

Physico-mechanical properties of extruded and sintered ceramics using pet coke and sewage sludge as admixtures

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Pet coke (PC) and sewage sludge (SS) have been separately used as admixtures into clayey raw materials for ceramic manufacturing by extrusion and sintering. Thermal analysis of the clay mixtures incorporating 6% of either PC or SS shows a significant shift of the solidification temperature to lower temperatures. The bending strength-in terms of modulus of rupture (MOR)-of the ceramic specimens produced does not change appreciably up to 6% content in PC or SS, indicating that the manufactured clay-based ceramics are able to tolerate low percentages of these admixtures. The specimen open porosity increases and the thermal conductivity decreases by increasing the admixture percentage, while both thermal conductivity and MOR increase with increasing sintering temperature. The results indicate that the utilization of PC and SS in ceramic manufacturing processes may lead to changes in processing parameters, to energy savings and to materials with improved thermal insulating properties.

Key words: Clay minerals, Secondary resources, Pet coke, Sewage sludge, Recycling, Ceramic manufacturing, Mechanical strength, Thermal insulation.

Introduction

Several secondary resources are currently under consideration as the raw materials or as admixtures into clays for ceramic manufacturing [1-4]. The aim of the present research is to separately examine the use of pet coke and sewage sludge as admixtures into a clay mixture used in standard ceramic production, and to investigate how the workability upon extrusion of the mixtures obtained is affected and how the mechanical strength, water absorption capability and thermal conductivity of the sintered ceramics vary with respect both to the admixture percentage and to the firing temperature.

Pet coke (abbrev. for Petroleum coke) (PC) in particular, a carbonaceous solid derived from oil refinery units (while other coke has traditionally been obtained from coal), is employed in common practice as an alternative fuel in both cement and ceramic industries [5, 6]. Due to the inherently low density of this by-product and the ability to act as an air-entraining agent during mixing, the addition of pet coke in the production of lightweight and low thermal conductivity cement paste and mortar products, has recently been examined, as an alternative to combustion [7]. Moreover, it has been considered for

processing porous silicon nitride by a slip casting method both to improve the properties of the suspension and as pore former upon sintering [8]. The innovative incorporation of this secondary resource in the clayey mixture that is attempted in the present study can also be advantageous for ceramic manufacturing, and thereby it represents a stimulating research subject.

On the other hand, large amounts of urban sewage sludge (SS) are daily produced, and, therefore, the safe and economically feasible disposal as well as the investigation of new environmentally-friendly applications for urban SS is imperative. In fact, with increasing concern over the disposal of this type of waste onto agricultural land [9] and growing social awareness about potential toxic incinerator emissions, it seems apparent that the recycling of sludge in building and construction applications, such as ceramic fabrication, can be considered as an important step in the right direction. Naturally, ceramic production starting from clays is a very common method, but it requires too much natural resources. Therefore, SS, as a possible substitute of clay, can be used to solve the environmental problems caused by this waste and to slow down the consumption of resources. The substitution of clayey raw materials for SS in the production of value-added traditional ceramics could also give place to cost savings due to the utilization of valuable wastes as secondary raw materials. Actually, SS contains a significant amount of energy, estimated to be from 2800 to 3500 kcal/kg. The incorporation of biomass material in brick clays is, generally, becoming an emerging technology for large

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scale applications, offering several potential advantages, such as safe and economical disposal of solid waste, solidification of toxic materials, i.e. heavy metals found in certain types of waste, and increased porosity of the bricks leading to increased thermal insulating capability and finally reduced fuel consumption [10]. Moreover, SS, containing large amounts of silica, alumina and lime, can be a good starting material for ceramics manufacturing. By controlling the initial mixture composition and by suitable heat treatment, a variety of ceramic crystalline phases will be obtained.

Recent studies have focused on the valorization of SS as an additive material to clay. Specifically, the reuse of SS without any treatment as primary material - mixed with clays in different proportions - in order to obtain structural ceramics with interesting behavior has been examined [11]. The influence of the firing temperature on the technological properties of red ceramics made of a kaolinitic clay incorporating a water treatment plant sludge has been evaluated [12]. Also, the gaseous VOC emissions during the firing processes for the production of ceramics with urban SS were monitored [13]. Moreover, the sintering behavior of dried SS and the related sintering mechanisms to produce a range of potentially useful ceramics, considering the effect of compaction pressure, sintering temperature and time, has been investigated [14, 15]. Furthermore, fabrication and characterization of ceramic products by thermal treatment of SS ashes mixed with different additives, including kaolin, montmorillonite, illitic clay and powdered flat glass, has also been attempted [16].

