Volcanic ash as flux in clay based triaxial ceramic materials, effect of the firing temperature in phases and mechanical properties

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Abstract

The study of possible incorporation of nontraditional starting powders is a contribution to the rational utilization of raw materials in the ceramic industry. The technological properties of solid waste problems (both urban and industrial) in many cases are not correctly studied and reported. The main objective of the present work is to study and demonstrate the applicability of the volcanic ash for the fabrication of clay based ceramic materials as the flux fraction for replacing feldspar. This paper deals with a particular raw material (volcanic ash) but the results can be extended to materials resulting from similar sources and properties. The milled volcanic ash was characterized and employed as a flux agent replacing feldspar in a model triaxial ceramic material (clay–quartz–flux) formulation. Previously, the volcanic ash was characterized. Differential Thermal Analysis and termogravimetry (DTA–TG) in order to establish the firing conditions were also carried out. Afterwards, the thermal treatments (900–1300 °C) conditions were studied: the firing temperatures were correlated with the shrinkage–porosity–density evolution.

The crystalline phase thermal evolution was also established and compared to the one observed in the model feldspar based material. Finally the mechanical properties of the obtained materials (flexural strength and dynamic elastic modulus) were evaluated. The results permitted to corroborate the applicability and establish some of the technological properties of ash based ceramic material.
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1. Introduction

The principal crystalline phases of the starting powders used for manufacturing traditional ceramics, also known as triaxial, are clays, quartz and feldspars [1]. In many cases the second and third are impurities of the principal clay source. However there are a lot of other inorganic resources that can be used as additives in the fabrication of this wide range of materials [1–11].

The study and the incorporation of nontraditional starting powders, is a contribution to the rational utilization of raw materials in the ceramic industry [12–26]. The technological properties of solid waste problems (both urban and industrial) in many cases are not correctly studied and reported. It is often overlooked that some wastes or materials like the volcanic ash are similar in composition when compared to raw materials, containing materials that are not only compatible, but beneficial to the manufacture of ceramics. The fabrication of products from waste is an advantage that may give the manufacturer a highly competitive position in the market due to the economic issues involved and the marketing opportunities particularly in reference to ecological aspects.

Traditional ceramics, white ware, sanitary ceramics, bricks, roof and floor tiles and technical ceramics, such as porcelain and mullite bodies, are usually highly heterogeneous due to the wide compositional range of starting powders and the natural clays used as raw materials, and the.

Therefore, there is a great incentive to use large amounts of suitable waste products as raw materials. Today it is a well-known fact that some waste materials are similar in composition

to the natural raw materials used in the ceramic industry and often contain materials that are not only compatible but also beneficial in the fabrication of ceramics. In view of the huge amounts of non-renewable mineral resources that the ceramic industry consumes, this similarity is of even greater significance. Although the volcanic ash is strictly a natural resource once it is deposited in the urban or sub urban areas during the volcanic eruptions it transforms into an urban waste with several effects in the human activities; and the approach should be things in common with other urban solid wastes.

There are several studies dedicated to describe the ceramic processes and properties of materials elaborated from industrial inorganic wastes [12–26]. These have been recently reviewed [12–14] but the application of some of these raw materials is usually found in more complex systems than bricks or red ceramic industry, like sanitary ceramics, porcelain tile, etc.

The Southern Volcanic Zone (33°–46°) of the Central Andes exhibits many volcanic systems which have been active during Upper Pliocene (< 3.5 Ma). Characterized as basaltic to andesitic stratovolcanoes, the Puyehue Volcano (40°35′S–72°08′W, in south-central Chile) and the Copahue Volcano (37°51′S–71°09′W, close to Argentina–Chile boundary) represent the latest evidences of explosive eruptions – strombolian and freatomagmatic types – which have delivered huge amounts of pyroclastic fragments affecting human communities as well as ecosystems. During the eruption west and northwest-winds prevailed, so that a fan-shaped area widening towards the east was deposited; this ash layer decreases in thickness as well as in grain size with increasing distance from the source [27–30].

On the 4th of July of 2011 the Puyehue Chilean volcano erupted, its activity produced a great amount of volcanic ash that deposited in the Argentinean territory and the south hemisphere; especially in the Patagonia, the ash deposit was significant and exceeded the 10 cm thick in much of the surrounding areas east of the volcano. In these cases ash is discarded and used at most as landfill. This paper proposes the use of this material in an application with more economic potential. The chemical, crystalline compositions and grain size distribution of the ash are not strictly homogeneous and are slightly variable within a range. This variation might be correlated with trajectory, distance to the origin and other characteristics of the deposit.

