IOP Conf. Series: Materials Science and Engineering **775** (2020) 012114 doi:10.1088/1757-899X/775/1/012114

Improvement of technological processes of production and application of liquid phosphate binders

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Abstract. The article presents the results related to the processes of liquid phosphate binder synthesizing based on nanotechnogenic raw materials. Such raw materials include alumina-containing sludge from non-ferrous metallurgy. It is established that with the use of alumina alkali sludge and phosphoric acid, it is possible to obtain mono- and disubstituted aluminophosphate binders, and on the basis of alumina-calcium sludge it is possible to obtain alumina-calcium phosphate binders. Particular attention is paid to rational technologies for the use of liquid aluminophosphate and aluminocalcium phosphate binders in the processes of obtaining protective impregnating coating compositions of chamotte linings and structural-chemical modification of piece refractories. The results obtained make it possible to predict an increase in the resistance and durability of widespread chamotte linings of industrial furnaces and other thermal units.

1. Introduction

One of the primary problems facing modern industry is the creation of refractory linings for furnace and thermal units with enhanced physical and thermal characteristics, including chemical resistance in aggressive environments. At operation in aggressive gas environments, high temperatures, in direct contact with molten metals, alloys and fluxes, the lining is subjected to severe destructive effects. The weak point of linings made from piece refractories is masonry or working seams. The destruction of the structure begins due to the penetration of various gases and melts into them. This is particularly observed in metallurgical, heating, thermal furnaces and in thermal aggregates of building materials industry.

The problem solution may be the creation of a lining of large-block elements based on heat-resistant concrete, which allows minimizing the number of working joints, and therefore increasing the durability and the lining service life. By modifying phosphate binders, it is also possible to increase physical and thermal properties of pieceless non-calcined refractories.

2. Materials and methods

Both hydraulic binders and chemicals (water glass, block silicate, various types of phosphate binders) can be used in the compositions of heat-resistant concrete as a binder. Refractory additives and aggregates for special concrete can be prepared not only from expensive and scarce materials, but also from secondary refractories, as well as the other refractory industrial waste.

Today, the replacement of scarce aggregates and finely ground additives with local or common materials, as well as the use of industrial waste in the production of refractory lining materials are important and promising tasks.

The most common and affordable binder for the manufacture of concrete mixes is Portland cement. A peculiar feature of obtaining heat-resistant concrete on Portland cement is the need for the introduction of refractory fine-ground additives that bind free lime released as a result of hydrolysis and hydration of clinker minerals.

Figure 1 shows graphs of changes in the strength of specimens of heat-resistant concrete on various types of binders during heating.

