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Recovery of Glazing Ceramic Sludge in Construction Materials

Fernanda Andreola, Luisa Barbieri, and Isabella Lancellotti

*Dipartimento di Ingegneria dei Materiali e dell'Ambiente, Università di Modena e
Reggio Emilia, Via Vignolese, 905/a, 41100 Modena, Italy. E-mail:
<andreola.fernanda@unimore.it>, <luisa.barbieri@unimore.it>,
<isabella.lancellotti@unimore.it >*

ABSTRACT

Ceramic glazing sludge deriving from the purification process of waste-water obtained by the glazing tile phase was mixed in equal proportion with glass cullet in order to obtain a high sintered product suitable to be used as floor /wall covering tiles. The characterization of fired samples includes the evaluation of both sintering parameters: water absorption, linear shrinkage and apparent density according to the ISO rules and sintering temperatures estimated by optical heating microscope. Satisfactory results were achieved from technological tests and SEM analysis showed a dense microstructure with crystalline phases similar to commercial glass-ceramic, identified by X ray diffraction. Besides, the obtainment of these products was achieved with energy saving due to the lower firing temperatures (about 1000°C) with respect to commercial products for floor/wall covering (about 1200°C).

INTRODUCTION

Italy is the 3rd largest floor and wall tile producer in the world, where the 80% of the total national production is manufactured in Sassuolo-Scandiano Ceramic District (mostly localized in a 300 km² area) in the Northeast Italy (Modena and Reggio Emilia). The floor and wall ceramic tiles industry represents a secure reference for the Italian economy with a production of about 600 million of m² [27° National Statistical Report, Confindustria Ceramica 2006].

The ceramic residues coming from tiles industry are due to the process and purification treatments and can be classified in two different ways as a function of both their production process and physical state. One group is composed of unfired rejects coming from steps prior firing (pressing, drying, glazing, etc.) and the other one consists in fired rejects, derived from tile selection, polishing, etc. The latter group includes residues as dust, solid and sludge (water content ranging from 40 to 80 wt%). Furthermore, the production process generates a series of sludge derived from water purification (clarification and glazing sludge) and the purification of firing and atomization gases (exhausted lime). At present, the current industrial reintroduction of

by-products into the same process is the best viable solution to combine environmental (reduction of dumping effluents and saving water consumption) and economic benefits.

However, one of the major environmental problems associated with wet glazed ceramic tile manufacturing processes is the correct removal of sludge arising from wastewater treatment [Busani, 1991; Blasco, 1992]. The industries having both wet milling and spray-drying step show a consolidate industrial practice, operating a close loop recycling of the glazing wastewater to the body preparation process (80-100%) [Confindustria Ceramica, 2008].

The problem appears when the companies have a partial cycle (without raw materials preparation and atomization steps) or use dry milling step for the raw materials preparation. In these cases the process is not able to support the wastewater and it makes necessary to separate the glazing sludge from the waters for purifying. Ceramic sludge are the solid waste produced by the waste water treatment plant of a ceramic factory, the ratio calculated of the glazing sludge amounts derived is about 90–150 g/m² of tile surface depending on the glaze applying processes [2° Integral Report, Confindustria Ceramica, 2008].

Normally glazes are formulated using silica (as major glaze component), fluxing agents (alkalis, alkaline earths, boron, lead, and so on), opacifiers (zirconium, titanium, and so on), and colouring agents (iron, chromium, cobalt, manganese, and so on). Glazing sludge (whose production in Ceramic District is evaluated in about 40,000 ton/y [ARPA, 2006] is codified in Europe as special waste and classified as hazardous or not hazardous (European Waste Code 10.12.11 or 10.12.12) as a function of heavy metals content. The sludge composition is strictly dependent on the particular manufactured glaze so it may contains heavy metals (Pb, Cd, Cu, Zn, etc.) and chemical compounds used for depuration (inorganic/organic coagulants and flocculants, etc.).

