CERAMIC TILES BASED ON LARGE AMOUNT OF POST-TREATED INCINERATOR BOTTOM ASHES

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ABSTRACT

Two new ceramic tile compositions based on 60 wt% secondary raw material (SRM) derived from pre-treated municipal solid waste incinerator bottom ashes and 40 wt% refractory clay were studied. The thermal and densification behaviours of the ceramic batches were evaluated by DTA/TG and dilatometric techniques, respectively. Sinterability was evaluated by measuring open and closed porosities (via gas-pycnometry), linear shrinkage and water absorption as a function of temperature. Crystallinity degree was valued during heating by High-Temperature X-Ray Diffraction (HTXRD) analyses at different temperatures as well. The results demonstrated that these ceramics are characterized *by sintering temperatures in the range of 1190-1240°C, low water absorption and high crystallinity whose main phase is anorthite. The obtained mechanical properties are comparable to commercial ceramic products, with flexural strength higher than 40 MPa. Preliminary results highlighted an opportunity to obtain new ceramics with suitable properties based on huge amount of incinerator bottom ashes.*

Key-words: ceramics, sintering, bottom ash, crystallinity

INTRODUCTION

Ceramic bodies, such as tiles, are heterogeneous materials, consisting mainly of natural raw materials with wide range of composition. (1) For this reason such bodies could tolerate different types of alternative raw materials.

The world production of building and tiles ceramics requires massive amount of natural raw materials and is based mainly on the traditional system clay-silica-feldspar. Nevertheless, several studies of different scientific groups made in the last decades are related to the substitution of conventional raw materials by other natural resources or industrial wastes. The major part of these works is concerning to the characterization and use of different alternative fluxing agents; this is a consequence of the high cost of feldspars and the limited number of appropriate deposits. Promising results were obtained using glass cullet, waste cathode ray tube of TV or PC monitor (CRT glass), different industrial residues and various volcanic rocks. (2- 4) Since the new fluxes have different chemical compositions some of the new ceramic batches show significant variations in the forming and firing behaviour. In general, the alternative fluxes form melts with lower viscosity than the corresponding feldspar ones; this decreases the sintering temperature and/or leads to formation of high percentage of glassy phase. (2, 4) However, the addition of higher amount of flux leads to an increase of amorphous phase in the final product, which can create a negative effect on the mechanical properties. In order to obtain sintering behaviour and mechanical characteristics similar to the industrial compositions feldspars are partially substituted.

Nevertheless, if the alternative flux is characterized by a high crystallization trend, the crystallinity of final ceramics might be increased. This effect can be obtained using glass-ceramic frits or waste residues with high crystallization trends (as slags and fly ashes).(5, 6) In this case, due to re-crystallization processes during the sintering and cooling steps, the amount of residual amorphous phase decreases, which leads to an improvement of the mechanical properties.(7)

One of raw materials appropriated for the ceramics industry is the bottom ash from municipal solid waste incineration (MSWI). In particular in Italy the 2010 generation of the MSW was nearby 32.5 million tons and an amount of incinerated waste around 5.2 million tons. (8) Solid outputs of incineration are represented by fly and bottom ashes that range from 3-5 to 20-35 %wt of the original quantity of waste, respectively. In this country in last years some companies, specialized in post-treatment technology of bottom ashes, were developed. The treatment of the incineration bottom ashes is based on a complex process of selection and physical/mechanical treatment (ageing, sieving and washing). After these treatments an inert material with silicon-based matrix, rich in iron, calcium and aluminium oxides is obtained. This product is mainly used in cements substituting extracted raw materials. Another interesting opportunity can be represented by materials such as ceramics, glasses and glass-ceramics. In the present work the aim was to obtain building ceramics based on huge amount of pre-treated incinerator bottom ashes (60 wt%) as an alternative raw material derived from municipal solid waste incinerator. In particular the pre-treated bottom ashes were used in intent to replace feldspar and quartz sand completely.

