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Abstract: Preliminary results on the production of new ceramic bricks by microwave-assisted sintering process employing MSWI bottom ashes are reported.

Microwave heating technique was compared with a conventional thermal treatment with the aims to: (1) study the influence of heat treatment method on crystallization behavior and microstructure of obtained samples; (2) define the crystallization evolution in microwave field; (3) gain an insight into the physical properties of the new samples.

Higher crystallinity and new crystal phases were observed in the samples prepared by microwave heating, where precipitation of new sodium rich crystal phases was observed, together with quartz and anorthite, formed in conventionally prepared samples.

The possibility to obtain novel bricks with huge waste amount, in a very short thermal cycle and at relatively low temperatures was demonstrated with significant reductions in the energy demand for their production. Finally, the samples obtained by microwave-assisted sintering are characterized by improved mechanical properties.

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Dear Editor

We would like to submit our paper entitled "New ceramic materials from MSWI bottom ash obtained by an innovative microwave-assisted sintering process" by R. Taurino, R. Rosa, E. Karamanova, L. Barbieri, S. Atanasova-Vladimirova, G. Avdeev, C. Leonelli and myself for publication in the "Journal of the European Ceramic Society".

Sincerely yours,

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Novel MSWA bricks, obtained with low cost microwave heat-treatment, were compared with conventionally treated samples. The results elucidate higher crystallinity, formation of new crystal phases and improved exploitation properties.

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3 **New ceramic materials from MSWI bottom ash obtained by an innovative**
4 **microwave-assisted sintering process**
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Abstract

Preliminary results on the production of new ceramic bricks by an innovative microwave-assisted sintering process employing MSWI bottom ashes are reported.

Microwave heating technique was compared with a conventional thermal treatment with the aims to: (1) study the influence of heat treatment method on the crystallization behavior and on the microstructure of obtained samples; (2) define the crystallization evolution in microwave field; (3) gain an insight into the physical properties of the new samples.

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The possibility to obtain novel bricks with huge waste amount, in a very short thermal cycle and at relatively low temperatures was demonstrated with significant reductions in the energy demand for their production.

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Keywords: bricks, MSW, sintering process, microwave.

Introduction

Recently, the predominant industrial waste treatments have been solidification and thermal processes, encouraging alternatives to land disposal and to manufacturing processes requiring extensive energy consumption. Concurrently, more efficient resource recovery alternatives should be studied. One of the main waste that can be considered as new raw material for ceramic and building sector is the bottom ash produced during the incineration of Municipal Solid Waste (MSW).

Among the methods for the valorization of bottom ash, the preparation of glass-ceramics, ceramics and glasses seem to be promising for converting MSWI (municipal solid waste incineration) bottom ash into novel materials that possess attractive mechanical and chemical properties¹⁻⁴

Particularly, several studies employing MSWI ash were carried out in order to evaluate the chemical durability of the vitrified products, the crystallization behavior of the parent glasses, the structure and properties of bulk glass-ceramics as well as the possibility to obtain different sintered ceramics and glass-ceramics by conventional heating technologies. Thermal treatment, such as sintering, has been proposed to convert MSWI bottom ash into ceramic-type materials¹⁻⁴. In

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addition to the many advantages of these eco-friendly new materials, a novel and innovative technology could be used to save energy and to improve the sintering processes. In this latter perspective, the use of microwaves represents an alternative sintering strategy to manufacture ceramic materials, with several potential benefits.

In particular, this study investigated the feasibility to combine clay and MSWI bottom ash in the production of bricks with properties comparable to those of conventionally made bricks. Publications, mostly in the form of patents, exist on this topic, mainly discussing methods of microwave drying of bricks⁵⁻⁹, nevertheless, no studies reported the microwave assisted sintering behaviour of bricks based on high amount of waste.

Since the MSWI bottom ash is a poor receptor of microwave energy, a “hybrid microwave sintering” process was used in this study to achieve the temperature necessary for preparing ceramic materials. In particular, a specific experimental set-up with a peculiar geometry was designed for preparing samples starting from an “end of waste” derived from the industrial processing of MSWI bottom ash.

Furthermore, the aim this paper was to study the influence of heat treatment schedule on the crystallization behavior and microstructure of the microwave-prepared ceramic materials. In addition, investigation was performed to gain an insight into the physical properties of the ceramics prepared by microwaves in comparison to those obtained by conventional heating^{1,10}, exploiting a conventional process

2. Experimental

2.1 Materials

The raw material used in this study is an artificial silica-based aggregate, rich in Ca, Al and Fe, with controlled grain size, derived from a MSWI bottom ash treatment plant in the North of Italy. The applied treatment mainly consists of three steps: (i) 3 months ageing of the as received bottom ash coming from several incinerators mainly in the North-Centre of Italy leading to uptake of CO₂ from the air, drying of excess water and partial oxidation; (ii) mill grinding to obtain two fractions with particle size of 0–2 mm and 2–8 mm; (iii) separation of metallic iron and aluminium by means of magnetic and eddy current systems.

The separated metals, appropriate for recycling, are ~ 8 wt% (7% Fe and 1% Al) of the total amount while the bottom ash recovered as secondary raw material (SRM) is ~80 wt%; the remaining ~10 wt% is water evaporated during the ageing treatment and unburnt organic part of the waste.

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In this study the fraction between 2–8 mm, which is the predominant part of the aggregate obtained, was used. The bottom ash appeared as a gray grainy powder. Its main chemical composition is given in Table 1. After 2 hours of heat-treatment at 600°C to definitively burn the organic residues, the bottom ash with the other raw materials were milled in a ball mill until a homogeneous particle size was obtained.

Other raw materials, used for the preparation of the ceramics batches, were industrial kaolin (K), Na₂CO₃ and corundum powder (Al₂O₃) (below 54 microns). The chemical composition of MSWI bottom ash (BA) and kaolin were examined by X-ray fluorescence spectroscopy (ARL ADVANT'XP X-ray fluorescence spectrometer) and the results are shown in Table 1.

2.2 Preparation of ceramic green bodies

Three different ceramic formulations were studied (Table 2). The ceramic batch (labelled C-b) was obtained by mixing 55 wt% of heat-treated BA and 45 wt% of kaolin (K) with 7 wt% of water. In the other two ceramics (labelled C-b-Al and C-b-Na) 5% of BA was substituted by fine (below 54 microns) corundum powder and Na₂CO₃, respectively.

Samples of 50 x 5 x 4 mm³ were prepared by cold isostatically pressing the above mentioned powders at 40 MPa with a dwell time of 30 seconds. These samples have been dried overnight before firing. The average green density was 1.8 ± 0.3 g/cm³ (calculated on the basis of the weight of the ignited sample). These samples were used for dilatometric studies of the sintering process.

2.3 Sintering of ceramic bodies

Conventional heating

In the conventional process, samples were heated in an optical dilatometry (Expert System Solutions, Misura HSML ODLT 1400) at 30°C/min up to 1000°C and held to this temperature for 5 min. The holding temperature and time were selected, using preliminary DTA and dilatometric results¹⁰.

Microwave hybrid heating experimental set-up

The microwave sintering experiments were carried out in a multimode microwave cavity operating at the frequency of 2.45 GHz (CEM MAS 7000-CEM, USA), which was equipped with a circular mode stirrer placed on the upper wall, in order to improve the heating homogeneity. The magnetron generator had a nominal maximum power of 950 W. Microwave power was set to its maximum in all the experiments. Surface temperature measurements were performed by means of a K-type thermocouple. The arrangement of the sample inside the microwave cavity is schematically

1 depicted in Fig. 1. As clearly visible, both a microwave-absorbing material layer (SiC) and a
2 microwave-transparent material layer (Al₂O₃) were used, the latter being positioned on the top
3 surface in order to avoid the reflection loss of the incident wave on the front surface between the
4 reactor and air. The MW absorbing layer is able to absorb the incident wave transmitted through the
5 MW transparent layer and consequently to generate heat. In terms of optimizing the arrangement of
6 the samples during microwave assisted sintering experiment, the dielectric properties of the selected
7 materials and the thickness of each layer are the most important parameters to control.

8 In this framework, several preliminary experiments allowed the selection of 7 mm and 13 mm as
9 the optimal thicknesses for the transparent and the absorbing layers respectively for sample with
10 size of 13 mm and 3.5 mm as diameter and height, respectively.