A recent article correctly describes these tephra [28] both geochemically and morphologically the volcano is described as well. The actual eruptive history, geochronology, and magmatic evolution of the Puyehue–Cordón Caulle volcanic complex was previously described [31,32].

The environmental impact of the Puyehue–Cordon Caulle 2011 volcanic eruption on Buenos Aires was exhaustively described in a recent article as well [29]. The characteristic of the eruption and the texture of the tephras were also exhaustively described recently [30].

The amount of ash usually deposited in this kind of events transforms it in a potential starting material for several applications. The application of the volcanic ash depends on several factors such as the mineralogy and chemical composition, so that the thorough understanding of physicochemical properties of the phases present in the raw materials can play a decisive role in the

evaluation of their technological potential. Then the true potential should be evaluated by the utilization of a representative starting material at laboratory scale. The ash has been proposed for building material fabrication, concrete, arsenic removal, geopolymer, and for other environmental application [33–36].

The sintering behavior of a volcanic ash has been studied recently [37] and the possible geo polimerization was also reported [38]. Some preliminary studies on materials elaborated from clay–ash mixtures were carried out by other authors. Both thermal analysis and mechanical characterization of some materials were presented [39].

The results of other high glass content mineral sources might be similar to the ones expected for the volcanic ash utilization. These have been widely explored in literature for some decades [37–43]. And the expected behavior of materials based in this kind of starting powders showed is similar to other alkali containing sources [44–48].

The objectives of the present work are to study and re-demonstrate the applicability of the volcanic ash for the fabrication of clay based ceramic materials as the flux fraction for replacing feldspar, to evaluate crystalline and non-crystalline phases of materials processed in different firing conditions. Finally the mechanical properties evolution with the firing temperature of a model triaxial material elaborated with a volcanic ash as fluxing agent was studied. Although this paper deals with a particular raw material but the results can be extended to materials originated in other volcanoes.

2. Experimental procedure

The employed ash was picked from the western coast of the Traful Lake (− 40.614148, − 71.546758), Argentina, (40 km west of the volcano): 40 kg were picked from the surface. The thickness of the ash homogenous deposit was around 20 cm, 60 days after the eruption started.

The volcanic ash presents a silico-aluminous composition and comes from high temperature–pressure conditions hence it principally consists in an amorphous glassy phase accompanied sometimes with some crystalline phases devitrified during the cooling [28].

During the heating treatments (above 1000 °C) of triaxial ceramics, the initial phases, usually crystalline, clay, quartz and feldspars suffer a series of chemical and physical processes at different temperatures between 500 °C and 1300 °C. These processes include decomposition, with gas emission, crystalline transformations, fusion and recrystallizations. Some of the products of these processes are amorphous and others present different grades of crystallinity. The actual temperature and conversion ratio of these reactions and processes depend on the clay type and fluxing components, together with the heating rate and atmosphere [1–11].

The Rietveld method has demonstrated to be an effective tool for quantitative phase analysis in diverse materials from XRD analysis [40,46,49].

The quantitative analysis of the amorphous/crystalline ratio is one of the most investigated and frustrating challenges in the diffraction research. Particularly in silicate materials, like in

Table 1
Chemical composition of volcanic ash and feldspar studied (ICP-AES).

Oxide	Ash (wt%)	Feldspar (wt%)
SiO_2	70.43	66.2
Al_2O_3	15.03	18.5
Na_2O	5.43	3.2
MgO	0.64	0.3
K_2O	2.76	11.3
CaO	1.45	0.2
TiO_2	0.50	0.01
Fe_2O_3	3.52	0.06

traditional ceramics, the particular amount of glass fraction influences the thermomechanical properties of the materials [45,46].

The volcanic ash was first characterized. A chemical composition analysis was performed evaluated by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Original crystalline phases and formed crystalline phases were analyzed by XRD (Philips 3020 equipment with Cu-$K\alpha$ radiation in Ni filter at 40 kV–20 mA, with 2θ between 3 and 70°, 2 s steps of 0.04°). The XRD patterns were analyzed with the program FullProf (version 4.90, July 2010) which is a multipurpose profile-fitting program, including Rietveld refinement to perform phase quantification. The amount of non-crystalline phases was evaluated employing the same method described in a previous article [10]. Formerly the phases were identified using phase analysis software (X'Pert HighScore, version 2.1.2).

Particle size distribution was performed by laser scattering (Malver-Mastersiezer 2000 with a dispersion unit (HYDRO 2000G) with 8000 rpm stirring and ultrasound.

