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The possible use of Bayer process cyclone fines for manufacture of abrasives(•)

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Abstract This paper deals with the feasibility of producing synthetic abrasives from a by-product of the Bayer process: the cyclone fines, through synthesis aided by mineralizers addition. The main result has been the production of a low temperature (1200–1300 °C) polish by adding fluoride mineralizers, that could be in clear competence with synthetic corundum obtained also in this work by a more traditional way: sodium removal, using of magnesium oxide as mineralizer, and high calcination temperatures (1700 °C).

Keywords Cyclone fines. Bayer process. Ceramic synthesis. Abrasives polish.

Posibilidad de uso de finos de ciclón del proceso Bayer para la fabricación de abrasivos

Resumen En este trabajo se demuestra la posibilidad de producir abrasivos a partir de un subproducto de la fabricación de la alúmina Bayer: los finos de ciclón, mediante la síntesis ayudada por la adición de mineralizantes. Un resultado importante ha sido la obtención de un pulimento a baja temperatura, (1.200–1.300 °C) mediante mineralizantes fluorados, que puede competir de forma clara con corindones sintéticos obtenidos, también en este trabajo, de forma tradicional: eliminación de sodio, utilización de óxido de magnesio como mineralizante y elevadas temperaturas de calcinación (1.700 °C).

Palabras clave Finos de ciclón. Proceso Bayer. Síntesis cerámica. Abrasivos. Pulimentos.

1. INTRODUCTION

Natural aluminous abrasives are mainly made of corundum or some others like emery, spinel, diaspore or sillimanite. However, the synthetic abrasives are mainly α-alumina with variable quantities of impurities, the most important of which is aluminium sodium oxide ($Al_{11}O_{27}Na_2$) or β-alumina[1 and 2]. Common alumina abrasives are elaborated by melting Bayer processed alumina at about 2000 °C. The typical alumina composition is 93–99 % α-alumina, 0.4-0.8 % Na_2O and 5-7 % β-alumina[3]. Another mostly α-alumina product is the so called tabular alumina produced by calcination of the Bayer product very near of its melting point, around 1900 °C [4].The nature and structure of the minor constituents largely control the abrasive character of these fused aluminas. They control not only the ultimate quality of the abrasive, but its friability. Impurities have an effect on the crystal habit of corundum itself, on its particle size and even on its intrinsic hardness. At equal purity levels friability generally tends to increase with increasing crystal size.

Cyclone fines are a by-product of the Bayer process and are made of mixtures of different aluminas and hydrates, which have not been completely calcined[5]. Due to their small particle size the fines are extracted from the top of the furnace and are collected in the cyclone or with an electrofilter. Fines are transported from the cyclone to a storage hopper. It is during this transportation that the abrasive behaviour of the residue was observed mainly in the corners of the pipes, which can be completely worn. As an average five kilograms of fines are generated from one tonne of bauxite[6].

The present work deals with the production of high quality polish abrasives using Bayer process cyclone fines that are rich in alumina content.

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According with the experience of aluminum producers, there is a transformation of transition aluminae into α-alumina in presence of fluorides, during the heating in the electrolysis process. In this work cryolite was used as mineralizer, following this idea.

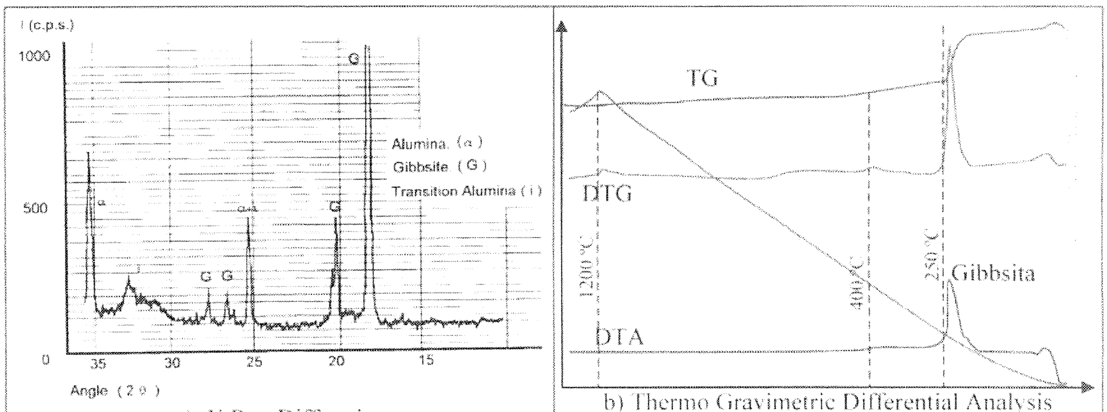
Some experiments were done at higher temperatures, as a different way of obtaining high abrasive features. If quite pure cyclone fines (sodium free) reach high temperature, a very high α-alumina conversion can be attained; the way for obtaining that sodium free cyclone fine was wet grinding. As the process must be sodium free, the mineralizer selected for these high temperature tests was magnesium oxide.

