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Prospects for the Development of New Types of Refractory Materials

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ABSTRACT: The article presents results of scientific research of development a new generation of refractory materials - fire-resistant concrete. As a scientific novelty of research, as a content of the composition of refractory concretes, it is recorded a new non-traditional filler -technogenic waste. As filler, incorporating a fire-resistant concrete, it is selected glinozemic waste from the gas processing plant. It is found that waste is required to be thermal activated after passing thermo differential and X-ray analyzes. Fire resistant concrete samples, which based on the heated mass at temperature 1200 ° C, are prepared and their mechanical strength indicators are studied

KEYWORDS: Refractory materials, high temperature, dryers, cement industry, mineral raw materials, gas reagents, liquid binders, burning process, physical-chemical indicators, granulometric composition**.**

I. INTRODUCTION

The development of a number of industries is directly related to the production of refractories. Refractory products are materials manufactured on the basis of mineral raw materials and characterized by their ability to maintain their functional properties under various conditions of service at high temperatures without significant violations. They are used to design furnaces, dryers and other high-temperature units, for carrying out a number of high-temperature metallurgical processes.

According to GOST R 52918-2008: refractory - non-metallic material with refractoriness not lower than 1580 ° C, used in units and devices for protection against the effects of thermal energy and gaseous, liquid, solid, corrosive reagents.

According to foreign data, the turnover of the world refractory market for 2014-2015 was estimated at 25 billion euros [1]. As can be seen from the diagram, (fig.1) the main consumer of refractories is ferrous and nonferrous metallurgy. A wide range of refractory materials on the world market makes the consumer especially attentive to the choice of the manufacturer of refractories.

II. OBJECT OF STUDY

Continuous optimization of existing technological processes in order to improve the quality of the product, as well as reduce the consumption of resources of time, energy and raw materials, is important for each company seeking to remain competitive in the market, both producing and consuming refractory products. Hence, one of the main global trends is the reduction in the unit costs of refractories.

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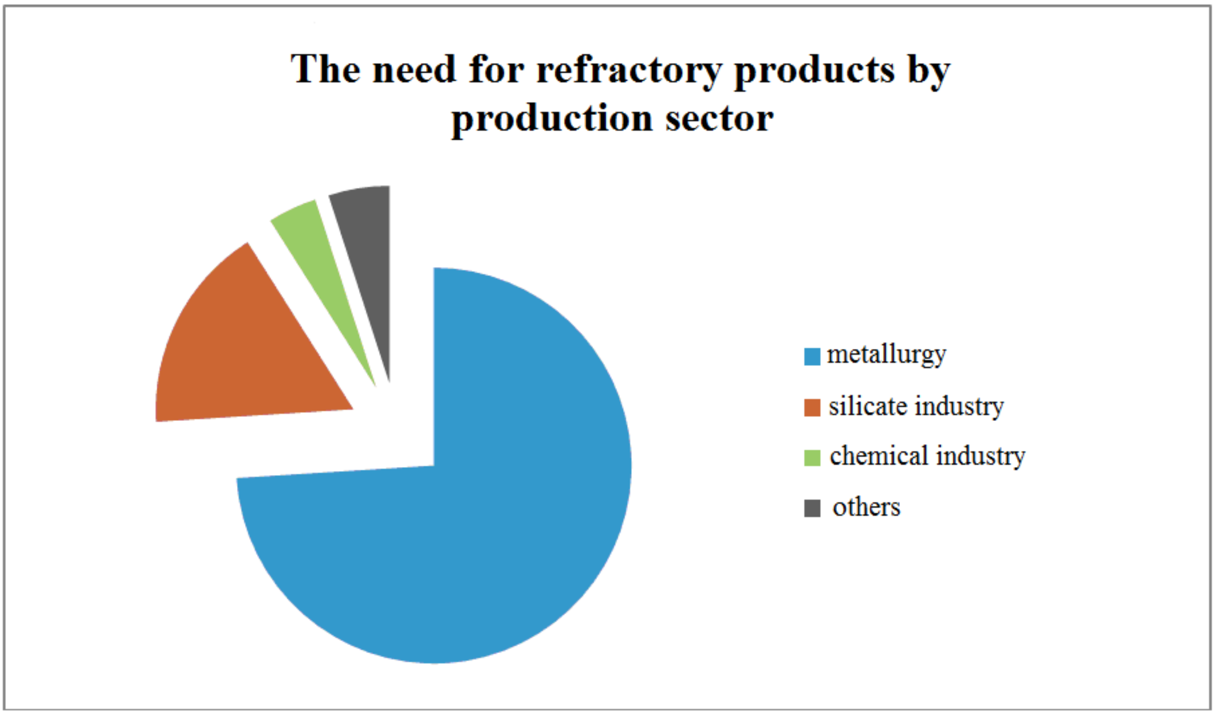

