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RESEARCH ARTICLE

PROPERTIES of POROUS CERAMICS PRODUCED by SINTERING TERRA ROSSA-ALKALI MIXES

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ABSTRACT

Porous ceramics were produced by sintering terra rossa (TR) with alkalis for void formation at 1000 °C. Little cylinders (25x25 mm) were prepared with TR to investigate the influence of alkali type (NaOH, Na_2CO_3 and KOH) and amount (8, 10 and 12% by weight of TR) on the physical, mechanical and microstructure of porous ceramics (PC). The highest compressive strength (32 MPa) was obtained in series with no alkalis. The addition of alkalis decreased the unit weight and compressive strength of PC due to decreased sintering temperature, increased foaming and excessive formation of glassy phase causing the brittle structure. The unit weight of the PC produced with NaOH and Na_2CO_3 was considerably low (0.62-0.70 g/cm^3) compared with PC comprising KOH (1.05-2.16 g/cm^3). Corresponding compressive strengths were 3.17-4.46 MPa and 7.68-25.87 MPa revealing that it can be used as a decorative alternative to clay brick and autoclaved aerated concrete blocks.

Keywords: *Compressive strength, Porous ceramics, Sintering, Terra rossa*

1. INTRODUCTION

Terra rossa (TR) is reddish, clayey to silty clayey soil widespread in the Mediterranean region occurs as a discontinuous layer ranging from a few centimetres to several meters formed on calcareous main material (limestone or dolomite bedrock) [1-3]. Most important characteristics of TR are their free Fe_2O_3 (hematite) content of up to 8% and is usually between 4-6%, which gives bright red colors to TR. Soil formed on the greyish-blue crystalline limestones of TR has been found to have very little residual material. The most important chemical process here is decalcification and the water-soluble $CaCO_3$ is removed by washing [5, 6].

Bricks, floor and roofing tiles, etc. are produced by a sintering process. Properties of these depend on the clayey material's chemical and mineralogical composition [7, 8]. Na_2O can significantly reduce the

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viscosity of the silicate melt by depolymerizing the silicate networks [9]. Ge et al. [10] observed that increasing the Na_2O contents reduced the viscosity of ceramic foams sintered. This caused expansion of the pores and reduced the bulk density of the product. SiO_2 itself is chemically inert.

Thermal expansion of SiO_2 is too little and resistance to thermal shock too much. Due to the high melting point (1723ºC), network modifiers such as alkali/alkaline earth oxides were added to the SiO_2 glass to break the bridging oxygen bonds in the Si-O-Si bonds and reduce the melting temperature of the glass [11-15]. Feldspar, talc and dolomites comprises important amount of Na_2O, K_2O, MgO and CaO that increases the flux amount and induce the formation of an amorphous phase which acts as binder [16-18]. Production of Red-fired ceramics (tiles, bricks etc.) continues in Anatolia today, with about 500 factories producing brick and roofing tiles using clay raw materials from alluvial deposits, which are important soils for agriculture. Therefore, researching new clay sources for red ceramics is inevitable [19]. Low thermal insulation properties and high weight of conventional bricks limits their usage at new buildings. Various pore-forming agents were used to develop thermal properties of sintered clay bricks [20]. Bricks as light as lightweight aggregates (LWA) could be produced by using expansion agents ($NaHCO_3$ and $CaCO_3$) [21].

A significant part of the area of Kütahya-Turkey was occupied by mountain terrains/high lands, which are built up of meta-carbonate rocks (marbles). The most characteristic types of red soil over carbonate rocks are Terra Rossa. The TR can be suitable as raw material in the brick and roofing tile industry. The present study presenting the results of a master thesis [22] motivated by a lack of data on the sintering properties of TR-alkali mixes. Accordingly, this paper aims to determine the contribution of these alkali oxides to the physical and mechanical properties of porous ceramics (PC) produced by TR.