2. CHARACTERIZATION OF CYCLONE FINES

The approximate composition of cyclone fines is: 13.5 % α-alumina, 16 % gibbsite and 70.5 % transition aluminas.

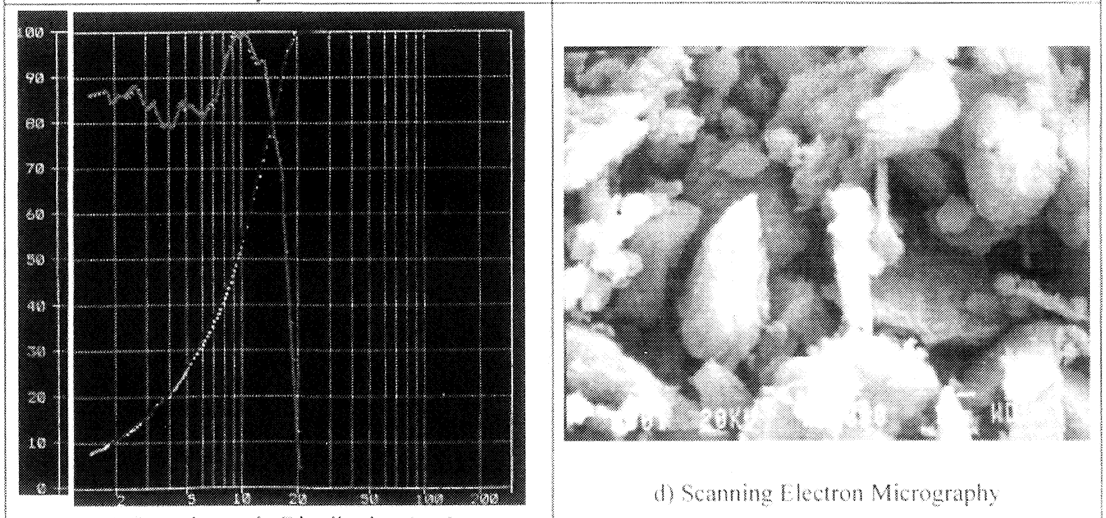
Cyclone fines had been characterised with various instrumental techniques such as: atomic absorption spectroscopy, X-Ray diffraction, differential thermal analysis, helium picnometer, particle size determination (Lumosed high reproductivity, $s^2<2$ %), abrasion measurements (IAD model AD–786, originally for quartz in clay materials. P=± 1 mg; $s^2<1$ %), scanning electron microscopy and fire loses during calcination[7 and 8]. Results are shown in figure 1 and table I.

As seen in figure 1, the raw cyclone fines are constituted of crystalline aggregates of various shapes and sizes (D_{50}=10µm,D_{100}=20µm); the high content of sodium and the high loss on ignition due to the presence of gibbsite must be emphasized, as well as the low real density and abrasiveness. The abrasiveness is calculated by determination of wheight loss of a metal mesh during the abrasion test[9], as shown in figure 2.



a) X Ray Diffraction

b) Thermo Gravimetric Differential Analysis



c) Granulometric Distribution (µm)

d) Scanning Electron Micrography

Figure 1. Characterisation of raw cyclone fines.

Figura 1. Caracterización de los finos de ciclón sin tratar.

Table I. Properties of the cyclone fines

Tabla I. Propiedades de los finos de ciclón

Chemical analysis, wt %	Na_2O	0.81
	K_2O	0.22
	MgO	0.06
	Fe_2O_3	0.2
	Al_2O_3	91
	CaO	0.03
Mineral analysis	α-alumina, %	13.5
	Gibbsite, %	16
True density, g/cm^3		3.192
Mean particle size, μm		10
Humidity		2.4
Fire losses, wt %	M.O.I. a 500 °C	6.8
	L.O.I. a 1200 °C	1.6
Abrasion (mesh test), mg		19

Figure 2. Effect of the abrasion on the test mesh.

Figura 2. Efecto de la abrasión en la malla de ensayo.

3. EXPERIMENTAL METHODS

Cyclone fines were calcined for studying the direct transformation without the aid of extrinsic mineralizers. This calcination has been carried out in a Thermoline Type 46100 furnace, a heating gradient of 5 °C/min was used. Calcination temperatures were chosen according to the transformation temperature of alumina into α-alumina. So 1000, 1100, 1200, and 1300 °C were used in a first trial[10]. Afterwards, the product was characterised as described in table II (only two experiments were done at 1400 and 1700 °C for comparison purposes).

