POSTER Nº24

INFLUENCE OF CLAYEY MATERIAL ON THE SINTERING BEHAVIOUR OF CERAMICS CONTAINING PAPER SLUDGE AND GLASS CULLET

G. Tonello[1*], E. Furlani[1], E. Aneggi[1], D. Minichelli[1], E. Lucchini[2], S. Bruckner[1] and S. Maschio[1]

[1]Università di Udine, Dipartimento di Scienze e Tecnologie Chimiche
Via del Cotonificio 108, 33100 Udine-Italy
[2]Università di Trieste, Dipartimento di Ingegneria dei Materiali e delle Risorse Naturali
Via A. Valerio 2, 34127-Trieste-Italy

Abstract
The sintering behaviour of several ceramics prepared using a previously selected mixture of incinerated paper mill sludge and glass cullet which was blended with 10, 20, 30 and 40 % wt of some natural clayey materials has been studied. Three natural commercial product were used: a red clay, a yellow clay and a kaolin. Mixtures of powders were blended by wet attrition milling, dried, sieved, pressed into specimens and then fired for 1 h at temperatures ranging from 1040 to 1140°C. The resulting materials were characterized by water absorption, shrinkage, hardness, bending rupture strength, crystallographic composition and microstructure. It was observed that all the materials containing kaolin reach good properties when fired at temperature greater than 1060 °C, the quantity of kaolin have little influence on their sintering behaviour. Conversely the optimal sintering temperature, and consequently the best physico-mechanical behaviour of materials prepared using red or yellow clay was found above 1080 °C and depends of their specific composition being affected by the amount of added clay. In addition, the blend containing 40 % wt of yellow clay can be fired into compact ceramic specimens at low temperature. A very low shrinkage coupled with high water absorption (> 20 %) was observed only for temperatures lower than 900 °C. The unespected event is explained by the formation of a low eutectic at 840°C.

Keywords: paper mill sludge; glass cullet; clayey materials; sintering;

Introduction

In a previous paper (1) we described production and characterization of some sintered ceramics obtained using mixtures of paper sludge (PS) and glass cullet (GC) from recycled colorless bottles; we demonstrated that materials containing 60 wt% of PS and 40 wt% of GC have good physico-mechanical properties independently of the type of PS used. Conversely, their shrinkage exceeds the limits established by the standards for tiles production. On the progress of that research, we have reported the results obtained with materials prepared by mixing the above mixture with increasing amounts of a natural red clay. It was demonstrated that the addition of 30 wt % of a natural red clay enables fast firing production of unglazed tiles. The present paper reports on production procedure and characteristics of fired ceramics containing the same blend PS/GC=60/40 added with 10, 20, 30 and 40 wt % of three different natural raw materials namely: a red quartzitic clay (RC), a yellow quartzitic clay (YC) and a high grade kaolin (K) in order to evaluate the influence of their chemical composition on the properties of the resulting fired materials which were characterized by shrinkage, water absorption and X-ray diffraction. The aim of the work is to demonstrate that the blend 60 wt % of PS and 40 wt % of GC, furtherly mixed with adequate amounts of natural raw materials, could be used in the production process of tiles. In addition, the target can be achieved by the use of different materials, the specific quantity being function of their chemical composition.

Materials and Methods

Paper sludge (PS) from recycled paper was first oven-dried at 150°C for 24 h and then incinerated at 850 °C for 2 h; the resulting material, ground to coarse powder was mixed with glass cullet (GC) from exhausted, Hg free, neon lamps. Natural clays used to balance the mixtures were: a red quartzitic clay (named RC), a yellow quartzitic clay (named YC) and a high grade Kaolin (K). The composition of the above materials, obtained by a Spectro Mass 2000 Induced Coupled Plasma (ICP) mass spectrometer is reported in table 1.

