ELABORAREA DE CĂRĂMIZI DIN ARGILĂ EXTRUDATĂ ȘI SINTERIZATĂ CU UTILIZARE BENEFICĂ DE “SOL DEGRADAT” CA ADITIV

DEVELOPMENT OF EXTRUDED AND SINTERED CLAY BRICKS WITH BENEFICIAL USE OF INDUSTRIAL “SCRAP-SOIL” AS ADMIXTURE

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In the current research, clay-based bricks with beneficial utilization of industrial “scrap-soil” as admixture were developed and characterized, in order to contribute to circular economy, environmental protection and conservation of natural resources. “Scrap-soil” is an industrial soil containing residues of steel scrap and/or steel making by-products as a result of their temporary storage in open steel industry soil spaces. Brick-shaped specimens were formed by extrusion of clay/”scrap-soil” mixtures in various proportions up to 9 %wt. industrial soil, and then fired at different peak temperatures (850-1100°C). Shrinkage and weight loss upon sintering as well as bulk density, porosity, mechanical strength and thermal conductivity of sintered ceramic microstructures were determined and studied as a function of the admixture percentage and firing temperature. The experimental results confirm that incorporation of “scrap-soil” into standard red ceramic bodies is feasible, as their shape, density, mechanical performance and thermal conductivity remain practically unaffected with increasing the admixture percentage. Moreover, the sintering temperature can be optimized either to obtain specific characteristics of the brick bodies or to attain energy savings.

Keywords: *“scrap-soil”, steel industry, clay bricks, extrusion, sintering, characterization.*

1. Introduction

The development of value-added products using secondary resources as substitute raw materials is of great interest for many researchers nowadays [1-4]. Special emphasis should be placed on resource optimization to minimize uncontrolled waste disposal [5]. Especially, steel making and steel refining industries generate huge quantities of by-products annually [6-10]. Considerable research has been conducted on the incorporation of various solid residues derived from metallurgical industries as admixtures into commercial clay bricks. Especially, raw material composition should be optimized to suit to specific ceramic product properties [11]. Metallurgical by-products, such as steel mill scale waste, steel making dust, steel slags and sludges, Waelz slag and quarry residues, containing useful metal oxides, have been evaluated for that purpose [12-18].

“Scrap-soil” in particular, is an industrial soil containing residues of steel scrap and/or steel making by-products as a result of their temporary storage in open soil spaces. It is usually directed for use in excavation works or is deposited to special dumps [19,20].

In the present study, clay brick specimens were manufactured from mixtures of steel industry scrap-soil and standard clayey raw materials by extrusion, and then fired at different temperatures. Their microstructure and physico-mechanical properties were characterized and are compared to reference material containing only clays, in order to determine the effect of scrap-soil addition. This work aims both at minimizing the environmental impact from the use of natural resources (clay minerals) and reducing the cost of scrap-soil safe disposal, with the development of value-added ceramic products, thus contributing to circular economy.

2. Materials and methods

2.1. Materials

Three different clays A, B and C, collected from Central Greece, were used in the present study and their chemical analysis is presented in Table 1. The clay mixture (“Viokeral” mixture) used in this research consisted of 50% A, 33% B and 17 % C clay type. The Viokeral mixture was utilized for manufacturing prototype (pr) and clay-based specimens loaded with various scrap-soil percentages.

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Table 1

Chemical analysis of clays used.

CLAY	PARAMETER (%)										
	Loss on Ignition (LOI)	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**K_2O**	**Na_2O**	**TiO_2**	**$CaCO_3$ (eq)**	**CO_2**
A	11.9	49.4	12.9	7.1	8.6	4.9	2.9	1.6	0.8	14.7	6.5
B	9.9	52.8	13.5	7.6	6.3	4.3	3.2	1.6	0.9	-	-
C	16.5	51.0	8.5	4.7	11.6	3.9	1.5	1.4	0.6	24.5	10.7

Table 2

Chemical composition of "scrap-soil".