Tablets were manufactured to test the cyclone fines calcination with sintering mineralizers. Different compositions were tested, from 1 to 7 % of fluoride additives. The manufacturing of tablets and the tests done after calcination were carried out as following:

The homogeneous mixture of fines and mineralizers was conducted in a rotating drum, by 30 min tumbling with ceramic cylinders. This mixture is pressed into a cylindrical shape, under a 45 MPa uniaxial hydraulic pressure.

The resulting tablets were sintered for one hour, under temperature conditions from 1000 to 1700 °C in the Thermoline furnace, heated at 5 °C/min, until the temperature is reached; after cooling, the samples were measured and then grounded in a ring mill for ten seconds.

Powders are then tested for abrasivity in the IAD model AD786 abrasion tester. These abrasives were characterised as described in table II.

Table II. Mean particle size and abrasiveness of different mixtures of cyclone fines and cryolite after calcination

Tabla II. Tamaño medio de partícula y abrasividad de diferentes mezclas de finos de ciclón y criolita después de calcinación

Temperature (°C)	**% Cryolite**							
	1	**3**	**5**	**7**	**1**	**3**	**5**	**7**
	Mean particle size (μm)				**Abrasiveness (mg)**			
1000	3	1.8	5	1.6	24	23	19	19
1100	2.5	–	5.5	2.8	22	–	24	20
1150	–	–	4.5	3.9	–	–	26	23
1200	3	5	4.3	5.0	25	24	29	28
1300	3.2	5	4.5	3.9	20	37	28	29
Averages	3	4	4.8	3.9	23	28	25	24
1400	–	6	–	–	–	33	–	–
1700	–	7	–	–	–	48	–	–
Averages	–	5	–	–	–	32	–	–

Synthetic corundum production was attained by previous sodium removal from the original powders. This was done by wet grinding. Fines were grounded in a SWECO I Vibrate-Energy Model M18/5 micronizer mill. The pulp density was 830 g of solid per litter of water. Two kilograms of alumina grinding bodies were used for similar amount of alumina fines.

The ground fines, sodium free, were shaped into tablets, some of them with the powders alone, and others mixed with 0.5 % MgO. The tablets were calcined at 1600 to 1700 °C. The quality of the sintering process is evaluated by measuring several parameters: row density (cD), density after sintering (sD), losses during calcination (L.C.), and linear contraction of the sintered pucks ($\Delta l/l_0$).

The tablets are afterwards grounded, and the polishing powder is then tested and analyzed.

4. RESULTS

This epigraph includes the different calcination tests made with the fines, including different ways of rising the hardness of the original material to get suitable properties to its final use as abrasives.

4.1. Low temperature calcination

4.1.1. Calcination of cyclone fines

Calcination is the way selected to transform the residual hydrate of the fines into a more stable and hard phase as alumina. In this way, the mechanical properties of cyclone fines can be upgraded simply by rising its temperature over 1000 °C.

The results of calcination are clearly shown by diffractometric analysis, as can be seen in figure 3. The evolution of the crystalline constituents is shown, as temperature increases from 1000 to 1300 °C.

Abrasiveness is about 20 mg for the material calcined alone at low temperatures. It is worth noting that even at high calcination temperatures (1600-1700 °C) abrasiveness only reaches 25 mg, will be shown later.

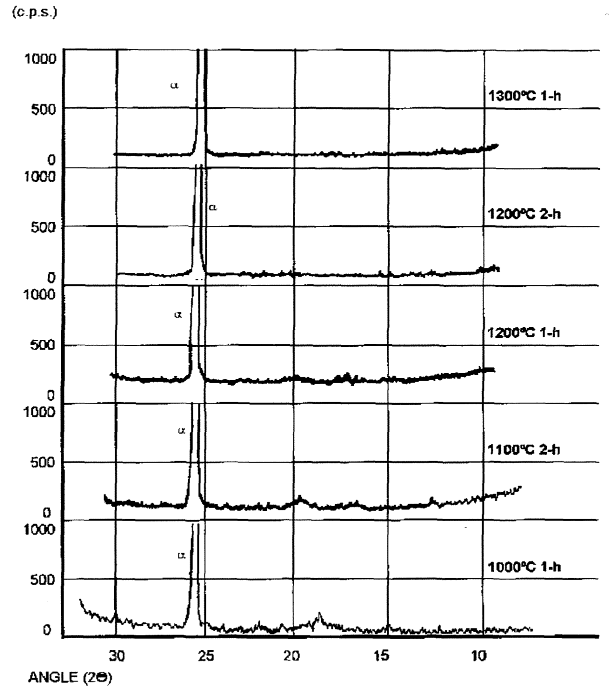


Figure 3. Diffraction patterns of cyclone fines calcined at different temperatures.