Experimental

Sample preparation

Three clay samples from different deposits in Central

Table 1. The composition of the clay raw materials used in the present study*.

Parameter	Constituent Clay (%)		
	A	B	C
L.O.I(**)	11.95	9.87	16.54
SiO ₂	49.40	52.79	51.02
Al ₂ O ₃	12.89	13.53	8.55
Fe ₂ O ₃	7.10	7.57	4.66
CaO	8.58	6.29	11.62
MgO	4.86	4.31	3.89
K ₂ O	2.88	3.19	1.55
Na ₂ O	1.56	1.57	1.42
TiO ₂	0.818	0.855	0.621
CaCO ₃ (eq)	14.72	-	24.46
CO ₂	6.47	-	10.75

*Source: TERRA S. A.,

**L.O.I. = Loss on Ignition.

Greece were selected and characterized. These clays are considered representative of the main types of clayey raw materials used by the ceramic industry (A, B and C). The composition of the three clays used is given in Table 1.

These clays, mixed in certain proportions typically utilized by the local brick manufacturing industry, were obtained from TERRA S.A. company, and the resulting mixture is referred to as “Viokeral” mixture. This clay mixture was used for all subsequent processing for manufacturing the prototype specimens and the specimens incorporating SS and PC.

Raw material characterization

Thermal Gravimetric and Differential Thermal Analysis (TGA and DTA respectively) were carried out on all raw materials used, namely i) the “Viokeral” mixture, ii) 100% SS, iii) 100% PC, iv) 6% SS in the “Viokeral” clay mixture and v) 6% PC in the “Viokeral” mixture. This was done in increments of 10 °C /min up to 1200 °C in order to determine mass and enthalpy changes. Figures 1-3 show the thermal analysis results for the “Viokeral” clay mixture, the “Viokeral” clay mixture containing the 6% SS and the “Viokeral” clay mixture containing 6% PC, respectively.

For the “Viokeral” clay mixture (Fig. 1), at 950 °C, the total mass loss is 11.7% (TGA). DTA analysis shows that, at low temperatures and up to about 150 °C, release of absorbed moisture is taking place and the process is endothermic.

From about 150 °C to about 500 °C, loss of chemically bound water takes place and the process is also endothermic. From 500 °C to about 800 °C several endothermic and exothermic peaks are observed. These are due to the combined effect of several decomposition reactions and the dehydroxylation of the silicate lattice. Combustion of trapped organic matter is also contributing [11, 17]. From about 810 °C to about 895 °C, the process is strongly endothermic, because of the thermal decomposition of carbonates. The DTG results indicate that the “Viokeral” mixture does not

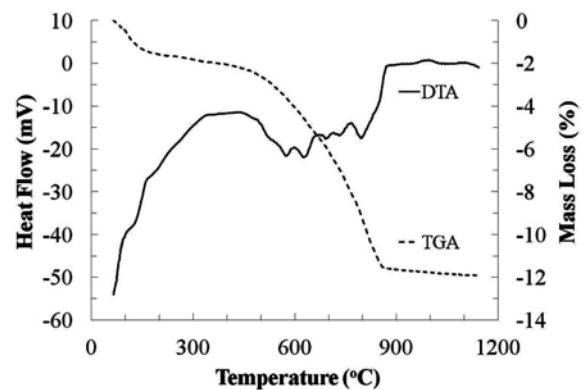


Fig. 1. Thermal analysis (TGA and DTA) for the “Viokeral” clay mixture.

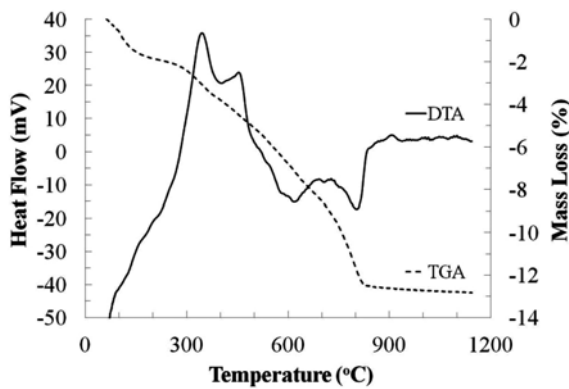


Fig. 2. Thermal analysis (TGA and DTA) for “Viokeral” clay mixture containing 6% w/w SS.

