OBTAINING SPHERICAL FRIT PARTICLES FROM CRYSTALLINE RAW MATERIALS

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1. ABSTRACT

Frit spheres were obtained with a diameter of less than 300μm from granules (produced in a spray dryer) made with particles of a mixture of natural raw materials of a crystalline character, milled in a jet mill until 90% of the particles had a diameter smaller than 10μm.

The resulting frit spheres, practically free of unmelted material of a crystalline nature, were obtained by putting the foregoing granules of crystalline raw materials through a vertical dilute phase tubular reactor running at 1700°C, which was specially designed to attempt to make this product.

2. INTRODUCTION

Ceramic frits are produced industrially by melting a homogeneous mixture of crystalline raw materials, with an appropriate particle-size distribution. The melt is usually quenched in water or cooled in air (between rollers), yielding irregular grains or sheets of frit. These products need to be milled prior to dry application.

For the correct dry application of a layer of frit particles onto a ceramic body, it is advisable for the frit particles to exhibit good flowability for uniform distribution. The greatest flowability is found with a spherical shape.

A literature survey was performed, which yielded a review article [1] on glass spheres, their applications and the methods used to produce them. One of the procedures used [2,3] started with a molten glass that was sprayed by applying a flame at high temperature and high speed. Another method employed glass particles that sphered by heating. A similar method to the former is used in the metallurgical industry to make metal spheres and alloys [4]. No procedure was found that allows making glass spheres directly from raw materials mixtures.

The purpose of present study was to obtain appropriately made spherical frit particles directly from the crystalline raw materials normally used for preparing industrial frits.

3. MATERIALS AND EXPERIMENTAL TECHNIQUE

3.1.- MATERIALS

The study was conducted by using two mixtures of selected raw materials with a view to obtaining two frits with quite a similar composition, referenced F-1 and F-2. The second frit is an industrial product and is marketed as a granular. Both yield transparent glazes in single-fire wall tile manufacturing processes. Table 1 presents their composition in oxides.

The standard raw materials employed in frit production were used in the batch formula.

The starting granules were obtained by spray drying a suspension of the raw materials mixture, with an appropriate particle-size distribution.

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[1] HENDRICKS, C. D. *Glass spheres.* En: SCHNEIDER, S J. Jr. (ed.). Ceramic and Glasses. Engineered materials handbook, Volume 4, Ohio: ASM International, 1991.

[2] BLAND, C. C. *Apparatus for production of glass beads by dispersion of molten glass.* U.S. Patent n° 3252780, May 1966.

[3] BLAND, C. C. *Method and aparatus for production of glass beads by dispersion of molten glass.* U.S. Patent n° 3243273, Mar 1966.

[4] GERMAN, R. M. *Powder metallurgy science.* Princeton: Metal Powder Industries Federation, 1984.

Oxide	F-1 (% by weight)	F-2 (% by weight)
SiO_2	57.50	61.8
Al_2O_3	7.10	7.8
B_2O_3	3.00	2.16
Fe_2O_3	0.12	0.12
CaO	10.90	11.78
MgO	1.46	0.71
Na_2O	0.57	0.50
K_2O	4.84	4.93
TiO_2	0.05	0.07
ZrO_2	<0.01	0.14
BaO	3.62	0.07
ZnO	10.13	9.30
SrO	<0.01	0.06
L.O.I.	0.44	0.29

Table 1. *Chemical analysis of frits F-1 and F-2.*

3.2.- EXPERIMENTAL TECHNIQUE

The reactor to be used needed to meet the following requirements:

- Granule residence time needed to be sufficiently high for the starting polycrystalline materials to vitrify.
- It needed to run at a temperature equal to or exceeding 1500°C, which is the peak temperature reached by industrial continuous kilns used for frit melting.
- Granule contact with the reactor walls needed to be avoided, as at the high wall temperature involved, the granules entering into contact with the walls would remain stuck. Consequently, the reactor needed to be vertical and have a sufficiently large diameter.

3.2.1.- Laboratory reactor

A reactor was built, depicted in Figure 1, based on an electric kiln of the type used to produce frits on a laboratory scale. The facility consisted of a 300-mm-long cylindrical chamber, with a 200-mm diameter, heated by electrical resistances. The granules were fed in continuously through the top of the reactor by a suitable proportioning device. The granules fell freely by gravity, crossing the chamber at high temperature. Under these conditions, the limit rate of fall was rapidly reached. The reactor diameter was appropriate to keep the granules from sticking to the walls.

