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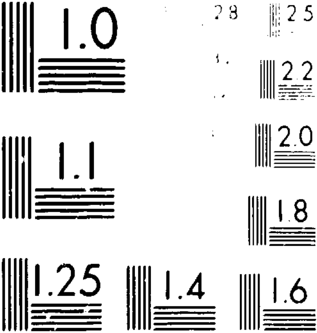
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MANUFACTURE OF HIGH ALUMINA PRODUCTS

Basic Information*

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ABSTRACT

Following the request of Messrs. Industrial Ceramics, Hyderabad, India, through UNIDO Headquarters Vienna, for an information on high alumina products manufacture, this paper was elaborated by the UNIDO-Czechoslovakia Joint Programme for International Co-operation in the Field of Ceramics, Building Materials and Non-metallic Minerals Based Industries in Pilsen. It presents the main principles of the manufacture of high alumina refractories usable at temperatures 1700 - 1800°C. The classification and characteristics of high alumina products are also presented. The production of each type of grog is described from initial raw materials, including the applied equipment, to properties of various grogs and advantages of some productions. The process of crushing and grinding of grogs is mentioned as well as the production of special bricks starting from mixing and composition of working blends to firing in kilns. Finally, the characteristic qualities of high alumina bricks are presented.

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I. INTRODUCTION

High alumina refractories usable at temperatures up to 1700 - 1800°C are manufactured on the base of mullite or corrundum grogs from very pure raw materials. The technical aluminium oxide and quality refractory clays or kaolins with a low content of impurities are used as the basic raw materials instead of natural raw materials as sillimanite, kyanite or bauxite. The grogs are produced either by electro-melting or by sintering of raw materials.

Electrically melted mullite and corrundum are produced in arc furnace, the temperature of melting being 1900 - 2000°C for mullitic grog and 2000 - 2200°C for corrundum grog. The principal difference between the electrically melted and sintered grogs is in the size and orientation of mullitic or corrundum crystals. Some advantages can be seen in the use of sintered grogs for the production of high alumina refractories in comparison with electrically melted grogs. Beside the constant volume in heating, the sintered grogs are characteristic by sufficient reactivity since their surface has a lot of small unevennesses which enable their binding with fine dispersed binding component. The grains of electrically melted grogs are on the contrary characteristic by smooth surfaces which form the bindings among grains during firing of products with difficulties.

The qualities of high alumina refractories manufactured on the basis of electrically melted grogs are lower than the qualities of materials produced on the basis of sintered grogs, especially as far as the bulk density and thermal shock resistance are concerned.

II. PRODUCTION OF SINTERED GROGS

Beneficiation of Raw Materials

Technical Aluminium Oxide

The technical aluminium oxide, containing 99.0 - 99.5% of Al_2O_3 is used in the production of mullite and corrundum grogs. The technical aluminium oxide is from the mineralogical point of view γ - modification in the state of transformation to the α modification containing residues of aluminium oxide hydrate (hydrargillite and boehmite). The particles of γ - Al_2O_3 form porous spherolites with diameter 20 - 70 μm. This structure causes the difficulties in recrystalizating sintering and blocks the mutual reaction of α -Al_2O_3 with SiO_2 during the creation of mullite. Therefore, it is not possible to obtain compact grog from non-beneficiated technical aluminium oxide. Preliminary fine grinding of aluminium oxide forms the necessary condition for its utilization during the manufacture of refractories of high density. The aluminium oxide is ground in drum mills, ball tube mills or vibrating mills. Grinding in drum or ball mills has low efficiency and high fineness of grist is difficult to reach. The vibrating mills are therefore used being able to reach high dispersity of grist. Ground aluminium oxide should contain 65 - 75% of particles under 2 μm. The amount of added iron by dry grinding in vibrating mill with iron grinding cells is negligible (0.05 - 0.1%). The grist must be demagnetized to remove occassional fragments of grinding cells.

Kaolin, Clay

The refractory clay or kaolin is added to the fine ground aluminium oxide during the production of mullite grogs in such an amount to obtain 72 - 74% of Al_2O_3 in fired grog. The clays are desintegrated in the clay shredder, dried in drum drier to the humidity under 5 or 1% (depending on the type of grog production) and ground under 0.5 mm. The kaolin used is dried and washed.