Local kaolinitic clay, together with quartz and potash feldspar with industrial grain size powders (mesh 200) were employed for the model triaxial formulation. (PG-La Toma SA, Argentina). The employed clay presents SiO_2: 61.8%; Al_2O_3: 27.9%; Fe_2O_3: 0.78%; MgO: 0.66%; K_2O% 0.76 and LOI of 7.7%. With 60 wt% of kaolinite and 40 wt% of quartz. The employed quartz presents 99.9 wt% purity. The feldspar crystalline composition is 50.0 wt% of microcline, 34.7 wt% oligoclase and 15.3 wt% of quartz.

A model triaxial formula was carried out (clay, quartz and feldspar mixture with 60–15–25 wt% as respective proportions). The milled (mesh 200) volcanic ash was introduced replacing the fluxing (feldspar) material (named C) and compared with the model formula with a potasic feldspar (named K) with a commonly employed amount of alcali (Table 1).

The starting powders were mixed with excessive water and dried over plaster mold up to optimum plastic condition (approximately 20% water content). Afterwards, the plastic index was evaluated by the Atterberg method. Prismatic ($8.0 \times 8.0 \times 50.0$ mm^3) samples were conformed by plastic deformation and naturally dried for 7 days.

The effect of heat treatment was evaluated by thermogravimetric analysis and differential thermal analysis (DTA–TG) simultaneously carried out on a Netzsch 409 C equipment up to 1100 °C with a heating rate of 5 °C/min, the sample size employed wash 200 mg and alumina was used as reference material.

Samples were fired at different temperatures with the technological ranges (900 °C, 1000 °C, 1100 °C, 1150 °C, 1200 °C, 1300 °C), with a heating rate of 5 °C/min and a 30 min soaking, in electric kiln. Density and open porosity of sintered samples were determined by the Archimedes method. Permanent linear contraction was also evaluated.

Finally the mechanical properties of the samples fired at different temperatures were evaluated. The flexural strength (σ_f) was measured on the bars with rectangular section using the three-point bending test (Universal testing machine INSTRON 4483). A span of 50 mm and a displacement rate of 2.5 mm/min were employed. And the dynamic elastic modulus (E) of the ceramics was measured by the impulse excitation technique with a GrindoSonic, MK5 "Industrial" Model [57,58].

The result obtained for the two studied materials (C and K) were correlated with the processing variables and properties, this brings information about the applicability of this material in the triaxial ceramic industries.

3. Results and discussion

3.1. Volcanic ash characterization

Table 1 shows the chemical composition of the volcanic ash and the potasic feldspar. At a first glance the chemical composition of the volcanic ash, with silica and alumina as principal elements, encourages the ceramic application; particularly the amount of alkali (and earth alkali) motivates the possible application as a fluxing agent. These are concordant with the EDX analysis performed by other authors [28].

The amount of silica is slightly higher than the model fluxing agent. On the other hand the amount of alumina is slightly lower. The total amount of alkali (Na+K) is higher in the feldspar. But, the feldspar contributes with more K and the ash presents a higher Na content. Finally, the alkaline earth (Ca+Mg) oxides contained in the ash is around 2 wt%, while the feldspar presents small amounts of these elements.

It is well known that the amount of alkali is related to the fluxing power of the fluxing agent [1]. But the K:Na ratio is also important because of the different viscosity of the resulting glassy and viscous phases at high temperature affecting the sinterability and properties of the final product. Potash feldspar presents an incongruent fusion behavior [1], soda one is a more energetic flux; furthermore the presence of earthen alkali oxides also will affect this and the sinterability of the triaxial material.

Finally the important amount of iron oxide (≈ 3.5 wt%) limits the application of this material in porcelain and white ceramics. But the rest of the clay based ceramics can be a possible industrial application of this raw material.

Figs. 1–3 show the SEM images of the as received and milled volcanic ash, respectively.

These are similar to the ones reported for similar ashes [28].

While the original powder presented rounded morphology, the milled powder presented sharp edges showing that during the milling pretreatment the grains suffered brittle fractures. These were expected because they are typical of non-crystalline materials, confirmed by the XRD analysis (Section 3.1.1). The grain
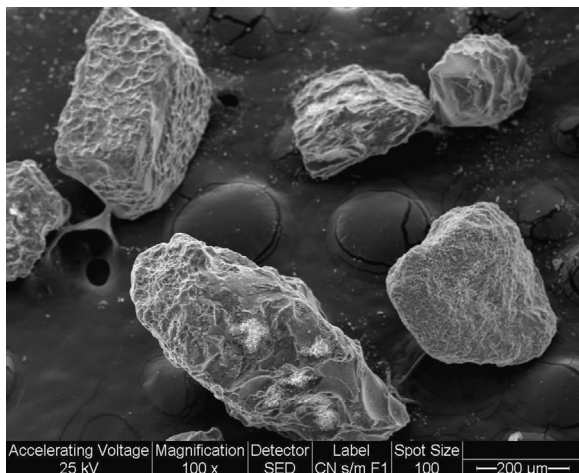
Fig. 1. SEM image of the coarse volcanic ash grains (× 100).

