RICE HUSK ASH (RHA) RECYCLING IN BRICK MANUFACTURE: EFFECTS ON PHYSICAL AND MICROSTRUCTURAL PROPERTIES

Fernanda Andreola*, Luisa Barbieri, Isabella Lancellotti
Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia,
Via P.Vivarelli 10, 41125 Modena, Italy

Federica Bondioli
Department of Engineering and Architecture, University of Parma
Parco Area delle Scienze, 181/A - 43124 Parma, Italy

***Presenting author email: andreola.fernanda@unimore.it,**
Tel: +39-0592056237, Fax: +39-0592056243

Abstract

In this work the screening results of the scientific activity conducted on the possibility to use rice husk ash (RHA) as silica precursor in ceramic field, such as raw material in the obtainment of clay bricks were reported. For the brick study an industrial mixture of two clays was used, the batch was prepared substituting the clays with different percentages of RHA (0-20 wt%) and the required quantities of water. The pastes obtained were extruded in a laboratory extrusor (P= 8-9 bar), dried and then fired in an industrial camera kiln (24 hrs total time, Tmax: 960°C and 6 hrs soaking time). The brick samples were undergone to technological analysis to determine: linear shrinkage and naphtha absorption after drying, (24-hour immersion) water absorption, linear shrinkage, weight loss, average flexural strength, apparent density after firing. To analyze the effect of the RHA presence microstructural (SEM/EDS) and mineralogical analysis (XRD) on the fired pieces were performed. From the tests conducted it is possible to note that RHA presence contributes to reduce the linear shrinkage during drying and firing while a contrary effect is observed for the water absorption. The carbon unburned content in the RHA contributes to increase the final porosity of the bricks indicating this agro-waste as pore forming component to obtain light weight clay bricks.

Keywords: rice husk ash (RHA), Ceramics, light weight Bricks

Introduction

On the basis of worldwide rice production (717 million tons per year in 2014), the total global rice husk ash amount could be around 35 million tons per year. Since, the rice husk is a low density material with a high calorific heat value (≈16 MJ/kg) which is widely used as a fuel for drying and for the parboiling process in the rice industry or in other industrial kiln (cement). The combustion produces a waste called rice husk ash (RHA). Every 1000 kg of milled paddy, about 220 kg (22%) of husk is produced, and when this husk is burnt, about 55 kg (25%) of RHA is generated [1]. RHA is an ash product with an unburned carbon percentage (~10%), which contains around 90% of amorphous silica. Generally, amorphous ash is formed during combustion (550-800°C) only at higher temperatures a crystalline ash is developed [2]. Some papers indicated that combustion temperatures below 700°C generates silica in the ash mainly as amorphous phase, which consists mainly of a disordered Si-O structure that is the product of decomposition and sintering of opaline or hydrate silica, without fusion. For higher combustion temperatures, the X-ray diffraction studies demonstrated that the ash begins to show a peak at $2\theta = 21.7°$, which indicates the beginning of crystallization of silicon dioxide in cristobalite [3-4]. Besides, increasing again temperature (1000°C), or as a result of further combustion of ash for a long time and at high temperatures (for example, to remove residual carbon), an increase in crystalline silica is noted and the trydimite development is observed. So, the final crystalline structure of silica is conditioned of combustion setting (time, temperature, heating rate, etc) .

The presence of silica is well known and a large number of scientific literature highlighted two main industrial uses. From the regulatory point of view, rice husk ash is not a residue, but it is considered in all respects a product, and as such it is marketed.

RHA is used during the production of high quality flat steel, due to their insulating properties (low thermal conductivity, low bulk density and high porosity), it is used as “tundish powder” to insulate the tundish container, prevents rapid cooling of steel and ensures uniform solidification casting process [3]. Moreover, in the cement industry, in the manufacture of low cost building blocks, and in the production of high quality cement as pozzolanic material [5]. The reactivity to lime of RHA depends on a combination of two factors, namely the high content of non-crystalline silica and the high specific area. Due to the presence of high silica content in ash, extraction of silica is satisfactory, there is a growing demand in the production of fine amorphous silica for cement and concrete used for bridges, marine environments and nuclear power plants[6]

Regarding the use of RHA as silica precursor in the ceramic field more studies are oriented to the obtainment of ceramics and glass ceramics. In particular, Prasad et al.[7] investigated the positive effect of rice husk ash in traditional Whiteware compositions completely replacing the quartz phase. Naskar et al. investigated the possibility to use this agro waste to synthesize lithium aluminum silicate (LAS) [8] and cordierite [9] glass ceramics. Replacement of kaolinite with RHA in the mixture composition yields higher amount of cordierite with lower crystallization temperature. Finally, the authors worked evaluating the effect of RHA addition in the obtainment of ceramic glazes [10], glass ceramic of the system $MgO-Al_2O_3-SiO_2$, [11,12] and in the Synthesis of $(Pr,Zr)SiO_4$ Ceramic Pigment [13].