For half a century, the specific consumption of refractories in the production of steel and alloys decreased by almost 3 times, in the glass industry, the specific consumption of refractories decreased by almost 4 times - from 15 to 4 kg per ton of glass, in nonferrous metallurgy over the same period they were reduced by half. In the cement industry, consumption was reduced by almost 10 times and in 2000 at individual enterprises of the cement industry amounted to 0.25 kg per ton of cement clinker. The most important factor that caused a significant decrease in the specific consumption of refractories is the use of new unshaped refractories. The class of unshaped refractories includes refractory concretes (concrete masses, mixtures, preformed products), which are basic, as well as gunning masses, rammed and ductile masses, mortars (refractory mortars) dry mixtures, refractory coatings, ceramic fibers and materials based on them [2].

Refractory concretes are mixtures of refractory aggregates and bonding, which, upon solidification, turn into stone-like material, capable of maintaining specified mechanical properties during prolonged exposure to high temperatures. Recently, the refractory industry in increasing quantities produces unburned refractory products. They can be regarded as refractory concretes on the grounds that, by analogy with ordinary concretes, they consist of refractory filler, inert at ordinary temperatures, and a binder of mineral or organic origin.

Refractory concretes differ from ordinary concretes, firstly, their refractoriness and sufficient strength in service conditions at high temperatures; secondly, they acquire their performance properties in the process of operation when exposed to high temperatures. Refractories of this type are widely used because in their production technology there is no complex and expensive technological process - burning. The advantages of refractory concretes over traditional refractory products are reported in [3].

III. RESEARCH METHODOLOGY

The technology of refractory concretes uses terminology that is somewhat different from the terminology used in the field of refractory ceramics.

Refractory powders, divided into fractions, used for the production of refractory concrete, called fillers (large, small, fine). Refractory powders containing all fractions necessary for the production of concrete and dry binders are called

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dry concrete mixes. Mixtures with water or liquid binders are called concrete mixes. Refractory concretes are classified by type of products made of them, by the type of binders and inert fillers used in their manufacture.

In our studies, we studied the possibilities of obtaining a filler from an alumina-containing waste of a gas chemical complex. In the Shurtan and Ustyurt gas-chemical complexes in the process of polymerization of polyethylene, aluminum oxide in active form, obtained by thermal treatment of natural bauxite at a temperature of 250-300 ^{0}C, is used as a catalyst. The content of aluminum oxide in the composition of the spent catalyst is more than 90%, and therefore, many researchers have studied it as a potential source of aluminum in order to obtain various types of materials and products [4,5]. In order to clarify the processes occurring during the heat treatment of alumina-containing waste, we carried out a differential thermal analysis of this waste on a derivatograph of the Paulik-Paulik-Erdey system at a speed of 10 K / min and a weight of 0.1175 g at the sensitivity of T-900 galvanometer; TG-200; DTA-1/10; DTG-1/10. Recording was performed under atmospheric conditions. The results are shown in Fig 1.