2. MATERIAL and METHODS

Terra rossa samples given in Fig. 1 were collected from the village of Çöğürler in Kütahya/Turkey. TR was ground by a ringed mill for 3 min to increase the surface area up to 4847 cm^2/g. Porous ceramics were produced by i) mixing TR with technical grade alkali oxides (NaOH, Na_2CO_3 and KOH >99% purity obtained from Detsan Chemicals Company in Eskişehir/TURKEY) at ratios of 8, 10 and 12% by weight of TR ii) keeping the mixtures in plastic bags for a day, iii) pressing with 2% water by weight of mix and 3 kN molding force to form 25x25 mm cylinders iv) drying 1 day at 20±2 °C in laboratory and 1 day at 105±2 °C in oven v) sintering at 1000 ºC in a tunnel kiln for 9 hours 45 minutes.

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Figure 1. Terra rossa on limestone layer in Çöğürler (Kütahya/Turkey) [22].

A total of 10 series with control (C) with no alkali addition were produced. Series with 8, 10 and 12% NaOH were labelled as N8, N10 and N12 respectively. Similarly, series with Na_2CO_3 or KOH were named as NC8, NC10, NC12 and K8, K10 and K12 respectively. Unit weight (UW) (TS EN 1097-6) [23], uniaxial compressive strength (UCS) of porous ceramics (PC) at 0.6 MPa/s loading rate was tested. Before the compressive strength test upper and lower surfaces of porous ceramics were smoothed with sandpaper. All the reported results are the means of three samples. Colorimetric analysis and optical microscopy analyses (broken surfaces taken from the centre of the samples) were conducted. To conduct a petrographic inspection, section samples were prepared from each terra rossa based porous ceramics respectively. Visual inspection was carried out under planar polarized light by using a petrographic microscope (Nikon Eclipse E200 Pol).

3. EXPERIMENTAL RESULTS

3.1. Characterization of the Terra Rossa

The TR was mainly composed of SiO_2, and Al_2O_3 (Table 1). The LOI of TR about 15.26 (wt%) was relatively high. By contrast, the number of alkaline oxides was very low. Fe_2O_3 (*hematite*) minerals content which gives red colors to TR as stated in literature [24] was 6.52%.

Table 1. Oxide content of terra rossa [22].

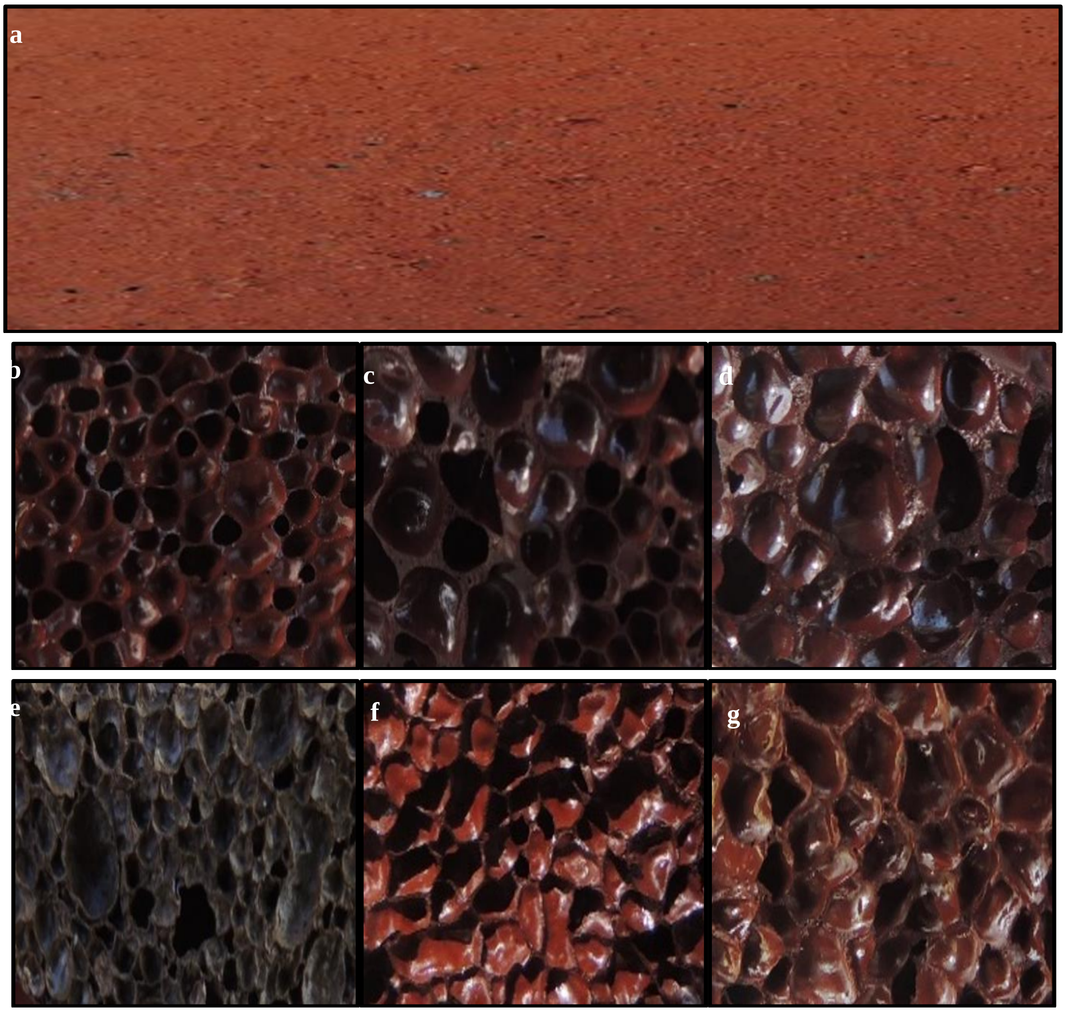
Oxide content	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	Na_2O	CaO	MgO	TiO_2	MnO	Cl	SO_3	*LOI
% mass	56.07	15.98	6.52	1.91	1.93	0.14	1.91	1.27	0.57	0.11	0.06	0.05	15.25