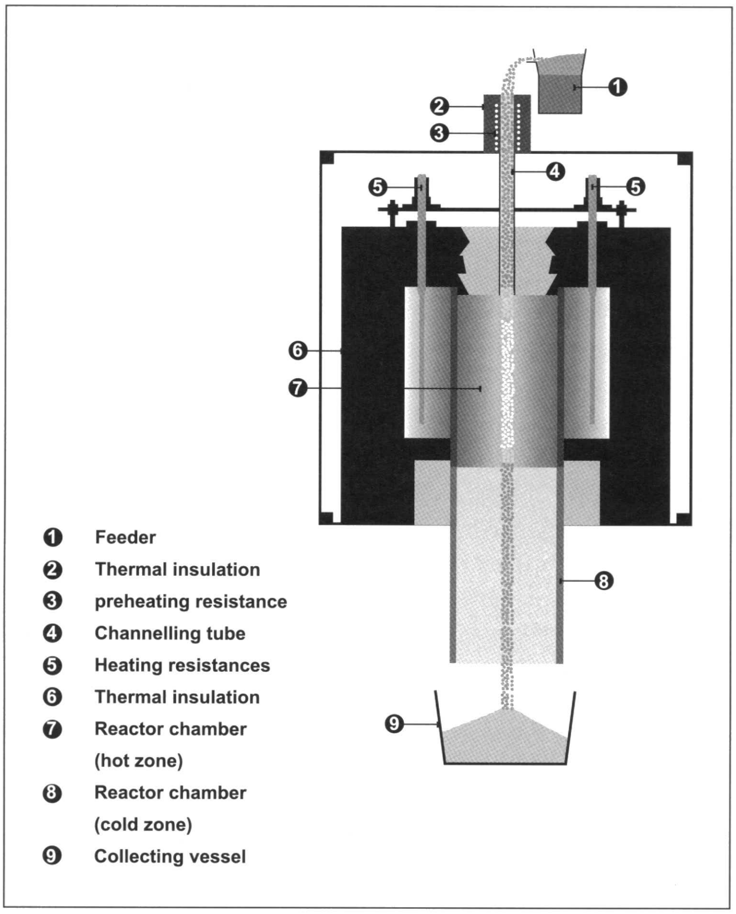

Figure 1. *Schematic illustration of the laboratory reactor.*

With a view to raising granule effective residence time in the reactor, two modifications were implemented stepwise in the reactor:

a) A device was designed and fitted at the reactor inlet to heat the granules, in order to shorten the reactor region that initially performed a preheating function (until the granules attained operating temperature), thus extending the effective reaction zone.

b) Subsequently, to carry out another series of tests, the reactor tube was lengthened without heating the added segment.

The fitted preheater consisted of a 400-mm long aluminium tube with a 30-mm-inner diameter, heated by an electrical resistance, and insulated from the ambient by refractory brick to reduce heat losses. Granule temperature at the preheater exit (the actual reactor inlet) was 700°C.

The reactor tube was extended by adding an aluminium tube to the reactor exit with the same diameter, as shown in Figure 1. This served to retard the cooling of the granules, which were initially poured directly into the collecting vessel.

3.2.2.- Pilot-scale reactor

Based on the experience acquired in the laboratory reactor, attempting to improve

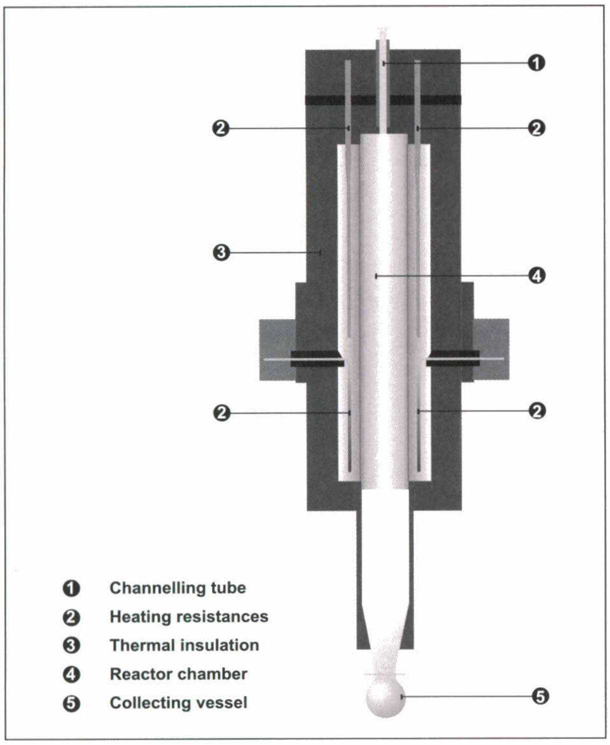

Figure 2. Schematic of the pilot-scale reactor.