ELEMENT	**Al**	**Ba**	**Ca**	**Cr**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Pb**	**Si**	**Zn**
CONTENT (% wt, dry basis)	1.17	0.13	7.15	0.07	0.24	24.3	0.21	1.78	0.38	0.25	0.26	0.18	1.07

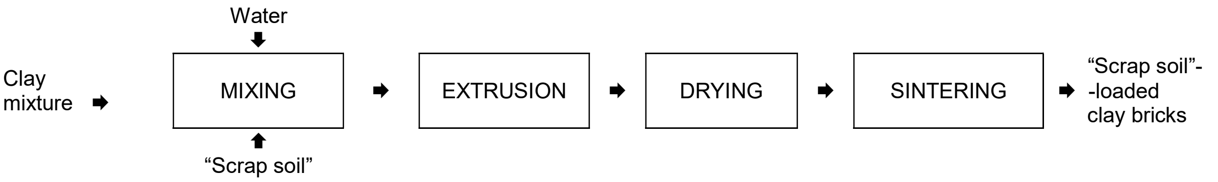


Fig. 1- Schematic diagram of the procedure followed for the production of "scrap soil"-loaded clay bricks (red ceramics).

The scrap-soil used in specimen preparation was provided by the "Aeiforos Metal Processing SA" company. The chemical composition of SS is presented in Table 2. It can be seen that main elements found in scrap-soil are iron and calcium.

Both raw materials used (clay mixture and scrap-soil) were crushed and sieved, resulting in fine aggregates (particle size <0.63mm).

2.2 Ceramic specimens

Ceramic bodies were produced by incorporating each time 0, 3, 6 and 9 %wt. scrap-soil in the aforementioned clay mixture. A schematic diagram of the proposed method is shown in Figure 1.

The clay/scrap-soil mixtures were kneaded with water to obtain a proper plastic mass for specimen shaping using a pilot-plant vacuum extruder provided with manual cutter. The ceramic rectangular cross section bars were 80mmX43.5mmX18mm. Extruded test specimens were weighed for moisture determination and then exposed to natural drying (for 12h) and then forced drying (at 110°C) until reaching a constant weight. Dried test pieces were fired following a protocol of gradual temperature increase up to a peak temperature in a programmable electric chamber furnace for only 15 min in order to minimize the energy consumption. The final (peak) sintering temperatures examined were 850°C, 950°C, 1025°C and 1100°C.

The ceramic microstructures obtained were characterized via SEM-EDX analysis. The determination of volume shrinkage (SVS) and weight loss (LOS) upon sintering, open porosity (OP) and total porosity (P), and also three-point bending strength (in terms of modulus of rupture, MOR), was conducted on fired brick specimens according to the ASTM C67 (Standard Test Methods for Sampling and Testing Brick and Structural Clay Tile). The thermal conductivity coefficient (k) was measured at 25°C using the guarded heat flow meter method (Anter Unitherm Model 2022). The tests are in accordance with the ASTM E1530 Standard (Test Method for Evaluating the Resistance to Thermal Transmission of Thin Specimens of Materials by the Guarded Heat Flow Meter Technique). All the results presented hereunder are the mean value of ten specimen measurements.

3. Results and discussion

3.1. Effect of scrap-soil addition

3.1.1. Ceramic specimen forming and appearance

The addition of the scrap-soil in percentages up to 9%wt. did not cause significant changes in the green clay mixture plasticity and extrusion behaviour upon specimen formation. The green specimens obtained had sufficient green strength required to ensure safe handling in the subsequent fabrication steps without any additive. Moreover, specimen color does not change significantly with increasing the scrap-soil percentage in the raw material mixture, upon firing at 950°C. Figure 2a depicts both the specimen weight loss (LOS) and volume shrinkage (SVS) variation resulting from the incorporation of scrap-soil into clay mixture sintered at 950°C. From this Figure, the incorporation of scrap-soil up to 9 %wt. content does not significantly affect both LOS and SVS.

3.1.2. Porosity/Bulk density

Open and total porosity as well as bulk density were determined from the immersion of the specimens in cold and boiling water as follows:

The samples were first immersed in distilled water (~25°C) for 24h. Cold water absorption (*WA_c*) and open porosity (*OP*) are obtained from the following equations (1-5):

$$WA_c(\%) = 100\frac{W_c - W_d}{W_d} \quad (1)$$

$$OP(\%) = 100\frac{W_c - W_d}{\rho V_s} \quad (2)$$

where: W_c = weight of saturated with cold water samples (g)
W_d = weight of dry samples (g)
ρ = density of water (1 g/cm^3)
V_s = geometrical volume of the samples (cm^3)

