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Utilisation of municipal incinerator grate slag for manufacturing porcelainized stoneware tiles manufacturing

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Abstract

Porcelainized stoneware tiles containing up to 20 wt.% of municipal incinerator grate slag have been fabricated by cold uniaxial pressing and conventional fast firing cycles. The sinterability of these samples was investigated from density and shrinkage measurements together with mechanical (Vickers microhardness and Young's modulus) and esthetical (spot resistance and colour parameters analysis) properties. The comparison with the porcelainized stoneware tiles containing no waste suggest a good compatibility between the ceramic body and the waste that does not significantly change the properties of the final products and the conditions of the firing cycle. Nevertheless, the porosity increase, proportional to the waste content, causes a decrease in density, shrinkage, spot resistance and whiteness.

Keywords: Incinerator slag; Mechanical properties; Sintering; Stoneware; Thermal properties; Tiles; Traditional ceramics; Waste materials

1. Introduction

Incineration represents the total oxidation process of the combustible materials present in the municipal and industrial wastes. The main aims of this technology (in Europe the combustion of untreated waste on a grate has a long tradition) are the reduction in volume, mass and toxicity of the waste, and recovery of energy produced in the combustion process. Although these advantages, during the incineration about 70 wt.% of the incoming waste is transformed into gases, leaving roughly 300 kg/t solid residuals, 250–300 kg/t slag and 20–30 kg/t ash for landfilling or reuse.[1] While the slag is classified as special waste because it is mainly constituted of Si, Al, Ca and Na oxides, the ash, containing significant concentrations of heavy metals, as well as trace amounts of organic pollutants, is classified as hazardous special waste in most countries[2] and must be deposited in special landfills equipped with careful control of the effluents. Currently the total of urban wastes in Italy amounts to 26.10^6 t/year, 7% of them is disposed to incineration. Considering that the quantitative of slag derived from the combustion process arises about 250–400 kg/t burnt residue,[3] it appears evident that its insertion into an alternative productive cycle might represent an alternative recovery option which is interesting from an environmental and economical perspective. This is in line with one of the most important task for the future, i.e. the minimisation of the consumption of traditional raw materials. A good opportunity seems to be offered by the ceramic industry. In fact, the Italian tiles industry, concentrated prevalently in an area of 300 km^2 in the north of Italy (Modena and Reggio Emilia provincies), represents a reference point for the country economy, having produced 606 million sq meters of tiles in 1999.[4] This industrial ceramic district represents the most important productive zone in Emilia-Romagna region with about 80% of the total national tiles manufactured. In particular, a product named porcelainized stoneware (in Italy is called gres porcellanato) is becoming more and more important with regard to its spread from very few market shares limited as to their application fields to more and more diversified ones; the result has been a clear increase in production volumes.

Porcelainized stoneware is an extremely hard and homogeneous ceramic product, originally unglazed, obtained by fast-firing of kaolin-based ceramic bodies

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and containing a large amount of fluxes (typical composition: 40–50 wt.% kaolin clays, 35–45 wt.% feldspars; 10–15 wt.% quartz). The obtained tiles, available in a large variety of colours, shape size and surface finish, are characterised by very low porosity (<0.01% expressed as water absorption as indicated in UNI EN 99) and are ideal for heavy-traffic areas subjected to mechanical and chemical stresses. From this short introduction, it is easy to understand that ceramic sector represents an important reference point for the recycling of incinerator wastes because, by using thermal cycles of sintering with maximum temperature around 1200 °C and time less than 1 h, the raw materials (clays, feldspars and quartz) develop silicatic crystalline phases and glassy matrices capable to block the wastes.

In the present work, grate slag coming from the municipal solid wastes incineration has been used as valuable source of minerals, including SiO_2, Al_2O_3, alkaline and alkaline-earth oxides for the mixing together with a traditional porcelainized stoneware ceramic body. Some technological and esthetical results obtained on the grate slag-containing products are compared to those reached for commercial porcelainized stoneware tiles.