The ceramic glazing sludge can be validated for use as substitute of natural raw materials in different industrial processes. Some examples are reported in literature: engobe formulations up to 5 wt% (Albuquerque et al. 2002) vitrification to produce new glazes [Monfort et al. 2003], bricks (5-10 wt%) and roofing tile formulations (about 60 wt%) [Ortelli and Vincenzini, 1983] but they seems only laboratory studies. Nowadays new emphasis is thrown on increasing recycling and recovery as new technologies and market development for recycled materials, in a global view to the benefits for future generations and environmental welfare. In this context this study in line with the Italian regulations is aimed at assessing the feasibility to obtain a ceramic building product suitable to be used as floor covering tiles from glazing sludge and glass cullet mixtures.

EXPERIMENTAL

Samples Preparation

For the study two sampling of sludge were chosen, representative of the waste as resulting from the glazing operation into an industrial cycle. The samples were dried in oven (110°C, 24 h) in order to eliminate the water content, then were mixed to obtain a representative material. Glazing sludge and glass cullet were ground separately, in order to obtain fine powders, two size were selected for the sintering process (<125 µm and <75 µm). Therefore, the two secondary

raw materials were mixed in equal proportion and sieved again to check the particle size distribution of the two mixtures (V125 and V75). The particle size distribution has been determined by using a laser size analyzer (Master Sizer Hydro 2000S, Malvern, UK).

The dried powders have been humidified to a water content of 6 wt% and uniaxially pressed at 40 MPa to produce round samples (40 mm diameter, 5mm thickness). The compacts have been dried at 105°C up to constant weight and then fired in an electrical laboratory furnace (Lenton, model AWF 13/12) at different temperatures (800, 900, 1000°C) with soaking times of 30 and 60 min. Besides the best mixture was fired in different industrial ceramic cycles in order to find the optimal operative conditions.

Test methods

On the samples prepared different analysis were performed in order to characterize them. The densification degree was studied by the determination of the water absorption (WA%), linear shrinkage (LS%) and apparent density (A.D). Water absorption of the fired samples was measured follows UNI EN ISO 10545.3. Linear shrinkage was determined by measuring the percentage change in the diameter of the samples from the green dried to the fired state using an electronic caliper following the equation:

$$LS\% = \frac{L_g - L_f}{L_g} \times 100 \quad (1)$$

being L_g and L_f the diameter of the green dried and fired specimens, respectively.

An envelope density analyzer with a dry medium (GeoPyc 1360, Micromeritics) was used to evaluate the apparent density of the fired samples. The LS%, WA% and A.D values obtained for five specimens were averaged for each composition. The sintering temperatures were estimated by optical heating microscope (HT Misura, Expert System Solutions, Italy) using heating rate 10°C/min up to 1400°C. Dilatometric measures were carried out by an optical dilatometer (Misura ODHT, Expert System Solutions, Italy) with a fast heating rate of 50°C/min up to 1000°C.

The crystalline phases in the fired samples were determined using a powder diffractometer (PW 3710, Philips Research Laboratories, Netherlands) with Ni-filtered $\text{CuK}\alpha$ radiation in 5-70° 2θ range and speed 1°/min, operating at 40 mA and 40 keV. Centre for Diffraction Data (ICCD) cards were used to identify the crystalline phases. The morphology and microstructure have been examined by scanning electron microscopy (SEM, Model XL40, Philips Research Laboratories) coupled with an energy dispersion spectroscopy (EDS) equipment.

The elastic modulus values have been determined using a non destructive impulse excitation technique (Lemmens Grindosonic Elektronika MK5, LTD). This test meets the ASTM 1259 testing method for dynamic elastic modulus.

Taking into account the presence of heavy metals in ceramic glazing sludge, leaching test following the UNI 10802 rule (BS EN 12457-2, 2002), were performed on the as-received sludge and on the sintered products. The samples were ground below 4 mm and immersed in distilled water (10/1 liquid/solid ratio) in capped bottles and agitated for 24h at room temperature (20 ± 5 C°). Solid residue was separated by filtration using a membrane 0.45 μm . On

each eluate, pH (pHmeter Crison – Basic 20) and specific conductivity (Radiometer Analytical - Meterlab CDM210) were measured. According to UNI EN ISO 5667-3 rule, the eluate was conserved for successive chemical analysis (ICP/AES) after acidification (pH=2 by HNO₃), metals and anions were determined: Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, Zn, sulphates, chlorides, fluorides, bromides and nitrates.