The samples were then immersed in distilled boiling water for 5h. Boiling water absorption (WA_b) and total porosity (P) are calculated as follows:

$$WA_b(\%) = 100\frac{W_b - W_d}{W_d} \quad (3)$$

$$P(\%) = 100\frac{W_b - W_d}{\rho V_s} \quad (4)$$

where, W_b = weight of saturated with boiling water samples (g)

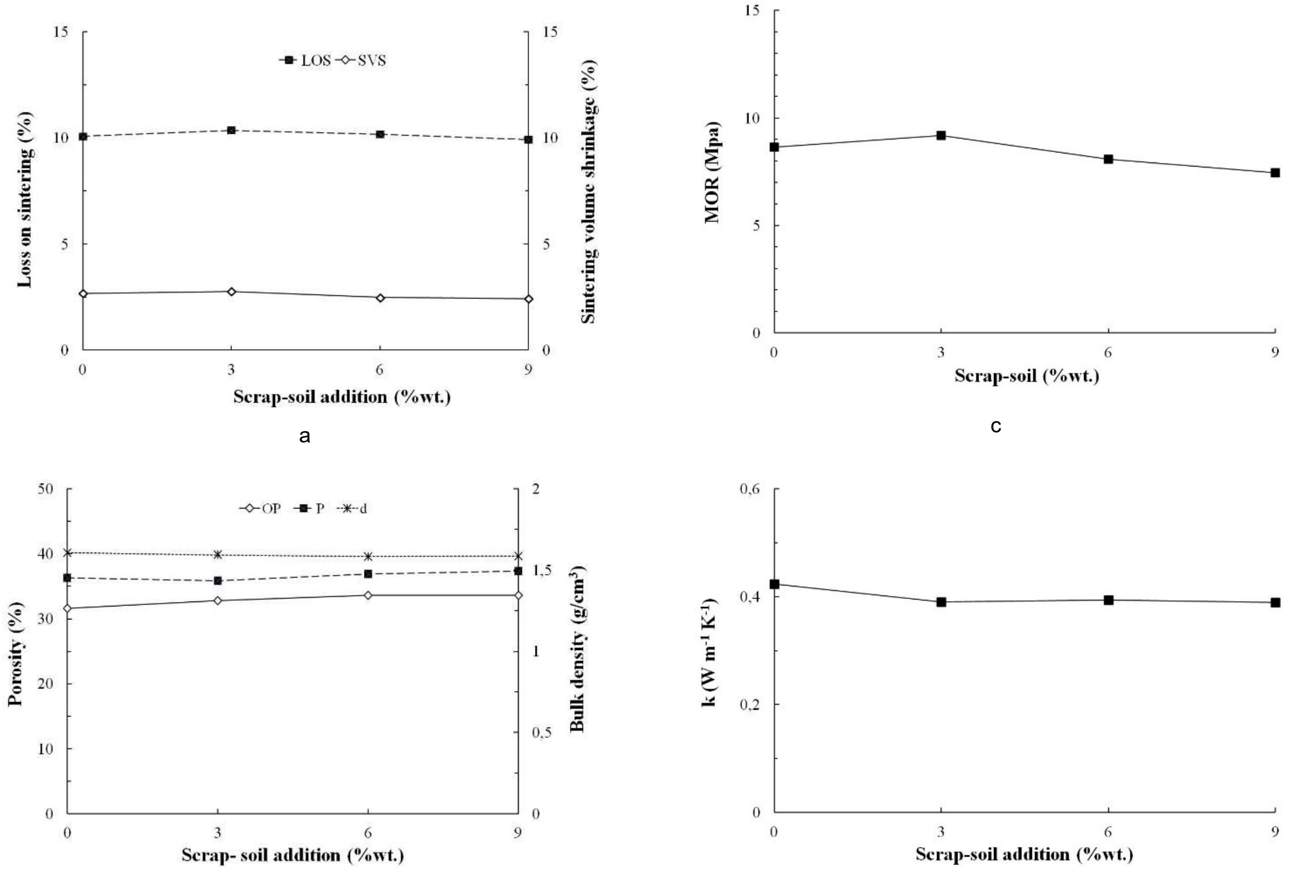
The specimen bulk density (d) is calculated from the following equation:

$$d(g/cm^3) = \frac{W_d}{V_s} \quad (5)$$

The influence of the % scrap-soil addition into the clay mixture on the porosity (open-OP and total-P) and bulk density of red ceramic specimens sintered at 950°C is presented in Figure 2b. It is evident that only the open porosity slightly increases with 3 %wt. scrap-soil utilization into the clay mixture, but further solid residue addition practically does not affect the residual porosity. At the same experimental conditions, the total porosity seems to be almost unaffected. Further processing of the previous experimental results shows that the bulk density of the specimens practically does not change by the scrap-soil percentage.

