

Resource and energy saving technologies of refractory linings of thermal units

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Abstract. In Russian practice, the vast majority of thermal units and other industrial furnaces are still built with the use of single-piece ceramic refractories. The purpose of research was to develop a wide range of special materials suitable for repairs of any linings of thermal units. In accordance with the purpose, this paper solved the following tasks: Selecting reactive binders used in the compositions of refractory concrete capable of structural modification of any refractory lining materials; Developing impregnating-coating compositions based on reactive binders capable of forming a protective coating with high adhesive strengthen linings; Developing compositions of refractory ramming mixtures, used for the repair of large fragments of linings and having high adhesion to any refractory lining materials; Checking the effectiveness of the technology in production environment. In this paper, we used not only standard techniques but also specially designed ones, in particular, to determine the adhesion of refractory coating to the refractory lining materials. The technology of repair works consists of application of some or all of the above solutions depending on the state of worn out lining of the thermal unit. Testing was carried out on many sintering plants of Samara region where rotary kilns are operated. The use of such chemically active substances as phosphate bonds and sodium silicate solutes in special refractory repair compositions with different functional purpose, allowed increasing the durability of liners of expanded fire clay rotary kilns as a result of reparatory works. Some items from the general technological scheme of repair works to restore the linings of heating units may be used in industrial furnaces in many industries.

1 Introduction

Technical progress in the construction of linings of industrial furnaces and other thermal units is associated with the introduction of new technology and modern refractory lining materials: single-piece ceramic and melt-molded refractories, prefabricated and monolithic refractory unfired concrete, dry mixes for applying repair mixtures by mortaring method and impregnating and impregnating-coating compositions for increasing the operation time of the linings of thermal units.

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Significant major developments in the field of creating refractory lining materials are focused primarily on heat-resistant concrete on various binders [1-5]. Their use in the construction and repair of linings of industrial furnaces and other thermal units makes it possible to mechanize refractory works, and reduce their labor intensity. Moreover, utilization of heat-resistant concrete in lining constructions can significantly increase the durability and longevity of linings by reducing the number of joints compared with brick versions of these structures.

Despite the undoubted advantages of heat-resistant concrete, in domestic practice single-piece kiln refractories (fireclay, magnesite, chrome magnesite, mullite, etc.) are still often used for the construction of linings - critical structures of thermal units, operating in many industries. Despite various aggressive media, which in addition to temperature effects have a significant disruptive effect on the single-piece refractories, fireclay ceramics in the form of bricks and other elements remains a traditionally widely used material for the manufacturing of linings of many thermal units. In this regard, a very actual issue is the development of effective resource and energy saving technologies of repairing thermal unit linings allowing them to extend their service life [6-10].

One of the directions of building materials and construction industry technologies development is the implementing of resource and energy saving technologies, including the efficient use of local materials and industrial wastes. In the Samara region there is a large number of chemical and petrochemical, metallurgical complexes and industries related to building materials which produce large volumes of mineral by-products and waste characterized by high levels of fire resistance, melting point, etc. These include aluminous chromous spent catalysts, high-alumina slurry-like (pasty) wastes, scrap of refractory products, as well as the waste of brickworks [10-12].

The use of these compounds in the repair plastic refractory mixtures (refractory concrete, gunned castable mixture and impregnating-coating compositions, ramming mixes and liquid adhesives for structural and chemical modification of ceramic refractories) makes it possible to create highly effective technologies for the reconstruction works in order to increase service life of the thermal unit lining.

Technologies applied earlier to increase the resistance and durability of linings of thermal units using heat-resistant compositions on various binders, did not lead to significant increase in service life of thermal units. Various plastic mixtures (concrete mixes, mortars and gunned castable mixtures and other compositions based on the dry refractory mixtures) applied on repair parts of the lining in the form of patches without taking into account the thermal expansion coefficient (TEC) of the basic lining material and repair structures, peeled off causing the heat unit to stop after just a few firings, i.e. after a very short period of work [7-9].

2 Materials and methods

In this regard, research tasks to provide an effective technology of lining repair in terms of significantly increasing its service life and operation of the heat unit are as follows:

- Search and application of reactive binders in liquid state, allowing by impregnation of refractory materials to carry out their structural and chemical modification that contributes, through the formation of the new refractory compounds in the pores, to increasing physical and thermal performance originally obtained at the factory.

