BOTTOM ASHES FROM BIOMASS COMBUSTION AS SECONDARY RAW MATERIALS IN PORCELAIN STONEWARE BODIES

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ABSTRACT

The ceramic industry is going to be deeply involved in the transition to a circular economy. Waste recycling could turn into a common practice to improve environmental sustainability of the manufacturing of silicate ceramics. Although this industry proved to be able to efficiently recycle its own processing residues – getting an index of reuse close to 100% for in-house residues – the recourse to pre- and post-consumption wastes from other sectors is still quite limited. Indeed, the main obstacle to a widespread recourse to waste recycling is the lack of knowledge about the effects of different kinds of waste on the technological behavior of semi-finished products along the productive line and technical performance of finished tiles. This work aims to evaluate the use of bottom biomass ashes as secondary raw material in porcelain stoneware bodies. Currently this type of waste is mostly used in cement conglomerates and as fertilizer, while studies on its possible use in the ceramic field, as a substitute for a traditional raw material, are still very limited. A bottom ash coming from a biomass thermoelectric power plant in Emilia-Romagna (Italy) was selected and characterized to determine its chemical, mineralogical, and thermal properties. The data indicated its employment in substitution of the fluxing component of the system. Therefore, the ashes were introduced in a classic porcelain stoneware batch in replacement of feldspars, in increasing amount (2-4-6wt%). The simulation at the laboratory scale of the industrial cycle allowed to identify a bottleneck relative to the rheological behavior of the slips, which can be easily managed by a slight deflocculant increase.

The semi-finished products were characterized for particle size distribution, specific weight of powders, bulk density, and flexural strength. It is worth noting that the mechanical properties of the unfired tiles were improved by the ash introduction. The powder compacts were then fired at different maximum temperatures (from 1000 to 1220°C) in order to follow the evolution of the technological properties and determine the gresification temperature (corresponding to maximum densification and water absorption <0.5%). Indeed, while the waste-free body achieved the desired properties at 1200°C, the introduction of biomass ash allowed the firing temperature to be lowered by 20°C (T_{md}=1180°C). Moreover, also for the fired specimens, an increase of the flexural strength positively correlated to the amount of waste was observed, despite the microstructure of ash-bearing bodies being characterized by pore sizes that are slightly coarser than in the waste-free body.

INTRODUCTION

The manufacture of ceramic products is constantly increasing all over the world, with a production of tiles around 13 billion square meters in the latest years [1], implying an ever-increasing demand for raw materials attaining an estimated global consumption beyond 300 million tons per year [2]. On the other hand, the progressive depletion of the main mineral deposits that this production rate imposes, is forcing the ceramic industry to look for suitable substitutes, which guarantee specific technological properties for the finished product. This situation represents a challenge for the ceramic industry, to make production completely sustainable in the long run – with a view to the transition to a circular economy – but ensuring the high technological performance of the product. Although to date the ceramic industry has proven to be able to recycle its own processing residues very efficiently, the use of wastes from other sources is currently rather limited. Indeed, the main obstacle to a widespread recourse to waste recycling is the lack of knowledge about its effect in ceramic tile manufacturing. In this context, a recent work of Zanelli and co-workers [3] overviewed the effect of waste recycling on the technological behavior and technical performance of ceramic tiles. Through a critical review of the available literature, the authors defined the maximum recommended amount of introduction of the secondary raw materials into the ceramic batches, so that the variations induced by the waste were tolerable in terms of technological behavior and technical performance of the finished products. The review of the data relative to bottom ashes from biomass combustion revealed that substantially no information is available on the technological behavior during body preparation, pressing and drying, while the firing process has been more widely investigated [4-14]. Despite the near absence of studies on the pre-firing steps, it emerges that they are the most critical, due to the high susceptibility of the ash to moisture (tendency to cementation), which can cause several problems in the storage and handling of the ashes. The goal of this work is to evaluate the technological feasibility of the biomass ash recycling in porcelain stoneware bodies, in relation to all the industrial steps of ceramic tile production (milling – granulation – shaping – drying – firing), in order to identify possible bottleneck along the manufacturing line. This was possible by simulating the industrial cycle at the laboratory scale, verifying the effect of the ash introduction not only on the fired products but also on the semi-finished ones.