3.1.3. Bending strength (Modulus of rupture)

The effect of the % scrap-soil addition into the clay mixture on the modulus of rupture (MOR) calculated upon three-point bending test of ceramic specimens sintered at 950°C is presented in Figure 2c. The results show that the embodiment of scrap-soil up to 6 %wt. results in a slight deterioration of MOR values by approx. 6.5%, while the reduction is more pronounced for further addition up to 9% (approx. 14%). It is noticeable that MOR graph line



a c

b d

Fig. 2 - The effect of %wt. scrap-soil admixture on: a) weight loss and volume shrinkage upon sintering, b) porosity (open, OP and total, P) and bulk density, c) modulus of rupture (MOR), and d) thermal conductivity coefficient-k, of clay-based red ceramics fired at 950°C.

is similar to other parameters examined such as weight loss and shrinkage graph and open porosity (see also Figures 2a and 2b).

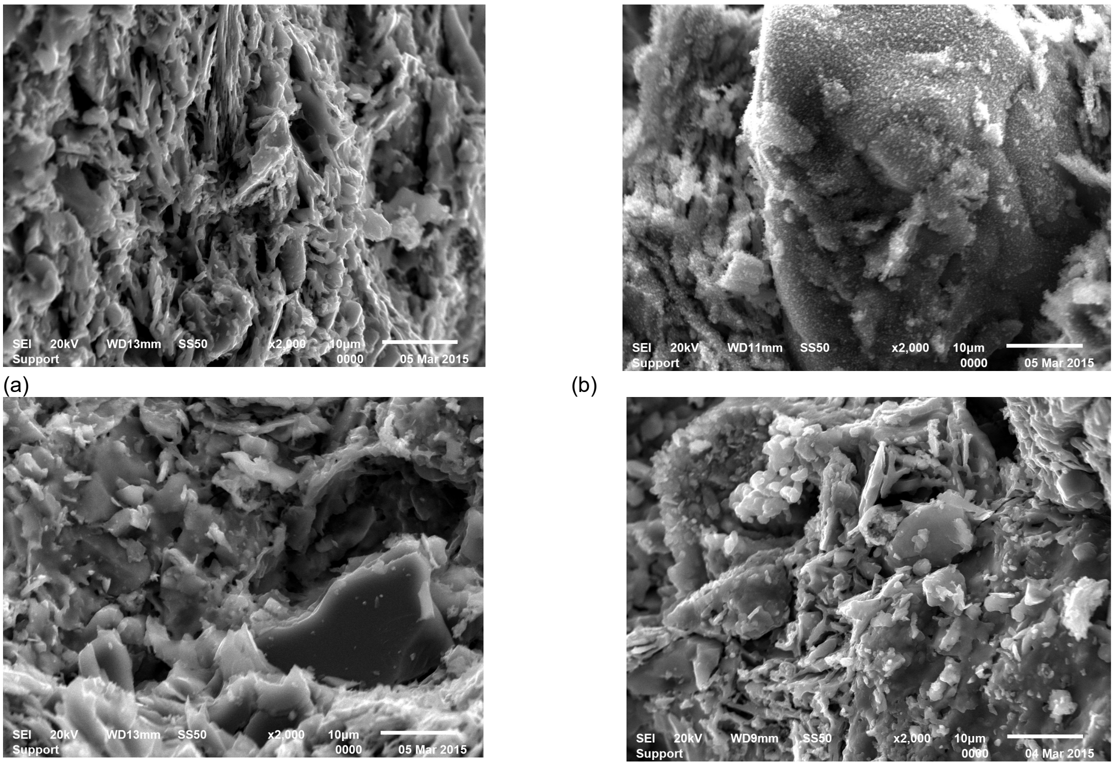
3.1.4. Thermal conductivity

Figure 2d depicts the variation of thermal conductivity coefficient (k) of red ceramics sintered at 950°C as a function of the scrap-soil percentage in the clay mixture. It is obvious, that the thermal conductivity of brick specimens sintered at 950°C is not noticeably affected (approx. 8%) by the scrap-soil addition even up to 9 %wt. This finding is expectedly in accordance with porosity trends presented in Figure 2, because porosity is reported to play an important role in thermal behaviour of clayey porous ceramic materials.

