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THEORETICAL BASIS AND PROSPECTS OF REFRACTORY MATERIAL PRODUCTION IN AZERBAIJAN

Irada Shirinzade[1], Irada Mammadova[2], Konul Aliyeva[3]

[1]*Azerbaijan University of Architecture and Construction. Prof.Dr.* irada.shirinzade@azmiu.edu.az

[2]*Azerbaijan University of Architecture and Construction, PhD, irada.mammadova@azmiu.edu.az*

[3]*College of Construction under the Azerbaijan University of Architecture and Construction, teacher, konul.alieva@azmiu.edu.az*

Abstract

For many years, refractory bricks have been imported from foreign countries to line the interior of furnaces in industrial enterprises located in our country. Azerbaijan obtains 80% of its refractory materials through imports from other countries (mainly from Russia). However, the increasing transportation costs necessitate the need to meet this demand at the expense of the country's domestic potential. According to research, there are natural raw materials for the production of aluminosilicate (chamotte brick) and silica (dinas brick) refractory materials in Azerbaijan. Preliminary research into the reserves and composition of Gizilja quartzite in the Khanlar region for the production of silica refractory materials, Kotandagh kaolin clay in the Gazakh region for aluminosilicate refractory materials, and Chanlibel clay in the Shamkir region for the production of refractory bricks confirms that these raw materials are suitable for the production of refractory bricks. Therefore, as a result of the analysis, it can be concluded that Azerbaijan has a raw material base for refractory materials such as fireclay bricks and Dinas bricks, and the increasing demand for these materials makes it necessary to develop the scientific basis for the production of refractory materials.

Keywords: *refractory materials, dinas brick, fireclay brick, quartzite, kaolinite*

Introduction

The level of production of refractory materials determines the macroeconomic situation of the country. Thus, the main consumers of refractory materials are ferrous and non-ferrous metallurgy, cement and glass production, construction materials, petrochemical industry and energy sector. Ferrous and non-ferrous metallurgy consume more than 75% of refractory materials produced in the world and have a decisive impact on the production of refractory materials. Refractory materials are the main and auxiliary materials for the construction of heating installations in metallurgy, construction materials production, energy and many other sectors of the national economy (Figure 1).

For many years, refractory bricks have been imported from foreign countries for lining the interior of furnaces in industrial enterprises located in our country. According to information [2], Azerbaijan obtains 80% of refractory materials through imports from other countries (mainly from Russia). However, the increasing transportation costs make it necessary to meet this demand at the expense of the country's domestic potential.

According to static data [1], the use of refractory materials worldwide in 2025 will be 57 thousand tons. It is predicted that this will be 72 thousand tons in 2030. In recent years, the development of industry in Azerbaijan has significantly increased the demand for refractory materials. The implementation of new projects serving the creation of various industrial sectors in the country creates a stimulus for the development of this sector.

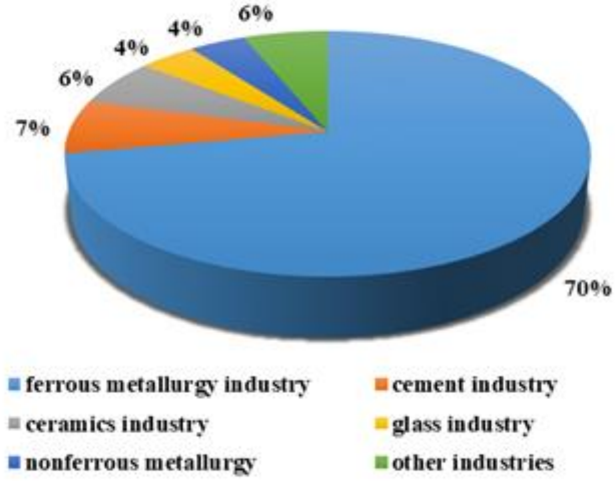

Figure 1. Areas of use of refractory materials

Main Part

Currently, up to 150 primary raw materials and about 100 inorganic substances are used in the refractory materials industry [3]. These raw materials are divided into 3 large groups according to their origin (genesis): natural, synthetic and man-made.

