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Glass-ceramic frits from fly ash in terracotta production

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Preliminary results of an investigation into the possible use of glass-ceramic frits from fly ash and glass cullet in terracotta (stoneware) tile manufacture are reported. Two new ceramics were studied and compared with a plant composition, containing 45 wt.% sodium feldspar. In the first ceramic batch 20% of the feldspar was substituted by frits and in the second the whole amount of feldspar was eliminated and replaced by 35% frits and 10% refractory waste. It was found that the addition of low viscous glass-ceramic frits decreased the sintering temperature by 50–100 °C. At the same time, due to formation of an additional crystal phase (i.e. pyroxene or anorthite) the new ceramics showed an improvement of 25–50% in bending strength.

Keywords: Fly ash, earthenware, glass-ceramics, sintering, phase formation, wmr 1321–9

Introduction

The production of tiling materials is one of the priorities of the traditional ceramic industry. As a result several studies, related to the substitution of conventional raw materials in tile-making (i.e. clays, sands and feldspars) by other natural resources (Carbonchi *et al.* 1999, Abadir *et al.* 2002, Gennaro *et al.* 2003, Ergul *et al.* 2007) or industrial wastes (Andreola *et al.* 2002, Barbieri *et al.* 2002, Dana & Das 2004, Torres *et al.* 2004, Bragança *et al.* 2006, Kurama *et al.* 2006), were carried out during the last decade. The major focus of these studies was based on the search for alternative fluxes as a consequence of the high cost of feldspars and the limited number of deposits that are suitable for ceramic manufacturing. Promising results have been obtained using glass cullet (Matteucci *et al.* 2002, Tucci *et al.* 2004, Bragança *et al.* 2006), waste cathode ray tube (CRT) glass (Andreola *et al.* 2008, Karamanova *et al.* 2007, Raimondo *et al.* 2007), different industrial residues (Dana & Das 2004, Torres *et al.* 2004, Kurama *et al.* 2006) and various volcanic rocks (Carbonchi *et al.* 1999, Gennaro *et al.* 2003, Ergul *et al.* 2007).

As the alternative fluxes have different chemical, phase and fractional compositions some of the new ceramic batches show variations of both forming characteristics and firing behaviour. In general, these fluxes form melts with lower viscosity than the corresponding feldspar ones; this decreases the sintering temperature or/and leads to the for-

mation of a greater percentage of glassy phase. For this reason, in order to obtain sintering behaviour and mechanical characteristics that are similar to the plant compositions, the feldspars can only be partially substituted. When glass cullet or CRT glass were used the optimal amount of the replacement was 5–10 wt.% (Matteucci *et al.* 2002, Tucci *et al.* 2004, Andreola *et al.* 2008, Karamanova *et al.* 2007, Raimondo *et al.* 2007).

The crystallinity of the final ceramics may be increased by using glass-ceramic frits (Siligardi *et al.* 2000, Zanelli *et al.* 2008) or compositions with high crystallization trends (Barbieri *et al.* 2002, Ergul *et al.* 2007). In this case, due to re-crystallization processes during the heat treatment, the amount of residual amorphous phase decreases. It can be assumed that increasing the crystallinity will have a positive effect on the mechanical properties (Hlavac 1983).

The aim of the present study was to evaluate the effect of sodium feldspar substitution in terracotta with glass-ceramic frits, based on 45 wt.% electric power station fly ash and 20% glass cullet. Similar glass compositions, produced by various industrial waste materials, have been well studied and used for syntheses of different glass-ceramic materials (Rawlings 1997, Karamanov *et al.* 1998, 1999, 2003, Rawlings *et al.* 2006).

Two different stoneware compositions were investigated and compared with a plant ceramic. In the first 20 wt.% of

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Table 1: Chemical compositions of used raw materials (wt.%).