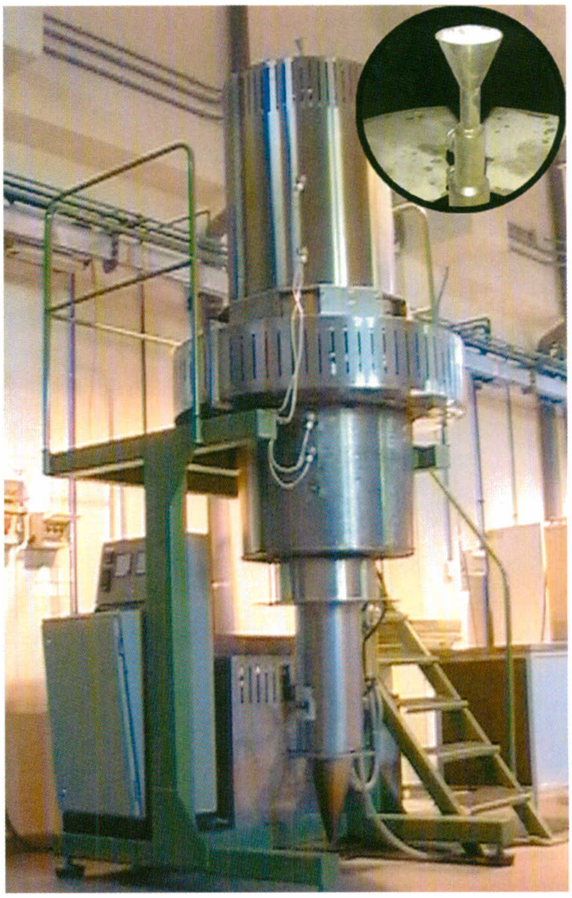

Figure 3. Assembly of the pilot-scale dilute-phase reactor.

its performance and run semi-industrial scale trials, a dilute-phase reactor was designed with the following characteristics:

- Operating temperature: up to 1700°C.
- Reaction tube length: 2 m.
- Reaction tube inner diameter: 0.2 m.

The reaction tube consisted of two consecutive zones with independent temperature regulation. Water was used as the cooling fluid in the powder feeder cooling system and in the area of the tube where the product was cooled. The electrical resistances used were Kanthal Super, quality 1800.

Figure 2 presents a schematic illustration of the pilot reactor involved and Figure 3 shows a photograph of the whole facility.

RESULTS AND DISCUSSION

Before conducting the tests described in this study, many others were performed, using different facilities to try and vitrify the polycrystalline components making up the granules of raw materials.

To be highlighted amongst the facilities used was the plasma reactor installed at ITC. This yielded promising results (10% of the polycrystalline materials initially present in the raw materials was vitrified). To improve the output, granule residence time in the reaction flame would have had to be considerably prolonged (tripled or quadruplicated). This involved a very high cost, and was therefore rejected, as the procedure was too expensive for the product to be competitive.

4.1.- LABORATORY REACTOR

4.1.1.- Tests conducted at 1500°C

The first experiments were carried out at an operating temperature of 1500°C, feeding in granules with a diameter smaller than 300μm. Figure 4 presents a photograph of the product obtained.

Quartz was used as a reference component to measure the extent of the vitrification attained, as quartz was the major polycrystalline material present in the starting mixture (57.5 to 61.8%, by weight) and because it was one of the materials with the highest melting temperature. The quartz residual content in the product was analysed by X-ray diffraction, from the height of the maximum intensity peak corresponding to this crystalline phase in the diffractogram (Figure 5). Using this procedure it was found that 40% of the starting quartz in the raw materials mixture had remained unmelted in the product.

