50
		47 – 53	54 – 57
Compressive strength after burning at 1500 °C	MPa	54 – 59	58 – 62
		60 – 65	66 – 72
Thermal resistance	A number of water thermal cycles	44-48	49-51
Fire shrinkage	%	0.25	0.19

		0,21	0,16
Thermal coefficient of linear expansion	10^{-6} deg^{-1}	<u>9,81</u> 9,64	<u>8,75</u> 8,57
Temperature of initial deformation under the load of 0,2 MPa	$^{\circ}\text{C}$	<u>1500</u> 1540	<u>1550</u> 1590

Note: Above the bar are ramming mixture properties; below the bar are properties of ramming mixtures modified with acidic aluminophosphates after the heat treatment at $t=200\text{ }^{\circ}\text{C}$.

5 Conclusion

Thus, the use of the industrial waste as fine-grained additives and fillers significantly reduces the cost of heat-resistant concretes and extends their use.

Increasing strength and correspondently thermal resistance of small-piece heat-resistant parts and products based on phosphate compositions can also be carried out using at the pressure of 5.0-15.0 MPa. The composition of mixtures in addition to the refractory clay can include both finely ground high-alumina fillers and small aggregates of aluminosilicate or high-alumina compositions. Almost all phosphate binders serve as grouting fluids, but the advantage is given to water-soluble aluminophosphate compounds [3; 5; 10].

The method of increasing the thermal stability of heat-resistant concretes practically on all types of binders considered, which consists of the introduction of refractory high-temperature fibers into the composition of concrete mixes, is quite simple. As a result of this technology heat-resistant concretes reinforced with fibers are formed. Kaolin wool, basalt fibers and also metallic fibers prepared from high-temperature alloys, e.g. nickrochrome, are possible to be used as fibrous refractory materials [12].

It has been established that the introduction of above-mentioned refractory inorganic fibers and metallic fibers in the amount of 3-4% of the total weight of the concrete mix increases its thermal stability by 1.2÷1.5 times.

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