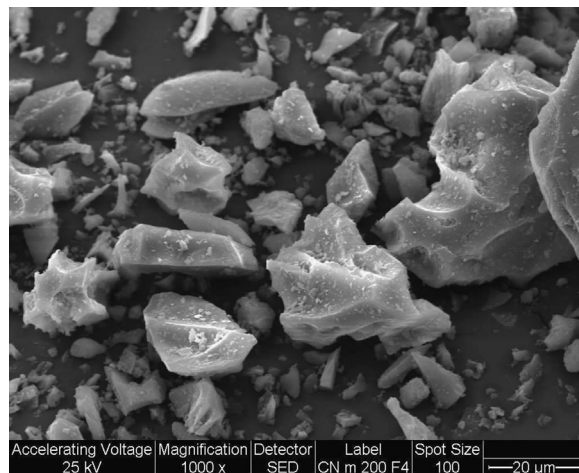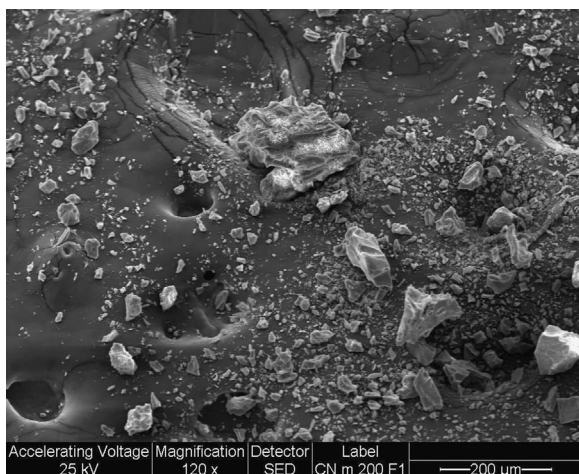Fig. 2. SEM image of the ball milled volcanic ash grains (× 120).

distribution cannot be established by the SEM images, but was measured by laser scattering.

3.1.1. XRD analysis of the volcanic ash

The XRD results are similar to the ones observed in similar ashes [28]. Fig. 5 shows the XRD pattern of the studied ash, it consists in a wide band around 24°, with small quartz peaks and plagioclase, were respectively quantified by the mentioned method; the results are shown in Fig. 4 as well. Although the chemical composition is similar to the traditional flux agent, noteworthy that the crystalline composition is different, since the main phase is amorphous and is accompanied by small amounts of quartz and feldspar, identified as plagioclase. Crystalline phases included in the refinements and their respective ICSD collection codes are shown in Table 2.

3.2. Triaxial material

3.2.1. Thermal evolution (DTA-TG)

The thermo-gravimetric (TG) analysis was performed simultaneously with the differential thermal analysis (DTA). Fig. 5 shows both curves for the ash based material (C). No differences

Fig. 3. SEM image of the ball milled volcanic ash (× 1000).

were observed with the thermal behavior reported for triaxial (clay–quartz–feldspar) materials [1,9–11]. Hence no important thermal processes inherent to the ash presence were observed.

Two mass losses could be identified below 1100 °C. The first correspond to the water evaporation (≤ 1 wt%) and the second one observed at 560 °C corresponds to the kaolinite decomposition to meta-kaolinite [1]. The second water loss was of approximately 3.1 wt%.

Three DTA peaks were identified at 104 °C, 560 °C, and 995 °C; the centroid temperature was chosen to identify the peaks because it is easier to establish. The first two peaks are endothermic and the third one is exothermic. The first one corresponds to the water evaporation observed also in the TG. The second (and more important) peak corresponds to the kaolinite decomposition also observed in the TG.

The third exothermal peak around 1000 °C may be attributed to either the spinel phase or mullite depending on several variables. In this work we are not the condition to decipher which is the phase formed at 1000 °C [5]. The quarts (α–β) transformation (573 °C) was not detected in the DTA curve, because it is overlapped by the kaolinite decomposition.