- Developing the technology for obtaining impregnating-coating compositions on the basis of reactive binders, which, due to capillary suction, should enter the surface pores of single-piece refractories, further contributing, after the heat treatment, to equalizing coefficients of thermal expansion of the working refractory and protective coating with high adhesion layer formed on its surface;

-Developing the technology for obtaining refractory ramming mixtures needed in the repair process of very large chipped holes of refractories and other potholes in the linings of thermal units. After hardening, ramming mixtures should have increased adhesion to the repaired surface because of applied binder;

-Testing new effective technology for repairing the lining, made of single-piece refractories or with refractory composites.

The expanded clay industry is currently operating single-drum and double-drum rotary kilns with the diameter of 2.5 m and the length of up to 40 m. The lining of rotary kilns of all constructions is carried out with the use of fireclay V-shaped and conventional bricks of the types SA or SB. As a result of construction specifics of rotary kiln lining, where except temperature loads there are also large dynamic loads on the lining during operation, vibration in particular, fireclay refractory brick work in some areas can be performed on dry basis, i.e. without mortar. But the lining of the burning zone of expanded clay burning rotating furnaces, where the process of raw granules blistering occurs, is performed mainly with fireclay refractory and mortar refractory. Fireclay lining of the burning zone is subjected not only to abrasive, i.e. mechanical action of claydite gravel solid crust, but also to the chemical attack from the possible occurrence of silicate melt due to accidental overheating. It is this chemical factor that is very important in the process of destruction of the fireclay refractory in the burning zone of the rotary expanded clay burning kiln.

3 Results

The silicate melt, resulting from partial melting of clay gravel, penetrates into the pores of the refractory fireclay. Fireclay brick in the lining is impregnated with silicate melt to a certain depth as a result of such exposure. According to the thickness of the fireclay lining, zonal structure is formed with different thermal expansion. This phenomenon eventually leads to internal stresses and peeling of individual zones of fireclay refractory [7].

Due to the fact that the thermal expansion turned out to be the major cause of failure of single-piece fireclay refractories, dilatometric studies were conducted to determine the thermal expansion coefficients of individual zones. Test results showed a great difference in thermal expansion coefficient values of these areas. The transition zone is fireclay, into which the melt diffused, and its structure is characterized by higher density and the absence of pores.

The difference in the coefficients of thermal expansion of the formed zones in fireclay lining leads to the destruction of single-piece refractories and promotes rapid failure of the lining as a whole. Fireclay refractory mortar used for laying the refractories in the burning zone is not fully sintered either leading to its scaling off and falling out from the joints. This also speeds up the process of destruction of the lining, leading in some cases to the falling out of worn bricks from the construction of rotary kiln lining.

Thus, both in single-piece ceramic refractories in the linings of the majority of thermal units, and in rotating expanded clay burning kilns, masonry joints are bottlenecks of these constructions. Therefore technological developments to enhance the durability and longevity of linings made with fireclay should be aimed at increasing the physical and thermal properties of a refractory (durability, heat resistance) and at improved adhesion characteristics of masonry mortars.

Analysis of binders and liquid binders used in refractory composites shows that the phosphate binders have the highest chemical reactivity. Even the use of orthophosphoric acid of a certain density for structural and chemical modification by impregnating a fireclay refractory of the type IIIA (National State Standard 390-96) gave a positive result. Table 1 shows the results of density and durability change in firebrick samples after impregnation H_3PO_4 solution and subsequent heat treatment and burning.

Table 1. Impact of fireclay refractory impregnation with orthophosphoric acid and subsequent heating on its physical and thermal parameters.

Refractory Type	The average density, g / cm ³ in the numerator and the compressive breaking strength, MPa in the denominator of refractory samples after impregnation and subsequent heating to a temperature of, °C.				
	200	500	800	1200	1500
Fireclay type SA, not subjected to impregnation	1.89/18.7	1.95/19.1	1.97/19.3	2.04/19.7	samples deformed
Fireclay type SA, impregnated with H ₃ PO ₄	2.11/45.4	2.19/42.9	2.11/38.7	2.08/39.6	2.04/41.3

Table 1 shows that the dense fireclay refractory impregnation with orthophosphoric acid has a positive effect on its physical and thermal parameters. Compressive breaking strength of the fireclay increases almost 2-fold, and the density increases by 1.1-1.5%. In addition to increasing durability, phosphate binders may provide improved chemical resistance to various melts at high temperatures, including silica, which are possibly formed in the burning zone of the expanded clay burning kiln. Studying the crystal-chemical structure of any metal phosphate, it can be stated that in the group PO₄³⁻ the central atom of phosphorus has double fully compensated bond (–P=O), which provides significant repulsion from many phosphates of a variety of corrosive media, including melts at high temperatures [1].