Figura 3. Difractogramas de finos de ciclón a diferentes temperaturas de calcinación.

4.1.2. Calcination of cyclone fines with cryolite

The degree of calcination of the hydrate can be controlled by changing the temperature, time and through the addition of mineralizers. The halogenated compounds (MgF_2 ,AlF_3) and boron element are quite effective with respect to improving the transformation into alumina, affecting the particle size[1, 4, 11 and 12].

The experimental results obtained for particle size and abrasiveness are shown in table II. Size is given as mean size, as specified by producers of most of polish materials. Actually, a commercial denomination "alumina 5" means five microns mean particle size.

Chemical analysis of synthetic alumina abrasive was done to see the evolution of volatile constituents and constitutional water with temperature of calcination. The results are shown in table III. Thermal analysis of the synthesis present very clearly the dehydration peak from gybsite at 250 °C, with a weight loss of 10 %. At 820 °C an exothermic peak is detected and at 1185 °C another exothermic one. The first one can be due to some transition alumina, and the second peak can be due to the β-phase as can be seen also in the diffraction patterns in figure 4. Small losses of interstitial water is detected accounting 7 % until 1200 °C. Sodium losses are considerable from 1300 °C to 1700 °C.

4.1.3. Discussion of results

After calcination to 1300 °C, without any addition to the fines, (Fig. 3) transformation is complete at

Table III. Chemical composition of the mixture fines-3 % cryolite, at different calcination temperatures

Tabla III. Composición química de la mezcla de finos con 3 % de criolita, a diferentes temperaturas de calcinación

Temperature (°C)	wt % Na_2O(+/- 0,05 %)	wt % Al_2O_3(+/- 2 %)
Without calcination	2.05	90
1000	2.10	94
1150	2.05	95
1200	1.95	96
1300	2.00	97
1400	1.90	97
1700	1.10	98

1100 °C after 2 h. The same occurs at 1200 and 1300 °C after 1 h.

In this case the abrasiveness for a mean particle size of 10 microns proved to be similar to the data achieved from non-calcined cyclone fines. This could be due to the existence of α-alumina aggregates in the raw fines and non isolated particles.

As shown in table II, the abrasiveness values of fines mixtures with 1% cryolite, after grinding the tablets and for similar particle sizes (3 microns), are around 23, without remarkable variations when calcinations is conducted between 1000 and 1300 °C. Regarding composition, α-alumina is present in all cases, but β-alumina appeared at 1100 °C.

Grounded tablets formed with cyclone fines and 3 % cryolite, have the higher abrasiveness of all the samples (average of 28 between 1000 and 1300 °C), specially those calcined at temperatures higher than 1250 °C (37). It can also be concluded that the presence of β-alumina –softer than α-alumina– increases with increasing calcination temperature, see figure 4, theoretically lowering the abrasive character of alumina polish, not only for his poor character but also because it decreases the amount of α-alumina. Nevertheless some comments must be made on this point.

In figure 5 (SEM micrograph), it can be seen that fines begin to desaggregate while the temperature increases. The definition of the elemental morphologies of the isolated crystals of varying sizes can be seen, due to the presence of a controlled amount of β-alumina, which helps grinding, specially when temperatures reaches 1700 °C (the case with highest abrasiveness: 48).