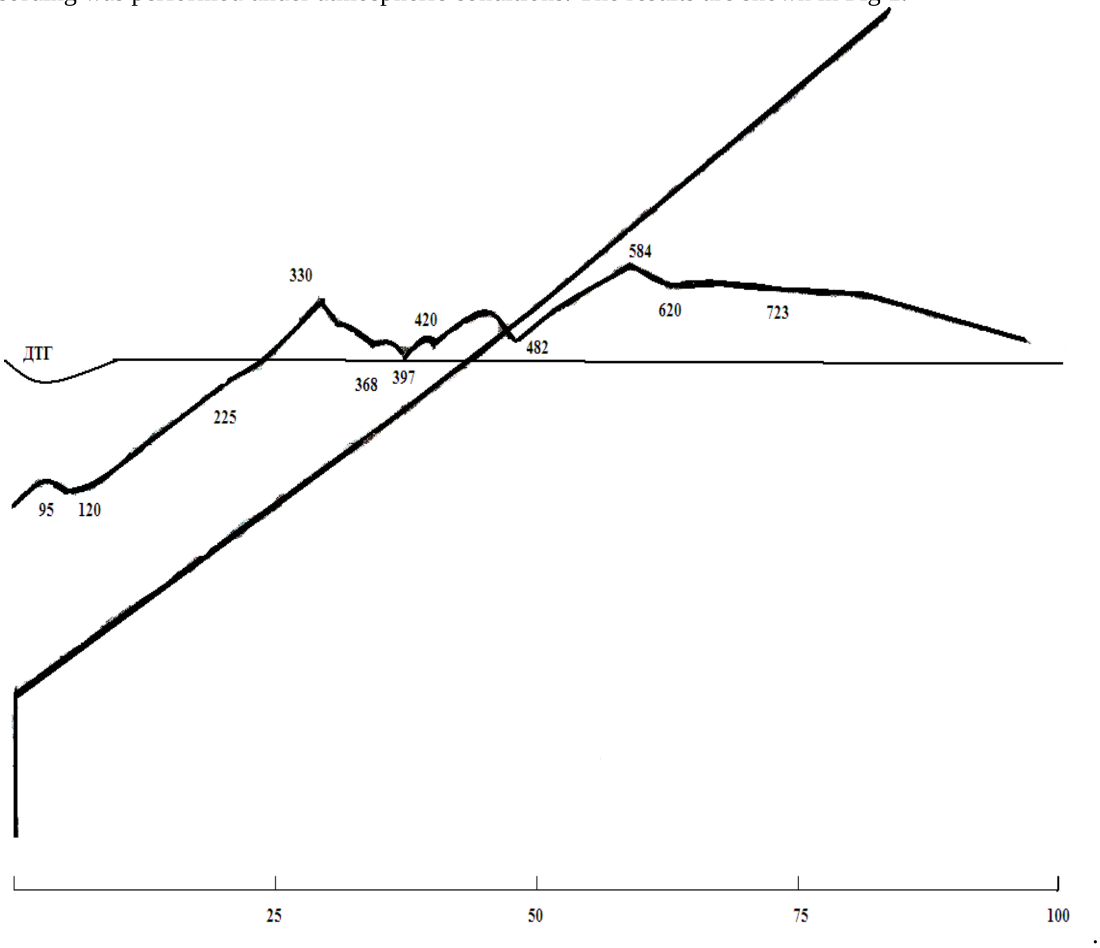

Fig.1. Thermogram of alumina-containing waste from the Shurtan Gas Chemical Complex.

On the heating curve of an alumina-containing waste sample (Figure 1), 8 endothermic effects were found at 95, 120, 368, 397, 420, 482, 620, 723 ° C and 3 exothermic effects at 225, 330 and 584 ° C. The appearance of the first two endothermic effects is due to the removal of water, and the rest with the processes of decomposition of aluminum hydrate. In the temperature range 60-180 ° C, the mass loss is 8.94% on the thermogravometry curve. A further increase in temperature leads to a gradual decrease in the mass of the sample. The total mass loss in the temperature range of 60-90 ° C along the thermogravometry curve is 20.43%. The appearance of exothermic effects associated with phase changes in the system.