RESULTS AND DISCUSSION

Chemical analysis showed that glazing sludge is characterized by high levels of SiO₂ and Al₂O₃ main components of ceramic matrix and the presence of alkaline and alkaline earth elements. Chromosphere oxides as Fe₂O₃ and TiO₂ derived from the glaze components. Among the heavy metals present, Pb, Cu and Cr show higher amounts, their leacheability is discussed in Table III. Glass cullet showed a typical composition of a sodium-calcium silicate glass as reported in the Table III.

The thermal behaviour of the powdered mixtures was studied by DTA and non-contact dilatometric techniques. DTA curves showed inflection points in the range 657- 665°C, corresponding to the glass transition temperature (T_g) and two exothermal peaks, one small at 450-460 °C (probably due to organic compounds decomposition) and the other indicating crystallization at 870°C. Moreover, the dilatometric curve allowed to estimate the initial sintering temperature and the temperature of maximum sintering rate. The sample V125 presents a thermal expansion until 730°C and successively starts to sinter; the temperature of maximum sintering rate (identified by the negative peak on the first derivate curve) is 861°C. Besides, from the hot microscope measure it was possible to obtain the characteristic temperatures of the mixtures with different particle size (Table II). The results achieved show plainly for both mixtures the reduction of sintering temperature with respect to traditional ceramic materials, encouraging the possibility to employ these mixtures (<125 µm and <75 µm) to obtain ceramic supports at lower temperatures. Successively the samples were submitted to different thermal treatments, in order to optimize the sintering conditions.

Table I- Chemical analysis (expresses in wt% oxide) of secondary raw materials used.

OXIDE	GLAZING SLUDGE	GLASS CULLET
SiO ₂	52,36	71,16
Al ₂ O ₃	19,37	2,39
CaO	5,73	9,98
MgO	2,43	2,03
Na ₂ O	3,9	12,63
K ₂ O	1,32	1,34
Fe ₂ O ₃	0,84	0,10
TiO ₂	0,45	0,02
BaO	0,54	0,12

ZnO	0,99	0,04
PbO	0,49	0,02
CuO	0,10	0,04
Cr ₂ O ₃	0,07	-
ZrO ₂	3,01	0,13
L.O.I	8,00	-
Others	0,50	-
TOTAL	100,4	100,00

Table II- Characteristic temperatures determined by heating microscope for the two mixtures prepared V125 and V75.

MIX	T (°C) sintering	T (°C) softening	T (°C) melting
V125	858	1090	1222
V75	802	876	1216

The particle size distributions chosen were favourable for the sintering process because smaller particles with a high reactivity fill the holes created by the larger one and thus increase the solid volume. The sintering degree of the mixtures as a function of thermal treatments was checked by linear shrinkage (L.S.%), water absorption (W.A.%) and apparent density (A.D.) (Table III).

During heating treatments, chemical, physical and mineralogical transformations occur in the samples that change their structure and mechanical properties. The most obvious effect is the dimensional change of the samples. Linear shrinkage increases as increasing temperature. This trend becomes important when it is recognized an enhancement of densification, this occurs for V125 samples treated at 1000°C with 30 min of soaking time and 900°C with 60 min of soaking time for V75 samples. From these results it is evident that the particle size distribution contributes to the sintering kinetic. In fact, at the same conditions sintered samples from finest powders shrink faster than those with coarse distribution (reached higher values of LS%), besides is obviously the decrease of beginning shrinkage temperature. Also the time revealed itself an important variable for the sintering. The water absorption, strictly related to both the material microstructure and the (open or interconnected) porosity, decreases when the temperature increasing. For samples V75 at 1000°C open-pore closure (WA% ~0%) is observed. Regarding the Young's modulus (E) values, it is possible to note a trend in agreement with the sintering parameters. The increase of the mechanical properties is due to the progressive densification process in function of the temperature.

Table III- Sintering parameters and mechanical properties for the two mixtures prepared in laboratory conditions.