11 Sintering experiments were conducted at three different maximum temperatures (800-900-1000°C).
12 In all cases an isothermal holding of 5 min was made.

23 *2.4 Characterization of samples*

24 The thermal behavior of the parent batches was estimated by differential thermal analysis, using
25 Netzsch STA 409 apparatus. The applied heating rate was 20°C min⁻¹ up to 1250°C. To study the
26 sintering process, bar samples (50mm x 5 mm x 4 mm) were fired in an optical dilatometer (Expert
27 System Solutions, Misura HSML ODLT 1400).

28 The chemical analysis was performed with XRF spectrometry (ARL ADVANT'XP X-ray
29 fluorescence spectrometer). Argon was used as the inert gas.

30 Physical characteristics of linear shrinkage (LS), water absorption (WA) and measurement of
31 weight loss of ignition (WLOI%) were performed according to ISO 10545-3¹². The apparent
32 density, ρ_a , of the sintered samples was estimated by precise measurement of dimensions and
33 weight of the sample, while the skeleton, ρ_s , and absolute, ρ_{as} , densities were determined by Ar
34 pycnometer (AccuPyc 1330, Micromeritic). The results were used to evaluate total P_T , closed P_C ,
35 and open P_O porosity according to the following equations 1-3:

$$36 P_T = 100 \times (\rho_{as} - \rho_a) / \rho_{as} \quad (1)$$

$$37 P_C = 100 \times (\rho_{as} - \rho_s) / \rho_{as} \quad (2)$$

$$38 P_O = 100 \times (\rho_s - \rho_a) / \rho_{as} \quad (3)$$

39 The experimental errors in the evaluations ρ_a , ρ_s , and ρ_{as} , were ± 0.03 , ± 0.01 and ± 0.01 g/cm³
40 leading to mistakes of at about 2% for the total and open porosity and at about 1 % for closed
41 porosity, respectively. The experimental errors for LS and WA were ± 0.5 % and 1 %, respectively.

1 XRD analysis was conducted to identify the crystalline phases obtained in conventional and
2 microwave treatment. The X-ray diffraction (XRD) pattern was recorded using a conventional
3 Bragg-Brentano powder diffractometer (Empyrcam, Panalytical) with a Ni-filtered Cu-K α radiation
4 using bracket holder. The scanning was done in the range of 2 θ angle from 5° to 70° with a step
5 size of 0.02°. The obtained peaks are compared with ICDD in order to identify the crystalline
6 phases.
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10 Microstructural and chemical analyses were carried out using Scanning Electron Microscopy, SEM
11 (JEOL, JSM 6390) and energy dispersive x-ray spectroscopy (INCA, Oxford Instruments). The
12 accelerating voltage was 20 kV, and the current I ~65 μ A. The analyses were made using fractured
13 samples, coated with Au.
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18 Fired products were characterized for mechanical properties like compressive strengths by an
19 electro-mechanical Instron 3300 (Instron, MA, USA).
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22 23 24 **Results and discussion**

25 26 *Thermal behavior*

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28 Fig. 2 shows the DTA plots of C-b, C-b-Al and C-b-Na. The endo-effects related to kaolinite
29 deoxydrilation are identical for all compositions (endothermic events around 540-560°C). The
30 crystallization exo-peaks due to reactions between the formed meta-kaolin and the phases from BA
31 and the first melting endo-effect for C-b-Al and C-b are detected at 985-980°C and 1160–1200°C,
32 respectively, for both samples. It can be concluded that the corundum powder does not influence the
33 crystalline phase formation and their subsequent melting, so that it can be considered as an inert
34 addition.
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38 On the contrary, the addition of Na₂O significantly decreases both temperatures of phase formation
39 and melting (approximately of 120 and 90°C, respectively), which highlights its obvious fluxing
40 effect.
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44 The sintering behavior of studied samples in the range 20–1000°C was evaluated by optical
45 dilatometer and the obtained results for the variations of linear shrinkages, as well as the used
46 temperature regime are plotted in Fig. 3.
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50 The densification curves show a shrinkage of about 0.3-0.5% at about 600°C due to the kaolinite
51 dehydration. Then, in C-b and C-b-Al samples the densification starts at about 900 °C and
52 practically ends after 3-4 min holding at 1000°C (i.e. after the formation of new phases according to
53 the DTA results). The reached shrinkage in C-b-Al is lower due to a reduced sintering rate (a
54 consequence of the addition of inert corundum powder).
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2 In C-b-Na samples, the densification starts at about 800 °C and finishes at about 950°C with a
3 shrinkage of about 2.5 %, which is similar to the C-b-Al one.
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5 *Physical and mechanical properties* 6

7 Table 3 shows the results of all density measurements of microwave and conventionally processed
8 samples, while Table 4 summarized the corresponding porosity values and the results for the linear
9 shrinkage (LS%), water absorption (WA%) and weight loss of ignition (WLOI).
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11 The differences in the absolute densities between C-b and C-b_{MW}, as well as between C-b-Al and C-
12 b-Al_{MW} might be attributed to a different crystallinity (i.e. higher is the crystallinity higher is ρ_{as}),
13 while the variations in C-b-Na indicate variation in the phase compositions due to the applied
14 method of heat-treatment.
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17 It can be noted that C-b-Na sample, treated with microwave heat-treatment at 1000°C, completely
18 melted inside the SiC “covering”, then the results are not reported in the table. It should be noted
19 that the same composition, treated by conventional heat-treatment, start to deform at about 1200°C
20 (i.e. at higher with 200°C temperature)¹⁰.
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23 The porosity evaluations in MW samples elucidate that the increasing of temperature decreases the
24 total porosity of 3-5 %, as well as that at higher temperatures some closed porosity is formed. At the
25 same time, in the C-b and C-b-Al samples, conventionally treated at 1000°C, the porosity remains
26 exclusively open, notwithstanding that the total porosity is similar to that of the corresponding MW
27 samples. Only in sample C-b-Na₁₀₀₀ some closed porosity was evidenced.
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30 The quality of a building brick can be measured by evaluation of its firing shrinkage and water
31 absorption (WA). A good quality brick can exhibit a linear LS lower than 8%, while according to
32 the criteria listed in CNS 382^{12,13}, a first class brick must have a WA value lower than 15%, a
33 second-class brick must have 15-19% water absorption and the third-class brick calls for WA lower
34 than 23%.
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37 Our results highlighted that all laboratory samples, sintered at 900 and 1000°C, categorically met
38 both criteria for a first class brick: indeed the linear shrinkage and the water absorption are below 4
39 % and 14%, respectively. In addition, because of the formation of closed porosity, WA values of C-
40 b_{1000MW} and C-b-Al_{1000MW} are lower than 10%, which is a particularly worth to note result.
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43 The weight loss for a normal clay brick usually is 15%^{12,13}. In the studied samples, due to the usage
44 of huge amount of pre-treated MSWI, WLOI results are significantly lower, which also can be
45 considered as an encouraging result.
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1 The most important engineering quality index for the building bricks is their compressive strength.
2 According to ASTM C-67¹⁴, the minimum required compressive strength of a paving brick
3 subjected to light traffic is 17.2-20.7 MPa¹⁵.
4

5 The compressive strength of samples obtained by conventional heat-treatment at 1000°C, as well as
6 of the samples obtained in microwave furnace at 900°C, were measured and compared. The results
7 are summarized in Fig. 4 and elucidate the all the obtained values (especially ones for C-b and C-b-
8 Al) significantly surpass the limit for the compressive strength.
9

10 Moreover, notwithstanding of the lower firing temperatures, the microwave heated samples at
11 900°C attained a high compressive strength of 60-65 MPa. This behavior is a consequence of the
12 difference in crystallinity and microstructure and will be highlighted in the next sections.
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20 *XRD analysis*

