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New porcelainized stoneware materials obtained by recycling of MSW incinerator fly ashes and granite sawing residues

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Abstract

Porcelainized stoneware is a flooring and covering material of the ceramic sector with versatile and modern characteristics similar to those of the natural stone. It is a compact product, extremely hard and homogeneous, generally not fully vitreous (unglazed) in its surface obtained by fast firing of the starting bodies, a mixture of kaolinitic clays, feldspars and quartz in an appropiate relationship. The final product is characterized by its almost zero porosity, being adequated to sustain heavy traffic intensity for interiors or for exteriors, both in modern or classic constructions with a wide range of aspects, designs and colors. According to the chemistry and mineralogical composition of the granite and incinerator wastes, this paper deals with the use of an incinerator fly ash of municipal solid wastes (MSW) and two different granite sawing residues in the obtaining of new types of porcelainized stoneware. By considering most of the physical and mechanical properties here determined, these modified porcelainized stoneware (MPS) materials are close to the conventional porcelainized stoneware and glass ceramics products.

Keywords: Incinerator and granite wastes; Recycling; Porcelainized stoneware

1. Introduction

1.1. Porcelainized stoneware material

Ceramic tiles have been used for some time as elements in construction, as an alternative to the natural stones. The development of the modern ceramic industry, in recent years in Europe, corresponds with the introduction of the traditional double firing techniques and later by the processing of fast single-firing in roller kills.

In the 1980s the material conception of porcelainized stoneware started in the ceramic sector. Actually, in the market there exists all type of decorations and colors of this product for different uses, Italy being the first producing country of this type of material. In Spain, the manufacture of porcelainized stoneware has grown spectacularly during recent years, where these materials have become of great interest in both industrial and research field.

Porcelainized stoneware material is extremely hard, high sintered and unglazed obtained by fast firing, in the 1200–1230°C range temperature, from a green pressed ceramic mixture, which contains an adequate relationship of kaolinitic clays, feldspars and quartz, in general, kaolinitic-illitic ceramic bodies with a large amount of fluxes [1–3]. "Porcelainized stoneware" means that the body is compact and vitrified by the presence of glassy phases to reach a residual porosity near to zero (characteristic of the porcelain). Thus, triaxial porcelains are formulated from ceramic pastes in whose ternary composition system (quartz, feldspar and kaolin) exist eutectic points, which allow the formation of an abundant liquid phase (vitreous) at high temperatures, which favours the growing of crystals, mainly of mullite ($3Al_2O_3{\cdot}2SiO_2$) [4,5].

Due to the attained microstructure, which confers high mechanical and physical properties, porcelainized stoneware construction materials show exceptionally high resistance to all type of tensions, such as thermal shock and impact resistance.

1.2. Incinerator fly ash and granite sawing residues

The problem in the large cities of the great quantity of domiciliary solid wastes (DSW) is continuously increasing.

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The incineration process reduces the waste volume by approximately 90%, but leaves considerable amounts of incineration residues: ashes and slags. Filter ashes are produced at a rate of 25–30 kg per 1000 kg of incinerated waste. Fly ashes contain basically Al, Ca and Si as oxide compounds, in addition to heavy metals and some traces of organic pollutants (e.g. polychlordibenzeno-dioxins and-furanes). Due to the toxic components, the incinerator fly ashes are classified in most of the European countries as toxic and dangerous residues. Therefore, they must be deposited in special landfills with careful control of effluents. This solution is costly and environmentally not fully satisfactory, making it necessary to find tecnological alternatives, that include the inertization and/or recycling of these solid residues. The most beneficial procedure would be to recycle and transform them into an inert and useful industrial product, taking advantage of their silicates content for the obtention of ceramic materials [6–9], as maybe the use of an incinerator fly ash of municipal solid wastes (MSW) from Madrid for obtaining the porcelainized stoneware.

On the other hand, the use of granite as feldspatic raw materials for the ceramic and glass industries is well known. Granitic rocks could be used in the formulation of glasses and triaxial porcelains by adequate design of the starting composition [10–12].