3.1.5. Microstructure

SEM micrographs taken on fracture surface of sintered bricks (Figure 3) indicate a relatively moderated variation in the ceramic microstructures obtained with increasing the scrap-soil addition from 0 up to 9 %wt. into the clayey raw material mixture (see Figures 3a to 3d), this being in accordance to the aforementioned results from the characterization of physico-mechanical properties

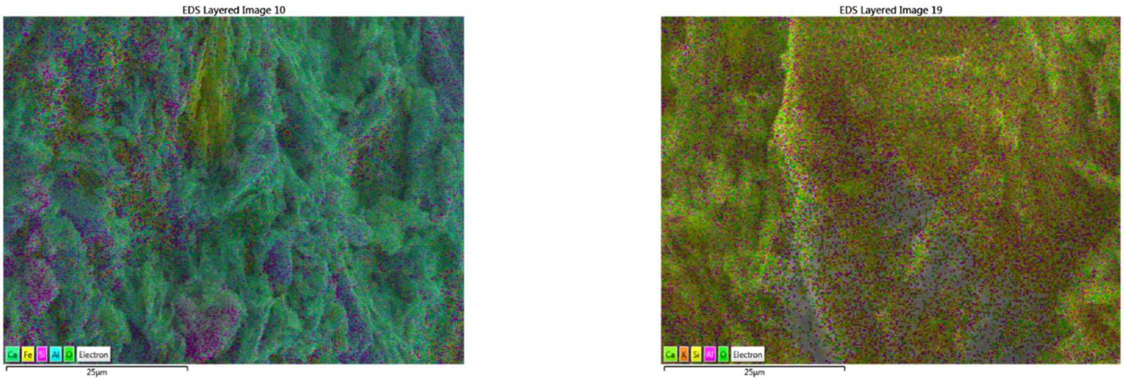
Both particles with irregular form and roundish shape are located in the ceramic bodies. As it can be stated from SEM mapping provided in Figure 4 for the fracture surfaces of Figure 3a-d respectively, the large agglomerates are predominantly composed of Al and Si that are associated with the clay mineral phase kaolinite.



(a) (b)

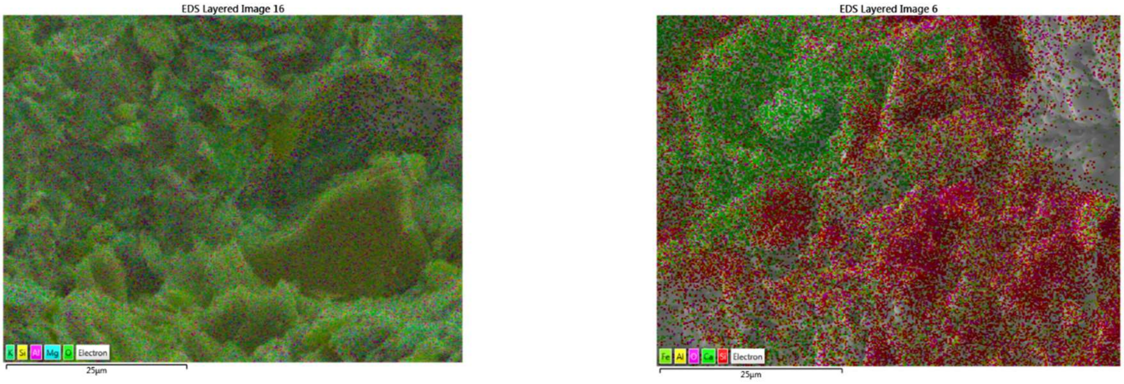
(c) (d)

Fig. 3 - Representative SEM micrographs of clay-based red ceramics fired at 950ºC, as a function of the wt.% scrap-soil addition: a) 0%, b) 3%, c) 6%, d) 9%.