EXPERIMENTAL

The present work used bottom ashes from biomass combustion, coming from a biomass thermoelectric power plant in Emilia-Romagna (Italy), as secondary raw materials in porcelain stoneware bodies. These bottom ashes represent combustion product of woody material, grass, pomace, and a mix of tree essences, treated at a declared combustion temperature between 700-1000°C. They are classified by the CER code (European waste catalog, directive 75/442/EEC) CER 10 01 01: Waste produced by thermal power plants and other thermal plants, defined as non-hazardous materials. In order to check their compatibility with a specific component of the ceramic batch, complying a determinate role (plastic component, fluxing component or skeleton), they were characterized from the chemical, thermal and mineralogical point of view. The chemical composition was determined by XRF-WDS (PW 1480, Philips) and reported in Table 1, together with the chemical composition of the other raw materials. The thermal behavior of the ashes was studied by HSM (Misura 3- 402ES/3, Expert System Solution) with a cycle of 10°C/min up to 1600°C, while the mineralogical composition was determined by XRPD analysis (X'PERT PRO, PANalytical). The results indicated a use of the ashes in substitution of the fluxing component of the system, i.e., feldspars. Therefore, four different porcelain stoneware batches were designed: a benchmark – consisting of 40wt% ball clays (plastic component), 45wt% feldspars (fluxing component) plus 15wt% of quartz sands (skeleton) – and three bodies with bottom ashes from biomass combustion in partial (2–4-6wt%) replacement of the feldspathic component. The maximum limit of ashes introduction (6wt%) was determined on the basis of literature results [3-14] and experimental tests. Indeed, laboratory tests indicated that the introduction of ashes implies a worsening of rheological behavior of the slips. This bottleneck can be easily managed in batches containing ashes up to 6wt%, by a slight increase in deflocculant (0.6wt% instead of 0.3wt%). On the other hand, a higher ashes introduction entails an excessive deviation from the technological behavior of conventional raw materials.

	BALL CLAYS		FELDSPARS		QUARTZ SAND		BOTTOM ASHES
wt%	**20**	**20**	**35**	**10**	**7**	**8**	**2-4-6**
SiO_2	60.16	65.39	68.98	71.29	84.07	93.76	43.10
Al_2O_3	26.53	22.13	19.22	16.04	7.71	3.27	8.71
TiO_2	1.40	1.11	0.18	0.28	0.04	0.09	0.45
Fe_2O_3	0.90	1.21	0.10	0.55	0.18	0.21	4.45
CaO	0.30	0.30	0.40	1.10	0.90	0.05	27.58
MgO	0.50	0.50	0.10	0.80	0.20	0.23	4.40
K_2O	2.40	2.11	0.20	7.02	6.10	1.85	5.36
Na_2O	0.40	0.50	10.51	1.40	0.20	0.14	1.20
P_2O_5	-	-	-	-	-	-	1.44
MnO	-	-	-	-	-	-	0.14
LOI	7.41	6.74	0.30	1.50	0.60	0.40	3.17
Total (%)	100	100	100	100	100	100	100

Table 1. *Chemical composition of raw materials used in porcelain stoneware batches (wt%). The chemical composition of the batches was calculated considering the contribution by weight of each raw material; bottom ashes were introduced in partial replacement (2-4-6wt%) of the total amount of feldspars.*

The four designed batches were prepared at the laboratory scale, simulating the industrial tile-making process. The raw materials were ball milled in a porcelain jar using dense alumina grinding media, 40% water and 0.06% deflocculant (sodium tripolyphosphate). Milled powders had a median particle diameter between 3.3 and 3.9 µm (Table 2). The slips were oven dried, de-agglomerated (hammer mill with grid of 500 µm) and manually granulated (sieve 2 mm, moisture ~8wt%). Powders were compacted with a hydraulic press (40 MPa) into 110 × 55 × 5 mm tiles, dried in an electric oven at 105 ± 5°C overnight and characterized for (Table 2): particle size distribution (ASTM C958), specific weight of powders (ASTM C604), bulk density (weight/volume ratio) and flexural strength (ISO 10545-4).

	unit	C0			C2			C4			C6		
d_{50}	µm	3.3	±	0.0	3.8	±	0.0	3.8	±	0.0	3.9	±	0.0
S.W.P.	g/cm^3	2.605	±	0.001	2.610	±	0.001	2.612	±	0.001	2.624	±	0.001
B.D.	g/cm^3	1.936	±	0.004	1.993	±	0.003	2.008	±	0.012	1.993	±	0.004
F.S.	MPa	3.08	±	0.14	3.25	±	0.12	3.25	±	0.06	3.65	±	0.18

Table 2. *Technological properties of semi-finished products.* d_{50}*= Median particle size; S.W.P.= Specific weight of powder; B.D.= bulk density; F.S.= flexural strength.*

Powder compacts were fast fired in an electric roller kiln (ER15; Nannetti, Faenza, Italy) at seven different maximum temperature (T_{max}) ranging from 1000 to 1220°C, with a thermal cycle of about 60 min cold-to-cold and 5 min of dwell time at T_{max}. The technological properties, determined after firing the specimens at the different T_{max}, are: linear firing shrinkage (i.e., 100(*L*m - *L*f)/*L*m where *L*f is the length of the fired tiles and *L*m is the length of the mold), water absorption, bulk density and open porosity (ASTM C373), specific weight of powders (ASTM C604) (Table 3). The flexural strength was determined only at gresification temperature (corresponding to maximum densification and water absorption ≤0.5%, i.e., 1180°C for C2-4-6 and 1200°C for C0) and over-firing T°C of 1220 for all samples (Table 3).