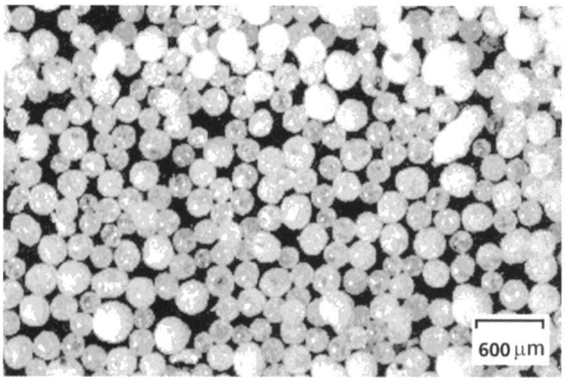

Figure 4. *Granules treated in the laboratory reactor at 1500°C.*

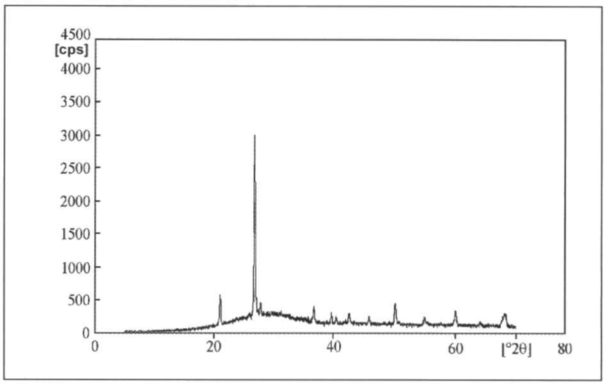

Figure 5. *Diffractogram of the granules treated in the laboratory reactor at 1500°C (D<200 μm).*

4.1.2.- Tests conducted at 1700°C

4.1.2.1.- Reactor length identical to that of point 4.1.1.

In view of the findings, it was decided to raise the reactor operating temperature to attempt to improve the degree of granule vitrification. Figure 6 presents a photograph of the resulting product, which can be visually observed to have a slightly glassier appearance than when the operation was run at 1500°C.

To quantify the outcome, the product was analysed by XRD. The result is shown in Figure 7. It was established from the diffractogram that 38% of the starting quartz had remained unmelted.

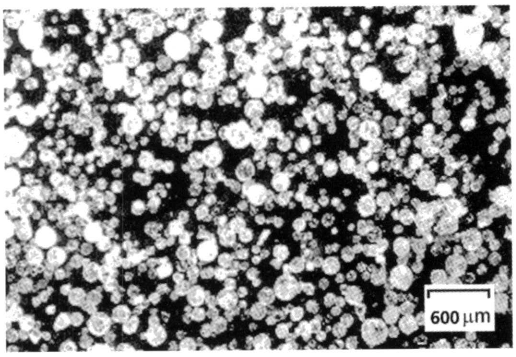

Figure 6. Granules treated in the laboratory reactor at 1700°C.

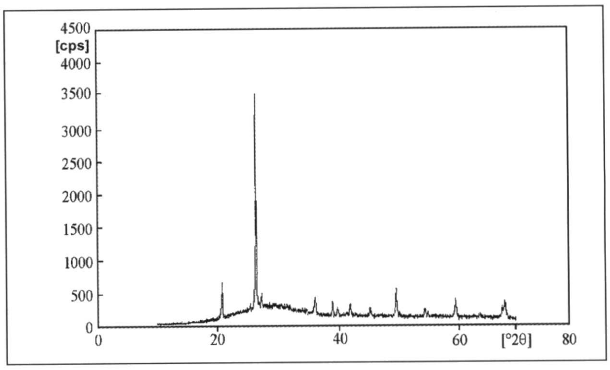

Figure 7. Diffractogram of the granules treated in the laboratory reactor at 1700°C.

As raising the operating temperature did not significantly improve the results, it was inferred that the bounding factor of the sphere vitrification overall process rate was not heat transfer by convection and radiation from the reactor walls to the granule surface, but the heat transmission step rate by conduction from the granule surface inwards into the granule. It was therefore considered that it would be more effective to raise granule residence time inside the reactor, and if this was not sufficient, to reduce granule size and/or the size of the particles making up the granules.