	Fly ash	Glass cullet	Glass-ceramic frits	Feldspar	Kaolin	Ball clay	Sand	Refractory residue
SiO ₂	49.8	71.8	57.1	70.4	51.6	59.4	90.2	60.3
Al ₂ O ₃	23.8	0.3	11.8	16.4	33.1	20.3	6.7	39.1
Fe ₂ O ₃ *	9.7	0.2	4.6	0.8	0.7	4.9	0.3	0.2
CaO	6.7	10.2	12.3	1.1	0.6	1.2	0.5	0.4
MgO	1.8	3.1	6.4	0.2	0.3	1.6	0.1	0.1
Na ₂ O	0.7	14.9	4.5	8.7	0.4	0.4	0.3	–
K ₂ O	2.2	0.4	1.4	0.6	0.3	0.6	0.1	–
L.O.I	4.9	–	–	1.8	13.8	12.5	2.2	0.2

*Iron oxides are presented as Fe₂O₃.

feldspar was substituted by frits, whereas in the second the whole feldspar amount was replaced by 35% frits and 10% refractory (chamot) waste.

The manufacture of 1 m² of tiling ceramic requires about 20 kg raw materials (i.e. the studied compositions offer the possibility of using 2–3 kg fly ash per m² terracotta). This implies that a medium stoneware production line with annual capacity of 1 000 000–1 200 000 m² could recycle 5–10 tons fly ash daily.

In the present study the sintering was evaluated by variations of linear shrinkage and water soaking. The phase transformation is estimated by dynamic thermal analysis (DTA)-thermogravimetric (TG) and X-ray diffraction (XRD) techniques. The bending strength of the final samples was also measured.

Materials and methods

The parent glass was prepared by mixing fly ash from an electric power generating station with glass cullet, dolomite and sand in the ratio 45 : 25 : 20 : 10. The melting (1 kg batch in a 500 mL mullite crucible) was carried out in an electric furnace at 1400 °C. After 1 h holding time the obtained melt was quenched in water and the resulting granulate (i.e. glass frits) was broken and milled. The chemical compositions (main elements) of the fly ash and glass cullet used and glass-ceramic frits obtained, G, are presented in Table 1.

The hypothetical viscosities of melts with fly ash, G and Na₂O·Al₂O₃·6SiO₂ feldspar (albite) compositions at 1100 and 1200 °C were estimated by the Lakatos method (Scholze 1990). The values obtained (i.e. 10^{5.7} and 10^{4.9} dPa s for the fly ash, 10^{5.0} and 10^{4.3} dPa s for the albite and 10^{4.6} and 10^{3.9} dPa s for the new glass composition) demonstrate that the fly ash cannot be used as a flux, whereas G can be considered as a sintering promoter. At the same time, due to the addition of dolomite and resulting high sum of CaO + MgO + Fe₂O₃,

the studied glass is characterized by a high crystallization trend. During secondary heat-treatment in the range of 900–1000 °C this composition formed 40–50 wt.% diopside solid solutions. Similar glasses are characterized by a good chemical durability and are successfully applied in the synthesis of sintered glass-ceramics (Karamanov *et al.* 1998, 1999, Piscicella *et al.* 2001, Rawlings *et al.* 2006).

The chemical compositions of the local ceramic raw materials used (i.e. kaolin, ball clay, feldspar and sand) and refractory residue are also shown in Table 2. The results showed that these materials may be used for tile-making but were inappropriate for the production of white porcelain or other quality ceramics: the ball clay had high percentages of iron oxides, CaO and MgO, the kaolin contained an elevated percentage of quartz, while the use of feldspar was characterized by 2% thermal losses and a reduced percentage of alkali oxides because of significant admixtures of clays and sand.

Three ceramic batches (Table 2), containing constant amounts of kaolin, ball clay and sand and different percentages of glass-ceramic frits, feldspar and refractory residue were prepared.