The production of granitic natural stone for buildings and public works reaches an important volume in the Guadarrama Mountains and in the Tietar river valley, both places in the autonomous community of Madrid in Spain due to the abundance of raw materials. Moreover an additional advantage of granite waste in comparison to other natural raw material is it has a very constant composition. The granitic industry generates an important quantity of residues as crashed material of different sizes; powder and mud residues are also originated from the sawmills and cutting machines. It is known that granitic rocks, according to their varieties, contain 25–40% of quartz; 3–10% of mica and the rest is constituted by diferent types of feldspars, including other minerals as impurities or trace amounts.

The percentage of feldspar in the granite is not negligible. Because this mineral takes part in most of the ceramic and vitreous materials, granite waste could be recycled [13]. Similary, other wastes have been considered as recycling secondary raw materials for the production of glass–ceramic tiles [14].

Recently the employment of granitic wastes has been considered of great significance for the production of new materials with characteristics of porcelainized stoneware. Due to the high quantity of quarries producing sawmill powders in the center zone of Spain and their feldspatic composition an other of the objectives of this investigation has been to characterized these residues and to formulate innovative compositions of porcelainized stoneware.

Therefore, the aim of this work is the chemical and mineralogical characterization of an incinerator fly ash, as well as the granite residues from the autonomous community of Madrid (Spain) for their utilization in the formulation of new ceramic construction materials such as porcelainized stoneware, with the main objective to determine the chemical and mineralogical composition of the final products, as well as their physical and mechanical properties.

2. Experimental

2.1. Characterization of residues and formulation of starting bodies

The raw materials used in this research have been: a type of fly ash (V) from a MSW incinerator plant, two granite muds (muds B and C) from Madrid, an industrial feldspar and clay, silica and alumina.

The chemical composition of the residues have been determined through wet way. X-ray diffraction patterns were recorded using Cu $K_{\alpha 1}$ radiation in a Philips PW-1730 difractometer, equipped with a graphite monochromator.

The starting compositions have been formulated attending two possible ways of utilization of these residues.

(a) From the composition of some granite muds B and C the body was formulated by correcting this composition of residues with silica and alumina, until obtaining a paste with silica/alúmina = 3.4, close to the existing one in a porcelanized stoneware studied previously by others authors [15]. These compositions were designated as corrected B and C.

(b) By sustitution in a porcelainized stoneware reference composition (40% clay, 40% feldspar, 20% quartz) [15] of a 10% of clay and feldspar by B granite mud and incinerator V fly ash, respectively. The compositions were designated as 1A and 1F. The raw materials have been mixed and homogenized with a turbulent motion dispositive during 10 min.

Bodies of 20 mm diameter and 5 mm thickness were obtained by cold axial pressing at 40 MPa. They were heat treated on refractory small tiles and submitted to a single firing cycle in a programmed furnace at heating rate of 50°C/min and held at the maximun temperature for 6 min. The cooling rate was also at 50°C/min. until reaching room temperature.

2.2. Sintering curves

In recent years there have been large advances in ceramic tile processing, which have allowed the shortening of the classic firing cycles (14 h) to fast firing cycles of 40–50 min. From previous research about porcelainized

stoneware and other ceramic products [16], a study of the water absorption and linear shrinkage versus firing temperature has been made. The water absorption (directly related to the open porosity) as well as the linear shrinkage are two physical parameters used for the drawing of the sintering graphs and definition of the firing range. Usually, these sintering curves allow the definition of the optimun processing conditions for obtaining the higher values of mechanical properties in the final products.

Water absortion was determined according to the UNE 99 standard, version E "Ceramic Tiles. Determination of water absortion".

2.3. Physical and mechanical properties

The density of the final materials was determined by using "Quantacrome" multipycnometer. This is an instrument specifically designed to measure the true volume of the samples after a fluid desplacement; in this case the gas is helium, which is recommended since its small atomic dimension assures with maximun accuraces its penetration into crevices and porers of the material.