4.1.2.2.- *Lengthening the reactor tube*

To increase granule residence time in the reactor a little, it was decided to lengthen the reactor cooling zone, delaying the fall into the cooled collector. The product obtained on lengthening the reactor exhibited a glassier appearance than the products produced before (Figure 8). This impression was confirmed by XRD analysis (Figure 9). The corresponding diffractogram shows that there were still unmelted quartz materials but in a lower proportion: 33% of the starting quartz in the raw materials mixture.

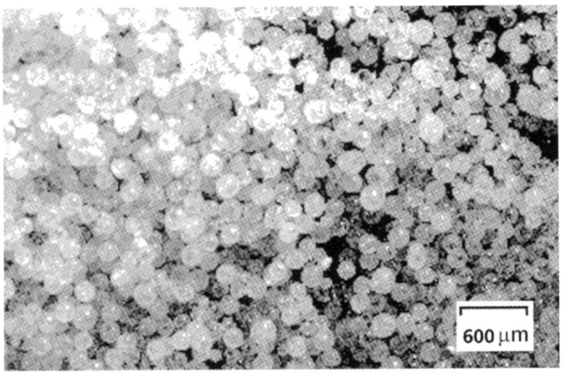

Figure 8. Granules treated in the lengthened laboratory reactor at 1700°C.

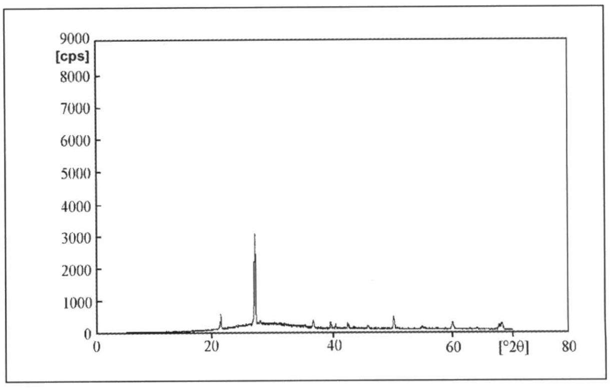

Figure 9. Diffractogram of the granules treated in the laboratory reactor with a lengthened chamber at 1700°C.

This outcome appeared to confirm the hypothesis that the bounding factor in granule vitrification was the rate at which the heat transfer step took place from the granule surface inwards into the granule. As it was not possible to lengthen the laboratory reactor effective zone, it was decided to build a larger reactor.

4.1.2.3.- Using granules made up of raw materials particles smaller than 10 μm (90% of the particles).

Before building the pilot-scale reactor, with a view to improving the extent of granule vitrification, a new attempt was made with the laboratory reactor using smaller size granules (fraction smaller than 100 μm), forming them with particles smaller than 10 (m, produced by milling the raw materials in a jet mill until 90% of the particles had a diameter smaller than this size.

Reducing granule size below 100 μm posed certain technical difficulties, as the granules were partially fluidised as a result of air movement, owing to natural convection inside the reaction tube.

To get around this problem, raw materials granules smaller than 300μm were used. The resulting product exhibited a greater degree of vitrification than the previous products (Figure 10). The visual impression was confirmed by XRD analysis. The diffractogram shown in Figure 11 was used to calculate the quantity of unmelted quartz, which was found to have dropped to 15% of the quartz initially present in the raw materials mixture.

As the product obtained in these last tests exhibited the best degree of vitrification produced up to this time, the product was applied dry to a fired body. The application was fired in an electric laboratory kiln at a peak temperature of 1120°C for 6 minutes. The resulting glaze exhibited an opalescent appearance instead of the desired transparent appearance. On examining the glaze with a stereoscopic magnifying glass (Figures 12 and 13), it was observed that the opalescence was caused by the presence of numerous tiny bubbles trapped in the glaze. These could either have been due to bubbles existing inside the vitrified spheres used to make the glaze, or to the porosity of the consolidated layer formed by dry application of the frit spheres.