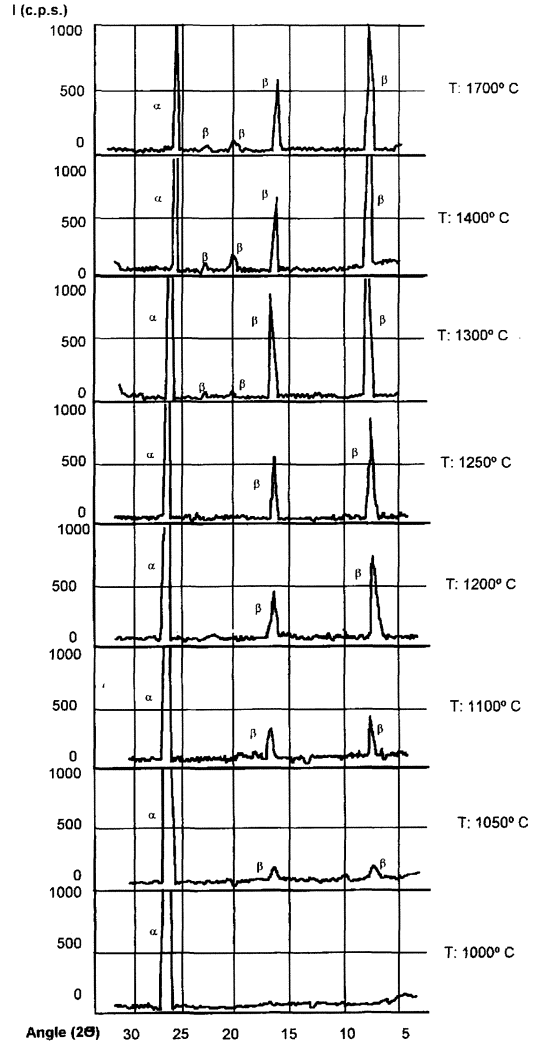
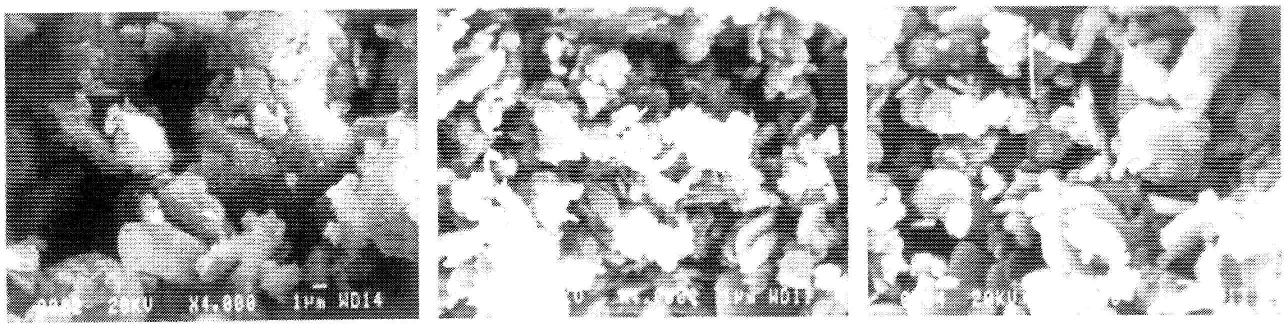


Figure 4. Diffractographs of the cyclone fines with 3 % cryolite, calcined for 1 h at different temperatures.

Figura 4. Difractogramas de los finos de ciclón con 3 % de criolita, calcinados durante 1 h a diferentes temperaturas.

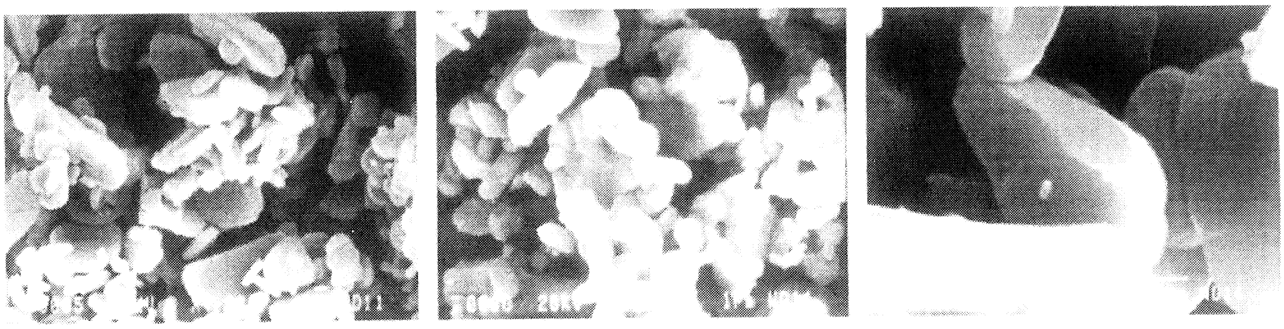
In table III it can be seen that the contents of aluminium and sodium, remain constant, at 2 % of Na_2O, until reaching 1700 °C when starts volatilisation. However, the amount of aluminium oxide increases due to the loss of constitutional water during calcination.

The tablets resulting from calcination of homogeneous mixture of fines with 5 % cryolite, after been ground, to an average size of 5 microns, show a gradually rising abrasiveness as calcination temperature increases as shown in table II. The abrasiveness clearly decreases compared to prior mixtures (average 25). The β-alumina appears at lower temperature (1100 °C). This could be the reason for the low abrasiveness levels; β-alúmina is not hard but fragile, and excess levels of β-alumina



Without calcining x4000 1000 °C x4000 1150 °C x4000

1200 °C x4000 1300 °C x4000 1300 °C x20000



1400 °C x4000 1700 °C x4000 1700 °C x15000

Figure 5. SEM Image of cyclone fines with 3% cryolite, calcined for 1 h at different temperatures.

Figura 5. Micrografía electrónica de barrido de los finos de ciclón con 3% de criolita, calcinados durante 1 h a diferentes temperaturas.

do not help in producing a suitable particle morphology and size distribution of the β-alumina particles, as controlled levels do.