Regarding the brick industry, the bodies used are generally very heterogeneous since they consists of clayed raw materials with a very wide–ranging overall composition [14]. Many studies demonstrated that heavy clay ceramics are potentially able to tolerate the presence of wastes from different sectors as industrial, urban and agricultural [15-17] and can be good candidate materials for recycling application. In general the additions, in terms of the quantity of waste that can be used in ceramic bodies, are rather modest (almost never more than 10 wt%) and the main effects (in addition to the energy savings during firing) include an increase on the porosity an a reduction of the shrinkage and the mechanical properties [15]. In particular, this work proposes to use RHA ranging from 5 to 20 wt% in substitution of the clays in the brick body due to the high silica content in the ash. A simulation of brick making in lab scale was performed and after drying and firing step the samples obtained were characterized.

Experimental (materials and methods)

For the brick study an industrial clay local mixture (Yellow clay and Grey clay) widely used was chosen. To prepare the mixture, the clays were dried and sieved to required particle size (<500 µm). The various compositions were prepared using a 1:1 ratio of each clay with different percentages (5, 10, 15 and 20wt%) of RHA in substitution and the required quantities of water (20-22wt%) to obtain the degree of plasticity suitable for pastes processed by extrusion. Laboratory brick samples in the form of bars (50mm x 120mm) were extruded (P= 8-9 bar), dried for 48hs at 110°C and then fired in an industrial camera kiln with a thermal cycle (24 hrs total time, Tmax: 960°C and 6 hrs soaking time). The brick samples were undergone technological analysis to determine the following parameters: linear shrinkage and naphtha absorption after drying, (24-hour immersion) water absorption, linear shrinkage, weight loss, average flexural strength, efflorescence, apparent density (Micromeritics, Envelop density analyzer) and CIELab colorimetry (Euromeccanica, UV-spectrophotometer X-Rite SP-60) on fired pieces in comparison to the standard one. Besides, microstructural (SEM/EDS) and mineralogical analysis (XRD) of the fired pieces were performed.

In order to characterize the rice husk ash and clays used, different techniques were performed: chemical by means of ICP inducted couple plasma, mineralogical by means of X-ray diffractometry for powders (XRD), particle size by means of laser particle size analyzer).

Results and Discussion

RHA characterization

The chemical analysis of the rice husk ash used, as received by the parboiled plant is reported in Table 1. It is possible to observe the high content of very pure silica and the high LOI associated to the presence of carbon unburned that was confirmed by the elemental analysis. The P_2O_5 is the main oxide after silica. Other oxides are all lower than 1.5wt%. In particular, the chromophore oxides as Fe_2O_3 and TiO_2, that can influence the colour developed in a ceramic matrix, are present only in traces. Regarding the elemental analysis defines that the hydrogen content is 0.15 wt%, the nitrogen content is 0.16 wt% while the carbon content is 8 wt% in accordance with the black color of the powdered ash.

From a mineralogical point of view, the Rietveld-RIR analysis of the XRD pattern showed that RHA is mainly constituted by amorphous silica (77.2 wt%) and, two polymorphous crystalline phases of silica: cristobalite low (17.2 wt%) and tridymite (5.6 wt%). The quantitative results underline that, as reported by Ibrahim [18], the thermal treatment performed on the rice to obtain the parboiled type favors the nucleation and growth of cristobalite phase which, in general, starts to appear at 900°C [19]. The presence of tridymite, instead, is governed by the kind and amount of impurities presents, this phase is stable for temperatures higher than 870°C this confirms the combustion process [20]. These results suggest that the ash can be used in bodies as leaning component. Leaning additives are materials that remains inert during drying and sometimes react during firing. They also play a role of plasticity reducing into the body, already used in heavy clay sector quartz sands, chamottes, fly ash, lean clay materials, etc [14,15].

Clays characterization

From the chemical analysis reported in Table 1 it is possible to observe the high content of silica (SiO_2) and alumina (Al_2O_3), characteristic components of ceramic materials. The presence of iron (Fe_2O_3), calcium (CaO) and magnesium (MgO) oxides characteristic of the ferruginous-calcareous clays responsible for the development of the red colour products after firing. On the contrary, alkaline oxides (Na_2O and K_2O) are present in small amounts. The percentage above 10 wt% of CaO indicates carbonates presence in the clays. Carbonates could cause aesthetic defects after firing (calcinelli) and are responsible for the final porosity of the bricks due to their decomposition (700-900°C) with develop of carbon dioxide within the firing cycle.