Vickers indentation was used to characterise the hardness (H_v) using a high quality microhardness tester Matzusawa. The samples were submitted to ten loads of 300 g, during 15 s each one. The fracture toughness, K_{IC}, was calculated using the equation (9):

$$K_{IC} = 0.048(c/a)^{-1.32}(E/H_v)^{0.4}H_v\sqrt{a}$$

Where E is the Young's modulus, that was previously determined by means of Knoop indentation.

3. Results and discussion

3.1. Chemical and mineralogical characterization of the residues

From the chemical analysis (Table 1) and X-rays diffraction (XRD) (Figs. 1–3) the chemical and mineralogical composition of the residues and raw materials used to design bodies composition have been determined. It is very clear from the fly ash analysis its high content in CaO and chloride, as well as silica, alumina and alkaline oxide. Concerning to the granite muds it can be appreciated their enrichment in alkalis, especially in potassium oxide. The iron oxide content are minor in the B than in the C mud. The corresponding coloration of the final products for this composition could be unsuitable for some applications.

The crystalline components of the V fly ash are: portlandite ($Ca(OH)_2$), calcite ($CaCO_3$), halite (NaCl), silvine (KCl), anhidrite ($CaSO_4$), probably coal (C), feldspar, etc. After the fly ash was washing with water in a suspension for 24 h, the diffraction patterns, which correspond to soluble salts such as NaCl and KCl, disappear or reduce their intensity (Fig. 1b), as well as the 8.3 Å diffraction. This reflection is very close to a form of microcrystalline silica, a compound capable of being removed through the paper filter.

Table 1
Chemical composition (wt.%) of the wastes and raw materials used for bodies composition design

	V fly ash	B mud	C mud	Clay	Feldspar
SiO_2	13.10	74.85	65.20	64.01	70.21
Al_2O_3	14.00	13.50	11.85	31.49	16.53
Fe_2O_3	1.40	1.13	11.66	1.18	0.06
CaO	62.00	1.02	2.73	0.25	0.55
TiO_2	–	0.11	0.12	0.50	0.05
MnO_2	–	0.05	0.11	–	–
K_2O	2.60	4.77	4.29	1.86	10.26
Na_2O	4.60	3.40	3.06	0.29	2.30
MgO	2.40	0.23	0.31	0.41	0.06
Cl^-	15.26	–	–	–	–
P_2O_5	–	0.05	0.22	–	–

From the corresponding XRD graphs of the muds (Fig. 2), it can be concluded, the presence of α-quartz, albite and orthoclase as main mineral phases. Furthermore, also detected are micaceous minerals and a small proportion of magnetite (and/or spinels), which are due to the metallic particles, as well as some of calcite coming from the cutting process.

The mineralogic analysis of clay and feldspar used in the formulation of the porcelainized stoneware samples are collected in the Fig. 3. The clay is highly enriched in kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$) containing a considerable quantity of quartz and micaceous minerals (illites). This clay shows a small proportion of orthoclase. The feldspar is basically orthoclase type including other alkaline feldspar (albite) and micaceous minerals (illite) as impurities.

3.2. Sintering curves

Figs. 4 and 5 show the sintering curves obtained for B and C compositions, which correspond to the corrected muds B and C, and Figs. 6 and 7 for 1A and 1F compositions, which are formulated by substituting in a triaxial porcelain the clay and feldspar by B granite mud and V fly ash, respectively.

The sintering curves show the variation of the water absortion, as well as the linear shrinkage versus the firing temperature. It can be seen from their open porosity, in general, that these bodies upon increasing the temperature, decrease the open porosity (considered as the capacity of material for absorption of water) and increases the linear shrinkage until reaching a maximum value which is later stabilized. The porosity is reduced progressively, being practically zero to a given temperature,