This fact predetermined the development of refractory mortar plastic compositions on orthophosphoric acid, performing the function of impregnating-coating compositions of refractory linings.

Due to the fact that the thermal expansion was the main cause of the single-piece fireclay refractories destruction, we conducted dilatometric studies of refractory protective coatings with a view of bringing their thermal expansion coefficient closer to the TEC of refractory fireclay.

Thermal expansion is the main cause of destruction of refractory lining materials. With the aim of making thermal expansion coefficients of fireclay masonry with phosphate coating closer, we offer profuse preliminary impregnation of the repaired surface with orthophosphoric acid. Fireclay basis as a result of its impregnation after heat treatment lowers its TEC, which becomes comparable to TEC of the fireclay phosphate mortar coating.

As the dilatometric studies in Research Institute KERAMZIT show, the coefficients of thermal expansion of fireclay, impregnated with H₃PO₄, and fireclay phosphate mortar coating are within $(7.57-8.63) \cdot 10^{-6} \text{ deg}^{-1}$ at temperatures 500- 900⁰C [7]. In order to determine the physical and thermal parameters, the samples of mortar coating were tested for compressive durability after heating. We also determined adhesive properties of these mortar compositions according to technique [7], the deformation temperature under load and thermal stability.

For preliminary assessment of the coating adhesion strength or adhesive strength with the base coat, coating of varying thickness and texture was applied on the brick, and after all kinds of heat treatment, the degree and nature of the coatingdestruction was visually assessed.

As the porous base, we used fireclay and high alumina bricks, i.e. the base coat corresponded to coating composition. Coatings were prepared using refractory mortar MIII - 39 and high-alumina mortar MMJI-62.

In addition to the above, we studied the microstructure in the contact zone between the binding substance and fireclay, and between the binding substance and melt. For this purpose, special fireclay samples were manufactured and coated with refractory coating (MMJI-62 + 70% orthophosphoric acid). These samples with coating were then subjected to thermal effects in contact with the raw clay melt. As a result of the experience, silicate melt interacted with the coating. The observed contact zone between the binding substance (coating) and the melt has a clear border, there is no significant penetration of the melt into the structure of coating; hence the reduction of potential appearance of micro fractures, which eventually lead to the destruction of the refractory. Contact area between the fireclay and the binding substance also has clear boundaries, but there is a small transition zone which gives good adhesion between the fireclay and refractory coating.

4 Discussion

Thus, the study of the microstructure of the refractory fireclay with applied coating showed a clear border of three zones: a zone of pure fireclay, a transition zone and a melt zone. The transition zone is fireclay, the structure into which H_3PO_4 penetrated by capillary suction, and after heat treatment there formed a dense structure with no open pores.

Dilatometric study of refractory protective coatings, conducted to determine the TEC, revealed a number of compositions of refractory phosphate coatings which can be used for the coating of the rotary expanded clay burning kilns. As the studies to determine the specific properties of phosphate binders show, they have high mechanical durability, chemical resistance, fire resistance, improved adhesion to ceramic refractories and wear resistance to expanded clay and its melt.

In addition to fire-resistant phosphate coatings to repair the linings of the rotary expanded clay burning kilns with large fragments of destruction, we developed refractory ramming mixtures which create reliable non-shrink layers on the working part of the liner.

Ramming mixtures in contrast to the developed heat-resistant concrete, designed to repair linings, have a number of specific differences arising from technological features of their sealing during restoration work in kilns and other thermal units. Sealing of ramming mixtures (monolithic concrete) during repairs can only be carried out by tamping method the consequence of which is the reduction of the amount of grouting fluid required for high-quality concrete packing.

After hardening of the repair layer of ramming mixtures, it is treated with impregnated coating compositions in order to avoid falling out of concreted fragment of the lining due to dynamic loads.

Taking this into account, we used the method of mathematical planning of the experiment to make adjustments of refractory ramming mixture compositions of phosphate hardening for repairs not only in rotary kilns, but also in the heating, melting and thermal engineering units and non-ferrous metallurgy.