The mineralogical composition of the clays, highlighted the presence of illite-mica, kaolinite, smectite and chlorite as clayed components and calcite ($CaCO_3$), quartz and K-feldspars. In the brick body clayed components have a plastic function essential for the workability of the pastes, carbonates and feldspars have a flux function, quartz and sand are the inert components necessary to build the structure of the product.

Table 1- Chemical analysis (wt%) of the clays and RHA used

OXIDE (wt%)	YELLOW CLAY	GREY CLAY	RICE HUSK ASH
SiO_2	52.67	50.41	81.0
Al_2O_3	11.02	12.16	0.05
TiO_2	0.58	0.61	0.03
Fe_2O_3	4.30	4.32	0.14
CaO	11.96	11.96	1.07
MgO	2.44	3.12	0.75
K_2O	2.44	3.12	1.39
Na_2O	0.54	0.72	0.0
ZnO	-	-	0.01
PO_4	-	-	3.23
SO_4	-	-	1.45
MnO	-	-	0.14
L.o.I (1100°C)	13.06	13.77	13.92
$CaCO_3$ (%)	18.5	19.5	-

Brick samples characterization

During brick making the water amount added necessary for kept the suitable plasticity increased with the increase of RHA introduced, raising 27% for the mix containing 20% of RHA. A possible explanation lies in the reduction of amount of plastic components (clays) in the mix with a less efficiency on the workability. The leaning function (not plastic) of RHA is positive because reduce the linear shrinkage during drying so as to avoid possible cracking of the pieces. In fact the LS% data obtained indicated a reduction of LS% as the function of RHA content in the mix with respect to the standard (Figure 1). By contrast, the naphtha absorption (NA) tests highlighted an increase of the permeability (open porosity) as a function of the RHA percentage (Figure 2). This trend is attributable to the higher quantity of water needs in the mixes to improve the workability of brick bodies. From these considerations it is possible to hypotisized that the introduction of RHA to clayed raw materials modify the behavior of the bodies in the drying phase.

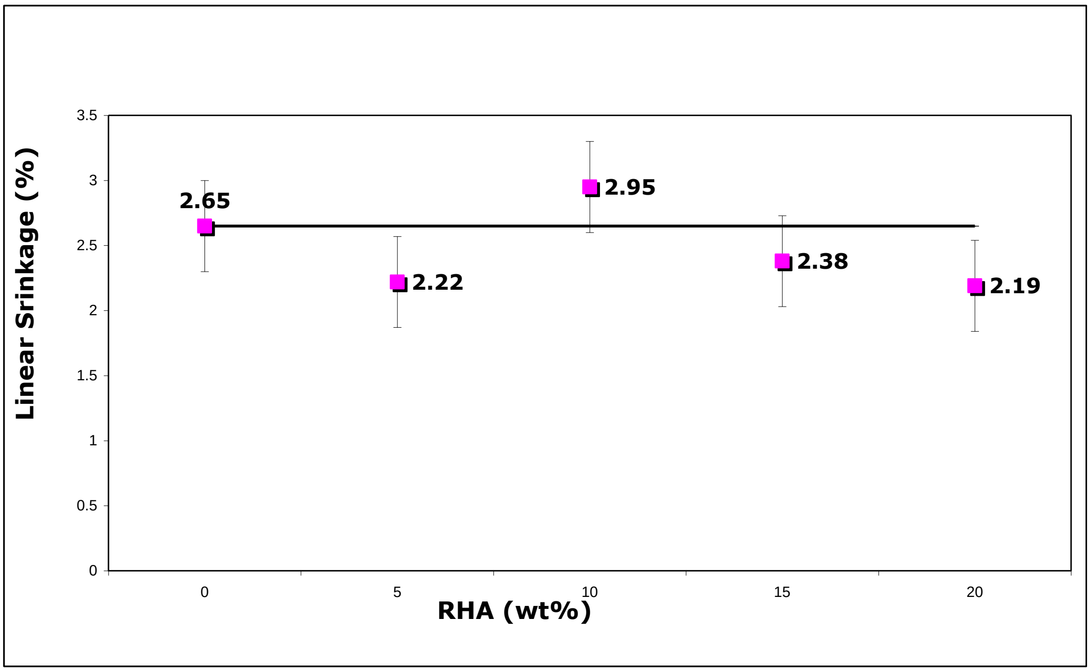


Fig.1- Linear shrinkage (LS%) for brick samples after drying step as a function of RHA content