21 X-ray diffraction analysis (XRD) was carried out to identify the crystalline phases in both
22 conventional and microwave processed samples.
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24 For the conventional samples, sintered at 1000°C (Fig. 5), the major phases were quartz (SiO₂)
25 [JCPDF file 01-078-1252] and anorthite (CaAl₂Si₂O₈) [JCPDF file 00-002-0523], with traces of
26 albite (Na₂O.Al₂O₃.6SiO₂) [JCPDF file 01-083-1610] in C-b-Na and corundum [JCPDF file 01-
27 071-1124] in C-b-Al.
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33 The results for the samples obtained by microwave treatments, at 800, 900 and 1000 °C, are
34 summarised in Fig. 6. This data clearly highlight an enhanced crystallization and appearance of new
35 phases.
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39 The microwave-sintered samples C-b_{MW} (Fig. 6a) showed that at 800°C the main phases are quartz
40 and gehlenite deriving from the initial BA waste component, while at 900°C the amount of these
41 phases decreases due to formation of anorthite and a new calcium aluminium oxide phase
42 (CaAl₂O₄) [JCPDF file 00-034-0440]. This process of phase transformations continues also at
43 1000°C, resulting in the higher final crystallinity in comparison with sample C-b₁₀₀₀ (see Fig. 5).
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48 The phase formation of C-b-Al_{MW} samples shows similar behavior as the one in C-b_{MW} with an
49 expected occurrence of inert corundum appearance.
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51 In our previous studies with conventionally treated C-b and C-b-Al samples¹⁰ it was demonstrated
52 that at 900°C, in accordance with the DTA results shown in Fig. 2, an evident formation of anorthite
53 is not yet observed. This difference clearly highlights one of the widely recognized drawbacks of
54 microwaves-assisted processes, i.e. the difficulty of exact temperature measurement, with a firing
55 temperature under-estimated of about 100°C. At the same time a faster heating rate of the samples
56 was estimated, indicating that microwave hybrid heating is an energy efficient method to fire these
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1 novel ceramic formulations. The final advantage of the microwave assisted was an undoubted
2 increase in the bending strength values of all samples.

3 X-ray diffraction measurement of sample C-b-Na_{900MW}, shows (Fig. 6c) that together with the
4 formation of sodian anorthite solid solutions [JCPDF file 01-084-0750], high amount of nepheline
5 ((Na,K)AlSiO₄) [JCPDF file 01-083-2372] was also formed. This interesting behaviour might be
6 related to a local formation of a “transitory sodium rich liquid phase” with low viscosity and
7 subsequent crystallization.
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9 In fact, in a heterogeneous system, such as the used bottom ash, a mixture of crystalline and
10 amorphous components^{1,16,17} with different melting temperatures is present. Generally, in similar
11 batches the alkaline and alkaline earth oxides are the most reactive components, resulting in the
12 formation of an intergranular thin liquid phase involving mass transport phenomena and locally
13 wetting of the solid grains. Thus, the addition of “free Na₂O” as a fluxing agent accelerates the
14 “local” melting at lower temperatures and improves the low temperature sintering. In this study a
15 further acceleration of this reaction mechanism could be due to the microwave irradiation itself,
16 which is known to act via a volumetric heat transfer of energy from the electromagnetic wave to the
17 solid sample^{7,8}. The localized formation of the liquid phases enhances the mechanism of heat
18 transfer and accelerate the ions diffusion at the interface with the solid grains. This peculiarity will
19 be studied in details in a future research.
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33 *SEM analysis*

34 The structure of final C-b₁₀₀₀, C-b-Na₁₀₀₀ and C-b-Al₁₀₀₀ samples were studied in detail by SEM-
35 EDS and the results were already published and discussed¹⁰. These observations highlighted that the
36 surfaces and the fractures of specimens heat-treated at 1000°C in a traditional electric furnace are
37 similar and are characterized by an irregular structures and open porosity. Some closed porosity was
38 observed only in C-b-Na₁₀₀₀, which can be explained with its lower crystallinity. The main
39 crystalline phases are residual α -quartz and newly formed plagioclase (anorthite or anorthite-albite
40 solid solution). Residual gehlenite, some pyroxene, as well as little glass or ceramic debris and fine
41 corundum particles (in C-b-Al₁₀₀₀) were also observed.
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52 Typical images at low magnification of surface (C-b₁₀₀₀) and fracture (C-b-Al₁₀₀₀), showing a
53 ceramic body with a suitable degree of sintering for bricks production^{18,19} and typical open porosity,
54 are presented in Figs. 7-a and 7-b, respectively. In Fig. 7-c the formation of closed porosity in
55 sample C-b-Na₁₀₀₀ is elucidated.
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1 Fig. 8 demonstrates typical images of the main crystal phases in the samples (together with the
2 corresponding EDS spectra). In Figs. 8-a and 8-b non-reacted α -quartz and gehlenite are shown,
3 respectively, while Fig. 8-c reports a glass piece from the parent BA. The presence of these residual
4 phases might be explained with their relatively large sizes (more than 10-20 microns), which
5 hinders their dissolution and/or transformation. At the same time, Fig. 8-d elucidates a typical
6 anorthite crystal. The anorthite s.s. crystals formed after only 5 min at 1000°C were not yet well
7 shaped, with their hexagonal habit that was not clearly visible and the crystals size was in the range
8 3-6 microns.
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11 In a previous study performed on similar compositions¹ heat-treated at 1200-1260° C for 1 h, it was
12 demonstrated that, with the increasing of temperature, gehlenite totally disappeared and the amount
13 of quartz significantly decreased leading to an increasing of the anorthite phase percentage. At high
14 temperature the single anorthite crystals got a very regular hexagonal shape but no significant
15 increase in their crystal size was observed.
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18 The structures of samples obtained by microwave treatment at different temperatures were also
19 studied by SEM-EDS. It was clarified that at 800°C, in accordance with the density and XRD data,
20 the processes of densification and the phase formation remain in their initial stages. This is
21 demonstrated in Figs. 9-a and 9-b, which show a “loose” bulk structure of sample C-b_{800MW} and a
22 small (10-15 microns) non-dissolved quartz particle, respectively.
23

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25 The crystallographic and pycnometric results demonstrated that after microwave treatment at 900°C
26 the samples C-b-Al_{900MW} and C-b-_{900MW} showed porosity, phase composition and mechanical
27 properties, similar to the ones obtained at 1000°C in traditional furnace. The SEM observations
28 confirmed these data highlighting also similar structure and morphology. In Figs. 10-a and 10-b are
29 presented the top surface of C-b-Al_{900MW} and the fracture surface of C-b_{900MW}, while Figs. 10-c
30 elucidates the newly formed anorthite crystals. It is interesting to note that these anorthite crystals
31 have a significantly smaller size with respect to those formed in the sample obtained by traditional
32 heat-treatment. A lower size of the formed crystal phase in ceramics, obtained by microwave
33 sintering was observed also in other compositions where a fast and volumetric heating was reached
34 and a uniform nucleation rate was recorded ex-post²⁰⁻²¹
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37 The increasing of temperature in samples C-b-Al_{1000MW} and C-b_{900MW} did not lead to a notable
38 improvement of the densification. However, the amount of tiny anorthite crystals increased, which
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1 might be mainly related to a better dissolution of the quartz phase thanks to localized formation of
2 liquid phase as discussed above. Fig. 10-d highlights a large quartz grain, where the dissolution
3 process is in an advanced stage.
4

5 The formation of nepheline, imbedded in Si and Al rich zone of sample C-b-Na_{900MW}, is shown in
6 Fig. 11-a, while melted glassy drops from C-b-Na_{1000MW}, inside the SiC capsule, is presented in
7 Fig. 11-b.
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10 From scientific point of view, notwithstanding of the lower mechanical properties, the results
11 recorded for the C-b-Na_{MW} samples are the most intriguing. It was already noted that sample C-b-
12 Na_{1000MW} totally melted inside the SiC “capsule”, while the corresponding sample, C-b-Na₁₀₀₀,
13 melts at about 1200°C. At the same time, the XRD analysis of sample C-b-Na_{900MW} (see Fig.6-c)
14 demonstrated the new formation of a high amount of nepheline, (Na,K)AlSiO₄, which was totally
15 absent in the samples obtained in conventional heat-treatment.
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18 The presence of nepheline phase cannot be explained by the chemical composition of the new
19 ceramic formulation and by its position in QAPF (Quartz, Alkali feldspar, Plagioclase,
20 Feldspathoid) mineralogical phase diagram^{22,23}. This observation rather indicates that nepheline
21 formation is a result of “local” reactions caused by MW heat-treatment. Most probably, the
22 crystallization of nepheline is a result of reaction between the metakaolin (Al₂Si₂O₇) and free Na₂O.
23 The melting temperature of nepheline is relatively high (>1500°C), but this phase has very low
24 eutectic temperatures with albite and other phases, which partially might explain the melting of the
25 sample C-b-Na_{1000MW}. This phenomenon will be studied in near future.
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38 **Conclusions**