EXPERIMENTAL PROCEDURE

Post-treated bottom ash derived from municipal incinerator was chosen in two fractions: fine **F** (0-2 mm) and coarse **L** (2-8 mm). These fractions were used together with a refractory clay (kaolin ceramic grade, Balco, Italy). The inert material contains iron (around 10% and 4%wt in fine and coarse fractions, respectively), calcium, aluminium and silicon oxides (variable in function of particle size) while kaolin clay contains silicon and aluminum oxides in a 1:3 SiO_2/Al_2O_3 ratio. Two ceramic batches, containing 60 wt % of **F** and **L** fractions and 40 % of a refractory clay were prepared: CFK (fine fraction/kaolin) and CLK (large fraction/kaolin). In order to prepare suitable press-powder, the raw materials were ground and sieved below 75 µm. Each batch composition was prepared by dry-grinding and then humidified with 6 wt.% distilled water; after that the green samples were pressed at 30 MPa. Bar samples (50 x 5 x 4 mm) were sintered in an electric laboratory furnace (Nabertherm) at 10°C/min heating and 1h dwell time at different temperatures (1100-1240°C range). Moreover, rectangular based samples (100×50×8 mm) were uniaxially pressed at 40 MPa with the samples used for strength measurements. These CFK and CLK samples have been dried overnight at 110°C and then fired in an electrical kiln, using 10°C/min heating rate up to 1210 and 1190°C, respectively, and with dwell time at the maximum temperature for 1 h.

The sintering process of the CFK and CLK in the temperature range of 20–1300°C was studied with a horizontal optical dilatometer (Expert System Solutions, Misura HSML OLDT 1400) using heating rate of 20 °C/min, while the thermal behavior was determined by differential thermal analyzer (Netzsch STA 409). The apparent density was estimated by an Envelope Density Analyzer (GeoPyc 1360, Micromeritics) using a dry-flow medium, while the skeleton and absolute densities by gas (Ar) pycnometer (AccyPy1330, Micromeritic) before and after crashing and milling the samples below 26 μm, respectively. These results of densities were used to evaluate total, closed and open porosity. For the semi- industrial fired samples measurements of linear shrinkage (LS%) and water absorption (WA%) according to ISO 10545-3 were also performed. Mechanical properties as elastic constants and flexural force completed the characterization. Crystalline phases formation as a function of the temperature were conducted by using a high-temperature X-ray diffractometer (HTXRD) with a heating chamber (HTK 16). Powders of mixtures (< 38 μm) were heated on platinum bar from room temperature to different temperatures (800, 950, 1000 and 1200°C for the CFK mixture and 800, 950, 1050 and 1200°C for the CLK mixture, respectively) at which the XRD scanning was performed. The temperatures were chosen on the basis of DTA results. The microstructure and crystal morphology of the fired samples were observed by scanning electron microscopy (JEOL JSM 6390) coupled with an energy dispersion spectroscopy equipment (INCA X-stream OXFORD).

RESULTS AND DISCUSSIONS

Figures 1 and 2 show the DTA-TG and dilatometric plots (left scale) of CFK and CLK, respectively, obtained at heating rates of 20^{o}C/min. At lower temperatures the DTA traces highlight diverse behaviour of CFK and CLK batches, which can be related to differences in their compositions. Due to a higher percentage of organic matter, the exothermic peaks in the range 300 – 450^{o}C and the related weight losses (dashed lines) are more intensive in CFK, as well as the endotherm nearly 700°C due to the $CaCO_3$ decomposition. The DTA and TG effects related to kaolinite dehydration are identical for the two compositions. The sintering curves elucidate that only the kaolinite decomposition at 530°C leads to linear shrinkage (at about 0.5 %). This means that the burning of organic residues and the decarbonization process can increase the porosity of samples. In the range 850-950°C about 2.5% shrinkage is observed in the both ceramics. These variations correspond to the exo-effects from the DTA curves (with peaks at 925 and 950°C for CKL and CKF, respectively). These effects can be explained by reactions of meta-kaolinite with oxides derived from the alternative raw material to form calcium aluminosilicates. The DTA traces show that melting of some of the formed crystalline phases is observed in the interval 1100-1170°C. However, this process does not lead to densification of the ceramics. Practically, the real sintering stars at 1200°C, which is in agreement with the second endo-effects by the DTA results. In this case the sintering in the range of first melting endo-effect is inhibited by recrystallization processes and the actual densification starts with the melting of the newly formed crystal phases.