Regarding fired samples the presence of RHA in the mix influences the sintering behavior. Higher amounts of RHA avoid the densification of the body due to carbon residue content presents into the composition. This residue decompose with gas development (CO_2) at the temperatures within firing thermal cycle (450-500°C) [21]. This phenomenon did not affected the LS% values achieved that remained almost constant and resulted similar to the based brick close to zero and in agreement with industrial tolerance (LS%<1%). On the contrary 24-hour immersion in distilled water tests shown an increase of WA% values as RHA content increases, presenting differences compared to the standard. Addition up to 10 wt% revealed satisfactory data in according to industrial tolerance (WA%=22%). It should be noted, however, that the values obtained are in accordance with the average porosity of roofing bricks which are around 30-35% [22]. This trend highlights an increase of open porosity as a function of RHA addition. Regarding the weight loss, all samples containing RHA achieved similar data about 13%. This percentage is in agreement with the weight loss deriving from the presence of both unburned carbon in RHA and carbonates. In agreement with other study RHA introduction contributes to obtain lighter bricks [16].

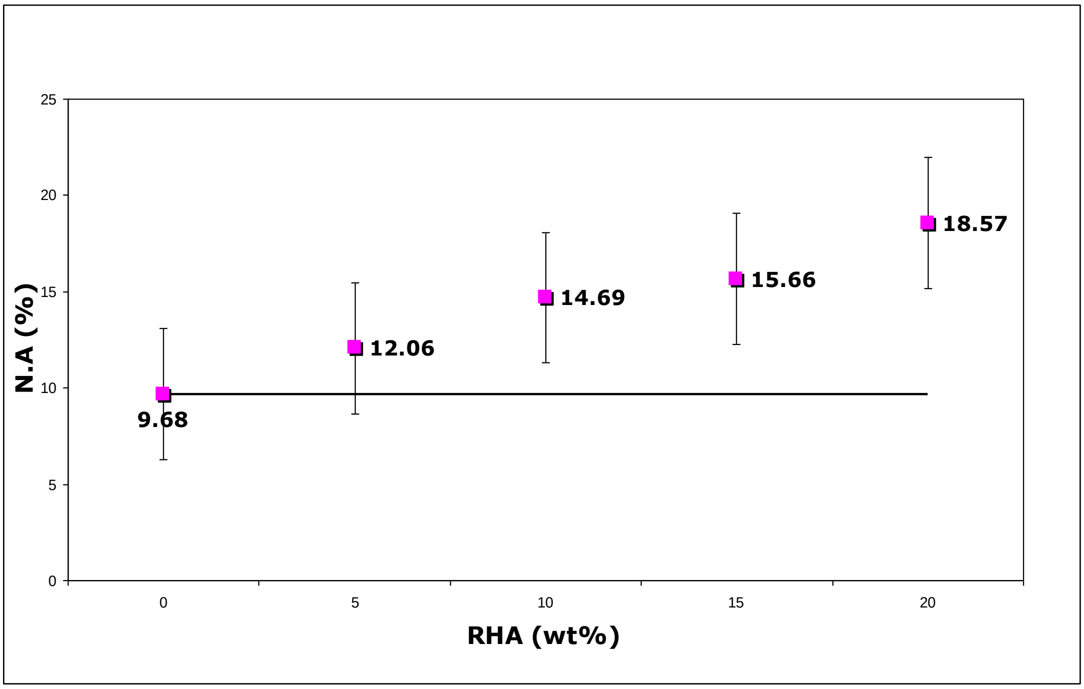


Fig.2- Naphta absorption (NA%) for brick samples after drying step as a function of RHA content

To determine possible interactions between RHA and clays bodies during firing, a mineralogical study of the different compositions was performed. As observed in the Figure 3, the patterns do not reveal specific reactivity between RHA and the clays used (there are not present neo formation phases), confirming its inert function.

Besides, is possible to observe the peaks of cristobalite and trydimite characteristic from the presence of RHA in the mixes, and their intensity increases with the increases of RHA percentage. This phenomena is in agreement with the literature where was found the development of cristobalite and trydimite when RHA is undergone at thermal treatment.[23].