Thermal Treat.	WA %		LS%		A.D (kg/m ³)		E(GPa)	
	V125	V75	V125	V75	V125	V75	V125	V75
800°C, 30 min	17.286	14.956	1.907	3.126	1690	1720	---	13.01
800°C, 60 min	15.387	13.163	2.748	4.228	1730	1750	14.22	19.11
900°C, 30 min	13.353	11.590	4.114	5.436	1820	1860	24.19	27.13
900°C, 60 min	12.900	9.713	4.403	5.492	1840	1880	26.88	27.95
1000°C, 30 min	4.791	0.883	6.876	10.337	2030	2260	38.22	50.45
1000°C, 60 min	2.434	0.250	8.028	10.602	2130	2270	42.13	51.05

The XRD analysis performed onto the sintered samples have highlighted that independently of particle size mixture all samples show quartz (SiO₂) as main crystalline phase (ICDD #63-532) and albite ordinate (NaAlSi₃O₈) (ICDD #9466), albite calcian ordinate (Na, Ca)Al(Si, Al)₃O₈ (ICDD #41-1480) and wollastonite-2α (CaSiO₃) (ICDD #2788) as minor phases. Kaolinite, corundum and calcite present phases in the glazing sludge disappeared during thermal treatments. Coarser quartz grains withstand to high temperatures and are present in the sintered product, but it is interesting to note that increasing the temperature, the residual amounts of quartz decrease due to the solubility in the glassy phase formed.

The new formed calcium(II) silicates phases probably derived from the solid state reactions between the calcium oxide (provided by calcite (CaCO₃) decomposition) with powdered silica and corundum derived from the glazing sludge. Mullite, the typical crystalline phase of porcelain stoneware products it is not present in these sintered materials. The formation of anorthitic phase interferes with the mullite formation since the anorthitic phase formation occurs at lower temperature than that necessary one for the mullite formation [Andreola et al. 1992]. This microstructural difference does not damage the final properties of the samples obtained, in Table V are reported the technical parameters compared to a commercial product for floor covering.

Microstructural study confirms the XRD analysis, besides puts out the effect of time and temperature on the microstructure. Sintered V125 samples showed that thermal treatments up to 900°C, 60 min is not enough to complete the sintering process. In fact they have a microstructure with grains not completely embedded in a high amount of glassy phase. Instead samples treated at 1000°C, 60 min show a high sintering degree with a residual closed porosity. Crystalline phases as wollastonite, albite and quartz (Fig.1a) with different morphology (needles, plates and grains) were observed. Comparing samples at the same temperature, the increase on the time highlighted an improvement of the sintering process due to the reduction of porosity and both diffusion and grown of crystallites (Fig.1b). Moreover, the investigation of sintered V75 samples at 900°C, 60 min confirmed the positive effect of particle size on sintering. These considerations are in agreement with the density data showed (Table III) where is possible to observe an increase of the density due to the viscous process of densification.