Component	SiO_2	Al_2O_3	CaO	MgO	B_2O_3	Na_2O	K_2O	Fe_2O_3	TiO_2	P_2O_5	PbO	Undeterm	LOI
GC	63.40	6.42	3.66	1.03	11.36	5.44	1.65	0.81	1.10	2.01	0.71	1.98	0.28
PS	23.01	17.40	18.48	15.99	<0.01	2.95	1.83	6.70	2.45	4.91	1.05	0.99	2.01
RC	58.34	18.16	3.15	2.00	0.49	1.27	2.83	7.64	1.21	1.45	<0.01	1.54	9.89
YC	59.48	17.46	4.07	2.21	0.21	2.39	2.22	4.72	0.87	1.68	<0.01	1.55	11.2
K	49.8	39.1	0.59	0.49	<0.01	1.08	1.45	0.34	0.51	1.28	<0.01	2.29	12.3

Tab. 1: Composition (wt %) and LOI (%) of Hg free glass cullet (GC), incinerated paper sludge (PS), red clay (RC), yellow clay (YC) and that of Kaolin (K) used as starting materials

Table 2 displays composition and symbolic names of the samples prepared. Blends (70 g of powder) were homogenized by ball milling for 24 h. Slurries were then dried in an oven for 24 h at 80°C.

Material name	RC1	RC2	RC3	RC4	YC1	YC2	YC3	YC4	K1	K2	K3	K4
Clay Quantity [wt %]	10	20	30	40	10	20	30	40	10	20	30	40
Incinerated PS [wt %]	54	48	42	36	54	48	42	36	54	48	42	36
Free GC [wt %]	36	32	28	24	36	32	28	24	36	32	28	24

Tab. 2: Composition of the samples prepared

After milling, the powders particle size distribution was evaluated using a Horiba LA950 laser scattering particle size distribution analyzer. PSD curves are represented with logarithmic abscissa. Dried powders were sieved through a 200 μm sieve and uniaxially pressed at 100 MPa into parallelepiped specimens (5x5x50 mm^3) for shrinkage and water absorption measurements. Sintering experiments were performed in air, by an electric muffle, at several temperatures in the range 1040-1140 °C with intervals of 20 °C using heating and cooling rates of 20 °C/min and a D-well time of 1h. Shrinkage on firing was evaluated, by a calliper, along the longest samples dimension (50 mm that of green specimens) using the ratio $(h_0-h_1)/h_0$ (subscripts 0 and 1 refer to the sample dimensions before and after the sintering).

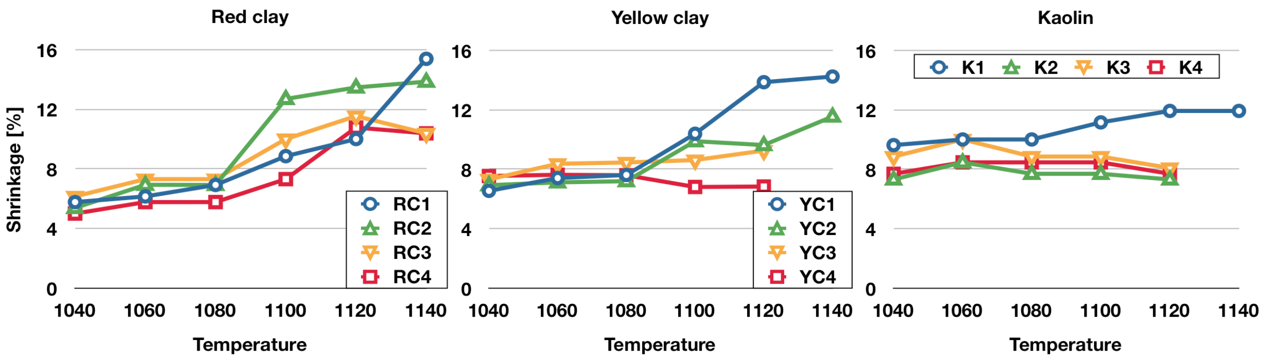

Fig. 1: Shrinkage of the samples prepared

Water absorption was determined following the norm EN99; in line with this norm, sintered samples were first weighed in air (W_1), then placed in a covered beaker and water boiled for 2 h. After boiling, samples were cooled in water to room temperature, dried with a cloth and weighed again (W_2). Water absorption was evaluated using the formula: $W (\%) = [(W_2-W_1) / W_1]\ 100$.

