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THE ENRICHMENT OF THE METAL GRADE ALUMINA TO α-Al_2O_3 MODIFICATION

The investigation on the production of special alumina from the metal grade alumina for ceramic industry was presented. Calcination experiments of the metal grade alumina were carried out with simultaneous addition of the different types of mineralizers. Basing on these results, a new method for enriching metal grade alumina was elaborated and industrially applied in Groszowice Alumina Plant for the production of the special alumina. Resultant special alumina exhibited physicochemical properties typical of ALCOA Alumina CL3000 or A15 and A3500. The economic analysis shows that the above method is cost-effective.

1. INTRODUCTION

Special alumina applied in the ceramic industry is the base material usually used for production of insulators (high voltage insulators, sparking plugs), wear resistance parts (lining, balls, cutting ceramics), oxide ceramics (electronics), and high quality Al_2O_3 ceramics (Oda and Shibusawa, 1986; Sleppy et al., 1991). Special alumina powders have to be of high chemical purity, i.e. the content of Al_2O_3 and alkalies must be from 99.85 to 99.99% and less than 0.1%, respectively. Simultaneously, alumina powder should be of high density, has small primary crystals, special degree of comminution, and electrical resistance (Martinswerk, 1988; Atomergic, 1988; Alcoa, 1991). Calcination of the aluminium hydroxide (gibbsite, bayerite, boemite) or the metal grade alumina with various types of mineralizers are usually used for production of special alumina on the industrial scale, although several other expensive methods are known in the world alumina technology (Dowihl and Kuhn, 1964; Gibas, 1970; Petzold and Ulbricht 1984). Calcination is a costly method, but adequate selection of mineralizers or their composition and quantity as well as other parameters should result in reduction of the production costs. Usually, only the temperature and quantity of the mineralizers were optimized (Hubicka, 1975; Hamano et al. 1991; Pyzalski et al. 1992). The problems of the formation of α-Al_2O_3 from various types of aluminium hydroxides (gibbsite, bayerite, boemite) containing different amounts of the harmful admixtures of alkalies were already presented by (Varhegyi et al., 1973; Faber and Srivastawa, 1976; Pyzalski and Wójcik, 1988, 1990) while problems concerning the use of fluorine mineralizers were discussed by Gibas, 1970; Petzold and Ulbricht, 1984; Hamano et al., 1991; Derdacka-Grzymek et al., 1990, 1992 .

From the most recent literature it appears that the mechanism of the action of fluorine compounds on the process of α-Al_2O_3 formation is not entirely explained (Hamano et al., 1991). The results of an extensive investigation presented in parts by Pyzalski and Wójcik, 1989, 1990; Wójcik and Pyzalski, 1990, led to a new technology of production of special alumina by calcination of bayerite obtained in the P & W Carbonization Process of gibbsite (aluminium

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hydroxides from Groszowice Alumina Plant) and metal grade alumina with the addition of mineralizers (Pyzalski and Wójcik, 1991; Adamczyk et al., 1991). The scheme of the general idea of this technology is shown in Fig. 1. Some results on the industrial production of special alumina from the metal grade alumina are also presented in this paper.

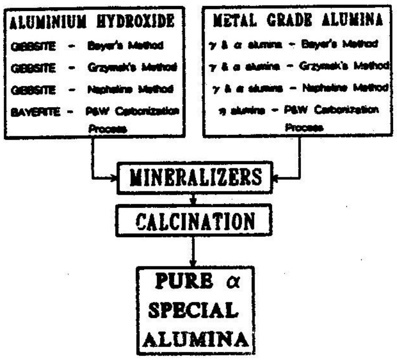

Fig. 1. Scheme of the general idea of the production technology of specjal alumina from different raw materials

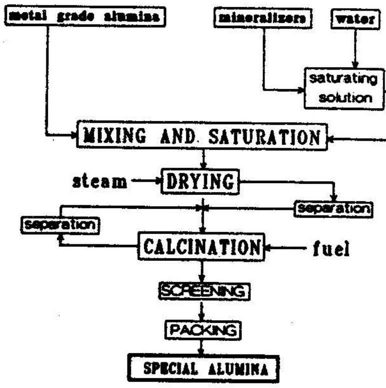

Fig. 2. Scheme of the general idea of the technology

2. PRODUCTION

Basing on the numerous experiments performed both in laboratory and on a larger scale, the technology of the production of the special alumina containing less than 0.05% of alkalies (recounting to Al_2O_3), more than 99.85% of Al_2O_3 and more than 97% of α-Al_2O_3 was elaborated for the commercial use. The scheme of the general idea of the technology is shown in Fig. 2, and the scheme of the industrial installation is shown in Fig. 3.