From table II it also can be seen that the abrasiveness increases with the calcination temperature as well as the particle size after grinding (3 to 6 microns), and the β-alumina content increases as well. The abrasiveness of the synthetized product with 7 % fluoride is even lower (average 23-24) than that of the 5 % cryolite alumina mixtures, as the β-alumina content is even higher. When using cyclone fines mixtures with 7 % cryolite there is some corrosion problems in the furnace, due to the high fluoride content.

4.2. High temperature calcination

4.2.1. Calcination of cyclone fines

Sodium is a deleterious element causing the production of β-phase. The removal of sodium from the fines is the goal of the wet grinding, washing out the element with water as the product is being grounded. By this way, the original content of 0.8 % Na_2O can be reduced to levels as low as 0.2 %. This lower sodium content is much more interesting for producing less fragile alumina during calcination. This also increases the melting point often related to hardness in these materials.

The variation of particle size and the corresponding abrasiveness for wet grinding, as a function of grinding time, is presented in table IV. A slight increase of abrasiveness with an increase of grinding time is observed.

Table V shows the results of the high temperature calcination process. The contraction increases with the calcination temperature as well as the sintered density, and the influence of the sodium is very important in the sintering process.

Table VI resumes the chemical analysis of mixtures before and after calcination, showing the sodium removal by washing and the effect of calcination on sodium level and alumina content.

X-Ray diffraction analysis shows the present components in the calcined samples. Figures 6 and 7 represent the corresponding patterns from each kind of mixture prepared for different temperatures.

Table IV. Particle size and abrasiveness as a function of grinding time of unimixed cyclone fines

Tabla IV. Tamaño de partícula y abrasividad según el tiempo de molido para finos de ciclón sin mezclar

Grinding time (h)	Mean particle size (μm)	Abrasiveness (mg)
1	5.6	13
2	2.5	16
4	2.0	17
8	1.1	18

Figure 8 shows the morphological analysis of the different powders, calcined at 1700 °C, in a sequence of micrograph, evidencing the evolution of the cyclone fines treatment. Cyclone fines ground washed show a progressive growth of the particle size and the development of more crystalline character when the calcination temperature increases.

The fines that were ground washed and with addition of MgO before sintering gave about the

Table V. Variation of the crude density cD, density after sintering sD, losses during calcination (L.C.) and linear contraction, $\Delta l/l_0$, with sintering temperature

Tabla V. Variación de la densidad en verde cD, densidad sinterizada sD, pérdida a la calcinación (L.C.) y contracción lineal, $\Delta l/l_0$, con la temperatura de sinterización

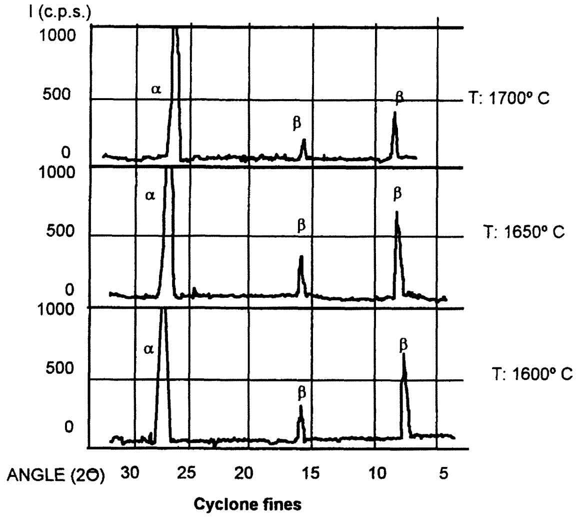
Temp. (°C)	1600				1650				1700			
Type	C.F.	C.W.	C.F. MgO	C.W. MgO	C.F.	C.W.	C.F. MgO	C.W. MgO	C.F.	C.W.	C.F. MgO	C.W. MgO
cD	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
sD	1.8	2.1	1.7	2.1	1.8	2.2	1.8	2.3	1.9	2.6	1.9	2.6
% L.C.	12	12	11.5	11.5	12	11	11.4	11.8	12	12	11.1	11.2
%Δl/lo(-)	9.6	16	10.8	15.8	10.3	18.2	12.6	19.0	14	22.4	13.6	21.7

(C.F.)	Cyclone fines without additive.
(C.W.)	Cyclone fines ground washed.
(C.F. MgO)	Cyclone fines with additive.
(C.W. MgO)	Cyclone fines ground washed with additive.