T(°C)		unit	C0	C2	C4	C6
1000	**L.S.**	cm/m	0.05 ± 0.07	-0.01 ± 0.03	-0.09 ± 0.01	-0.17 ± 0.05
	W.A.	%	13.36 ± 0.13	11.87 ± 0.09	11.70 ± 0.07	12.17 ± 0.07
	B.D.	g/cm^3	1.931 ± 0.005	1.994 ± 0.002	2.002 ± 0.005	1.987 ± 0.003
	O.P.	%	25.81 ± 0.12	23.66 ± 0.03	23.42 ± 0.09	24.19 ± 0.15
1100	**L.S.**	cm/m	2.30 ± 0.21	1.64 ± 0.02	1.12 ± 0.04	0.77 ± 0.01
	W.A.	%	9.66 ± 0.11	8.77 ± 0.01	9.40 ± 0.09	10.45 ± 0.08
	B.D.	g/cm^3	2.047 ± 0.004	2.098 ± 0.003	2.080 ± 0.006	2.045 ± 0.002
	O.P.	%	19.71 ± 0.18	18.39 ± 0.00	19.53 ± 0.12	21.37 ± 0.14
1130	**L.S.**	cm/m	2.99 ± 0.00	3.08 ± 0.01	2.29 ± 0.08	1.71 ± 0.01
	W.A.	%	7.42 ± 0.06	6.13 ± 0.09	7.16 ± 0.14	8.20 ± 0.14
	B.D.	g/cm^3	2.136 ± 0.004	2.196 ± 0.002	2.157 ± 0.004	2.112 ± 0.005
	O.P.	%	15.85 ± 0.09	13.47 ± 0.19	15.44 ± 0.28	17.31 ± 0.25
1160	**L.S.**	cm/m	4.57 ± 0.02	4.76 ± 0.03	4.31 ± 0.08	3.58 ± 0.13
	W.A.	%	4.39 ± 0.06	2.56 ± 0.07	2.82 ± 0.11	3.84 ± 0.14
	B.D.	g/cm^3	2.261 ± 0.002	2.339 ± 0.000	2.312 ± 0.009	2.254 ± 0.006
	O.P.	%	9.93 ± 0.12	5.98 ± 0.17	6.53 ± 0.23	8.65 ± 0.30
1180	**L.S.**	cm/m	5.27 ± 0.02	5.13 ± 0.07	4.87 ± 0.04	4.65 ± 0.09
	W.A.	%	2.60 ± 0.02	0.53 ± 0.03	0.26 ± 0.00	0.54 ± 0.05
	B.D.	g/cm^3	2.327 ± 0.005	2.371 ± 0.001	2.364 ± 0.003	2.333 ± 0.004
	O.P.	%	6.04 ± 0.03	1.34 ± 0.07	0.62 ± 0.00	1.26 ± 0.27
	F.S.	MPa	32.34 ± 0.95	34.85 ± 2.37	36.44 ± 1.28	37.44 ± 1.27
1200	**L.S.**	cm/m	5.56 ± 0.03	4.80 ± 0.08	4.46 ± 0.04	4.34 ± 0.04
	W.A.	%	0.41 ± 0.07	0.13 ± 0.03	0.09 ± 0.05	0.09 ± 0.05
	B.D.	g/cm^3	2.356 ± 0.004	2.334 ± 0.004	2.319 ± 0.004	2.312 ± 0.004
	O.P.	%	0.97 ± 0.17	0.31 ± 0.07	0.21 ± 0.12	0.21 ± 0.12
	F.S.	MPa	31.54 ± 0.58	31.16 ± 1.48	34.65 ± 0.81	40.31 ± 1.48
1220	**L.S.**	cm/m	5.46 ± 0.07	4.17 ± 0.10	4.46 ± 0.04	4.35 ± 0.03
	W.A.	%	0.14 ± 0.03	0.12 ± 0.11	0.08 ± 0.03	0.08 ± 0.03
	B.D.	g/cm^3	2.350 ± 0.004	2.276 ± 0.007	2.221 ± 0.002	2.210 ± 0.006
	O.P.	%	0.32 ± 0.32	0.28 ± 0.25	0.18 ± 0.07	0.18 ± 0.07
	F.S.	MPa	30.29 ± 2.06	32.22 ± 1.52	35.99 ± 0.71	38.3 ± 1.68

Table 3. *Technological properties of finished products fired at different temperatures. L.S.= linear firing shrinkage; W.A.= water absorption; B.D.= bulk density; O.P. = open porosity; F.S.= flexural strength.*

The microstructural evolution between the gresification and over-firing temperatures was observed by scanning electron microscopy (JSM-6010 LA InTouchScope, graphite sputtered polished surface, JEOL, USA).