The first composition (labelled C-0) was used for production of terracotta tiles in the ceramic plant Isida- Elin Pelin (Bulgaria). The heat-treatment in the manufacturing kiln took 3 h; the sintering temperature was 1170–1180 °C and the holding time was about 10 min. The non-glazed samples obtained from this production cycle were characterized by an apparent density of 2250 ± 80 kg m⁻³, linear shrinkage of 6.0 ± 0.3%, water soaking of 4.6 ± 0.4 wt.% and bending strength of 31 ± 3 MPa.

In the C-1 batch 20 wt.% of the feldspar were substituted by glass frits. In C-2 the feldspar was totally replaced by 35% frits and 10% refractory chamot waste, used as an inert material to balance the Al₂O₃ percentage in the final composition.

Table 2: Batch compositions of studied ceramics (wt.%).

	Kaolin	Ball clay	Sand	Feldspar	Glass-ceramic frits	Refractory residue
C-0	6	31	18	45	–	–
C-1	6	31	18	25	20	–
C-2	6	31	18	–	35	10

All raw materials were milled and sieved below 63 μm . Parent batches with water content of 6% were prepared and homogenized and green samples with initial size of 50 mm \times 30 mm \times (4–5) mm were obtained by pressing at 30 MPa.

A series of five samples of each composition were heated for 40 min at 1050, 1100 and 1150 $^{\circ}\text{C}$ at heating and cooling rates of 15 $^{\circ}\text{C min}^{-1}$. Then, the densification was estimated by measuring the linear shrinkage, $\Delta L/L_0$, water soaking, W , (3 h at 98 $^{\circ}\text{C}$) and apparent density, ρ_a (by water Archimedes balance).

The phase transformations of parent batches were estimated by DTA-TG analysis (MOM Paulin-Paulin) using samples of approximately 500 μg and a heating rate of 7.5 $^{\circ}\text{C min}^{-1}$. The phase composition of final ceramics was evaluated by XRD analysis (Philips PW1810 and $\text{CuK}\alpha$ radiation). The bending strength was evaluated by the three-point method (BDS).

Results

DTA traces of the three batches show similar behaviour in the temperature range 20–700 $^{\circ}\text{C}$: endothermic effects at 100–120 $^{\circ}\text{C}$ due to loss of ‘physical’ water between the layers of the clay structures and at 450–55 $^{\circ}\text{C}$ because of dehydroxylation and the formation of metakaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). The corresponding TG losses were 2.4, 2.0 and 1.9 wt.% at 90–120 $^{\circ}\text{C}$ and 3.7, 3.4 and 3.0% at 450–600 $^{\circ}$ for C-0, C-1 and C-2, respectively.

In the range 700–1250 $^{\circ}\text{C}$ the TG traces showed no weight changes whereas the DTA curves (Figure 1) indicate some differences. In C-0 only a large endothermic effect was observed at 1000–1250 $^{\circ}\text{C}$, which can be related to the melting of the feldspars and the following quartz dissolution (Karamanov *et al.* 2006). At the same time, due to crystallization of the glass-ceramic frits, C-1 and C-2 showed exothermic effects in the range of 900–950 $^{\circ}\text{C}$. The melting endothermic effect in C-2 was more intensive than that of C-0, whereas in C-1 it overlapped with an exothermic peak at 1150 $^{\circ}\text{C}$.

Figures 2, 3 and 4 show the variations of linear shrinkage, water absorption and apparent density at 1050, 1100 and 1150 $^{\circ}\text{C}$, respectively. The results highlight the similar sintering behaviour of C-0 and C-1 and the diverse behaviour of C-2.

In order to clarify the densification process new samples were sintered for 20 and 60 min at 1150 $^{\circ}\text{C}$ (C-0 and C-1) and at 1050 $^{\circ}\text{C}$ (C-2). The corresponding variations of linear shrinkage, water absorption and apparent density are reported in Figures 5, 6 and 7, respectively.