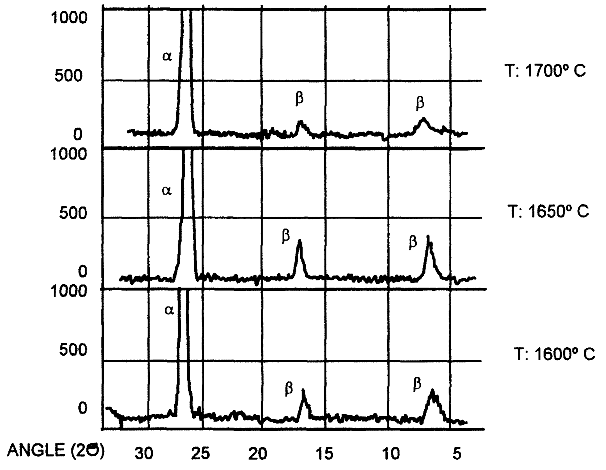
Table VI. Chemical composition of the samples studied

Tabla VI. Composición química de las muestras estudiadas

Sample	Calcination temperature	wt %					
		wt % Na_2O	wt % K_2O	wt % MgO	wt % Fe_2O_3	wt % Al_2O_3	wt % CaO
C.F. MgO	1600	0.64	0.16	0.44	0.2	99	0.05
C.F. MgO	1650	0.72	0.32	0.44	0.2	99	0.05
C.F. MgO	1700	0.64	0.24	0.44	0.2	99	0.10
C.F.	Uncalcined	0.80	0.22	0.06	0.2	91	0.03
C.F.W.	Uncalcined	0.32	0.12	0.08	0.2	93	0.02
C.F.W. MgO	Uncalcinated	0.24	0.20	0.43	0.2	91	0.04



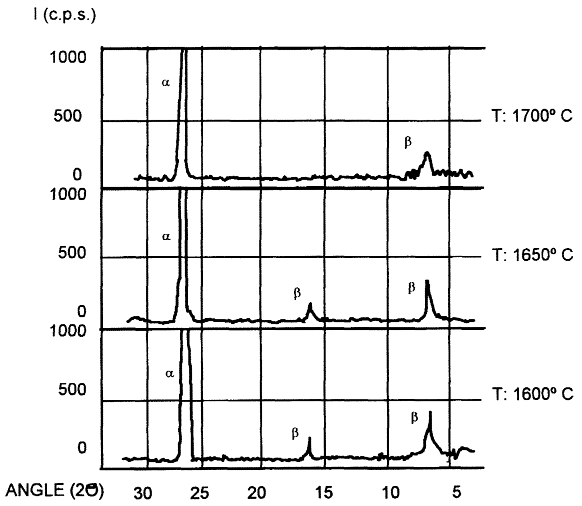
Cyclone fines



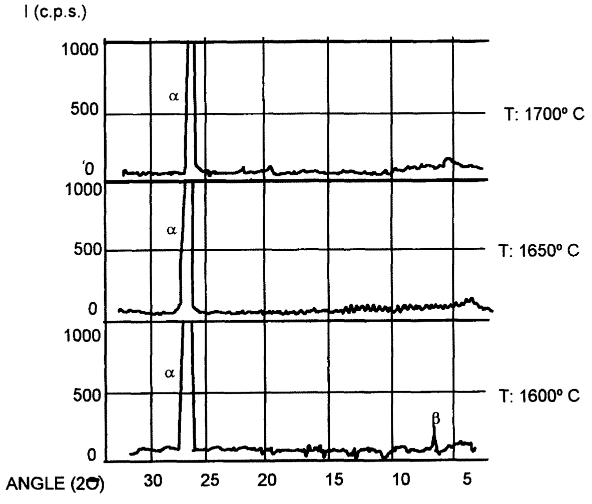
Cyclone fines with MgO

Figure 6. XR D pattern or spectra of the cyclone fines, calcined for 1 h at different temperatures.

Figura 6. Difractogramas de los finos de ciclón, calcinados durante 1 h a diferentes temperaturas.



Cyclone fines washed and ground



Cyclone fines washed and ground mixed with MgO

Figure 7. XR D of cyclone fines, washed and ground. Calcined for 1 h at different temperature.

Figura 7. Difractogramas de finos de ciclón lavados y molidos. Calcinados 1 h a distintas temperaturas.

same abrasiveness, except at 1700 °C where a strong increase is observed (table VII).

