Essential Readings in Light Metals: Alumina and Bauxite.
Edited by Don Donaldson and Benny E. Raahauge.

THE USE OF BAYER ALUMINA FINES FOR OTHER INDUSTRIAL PURPOSES

P.García, R.Zapico, J.MªAyala, J.P.Sancho
Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica
Escuela de Minas. Universidad de Oviedo -33004-. Spain

ABSTRACT

Bayer Plants, in particular with american designed calciner, producing alumina from different bauxites, as in the San Ciprián (Lugo, Spain) plant, have the production of variable amounts of alumina fines when the metallurgical alumina is obtained, this fines if not separated in the plant go to the reduction plant, where they causes troubles to the process.

This paper resume the work done in order to get profit of this fines ($\leq 43\mu m$) for obtaining refractory and ceramic products of higher added value as: mullite and especial aluminas whit different sodium content.

INTRODUCTION

Bayer aluminas are denominated "metallurgical aluminas" because they are used in the Hall-Heroult process to produce aluminium in the reduction plants.

Both Bayer and Hall-Heroult processes are developed to produce very pure products as well as producing it with the higher performance. To achieve it, fines ($\leq 45\mu m$) with high Na content are undesirable, mainly because the behaviour of this powders in its solution in cryolite bath is complex, disturbing the cell process, mainly, producing sludges and deposits that decrease the Faraday ratio (1).

This alumina fines can be very well mixed with pure kaolin for obtaining mullite by the convenient sintering process. Also they can be treated to obtain especial aluminas. Both products are used in the refractory and ceramic industries.

As Kingery (2) say ceramic is a material that have a main component that is an inorganic non metallic compound. Campos-Lóriz (3) define ceramics as polycristalin materials, non metallics and inorganic of high smelting point. There are a lot of materials that have this above defined properties. Between then we have intended to produce mullite and aluminas of comercial interest from kaolin and the above defined fines.

CHARACTERIZATION OF THE RAW MATERIALS

It has been characterized physically as well as chemically, the ciclon fines and the ≤ 43 fraction from alumina produced in San Ciprian Factory (Lugo-España). The kaolin from Asturias, stone kaolin, also has been studied and analyzed. Both materials: alumina powder and kaolin are the base for mullite production.

Parameters evaluated and the test done have been:

* True density (Picnometer Helium) α content (XRD) (4), gibbsite content (DTA) (5), specific surface (BET), size distribution (Lumosed) and fire losses (MOI 500°C, L.O.I. 1200°C) (6).

Table I has the values of the parameters from the alumina fines in comparison with regular metallurgical alumina.

Chemical analysis has been done by A.A.E. Al and Na were quantified and data are collected in Table II.

Table III has the chemical analysis, loss on calcination (600°C), density and granulometry of the kaolin used.

Table I.- Physical properties of alumina fines.

Property	Sample		
	Ciclon fines	Fraction <43μm	Alumina
True density (g/cc)	3,192	3,430	3,448
% Corindon	13,5	5,5	3,2
% Gibbsite	16,0	2,0	0,3
Humidity 110°C	2,4	2,4	2,5
MOI 500°C	6,8	1,4	1,0
LOI 1200°C	1,6	0,7	0,5
BET (m^2/g)	34,5	47,7	55,2
Average diameter of particle (μm)	11	22	83
Global density	0,8	0,9	1,0

Table II.- Chemical analysis of alumina.

Sample	% Al_2O_3	% Na_2O
Ciclon fines	83	1,0
A-1 (<43 μm)	94,4	0,54
A-2 (<43 μm)	93	0,4
A-3 (<43 μm)	96	0,27
Alumina	96	0,40

Table III.- Kaolin characteristics.

	Natural	Treated (*)
SiO_2	46	54
Al_2O_3	38	40
Fe_2O_3	0,22	0,25
K_2O	0,1	0,15
Na_2O		0,01
CaO	0,11	0,14
MgO	0,05	0,08
Loss on ignition: LOI (600°C) P.C.	14	0,8
Density		2,555

(*) Kaolin has been washed with amonia and diluted chloridic acid and calcined at 600°C. Calcination was done for the elimination of the constitutional water, between 500-600°C.

EXPERIMENTAL WORK

Production of special alumina powders

Raw material preparation for alumina powders fabrication

Sodium content in both, ciclon fines and alumina fines, is quite high for their utilization as materials for high purity ceramic products. Something similar happens with the size of the alumina particles (7,8).

Sodium content reduction in alumina fines

Sodium was partially eliminated from fines until a low level enough for its use. Samples of alumina were washed with destiled water under mechanical stearing. Pulp density was 10% and the washing time one hour. After this time liquid/solid separation is done, repiting anew the washing with the same parameters. After four washing operations the final product was characterized.