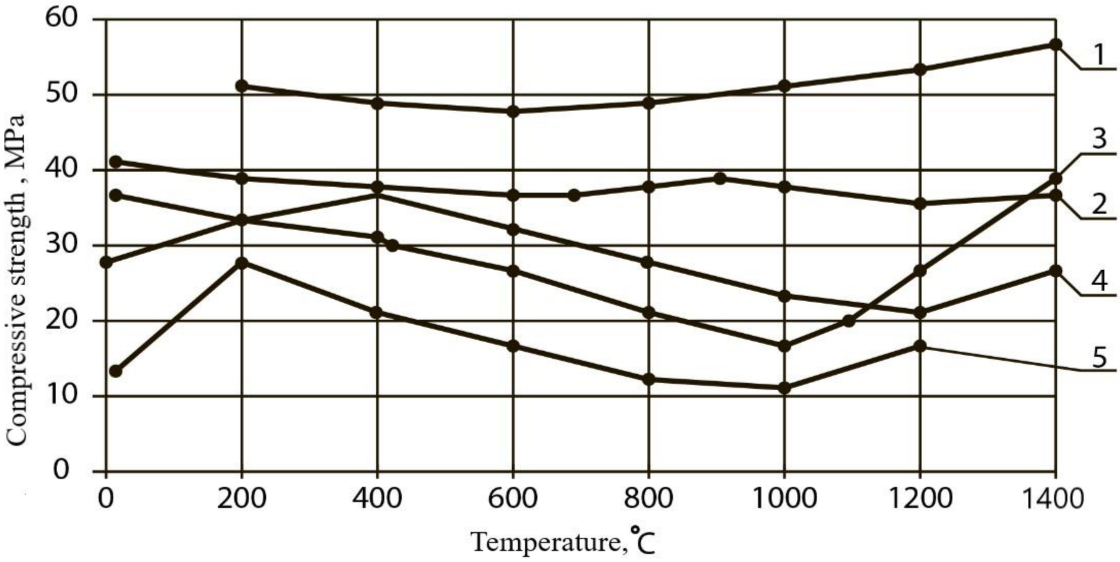

Figure 1. Schedule of change in strength of heat-resistant concrete specimens on various types of binders at heating: 1 - Phosphate binders; 2 - liquid glass; 3 - high alumina cement; 4 - alumina cement; 5 - Portland cement + refractory additive.

As it can be seen in Figure 1, the best strength indicators are shown by heat-resistant concrete with phosphate binder, and the strength of heat-resistant concrete with Portland cement is significantly reduced in the temperature range 400-1000°C.

This is due to calcium hydrosilicates and hydroaluminates dehydration, ending at 800°C, therefore, when assigning or designing the concrete composition, one should strive to obtain a higher grade because of lower water-binding ratio. [1]

Another way to increase refractory lining materials efficiency is to use liquid phosphate binders as a substitute for various heat-resistant compositions, as well as an impregnating composition of ceramic piece refractories.

Liquid phosphate produced by the chemical industry of the Russian Federation, such as aluminochromophosphate binder and aluminoborophosphate binder are very scarce and expensive. Orthophosphoric acid used as a mixing fluid for heat-resistant phosphate solutions and concrete does not make it possible to obtain materials with enhanced physical and thermal parameters. It should be noted that only technical materials, such as alumina hydrate Al $(OH)_3$, boron and chromium oxides are used in the production of such binders as aluminochromophosphate binder aluminoborophosphate binder.

Chemical industry produces in small quantities acidic water-soluble phosphate binders based on $Al(OH)_3$ and H_3PO_4, which are monosubstituted $Al(H_2PO_4)_3$ and disubstituted $Al_2(HPO_4)_3$

aluminophosphates.

The technical advantage of using acidic water-soluble aluminophosphate binders in heat-resistant solutions, concrete and other refractory lining materials production over phosphoric acid is that these compounds: $Al(H_2PO_4)_3$ and $Al_2(HPO_4)_3$ become dehydrated, crystallized and stable during heating cristobafite mineral $AlPO_4$, the melting point of which exceeds 2000°C [2].

At the Samara Metallurgical Plant, sludge alumina-containing wastes are formed in large quantities, which are nanotechnogenic raw materials. As a result of the process such as chemical treatment of aluminum metal-containing parts in an alkali solution of NaOH, a sludge-like precipitate is formed at the molecular level in the form of Al $(OH)_3$ hydroxide. This aluminum-alkaline slurry or alkaline etch slurry of aluminum is accumulated at the bottom of the etching baths, which is a light gray creamy mass.

Further, aluminum-alkaline sludge with a pH > 12.5 at modern wastewater treatment plants is mixed with carbonate sludge in order to eliminate alkalinity. Calcium sludge formed as a result of dehydration in the form of a cheesy sludge is transported to a landfill for burial of industrial waste.

The chemical composition of high alumina sludge waste is presented in table 1.

Table 1. Chemical composition of sludge waste

Samole	Component Content, %							
	Al_2O_3	CaO	Fe_2O_3	SiO_2	MgO	R_2O	SO_3	п.п.п.
Aluminum Alkali Sludge	43-59	0,3-1	1,5-2,5	0-1,3	0-4	2,5-10	0-4	30-35
Calcium Alumina Sludge	14,6	26,32	0,8	8,16	8,24	1,36	1,58	38,88

3. Processes occurring at the structural-chemical modification of refractory lining materials

At the Department "Production of Building Materials, Products and Structures", Samara State Technical University, studies were conducted to develop a method for synthesizing liquid phosphate binders used for the preparation of heat-resistant concrete and mortars. The processes of structural-chemical modification of ceramic refractories have also been studied. This method consists in mixing in a certain ratio of nanotechnogenic sludge waste with phosphoric acid of a certain concentration. Nanoscale sludge waste, as shown by studies [3] is in the range of 20-80 nm, which is 1000 times thinner than any cement particles.