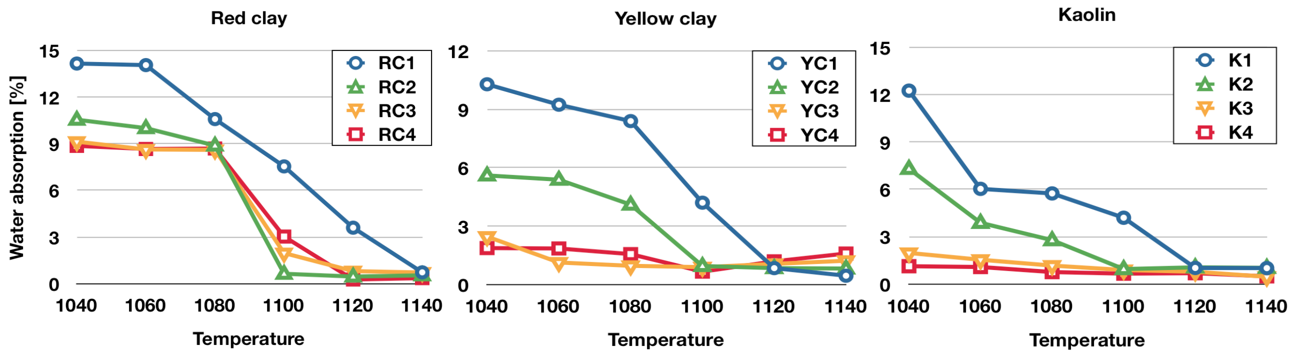

Fig. 3: Water absorption of the samples prepared

Crystal phases of the starting components and those of the fired materials were identified by X-ray diffraction (XRD) analysis which was carried out on a Panalytical X'pert Pro Detector X'celerator; monochromated CuKα_1 radiation (40 kV , 40 mA) was used. The presents of quartz, nontronite, halloysite and kaolinite were identified in the red clay whereas only silica and kaolinite were detected in the yellow clay. Kaolin mainly contains kaolinite togheter with a small quantity of quartz. Incenerated PS contains a great quantity of calcium carbonate and small amounts of illite-montmorillonite and coesite.
Samples prepared using the red clay and fired at 1100°, showed samples the presence of akermanite-gehlenite, wollastonite and augite. Same phases where identified also on samples containing the yellow clay. Conversely specimens containing kaolin displayed the presence of wollastonite, diopside and akermanite.
The above phases were revealed independently of materials composition. The presence of 10 or 40 %wt of clay or kaolin only modifies the relative fraction of a single phase.

Conclusions

Water absorption, directly related to the open porosity, and linear shrinkage are physical parameters used for drawing the sintering curves which allow for optimization of firing cycles focused to obtain materials with good mechanical properties. It means that small differences of sintering temperature, always possible using industrial fast firing cycles or of chemical composition of the used waste materials must not lead to fired products with variable properties. It follows that it is necessary to formulate materials that exhibit little oscillations of shrinkage and water absorption with changing the top sintering temperature. It can be observed that materials containing 30 or 40 wt % of YC, RC or kaolin are in line with the above request. Nevertheless also the other compositions (namely 10 and 20 wt %) could lead to mixtures of powders suitable for the industrial production of tiles, but the properties of the resulting product could suffer of performances variability. The use of high grade expensive raw materials (namely Kaolin) in spite of a Fe rich clay not lead to great advantages in terms of water absorption or shrinkage.
Concluding the above investigation, it can be stated that the addition of 30% wt of RC, YC and K to the original PS/GC (60/40) mixture, leads to powders composition that could be suitable for the industrial production of tiles. With such formulations, final products should also tolerate the unavoidable variability of the waste which shall be reflected in higher or lower optimal sintering temperature of the materials. On the other hand, if lower quantities of natural clayey materials are added, the properties of the corresponding materials are greatly affected by small variations of chemical compositions or sintering temperature and therefore the industrial production of tiles could be compromised.

Acknowledgment

The Italian region Friuli Venezia Giulia is gratefully acknowledged for financial support.

References

Asquini, L., Furlani, E., Bruckner, S., Maschio, S., 2008. Production and characterization of sintered ceramics from paper mill sludge and glass cullet. Chemosphere,71, 83-89