All waters from the four washing operation give different sodium content. The percentage of Na extracted were: 46%, 9%, 2% y 1%, of Na_2O, aproximately.

Sodium content in the four residua also were evaluated. These values are represented in Table IV.

Table IV.- Sodium content in the alumina fines

Sample	% Na_2O Without wash	After washing
A-1 (<43μm)	0,54	0,26
A-2 (<43μm)	0,40	0,19
A-3 (<43μm)	0,27	0,13
Ciclon fines	1,0	0,27

Sodium is washed out in the operations but the aluminum content of the waters is nule, according with our prior estimations.

Alternativelly to the granulometric separation -dry via- to obtain the fine fraction, alumina was washed as it was sieved in wet. In the same operation alumina fines with low soda content were obtained (0.15% Na_2O).

Grinding of fines

Reduction average diameter of particle, was made dry and by the wet procedures, using in both cases a ball mill with alumina grinding media; samples A-1 (< 43) and A-2 (< 43) with average diameters of 22 and 20 μm were wet grinded with a pulp density of 10% during 20 hours. $\bar{D}p$ was measured in "Lumosed" resulting 4 and 5μm, respectively.

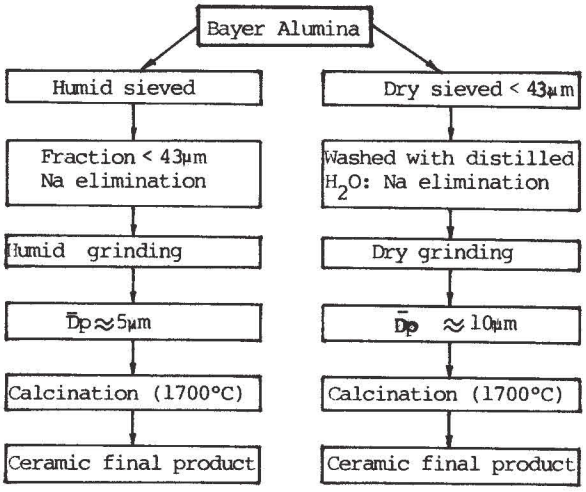
Sample A-3 (< 43 μm) was grinded dry and time influence on the diameter was studied. Diameters after 2,6 and 12 hour were 15, 14 and 11 μm respectively.

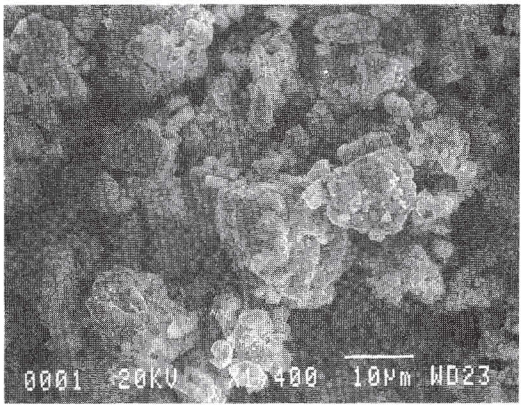
Especial alumina powders production

Powders from alumina fines (washed and grinded) are calcinated afterwords to obtain ceramic powders. The furnace used was a Lindberg programable one with heating and cooling ramps and high temperature acuracy.

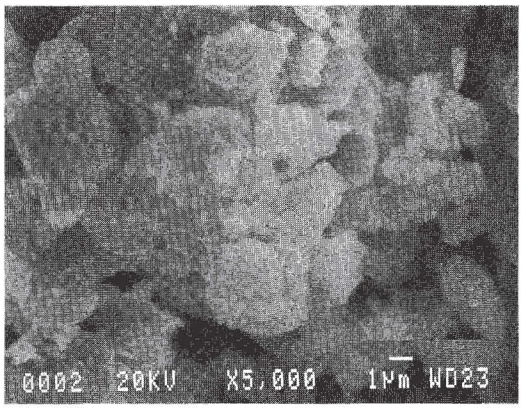
Alumina has been submited at 1700°C for 6 hours to produce a well cristalized α phase. Powder were XRD studied and microscopicaly observed. Seudoexagonal forms are present (see micrographies). Figure 1.

Flow diagrams for ceramic alumina production





a)



b)

Figure 1.- S.E.M. of the particle 43 m of industrial alumina heated at 1700°C, 6 h.
a) group view
b) particle detail

Mullite production. Raw materials preparation for the mullite fabrication

The following information describes the steps given for the obtention of mullite treating at high temperature a mixture of kaolin plus alumina fines. Raw material were described in paragraph 2.