3.2.2. Sintering

Porcelain stoneware consists of a vitreous phase in which residual minerals (quartz and feldspars) and newly formed phases (mullite) are dispersed. Such a vitreous phase, being quantitatively predominant, governs the viscous flow sintering and strongly affects the geometrical characteristics of tiles as well as their mechanical, tribological and functional properties [5]. Besides its key-role, little is known about the chemical and physical features of this vitreous phase. In the literature—along with a set of phase compositions of porcelain stoneware tiles indicating that the vitreous phase ranges from 45 to 80 wt% [1,5].

Fig. 6 compares the linear shrinkage. The ash formula presents a higher contraction than the model mixture in all the temperature range (except after 1300 °C). The standard formula (K) presents a gradual evolution of the linear contraction in the technological range (treatments below 1250 °C) and is slightly more abrupt after higher firing temperatures (1300 °C). On the other hand the
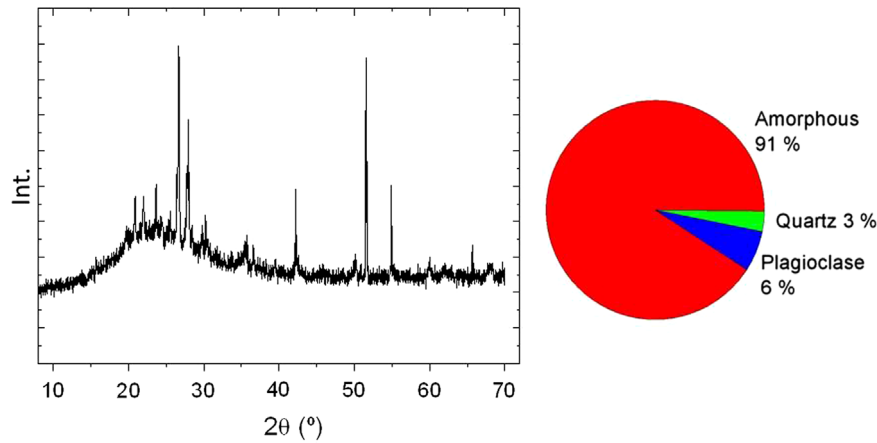
Fig. 4. XRD pattern and phases quantification of the employed volcanic ash.

Table 2
Crystalline phases included in the refinements and their respective ICSD collection code.

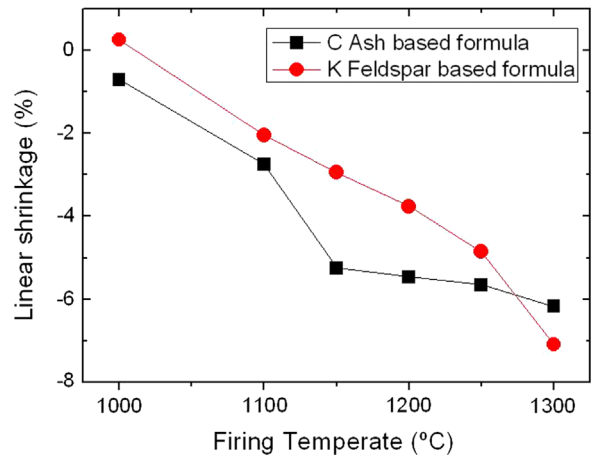|	Phase	ICSD collection code
Clay	Kaolinite	68697
	Muscovite /Illite 2M₂	34921
SiO₂ phases	Quartz	40009
	Cristobalite	74530
	Amorphous Silica (Cristobalite high)	162617
Feldspar	Na–Ca Feldspar (Oligoclase: Albite low)	36279
	K Feldspar (Microcline)	34786
	K Feldspar (Sanidine)	39747
Neo mineral	Mullite	66263

Fig. 6. Linear shrinkage of the two triaxial (clay–quartz–flux) materials fired at different temperatures.
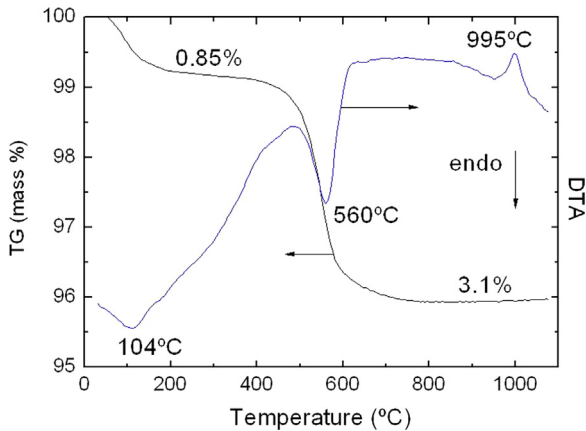

Fig. 5. Thermal analysis of the ash based material (TG–DTA).