(a) (b)

Fig. 4 continues on next page



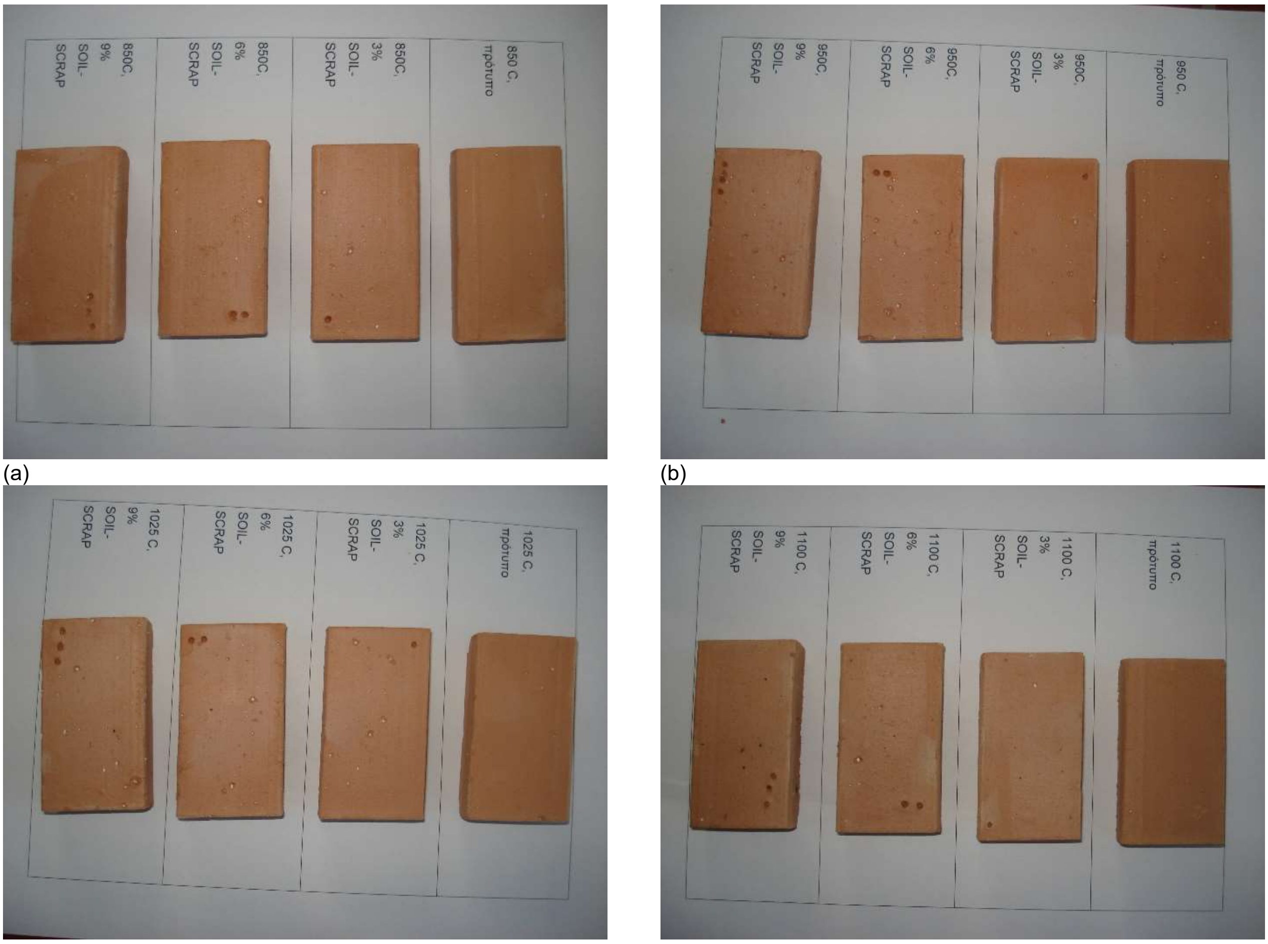
(c) (d)

Fig. 4 - SEM mapping of clay-based red ceramics as a function of the wt.% scrap-soil addition (see Figure 3a-d respectively).

3.2 Sintering temperature effect

Representative macrophotographs of clay bricks, either prototypes (0%) or with 3, 6, 9 %wt. scrap-soil admixture, sintered at 850, 950, 1025 or 1100^{o}C are provided in Figure 5. From this Figure, integral red-brownish fired specimens were produced, in all cases examined.