Production of sintered corrundum grog

The briquettes are prepared from fine ground aluminium oxide by mixing with water and bonding agent which secures the strength of briquettes after drying. Either sulphite liquor is used as a binder in the amount of 1 - 1.5% of dry mixture or 1.5% solution of methyl cellulose in the amount of 6 - 8% in the mixture. Depending on the way of briquettes manufacture and the type of technical aluminium oxide used, the relative moisture content alternates from 8 to 18%. The blend is mixed in a two-axes blender. Depending on the type of firing, either briquettes or standard shapes are pressed. Dried briquettes are fired in rotary kilns at temperatures 1900 - 1950 ^{o}C for 1 - 3 hours. Standard shapes are fired in lowprofiled tunnel or hood-type kilns at temperatures 1880 - 1900 ^{o}C with longer firing cycles.

The properties of corrundum grogs of three different products are presented at table 1.

Production of sintered mullite grog

Fine ground aluminium oxide and ground dry plastic refractory clay or washed kaolin with Al_2O_3 content minimally 40 - 42% and with low content of Fe_2O_3 and alkalies at least under 2% are the initial raw materials for the production of sintered mullite grog. An important precondition of the production of sintered mullite grog with homogenous structure

Table 1: The Properties of Sintered Corrundum Grogs

type of corrundum / component/property /%/	Tabular Al_2O_3 /USA/	Sintered corrundum /Japan/	Sintered corrundum /USSR/
Content			
Al_2O_3	above 99.5	99.5 - 99.6	99.1 - 99.5
SiO_2	up to 0.06	0.06 - 0.14	0.04 - 0.16
Fe_2O_3	up to 0.06	0.05 - 0.09	0.06 - 0.16
Na_2O	up to 0.1	0.11	0.1 - 0.25
Apparent porosity	**below 10**	**2.5**	**below 7**
Bulk density $g.cm^{-3}$	3.65 - 3.8	3.7	3.6 - 3.7

is a perfect homogenization of raw materials. The initial components are mixed in a ratio securing the Al_2O_3 content in grog 72 - 74%. The mixing is done either in high-speed muller with partially increased moisture content of mixture to about 10% or in ball tube or drum mill. Homogenized blend is moistened in two-shaft blender to relative moisture content 20 - 23% with addition of 0.5 - 1% of binder (sulphite liquor or methyl cellulose). The briquettes or standard shapes are extruded from moistened blend in a vacuum pug. The briquettes are predried and fired in a rotary kiln at the temperature 1700 - 1750°C. The standard shapes are dried to the relative moisture content under 2% and fired in tunnel or hood kilns at the temperature round 1700°C. The disadvantage of rotary kilns is the low degree of mullitization and non-stable density of good fractions of grog. Moreover, a considerable amount of flue dust occurs during firing of grog in rotary kilns. Grogs fired in tunnel or hood kilns on the contrary have stable density with good degree of mullitization and no problems with a flue dust occurrence.

Table 2 presents the qualities of mullite grogs of four producers with different ways of homogenization of initial raw materials and different ways of firing.

Crushing and grinding of grogs

Sintered grogs are difficult to crush and grind due to their high strength and hardness. They cause considerable abrasion of grinding equipment. Jaw crushers are used for crushing, tapeled granulators for grinding. The ball tube and vibrating mills are used for grinding of fine fractions. A ground grog is usually separated to fractions 2 - 3 mm (2 - 5 mm), 0.5 - 2 mm and under 0.5 mm. The iron must be eliminated from all fractions by electromagnetic separation to reduce the iron content under 0.1%.

Table 2: The Properties of Mullite Grogs

Producer / Component/ property /%/	Mullite Corporation /USA/	Cawood /Great Britain/	PM /Poland/	Mullite II /Czechoslovakia/
Content				
Al_2O_3	71	73	72.5 - 73.5	72
Fe_2O_3	1.4	0.53	0.5 - 0.9	1.4
TiO_2	3.0	0.15	0.3 - 0.4	1.2
Na_2O+K_2O	0.05	0.9	0.4 - 0.7	1.3
Apparent porosity /%/	-	3	4 - 8	8.4
Bulk density /$kg.m^{-3}$/	2 850	2 850	2 650 - 2740	2 750
Mullite content /%/	-	92.8	86 - 95	70 - 74
Corrundum content /%/	-	4.4	3 - 8	12 - 20
Method of homogenization	-	common grinding in ball tube mill	in blunger, mixing of blunged kaolin with Al_2O_3	high speed mixer
Firing	rotary kiln	tunnel kiln	rotary kiln	tunnel kiln

A part of fine grog under 0.5 mm is ground in ball tube or vibrating mills to fineness under 60 µm or 90 µm. This portion is used as a bond or its part in operating blends.