Fig. 7. Porosity and density evolutions with the firing temperature of the ash based triaxial materials (C) and the standard (K) triaxial material.

ash based material (C) presented an abrupt contraction increase up to 1150 °C treatments and a slight increment (nearly constant) evolution with the firing temperature over this sill. The observed differences are not significant in relation to the application of technology, as they are not excessive.

Fig. 7 shows porosity and density evolution with the firing temperature for both materials (C and K). The porosity decrease with the firing temperature is evident for C material evidencing the sinterization of the material. The porosity is lower than the standard material in almost all the temperature range. The
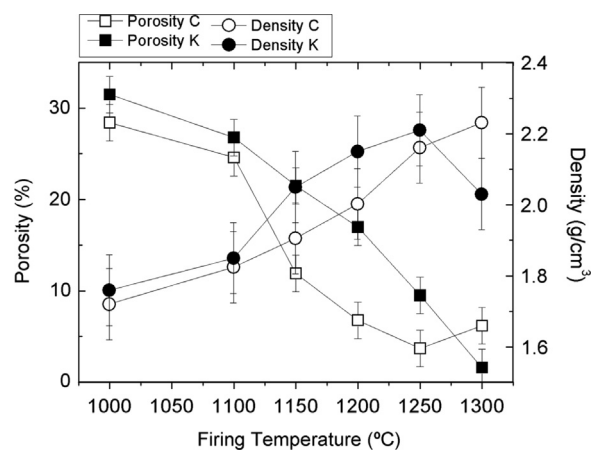
decrease is more important, with an abrupt decrease in the porosity between 1100 °C and 1150 °C. Similar inflection was observed for the contraction, and the sinterization of the standard material is more gradual in this temperature range. Moreover the porosity is low ($\approx 2\%$) for the 1300 °C treatments for the K

material, null porosity was not achieved, this was expected due to the employed clay source a. On the contrary the C material presents the lowest porosity for the 1250 °C treatments and an increase in the porosity after 1300 °C treatments, evidencing that the maturity of this formula is lower (at least 50 °) and at higher temperature treatments some pores are developed perhaps as a consequence of the decrease in the gas solubility [1].

These behaviors can be explained in terms of the fluxing elements introduced through the feldspar or the studied ash. The amount of fluxing elements is slightly higher for the employed potash feldspar, but the fluxing power of the corresponding alkali composition (Na and K) and earth alkali is higher. Second the measured Ca and Mg are active secondary fluxing agents, and at lower temperatures [5]. In addition the effect of the iron oxide in these conditions is also fluxing. Finally the amount alumina incorporated throw the fluxing agent should be pointed out, because it can be assumed that it is proportional to the viscosity and the surface tension of the formed glassy (or viscous) phase [5]. Because of this the sintering of the C material is expected to be lower, as observed.

The density behavior is opposite to the one observed for the porosity showing the abrupt change around 1150 °C and the de-sinterization after 1300 °C treatments for the C material accompanied by the formation of macropores [1,9–11]. Porcelain-like bodies typically attain bulk density in the 2.3–2.5 g/cm^3 range, while the values achieved in this work are around 2.2 g/cm^3; associable to 2–4% open porosity, that is detrimental to other technological properties.

3.2.3. Crystalline (and non-crystalline) phase thermal evolution

In order to elucidate the phase evolution after firing cycles with different maximum temperatures the XRD-Rietveld analysis was carried out to the C samples fired with the mentioned range and compared with the same quantification performed to the standard formula K, with potasic feldspar as fluxing agent [49–51].

The Rwp parameter contemplates the refinement goodness. Typical values of Rwp range from a few percent for very accurate refinements to 20–30% for X-ray refinements, depending in part on the counting times used, the degree of preferred orientation,

and the number of variable parameters. The refinements were adequate; the Rwp values were, in all the cases, between 10 and 30%. The amorphous (glassy) phase quantification was also performed [52–56].

Figs. 8 and 9 show the phase evolution as a function of the maximum temperature of the firing program. The initial was principally kaolinite, but presented a small amount (10%) of illite in the initial phase proportion, in Figs. 8 and 9 the clay phases were grouped.

As expected in this triaxial mixture the observed feldspars consisted principally in plagioclase (Na–Ca feldspar) and micro-cline (K-feldspar), at high temperature (over 1150 °C) Sanidine (a high temperature K-feldspar [1]) was detected, confirming the incongruent fusion of this employed feldspar [1]. In Figs. 8 and 9 the three feldspars were grouped. In both materials the clay decomposition was observed as detected in the TG.