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40 The possibility to obtain new ceramics, based on high amount (up to 55 wt%) of pre-treated bottom
41 ash from municipal solid waste incinerators, using microwave heat-treatment was shown. Samples
42 with parameters (firing shrinkage, water absorption and compressive strength), corresponding to the
43 standards for traditional clay bricks were obtained in extremely short heat-treatment of 5 min a
44 temperature of 900°C. The volumetric heating, characteristic of microwave assisted processing, led
45 to uniform formation of new anorthitic crystals and, when Na carbonate was added, also nepheline
46 was found. The experimental set-up used for microwave hybrid heating contributed to a shift in
47 temperature measurements of about 100°C lower than real temperature, nevertheless peculiar
48 features were recorded with XRD, SEM and EDS observations.
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1 The efficient heat transfer phenomenon due to microwave irradiation coupled with the use of MSWI
2 bottom ash contributed to the manufacture of a particularly environment-friendly ceramic material
3 characterized by energy and natural materials savings.
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8 **Acknowledgments**

9

10 The authors are grateful for the financial support deriving from the program of mobility, scientific
11 and cultural collaboration of the University of Modena and Reggio Emilia with the Institute of
12 Chemical Physics of the Bulgarian Academy of Sciences (Sofia, Bulgaria) – 2012-2013.
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Table 1. Chemical composition (wt%) of two raw materials used (K = kaolin; BA = MSWI bottom ash).

OXIDE	K	BA
SiO ₂	52.5	46.8
TiO ₂	0.5	0.7
Al ₂ O ₃	33.3	9.8
Fe ₂ O ₃	0.6	4.3
CaO	0.2	18.6
MgO	0.4	2.9
K ₂ O	0.9	1.0
Na ₂ O	0.1	4.5
B ₂ O ₃	0.0	0.6
MnO	0.0	0.3
ZnO	0.0	0.3
PbO	0.0	0.3
SO ₃	0.0	1.0
P ₂ O ₃	0.0	1.2
CuO	0.0	0.5

Table 2. Chemical composition (wt%) of the studied ceramics

Oxide	C-b	C-b-Al	C-b-Na
SiO ₂	54.2	51.5	52.7
TiO ₂	0.7	0.7	0.7
Al ₂ O ₃	22.2	26.9	22.1
Fe ₂ O ₃	3.1	2.7	2.8
CaO	11.6	10.5	10.7
MgO	2.0	1.8	1.8
K ₂ O	1.0	1.0	1.0
Na ₂ O	2.8	2.6	5.9
B ₂ O ₃	0.4	0.3	0.3
MnO	0.2	0.2	0.2
ZnO	0.2	0.2	0.2
PbO	0.2	0.2	0.2
SO ₃	0.6	0.5	0.5
P ₂ O ₃	0.8	0.7	0.7
CuO	0.3	0.3	0.3

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Table 3. Apparent (ρ_a), skeleton (ρ_s) and absolute (ρ_{as}) densities of microwave and conventionally-processed samples.

Sample	Processing route	Temperature (°C)	ρ_a (g/cm³)	ρ_s (g/cm³)	ρ_{as} (g/cm³)
C-b₁₀₀₀	Conventional	1000	1.86	2.67	2.69
C-b_{1000MW}	Microwave	1000	1.92	2.61	2.73
C-b_{900MW}	Microwave	900	1.89	2.67	2.73
C-b_{800MW}	Microwave	800	1.80	2.72	2.73
C-b-Al₁₀₀₀	Conventional	1000	1.95	2.77	2.78
C-b-Al_{1000MW}	Microwave	1000	1.92	2.82	2.84
C-b-Al_{900MW}	Microwave	900	2.00	2.72	2.73
C-b-Al_{800MW}	Microwave	800	1.79	2.78	2.81
C-b-Na₁₀₀₀	Conventional	1000	1.92	2.62	2.74
C-b-Na_{1000MW}	Microwave	1000	-	-	-
C-b-Na_{900MW}	Microwave	900	1.82	2.66	2.69
C-b-Na_{800MW}	Microwave	800	1.72	2.70	2.76

Table 4. Total porosity (P_T), open porosity (P_o), closed porosity (P_c), linear shrinkage (LS%), water absorption (WA%) and weight loss of ignition (WLOI) of microwave and conventionally-processed samples.

Sample	Temperature (°C)	P_T (%)	P_o (%)	P_c (%)	WA (%)	LS (%)	WLOI (%)
C-b₁₀₀₀	1000	31	30	1	14	4	7.3
C-b_{1000MW}	1000	30	26	4	6	2.5	7.4
C-b_{900MW}	900	31	29	2	8	2.5	7.2
C-b_{800MW}	800	34	34	0	13	0.5	6.3
C-b-Al₁₀₀₀	1000	30	29	1	13	3.5	6.9
C-b-Al_{1000MW}	1000	32	30	2	10	3	8.3
C-b-Al_{900MW}	900	27	26	0	9	2	7.8
C-b-Al_{800MW}	800	36	35	1	13	0.5	7.1
C-b-Na₁₀₀₀	1000	30	26	4	12	3.5	10.6
C-b-Na_{900MW}	900	32	30	2	8	2.5	11.8
C-b-Na_{800MW}	800	36	34	2	12	2.0	10.4

Figures captions

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3 Figure 1. A scheme of the geometry adopted for the hybrid heating experiments within the
4 microwave furnace.

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6 Figure 2. Non-isothermal DTA results of C-b (dot line), C-b-Al (solid line) and C-b-Na (dash line)
7 compositions.
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10 Figure 3. Dilatometer results for compositions C-b, C-b-Al and C-b-Na at heat-treatment of
11 30°C/min heating rate, 5 minutes holding at 1000°C and free cooling.
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15 Figure 4. Compressive strength (σ_c) of the samples conventionally-processed at 1000°C and
16 microwave processed at 900°C.
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19 Figure 5. XRD spectra of C-b₁₀₀₀, C-b-Na₁₀₀₀ and C-b-Al₁₀₀₀ samples after conventional heating.
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21 Q: α -quartz [JCPDF file 01-078-1252], A: anorthite [JCPDF file 00-002-0523]; Co: corundum
22 [JCPDF file 01-071-1124]; Al: albite [JCPDF file 01-083-1610].
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26 Figure 6. XRD spectra of a) C-b, b) C-b-Al and c) C-b-Na samples treated by microwave . Q: α -
27 quartz [JCPDF file 01-082-0511], A: anorthite, sodian [JCPDF file 00-020-0528], Ca: calcium
28 aluminum oxide [JCPDF file 00-034-0440], N: nepheline [JCPDF file 00-019-1176], G: gehlenite
29 [JCPDF file 01-087-0968].
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33 Figure 7. SEM images of: a) C-b₁₀₀₀ sample surface, b) C-b-Al₁₀₀₀ sample fracture and c) closed pore
34 in C-b-Na₁₀₀₀ sample.
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37 Figure 8 SEM images and spectra of: a) quartz particle (Q) and Corundum (C) in C-b-Al₁₀₀₀ sample,
38 b) gehlenite (G) in C-b-Al₁₀₀₀ sample, c) glassy (g) debris in C-b-Na₁₀₀₀ and anorthite crystal (A) in C-
39 b₁₀₀₀.
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42 Figure 9. a) SEM image of C-b_{800MW} sample fracture and b) SEM image and EDS spectrum of
43 Quartz particle (Q) in C-b_{800MW} sample.
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46 Figure 10. SEM images of a) C-b-Al_{900MW} sample surface, b) C-b_{900MW} sample fracture, c) a
47 typical zona of tiny plagioclase crystals in C-b_{900MW} sample and d) quartz grain (Q) in stage of
48 dissolution in C-b_{1000MW} sample.
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51 Figure .11. a) SEM image and EDS spectrum of large (15-25 microns) nepheline structure in C-b-
52 Na_{900MW} sample and b) SEM image of “melted” part of sample C-b-Na_{1000MW}.
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Fig. 1