III. PRODUCTION OF SPECIAL BRICKS

Composition and Mixing of Operating Blends

The mullite corrundum materials with Al_2O_3 content 80 - 90% can be produced by the use of mullite and corrundum grogs, for example combinating corrundum grog with mullite bond. The density of products can be influenced by mutual ratio of coarse and fine fractions of grog and bond. The maximum grain size of grog is 2 - 3 mm for corrundum products and 3 - 5 mm (depending on the size of products) for mullite or mullite-corrundum products. The amount of fine portions of grog and bond should not exceed 45% in working blends as their higher content causes difficulties in pressing (cracks).

The optimal grain size distribution for a corrundum working blend is as follows:

45% of grog	0.5 - 3 mm (0.5 - 2 mm)
10% of grog	0.06 - 0.5 mm
45% of bond	under 0.06 mm

The fine ground corrundum grog under 0.06 mm or the mixture of fine ground grog and ground technical aluminium oxide are used mostly as a bond.

The optimal grain size distribution for mullite and mullite-corrundum working blends:

50% of grog	0.5 - 3 mm (0.5 - 5 mm)
10% of grog	0.09 - 0.5 mm
40% of bond	under 0.09 mm

The mixture of fine ground mullite grog with washed kaolin, fine ground clay or mullite mixture (original mixture for production of grog) is used mostly as a bond.

Mixing is done by ordinary method in high speed mixers. Relative moisture content of working blends fluctuates from 3 to 6%, depending on the porosity of grog. The carboxyl methyl cellulose or 0.5% of sulphite liquor are added to working blends to increase the strength of green bricks.

Shaping and Drying of Products

High alumina products are shaped by dry pressing on hydraulic or friction presses by the pressure 60 - 100 MPa. The pressing should be double-action one with deaeration and it is necessary to reach high density of pressings. Complicated shapes can be prepared by manual ramming with the use of pneumatic hammers.

The isostatic pressing can be applied successfully in manufacture of corrundum products. It enables to use high pressures 150 - 200 MPa for pressing products from fine grain working blends.

Pressings made by dry method are permeable enough and cause no difficulties during drying which can be therefore intensive. Pressings are dried in tunnel driers mainly.

Firing

Products with high content of aluminium oxide are fired in tunnel or hood kilns. The height of setting alternates prevalently from 0.6 to 1 m. The products are fired at high temperatures and higher setting would cause deformation of lower parts of the setting. Firing temperature depends on the type of fired products. This dependency is expressed in table 3.

Table 3: Firing Temperature of Special Bricks

Type of Bricks	Firing Temperature /°C/
mullite	1580 - 1620
mullite-corrundum	1650 - 1700
corrundum	1750 - 1850

The average temperature rise during preheating is 30 - 35°C/h, the average temperature decline during cooling 55 - 60°C/h. The holding time at maximum temperature is determined by the firing temperature and by the type and size of fired bricks. It alternates from 5 to 10 hours.

Typical Properties of High Alumina Products

Table 4: Properties of High Alumina Special Bricks

Property	Type of bricks		
	mullite	mullite-corrundum	corrundum
Content /%/			
Al_2O_3	69-73	80-85	99
SiO_2	-	-	-
Fe_2O_3	0.8-1.2	0.8-1.2	-
Apparent porosity /%/	16-22	16-22	14-18
Crushing strength /MPa/	40-80	50-80	70-100
Refractoriness under load 0.2 MPa /°C/	1600-1650	1650-1700	1700

IV. FINAL NOTE

The UNIDO-Czechoslovakia Joint Programme in Pilsen was requested by Messrs. Industrial Ceramics, Hyderabad, India, through UNIDO Headquarters Vienna, for the information concerning the manufacture of high alumina products. The publication was elaborated on the basis of this request since this subject can be the matter of interest of other developing countries intending to expand their production of refractories in this field.

The high alumina products represent special refractories, usable at the temperatures up to 1800°C. For a country with necessary raw material reserves, these products can become an interesting object for export. On the other hand, a large experience in production of refractories is required to meet all the necessities of high alumina products manufacture.

The paper presents the principles of high alumina products manufacture. The UNIDO-Czechoslovakia Joint Programme is ready to assist to any developing country in case a more detailed information is requested.

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