According to the standard (GOST 28874), refractory materials are classified according to the following characteristics: according to their chemical and mineralogical composition; according to their refractoriness; according to their density; according to their purpose; according to the molding method; according to their shape and size.

According to their chemical mineralogical composition, refractory materials are: siliceous, aluminosilicate, aluminate, aluminate-lime, magnesian, magnesian-lime, lime-based, magnesian-spinel, magnesian-silicate, chromium, zircon, oxide-containing, carbonaceous, oxide-carbonaceous, carbide-silicon and oxygen-free.

The chemical composition of most of the listed refractory materials is made up of oxides that are difficult to melt: MgO - melting point 2800^0C; CaO - 2614^0C; Al_2O_3 - 2050^0C; SiO_2 - 17300C; Cr_2O_3 - 2299^0C; ZrO_2 - 2700^0C.

Sometimes these materials can be divided into 2 groups according to the origin of the raw materials: clay-containing and non-clay-containing. The ratio between them is 55.4/44.6%.

By their purpose, refractory materials are divided into refractory (1580 - 1770°C), high-fire (1770 - 2000^0C) and very high-fire (more than 2000^0C) materials.

The classification of raw materials for refractory materials is given in table 1.

Table 1. Classification of raw materials for refractory materials [3]

s/s	Type of refractory material	Types of raw materials according to their origin		
		naturally	synthetic	technogenic waste
1	Silicon-containing, SiO_2	Quartzite, marshallite, quartz, opal, diatamite, quartz sand	Silicate glass (lechatelierite), glass fibers	Microsilica, quartzite slurry
2	Aluminosilicate, $Al_2O_3 \cdot SiO_2$; corundum, Al_2O_3; (Σ(Al2O3 + SiO2) > 70)	Refractory clay, kaolin, topaz, kyanite, andalusite, sillimanite, low-iron bauxite, quartz sand	Tabular corundum, corundum alloy, mullite alloy, aluminosilicate glass fibers	Corundum slurry, pyrophyllite, aluminum oxide powder, alumothermic resins
3	Magnesium-containing, MgO ($MgO \geq 85$)	Magnesite, brucite, hydromagnesite, huntite, bischofite	Periclase	Fumes generated in caustic magnesite production
4	Magnesian-spinelide refractory material, $MgO–Cr_2O_3$, $MgO–Al_2O_3$, $MgO–FeO–Al_2O_3$	Magnesite, chromite, chrome-spinelite, magnochromite, alumochromite	Periclazochromite, spinel, ghersinite	Aluminochrome catalyst (petroleum chemistry), ferrochrome carbon resin
5	Magnesium-silicate refractory material, $MgO–SiO_2$ ($\Sigma(MgO+SiO_2) \geq 60$)	Dunite, olivine, serpentinite, talc, talcomagnesite	Dolomite alloy, dunite alloy, forsterite alloy	Ferrochrome tailings, waste obtained during the enrichment of chrome ore
6	Magnesian-lime refractories, MgO–CaO ($MgO \geq CaO$)	Dolomite, dolomitized magnesite, limestone and chalk	Dolomite alloy	Volatile dusts collected during the extraction of carbide and $Ca(OH)_2$
7	Carbon-containing refractory materials, $C + RO + RO_2 + RO_2 + R_2O_3$ (C = 4÷40)	Graphite, shungite, anthracite, quartz	Artificial graphite, technical carbon	Waste from furnace electrodes
8	Zirconium-containing refractory materials, $ZrO_2–SiO_2$	Baddaleite, zircon	Baddeleyite alloy	Recycling materials
9	Silicon carbide refractories, SiC	uartz, shungite, graphite, coal	Silicon carbide	Gravity discharge of electrodes ($SiC + SiO_2$)

10	Aluminated-lime refractories, Al_2O_3–CaO (CaO = 8÷30)	Limestone, bauxite, chalk	Bonit	Aluminothermic slags
11	Special types of refractories containing oxides, RO, R_2O_3, RO_2	Berill, kassiterit	BeO, Cr_2O_3, Y_2O_3, SnO_2	Recycled refractories, recycled ceramics

Silica-containing refractory materials themselves are divided into groups such as quartz glass, dinas and quartz. The main raw material for refractory materials with this composition is quartzite. The content of SiO2 in quartz glass should be more than 98%, in dinas - more than 93%, and in quartz - more than 85%. As can be seen, the composition of the rock should be sufficiently pure.

