Low-Alkaline Fine Alumina for Ceramic Industry

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Abstract

Borovichi Refraktories Plant (BKO) was fulfilled experiments for the study of the properties and search for method of processing alumina and aluminum hydroxide to produce fine alumina with the highest content of alpha-phase, free from impurities of metal iron, with a minimum content of sodium oxide. Was developed by method for producing and creating alumina with a low (less than 0.08 %) content of alkaline oxides, high dispersion (average particle size of 1.2-1.3 microns, the maximum size of no more than 4 microns), chemically pure (Al_2O_3 content of more than 99.5 %) and phase purity (alpha phase content in the crystalline phase of more than 99 %), designed for the production of corundum technical ceramics, fully consistent with imported reactive alumina brand CT 1200 SG manufactured by Almatis.

Keywords: Alumina, chemical purity, phase purity, alpha phase Al_2O_3, grading, corundum technical ceramics

1. Introduction

In the manufacture of corundum ceramics for special purposes, it is necessary to use the original alumina of a high degree of dispersion (average particle size 1.2-1.3 microns, maximum size no more than 4 microns) and purity: both phase (alpha phase content more than 99 %) and chemical (Al2O3 content more than 99.5 %). This significantly limits the content of alkaline oxides (Na2O – not more than 0.08 %), in out-beanie the formation of the glass phase, iron oxide (Fe2O3 – not more than 0.08 %) and other under-impurity oxides: SiO2 – not more than 0.08 %, CaO – not more than 0.04 % and MgO not more than 0.07 %, the content of which significantly affects the content of the main phase of corundum, due to the formation of new phases in the synthesis of multicomponent compounds. Due to the fact that the domestic industry does not offer such an alumina material, ceramic manufacturers, as a temporary measure, use imported reactive alumina. Development of BKO to obtain low-alkaline fine alumina for the ceramic industry was carried out within the framework of the import substitution program.

2. Development of the Method of Obtaining

The use of alumina hydrates (mono - trihydrate) and metallurgical alumina was tested as starting materials. Metallurgical alumina has the least losses during calcination, its use is recognized as the most acceptable. The use of Al_2O_3 phase transition mineralizers in the alpha form is recognized as inappropriate due to the high chemical purity requirements for the product. High-temperature firing of the initial metallurgical alumina is the only "clean" method for producing corundum. Several well-known methods for producing high-calcined alumina were tested: firing in a rotary kiln, firing a powdered product in a special muffle in a tunnel kiln, firing a briquetted pre-crushed to a fraction of less than 0.063 mm. the First two methods, according to the results of the production of pilot batches, were rejected due to the low yield of a suitable product: in a rotary kiln, high losses with a dust-carrier, in a Tunel kiln, a low yield of α-Al_2O_3.

3. Elimination of Metal Iron

Grinding of alumina in a vibratory mill with steel lining and steel grinding media, used for the production of refractories, leads to grinding of metal iron, from which it was necessary to get rid of.

The use of magnetic separation, as shown by the practice of its use, has not led to the disposal of ground iron, although it reduces its content.

To solve this problem, it is necessary, as shown by the experimental work performed by the BKO Central Plant's Laboratory (CPL), the use of special equipment:

- mill lining with a special material that excludes contact of the milled material with the inner metal surface of the vibrator body. For this can be used: polyurethane or corundum plates (tiles).
- the use of corundum grinding media.

The carried-out work showed that the application of the corundum lining the inner surface of the vibratory mill and corundum grinding bodies eliminate the presence of metallic iron in the form of free grinding of the finished product.

4. Development of a Method of Purification from Excess Alkaline Oxides

The most suitable for the manufacture of special corundum ceramics is low-alkaline alumina grade GN according to GOST 30559-98 with a normalized limit of alkaline oxides of 0.1 %. This type of alumina is not produced in Russia. Metallurgical alumina grades G-00 and G-0 according to GOST 30558-2017, contains 0.2 to 0.5 % alkaline oxides. Therefore, additional chemical cleaning is required to reduce the content of these oxides.

The following methods of purification of alumina and alumina hydrate from excess sodium oxide were tested:

- Flushing of ground technical alumina or aluminum hydrate with azeotropic ethyl alcohol in a propeller stirrer;
- Wet grinding of technical alumina or aluminum hydrate in an azeotropic ethyl alcohol mixture;
- Treatment with hydrochloric acid of technical alumina or aluminum hydrate with post-blowing treatment of the dissolution product with ammonia water, isolation and calibration of aluminum hydroxide.

Laboratory testing of methods did not lead to positive results. Reduction of sodium oxide is not observed.