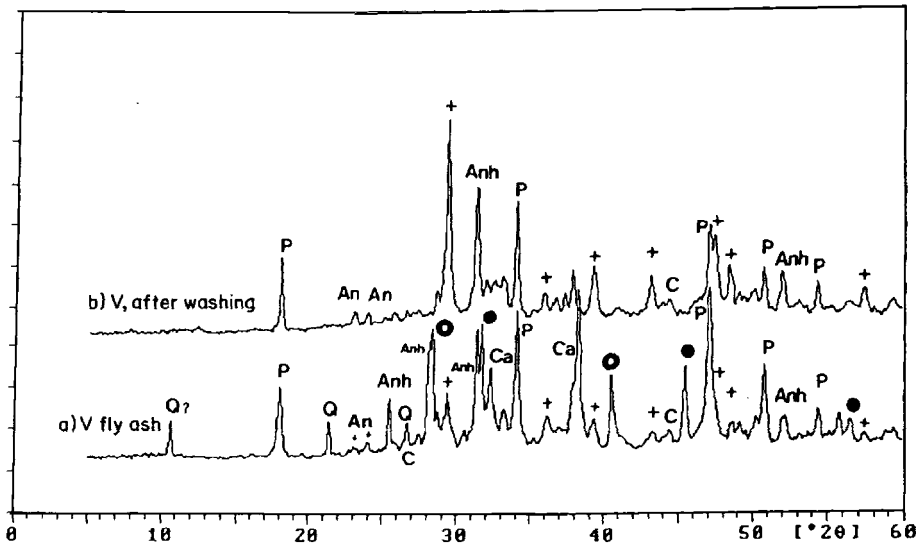

Fig. 1. Analysis by XRD of the F ash: (a) from the incinerator plant; (b) after washing with boiling water. P: portlandite; Q: quartz; An: anorthite; Anh: anhidrite; +: calcite; ●: halite; ○: silvine; Ca: free lime; C: free coal.

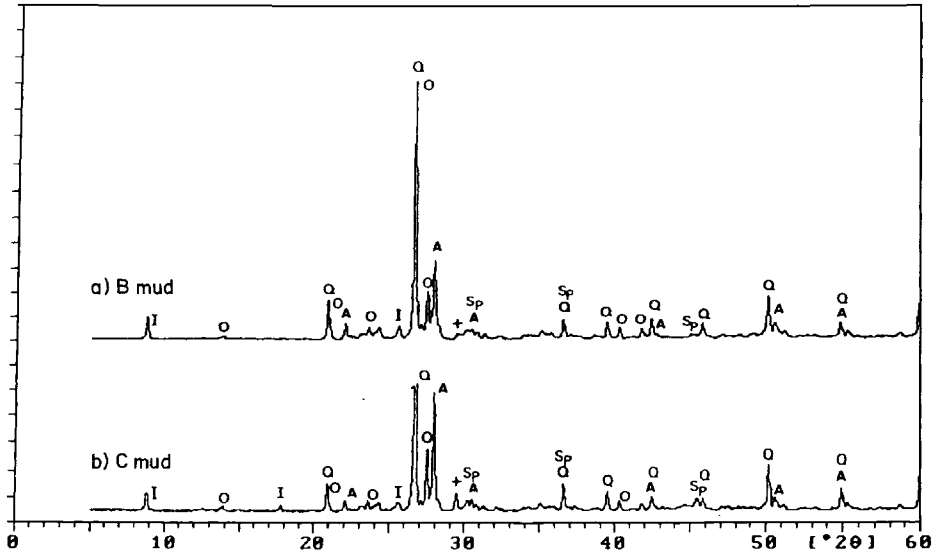

Fig. 2. Analysis by XRD of the muds: (a) B mud; (b) C mud. I: illite; O: orthoclase; Q: quartz; A: albite; +: calcite; Sp: spinel.

depending on the waste type and on the composition of the original body. The evolution of the linear shrinkage, as well as of the water absorption, fits well with the sintering process of ceramic products and it is affected by the formation of a vitreous phase or "transitory liquid", which improves this sintering process. In the porcelainized stoneware bodies the viscosity of the system does not suffer a normal decrease with temperature. This is reduced by the formation of mullite ($3Al_2O_3$ $2SiO_2$) and the dissolution of the quartz, which contributes to the increment of the firing process of these products [2].