The main raw material for silica-containing refractory materials is quartzite. The composition of quartzite mainly consists of SiO2 (quartz, opal and chalcedony). Quartzite rock is formed by metamorphism (change in shape due to high pressure and temperature in the deep layers of the earth). Quartzite is a rock with an average density of 2.68 g/cm3 and a compressive strength of 100-450 MPa.

A quartzite raw material deposit for 2 dinas bricks has been registered in the State Balance of Azerbaijan. These are the Gizilja deposits in the Khanlar region and the Chovdar deposits in the Dashkesan region. Both deposits are in reserve. It should be noted that the chemical and mineralogical composition of these deposits has not been sufficiently studied, and the areas of application have not been investigated. According to preliminary studies, the stones extracted in the Gizilja deposit are plagioporphyry rocks. This rock is of volcanic origin, and its composition includes quartz, plagioclase and amphibole, pyroxene minerals. Sometimes mixtures of biotite and magnetite are also found in its composition.

The quartzite of the Chovdar deposit has also not been sufficiently studied. According to the information of "AzerGold" CJSC [4], it is noted that only this deposit consists of derived quartzites of the Upper Biagio age, that is, mineralization occurred mainly within quartzite - highly metamorphosed quartz-rich rocks. As a result of hydrothermal processes, barite, gold and copper sulfide deposits are also found in the rocks belonging to the deposit (there are gold and copper deposits in Chovdar). According to preliminary studies [5], the amount of gold in some parts of the deposit varies significantly. It is on average at the level of 8-10 g/t. Therefore, the use of quartzite from this deposit as a raw material for dinas bricks is not yet relevant. As a result of studying the mineralogical composition of the rock of the Chovdar deposit, it was determined that, in addition to gold, the rock contains quartz, limonite, hematite and other minerals.

The main raw material for magnesian refractories (magnesian-lime, magnesian-spinel, magnesian-silicate) is magnesite rock. The refractoriness of magnesian materials is higher than others (the melting point of MgO is 28000C). However, according to static data and the list of "Minerals of Azerbaijan", magnesite deposits have not been registered in the territory of Azerbaijan. Therefore, the organization of the production of magnesian-containing refractories is not considered promising.

The main raw materials for aluminosilicate-containing refractory materials (aluminosilicate, aluminate, aluminate-lime) are refractory clays. These clays are called kaolin clays due to their mineralogical composition. The most widely used refractory materials in this group are chamotte and mullite refractory materials.

Raw materials for aluminosilicate-containing refractory materials are available on the northeastern slopes of the Lesser Caucasus in the territories of Khanlar, Dashkasan and Gazakh regions in Azerbaijan. Preliminary exploration work has been carried out on the Kotandagh clay deposit in the Gazakh region and on the Chanlibelgil deposit in the Shamkir region, and the reserves of the deposit have been calculated. According to the studies conducted, the rock of this deposit mainly consists of kaolinized clays. The Khoshyal kaolin deposit in the Shamkir region has been studied in recent years and its use in the production of refractory materials has been recommended. According to preliminary studies conducted by the staff of the Department of Materials Science of the Azerbaijan University of Architecture and Construction, the amount of kaolinite mineral in the rock of the Kotandağ deposit is 39.8%. It is known that clays containing more than 23% kaolinite can be used as raw materials in the production of refractory materials (chamotte bricks) [6]. The staff of the department also studied the chemical and mineralogical composition of the Chanlibel deposit, and it was found that the amount of kaolinite mineral is 38%. Therefore, Kotandağ clay and Chanlibel clay are high-quality raw materials for the production of refractory bricks.