2. Experimental procedures

Cylindrical samples of 4×0.5 cm were produced by using grate slag from the Reggio Emilia (Italy) municipal solid waste incinerator (mainly constituted of Si, Al, Na and Ca oxides). As suggested by previous results, with respect to the ash only this kind of powder is compatible with the ceramic bodies because of the high content of NaCl and organic substances present in the ash responsible of corrosive phenomena in the plants and defects (mainly bubbles and pores) in the final products.[5] The incinerator wastes were analized by using the SEM and EDX techniques. The morphology (Fig. 1a) and chemical analysis (Fig. 1b) of the grate ash shows a powder with an irregular shape containing a glassy phase mainly constituted by Si, Ca and Al. For the fly ash spherical and elongated crystals from SEM image are well evident (Fig. 2a). The corresponding crystalline phase is halite (NaCl) as detected by EDX analysis (Fig. 2b).

The grate slag were added in a typical porcelainized stoneware body (chemical analysis in oxides wt.%: 67 SiO_2–19 Al_2O_3–4.5 (Na_2O+K_2O)–2.5 others—7 loss ignition) in 5, 10 and 20 wt%. Higher amounts produced swelled fired samples having too high porosity and very poor mechanical and surface properties.[5] The compacts were obtained from the powders humidified with distilled water at 6 wt.% by cold pressing at 400 kg/cm^2. Sintering of the pellets was carried out in a laboratory electric furnace following four firing schedules reaching different maximum temperatures from 1140 to 1200 °C, at regular intervals of 20 °C, with a soaking time of 15 mins and natural cooling to room temperature.

2.1. Density and shrinkage

Apparent density measurements were carried out on the sintered samples using the Hg displacement method described elsewhere.[6] Linear shrinkage was determined with an electronic digital calliper as the dimension difference between the green (L_1) and the fired material (L_2) by using the Eq. (1)

$$LS\% = L_1 - L_2/L_1 * 100 \quad (1)$$

2.2. Mechanical properties

Vickers microhardness values were determined on the polished surface of the fired tiles using an indenter (Matzusawa microhardness tester DMH-2) for 15 s at different loads between 25 g and the maximum load tolerable by the sample corresponding to the formation of microfractures. Elastic Young's modulus E was determined by the impulse excitation technique (Lemmens GrindoSonic MK5). This test meets the ASTM 1259 testing method for dinamic Young's modulus.[7]

2.3. Spot resistance

The fired samples were subjected to the methylene blue spot test, that represent an indirect determination of the open porosity of the material. The surface of samples has been exposed to the action of a HCl solution (3% v/v) for 24 h in order to observe possible alterations or loss of the initial surface, then some drops of the methylene blue solution have been sprinkled on the zone pre-treated with the acid. After 24 h the surface washed with distilled water has been observed.

2.4. Colour test

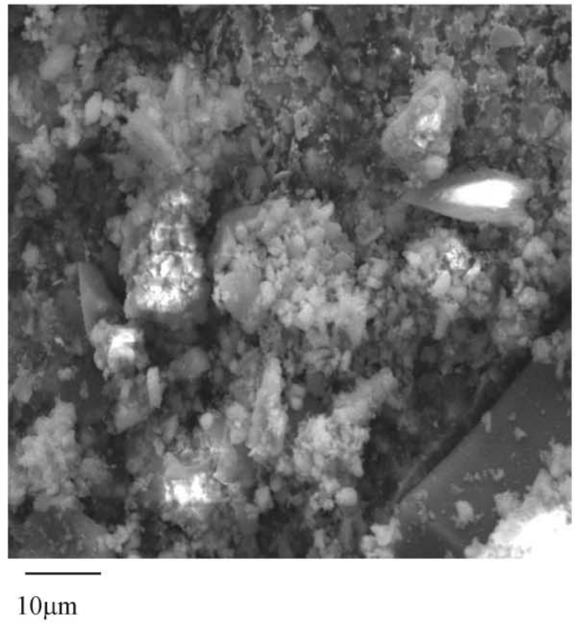
In order to determine the effect of the grate slag addition on the esthetical properties, fired samples were analysed using a UV-vis spectrophotometer (Perkin Elmer, Lambda 19) with a software for colour measurements. The parameter CIELab L^*, a^*, b^* were calculated by the Hunter method.[8]