In addition, two more cleaning methods were tested for testing:

- Method of purification of alumina hydrate with hot water during grinding.
- Method of purification of crushed pre-annealed alumina with hot water.

Testing of the first of the additional methods was carried out on the equipment of the experimental-technological line of LLC "Functional materials". The results are shown in table 1. A 1.7-fold decrease in the sodium oxide content was achieved.

Table 1. Results of chemical analysis of aluminum hydroxide after washing from sodium oxide with hot water and hot water with boric acid addition during grinding in a bead mill.

Material	Method	Al_2O_3	Fe_2O_3	SiO_2	CaO	MgO	Na_2O
The hydrate of aluminum oxide – source		96,70	0,19	1,67	0,11	1,13	0,23
Aluminum oxide hydrate - hot water wash	1	96,80	0,03	1,10	0,10	0,82	0,13
Aluminum oxide hydrate – washing with hot boric acid solution	2	98,20	0,01	0,60	0,43	0,55	0,16

Testing of the second – in the laboratory of chemical analysis of CPL JSC "BKO". Table 2 shows the results of testing the method.

Table 2. Results of chemical analysis of alumina GRT after washing of sodium oxide by boiling in the distillate.

Material	Al_2O_3	Fe_2O_3	TiO_2	SiO_2	CaO	MgO	Na_2O	K_2O
Reactive alumina grade GRT– source	99,50	0,05	0,001	0,03	0,05	0,08	0,28	0,01
Washing with distillate. 6-times boiling. 1st experience	99,70	0,017	0,001	0,024	0,04	0,063	0,161	0,005
Washing with distillate. 6-times boiling. 2nd experience	99,60	0,022	0,001	0,030	0,023	0,081	0,191	0,021
Washing with distillate. 12 times boiling in the 2nd experiment	99,70	0,023	0,001	0,028	0,022	0,081	0,145	0,021
Washing with distillate. 18 times boiling in the 2nd experiment	99,70	0,020	0,000	0,020	0,020	0,060	0,150	0,010

Tests of the methods of washing the burnt crushed alumina and alumina hydrate with hot water during grinding showed a positive result – almost a two-fold decrease in the content of sodium oxide.

The method of washing with hot water pre-annealed and crushed alumina reactive GRT gave the best of all the tested methods the result. It was decided to use it in the production of the pilot batch.

5. Production of Pilot Batches

To confirm the developed method, two experimental batches of alumina with special requirements were produced. The results of the pilot batches are shown in table 3. All indicators meet the requirements for low-alkaline alumina for the production of corundum ceramics for special purposes.

Table 3. The Results of the production of experimental batches of alumina.

Date	Place of Manufacture	Manufactured alumina Properties Name	Value	Required Value	Degree of compliance	Shipment
Sept. 2018	CPL Tunnel Furnace, Vibratory mill grinding with corundum lining and grinding bodies	Chem. cont., %				Shipped 400 kg
		Al_2O_3	99,7	more 95	executed	
		Fe_2O_3	0,02	no more 0,03	executed	
		SiO_2	0,01	no more 0,08	executed	
		CaO	0,04	no more 0,04	executed	
		MgO	0,05	no more 0,07	executed	
		Na_2O	0,08	no more 0,08	executed	
		Content of alpha-Al_2O_3	99,0	more 99	executed	
		D_{50}	1,25	1,2-1,3	executed	
		D_{90}	2,99	no more 3,6	executed	
Oct. 2018	CPL Tunnel Furnace, Vibratory mill grinding with corundum lining and grinding bodies	Chem. cont., %				Shipped 200 kg
		Al_2O_3	99,7	more 95	executed	
		Fe_2O_3	0,01	no more 0,03	executed	
		SiO_2	0,01	no more 0,08	executed	
		CaO	0,02	no more 0,04	executed	
		MgO	0,04	no more 0,07	executed	
		Na_2O	0,0.	no more 0,08	executed	
		Content of alpha-Al_2O_3	99,2	more 99	executed	
		D_{50}	1,30	1,2-1,3	executed	
		D_{90}	2,99	no more 3,6	executed	

6. Summary

As a result of the study, was developed a method of obtaining and creating a special. alumina with low (less than 0.08 %) content of alkaline oxides, high dispersion (average particle size 1,2-1,3 microns, maximum size no more than 4 microns), chemically pure (Al_2O_3 content more than 99.5 %) and phase purity (alpha-phase content in the crystalline phase more than 99 %), fully corresponding to imported reactive alumina of CT 1200 SG brand manufactured by Almatis.

According to the developed method, technological documentation has been compiled, and technical conditions for the developed product.