Fine particles of nanotechnogenic raw materials (sludge waste) interact with phosphoric acid at normal temperature, forming a mixture of liquid phosphoric acid solutions without sediment. The data control of phosphate binders for sedimentation stability showed that within two years no precipitate is formed in these solutions [4]. The synthesized liquid phosphate binders (aluminophosphate:Al $(H_2PO_4)_3$ and $Al_2(HPO_4)_3$ and alumina-calcium phosphate) showed very high technical efficiency in the studies concerning the improvement of physicothermal characteristics of phosphate solutions (chamotte coatings). Performance indicators in the processes of ceramic refractories increased due to their structural-chemical modification by impregnation with these binders [5].

In connection with the foregoing, to develop the compositions of heat-resistant solutions-coatings of chamotte linings phosphate binders based on alumina-containing sludge wastes were chosen as the binder. Crushed fireclay sand and finely ground additives such as chamotte mortar MSH-39 according to GOST 6137-2015, spent catalyst IM-2201 - aluminum-chromium petrochemical waste were used as raw materials. Chemical compositions of finely ground fillers and some of their physico-thermal indicators are shown in table 2.

The solutions samples were tested for compressive strength after heating, with the determination of thermal stability. The compositions and some properties of the solution-coatings are given in table 3 and 4.

The tests showed that, the compressive strength of the solution-coatings samples is sufficient for their use in the lining of thermal units. However, to provide more complete conclusion concerning the solutions suitability as protective coatings, it is necessary to know their adhesion strength to refractory or adhesion.

The adhesion strength of solutions (adhesion) was determined using a PSO MG4 adhesive meter.

The layer thickness of the weighed coating on the surface of the CHA type chamotte refractory did not exceed 5 mm.

Table 2. Chemical compositions of finely ground fillers

№	Sample	Composition, mass %									True density, g/sm^3	Fire resistance, ^{0}C
		Al_2O_3	SiO_2	Fe_2O_3	FeO	CaO	MgO	Cr_2O_3	R_2O	SO_3		
1	Fireclay Mortar	36.6	56.7	3.2	-	-	-	-	0.4	0.15	2.5-2.67	1730
2	Spent Catalyst IM 2201 - aluminum-chromium waste of the Novokuybyshevsk petrochemical plant	73-75	7-9	0-0.15	-	-	0.3-0.6	13-15	0-0.9	0-1.1	4.1-4.3	2000

Table 3. Basic physical and mechanical properties of heat-resistant solutions

№	solution composition, kg/m^3	The average density of the mortar mixture, kg/m^3	The compressive strength of samples, MPa, depending on the heating temperature, °C							
			20 (7 days)	200	400	800	1000	1200	1300	1400
1	Fireclay Mortar - 460 Fireclay sand - 1050 CalciumAluminate Phosphate Binder - 560	2035	12.4	31.6	30.1	38.4	38.6	36.1	36.5	-
2	Spent catalyst IM-2201 - 460 Fireclay sand - 1050 CalciumAluminate Phosphate Binder - 5.0	2040	19.1	25.6	33.1	31.8	33.8	35.0	35.7	33.4

Note: density of calcium-aluminum phosphate binder ranged from 1.45-1.48 g/cm^3

As it can be seen from tables 3 and 4, the strength indicators of phosphate solutions of the coatings are high enough. In our opinion, as for the adhesion strength of the coating solutions, such elevated values are explained by the fact that the chamotte substrate is impregnated with a phosphate binder on its surface. Further heat treatment leads to hardening of the refractory surface layer, which helps to equalize the coefficients of thermal expansion of the coating solution with chamotte [6].

Table 4. Thermal and adhesive properties of heat-resistant mortar solutions

№ composition according 2	Adhesive strength of solutions with a chamotte substrate, MPa after heating at a temperature of °C						Heat resistance, water heat exchangers
	20 (7 days)	400	800	1000	1300	1400	
1	3.2	3.4	3.5	3.7	3.6	-	24
2	2.6	2.8	2.9	3.1	3.2	3.6	26

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It was also noted that during the preparation of a phosphate coating solution in the mixer, the chamotte aggregate is completely impregnated with a grinder, i.e. calcium-aluminum phosphate binder. Further heating of the aggregate in the solution leads to its hardening, which has a positive effect on the physical and thermal properties of protective phosphate coatings.