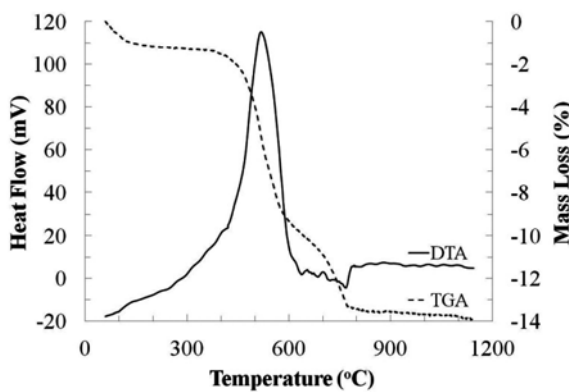


Fig. 3. Thermal analysis (TGA and DTA) for “Viokeral” clay mixture containing 6% w/w PC.

belong to the Kaolinitic group of clay materials since the characteristic peak of the kaolinitic clays, which occurs at about 980 °C, is absent.

Incorporating 6% w/w SS into the “Viokeral” mixture (Fig. 2), changes dramatically the enthalpy behavior seen in Figure 1 (100% “Viokeral” clay mixture). The endothermic peaks seen at intermediate temperatures are dampened off, while the highly endothermic peak between 810 °C and 895 °C has basically disappeared as a result of the exothermicity of the burning of the organic material of SS. This has been ascertained from a separate DTA analysis of 100% SS (not shown). Another important aspect of Figure 2 is that levelling off of both the enthalpy changes and mass loss occurs at about 45 °C lower temperatures, compared to Figure 1, most likely because of the contributing thermal energy of the SS.

The incorporation of 6% w/w PC (Figure 3) into the “Viokeral” mixture, changes even more dramatically the enthalpy behaviour seen in Figure 1 (100% “Viokeral” clay mixture).

There is a highly exothermic peak at about 530 °C due to burning of PC which entirely overwhelms the endothermic decomposition reactions observed in Figure 1. Moreover, the levelling off of both the enthalpy changes and mass loss occurs at even lower

temperatures, at about 90 °C lower temperatures, compared to Figure 1. In both cases (6% SS and 6% PC) TG analysis (mass loss) confirms that basically all organic material is combusted.

These findings could have important implications, in terms of energy savings, in an industrial scale application of these two processes, i.e., incorporating SS or PC or both into clayey raw materials.

Specimen preparation and characterization

All specimens were prepared in the same way using a standard pilot-plant procedure and equipment [18]. First, the clay raw materials were ground and mixed with either SS or PC in various proportions. Then the resulting mixture was homogenized thoroughly and water was added to form a plastic mass for extrusion in a specific apparatus. The plasticity of the mass was evaluated. The optimum water content of the plastic mixtures varied between 19 and 21%. Higher or lower water contents gave improper plasticity: below 18% water content, surface and possibly bulk cracking of the specimens was evident, while above 22% water content, sticking of the plastic mass in the internal parts of the extrusion apparatus occurred, making extrusion progressively difficult. All specimens prepared were dried at room temperature for 48 h followed by oven drying at 110 °C for 24 h. The specimens were then sintered in a computer controlled furnace. The first step was heating to 500 °C, which was reached after heating after a 5 h period at a rate of about 1.7 °C/min, followed by further controlled heating up to the sintering temperature at a rate of 4.5 °C/min. All specimens remained at the sintering temperature for 15 min (except for a separate series of specimens containing 6% PC that were allowed to remain for 720 min at $T_{\text{sint}}=950$ °C), and then were gradually cooled to room temperature in the furnace.

In order to determine water absorption, the fired samples were weighed before and after immersion in water for 24 h. The 3-point bending test was used to determine the modulus of rupture of the solid specimens using an automated Galdabini CTM/5 tester. All measurements were performed on 30 solid specimens of each composition, and the average values are reported in the results (Figures 5, 6 and 9).