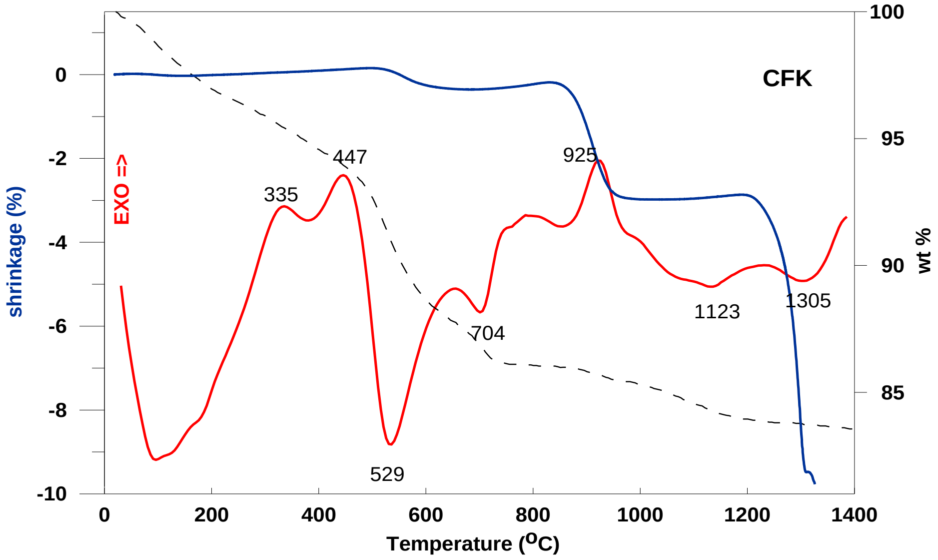


Figure 1 – DTA/TG and Dilatometric curves of CFK composition.

In order to elucidate the sintering behavior samples were heat-treated for 1 h at different temperatures in the range 1100-1250°C. The results for the linear shrinkage and water absorption of both ceramics are summarized in Figure 3, while the information for the variations of open and closed porosities are reported in Figure 4.