Optimal compositions of monolithic ramming mixtures are as follows:

Composition 1: refractory clay or kaolin - 10%, aluminum chromous waste ИМ -2201-30%, the fine corundum (fr.<1.25), aggregate - 20%, high alumina sand - 40%, grouting fluid - orthophosphoric acid or acidic aluminophosphate binder.

Composition 2: refractory clay or kaolin - 10%, zircon concentrate КЦ -1 - 30%, the fine corundum (fr.<1.25), aggregate - 20%, high alumina or fireclay sand - 40%, grouting fluid and consistency of ramming mixture are similar to composition 1.

Acidwater soluble aluminum-calcium-phosphatic or aluminum-phosphatic binders were prepared by synthesizing the corresponding slurry-like nano-technological raw materials - pasty waste from Samara Metallurgical Plant with orthophosphoric acid. For aluminum-phosphatic binder we used slurry of alkaline etching of aluminum, and for aluminum-calcium-phosphatic binder we used aluminum-calcium-phosphatic slurry [5; 13-17].

Samples of ramming mixtures with optimal compositions were used for testing dependencies of their strength characteristics on the technological production parameters; thermo-mechanical and thermo-physical properties at different temperatures; we also determined strength characteristics of the system "refractory lining - ramming mixture", showing good adhesion of developed compositions to single-piece and concrete products used to repair the linings of industrial furnaces with aggressive media.

Developed resource saving technologies of heat-resistant concrete, as well as the way of repairing linings of industrial furnaces with ramming mixtures, were industrially approved at Samara Metallurgical Plant, Samara Bearing Plant, KERAMZIT in the city of Samara.

Based on the results of industrial tests, the management of Samara Metallurgical Plant and Samara Bearing Plant decided to build the sites for production of heat-resistant concrete with capacity of 1500-2000 tons / year.

From October 1982, the system of Samara Metallurgical Plant includes the operating station with capacity of 0.5 thousand of tons per year for the manufacturing of products made of heat-resistant concrete and soluble silicate phosphate binders for linings of the heating, melting and thermic furnaces. This station provides the needs of the enterprise in the required reserve of refractory lining materials.

The economic benefit of production and use of refractory concrete instead of firing ceramic refractories is more than 1.54 million rubles / ton (in prices of 2013).

According to their technical and economic indicators, developed heat-resistant concrete considerably exceeds single-piece ceramic refractories: fireclay, magnesite chrome, and high-alumina. Lining material consumption per 1 ton of aluminum alloys at Samara Metallurgical Plant decreased by 9.5-12.6%; for 1 ton of steel billets, bearings on the Samara Bearing Plant - by 13.5-16.5%.

Conclusions

Currently, many industrial enterprises in the Samara region are in need of non-waste technologies, i.e. in their structures the formed byproducts must be processed into materials that will be further needed, either for repair of various technological equipment, or for the manufacture of building materials complying with a particular regulatory document, possibly the National State Standard.

If we turn to the experience of leading or developed countries, we can see that their attitude to any industrial waste produced even in small quantities is quite different than that in Russia, where landfills or disposal sites for wastes are systematically organized.

In these countries (USA, Canada, Japan, Britain, France and others.) the problems of industrial waste utilization become relevant already at the stage of laboratory or experimental studies, even at pilot-scale testing, when a new technology is only launched into the production, and it is impossible to avoid the formation of certain by-products, i.e. industrial waste.

Thus, in particular the use of high-clay wastes of some industrial enterprises of the Samara region made it possible to obtain high quality specific refractory compositions: phosphate impregnating-coating compositions, ramming mixtures of phosphate hardening, and others, which are the basis of resource and energy saving technologies for repairing the linings of thermal units.

At present, the environmental situation both in the Samara region, and other regions and areas of the Russian Federation determines the need to implement the broad utilization of industrial waste, resulting in reduced energy costs, traffic volumes, the cost of building materials, the area of land occupied by disposal sites, and in many cases eliminating the creation of new quarries.

Naturally, the responsibility for making tons of waste lies on the enterprises in which they were formed. These organizations (plants) and other institutions have to pay significant sums of money for the storage of industrial waste in special landfills or storages.

Therefore, many of the technological solutions presented in this article will allow the majority of enterprises of the Samara region to transfer their funds to the implementation of certain developments on the use of their own waste for the production of special materials and addressing their own pressing needs.

The article presents the real, i.e. the necessary recommendations for the use of specific industrial waste in certain enterprises of the Samara region where they are formed, for utilizing in rational production technologies.

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