As mentioned, the ash consists principally in an amorphous phase. Hence the amount of amorphous phase is comparatively higher in all the range: this could affect the mechanical properties of the ceramics (this is observed in Section 3.2.4); the amount of amorphous phase at different firing cycles for the studied materials (C and K) can be observed in Fig. 10. After 1300 °C the mount of amorphous phase in both materials studied is similar. The increase the C material is smaller than the one observed in the K material. Moreover the amount of
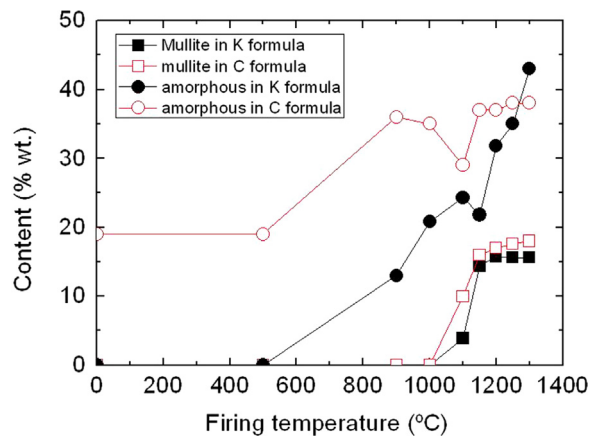

Fig. 9. Amorphous phase and mullite content as a function of the firing temperature.
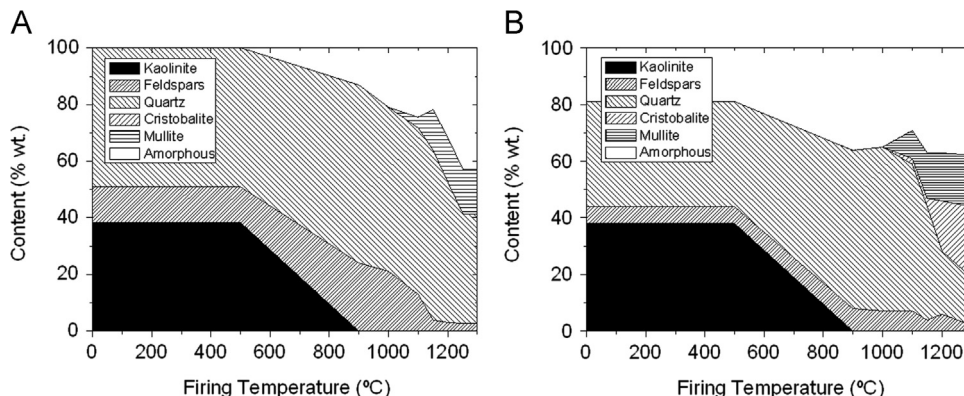

Fig. 8. Crystalline phase composition as function of the firing temperature by the Rietveld method; (A) for the ash based triaxial material and for the feldspar based triaxial material (K).
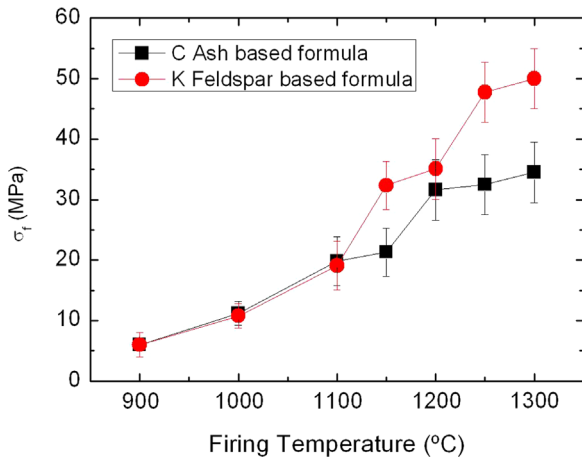
Fig. 10. Flexural strength (σ_f) as a function of the firing temperature.

Fig. 11. Dynamic elastic modulus (E) as a function of the firing temperature.

non-crystalline phases evaluated for the materials fired at higher temperatures (≤ 1200 °C) is similar for the two studied materials (C and K).

Since about 36% kaolinite is present in the batch, the maximum amount of mullite expectable is approximately 18%; mullitization is almost total at 1300 °C (and differences between feldspar and ash).

C material presents an important amount of cristobalite in the materials processed at high temperatures (over 1150 °C), this was not observed in the standard composition (K). Formation of cristobalite is rather common in silica-rich glasses.