Mullite has the chemical formula: $3Al_2O_3.2SiO_2$ (28.2% SiO_2 and 71.8% Al_2O_3) with this data mixtures of kaolin and alumina fines were prepared, once both materials were grinded together in the proper amounts.

According with the composition of Tables 2 and 3 the corrected percentages of kaolin and alumina to get the SiO_2/Al_2O_3 relationship corresponding to mullita are: 52,5% of kaolin and 47,5% of alumina.

Once grinded and mixed the raw materials were homogenized with the purpose of getting full mullitization and a final product without other mineral fases present.

Thermal treatment of raw materials

The mixture kaolin plus alumina fines is pressed in cilinder pucks of one by one cm^2.

First of all the time was fixed: 1 hour, and the experimental variable was the temperature: 1500 and 1600°C were tested. XRD of the pucks was done. The amount of mullite increases with temperature, but in both cases some α alumina rested unreacted. (See figure 2).

From the prior studies and some bibliografic data (9, 10, 11 and 12) the temperature was fixed. 1600°C and the time varied between 3 and 6 hours.

XRD analysis do not showed any α-alumina present, being both very similar in relation with the mullite content.

In order to decrease time of transformation two other test were carried out at 1700°C: 60 and 90 minutes.

XRD graphs (Fig. 2 shows no α-alumina present and mullite has better cristalization parameter). Both samples are very similar and also similar to the standard sample (BCR) of the Commision of the European Communities that has 97% mullite and 3% vitreous phase.

Chemical composition of the mullite obtained is:

