PRODUCTION OF FINE-GROUND NK-Alumina 11 AND NK-Alumina 14 FOR LOW-CEMENT REFRACTORY CASTABLES

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This article characterizes fine-ground NK-Alumina 11 and NK-Alumina 14 developed in PKF "NK" for low-cement refractory castables. The quality indicators of the developed aluminas are not inferior to international analogs.

Keywords: unshaped refractories, alumina, microsilica, low-cement refractory castable (LCRC).

Current development trend in the refractory industry comprises an increase in the production volume of low-cement refractory castables (LCRC) due to a decrease in energy, material, and labor costs in their manufacturing. The advantages of LCRC include a low CaO content and an efficient structure, increasing the service life of the lining of thermal units for various purposes.

The matrix part of LCRC usually includes components such as calcined and/or reactive alumina, microsilica, high-alumina cement, deflocculating agents, and additives for adjusting the setting time, as well as a fine-dispersion filler. Thus, LCRC, in contrast to traditional concrete (CaO > 3.5%), contains a deflocculating agent and a highly dispersive component (>2% of submicron particles in castable) [1]. The presence of highly dispersive powders (reactive alumina and microsilica) in the LCRC composition increases the particle packing density. This causes an increase in the castable density, a decrease in porosity, and an increase in the proportion of small pores (the latter is especially important).

The key current suppliers of highly dispersive materials for LCRC are international companies such as Almatis, www.almatis.com (reactive alumina), Nabaltec, www.nabaltec.de (reactive alumina), and Elkem, www.elkem.com (microsilica). In some Russian industries, microsilica is formed during the cooling and filtering of furnace gases while producing metallic silicon, ferrosilicon, and other silicon alloys in electric arc furnaces. Microsilica collected from gas cleaning systems is widely used for producing building materials, binders, and modifiers to build concrete. Attempts to use Russian microsilica in LCRC replacing imported microsilica have not become widespread [2]. Russian reactive alumina is currently produced only by the Borovichi Refractory Plant.

In LCRC, microsilica, in contrast to reactive alumina, affects its phase composition after hardening. According to Boris (2014) [3], the main products of high-alumina cement hydration are crystalline hydrate CAH_{10}, which is formed at temperatures below 21°C, crystalline hydrate C_2AH_8, and amorphous AH_3 (21 – 35°C), as well as crystalline hydrates C_3AH_6 and AH_3 (>35°C). Crystalline hydrates CAH_{10} and C_2AH_8 are metastable and are converted into C_3AH_6 and AH_3 depending on different conditions (e.g., temperature and water-cement ratio). During concreting in winter conditions, mainly CAH_{10} hydrates are formed, whereas C_2AH_8 and C_3AH_6 are formed in summer conditions. In the presence of microsilica, the CASH phase is formed in addition to the above hydration products.

When using microsilica, the refractoriness and corrosion resistance of LCRC are reduced. Therefore, in recent years, microsilica is replaced by alumina [4]. At high temperatures, LCRC based on a matrix of alumina outperform microsilica concretes in terms of ultimate strength during bending in a hot state. Only an alumina matrix can provide sufficient concrete strength above 1500°C. Even a small SiO_2 content in concrete (only approximately 0.5%) negatively affects high-temperature strength. This is especially factual in the production of critical concretes exposed to erosion and me-

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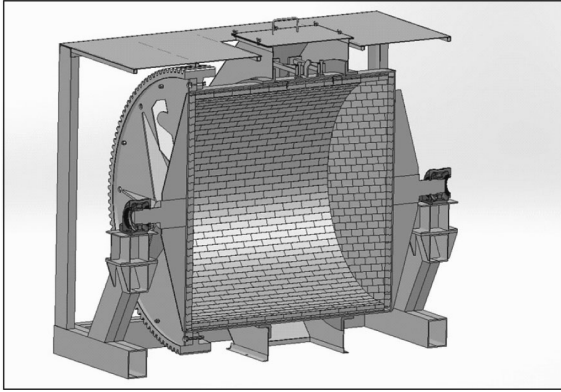[3] zroman7777@mail.ru

Fig. 1. Discontinuous dry grinding ball mill of PKF "NK."

chanical stress at high temperatures. Under these conditions, only an alumina matrix seems to be the only solution [5].

In the mid-temperature region (600 – 1600°C), the highly active products of the binding LCRC destruction undergo deep phase and structural transformations taking place in the solid state and aimed at the approximation of the heterogeneous composition to the chemical and physical equilibrium with temperature. The most important physical and chemical processes in this temperature range are concrete sintering and the recrystallization of mineral phases, which determine the formation of a crystalline intergrowth and a ceramic structure of the material. When using a matrix based on the reactive alumina above 1300°C, a high-temperature compound CA_6 is formed (melts incongruently at 1850°C). The CA_6 yield is determined by the alumina content. When using high-alumina cement (>70% Al_2O_3), the alumina content in the matrix should be 2.5 times higher than that of cement for the complete transition of CaO to CA_6. In concretes based on chemically pure raw materials, CA_6 is formed owing to the solid-phase interaction with the formation of a strong crystalline intergrowth among particles [5 – 7].