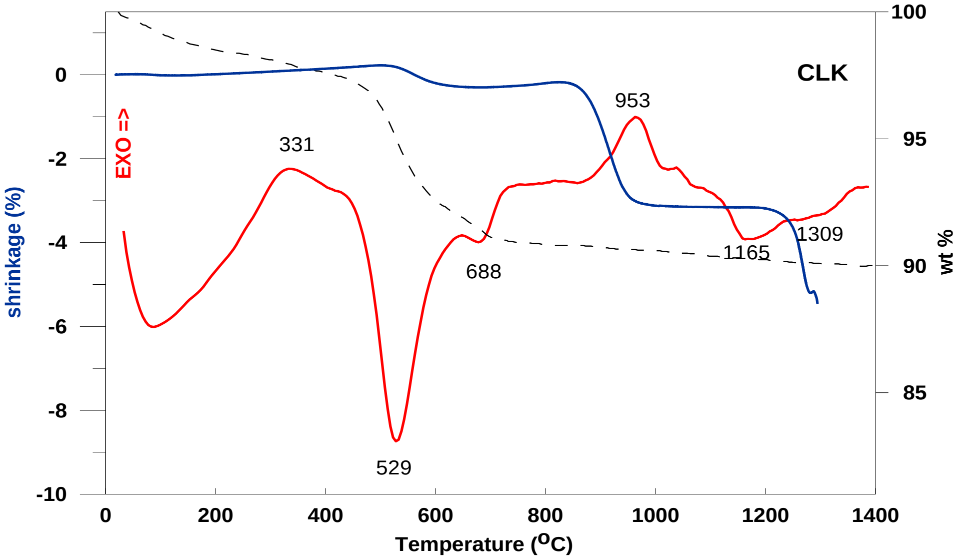


Figure 2 – DTA/TG and Dilatometric curves of CLK composition.

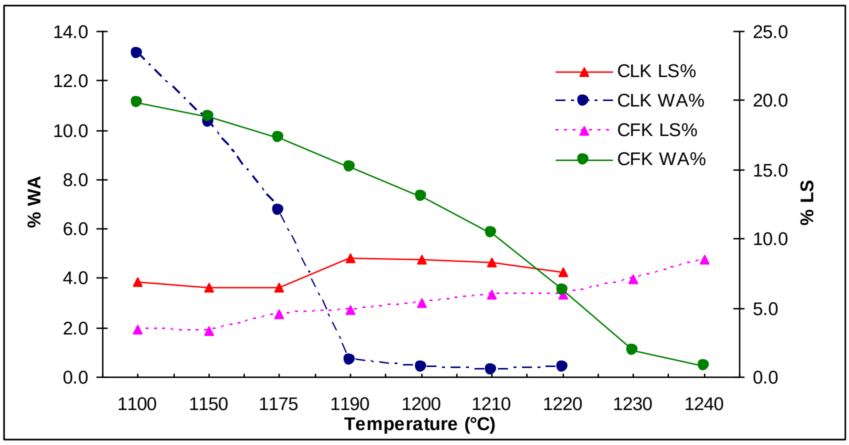
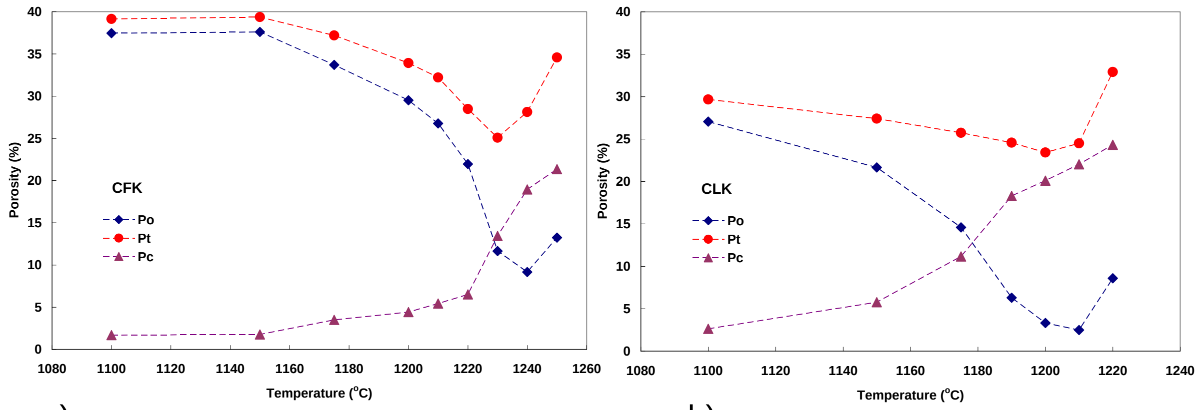


Figure 3 - Water absorption (WA%) and linear shrinkage (LS%) vs. firing temperature for CFK and CLK specimens.