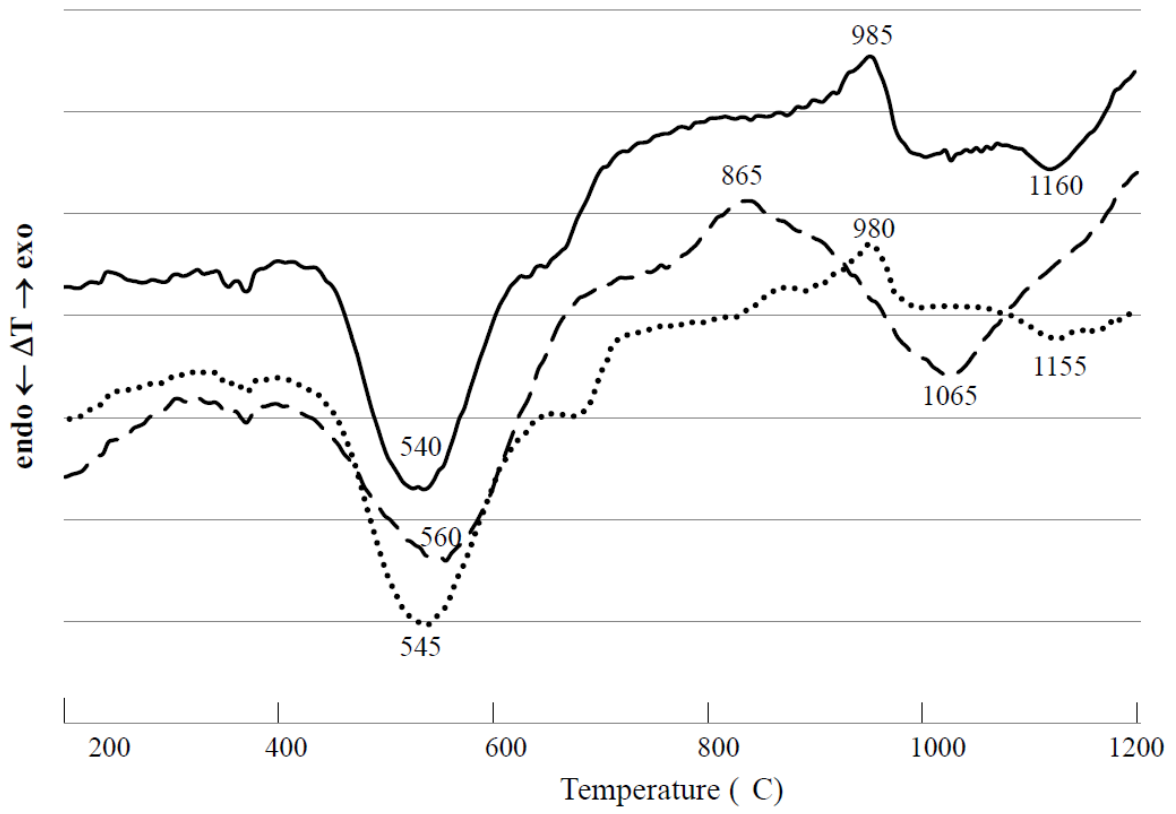


Fig. 2.

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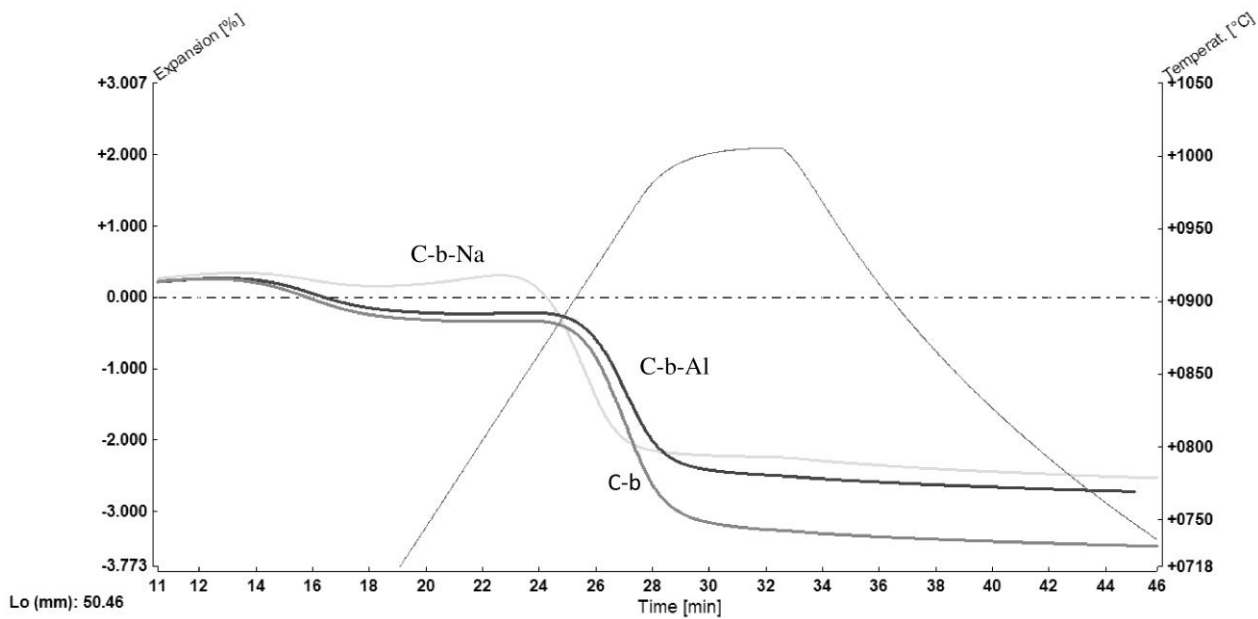


Fig. 3.

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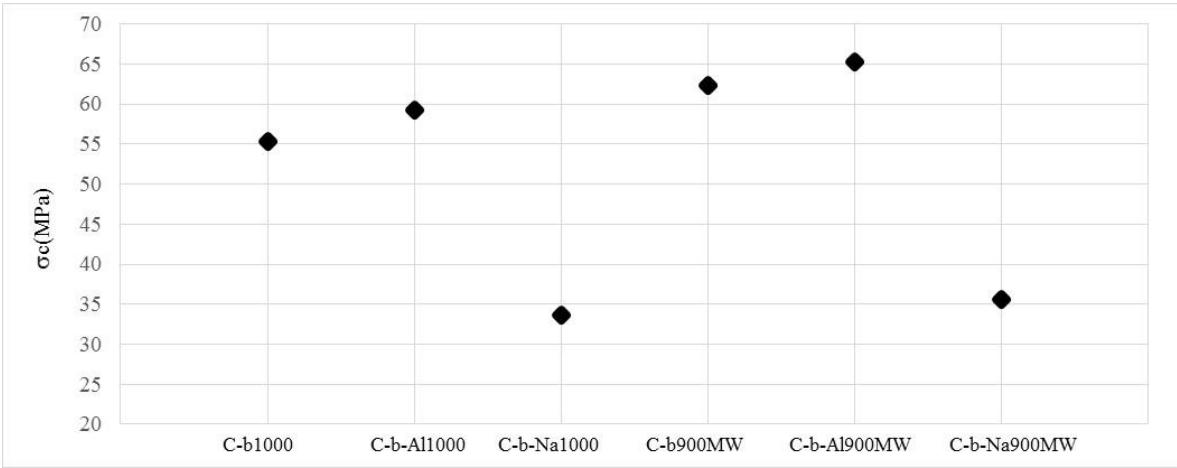