RESULTS AND DISCUSSION

The biomass bottom ashes under study are characterized, from the chemical point of view, by relatively high contents of SiO_2, CaO and Al_2O_3. These features appear to be in line with the literature chemical data relative to ashes coming from the combustion of agricultural and forest residues and from a mix of these [15-17]. These kinds of ashes are indeed mainly composed of Si, Ca, Al, Ti, Fe, Mg, Na, K, S and P [18], even if the relative concentration of a specific element is a function of the biomass from which the ashes originated. Compared to the feldspars they have replaced, these bottom ashes show peculiar features, with a lower content of SiO_2 and Al_2O_3 (~43 and ~9wt%, respectively) and higher amount of CaO, Fe_2O_3, MgO and K_2O (Table 1). Their qualitative XRPD analysis indicates the presence of quartz, orthoclase, leucite, wollastonite, cristobalite, akermanite, calcite and portlandite (Figure 1), also in this case mostly matching the literature data relative to biomass bottom ashes [19-20].

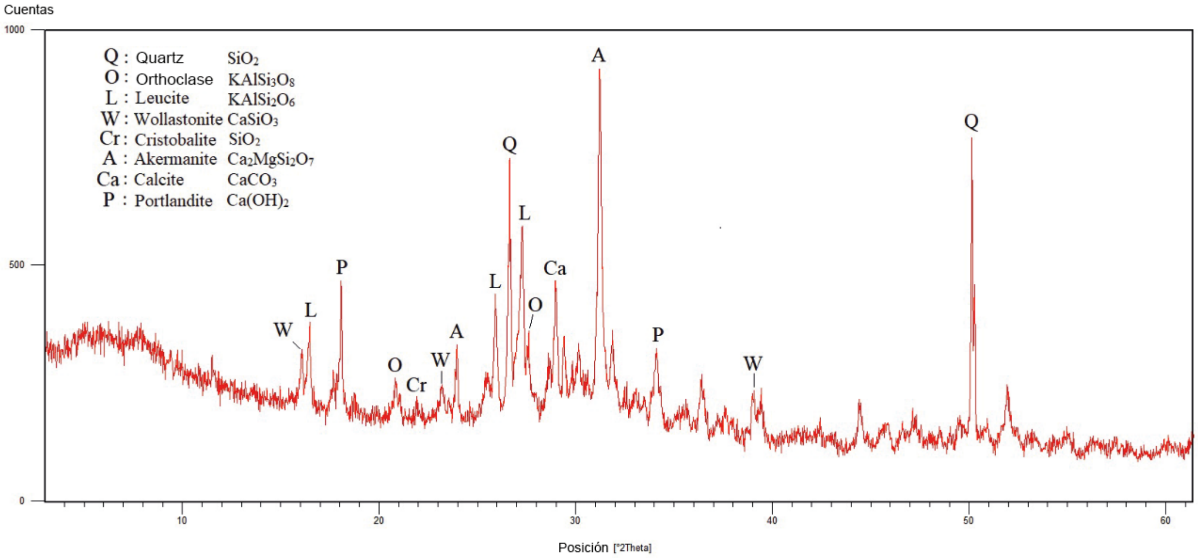

Figure 1. *XRPD pattern of biomass bottom ash under study.*

With regard to the thermal behavior of the ashes, the data collected by the hot stage microscope allow good fusibility to be observed, comparable with that of the conventional feldspars used in the porcelain stoneware production.

The biomass bottom ashes were therefore introduced in a typical porcelain stoneware batch (C0) in partial substitution (2-4-6wt%) of feldspars, in order to obtain four different batches, which underwent the simulation of the industrial tile making processing at the laboratory scale. The addition of the ashes had a significant impact in the first step of production, i.e., wet milling. Their presence led to a worsening of the rheological properties of the slip with a significant increase in viscosity. Anyway, this bottleneck was easily overcome thanks to a slightly addition of deflocculant (from 0.3 to 0.6wt%). This correction allowed adequate wet milling, obtaining bodies with very similar particle size distribution (Table 1, d_{50}; Figure 2). Otherwise, the presence of the ashes did not modify the technological behavior of porcelain stoneware bodies during the granulation, shaping and drying steps. This low impact was observed also for the technological properties of semi-finished products (Table 2), characterized by small variations.