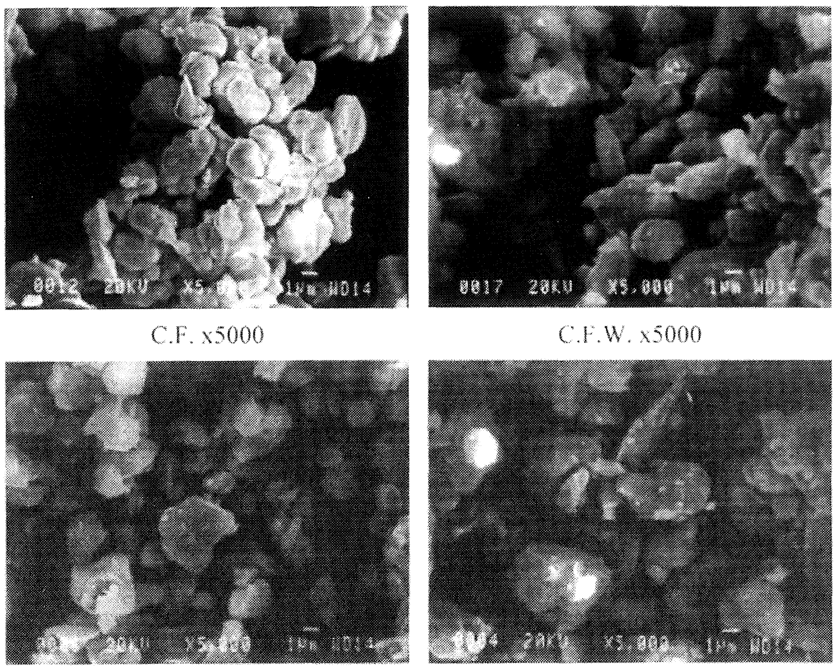
4.2.2. Discussion of results

It can be seen from table IV for unmixed cyclone fines that a decrease from about 6 to 1 micron in particle size results in an abrasiveness increases from 13 to 18.

The contraction of tablets increases with the calcination temperature as well as the sintered density, and the influence of the sodium contamination in the alumina is very important in the sintering process, due to its fluxing character.

The presence of β-alumina is observed when calcining cyclone fines and the intensity of the reflection peaks decreases when the calcination temperature increases until 1700 °C due to sodium volatilization. The peak is not present when cyclone fines, ground washed, are calcined to 1700 °C. Intensity of β-alumina reflection peak decreases in washed cyclone fines due to its lower sodium content. Washing is a better sodium removal method than high temperature volatilisation.

The abrasiveness of a material depends on the particle size and the characteristics of the alumina. In this case, the different mixtures studied have approximately the same particle size. However the greatest abrasiveness correspond to the ground washed fines with MgO addition when calcined to 1700 °C as shown table VII.



C.F. x5000 C.F.W. x5000

C.F. MgO x5000 C.F.W.MgO x5000

Figure 8. SEM micrograph of cyclone fines calcined at 1700 °C.

Figura 8. Micrografía SEM de finos de ciclón calcinados a 1700 °C.

Table VII. Average particle size (mm) and abrasiveness (mg) of high temperature sintered fines, after grounding

Tabla VII. Tamaño medio de partícula (mm) y abrasividad (mg) de finos sinterizados a alta temperatura, una vez molidos

Temperature	F.C.		C.W.		C.F. MgO		C.W. MgO	
	mm	mg	mm	mg	mm	mg	mm	mg
1600	5.5	23	4.5	10	4	21	4	19
1650	4.0	28	5.0	18	5	22	4	20
1700	5.5	22	5.5	19	5	19	5	33

The abrasives produced from washed cyclone fines, doped with MgO and calcined to 1700 °C, has sodium content in the same level as commercial abrasives[5]. These fines shown in figure 8 have no aggregates and present different particle sizes and shapes.

Fines, when sintered with magnesium oxide, result in products similar to the fluoride sintered material (Fig. 5), but with different particle shape and hardness.

5. CONCLUSIONS

The calcination of the fines at low temperatures (1000-1300 °C) produces a powder formed by α-alumina and β-alumina with low abrasive character: 18 mg in the mesh test. This abrasive character, for the same particle size, increases to 25 mg when the calcination temperature increases (1600-1700 °C).

This work has demonstrated the possibility of rising the fines hardness, avoiding the high-temperature processes, by varying the particle size and shape using cryolite as additive. The abrasive is then produced at low temperatures (1000-1300 °C) and after grinding a powder with a high abrasive character is obtained in most of the cases. The best abrasive behaviour was detected for the mixture containing 3 % cryolite. Corundum was present, but also with a certain β-alumina content. This could made a good abrasive in spite of their high fragile character. The polishing effect on metals and minerals of these synthetic products of low temperature is very similar to that for commercial polishing powders, but it could be an interesting product due to its low prize.

The sintering of washed and ground cyclone fines, with the addition of 0.5 % magnesium oxide as mineralising-sintering agent, produces, after calcination up to 1700 °C, a powder with a quite high abrasive character, without the presence of β-alumina, since the amount of sodium present has decreased to 0.2-0.3 %. However the abrasiveness is not better than that obtained at low temperature adding 3 % cryolite.

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