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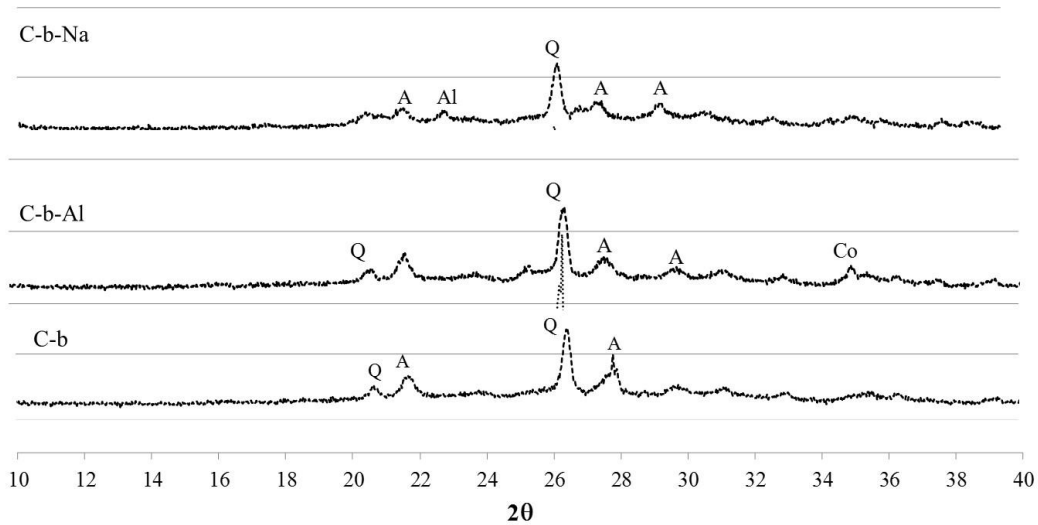
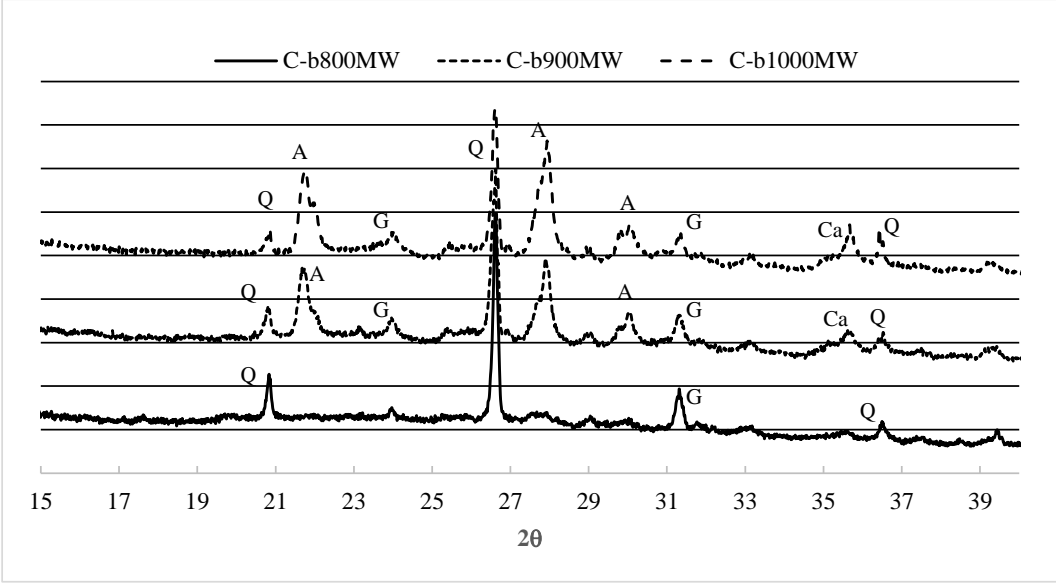
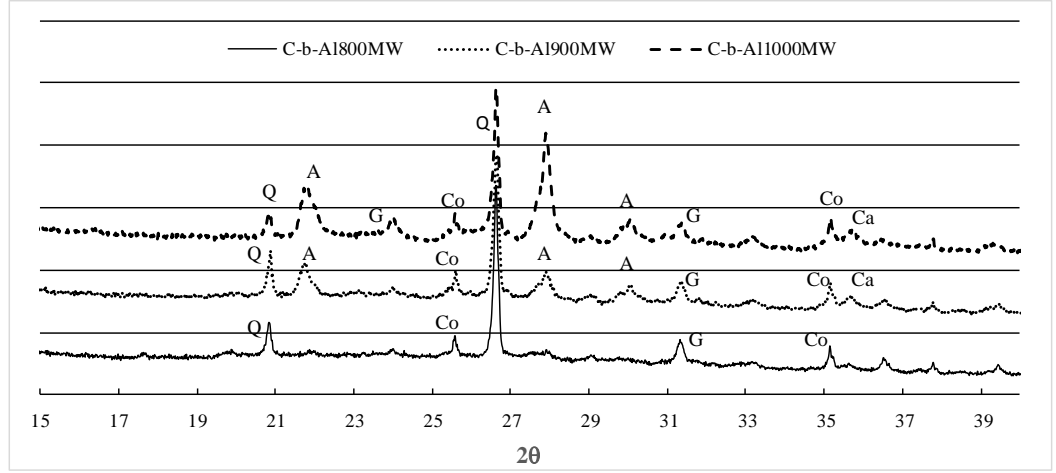