Since refractory materials are mainly made from natural raw materials, the raw materials are not ready for the production process. Raw materials are subjected to a number of complex processes, such as extraction from quarries, transportation, crushing, grinding and enrichment. During the production of aluminosilicate refractory materials, refractory clays and other natural raw materials are first crushed in clay rollers. Then, they are finely ground in mills and collected in bunkers, raw materials and materials are dosed and mixed and sent to the molding unit. Refractory bricks are usually molded in 2 ways: by plastic method and by pressing method. Molded products are subjected to a drying process. The product is dried at a temperature of 80-2000C. The drying temperature is selected according to the molding mode of the product. During the drying process, a decrease in volume (drying-shrinkage) occurs as water is separated from the material. During drying, 65-75% of the moisture in the material evaporates. During drying, the physically and mechanically bound water in the material is released, and the product gains a certain degree of strength.

The most important indicators of refractory materials, namely, fire resistance, density and strength, increase during the burning of the material. This is due to the occurrence of complex physical and chemical processes. The burning mode of refractory aluminosilicate materials is selected depending on the composition of the raw materials, the size and shape of the product. The burning process in this type of materials is usually divided into 3 stages: heating, holding at high temperature and cooling.

Since the main raw material for refractory materials such as fireclay bricks is kaolin clays, the processes occurring during combustion in these types of clays are of great importance. The mineral that affects the main phase formation process is the kaolinite mineral. The following processes occur in the kaolinite mineral during combustion: an endothermic effect is observed in the range of 450-6000C; three are observed at 900-950^{0}C, 1150-1300^{0}C and 1210-1320^{0}C. The endothermic effect occurs due to the dehydration of kaolinite. According to the authors, metakaolin is formed during the dehydration of kaolinite [7].

Most researchers believe that metakaolin is an intermediate phase in the process of kaolinite being heated to form mullite.

$$Al_2O_3{\cdot}2SiO_3 \cdot 2H_2O \rightarrow Al_2O_3{\cdot}2SiO_2 + 2H_2O$$

or

$$Al_2[Si_2O_5](OH)_4 \rightarrow Al_2[Si_2O_7] + 2H_2O$$

Unlike the endothermic effect, the first exothermic effect occurs in a very small temperature range (900-950^{0}C). There are 2 different opinions about the cause of this exothermic effect. Some note that γ - Al_2O_3 is formed in the indicated temperature range. The formation of the second exothermic effect (1150-1300^{0}C), according to researchers, is associated with the formation of mullite. It is also believed that cristobalite is formed at this time. The third exothermic effect is associated with the completion of the crystallization of mullite and cristobalite.

$$3(Al_2O_3 \cdot 2SiO_2) \rightarrow 3Al_2O_3 \cdot 2SiO_2 + SiO_2$$

The production technology of Dinas brick is as follows: quartzite rock is ground to a size of 0.1-5 mm, 3-5% lime is mixed with quartzite to form milk of lime, molded and burned in tunnel-type kilns. The maximum burning temperature of Dinas brick is 14500C. In order to obtain high-quality Dinas brick, it is necessary to approach the burning process with special sensitivity. The process of increasing the temperature should be carried out very slowly, especially during the transition of quartz from one form to another. Because at this time a liquid phase is formed in the system, which fills the gaps between the quartz crystals and relieves the tension. When the temperature is increased rapidly, the amount of liquid phase is less. The refractoriness of Dinas brick should be higher than 1640^0C.

Conclusion

Therefore, as a result of the analysis, it can be concluded that Azerbaijan has a raw material base for refractory materials such as fireclay bricks and Dinas bricks. Since magnesite rocks are not found in the country, the production of magnesian refractory materials is not considered relevant. In recent years, the creation of Industrial Parks and the opening of new industrial enterprises in all regions of the country have increased the demand for refractory materials, which are one of the important materials for the construction of such enterprises. The demand for refractory materials necessitates the development of theoretical and scientific foundations for the production of these materials.

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