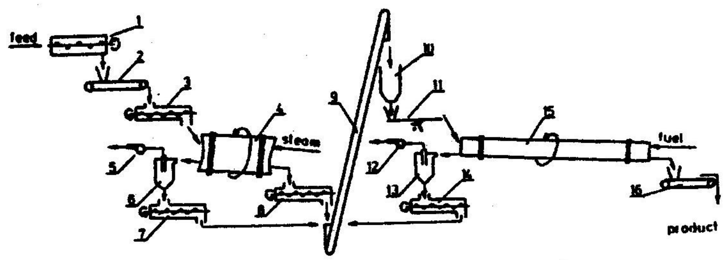

Fig. 3. Scheme of the industrial installation: 1 - rotary mixer, 2-16 - belt conveyor, 3-7-8-14 - feeders, 4 - drying rotary drum, 5-12 - exhauster, 6-13 - cyclone, 9 - skip conveyor, 10 - buffer bin, 11 - vibratory feeder, 15 - calcinator

2.1. General description of the technology

The idea of the presented technology is to beneficiate the ordinary aluminium hydroxide or the metal grade alumina by the saturation of the grains of aluminium hydroxides or the metal grade alumina with the solution containing selected mineralizers, drying of the saturated material and its calcination in the rotary kiln. The following main steps can be distinguished:

1. The precise saturation of a raw material allows a uniform spreading of the mixture of mineralizers on the surface of grains.
2. The drying of the saturated materials favours the accurate feeding into the calcinator and its stable operation.
3. The calcination carried out at proper temperature, rpm, draughts and feed leads to special alumina with required physicochemical properties.
4. The hot special alumina is then transported into the silos and classified on sieves.
5. The ready product is next packed and attested.

2.2. Materials

The metal grade alumina originated from Bayer's technology was used as a base raw material. Table 1 shows the physicochemical properties, Fig. 4 shows XRD diffraction patterns of α-Al_2O_3 and β-Al_2O_3, and Fig. 5 presents the morphology of grains.

Mineralizers A, B and C (patented), industrial water for the saturation of the alumina, fuel for heating of the calcinator, steam for drying the saturated alumina and electrical energy were used in this technology.

Table 1. Physicochemical properties of the metal grade alumina

Component	Chemical composition (%)	Particle size (%)	
$Na_2O + K_2O$	0.6	> 150 μm	6.0
SiO_2	0.05	100-60 μm	36.0
Fe_2O_3	0.03	60-45 μm	29.7
$TiO_2 + V_2O_3 +$ + $Cr_2O_3 + MnO_2$	max 0.03	< 45 μm	27.6
L.o.i	1.1		
Al2O$_3$	98.5		
α-Al_2O_3	40.0		

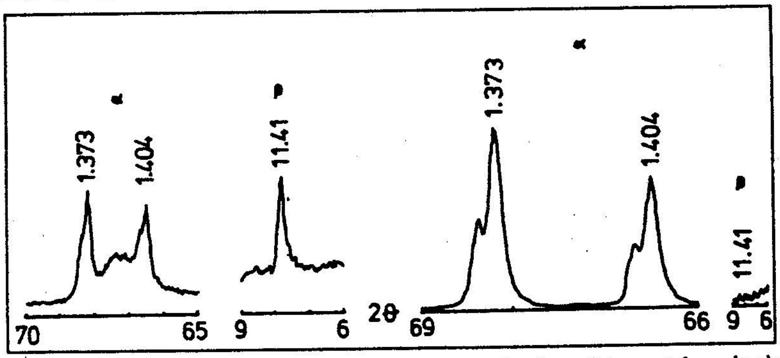

Fig. 4. XRD diffractograms of α-Al_2O_3 and β-Al_2O_3 examination of the metal grade alumina (left) and the special alumina (right)

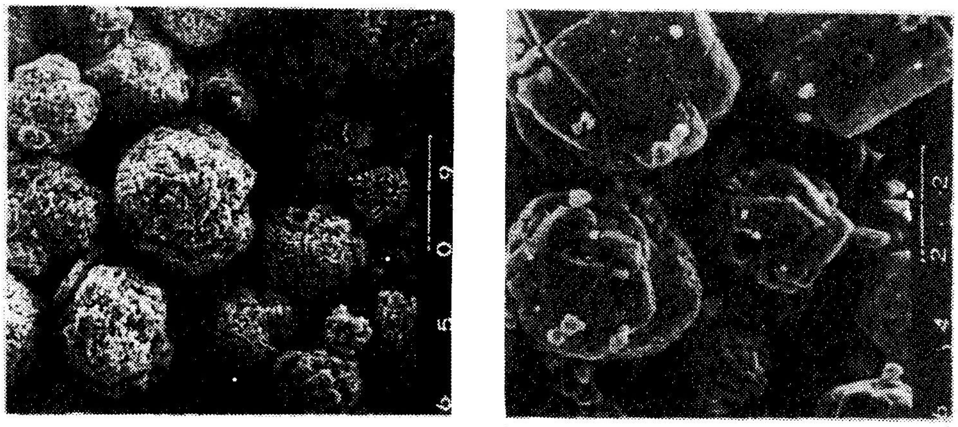

Fig. 5. SEM of the metal grade alumina (left) and the special alumina (right), (x300, 1 cm = 33 μm)