3. Results and discussion

3.1. Density and shrinkage

The sintering study, aimed to evaluate the change due to the insertion of the grate slag on the fired tiles characteristics, was carried out by comparing apparent densities

(a) SEM image grate slag



(b) EDX grate slag

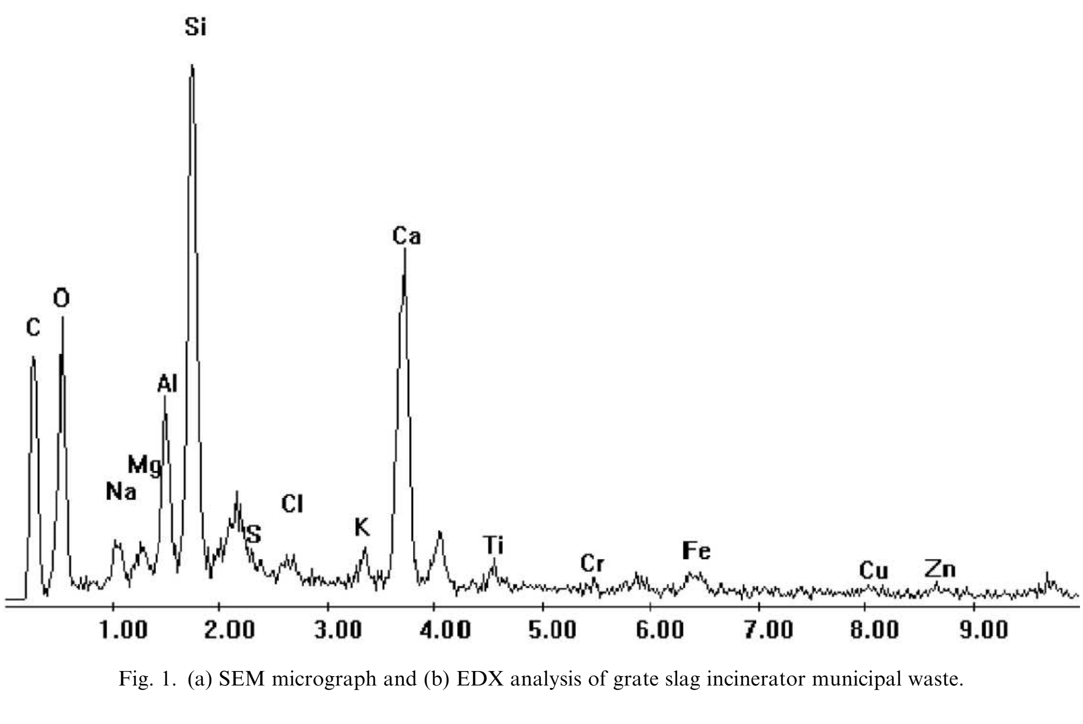
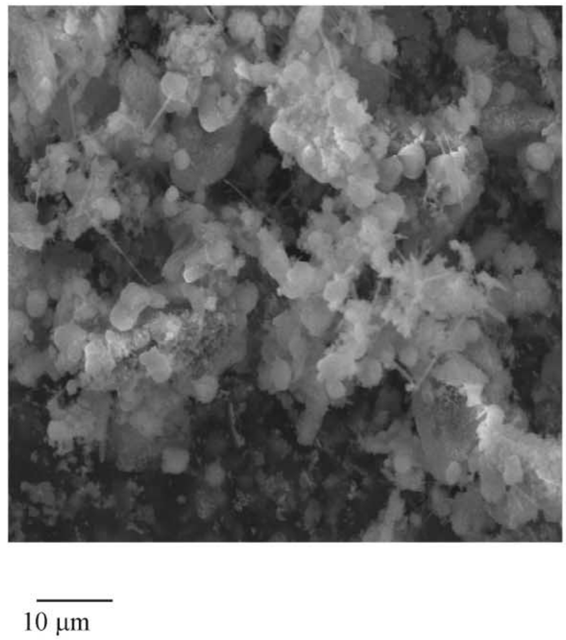


Fig. 1. (a) SEM micrograph and (b) EDX analysis of grate slag incinerator municipal waste.

and linear shrinkage values. Fig. 3 shows that the optimum sintering temperature for the grate slag-containing materials seems to be 1180 °C (instead of 1200 °C, characteristic temperature of the porcelainized stoneware) after that it swells. For each temperature the addition of the waste in the ceramic body decreases both the shrinkage and the density because of the increase in the porosity and the change in the microstructure.