Specifically, a slight increase in the bulk density and flexural strength in the prototypes containing ashes, indicating an improvement in compaction and mechanical properties, due to the presence of the ashes themselves. Powder compacts were then fast fired at seven different maximum temperatures (T_{max}): 1000-1100-1130-1160-1180-1200-1220°C, and their technological properties, determined after firing, are reported in Table 3. In contrast with the semi-finished products, the ashes significantly influenced the firing behavior. In regard to linear shrinkage, it decreased with the amount of ashes (Figure 3). Actually, the growing increase in ashes, from 2 to 6wt%, led to a progressive reduction in linear shrinkage values, less pronounced for batch C2. Moreover, the waste-bearing bodies reached their max shrinkage at 1180°C, showing similar values among them and also close to the benchmark. In any event, after this temperature, they exhibited a turnaround, suggesting an expansion of the ceramic bodies. On the other hand, the waste-free body C0 kept shrinking up to 1200°C, reaching the highest value of the set (5.56 cm/m), and remained stable even at the highest temperatures of 1220°C.

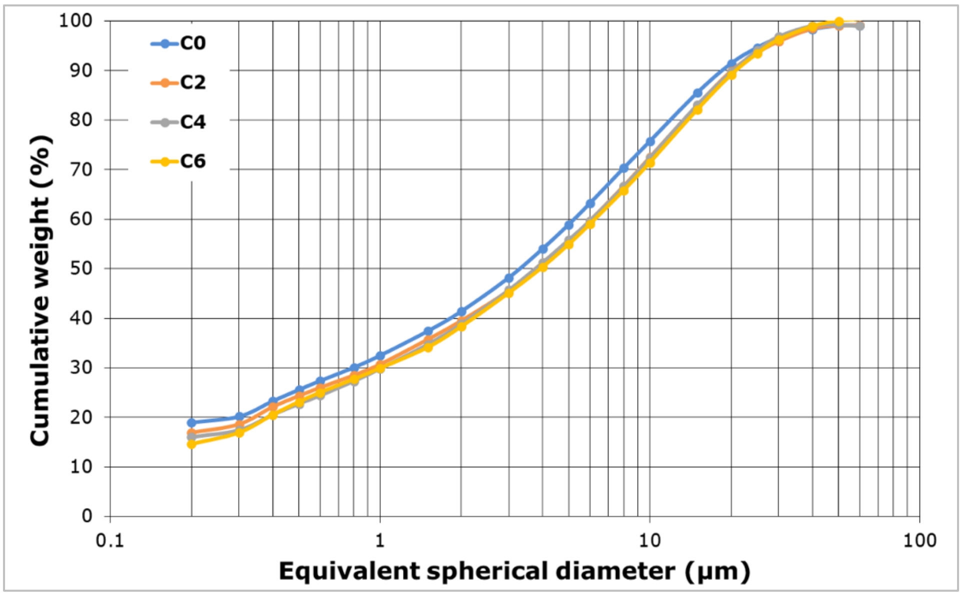

Figure 2. *Particle size distribution of batches C0-C2-C4-C6.*

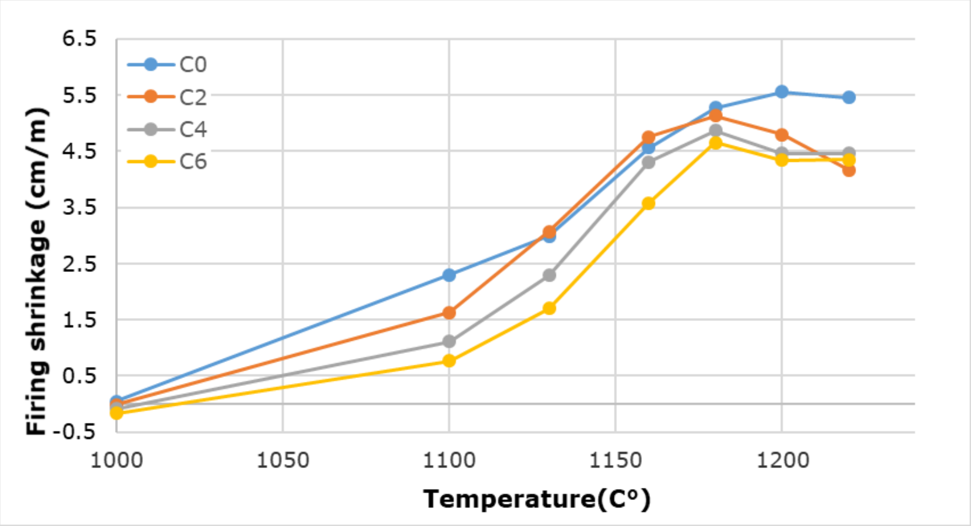

Figure 3. *Linear firing shrinkage of finished products fired at different temperatures.*

Taking into account the water absorption and the bulk density, the two fundamental parameters in the construction of the gresification curves, it is possible to observe their evolution with the increasing temperature in Figure 4. At the lowest temperature of 1000°C the batches containing ashes are characterized by a slightly higher bulk density with respect to the benchmark, corresponding to a lower water absorption, in agreement with the open porosity data (Table 3). In the temperature range between 1000 and 1100°C it is no longer possible to observe a clear distinction in behavior between the waste-bearing batches and the reference, mostly because of the sample C6, characterized by a slower densification rate with respect to batches C2 and C4. Starting from 1100°C there is, for all the samples, a change in the slope of the curves with a significant increase in density and a corresponding decrease in water absorption, indicating an increase in sintering kinetics.