*LOI: Loss on ignition

3.2. Evaluation of Physical and Mechanical Properties

The pore structure of porous ceramics products with different alkali types and amounts were shown in Fig. 2. The iron element in oxidation state II was oxidised to state III after sintering could be responsible from darker colors of porous ceramics [25, 26]. Alkali type and amount significantly affected the colors of the porous ceramics as illustrated in Table 2. Numerical values of color analysis were given in Table 2. Different colors were observed due to the type and amount of alkalis. The increase in NaOH content significantly reduced a* and b* values of the N series.

Alkalis lower the melting temperature in N and NC series. The unit weight and the compressive strength decreased with the increase in the alkali ratio. The pore sizes in N and NC series continued to increase gradually with increasing alkali content. Enhancement of foaming due to higher alkali amounts was probably responsible for these dicreasements. However, in contrast, with the increase in KOH amount the pore sizes of K series were reduced while the UW and UCS of K series increased considerably. Maximum UCS was achieved for the K12 series. Homogeneous distribution of pores observed in K series. Contrary to other alkali series, increase in KOH amount considerably increased the compressive strength of porous ceramics.



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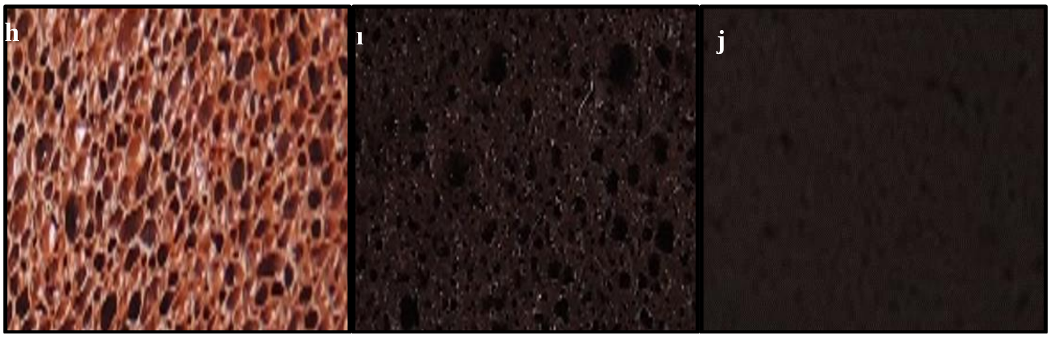

Figure 2. The cross-section of (a) C, (b) N8, (c) N10, (d) N12, (e) NC8, (f) NC10, (g) NC12, (h)K8, (ı) K10 and (j) K12 [22].