Quartz (SiO_2) and mullite ($3Al_2O_3{\cdot}2SiO_2$) are the only crystalline phases present in the samples containing no waste after firing. The addition of grate slag causes some changes. Mullite phase starts to disappear and simultaneously appears a new phase, anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$)

(a) SEM image fly ash



(b) EDX fly ash

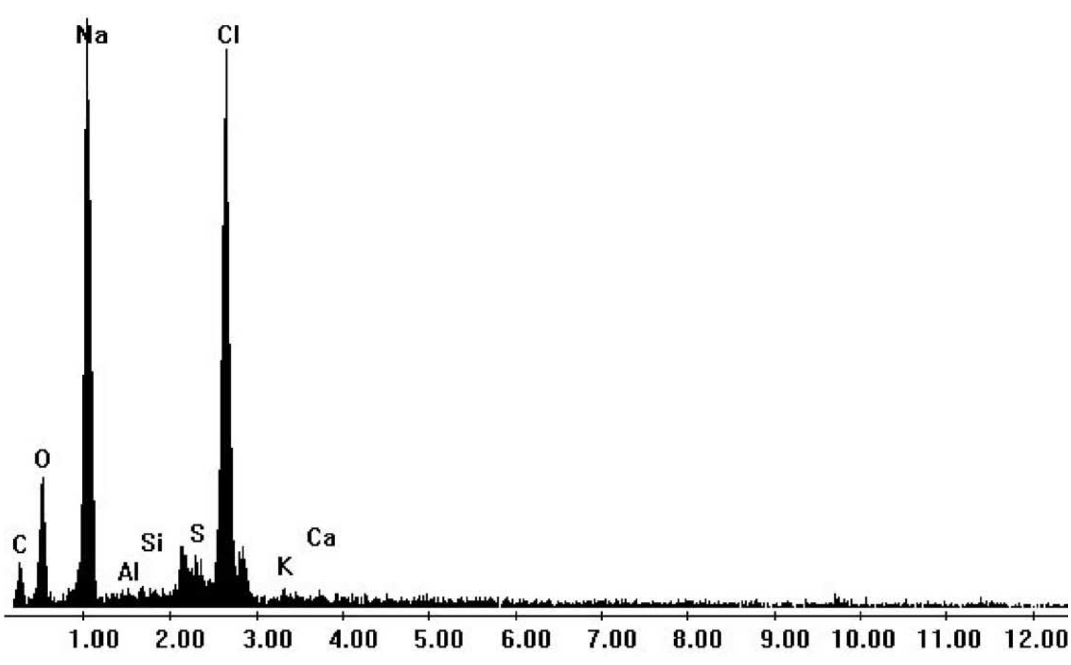


Fig. 2. (a) SEM micrograph and (b) EDX analysis of fly ash incinerator municipal waste.

in samples added with 5 wt.%. Higher amounts of grate slag provoke the growth of anorthite and the disappearance of mullite phase as a function of the percentage added. For all the samples studied quartz is the main crystalline phase. Fig. 4 reports the XRD spectrums obtained for fired samples without and added 20 wt.% grate slag.