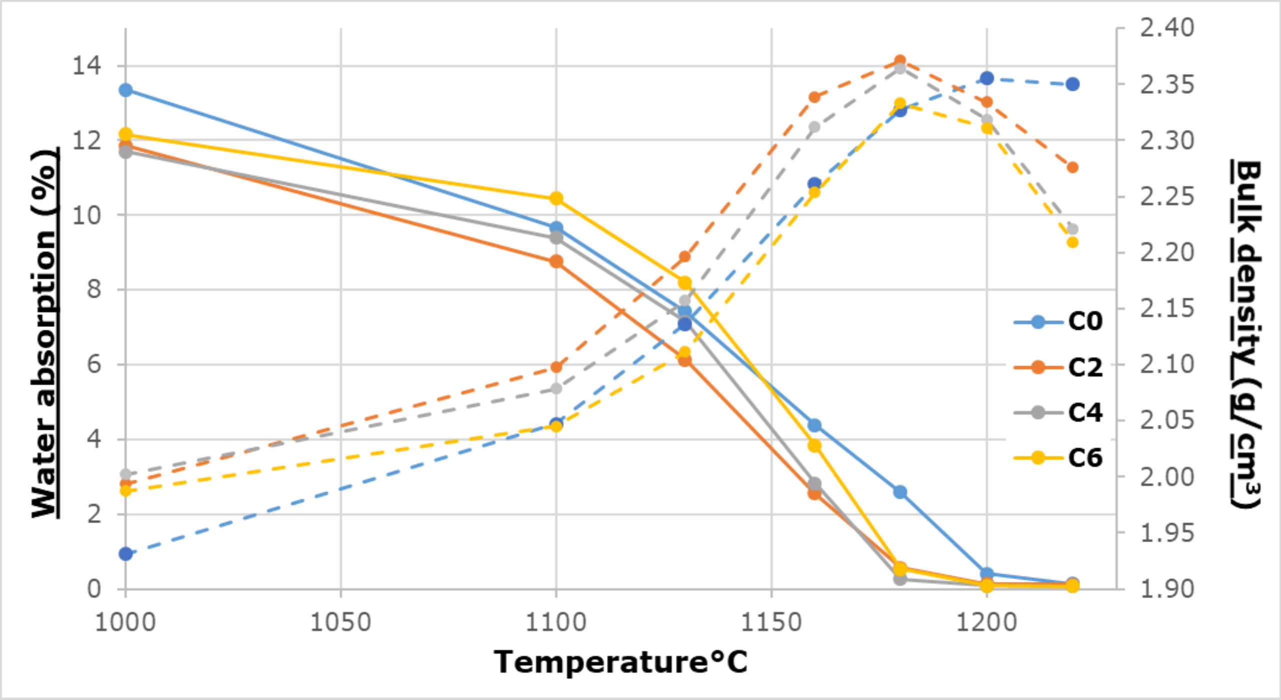

Figure 4. *Gresification curves for batches C0-C2-C4-C6.*

At 1180°C the batches with bottom ashes reached their maximum density, with values very similar for C2 and C4, slightly lower for C6; at this same temperature they also show values of water absorption ≤0.5%, which allow definition of 1180°C as their adequate firing T°C. Actually, even if at 1200°C the water absorption is even lower for these bodies, they suffer from a significant loss of density, which, in accordance with the linear shrinkage data, indicates an expansion of the ceramic body, more accentuated at the maximum tested T°C (1220). On the other hand, for the benchmark the sintering process is still going on at 1180°C, as witnessed by the high water absorption (2.6%) and increasing density values. Indeed, for this batch the densification is accomplished at 1200°C, 20°C higher than the samples containing ashes. Nevertheless, it may be noted that C0 is characterized by a more pronounced stability at high temperature with respect to the other batches.

This feature is also mirrored by the microstructure evolution of the bodies between the maximum densification temperature (T_{md}, Figure 5) and that of over-firing (Figure 6). At the T_{md} all the batches show a compact bulk structure with relics of quartz crystals and rounded isolated closed pores, from a few µm up to 10 µm, dispersed in an abundant amorphous phase (liquid at HT), which has promoted the sintering process by reducing the voids and increasing the density of the ceramic matrix. In detail, it is possible to observe that the reference batch shows a lower number of pores with respect to the other samples, which are also smaller in size. Passing to the over-firing temperature (Figure 6), it appears clear how the changing in the technological properties has affected the microstructure. Indeed, the reversal of linear shrinkage and the significant loss of density for the waste-bearing batches, can be read in the SEM micrographs through the presence of enlarged closed pores. These large pores, with a diameter up to 60 µm, indicate the occurrence of de-sintering processes related to bloating phenomena, which can lead to pyroplastic deformations.