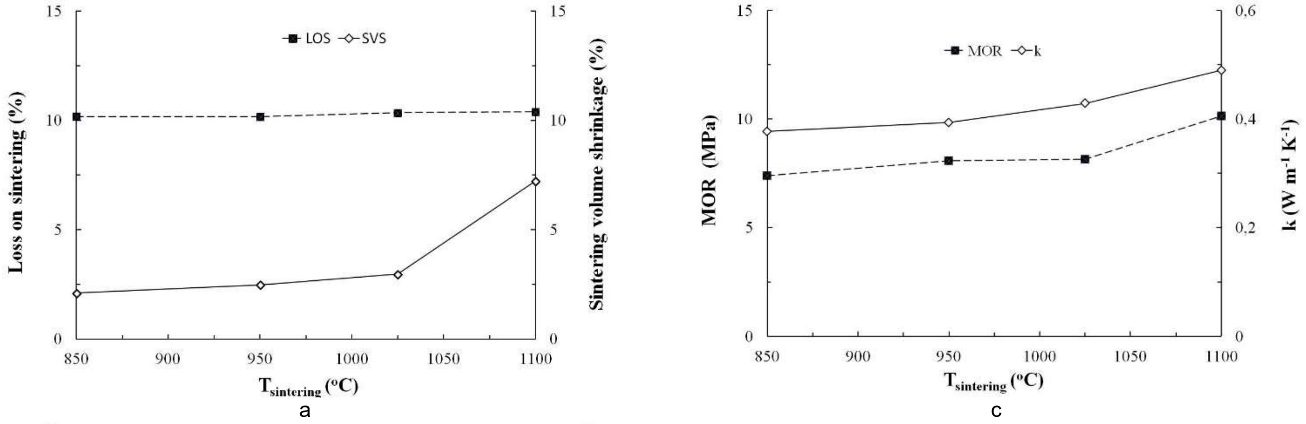
The effect of firing temperature on sintering behavior and physico-mechanical properties of ceramic bodies with 6 wt.% scrap-soil admixture is presented in Figure 6. It can be seen from Figure 6 that the increase in sintering temperature from 850^{o}C up to 1025^{o}C has no or relatively restricted effect on the properties examined. However, further heating, from 1025^{o}C up to 1100^{o}C results in clearly more intense variation (SVS ≈+200%, OP ≈ -20%, MOR ≈ +20%, k ≈ +15%) due to higher densification, probably associated with liquid phase phenomena occurring upon sintering and binding the materials produced.



(a) (b)

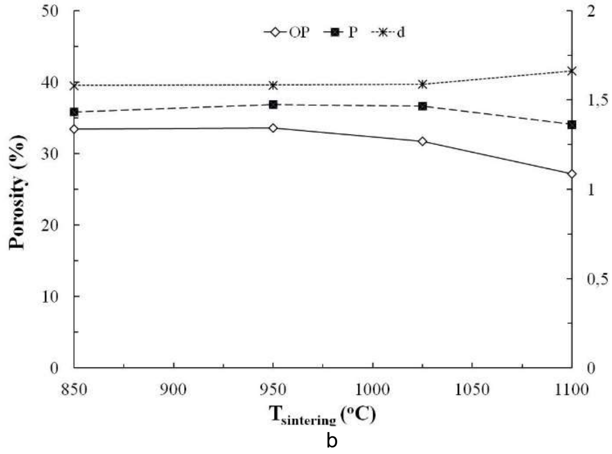
(c) (d)

Fig. 5 - Representative photographs of clay brick specimens (80mmX43.5mmX18mm), either prototypes (0%) or with 3, 6, 9 %wt. scrap-soil admixture, fired at 850°C (a), 950°C (b), 1025°C (c) and 1100°C (d).