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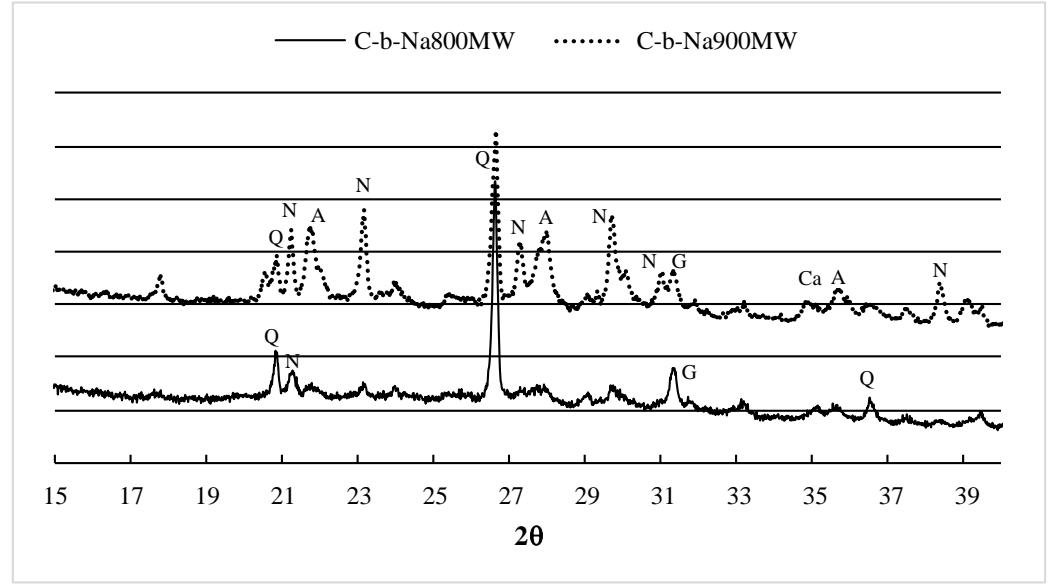
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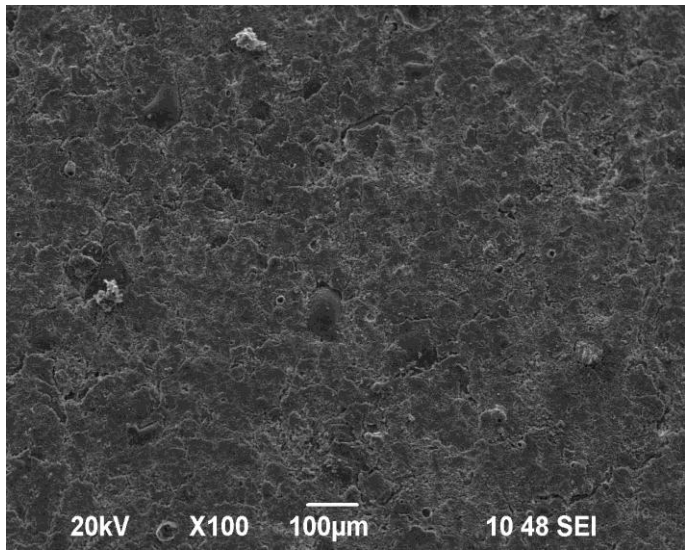
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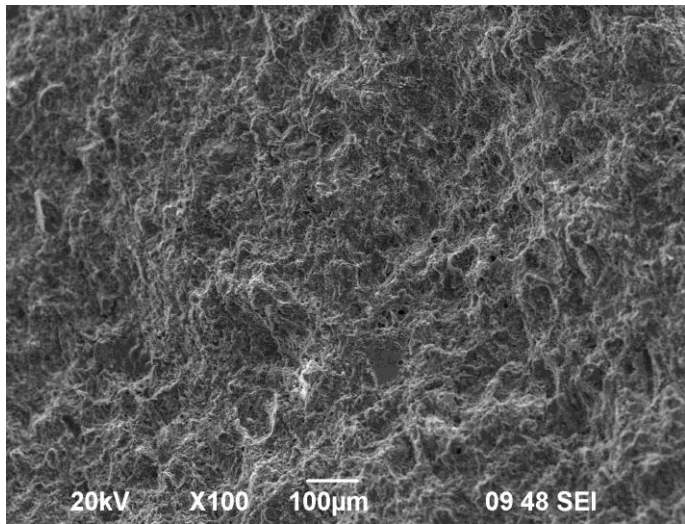
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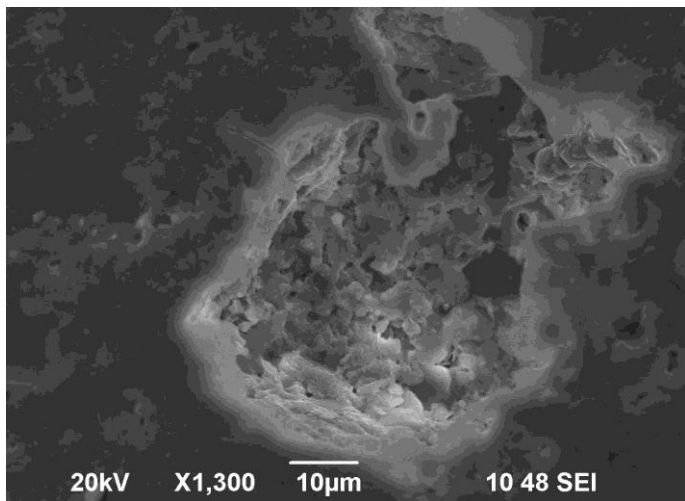
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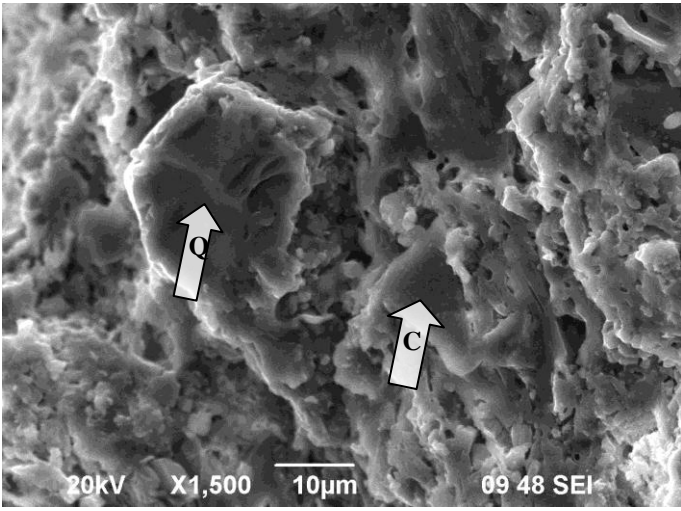
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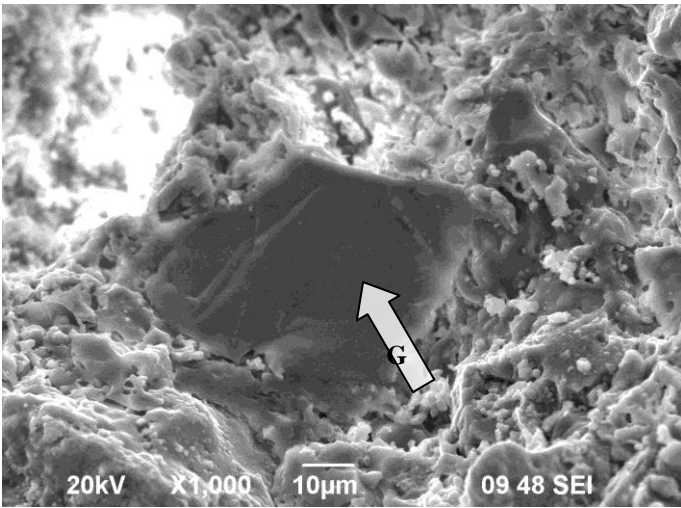
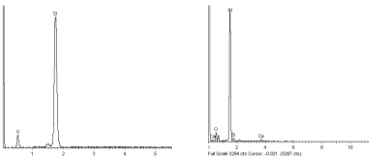
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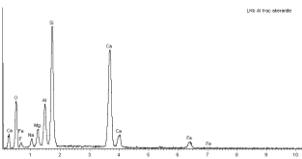
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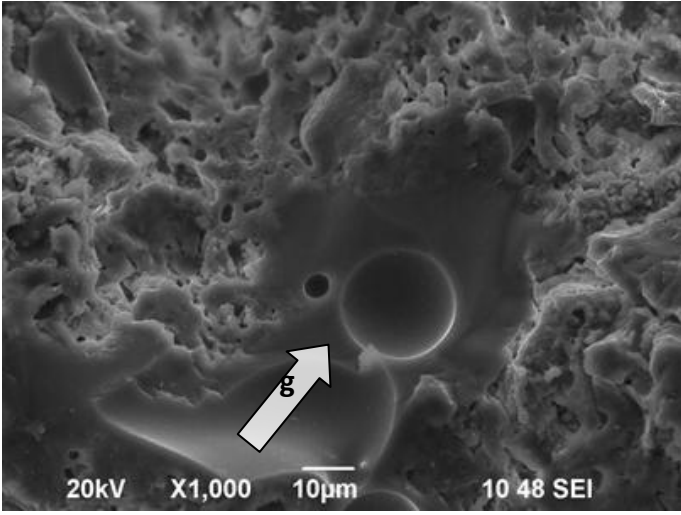
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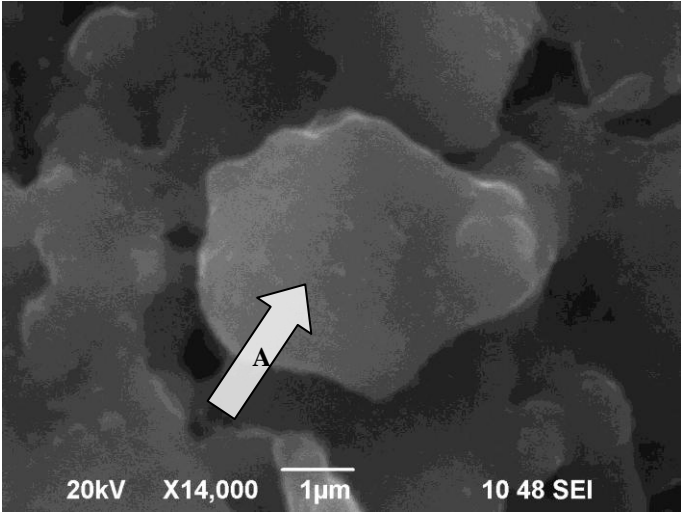
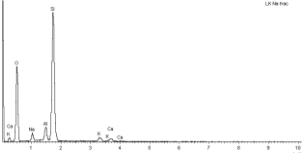
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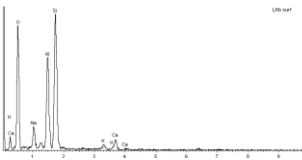
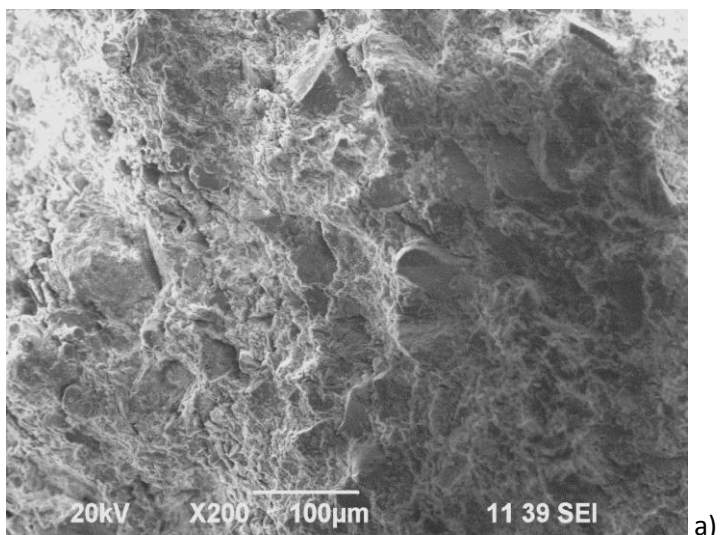
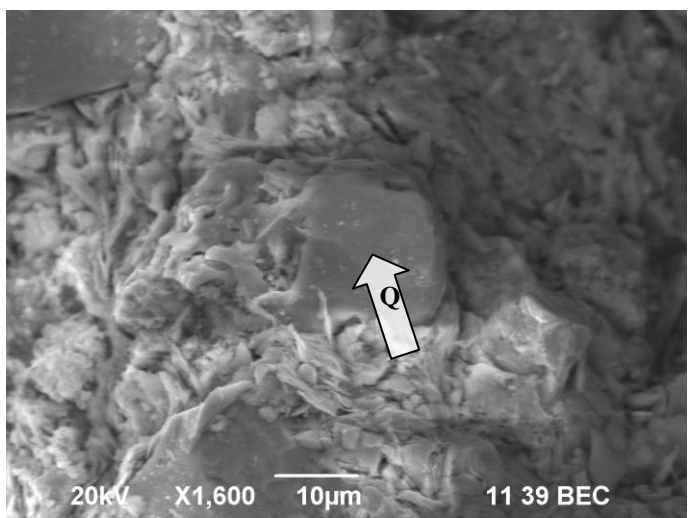