2.3. Metods of the examination

The specimens of the metal grade alumina and the special alumina collected during production were examined as follows:

a) the level of contamination were determined by chemical and spectroscopic (ASA) analyses,

b) the phase composition was examinated by XRD method with Philips diffractometer and Cu lamp. The contents of α-Al_2O_3 and β-Al_2O_3 were marked on the basis of the internal standard method and the intensity of peaks of α-Al_2O_3 (d=1.373Å) and β-Al_2O_3 (d=11.41Å),

c) the densities of specimens were calculated from the pycnometric measurements with pure kerosene and redistilled water,

d) the granulometric distributions of grains were determined from sedimentation analysis with Sartorius apparatus,

e) the morphology of specimens was observed using EMS method with JEOL type,

f) the grindability tests were described by comminution of specimens in the rotary-vibration mill.

2.3. Controlling

The control of the technology of calcination process was made by:

a) checking of the saturation procedure of the metal grade alumina with the solution containing mineralizers,

b) concentration of mineralizers,

c) inspection of the drying process,

d) precise checking of the feeding of the material into the calcinator,

e) precise supervision of the calcination procedure,i.e.:

ii. check-up of the temperature of the calcinator in several marked points,

ii. check-up and regulation of the fuel into the burner,

iii. check-up of the pressure of the primary air and the secondary air from the heater into the burner,
iv. check-up and regulation of the air draughts,
v. check-up of the materials losses,
vi. current check-up of the mechanical, electrical and controlling devices,
vii. current check-up of the production of the special alumina,
viii. production yield,
ix. weight by volume and density,
x. contents of α-Al_2O_3 and sieve testing and packing.

3. RESULTS

Following the evaluated technology, about 40 tons of the beneficiated special alumina were produced in two separated cycles of the calcinator operation.

The technical parameters of 20 m long calcinator were as follows:

- average yield	- 150 kg/h,
- average fuel consumption	- 1440 l/h,
- primary air pressure	- 2.5 atm,
- kiln speed	- 1.25 rpm,
- calcination temperature	- 1350°C,
- draught losses	- max 5%.

3.1. Properties

The detailed specification of the physicochemical properties of the produced alumina is shown in Table 2.

Resultant special alumina contains more than 97% of α-Al_2O_3 with the density of 3.967 g/cm^3 (Fig. 4). The chemical analysis confirms the required purity of the special alumina with the contents of alkalies less than 0.025%. On the other hand, the content of SiO_2 in the produced special alumina increased from 0.05% to 0.083%. It was caused by the fire-clay lining in the cool end of calcinator. The application of a calcinator with high alumina lining would eliminate this problem. Other physicochemical properties, e.g. content of Al_2O_3, α-Al_2O_3, l.o.i., density, etc., were better than assumed. The interesting particle size distribution of the produced special alumina was observed. Table 2 shows that the grains of the range fraction from 45 to 100 μm are dominant. The particle size distribution of the examined samples indicates that the specific surface area ranged from 0.4 to 1.5 m^2/g according to BET. The microscopic observations revealed that the grains of the special alumina were composed from the aggregates consisting of the fine primary spherical crystals of α-Al_2O_3 of 1.5-5 μm size (Fig. 5). It can be easily visible that the grains are joined in the loose structure.

A sample of the produced special alumina was tested in the two chambered rotary-vibration mill. The first chamber was charged with the Polish alumina, the second one with the ALCOA CL3000, while the amplitude and frequency parameters were identical. Test results show that after one hour of grinding the first sample exhibited d_{50} = 16 μm while CL3000 sample had only 20.3 μm of the average diameter. ALCOA alumina needs longer time for a similar stage of the comminution because of the tabular form of grains joined with each other into a more compact structure (Fig. 6). It is obvious that the positive result of the grindability test for the Polish special alumina allows us to save energy necessary for comminution of such hard material as α-Al_2O_3 in ceramics technology.