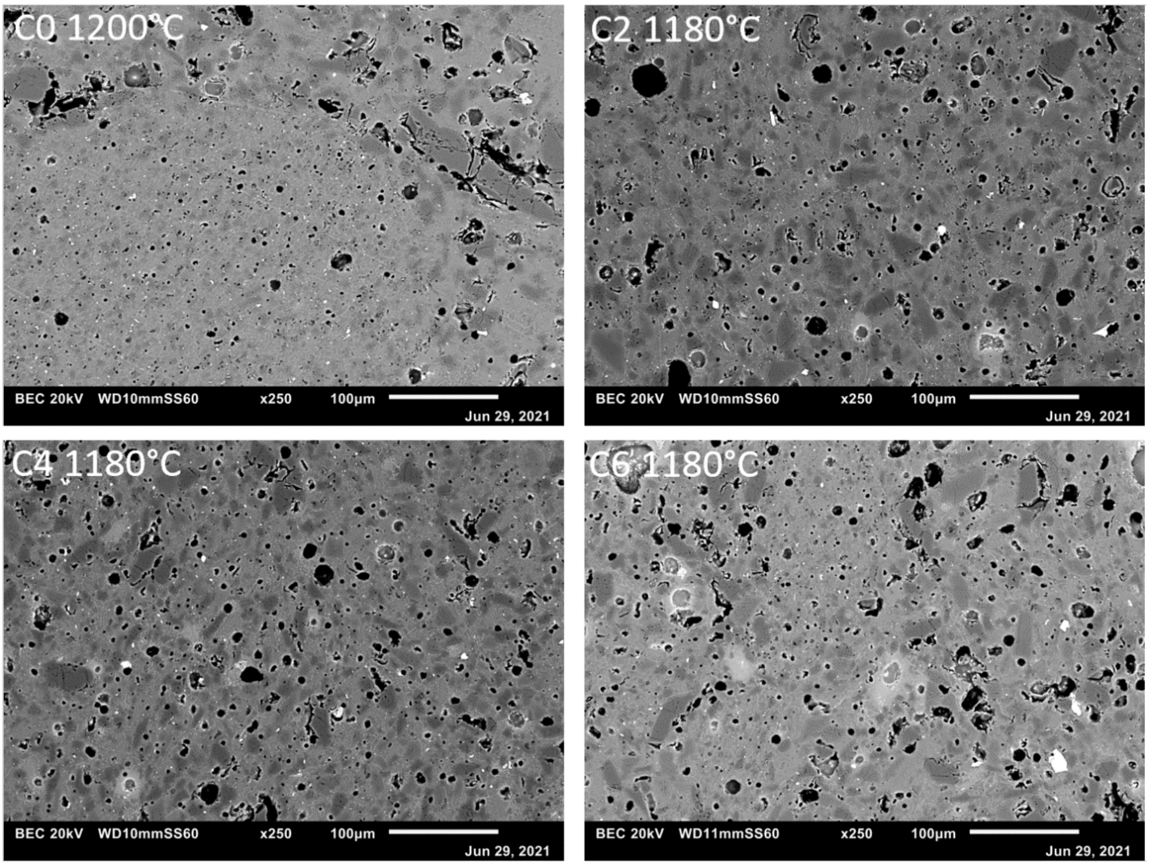

Figure 5. *SEM micrographs of bodies fired at T_{md} (1200°C for C, 1180°C for C2-C4-C6).*