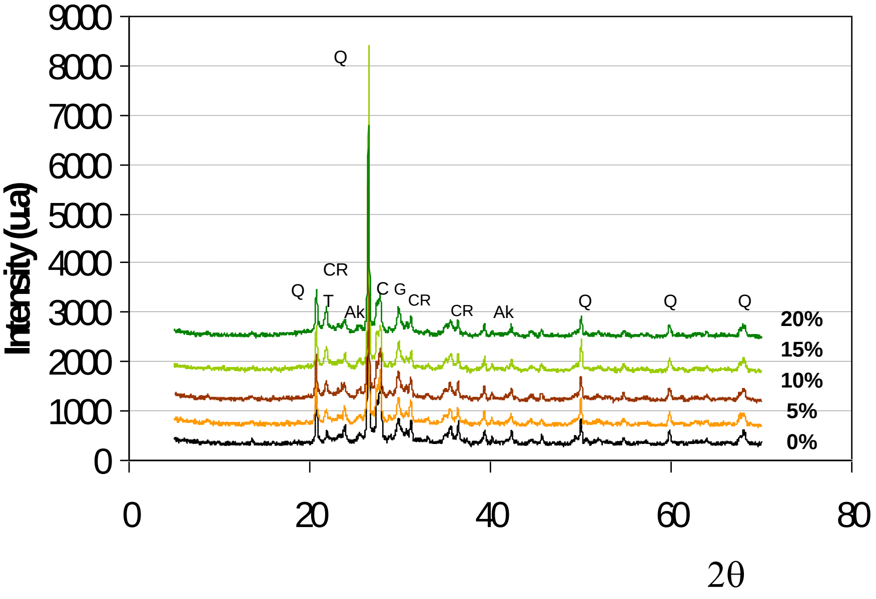
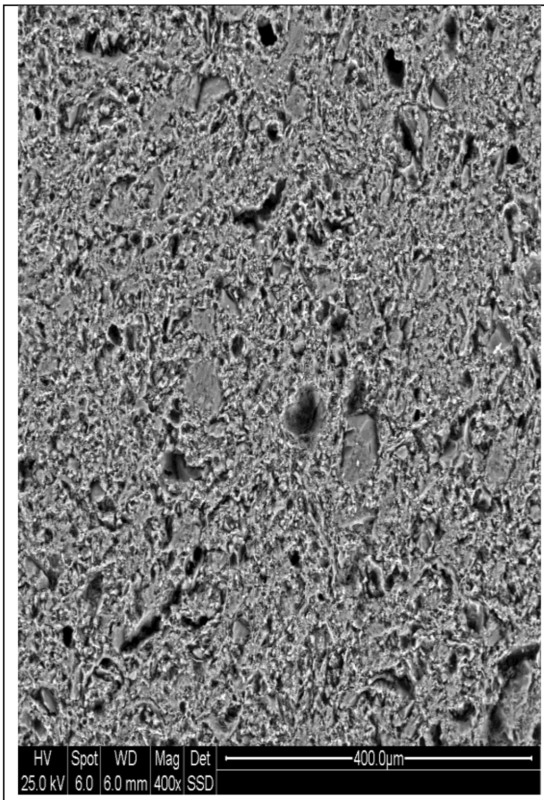
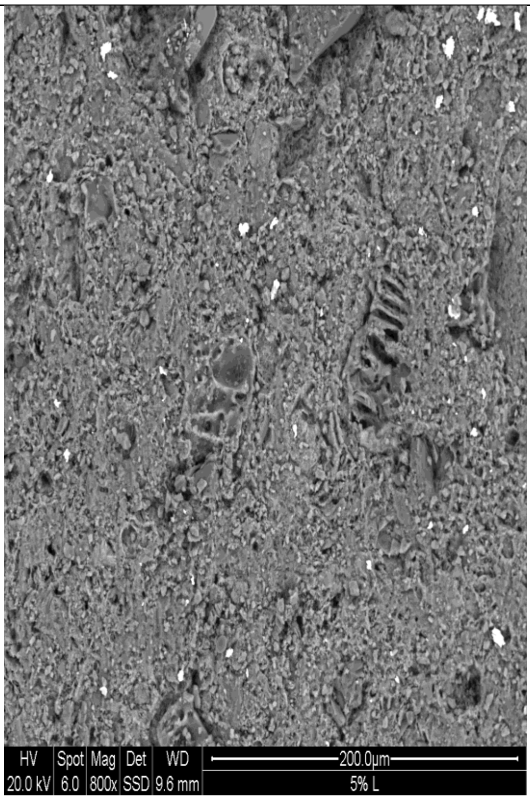


Fig.3 RXD analysis of brick samples fired in industrial cycle containing: 0-20 wt% of RHA (Q=quartz; CR=cristobalite; T=trydimite; C=calcite; Ak=akermanite; G=ghelenite)

Microstructural analysis by SEM/EDX on fired brick samples containing RHA compared with the standard one were reported in Figure 4. The reference brick sample highlights the typical ceramic brick matrix composed by Ca-Mg silico-alluminates, Ca-Mg silicate (diopside) and quartz grains unreacted during firing (Fig.4a). These findings are in agreement with the crystalline phases identified in XRD spectra, also confirmed by EDX analysis. From the cross section micrographs of samples containing 0, 5, 10 and 20%wt RHA it is possible to note that the ceramic matrix and composition are similar to the reference, but there is an evident presence of close porosity that increases with the RHA content (Fig.4b, c, d) . Besides, with SEM/EDX analysis it was possible verifiy the evolution of the agro-waste after firing. The microphotographs show zones with the morphology of RHA (same skeletons) embedded into the ceramic matrix. These cavities are empty where a part of the original ash was replacement by an inorganic compound rich in Si-composition, confirming the combustion of the organic component during firing (Fig.4b, c, d).