Water absorptivity (WA) was calculated from the following equation:

$$WA (\%) = 100 (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}} \quad (1)$$

where: W_{wet} = the specimens (30) weight when saturated with water (g)

W_{dry} = the specimens (30) weight when dry (g)

The open porosity (OP) is defined as the volume of open pores of the specimen as a percentage of the sample volume and is calculated from the following

relation:

$$OP (\%) = 100 (W_{\text{wet}(C)} - W_{\text{dry}}) / (\rho \cdot V_s) \quad (2)$$

where: ρ = water density (1 g/cm³)
 V_s = specimen volume (cm³)

The modulus of rupture (MOR) in MPa was calculated from the following relationship:

$$M.O.R. = (3PL) / (2BW^2) \quad (3)$$

where: P = the fracture load (N)
 L = half of the span between the supports of the bend ring (mm)
 B = the width of the specimen (mm)
 W = the height (thickness) of the specimen (mm).

Results and Discussion

Sewage Sludge (SS) as admixture

Fig. 4 shows the effect of adding SS into the ‘Viokeral’ clay mixture on water absorptivity and the open porosity. Actually, both increase with increasing

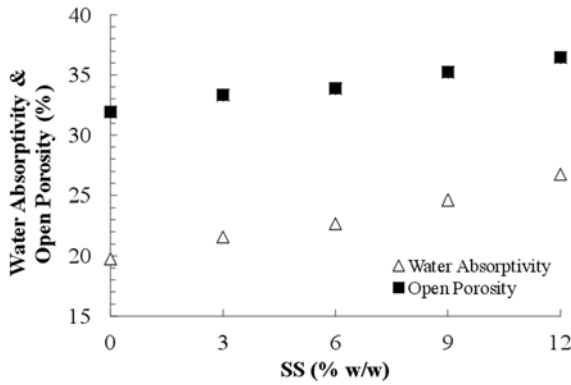


Fig. 4. The effect of adding SS into the ‘Viokeral’ clay mixture on water absorptivity and open porosity of the sintered specimens ($T_{\text{sint}} = 950^\circ\text{C}$).

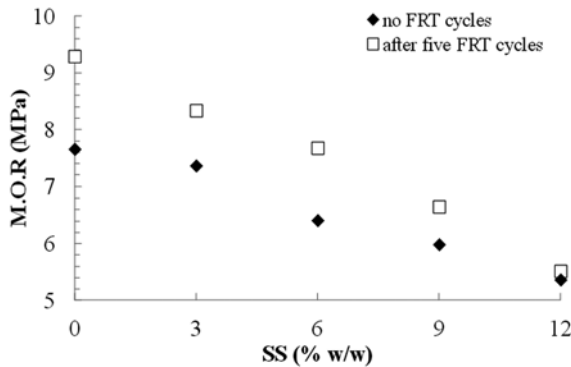


Fig. 5. Modulus of Rupture of the sintered specimens incorporating SS ($T_{\text{sint}} = 950^\circ\text{C}$) both before and after subjecting them into 5 cycles of Frost Resistance Testing.

percentage SS, this being attributed to the increased porosity of the specimens as a result of the burning of the organic fraction of their mass. Weight loss from the sintering process varied from 9% for the ‘Viokeral’ clay mixture to about 13.5% for the clay mixture containing 12% SS.

Figure 5 shows the modulus of rupture of the specimens both before and after subjecting them into 5 cycles of Frost Resistance Testing (FRT).

MOR is inversely proportional with % SS content of the clay mixture, and this is attributed to the increased porosity of the ceramic specimens as SS increases. Up to about 3% SS, the decrease in MOR is not significant (about 2.5%), while it becomes significant at 6% SS (about 13%). It appears that incorporation of SS below 5% does not affect the MOR significantly.

Rupture behaviour after subjecting the specimens to a 5 cycle Frost Resistance testing is also shown in Figure 5. At 0% SS, the MOR of the sintered clay specimens shows a significantly increased strength compared to that of the corresponding specimens not subjected to frost resistance. The increase is about 25% at 0% SS and it decreases gradually as SS is incorporated into the clay mixture, eventually tapering off at 12% SS. This behaviour is under investigation and, to our knowledge, it has not been reported in literature before. The measured strengthening of the specimens may be due, at least in part, to the incorporation of magnesium and calcium salts into the specimen pores. As pore size distribution is not known (has not been measured at present) as a function of SS and also before and after frost resistance testing, it is not currently possible to reach any solid conclusion.

Figure 6 shows the effect of sintering temperature on the MOR of specimens containing 6% SS and at sintering temperatures of 850, 950, 1050 and 1150 °C.