3.2. Mechanical properties

The effect of the grate slag into the ceramic tile on the microhardness was studied using the Vickers microindentation technique on the tiles sintered to the best conditions above established (i.e. 1200 and 1180 °C for the porcelainized stoneware and municipal incinerator grate slag-containing tiles, respectively). Table 1 reports the microhardness values measured at the only load corresponding to 50 g. In fact, the measurements made by using 25 g present a high scattering in the results (standard deviation around 40–45%), due to the difficult of the operator in reading the length of the two diagonals (results affected by instrumental and human error). Higher loads are too much for the samples slag-containing, presenting a major fragility with respect to the porcelainized stoneware. Limiting the attention on the data collected with the 50 g load, it is possible to observe no differences between the characteristic value of the porcelainized stoneware and those of the waste-added tiles. Moreover, it is to be noticed that the addition of the waste causes a diminution of the mechanical resistence (10 wt.%). In fact, the microfracture formations appear at lower loads probably due to the increase in the porosity of the material and a change in the crystalline phases (increase of anorthite percentage) corresponding to a change of microstructure.

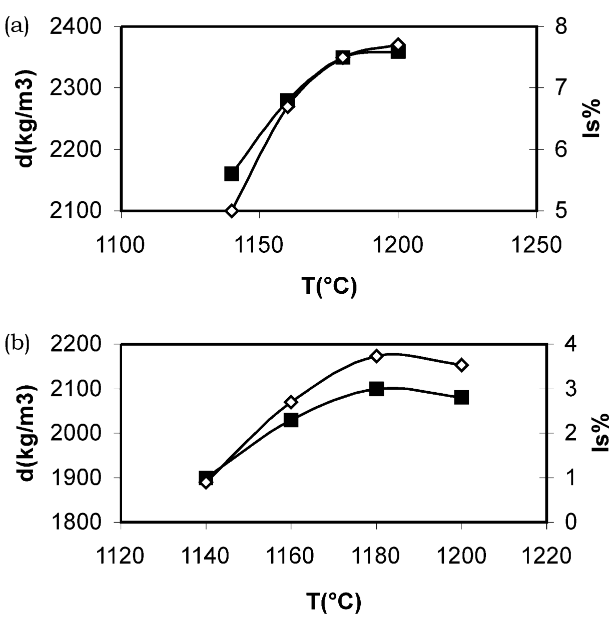


Fig. 3. Apparent density (■) and linear shrinkage (◇) trend as function of temperature for samples: (a) porcelainized stoneware; (b) containing 20 wt.% of grate slag.

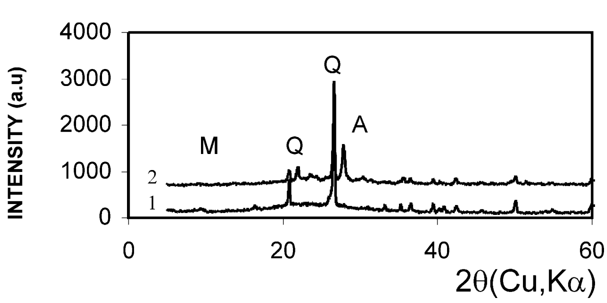


Fig. 4. XRD pattern for the powdered samples: (1) porcelainized stoneware; (2) containing 20 wt.% of grate slag.

The elastic modulus of ceramic materials was determined using the ultrasonic technique with a good approximation.[7,9] As a matter of fact, Young's modulus provides information on the microstructure, it is an index of the rigidity degree and therefore of material compactness. The calculated E values obtained by resonant frequency showed a dependence of the amount of grate slag added. In fact, an important decrease (30%) is evident passing from about 72 GPa (porcelainized stoneware tile sintered at 1200 °C) to 50 GPa (20 wt.% of grate slag-containing sample). These results allow to conclude that the addition of grate slag provokes an increase of the porosity and a decrease of the rigidity of the material.

3.3. Spot resistance

The spot resistance test (Fig. 5) points out an increase of the spot colour intensity with respect to porcelainized stoneware (GP), proportional to the waste content in the sample. In fact, the presence of grate slag amount provokes some microporosity and the change in the microstructure. Similar effect is observed in samples added with electrofilter fly ash.