According to TS EN 771-1 [27], hollow bricks are required to have a compressive strength of at least 2 MPa and the unit weight of them ranges between 600-700 kg/m^3. According to TS EN 771-4 [28], autoclaved aerated concrete blocks must have a compressive of 2.2 MPa and their unit weight values are 350 to 500 kg/m^3 [28]. Control series had a unit weight of 2.3 g/cm^3 and compressive strength of 32 MPa. The unit weight of the PC produced with NaOH and Na_2CO_3 was considerably low (0.62-0.70 g/cm^3) compared with PC comprising KOH (1.05-2.16 g/cm^3). Corresponding compressive strengths were 3.17-4.46 MPa and 7.68-25.87 MPa revealing that it can be used as a decorative alternative to clay brick and autoclaved aerated concrete blocks.

Table 2. Color Codes, physical and mechanical properties of porous ceramics [22].

		Sample codes									
		C	N8	N10	N12	NC8	NC10	NC12	K8	K10	K12
Color codes	L*	35.54	32.97	37.26	37.89	40.29	38.05	37.88	39.09	34.25	35.08
	a*	19.15	9.12	5.73	5.17	2.76	7.93	8.25	11.43	12.24	12.80
	b*	17.97	5.05	3.10	2.55	10.16	5.28	4.23	8.76	10.45	11.35
Properties	WA	6.25	0.98	1.09	2.41	0.91	1.38	1.95	0	0	0
	UW (g/cm^3)	2.30	0.67	0.64	0.62	0.70	0.68	0.65	1.05	1.73	2.16
	CS (MPa)	32.13	3.82	3.55	3.17	4.46	4.31	3.94	7.68	14.16	25.87

Note: The "L" axis gives the lightness: a white object has a L value of 100 and the L value of a black object is 0. The shades of grey, are on the L axis. The "a" axis is the green-red axis and the "b" axis goes from blue (-b) to yellow (+b).

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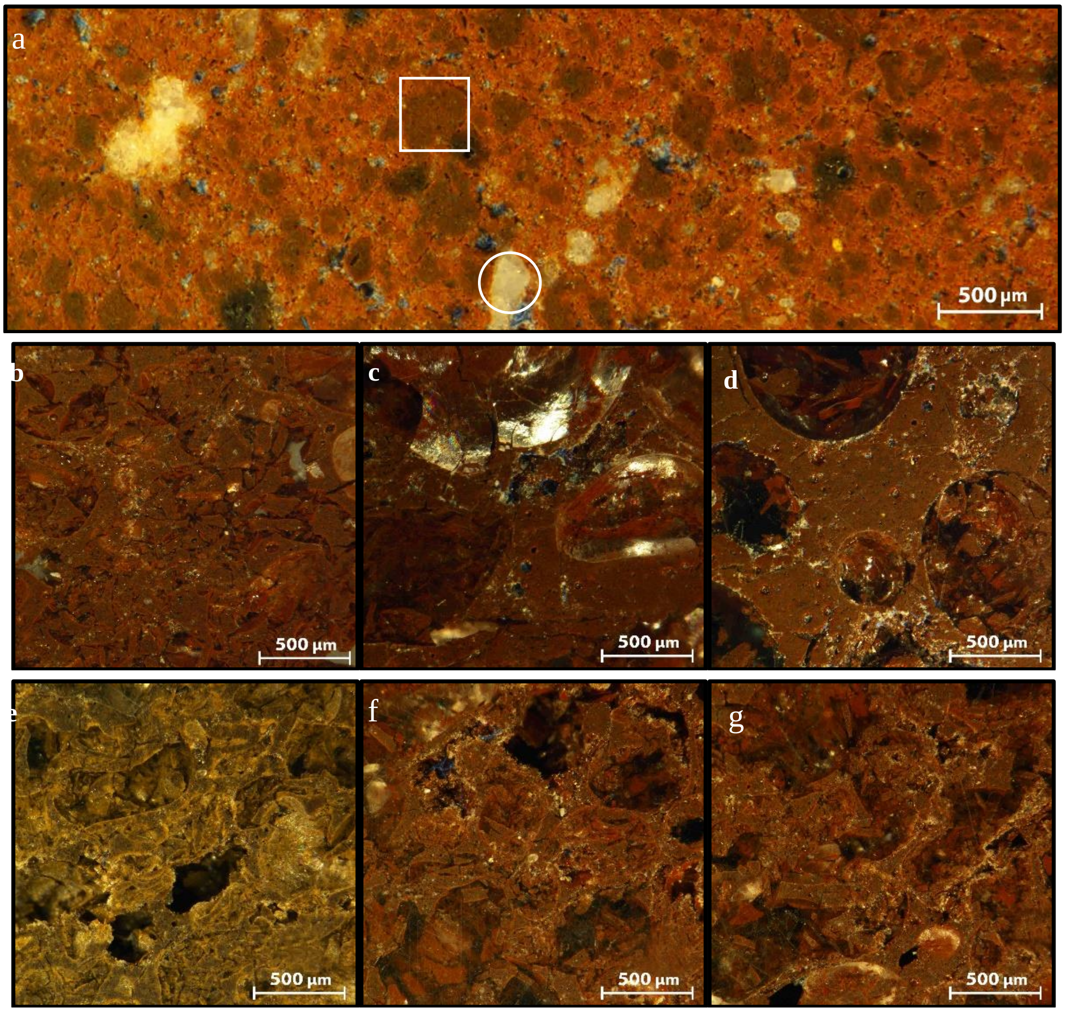
3.3. Evaluation of Optical Microscopy Images