Fig. 8

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a)



b)

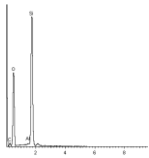
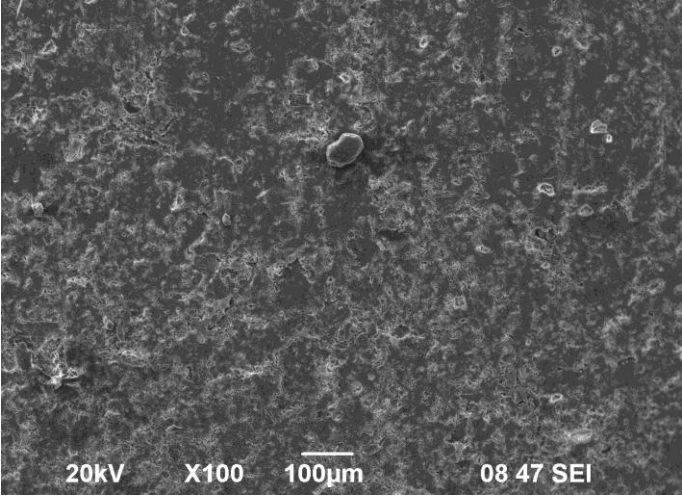
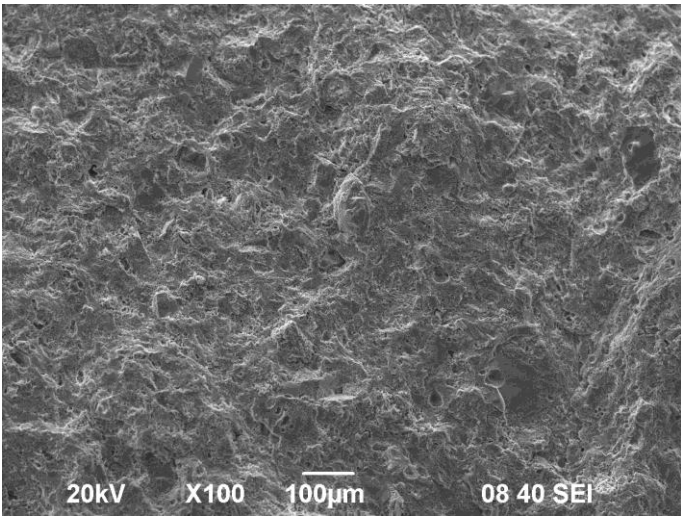


Fig. 9

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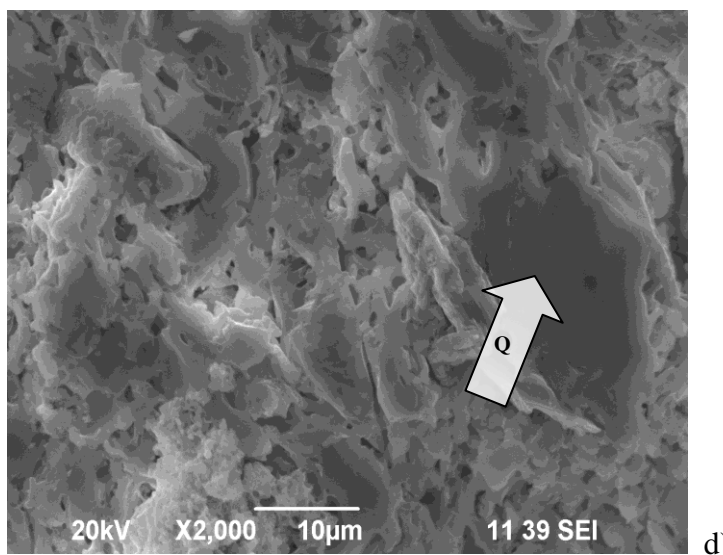
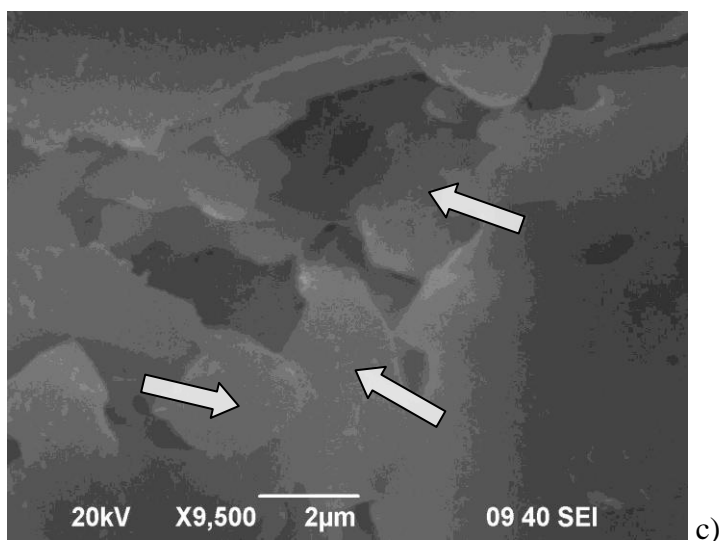


Fig. 10.

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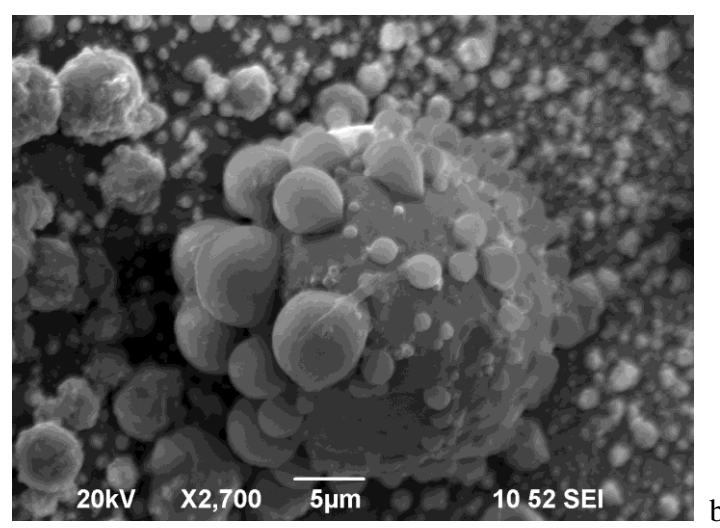
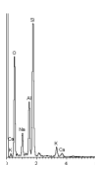
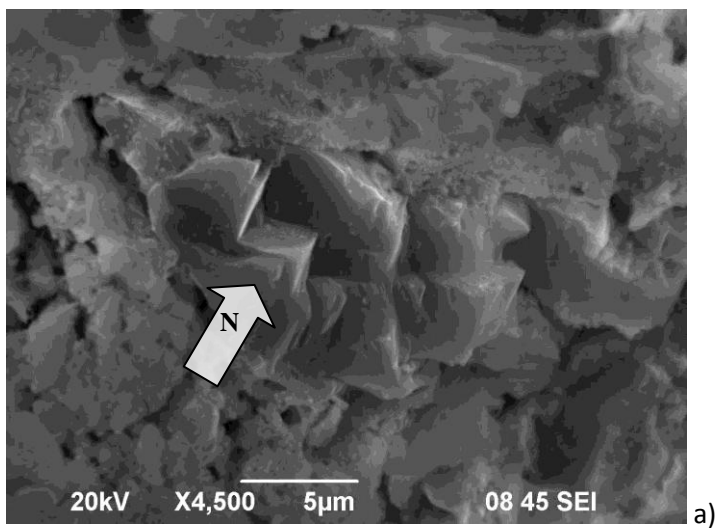


Fig.11.