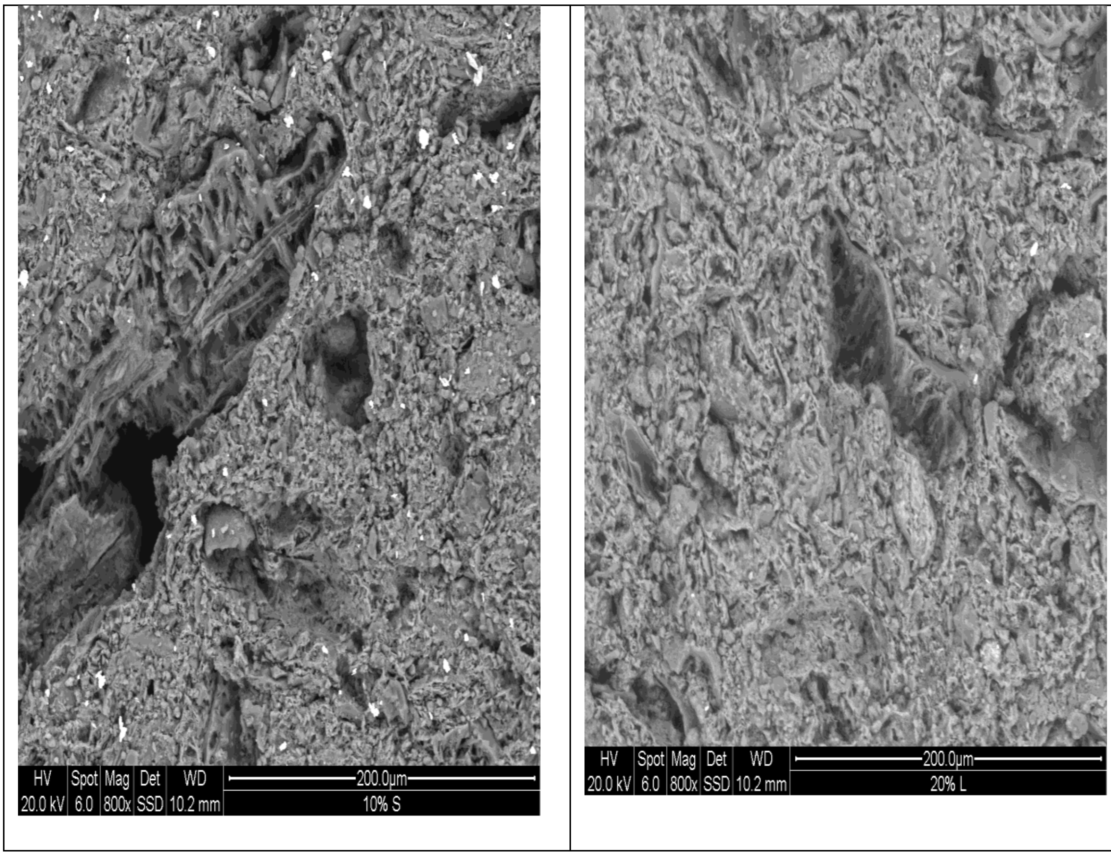


Fig. 4- cross section SEM micrographs of the different brick samples fired in industrial cycle containing: a) 0%; b) 5%; c) 10%; d) 20% of RHA.

Measurements according to UNI 8635-13 for discontinuous roofing products (slab blocks) were carried out to verify the flexural strength of specimens. For this brick category the values fluctuate between 12-20 MPa [22]. Figure 5 shows a decreasing trend of the flexural strength of specimens depending on the amount of rice husk ash into the body. Flexural strength is a parameter highly dependent on microstructure, porosity and mineralogical composition (percentage of components and their granulometry, amount of carbonates and inert components). This trend can then be traced back to the increased closed porosity in the material resulting from the increasing addition of RHA, as evidenced by microstructural analysis (Fig.4). According the method used, the industrial tolerance considerer suitable products with F.S above 10 MPa for use as a supporting masonry, therefore, only those containing 5 wt% ash may be employed in this field.