The cristobalite can be deleterious for the mechanical properties of this kind of materials. Also a much more important care should be taken in the firing cycle during the cooling stage because of the volume change of the cristobalite transformation at low temperature (200–270 °C).

Finally it has been stated that the mullite presence in this kind of materials is important for development of adequate mechanical properties [1]. Fig. 10 shows the results of the XRD-Rietveld mullite quantification performed for the different materials studied. The mullite content evidences that the mullitization starts between 1000 and 1100 °C and is complete after 1150 °C treatments. The differences and the slight increase observed in the C material at higher temperatures, might be caused by the difficult of the accurate quantification the non-crystalline phases and have no technological implication.

3.2.4. Mechanical properties (σ_f and E) of the triaxial materials

As expected both mechanical properties are correlated with the sinterization and the firing temperature. These can be easily observed from Fig. 11, which plot both mechanical properties with the firing temperature and open porosity.

The obtained values of flexural strength (σ_f) and the elastic modulus (E) are slightly lower than porcelain like ceramics, in both firing temperature ranges: earthenware and stoneware. This can be explained in terms of the observed porosity the typical 35 MPa minimum is achieved only after 1300 °C firing cycles [1–11]. The achieved strength for treatments, below 1100 °C, is
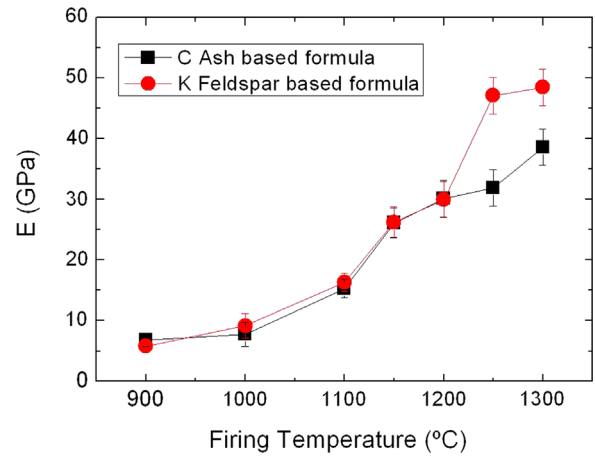
equivalent for the both materials studied, showing than below this temperature the role of the ash (and quartz) is only filler.

The elastic modulus shows a similar behavior to the strength, at lower temperature treatments the resulting materials present equivalent values. But at higher temperature cycles the elastic modulus of the ash based material (C) presents lower E values. Taking into account the fact that the mullite and amorphous proportions are similar for both studied materials, the differences observed might be explained by the porosity and cristobalite presence in the C material.

4. Conclusions

The volcanic ash, once deposited, results in a major problem in urban and agricultural areas. It becomes a solid waste with important consequences in all activities, including human health and animal livestock. A rapid collection of the ashes would allow obtaining an ash with better quality and purity. And the rapid restart of the previous economic activities. The possible application will undoubtedly encourage the recollection.

The present study presents additional information about the possible utilization of volcanic ashes as raw materials for ceramic materials, particularly, as the fluxing agent in a triaxial (clay quartz flux) formula. A representative sample of volcanic ash was characterized and a triaxial (clay–quartz–flux) formulation was performed and compared with the model (feldspar) one. The chemical thermal processes and the sinterability were determined. The actual temperature of this processes were also established.

The sintering and thermal evolution of the mechanical properties of the ceramic produced were also studied and compared with a model triaxial (clay–quartz–feldspar) formula. It was shown that with thermal cycles similar to those used for manufacturing traditional ceramics the obtained ceramics presented appropriate textural and mechanical properties comparable with materials produced with the traditional raw materials: feldspar.

Particularly a decrease in the maturation temperature range was observed. No important difference in the mullitization behavior was observed. Properties of the obtained materials present similar correlations with the processing variables but with a slight decrease in the mechanical properties explained by

the porosity presence (2–4%) and cristobalite, the first one can be improved by the optimization of the processing variables (particle size, firing cycle, other secondary fluxes addition.

The usage of different feldspars is established for different triaxial ceramics earthenware, stoneware or porcelain like materials, and is based in performance, cost and availability.

The possible application of the volcanic ash would result in a decrease in the energy consumption related to the feldspar production. Besides, the lower hardness would reduce the milling operation in the ceramic pretreatment cost. The disadvantage of employing this mineral would be the higher presence of impurities, the starting particle size inhomogeneity, and the possible long term unavailability.

Acknowledgments

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