The corrected compositions of the B and C muds, show their maximum linear shrinkage and minimum water absorption values at about 1200°C, the C mud being the one which depicts smaller absorption values. On the other hand, the bodies of porcelanized stoneware have been sintered at 1250°C in the case of 1F and at 1300°C in the case of 1A samples. Concerning the shrinkage values, these are smaller than sintered muds (B and C compositions). In any case, it has been proved that the unilateral addition of ash and granite mud to a conventional paste implies an improvement of the sintering process; more concerning the values of water absorption, than the obtained linear shrinkage values.

3.3. Chemical and mineralogical composition of the tested bodies

The sintering behavior is closely related to the mineral phases formed during the firing process and the materials

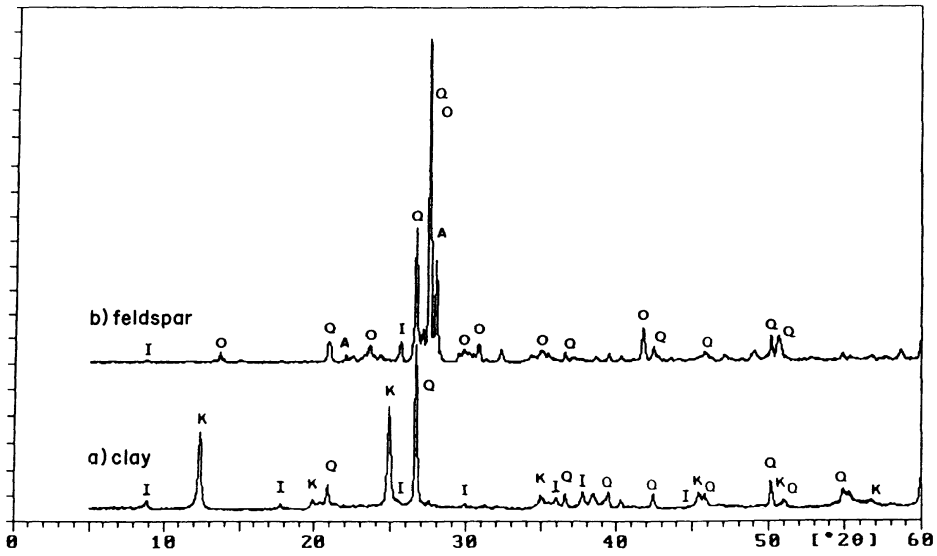

Fig. 3. Analysis by XRD of the raw materials: (a) clay; (b) feldspar. I: illite; O: orthoclase; Q: quartz; A: albite; K: kaolinite.

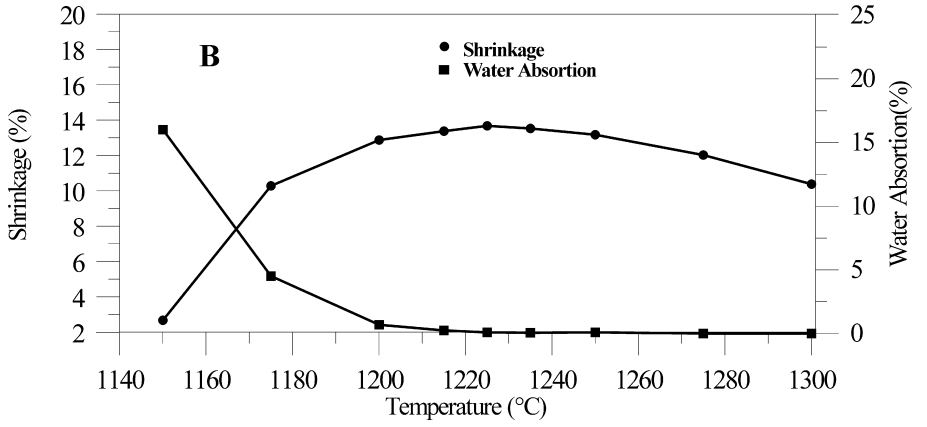

Fig. 4. Sintering curves of the B composition.