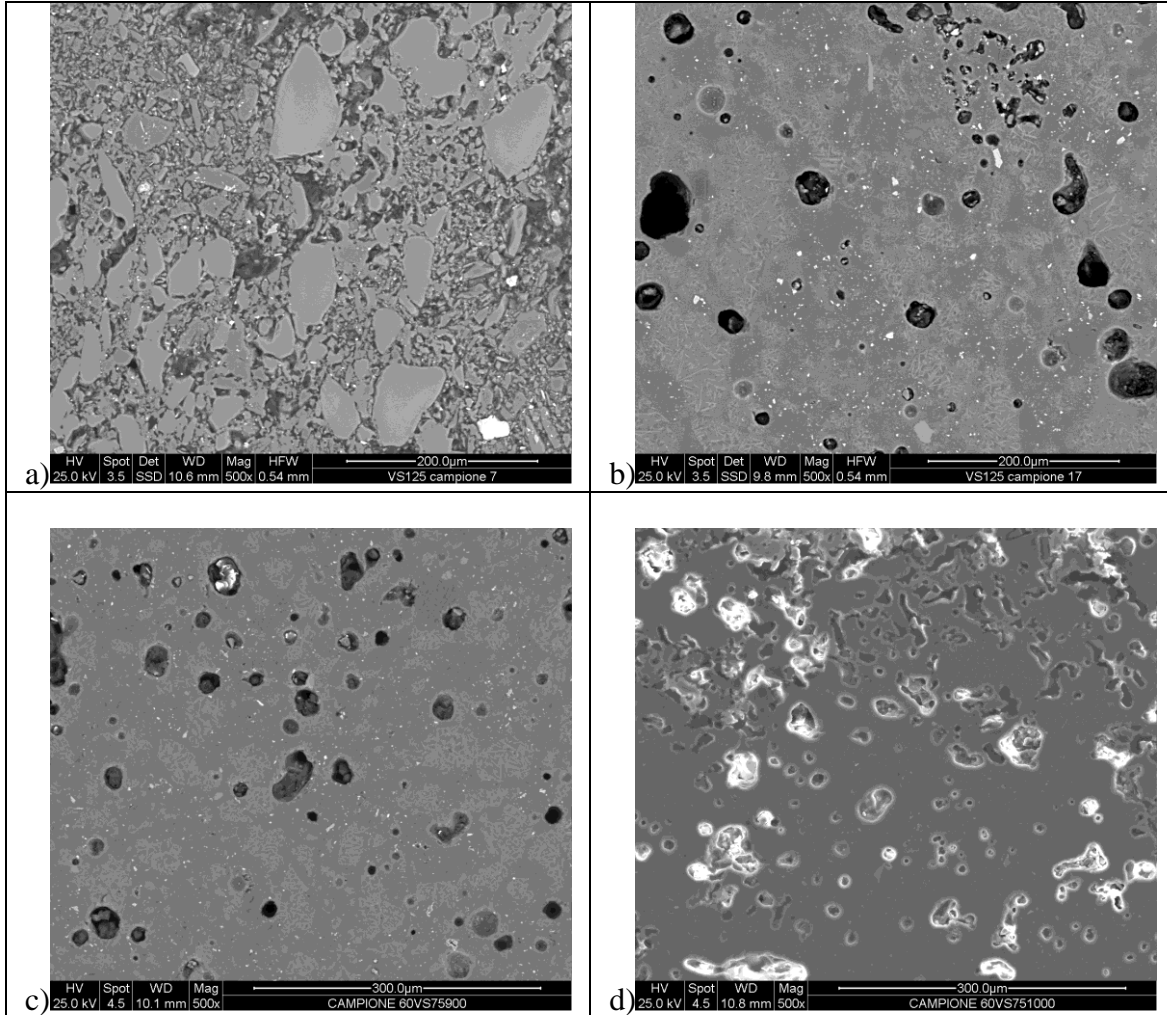


Fig. 1- SEM micrographs of: a) V125 900 °C, 60 min.; b) V125 1000°C, 60 min.; c) V75 900°C , 60 min and d) V75 1000°C, 60 min.

Leaching Test

At the moment the Italian environmental legislation does not contemplate an applicable test to check the leaching onto the end products such as "ceramic tiles" obtained from secondary raw materials (SRM), for this reason we have referred to the advisable methodology for granular and monolithic residues with moderate and irregular shape [UNI 10802]. The glazing sludge (using as secondary raw material) contains small amounts of heavy metals as Pb, Cu, Cr, Ni, Ba, etc. In order to evaluate if thermal treatment is suitable for its recycling, an investigation of harmful substance mobility was performed on the fired samples. Metals mobility has been evaluated by direct comparison of the leachate of as received sludge and the sintered materials thermally treated. For this analysis only V125 and V75 samples fired at 1000°C, 60 min were considered.

Table IV- Leaching test for glazing sludge and the V125 and V75 sintered samples compared to the Italian Standards.

ANIONS/ELEMENTS	GLAZING SLUDGE	VS125	V75	Italian regulation limit All.3-D.M 05/02/98
pH a 20°C	8.63	9.82	9.91	5.5-12.0
Specific conductivity (µS/cm)	145	62.0	65.4	-
Nitrate (mg/L)	<0,02	<0,02	<0,02	50
Sulphate (mg/L)	15,8	2,0	2,7	250
Chloride (mg/L)	8,45	0,27	0,43	200
Fluorine (mg/L)	1,17	0,035	0,012	1.5
Cr (µg/L)	18.5	11.4	6.30	50
Cd (µg/L)	<1	<1	<1	5
Ni (µg/L)	1.60	1.60	1.80	10
Cu (µg/L)	37.9	2.10	3.33	50
Pb (µg/L)	184.8	3.80	1.20	50
Al (mg/L)	0.50	0.5	0.60	--
As (mg/L)	<0.05	<0.05	<0.05	0.05
Ba (mg/L)	<1	<1	<1	1
Co (mg/L)	<0.02	<0.02	<0.02	0.25
Fe (mg/L)	<0.02	<0.02	<0.02	--
Mn (mg/L)	<0.02	<0.02	<0.02	--
Se (mg/L)	<0.02	0.1	0.10	0.01