The XRD spectra of the final ceramics (C-0 and C-1 after 60 min at 1150 $^{\circ}\text{C}$ and C-2 after 60 min at 1050 $^{\circ}\text{C}$) are plotted in Figure 8.

Discussion

The ceramics C-0 and C-1 showed negligible densification at 1050 and 1100 $^{\circ}\text{C}$: the linear shrinkage was 1–2.5% and the water absorption was 9–12%. The sintering process practi-

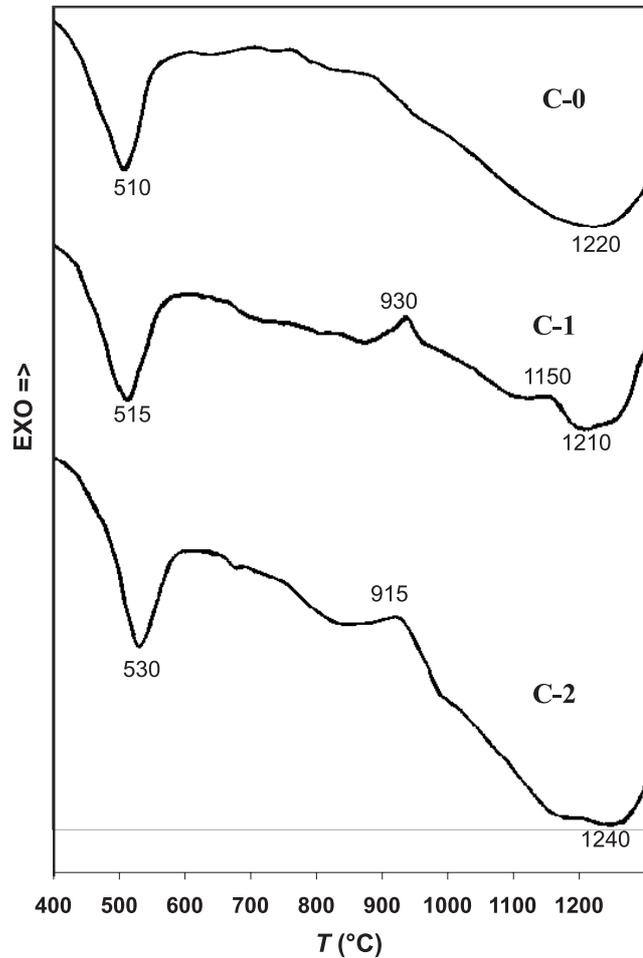


Fig. 1: DTA of studied ceramic batches.

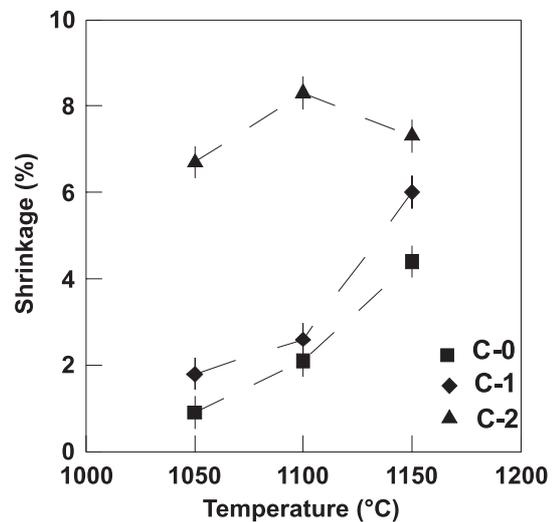


Fig. 2: Linear shrinkage of studied ceramics at different firing temperatures.

cally started after the melting of feldspars at 1150 $^{\circ}\text{C}$. At this temperature W decreased by two times in C-0 and reached 1.4% in C-1 (i.e. a significantly lower value than the plant samples, fired at 1170–1180 $^{\circ}\text{C}$). The improved sintering of