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Also in our studies were given radiographic studies of this waste. X-ray analysis was carried out on a diffract meter brand Dron-4. On radiographs of the initial waste (Figure 2-1), diffraction peaks characteristic of hydrargillite Al_2O_3 were found. $3H_2O$, boomite $Al_2O_3.H_2O$, diaspore AlOOH and bayerite. The intensity of bohmite reflexes is noticeable, and the remaining phases are extremely insignificant. The diffractogram (Fig.2-2) of the used catalyst differs from the X-ray diffraction of the initial one by a decrease in intensity or by the disappearance of noticeable bohmite reflexes and the appearance or enhancement of some of the hydrargillite reflexes. The nature of the diffractogram curve becomes more amorphous. After roasting at a temperature of 1200 ° C, diffraction maxima with low intensity appear on the X-ray diffraction pattern (Figure 2-3), reflecting the bayerite-polymorphic modification of aluminum hydroxide, as well as reflexes characteristic of diaspora and β-alumina. The nature of the obtained diffraction patterns of the initial and spent alumina-containing catalyst indicates the occurrence of successive low-temperature transformations of aluminum hydroxides, which are associated with the decomposition of various modifications of aluminum hydrates.

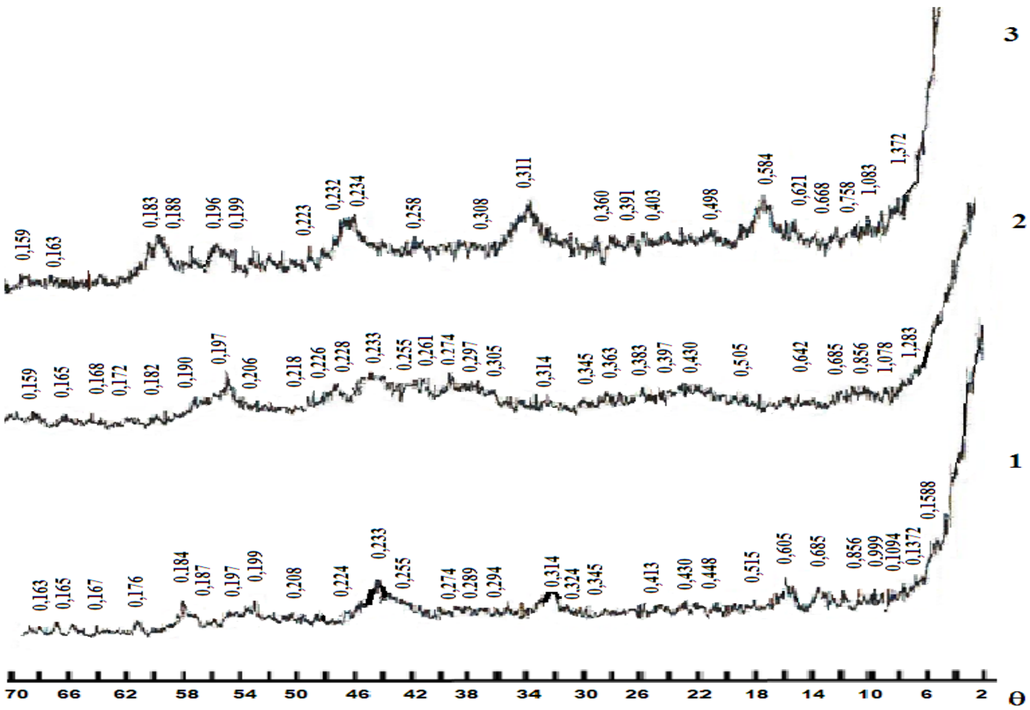

Fig.2. Radiographs of the original (1), spent (2) and thermo-treated (at T = 1200 ° C) alumina-containing waste (3).

Table 1 summarizes some of the physicochemical properties of alumina-containing waste before and after burning.

Based on the data obtained, we have made assumptions that this waste can be fully applied as a filler for the production of refractory concrete.

There is a lot of information, as a binding component, in the literature, [4-6], but mainly the authors refer to the use of aluminophosphate binders, as the most easily available binder with a relatively low cost. During our research, various samples of refractory concrete were obtained, consisting of the bonding and unburnt and calcined alumina-containing waste at temperatures of 1000 and 1200 ° C.

Table 1.
Physico-chemical indicators of alumina-containing waste

№	Indicators	Spent catalyst	Spent catalyst T_{burn}=1200°C
1.	the diameter of the granules	from 1 to 4мм	from 1 to 3мм
2.	Color	dark brown	white
3.	bulk weight, g/ $см^3$	1,091	0,88

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4.	granulometric composition: <3 mm <1 mm	3.9%; 96,1%	3,68%; 96,32%
5.	water absorption, %	35,48	40,30

The ratio of alumina-containing waste: binding varied in the range of 70-80: 30-20 (see Table 2). The preparation of the mass was carried out according to the traditional technology of concreting [7].