3.4. Colour tests

In the ceramic industry, the CIELab method is the most utilised to determine the whiteness and colour of

Table 1
Vickers microhardness (measured at 50 g) and Elastic modulus (E) values for the porcelainized stoneware tile (GP, 1200 °C, 15′ soaking time) and porcelainized stoneware tiles grate slag containing (1189 °C, 15′ soaking time)

Sample	Microhardness Vickers (GPa)	Elastic modulus E (GPa)
GP	7.0±0.3	71.6±0.1
S (5 wt%)	7.0±0.3	64.2±0.1
S (10 wt%)	6.9±0.2	59.9±0.1
S (20 wt%)	7.0±0.3	48.4±0.1

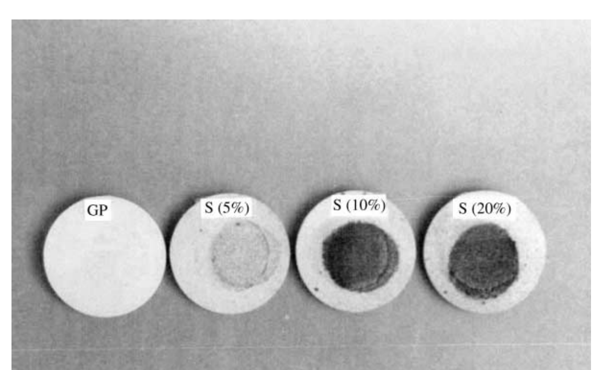


Fig. 5. Photograph of the spot resistance test on samples containing different grate slag amounts.

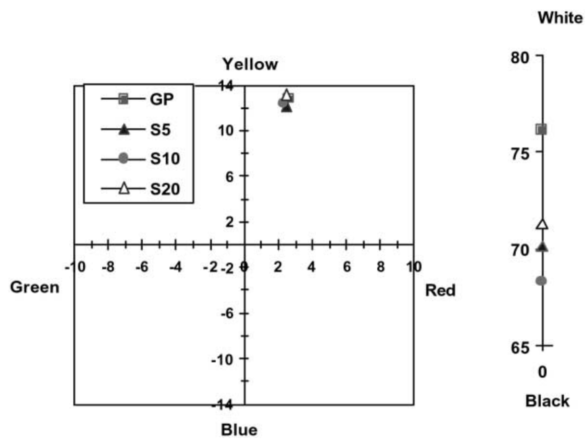


Fig 6. Hunter L^*, a^*, b^* parameters for samples: (GP) porcelainized stoneware; (S5) 5 wt.%; (S10) 10 wt.%; (S20) 20 wt.% grate slag addition.

the tiles by measuring the three parameters L^* (brightness) from absolute white $L=100$ to absolute black $L=0$, a^* (red-green), b^* (yellow-blue) elaborated from the visible spectra.[8]

From the results obtained, a decrease in L^*, a^*, b^* parameters was observed as a function of the waste content. From Fig. 6 it appears evident that the variation of the a^* and b^* Hunter parameters is not significant. Since the esthetical properties of the porcelainized stoneware and its whiteness are more important, a decrease of L^* parameter as a function of the waste present in the body can affect its marketing. The apparent L^* improvement for 20 wt.% grate slag containing sample can be due to a narrow range of sintering derived from the presence of a glassy phase formed that causes an increase of the meltability.

On the basis of these results, it can be concluded that the addition of grate slag should be made in glazed single firing products rather than in high-quality ceramics as unglazed porcelainized stoneware.

4. Conclusions

Studies have been carried out to investigate the sintering, mechanical and esthetical (spot resistance and colour) properties of municipal incinerator grate slag-containing tiles compared to those of porcelainized stoneware ones. The aim is to present an alternative recovery option environmental and economically interesting of this kind of waste in an important industrial sector, the ceramic one, without modifying substantially the process and technological conditions. As a matter of fact, the introduction of the municipal incinerator grate slag in a porcelainized stoneware, a ceramic body with a high sintering degree, does not significantly change the properties of the final products and the conditions of the firing cycle. The most evident effect is represented by the porosity increase, proportional to the waste content, that causes a decrease in density, in shrinkage, and in spot resistance. Furthermore, additions up to 10 wt.% of grate slag do not have a negative influence on the esthetical characteristic of the fired tiles.

These results suggest that the ceramic sector might represent a suitable alternative to use this kind of waste product, but is advisable for the utilisation on ceramic bodies less valuable than the porcelainized stoneware for example fast firing glazed tiles.

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