Reactive alumina refers to the alumina fully ground to the primary crystal d_{50} of 0.6 to 3.3 μm and having a mono-,

bi-, and multimodal distribution [4]. The raw material for its production is anhydrous alumina. In the industry, one of the most common methods for producing anhydrous alumina is the Bayer wet process. Sodium aluminate is extracted from bauxite using an alkaline solution from which the aluminum hydroxide is precipitated. Anhydrous alumina is obtained via calcination [8, 9].

The existence of α-, β-, and γ-Al_2O_3 forms has been established in several crystalline modifications of alumina, and only α- and γ-forms are considered pure alumina. β-Al_2O_3 is essentially a compound of the type $R_2O \cdot 11 – 12Al_2O_3$ (R is Na or K) and $RO \cdot 6Al_2O_3$ (R is Ca, Ba) formed during electric melting (slow cooling) or the recrystallization of corundum in the presence of impurities [8]. α-Al_2O_3 has crystals in the form of rhombohedrons and represents a white powder with a particle size of 10 – 60 μm in the form of porous spherulites. The NK-Alumina 11 and NK-Alumina 14 developed at PKF "NK" were obtained through the dry grinding of this material and contain at least 90% and 95% of α-Al_2O_3, respectively (Table 1).

Notably, ground alumina contains underground porous agglomerates. However, spherulites comprising individual crystals of Al_2O_3 absorb a part of gauged water and therefore affect the rheology of concrete. Consequently, when placing concrete, adding extra water to impart the necessary molding properties is essential [10]. Extremely fine grinding can be obtained using surface-acting agents (SAA). The experience of grinding alumina under production conditions showed that grinding with SAAs enabled an increase in its specific surface area by 25 – 28%. When the initial alumina is ground, its spherulite structure is destroyed. The surface of new particles formed during grinding adsorbs SAAs, thereby eliminating their aggregation. Further, SAAs penetrate into material microcracks and thereby reduce the resistance of alumina to grinding (wedging stresses appear in microcracks). Fine and ultrafine mechanical grinding is performed in various devices, i.e., in ball, planetary, vibration, or jet mills and attritors (www.eirich.com, www.netzsch.com) [11]. The sim-

TABLE 1. Characteristics of the Bimodal Alumina Developed by PKF "NK" and Some of Their International Analogs

Alumina brand	D_{50}, μm, maximum value	D_{90}, μm, maximum value	Specific surface, cm²/g, minimum value (laser diffraction)	Content of α-Al_2O_3, not less than, %	Chemical composition, wt.%			
					Al_2O_3, maximum value	SiO_2, maximum value	($Na_2O + K_2O$), maximum value	Fe_2O_3, maximum value
NK-Alumina 11 (PKF "NK")	3.3	10	11000	90	99	0.12	0.3	0.03
NK-Alumina 14 (PKF "NK")	2.5	5.5	14000	95	99	0.03	0.3	0.03
CL 370* (Almatis)	2.5	—	3.0 m²/g (BET)	—	—	—	0.1	—
E-SY 1000* (Almatis)	1.7	—	2.0 m²/g (BET)	—	—	—	0.2	—
NO 615 – 30* (Nabaltec)	2	—	5.0 m²/g (BET)	96	99.6	0.05	0.2	0.03
NO 625 – 30* (Nabaltec)	2	—	3.0 m²/g (BET)	96	99.7	0.05	0.1	0.03

* Parameter values given by the manufacturer are indicated.

plest device is a ball mill, which explains the choice of this grinding unit (Fig. 1). The technical characteristics of the mill of the PKF "NK" are presented below:

Productivity, kg/day . . . . 450 – 700
Specific power consumption, kW·h/kg . . . . 1.6 – 2.0
Electric motor power, kW 37
Drum volume (with lining), m^3 . . . . 3.1
Lining and grinding media material . . . . Corundum

When the mill rotates, the grinding bodies rise along with the drum in the direction of rotation until the force of gravity exceeds the sum of all other forces acting on the body. After reaching the critical height, the grinding bodies roll down and grind the material, rubbing the material against the surface of the lining or other balls, or crushing the material with impacts when falling. To eliminate the contamination of the ground material, corundum lining and corundum grinding bodies were used. Experience has demonstrated that the intensity of its grinding is influenced by technological parameters such as the rotational speed of the mill, number and shape of grinding bodies, weight of the material loaded for grinding, and duration.

The following classification of powdery materials is often used:

– ultrafine powders are 1 – 100 nm;
– finely dispersed powders are 100 nm to 10 μm;
– medium dispersed powders are 10 – 200 μm;
– coarse powders are 200 – 1000 μm [12].

Considering this classification, the developed alumina powders can be classified as finely dispersed. This approach to the name of the developed materials well characterizes their dispersion ability.

According to Schnabel, et al. [5] and Kashcheev [13], materials with a wide particle size distribution (bi- and multimodal distribution) are characterized by a denser packing than materials with monomodal grain distribution. NK-Alumina 11 ($d_{50} < 3.3$ μm) and NK-Alumina 14 ($d_{50} < 2.5$ μm) have a bimodal distribution and comprise a submicron fraction (μm) in an amount of 15 – 20% and 25 – 30%, respectively. High-alumina cement grains used for LCRC (e.g., Secar-71) are known to have d_{50} of 10 – 15 μm and d_{90} of 45 – 50 μm. Considering the grain composition of the matrix components (alumina and high-alumina cement), it can be observed that the developed alumina completes the binder granulometry, thereby providing a high level of the performance properties of concretes based on them.

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