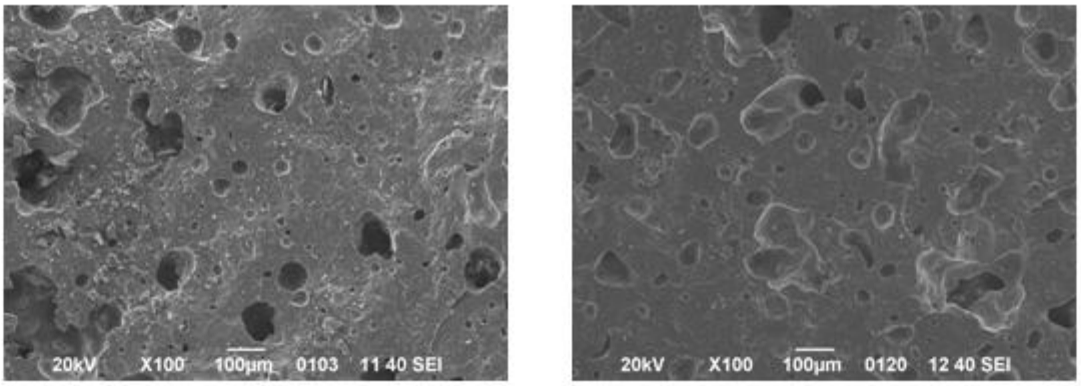
These results are in a good agreement with the dilatometric ones and highlight that an intensive sintering begins after 1160-1180°C. The densification of CLK composition is carried out at lower temperature. At 1200-1210°C well sintered samples with WA % near zero and about 20 % closed porosity is formed; at higher temperature starts an overfiring phenomenon. At the same time, the optimal sintering temperature range of CFK composition is 1230-1240°C, where the WA% values are within 1.4-0.8% and the closed porosity is below 20 %.



a) b)

Figure 4 - Open porosity (P_o), closed porosity (P_c) and total porosity (P_T) for CFK (a) and CLK (b) specimens vs. firing temperature.

SEM images of the final samples presented in Figure 5 confirmed the results obtained by pycnometry, an elevated closed porosity. Detailed photos of the closed porosity in the ceramics studied (Figure 6), permits to observe a high crystallinity and an indented pore’s surface (which is an untypical microstructure for the traditional ceramic matrix). Probably, this fact is a consequence of the crystalline phase formation during the sintering and cooling processes.



(a) (b)

Figure 5 - SEM Photographs of: a) CLK fracture fired at 1210°C, 1h; b) CFK fracture fired at 1240°C.