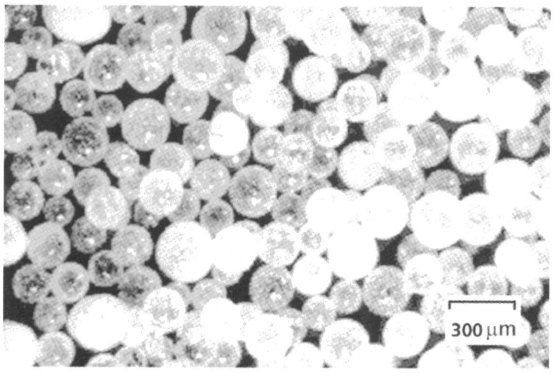

Figure 10. *Granules sized <300μm made up of raw materials particles sized <10μm (90%), treated in the laboratory reactor with a lengthened chamber at 1700°C.*

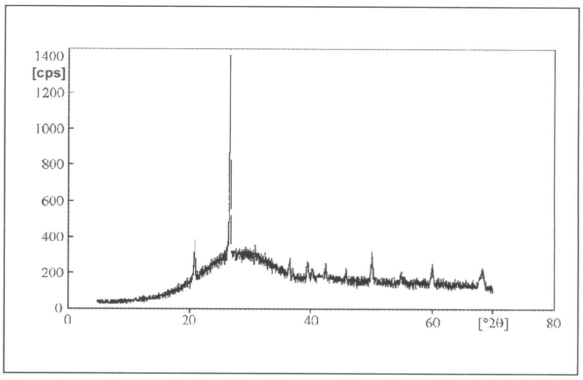

Figure 11. *Diffractogram of the granules treated in the laboratory reactor at 1700°C.*

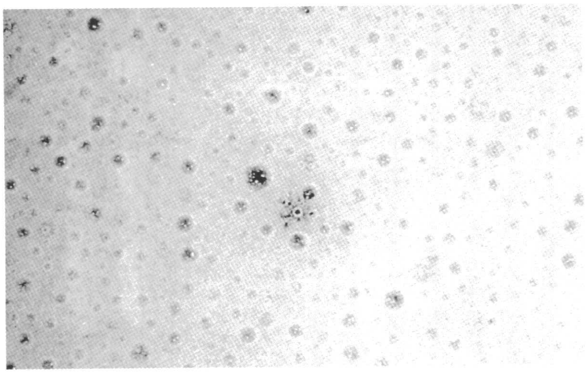

Figure 12. Appearance of the glaze obtained with the spheroidised frit of Figures 10 and 11.

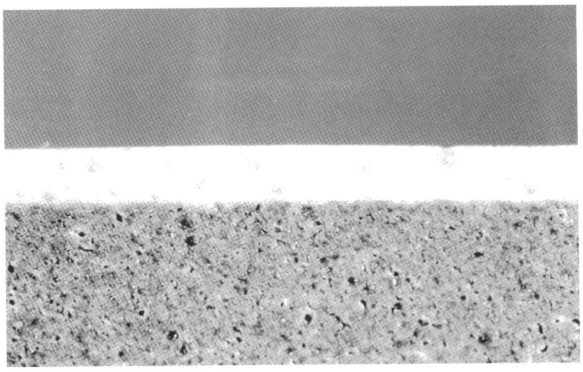

Figure 13. Appearance of the cross section of the glaze obtained with the spheroidised frit of Figures 10 and 11.

4.2.- PILOT-SCALE REACTOR

In view of the findings, a reactor with analogous characteristics was designed, which was longer than the laboratory reactor, to raise granule residence time inside the reactor, as this could significantly affect the quartz content of the product made by heat treatment. The tests were run at 1700°C with granules sized <300μm, consisting of raw materials particles smaller than 10 μm (90% of the particles).

4.2.1.- One heat treatment

The frit spheres produced as a result of the passage of the raw materials granules through the reactor exhibited a very good appearance. The spheres made were transparent, homogeneous beads, although the presence of very small air bubbles could be observed (Figure 14).

Based on the diffractogram of these spheres (Figure 15), the residual quartz content was estimated at 3% of the starting quartz, i.e., 1% of the total resulting frit sphere mass, which meant a very important reduction.

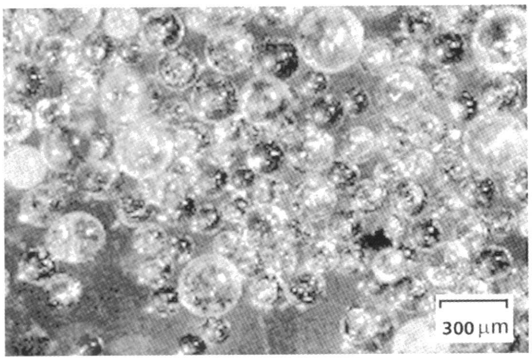

Figure 14. Appearance of the product obtained with a single granule passage through the reactor.