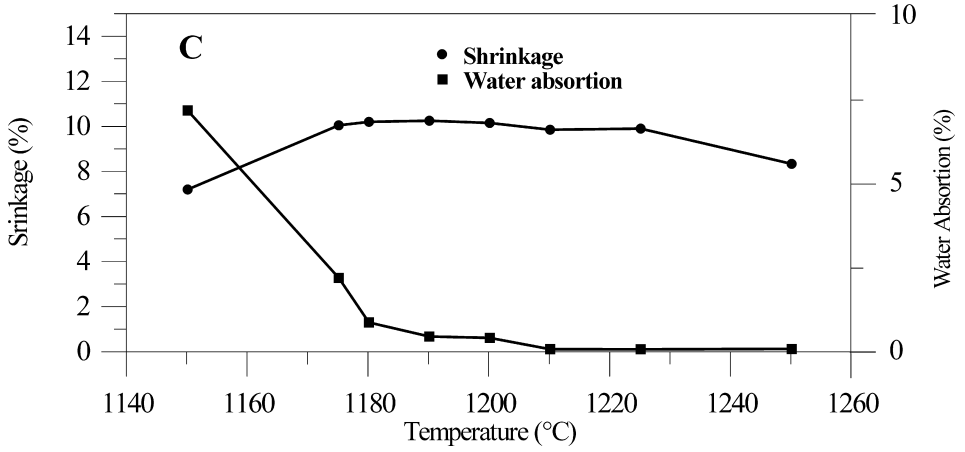

Fig. 5. Sintering curves of the C composition.

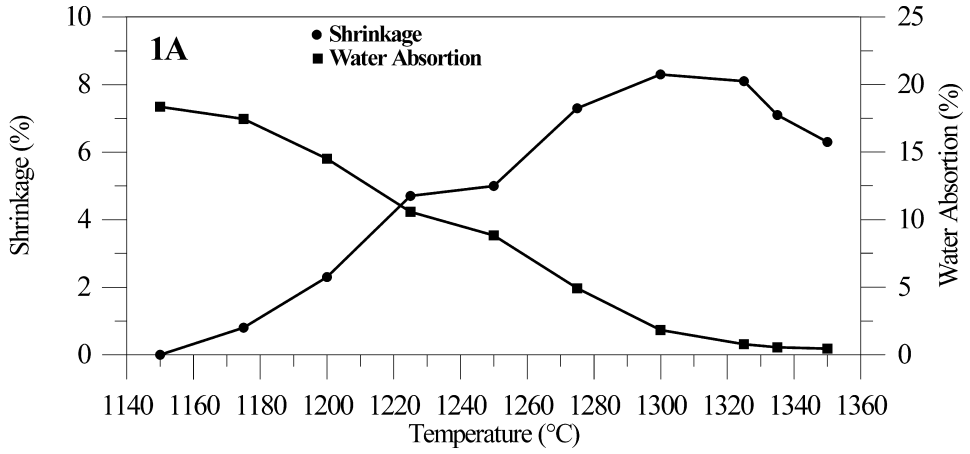

Fig. 6. Sintering curves of the 1A composition.

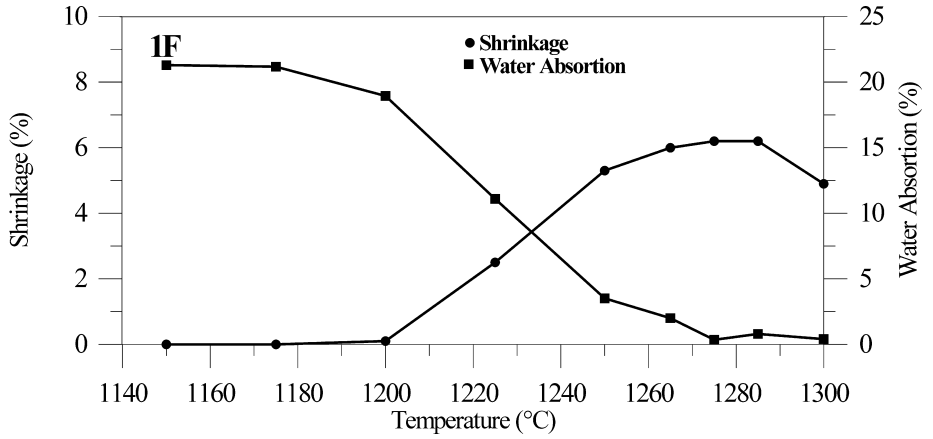

Fig. 7. Sintering curves of the 1F composition.

obtained by fast firing show the smaller percentage of water and maximum shrinkage.