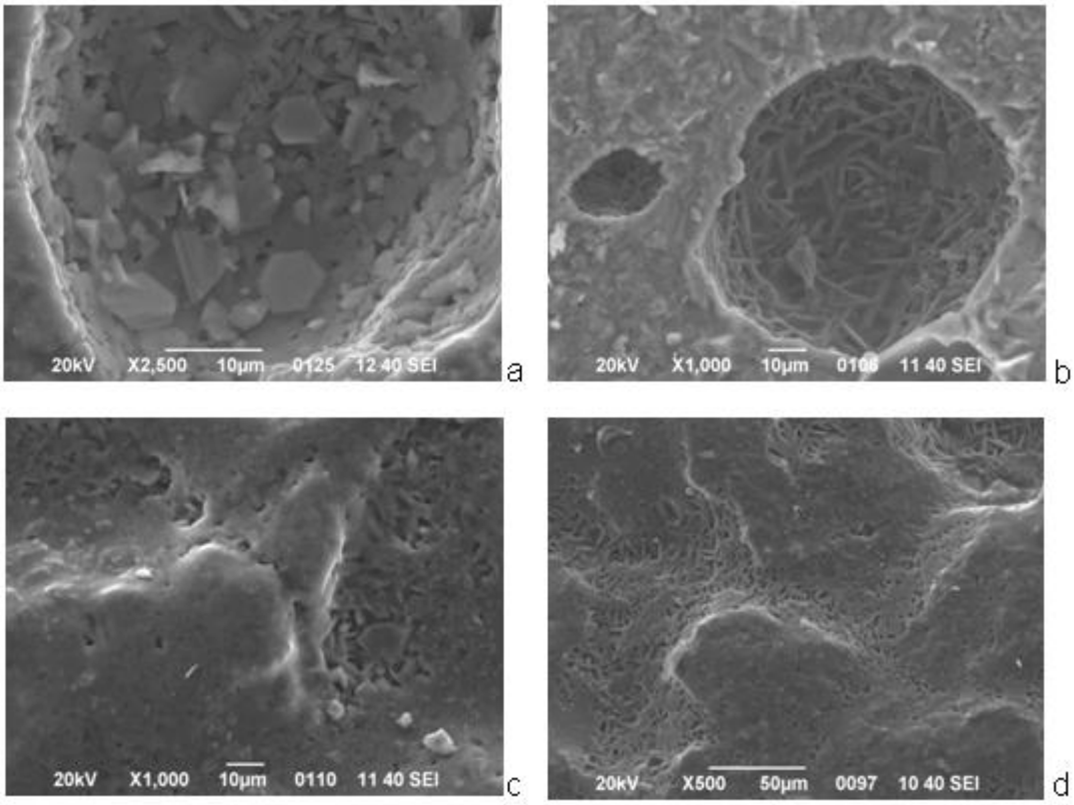


Figure 6 - SEM details of: a) CFK fracture fired at 1240°C for 1 h; b) CLK fracture fired at 1210°C for 1h; c) CFK surface and d) CLK surface, respectively.

X-ray analysis on both ceramic compositions confirms the high crystallinity, identifying anorthite ($CaAl_2Si_2O_8$) and pyroxene solid solution as main crystalline phases. It can be assumed that crystallization processes takes place during the sintering and cooling steps, decreasing the amount of amorphous phase in the materials. The phase transformations during heating shown the formation of gehlenite ($Ca_2Al(AlSi)O_7$) and anothite around 920°C for the two compositions. For CLK composition at 1200°C the gehlenite and anothite melt and only remaining one traces of quartz (Figure 7). The crystallization of anorthite during cooling and the high crystallinity of final CLK ceramics are also well elucidated in Figure 7. While for the CFK composition during heating at 1200°C the gehlenite and part of quartz melt but the amount of anorthite phase increases (i.e. a recrystallization process takes places); traces of hematite are also observed at this temperature (Figure 8). During cooling from 1200°C to 950°C (see Figure 8) additional crystallization of anorthite carries out, resulting in final ceramics with a high degree of crystallinity.

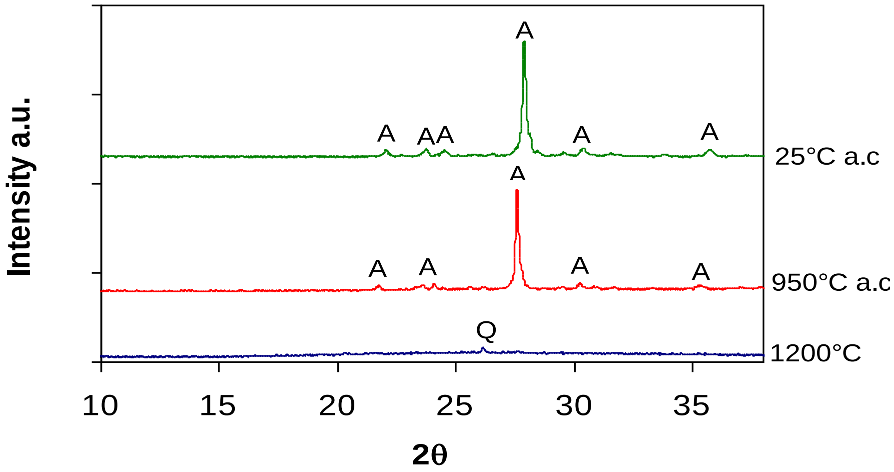


Figure 7 - XRD spectra of CLK composition after cooling (a.c) at 950 and 25°C compared to 1200°C spectrum. Q: quartz and A: anorthite.