Positive results were obtained from pH and specific conductivity measures; pH values for the end products are within the rule range (5.5-12.0) and the conductivity values are lower than the as received sludge. These data confirmed that the residual glassy phase presents into the sintered materials succeed to block the ions embedded in the matrix showing a lower release with respect to the materials before thermal treatment.

Regarding metals leaching the glazing sludge shows a high release of some heavy metals, in particular lead value surpass the regulation limit. This residue derives from the glazing phase

and it is constituted by glassy phase and other components (pigments, oxides) which are not capable to bond heavy metals which can be released.

By analysing the different materials leaching, it is possible to observed that V125 and V75 sintered samples show significantly reduced values with respect to the sludge before thermal treatment in fact the mobility of metals like Pb, Cu, Cr, and anions as chlorine and sulphates is strongly reduced.

Semi-Industrial experimentation

Satisfactory laboratory scale and leaching tests results permitted to hypothesize the obtainment of floor or wall tiles at lower temperatures (900-1000°C) than commercial products (1100-1200°C) using secondary raw materials.

The semi-industrial scale activity has been carried out within a collaboration with a ceramic company where the samples were fired. In this phase of the work only the mixture prepared from powders < 75 µm was considered. The experimentation consisted in the preparation of the samples by a similar laboratory procedure as describe above and in their treatment at different firing industrial cycles in order to individuate the optimal firing conditions. On the base of the laboratory results, three industrial firing cycles were chosen at 960°C, 50 min; 1020°C, 54 min and 1087°C, 41 min. The sintering degree was checked by the determination of sintering parameters (W.A%. L.S% and D.A). Young's modulus measures completed the characterization.

Table V- Sintering parameters and mechanical properties for samples fired by industrial cycles

Industrial Thermal Treat.	Water Absorption WA %	Linear Shrinkage LS%	Apparent Density A.D (kg/m³)	Young's modulus E(GPa)
(960°C, 50 min.)	8.2÷11.0	5.55 ÷ 6.25	1908	21.68 ÷ 31.14
(1020°C, 54 min.)	6.6÷8.6	6.72 ÷ 7.42	2025	34.51 ÷ 37.54
(1087°C, 41 min.)	0.04÷0.09	11.34 ÷ 11.72	2281	57.03 ÷ 57.63
Commercial product	<0.5÷3	7.0-8.0	2200	----

From the data reported it is possible to note that the optimum temperature range is around 1020-1080°C, in particular regarding water absorption at 1087°C, the low values permits to classify these materials into BIa Group according to UNI EN 14411 (all.G) rule (BIa W.A% ≤ 0.5%). The properties achieved by these samples are comparable with those corresponding to commercial products using firing cycles at 1200-1250°C. Regarding L.S% the mix glazing sludge and cullet glass favoured the sintering process but the samples show L.S% values higher than the industrial requirements; this fact can causes calibration problems after firing. In order to optimize the linear shrinkage, future developments of the research has scheduled the reformulation of the mixture introducing a reducing plasticity material.

CONCLUSIONS

This work proposes sustainable solutions in residential and non-residential buildings by using ceramic products obtained from secondary raw materials and fired at lower temperatures than traditional industrial cycles. More than 50% of all materials extracted from earth are transformed into construction materials and products. The possibility to avoid the use of natural raw materials, reducing the impact derived from the extraction and the preparation give to this research an important environmental footprint in the sustainability field. Considering that these products containing large amounts of post-consumer materials, they can be benefited to the market, taking into account the new certifications as LEED (Leadership in Energy and Environmental Design).

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