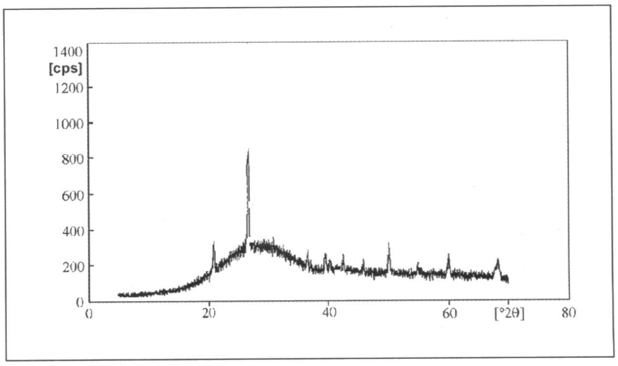

Figure 15. Diffractogram of the product obtained with a single granule passage through the reactor.

4.2.2.- Two granule passages through the reactor

To have an impression of the improvement that could be achieved in the quality of the resulting product by lengthening the 2-m reaction tube (effective zone) by a further one or two metres, the frit spheres obtained in the treatment described in point 4.2.1 were put through the reactor again.

On performing the second heat treatment, the quartz percentage dropped to 1.2% of the starting quartz, i.e., 0.4% of the total sphere mass. In other words, 99.6% of the polycrystalline materials initially present in the raw materials vitrified.

4.3.- TESTS IN THE PILOT REACTOR TO PRODUCE A SPHEROIDISED FRIT FOR INDUSTRIAL USE

Considering the last findings, and in order to verify the feasibility of the studied procedure for producing spheroidised frits for industrial application, a batch formula was used, which was similar to the one employed in making an industrial frit marketed for dry application as a granular. This industrial frit, whose oxide composition is detailed in Table 1, was referenced F-2. It is usually applied industrially in two different granule size ranges: a) in granules sized <300 μm; b) in granules sized <100 μm.

For comparative purposes, frit spheres were produced in the pilot-scale reactor from raw materials granules sized <300(m, made from particles sized <10 (m (90% of the particles). The resulting product was separated into the same size fractions used in marketing the industrial product, i.e., a size fraction <300 μm (termed coarse) and a size fraction <100 μm (termed fine).

4.3.1.- Product characterisation

4.3.1.1.- Observation with a magnifying glass

Figure 16 presents a photograph of the resulting fine product fraction and Figure 17 one of the coarse product fraction.

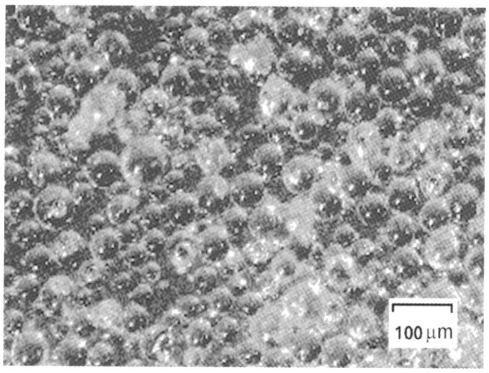

Figure 16. *Appearance of the product obtained in the pilot-scale reactor. Fine fraction (D<100 µm).*

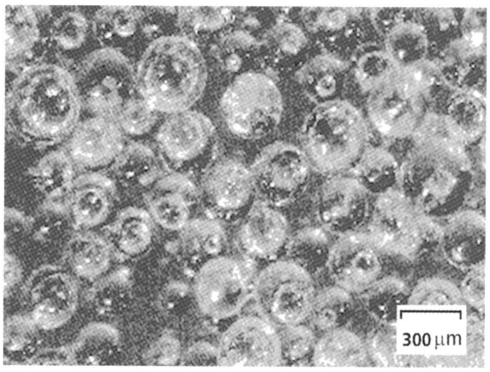

Figure 17. *Appearance of the product obtained in the pilot-scale reactor. Coarse fraction (D<300 µm).*

The micro-spheres can be observed to contain very small inner bubbles. This internal porosity is a little more pronounced in the larger-size spheres.

4.3.1.2.- X-ray diffraction

XRD analysis was performed of the two resulting sphere fractions. Both were found to have a quartz content of less than 0.5% of the total mass, which lies at the detection bound of the available XRD instrument, so that no result was found.