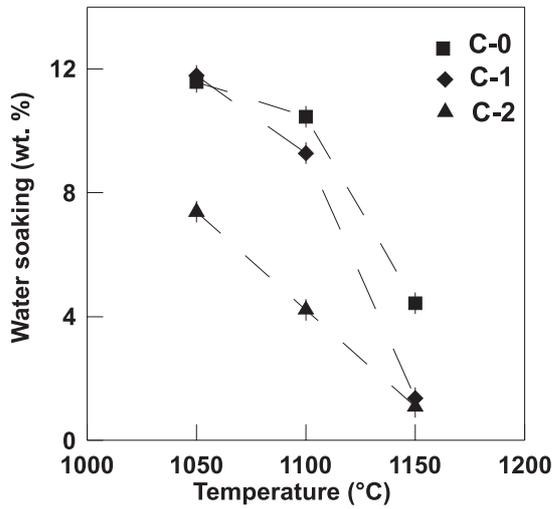


Fig. 3: Water soaking of studied ceramics at different firing temperatures.

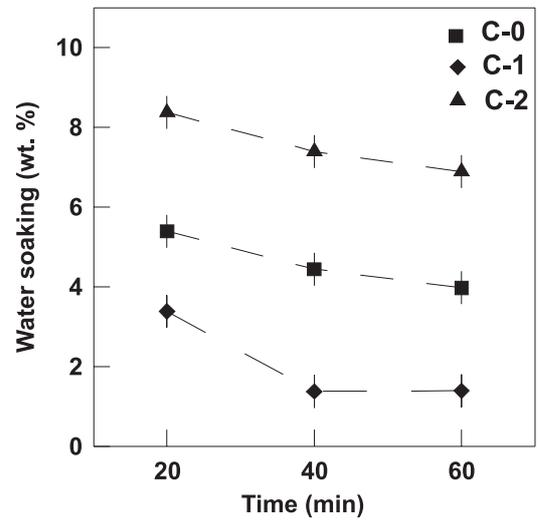


Fig. 6: Water soaking of studied ceramics at different holding times.

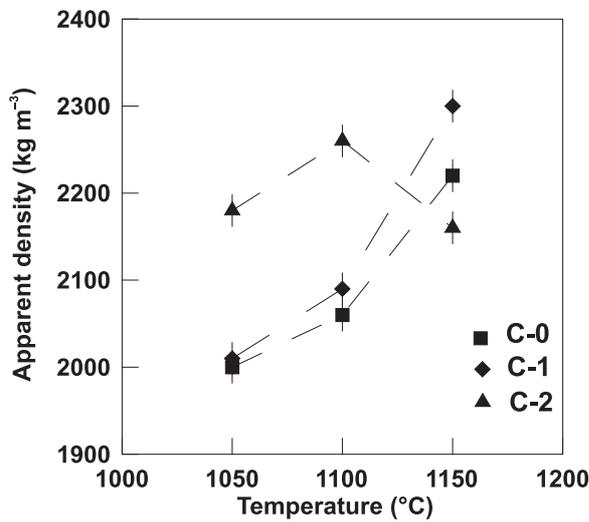


Fig. 4: Apparent density of studied ceramics at different firing temperatures.

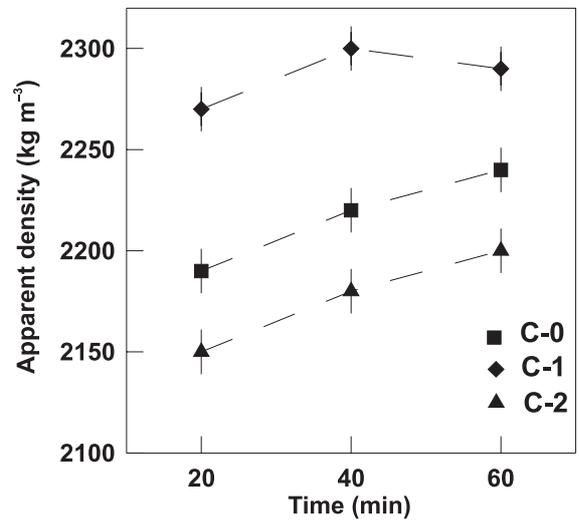


Fig. 7: Apparent density of studied ceramics at different holding times.