The chemical composition of the tested bodies is shown in Table 2. By XRD it has been detected the crystalline phases of the fired samples at the corresponding temperatures (Fig. 8a–d).

Therefore, it has been demonstrated that the firing products of the corrected B and C muds, at temperatures of 1225 and 1190°C respectively, are constituted by quartz and a small percentage of partly dehidroxilated mica minerals coming from the granite waste. The 3.46 A residual peak is attributed to the illite mineral structure [17]. In the corrected composition B the feldspar component has melted at 1225°C, while in the C one it seems that at 1190°C stays a rest of crystalline feldspar (albite and orthoclase). Furthermore, in this mud some phases containing iron oxides, such as hematite and spinel, are formed. On the other hand, in the bodies in which composition different percentages of clay and feldspar have been substituted by mud and fly ash (Fig. 8c and d) mullite has been formed, but in a very small quantity or with a very incipient crystalline character at 1350 and 1275°C, respectively. Mullite is formed by the reaction of the metakaolinite that is provided by the dehydroxilation process of the kaolinitic materials. This mullite phase is hardly detected by XRD, which indicates that it can be considered as a primary mullite or that their volume fraction and size is extremely small. Scanning electron

Table 2
Chemical composition of the tested bodies

Wt.%	R	B	C	1A	1F
SiO_2	73.54	69.65	61.54	74.71	66.85
Al_2O_3	19.28	20.48	18.09	17.50	18.76
Fe_2O_3	0.50	1.01	10.58	0.49	0.62
CaO	0.36	0.92	2.44	0.44	6.42
TiO_2	0.23	0.09	0.09	0.19	0.22
MnO_2	–	0.05	0.1	–	–
K_2O	4.85	4.43	3.81	5.14	4.02
Na_2O	1.03	3.14	2.74	1.35	1.25
MgO	0.19	0.18	0.28	0.17	0.35
Cl^-	–	–	–	–	1.51
P_2O_5	–	0.05	0.20	–	–
Total	99.98	100	99.91	99.99	100

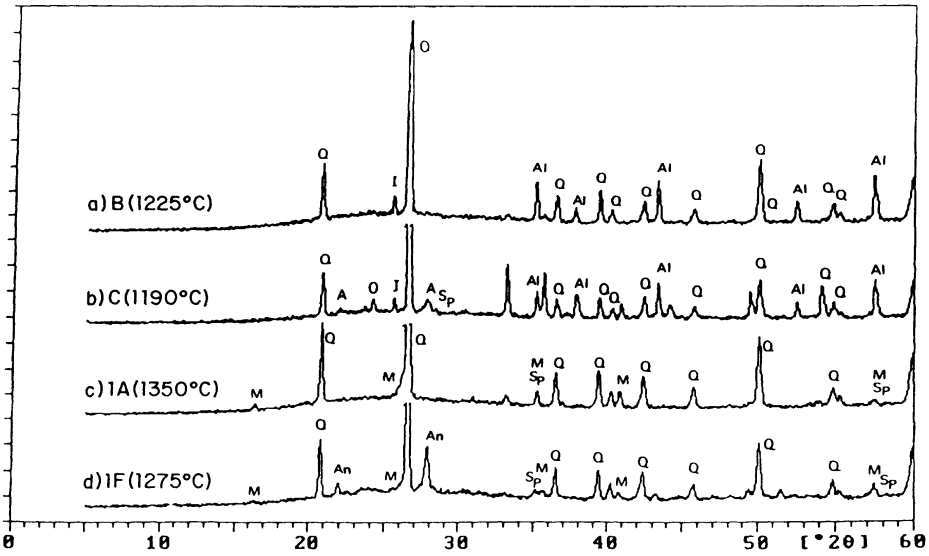

Fig. 8. XRD diagrams of the samples corresponding to the firing temperature which gives rise to minimal absorption values of water: (a) corrected composition B (1225°C); (b) corrected composition C (1190°C); (c) porcelainized stoneware 1A (1350°C) and (d) porcelainized stoneware 1F (1275°C). Q: quartz; Al: alumina; I: illite; Sp: spinel; M: mullite.

microscopy (SEM) will allow the identification of this phase. The corresponding study is in progress.