4.3.1.3 .- Measurement of flowability

It is very important for products destined for dry applications to exhibit good flowability, as this property determines the greater or lesser uniformity of the consolidated layer produced on application, which affects end glaze quality.

As a characteristic flow parameter, the angle of the vertex of a cone of material formed by powder flowing freely from a set height was used. As this parameter (θ) increases, the material flows better.

The flowability of the product made in the pilot-scale reactor (Coarse fraction) was measured and compared with that of similarly sized glass spheres. A flow value of 62.6° was found for the glass spheres, while the product obtained in the pilot-scale reactor yielded a practically identical value of 63.8°. The flowability of the product made in the pilot-scale reactor was therefore equivalent to that of spherical glass granules, and better than that of the glaze agglomerates produced by granulation or spray drying, and than that of the frits in granular form.

4.3.2.- Application of the product and firing of the glazed piece

A screen-printing application was performed with the product obtained in the reactor °Coarse fraction) and of the industrial product (granular), with the same size distribution, on stoneware bodies. The applications were fired in a pilot roller kiln at Esmalglass, S.A.

The quality of the glaze obtained from the frit vitrified in the reactor was similar to that found on applying the industrial granular with the same composition, as Figures 18 and 19 show.

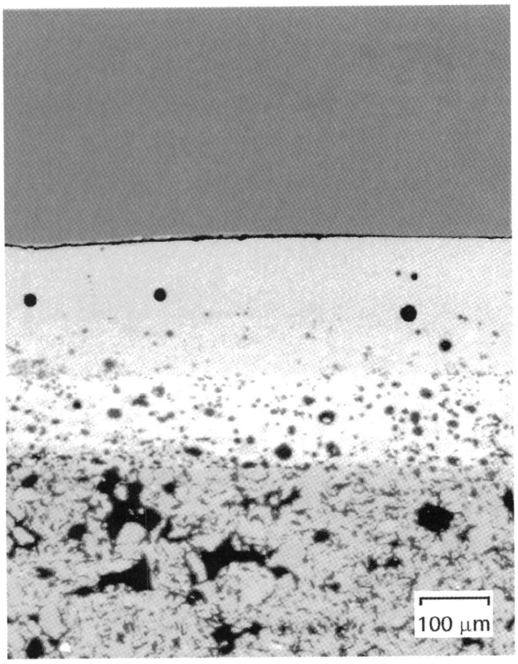

Figure 18. *End glaze on applying the industrial granular.*

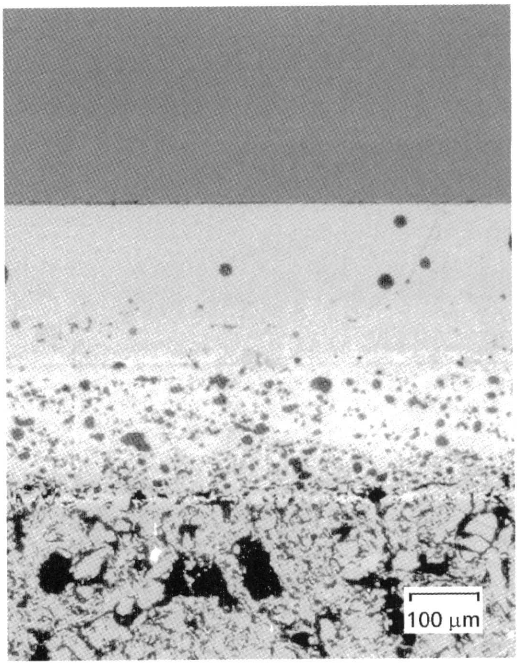

Figure 19. *End glaze on applying the spheroidised frit.*

5. CONCLUSIONS

1.- Suitable technology is available for producing spheroidised frit grains with a quartz content of less than 0.5% from granules sized <300μm, made up of particles of raw materials sized <10μm.

2.- The flowability of the spheroidised frit in this study is of the same order (a little better) than glass spheres with the same size distribution and considerably better than that of glaze agglomerates produced by granulation or spray drying, and than that of granulars.

3.- This quality makes the spheroidised frit particularly useful for use in dry application systems in glazing lines and presses that require using materials with great mobility and low abrasive power.

4.- The quality of the end glaze obtained on firing tiles coated with the spheroidised frit made in this study equalled that obtained on applying an industrially produced granular with the same composition to the same body.