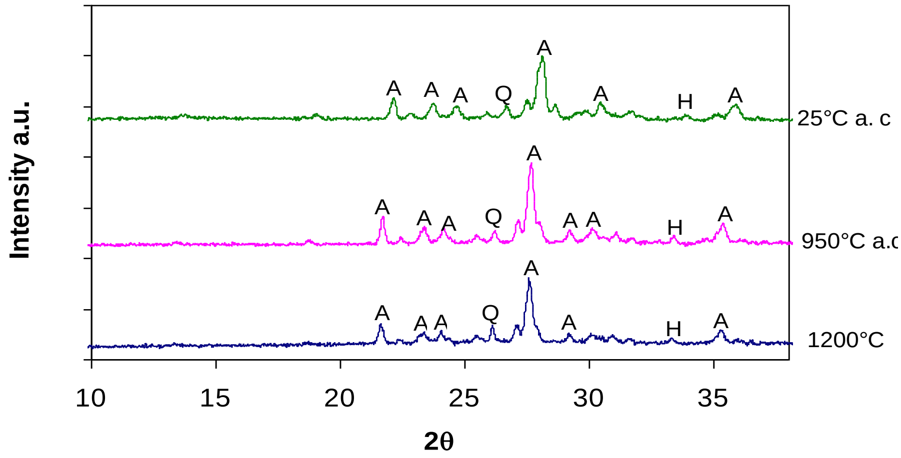


Figure 8 - XRD spectra of CFK composition after cooling (a.c) at 950 and 25°C compared to 1200°C spectrum. Q:quartz, H: hematite and A: anorthite.

Semi-industrial samples of the both compositions, fired at appropriate temperatures (at about 1190 and 1210°C for CLK and CFK, respectively) were obtained and their technological properties were measured and the values are reported in Table 1. The sintering parameters (LS% and WA%) and the porosity values are in agreement with ones from the laboratory studies for the same temperature ranges. Notwithstanding that the semi-industrial specimens present 26-28% total porosity, the materials show mechanical properties higher than those prescribed in the EN ISO rule for high sintered commercial tiles (BIa group; WA≤0.5%, B.S>35 MPa) (9) and good values of Young's modulus and Mohs hardness. These positive results can be related to the elevated presence of anorthite after firing and the low amount of glassy residual phase. Finally, the mixtures show moderate thermal expansion coefficients (α) between 20-400°C (Table 1) suitable for avoiding the common glazes defects in firing (crazing, cracking).

Table 1 - Technological properties: linear shrinkage (LS%), water absorption (WA%), calculated porosities, bending strength (B.S.), Young's modulus (E) and thermal expansion coefficient (α) for the semi- industrial fired samples CLK and CFK.

Properties	CFK	CLK
LS (%)	6.48	4.05
WA (%)	4.71	2.56
P_o (%)	20.6	15.7
P_C (%)	5.40	11.5
P_T (%)	26.0	27.3
B.S. (N/mm^2)	47.67	42.09
E (GPa)	49.17	45.12
$\alpha \times 10^{-6}$ (°C^{-1})	6.14	6.22

CONCLUSIONS

The presented study shows the feasibility to use high amounts of pre-treated bottom ash as alternative raw material in clay-based ceramics compositions. The new ceramics were tailored to completely replace feldspar and quartz sand and may be satisfactorily well-explained through SiO_2-Al_2O_3-CaO-Fe_2O_3 system with crystalline phases as anorthite, quartz and traces of hematite. This kind of residue permits to obtain building materials with technological properties similar to commercial ones without use of traditional fluxes and inert materials. According to the UNI EN ISO standards the obtained tile samples could be classified into BIb and BIIa groups (WA% values within 2-5%) but having mechanical properties higher than those prescribed for high sintered materials (B.S. > 35 MPa for BIa group).

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