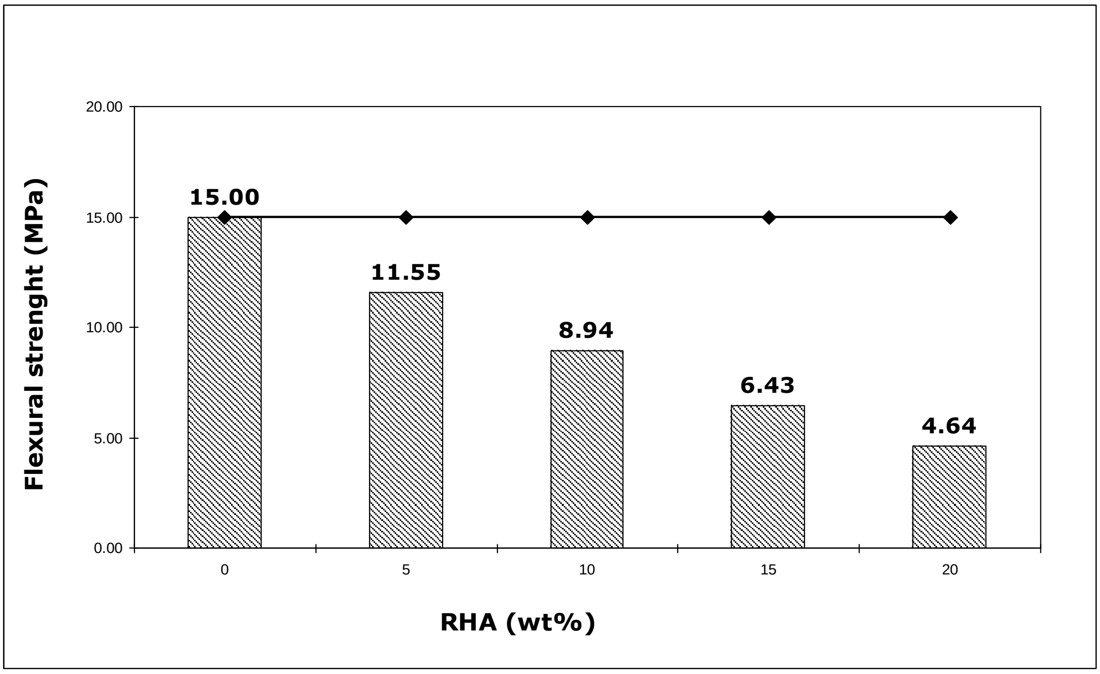


Fig.5- Flexural strength (MPa) for brick samples after firing step as a function of RHA content

Conclusions

This research has reveals that RHA, can become a raw material for brick products due to a high silicate content which have mainly plasticity reducing effect on the brick bodies. Contributing to reduce the linear shrinkage during drying and firing. This effect is in agreement with the XRD spectra confirming that RHA did not interact with the clays in the solid-state reactions during firing. there are not observed neo formation crystalline phases. Besides, the carbon unburned content in the RHA contributes to increase the final porosity of the bricks indicating this agro-waste as pore forming component to obtain light weight clay bricks to use as ceiling materials.

With substitutions up to 5 wt% of into the bricks bodies, the main properties tested were in accordance to the recommended values for roofing bricks. Bricks containing higher amounts of RHA could be used in light weighted faced load bearing walls where moderate strengths and penetration protection (porosity/permeability) are required.

References

[1] Koteswara, R., Pranav, D.: Stabilization of expansive soil with rice husk ash, lime and gypsum- an experimental study. Int. Journal of Engineering Science and Technology (IJEST), 3(11) 8076-85 (2011)

[2] Bronzeoak Ltd., 3 MWe Rice Husk Power plants in Indonesia: a Feasibility Study. Internal Report, Indonesia (2001)

[3] Kumar, A., Kalyani M., Kumar D. and Parkash O.: Properties and Industrial Applications of Rice husk: A review International Journal of Emerging Technology and Advanced Engineering Website: www.ijetae.com. ISSN, 2(10) 2250-2459 (2012).