Table 2. Physicochemical properties of representative samples of special alumina produced in two cycles

Component	I production cycle			II production cycle		
	Sample No 1	Sample No 2	Sample No 3	Sample No 4	Sample No 5	Sample No 6
Chemical composition (%)						
$Na_2O + K_2O$	0.033	0.007	0.011	0.023	0.042	0.011
Fe_2O_3	0.020	0.007	0.010	0.025	0.005	0.015
CaO	0.039	0.020	0.020	0.016	0.015	0.037
SiO_2	0.073	0.092	0.086	0.080	0.070	0.100
B_2O_3	0.006	0.014	0.025	0.030	0.012	0.010
MgO	< 0.001					
TiO_2	< 0.003					
Cr_2O_3,	< 0.001					
Mn_2O_3	< 0.001					
CuO	< 0.001					
Al_2O_3	>99.82	>99.85	>99.84	>99.82	>99.85	>99.82
L.o.i. 1150°C, 6h	0.19	0.19	0.15	0.19	0.16	0.11
Particle size (%)						
> 100 μm	13.1	12.3	5.4	7.2	10.0	5.8
100-60 μm	55.1	51.9	50.9	46.5	52.2	56.0
60-45 μm	24.4	24.5	29.0	30.7	27.1	26.8
< 45 μm	7.4	11.4	14.8	15.6	10.3	11.4
α-Al_2O_3, %	95.5	96.3	97.7	96.5	97.6	97.3
Density, g/cm^2	3.961	3.970	3.972	3.963	3.969	3.969

3.2. Economy

Basing on the material and energy balances and evaluations of the starting costs, the following production costs calculated in % per 1 ton of Al_2O_3 were achieved in our conditions of commercial scale production of special alumina:

- cost of the metal grade alumina - 52%,
- cost of the fuel - 11%,
- cost of the electrical energy - 3%,
- cost of the mineralizers - 16%,
- cost of the labour - 15%,
- others - 3%.

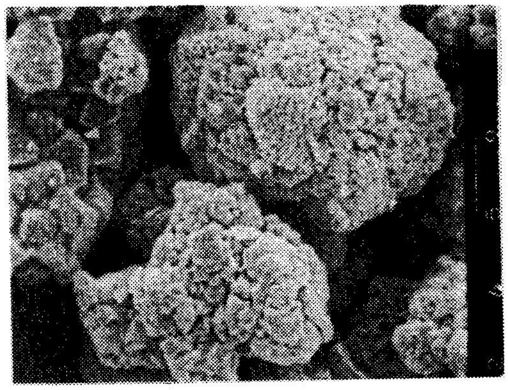

Fig. 6. SEM of ALCOA alumina CL 3000, (x300, 1 cm=33 μm)

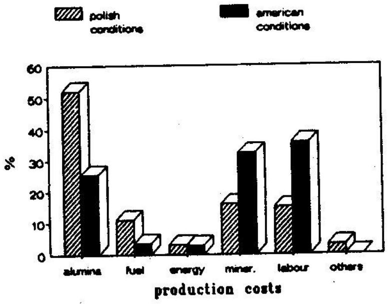

Fig. 7. Comparison of the production costs of the special alumina in the Polish and American conditions (prices in 1991)

On the other hand, taking prices of materials, energy, fuel, etc., officially from The World Almanac and Book of Facts (The World Almanac, 1992), a very interesting comparison of the production costs appears. These prices were as follows:
- metal grade alumina - about 200 \$/ton,
- electrical energy - 3.74 c/kWh,
- diesel fuel - 0.50 \$/gallon,
- mineralizers (MERCK) - 35 \$/kg,
- average hourly earning - 7.64 \$/hour.

Anticipated production costs calculated in % per 1 ton of Al_2O_3 are as follows:

25.6% - cost of the metal grade alumina,
13.4% - cost of the fuel,
2.8% - cost of the electrical energy,
32.4% - cost of mineralizers,
35.8% - cost of the labour.

Figure 7 shows the graphical comparison of these two calculations. Comparison of prices of the special alumina in the World Market with the production costs indicates that our technology is very profitable.

3.3. Application

The produced special alumina was successfully tested in the laboratory and on the semi-technical scale in Sparking Plug Factory in Poland. Results confirmed the high quality of our product and its usability for sparking plug production.

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W artykule przedstawiono wyniki badań nad wzbogacaniem hutniczego tlenku glinu w celu otrzymania wysokiej czystości specjalnego tlenku glinu w odmianie korundu (α-Al_2O_3). Hutniczy tlenek glinu kalcynowano z jednoczesnym dodatkiem różnych mineralizatorów. Na podstawie wyników tych doświadczeń opracowano technologię produkcji specjalnego tlenku glinu, polegającą na nasączeniu hutniczego tlenku glinu roztworem zawierającym wybrane mineralizatory, jego wysuszeniu i skalcynowaniu w piecu obrotowym. Technologię sprawdzono w warunkach przemysłowych w Fabryce Tlenku Glinu w Groszowicach koło Opola. Otrzymany produkt posiadał właściwości fizykochemiczne typowe dla specjalnych tlenków glinu typu ALCOA CL3000, A15 lub A3500. Analiza ekonomiczna wykazała, iż proponowana technologia jest ekonomiczna.