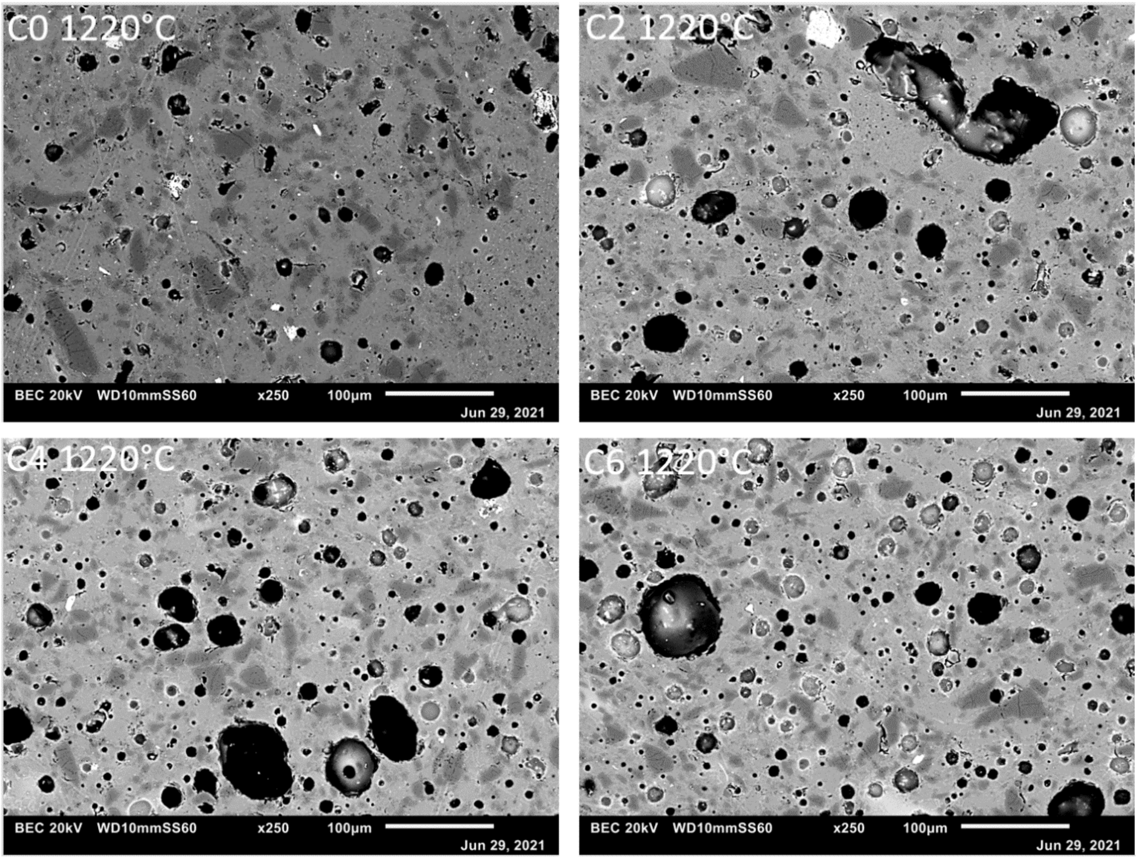

Figure 6. *SEM micrographs of bodies that underwent over-firing at 1220°C*

CONCLUSIONS

This study investigated the feasibility of biomass bottom ash recycling in porcelain stoneware bodies. The work has been carried out through the simulation of a ceramic industrial cycle on a laboratory scale, monitoring the variations of the main technological parameters following the introduction of the ashes in a typical porcelain stoneware batch. Due to their physical and chemical properties, the ashes were introduced in the ceramic batch in partial substitution of feldspars, up to 6wt%. The simulation of the industrial manufacturing process, allowed only one bottleneck, related to the rheological behavior of the slips, to be identified. The presence of ashes, in fact, induced a considerable increase in the viscosity of the slip during the wet milling, which was overcome by a slight deflocculant addition, involving a total of 0.6% on the dry mass. There were no further bottlenecks in the process simulation. Indeed, already from the characterization of semi-finished products, it emerged that the ashes improved some technological properties, such as mechanical strength. Improvement of mechanical properties was also confirmed in the fired specimens. On the other hand, no significant variations with respect to the other technological parameters were identified, certifying that the introduction of ashes, within certain limits, guarantees the maintenance of the required properties of the semi-finished products along the production line. As for the firing behavior, the introduction of ashes allowed the firing temperature to be lowered by 20°C (1180°C) with respect to the waste-free batch (1200°C), while maintaining good levels of densification, with bulk density around 2.4 g/cm^3. However, the waste-bearing batches exhibited a tendency to instability at high temperatures, so that the gresification window tends to be rather narrow. In this sense, it is important to identify the exact firing temperature of the bodies, in order not to incur phenomena related to the over-firing of ceramic products, such as bloating, as suggested by SEM results. Taking into account all the collected data, the ceramic product obtained from C4 batch is the best choice among the tested ones, showing values perfectly matching the standard requirements for porcelain stoneware; while the 6wt% replacement, represents the limit of introduction for this type of formulation. The results obtained are therefore promising from an industrial point of view, but it should be remembered that the chemical and mineralogical composition of biomass bottom ashes is extremely variable, depending not only on the biomass of origin but also on the processes with which were generated. The characterizations of the ashes themselves before use are therefore of fundamental importance. On the other hand, it should be also remembered that these ashes are classified by the CER code (European waste catalog, directive 75/442/EEC) as non-hazardous materials, and, in view of this and the maintenance of the required properties for ceramic products (with the potential lowering of the firing temperatures), they represent an excellent candidate for further technological investigations.

ACKNOWLEDGEMENTS

This work was undertaken within the CNR project "*Capitale naturale e risorse per il futuro dell'Italia (FOE 2020)*" as deliverable "*Utilizzo razionale di risorse tramite riduzione di materia prime critiche, valorizzazione degli scarti e riciclo efficace*" (Dipartimento di Scienze Chimiche e Tecnologie dei Materiali – DSCTM). *CUP=B85F21002120005*

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