Table 2
The compositions of the experimental masses of refractory concrete

The compositions	Components			
	RE initial	RE burning =1000°C	RE burning =1200°C	AΦC
A-1	80			20
A-2	70			30
A-3		80		20
A-4		70		30
A-5			80	20
A-6			70	30

IV. RESEARCH RESULT

The weighed components were placed in a plastic container and mixed for 3-5 minutes. Then the mixture was placed in a 70x70x70 mm mold, pre-lubricated with glycerin on the inside. The pressing was carried out in hydraulic presses at a pressing pressure of 10-15 MPa.

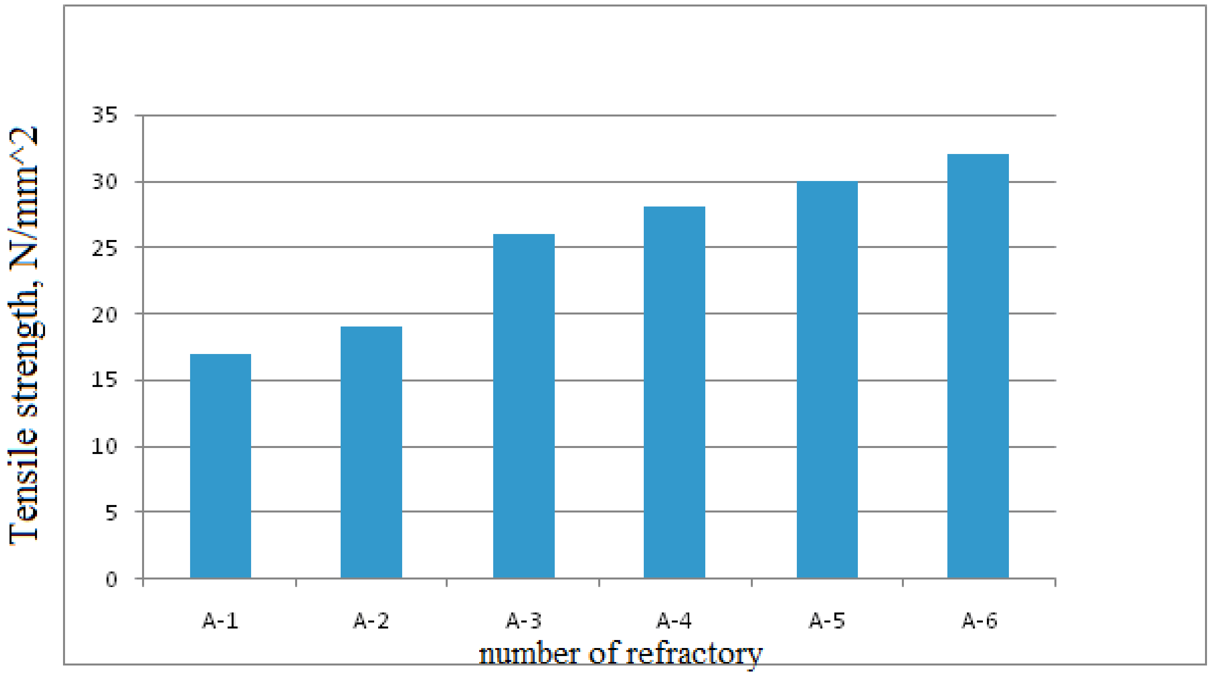

Figure 3. The effect of the composition on the tensile strength of refractory concrete

After exposure to ambient conditions (average temperature - 25 ° C, humidity 46-60%), the samples were subjected to mechanical stress. The data obtained are shown in Fig.3

Thus, studies have shown that it is possible to obtain refractory concrete - as a new refractory material to replace refractory products. Alumina-containing wastes from a gas-chemical complex were investigated for use as refractory concrete filler. As a result of physicochemical studies, it has been established that this waste becomes as a "dead" filler after burning at 1200 ° C and can be quite used as a highly refractory filler. The obtained samples are further studied in terms of their refractoriness and chemical resistance, which will be reported in future publications.

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