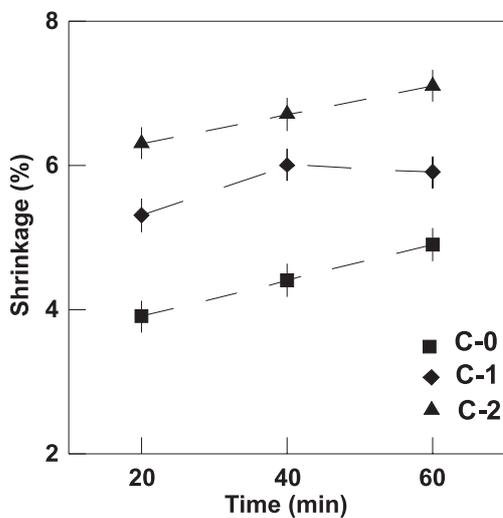


Fig. 5: Linear shrinkage of studied ceramics at different holding times.

C-1 at 1150 °C was also confirmed by the higher shrinkage and apparent density.

In C-2 a considerable densification was already observed at 1050 °C while at 1100 °C both W and ρ_a reached the parameter values of plant ceramic. At 1150 °C overfiring was observed: the water absorption decreased to 1.0% and due to the formation of greater closed porosity, the apparent density and shrinkage decreased. This behaviour was a result of the addition of 35% glass frits, which, at higher temperature, led to the formation of an abundant amount of low viscous melt.

The C-2 composition was also characterized by high $\Delta L/L_0$ percentages, which indicated a superior initial porosity of the green samples. Similar results have been reported in other studies with glass-ceramic frits (Zanelli *et al.* 2008) and other alternative raw materials (Abadir *et al.* 2002, Gennaro *et al.* 2003). The firing shrinkage in C-2 could be decreased

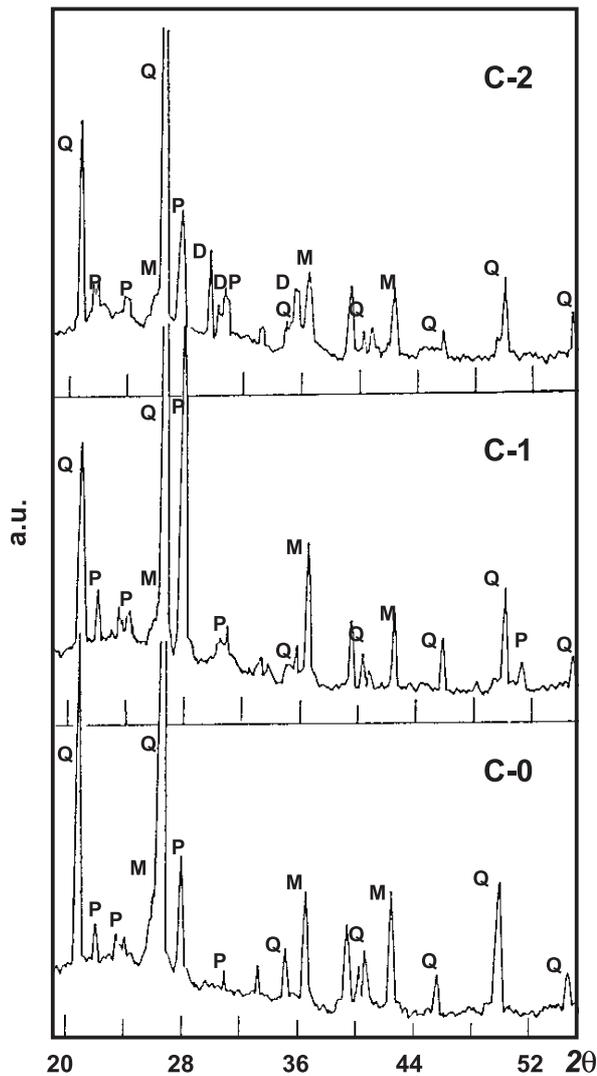


Fig. 8: XRD spectra of final ceramics: Q, quartz; M, mullite; P, plagioclase phase; D, diopside solid solution.

by increasing the amount of clay in the batch or by higher pressure.