The effect of the impregnation of aggregates and the chamotte base of the lining with liquid aluminophosphate and alumino-calcium phosphate binders on their physicomechanical properties was tested on samples of 50×50×50 mm. The samples were impregnated using a vacuum chamber. When the discharge in the chamber is 2.6 kPa, the air is completely removed from the open pores of the ceramic refractory, and the pore space is filled with liquid phosphate binders. After the impregnation, the samples were kept in air for 15 minutes, and then they were heated at the temperatures 200, 500, 800, 1000, 1200 and 1500°C maximum during 2 hours. After each heating the average density of the samples and compressive strength were determined.

The test results are given in table 5 show that the impregnation of chamotte positively affects their physical and thermal properties.

Table. 5 Effect of impregnation of chamotte refractory with liquid phosphate binders, followed by heating of aluminosilicate (chamotte) refractory on physical and mechanical properties

Aggregate	The average density g/cm^3 in the numerator and the compressive strength (R), MPa in the denominator of refractory samples after heat treatment at 200°C and subsequent heating to a temperature of °C					
	200	500	800	1000	1200	1500
Non-impregnated chamotte	1.93/20.60	2.01/19.70	2.08/23.70	2.05/20.80	2.03/19.60	2.03/19.4
Chamotte impregnated with a solution of monosubstituted aluminophosphate $Al(HPO_4)_3$	2.15/37.60	2.18/37.09	2.10/37.80	2.12/38.00	2.10/38.50	2.00/19.4 (1300°C)
Chamotte impregnated with a solution of disubstituted aluminophosphate $Al_2(HPO_4)_3$	2.17/40.9	2.20/41.2	2.20/41.4	2.19/41.1	2.18/42.2	2.17/42.9
Chamotte impregnated with an aluminum-calcium phosphate binder	2.19/44.3	2.20/46.2	2.21/46.7	2.20/45.9	2.19/45.7	2.18/47.1

Firstly, in impregnated chamotte, the compressive strength after heating increased in 1.3-1.8 times, and the average density by 1-1.5 %. Moreover, at high temperatures, the average density of impregnated chamotte by 1-1.3 % decreases due to the sublimation of P_2O_5.

The increase in the strength of chamotte samples impregnated with liquid aluminophosphate binders is explained by the fact that during the heat treatment strong crystals of $AlPO_4$ and others are formed. These compounds are formed as a result of the heating of $Al(H_2PO_4)_3$ and $Al_2(HPO_4)_3$ binders above 500°C, as well as at high temperature during the interaction of minerals containing Al_2O_3 in chamotte, such as mullite - $3Al_2O_3 \cdot 2SiO_2$, sillimanite - $Al_2O_3 \cdot SiO_2$, with liquid aluminophosphate bonds. [2] It should also be noted that with an increase in the degree of hydrogen substitution by metal aluminum in liquid aluminophosphate binders, the strength of chamotte samples during their structural-chemical modification also increases up to 10-15 %. And the use of liquid aluminum-calcium phosphate binder for the impregnation of chamotte samples allowed increasing their strength by almost 1.8-2 times. This is probably due to the presence of a large set of water-soluble salts in the alumina-calcium phosphate binder: acid aluminophosphate, calcium phosphate, magnesium phosphate and others. This follows from the study of the chemical composition of calcium-aluminum sludge (table 1).

X-ray diffraction analysis of chamotte samples impregnated with phosphate binders and heated to 1000°C showed the appearance of cristobafite crystals $AlPO_4$. Analyzing the results of physical and thermal tests and the phase composition of chamotte samples, we can conclude that the impregnation of aggregates in solutions coatings and chamotte lining with phosphate binders has a positive effect on the firing characteristics of the solutions of the chamotte base lining coatings.

4. Conclusion

Based on the foregoing, it becomes possible to develop a technology for increasing physical and thermal properties of aluminosilicate chamotte by impregnating refractories in solutions of phosphate binder synthesized on sludge waste base and heat treatment at a temperature of 200-500°C. As a result of such technological redistributions, fireclay refractory acquires practically new physical and thermal parameters: compressive strength and thermal resistance increase in 1.5-2 times.

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