The MOR increases gradually with increasing sintering temperature up to 1050 °C. Apparently, between 1050 °C and 1150 °C, phase transition, possibly the formation of a glass-ceramic phase, occurs. Besides, at 1150 °C, the specimens show a sharp shrinkage and change in

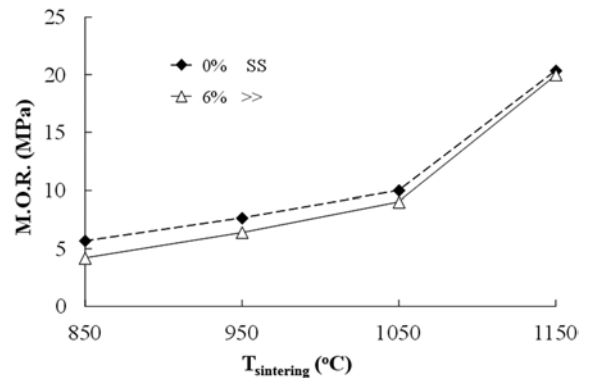


Fig. 6. The effect of sintering temperature on the MOR of specimens containing 0 and 6% w/w SS.

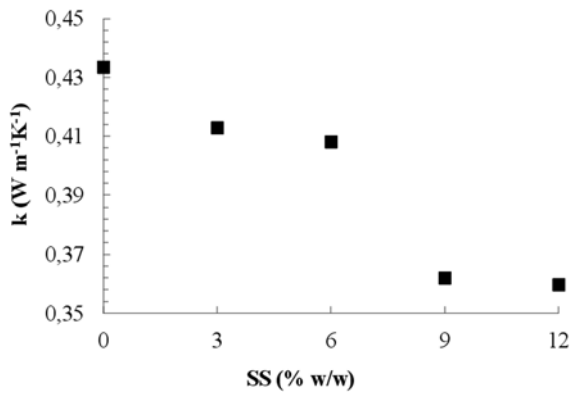


Fig. 7. The variation of the thermal conductivity coefficient at 25 °C (k) with the % SS content in the clay mixture of the sintered ($T_{\text{sint}} = 950$ °C).

coloration. Also, water absorptivity disappears and hardness increases over 10-fold. For sintering temperatures between 850 °C and 1050 °C, the MOR increases significantly nearly by 40%. This significant strengthening is also under investigation, and a decreased porosity or a change in pore size distribution may be partly or in whole contributing.

The results in MOR increase may be correlated empirically with the following equation:

$$\text{MOR}_p = \text{MOR}_0 e^{-\lambda p} \quad (4)$$

where: MOR_p and MOR_0 = the modulus of rupture of specimens with porosity p and 0 respectively (MPa)

λ = an empirical constant

This is consistent with the behavior of porous materials described by the Rice empirical correlation [19].

Figure 7 shows the variation of the thermal conductivity coefficient measured at 25 °C with the % SS content in the clay mixture of the specimens.

The observed decrease in thermal behaviour with increasing the SS percentage correlates well with the measured increase in open porosity (Figure 4).

Pet Coke (PC) as admixture

Figures 8-10 show the water absorptivity, the MOR and the coefficient of thermal conductivity respectively, when Pet Coke (PC) is incorporated into the clay mixture.

In Figures 8, 9 and 10, by adding PC up to 6% into the clay mixture, more or less similar behaviour to that seen in Figures 4, 5 and 7 (where SS was added) is observed. In fact, water absorptivity and open porosity increase, while MOR and thermal conductivity decrease, with increasing the PC percentage in the clay mixture. Increasing porosity leads to lowering of MOR and thermal conductivity. Again, a decrease of 6.5% in strength (as expressed by the MOR values), as well

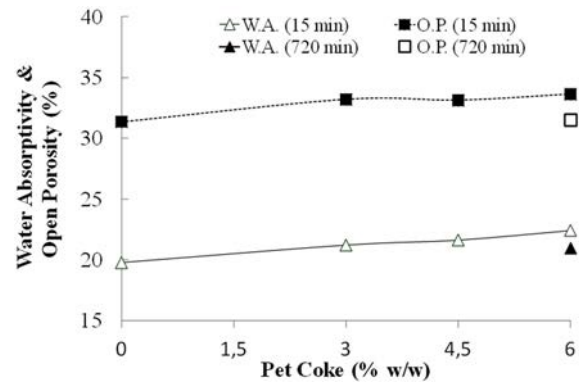


Fig. 8. The effect of adding Pet Coke (PC) into the "Viokeral" clay mixture on water absorptivity and open porosity of the sintered specimens ($T_{\text{sint}} = 950$ °C).