The linear shrinkage of C-0 at 1150 °C and C-2 at 1050 °C increased regularly with the holding time, which is a typical behaviour at densification by viscous flow (Kingery *et al.* 1976, Hlavac 1983). The variations of the other two parameters were also similar.

The results for C-1 after 20 min at 1150 °C holding were better than the values for C-0 after 60 min at the same temperature, which demonstrates the improvement of the densification in the composition with glass-ceramic frits. After 40 min the C-1 results were optimal; after 60 min holding the shrinkage and the apparent density started to decrease, which indicates the beginning of overtiring.

The addition of glass-ceramic frits not only decreased the sintering temperature and time, but also led to improved mechanical characteristics. The bending strength of C-0 and C-1 after 60 min at 1150 °C showed values of 33 ± 3 and 41 ± 4 MPa, respectively. A very high bending strength of 49 ± 3 MPa was measured for C-2 after 60 min at 1050 °C (i.e. at 100 °C lower temperature and at an inferior degree of

sintering). The enhancement of the mechanical properties can be related to the modifications of phase compositions in the ceramics containing glass-ceramic frits.

The XRD spectrum of the plant composition is typical for earthenware and shows high amount of glassy phase, residual quartz (Q), plagioclase phase (P) and some mullite (M). The plagioclase phase is un-reacted albite, whereas the mullite is the product of metakaolin transformations.

At the same time the C-2 sample shows an amorphous halo, a lower amount of quartz, some plagioclase and mullite, as well as diopside solid solutions (D). The decrease in the amount of quartz was mainly due to the removal of feldspar raw material, and the plagioclases are feldsparic admixtures in the plastic materials used; the diopside, formation of which is indicated by the DTA exothermic peak at 915 °C, arose from the glass-ceramic frits. These results emphasize the significant increase in the bending strength after the addition of 35% frits, which can be related to the pyroxene crystallization, which reinforces the glassy matrix of the final ceramic.

The XRD spectrum of C-1 shows a decrease in the quartz and an increase in the plagioclase phase. The accelerated quartz dissolution was due to the lower viscosity of melt formed, while the greater amount of plagioclase phase can be related to the formation of anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) solid solutions. In fact, anorthite and albite form continuous solid solutions, in which the melting temperature drastically increases as a function of the anorthite part. No pyroxene phase was observed, which indicates that at temperatures greater than 1050–1100 °C the diopside solid solutions melted and then participated in the formation of a new anorthite plagioclase phase. The DTA exo-peak at 1150 °C probably indicates this re-crystallization process.

The formation of the anorthite crystal phase has also been observed in other ceramic compositions with Ca-rich alternative fluxes (Andreola *et al.* 2002, Barbiri *et al.* 2002, Dana & Das 2004).

Conclusions

The possibility of using glass-ceramic frits, obtained from 45 wt.% fly ash and 25% glass cullet, in terracotta manufacture was studied. Two ceramic compositions, with partial and total substitution of the feldspar, were investigated and compared with a plant earthenware ceramic.

The preliminary results obtained show that the addition of the low viscous glass-ceramics frit significantly decreased the sintering temperature and time. At the same time, due to formation of an additional crystal phase (i.e. pyroxene or anorthite), the new ceramics were characterized by improved bending strength.

The higher percentage of glass frits in batches of these new ceramics (i.e. 20 and 35 wt.%) offer the opportunity to recycle 2–3 kg fly ash per m² terracotta.

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