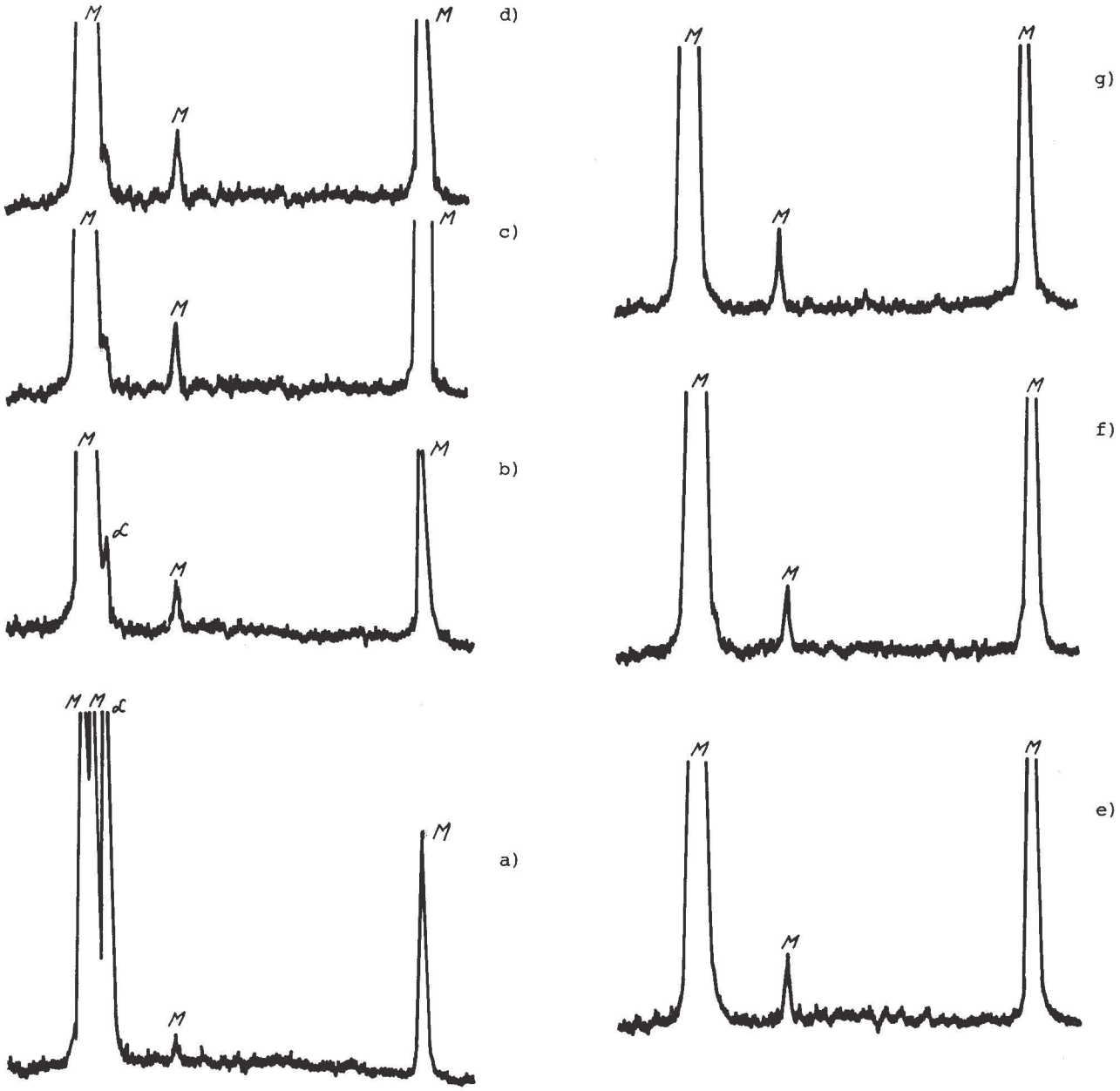


Figure 2.- X-Ray diffraction diagram of the mixture kaolin and alumina fines, heated:

a) 1500°C 1 h
b) 1600°C 1 h
c) 1600°C 6 h
d) 1600°C 3 h
e) 1700°C 1 h
f) 1700°C 1 h, 30 min.
g) mullite (RM 301)

Table V.- Analysis of mullite.

SiO_2	30,6%
Al_2O_3	66%
Fe_2O_3	0,6%
CaO	0,14%
MgO	0,06%
Na_2O	0,4%
K_2O	0,7%

Mullite content

Standards with 90, 85 and 80% mullite were prepared using the upmentioned mullite standard and (7%)F_2 Ca as an internal standard and quartz; all of them certified standards.

Samples were mixed 24 hours and used with the XRD but with a special precautions to avoid preorientation, by using an aparatus developed for this purpose by RLF.

Picks analyzed are the corresponding to the (110) reflexions with a reticular distance of d = 5,39Å for the mullite and (111) with d = 3,16Å for the fluorite. The relationship between the mullite content and the height of picks is represented by the following equation:

$$\% \text{ Mullite} = 43,4518 + 0,0469\ I \quad (r = 0,99)$$

Percentage of mullite of samples obtained in laboratory are 80% and 85% for the 1600°C-3h and 1700°C-1h, respectively with error limit of 3%.

CONCLUSIONS

A quite good alumina corindon of fine size and low sodium content has been obtained by washing and calcining until 1700°C alumina fines (≤45µm).

Mullite also is produced by using local kaolin and alumina fines, the product is well transformed at relatively low temperature and time.

Tabular alumina will be produced by heating to a higher temperature as a continuation of this work.

ACKNOWLEDGMENTS

It is very much acknowledged the collaboration of the INESPAL Company of Spain for the raw materials providing.

REFERENCES

1.- G.Gopienko & N.Siraev.
An effect of the Alumina quality on the Aluminium electrolysis process.
Light Metals 1985.

2.- W.D.Kingery, H.K.Bowen and D.R.Uhlmann.
Introduction to ceramics.
2nd Edition. John Wiley & Sons. Inc. 1976.

3.- D.Campos Lóriz.
Los materiales refractarios: Generalidades y clasificación.
Revista de Metalurgia (CENIM). Vol.16, nº2. 113. 1980.

4.-
Determination of alpha-alumina in calcined alumina.
Alcan Arvide. 1976.

5.- MªP.García Coque
Caracterización de alúminas Bayer modernas para electrólisis del aluminio.
Tesis Doctoral. Oviedo. 1989.

6.- M.A.Llavona, F.Blanco, MªP.García, J.P.Sancho, and L.F.Verdeja
Some new consideration on the measurement of humidity, MOI and LOI.
Light Metals 1988.

7.- G.Maczure, K.S.Moody and J.T.Kennedy.
Alumine.
Ceramic Bulletin. Vol.69, nº 5. 1990.

8.- E.Dorre, H.Hubner.
Alumina. Processing. Properties and Applications.
Springer - Verlag. Berlín. 1984.

9.- S.Somiya, F.D.Davis and J.A.Pask.
Mullite and mullite matrix composites.
The American Ceramic Society, Inc. 1990.

10.- K.C.Liu.
Mullite formation by reaction sintering of Kaolinite-alumina.
Tesis Doctoral. Universidad de Berkeley. 1990.

11.- L.Tcheichul and S.Butschkav.
Un aporte al problema de la mullita.
Cerámica y Vidrio. Enero-Febrero. 1975.

12.- S.Cohen, A.R.Rossini and T.G.Kernel.
Nuevo proceso para la formación de la mullita.
Cerámica y Vidrio. Septiembre-Octubre. 1971.