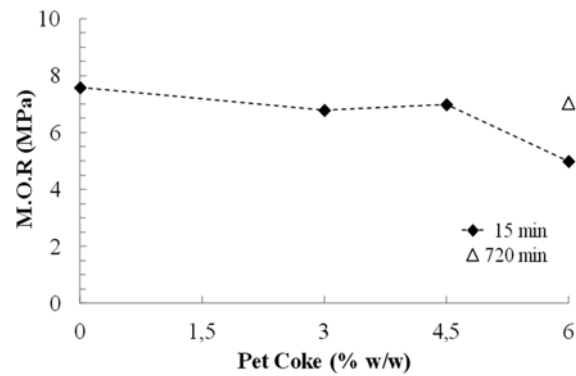


Fig. 9. The effect of adding Pet Coke (PC) into the "Viokeral" clay mixture on MOR of the sintered specimens ($T_{\text{sint}} = 950$ °C).

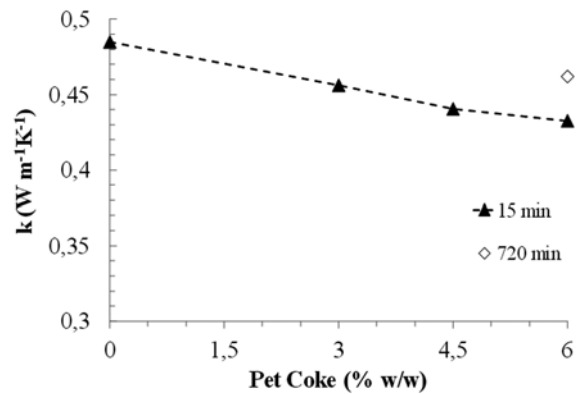


Fig. 10. The effect of adding Pet Coke (PC) into the "Viokeral" clay mixture on the thermal conductivity coefficient (k) of the sintered specimens ($T_{\text{sint}} = 950$ °C).

as of 10.2% in thermal conductivity, are rather insignificant up to 4.5% PC addition. This indicates that PC can be incorporated into clays up to about 5% without substantially affecting mechanical strength but with substantial gains in thermal insulation and possibly reduced fuel consumption and air pollutant emissions. This last aspect is also under present investigation.

In all cases, specimens were allowed to remain at the sintering temperature of 950 °C for 15 min. However,

separate runs were also carried out using specimens from the same batches (6% PC) that were allowed to remain at 950 °C for 720 min instead of 15 min. The results are also shown in Figures 8-10. It is noted that water absorptivity decreases while MOR and thermal conductivity increase as sintering time is substantially increased. This is most likely due to changes in porosity and pore size distribution. The effect is probably diffusion controlled.

Conclusions

Using either pet coke (PC) or sewage sludge (SS) as admixtures up to about 6% w/w into clayey materials for ceramic production:

a) the workability of the plastic mass formed for extrusion is not affected.

b) the mechanical strength of the ceramics manufactured by extrusion and sintering does not change appreciably.

c) the coefficient of thermal conductivity decreases, one of the most significant findings, indicating the creation of more porous microstructures.

d) the solidification temperature shifts to lower temperatures, especially with the incorporation of pet coke. In this case, smaller amounts of energy could apparently be used upon future commercialization of the procedure, thus leading to fuel savings, and optimum firing temperatures in a full scale operation could potentially be modified. Also lower air pollutants could be emitted as a result and some toxic pollutants such as heavy metals could be solidified into the ceramics so-produced. The disposal of SS can possibly be done in a closed loop system where part of SS can be directly mixed with the raw clayey materials to form the plastic mass, and the rest of SS be dried off with part of the exhaust gases from the sintering process and subsequently be used as an additional fuel.

In conclusion, the manufacturing of such ceramics with increased insulation capabilities could lead to energy savings in buildings. An increased porosity in these materials would not affect their performance, as they, normally, do not come in contact with water and are not exposed to water. The results are encouraging showing that the incorporation of low amounts of low price and easily available pore-formers such as SS and PC in clays for the fabrication of extruded ceramics is possible without significantly sacrificing mechanical strength, while energy savings and increased thermal insulation can be achieved.

Acknowledgments

This research was supported in whole by a grant from "Terra S.A.", A' Industrial Area, Larissa, Greece.

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