Even more, due to the fact that in these "porcelainized modified stoneware materials" are identified some reflections of spinel (or γ-alumina), it is confirmed that this mullite has not been sufficiently developed. Finally, in the case of the 1F composition, obtained by substitution of feldspar by incinerator fly ash, it has been proved that the formation of anorthite crystals occurs jointly with the incipient or primary mullite.

3.4. Physical and mechanical properties

The properties determined in these new materials obtained from fly ash and granite residues have been density and mechanical properties (Table 3).

With respect to the density values of samples showing lower values of water absorption and maximum linear shrinkage they are in the 2.13–2.73 kg/dm^3 range. These density values are, in general, very close to the commercial porcelainized stoneware and they are a consequence of the particle sintering and microstructure [2].

The mechanical properties by indentation methods, here determined, were: Vickers microhardness (H_v), Young modulus (E) and stress intensity factor or toughness (K_{IC}) (Table 3). These results are in the range and/or higher of similar materials used as pavements.

The H_v values are in the 6.1–6.7 GPa range, being very close to porcelainized stoneware [2]. Elasticity modulus is between 106–227 GPa, being very high the value for the C (1190°C) material and ranging in the glass–ceramics products [18].

The most interesting results in the case of K_{IC} has been obtained for the C (1190°C) and 1A (1350°C) materials with values of 2.5 and 2.3 MPa m$^{1/2}$, respectively. These values are higher than those corresponding to the porcelainized stoneware and conventional glass ceramics [18]. Values obtained for others materials here investigated (B and 1F) are in the range of the mullite values [19].

Table 3
Mechanical properties and density

Sample	H_v (GPa)	E (GPa)	K_{IC} (MP am$^{1/2}$)	ρ (kg/dm^3)
B-1225°C	6.3	106	1.7	2.28
C-1190°C	6.4	227	2.5	2.73
1A-1350°C	6.7	152	2.3	2.24
1F-1275°C	6.1	106	1.6	2.13

Research is now in progress in order to determine the relationships between the microstructure and mechanical properties of the final products.

4. Conclusions

From the XRD results the mineralogical composition of the tested bodies are: corrected B and C muds, at temperatures of 1225 and 1190°C respectively, are constituted mainly by quartz. The feldspar component has melted. In the C mud it seems that at 1190°C stays a rest of crystalline feldspar (albite and orthoclase) and some iron oxides, such as hematite and spinel, are formed.

In 1A and 1F (at 1350 and 1275°C, respectively), quartz and mullite are detected This crystalline phase could be in volume fraction or size small.

The density values of the final products they are in the 2.13–2.73 kg/dm^3 range. Similar values to the commercial porcelainized stoneware, in general.

The results for mechanical properties determined by indentation methods have been: The Vikers microhardness (H_v) values in the 6.1–6.7 GPa range are very close to those of porcelainized stoneware.

Elasticity modulus (E) is between 106 and 227 GPa, being very high the value for the C (1190°C) material and ranging in the glass–ceramics products.

In the case of stress intensity factor or toughness K_{IC} for the C (1190°C) and 1A (1350°C) materials, values of 2.5 and 2.3 MPa $m^{1/2}$ have been obtained. They are higher than those corresponding to the porcelainized stoneware and similar to conventional glass–ceramics. Values obtained for others materials investigated, B (1225°C) and 1F (1275°C) are in the range corresponding to the mullite.

By considering these results, the final materials could be an interesting new type of construction material MPS, with promising applications in the field.

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