[4] Della V P, Kuhn I, Hotza D.: Rice husk ash as an alternate source for active silica production [J], Materials Letters, 57(4) 818-821 (2002)

[5] Antiohos, S.K., Tsimas S.: Rice husk ash (RHA) effectiveness in cement and concrete as a function of reactive silica and fineness, Cement and Concrete Research 61–62, 20–27 (2014)

[6] Chandrasekar, S., Satyanarayana, K. G and Raghavan P.N. : Processing, Properties and Applications of Reactive Silica from Rice Husk-overview, J. Materials Science, 38, 3159-3165 (2003)

[7] Prasat,C.S., Maiti, K.N., and Venugopa, R.: Effect of the substitution of quartz by rice husk ash and silica fume on the properties of whiteware compositions, J. Ceram. Int., 29(8), 907-914 (2003)

[8] Naskar, M.K., Chatterjee, M.: A novel process for the synthesis of lithium aluminum silicate powders from rice husk ash and other water-based precursor materials, Mat. Letters, 59, 998-1003 (2005)

[9] Naskar, M.K., Chatterjee, M.: A novel process for the synthesis of cordierite ($Mg_2Al_4Si_5O_{18}$) powders from rice husk ash and other sources of silica and their comparative study, J. Euro. Ceram. Soc., 24, 3499-3508 (2004)

[10] Bondioli, F., Barbieri L., Ferrari, A.M., Manfredini, T. : Characterization of Rice Husk Ash and Its Recycling as Quartz Substitute for the Production of Ceramic Glazes, J Am Ceram Soc, 93(1), 121-126 (2010)

[11] Martın M.I., Andreola, F., Barbieri, L., Bondioli F., Ferrari, A.M., Lancellotti I., Ma.Rincón, , J., Romero M.:,Crystallisation and microstructure of nepheline–forsterite glass-ceramics", Ceramic International, 39(3) 2955–2966 (2013)

[12] Andreola, F., Martín, M.I., Ferrari, A.M., Lancellotti, I., Bondioli F., Rincón, J.Ma., Romero M., Barbieri L.:Technological properties of glass-ceramic tiles obtained using rice husk ash as silica precursor, Ceramics Journal, 39(5) 5427–5435 (2013)

[13] Bondioli F., Andreola, F., Barbieri, L., Manfredini, T., Ferrari, A.M.:Effect of Rice Husk Ash (RHA) in the Synthesis of (Pr,Zr)SiO_4 Ceramic Pigment, J. Euro. Ceram. Soc., 27, 3483-3488 (2007)

[14] Dondi, M., Fabbri, B.: The production of bricks in Italy (La produzione del laterizio in Italia), Faenza Ed., (1995) in Italian language

[15] Dondi, M., Fabbri, B., Marsigli M.: Industrial recycling of an urban wastes in brick production - A review, Tile&Brick Int., 13(3), 218-225 (1997)

[16] Hossain, T., Kumar, S., Sarker, Basak, B.C.: Utilization potential of rice husk ash as a construction material in rural areas, Journal of Civil Engineering (IEB), 39 (2) 175-188 (2011)

[17] Barbieri, L., Andreola, F., Lancellotti, I., Taurino, R.: Management of agricultural biomass wastes: Preliminary study on characterization and valorisation in clay matrix bricks, Waste Management, 33 (11), 2307-2315 (2013)

[18] Ibrahim D.M.: Crystallite growth of rice husk ash silica, Thermochimica Acta, 45, 79-85 (1981)

[19] Ibrahim, D.M., El-Hemaly, S.A., Abdel-Kerim, F.M.: Study of rice husk ash silica by infrared spectroscopy, Thermochimica Acta, 37, 307-314 (1980)

[20] Floerke O.W.: The crystalline forms of SiO_2 and their transformation behavior, Ber. Deut. Keram. Ges., 38(3), 89 (1961)

[21] Genieva, S.D., Turmanova, S.C., Dimitrova, A.S., Vlaev, L.T: Characterization of RHA and products of its thermal degradation air or nitrogen atmosphere, J. of Thermal analysis and Calorimetry, 93 (2), 387-396 (2011)

[22] Fabbri, B. Dondi, M.: Characteristic and defects of bricks, Ed. Faenza (1995) in italian language

[23]. Shinohara, Y., Kohyama, N.: Quantitative analysis of trydimite and cristobalite cristallized in rice husk ash by heating, Industrial Health, 42, 277-285 (2004)

Figure Captions

Fig.1 Linear shrinkage (LS%) for brick samples after drying step as a function of RHA content

Fig.2 Naphta absorption (NA%) for brick samples after drying step as a function of RHA content

Fig.3 RXD analysis of brick samples fired in industrial cycle containing: 0-20 wt% of RHA (Q=quartz; CR=cristobalite; T=trydimite; C=calcite; Ak=akermanite; G=ghelenite)

Fig. 4-Cross section SEM micrographs of the different brick samples fired in industrial cycle containing: a) 0%; b) 5%; c) 10%; d) 20% of RHA.

Fig.5 Flexural strength (MPa) for brick samples after firing in industrial cycle as a function of RHA content