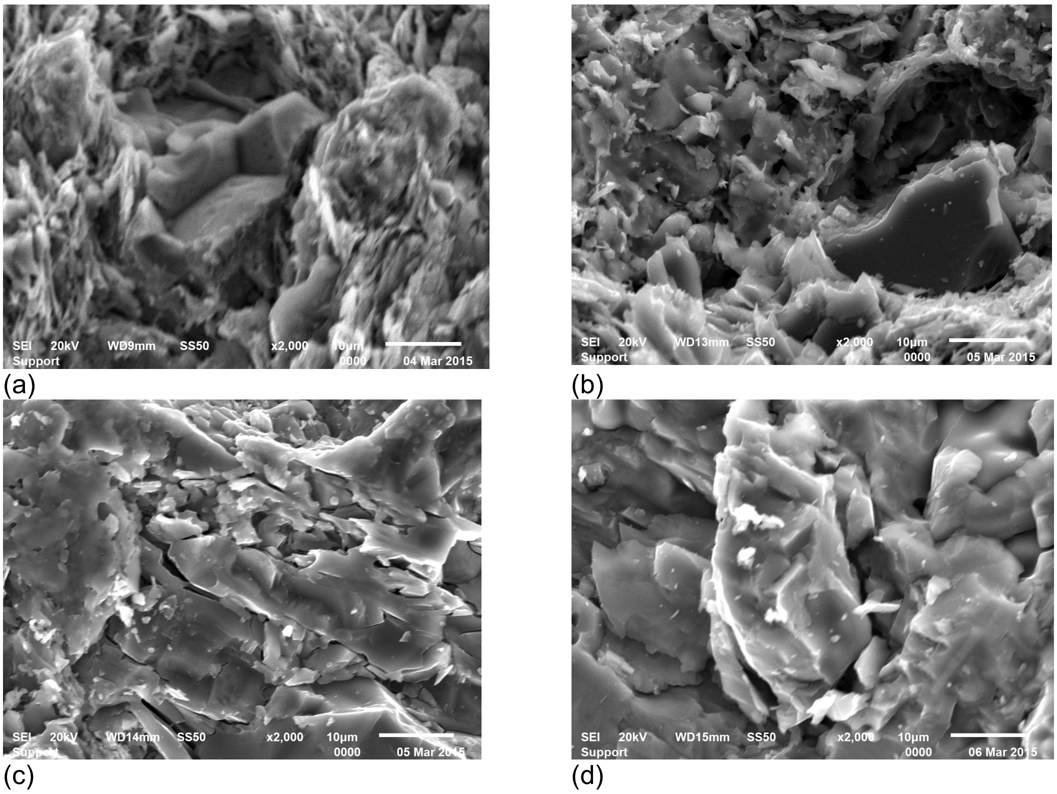
a

c



b

Fig. 6 - The effect of firing temperature on (a) weight loss (LOS) and volume shrinkage (SVS) upon sintering, (b) open porosity (OP), total porosity (P), bulk density, and c) modulus of rupture (MOR) and thermal conductivity coefficient-k, of clay-based red ceramic bodies with 6%wt. scrap-soil admixture.



(a)
(b)
(c)
(d)

Fig. 7 - Representative SEM micrographs of clay-based red ceramics with 6%wt. scrap-soil admixture, fired at 850ºC (a), 950ºC (b), 1025ºC (c) and 1100ºC (d).

In Figure 7, SEM micrographs of 6 %wt. scrap-soil content brick bodies fired at different peak temperatures are provided. From this Figure, a porosity decrease and an extended diffusion possibly combined with viscous flow phenomena occurred in the ceramic matrices are revealed, when increasing the sintering temperature from 850°C and 950°C (Figures 6a and 6b) to 1025°C (Figure 6c) and especially up to 1100°C (Figure 6d), thus explaining the above mentioned clear increase in both modulus of rupture (MOR) and thermal conductivity coefficient (k) of the clay bricks with sintering temperature, respectively.

4. Conclusions

- Brick-shaped red ceramic bodies were successfully obtained, from standard clay mixtures incorporating "scrap-soil" derived from steel making industry, by employing extrusion and sintering.
- The beneficial utilization of low percentages of scrap-soil (up to 6 %wt.) is attained with tolerable variations in the physico-mechanical and thermal properties of the brick specimens fired at 950°C, thus potentially contributing, at least partly, to safe management and minimization of this largely available heavy industrial soil.
- The increase of the % scrap-soil amount incorporated in the clay mixture does not seem to impart a significant effect on the ceramic microstructure, while increasing the sintering temperature from 850°C to 1025°C, and especially up to 1100°C, enhances brick densification, thus leading to more compact microstructures with reduced residual porosity and increased modulus of rupture and thermal conductivity, respectively.
- In terms of the thermal insulation properties of the ceramic bodies and energy consumption savings, the optimum sintering temperature appears to be 950°C.

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