Fig. 3 (a) presents the C series. The microstructure suggests quartz (white circle) and hematite particles (white square) in size up to 2 cm embedded in the liquid phase. Since the grain size of the liquid phase was considerably fine the mineral type could not be determined by optical microscopy.



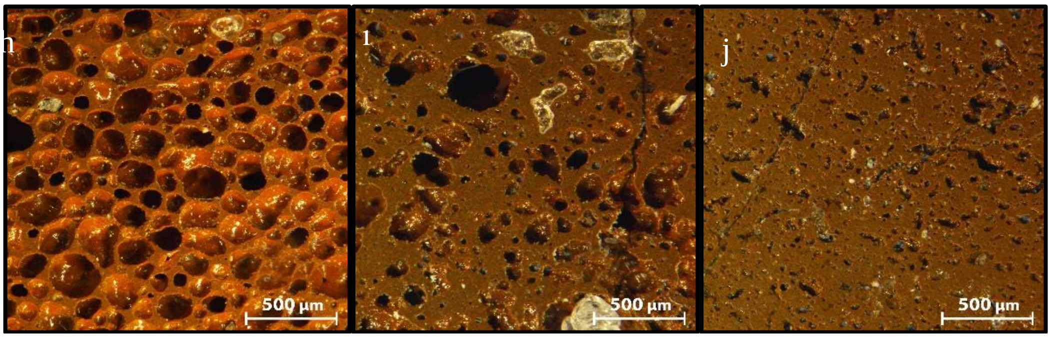


Figure 3. Optical microscopy images of (a) C, (b) N8, (c) N10, (d) N12, (e) NC8, (f) NC10, (g) NC12, (h)K8, (ı) K10 and (j) K12 [22].

Some cracks were observed in all samples because of the shrinkage of the binding matrix. This was more pronounced for series produced with 12% alkalis. For K series closed pores were more spherical. N and NC series have more unconsolidated grains compared to the K series. It was concluded that the increasing KOH enhanced the vitreous structure. The compressive strength of porous ceramics enhanced up to 26 MPa for K12.

4. CONCLUSIONS

There are difficulties in finding suitable clay fields used as brick raw material and in obtaining clay from these fields. New brick factories are not licensed. A compact material having a unit weight of 2.3 g/cm^3 and compressive strength of 32 MPa obtained by sintering terra rossa. According to us high content of Fe_2O_3 acted as a flux increasing the compactness of the material and enhancing the mechanical strength. The addition of alkalis decreased the unit weight and compressive strength of PC. Porous ceramics with a unit weight of 1.05-2.16 g/cm^3 and compressive strengths of 7.68-25.87 MPa were produced using KOH as an expansion agent. Porous ceramics can be used as a decorative alternative to clay brick and autoclaved aerated concrete blocks. Potassium felsdispates can be used as cheaper alkali source. The incorporation of expansion agents in TR can be a viable procedure, which turns TR into decorative porous ceramics.

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