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The possibility to recycle solid residues of the municipal waste incineration into a ceramic tile body

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The feasibility of utilising solid residues of the municipal wastes incineration such as grate (bottom) ash and electrofilter and sleeve filter fly ash, in combination with a porcelain stoneware body, in the preparation of tiles has been investigated. While the chemical, mineralogical, thermal and rheological characterisation of the waste raw materials carries out some problems arising by using fly ash, these seem to be overcome with the bottom ash. The introduction of up to 20 wt% of this powder into the ceramic body does not substantially change the mineralogical and thermal behaviour of the product.

1. Introduction

The classical hierarchy of principles of waste management in European Policy established prevention as first priority, followed by recovery and finally by safe disposal of the waste. The first concept is applicable to a "quantitative" prevention, that is the reduction of waste production and its hazardousness. As far as municipal solid waste is concerned, it is clear that the reduction of waste production must pass through a change in the way of producing and consuming: longer life products, less packaging, more product reuse. However, this change of mentality has not yet taken place, therefore waste incineration with energy recovery can be seen as a suitable technology to reduce the volume and the hazardousness of the municipal waste. During incineration about 70 wt% of the incoming waste is transformed into gases, leaving roughly 300 kg/t solid residuals, 250 to 300 kg/t grate ash and 20 to 30 kg/t fly ashes for landfilling or reuse [1]. In the European Union, approximately 30×10^6 t of wastes are thermally treated in about 500 incinerators producing yearly 9×10^6 t bottom and 0.75×10^6 t incinerators ashes [1]. These numbers are expected to rise because of decreasing volume and numbers of landfill deposits for untreated waste and changing legal regulations for countries where only a small part of the overall waste is thermally treated. As far as the chemical nature of these residues is concerned, the grate ash is classified as special waste because it is mainly constituted of Si, Al, Ca and Na oxides, while the electrofilter and sleeve filter ashes containing significant concentrations of heavy metals, as well as trace amounts of organic pollutants, are classified as hazardous special waste in most countries [2] and must be deposited in special landfills equipped with careful control of the effluents. In recent times, the attention is being focused on new technologies for the recovering (recycling) of waste materials, including the vitrification, devitrification and the incorporation into ceramic matrices [3–8]. The Italian ceramic tile industry, situated prevalently in an area of 300 km^2 in the north of Italy (Modena and Reggio Emilia provincies), represents a reference point for the Italian economy having produced about 600 million sq meters of tiles in 1999 [9]. This zone in the Emilia-Romagna region produces around 80% of the national tiles production. Inside this industrial sector, unglazed sintered tiles (porcelain stoneware) are becoming more and more important with regard to its spread from very few market shares to more and more diversified ones due to its technical and aesthetical advantages; the result has been a clear increase in production volume. In 1999 the domestic production has reached more than 200 million m^2/year, equal to about 36% of the total output in Italy [9]. The porcelain stoneware is fired in rapid cycles (30–45 minutes) at maximum temperatures of 1200–1230°C, obtaining a product with high physical, structural and mechanical characteristics due to the high level of sintering [10].

In the present study a detailed chemical, mineralogical and thermal characterisation of solid residues of the municipal wastes incineration was performed in order to investigate the possibility to introduce this kind of waste materials into a ceramic tile body. Thermal, mineralogical and rheological preliminary results obtained from the addition of incinerator solid residues to a representative porcelain stoneware body are also presented.

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2. Experimental procedure

2.1. Materials

The solid wastes used in this research were bottom ash and electrofilter and sleeve filter fly ash coming from the municipal incinerator of Reggio Emilia (Italy). A traditional porcelain stoneware ceramic body (called gres porcellanato in Italy) was considered as matrix to obtain ceramic tiles. For the as-received grate ash drying at about 100°C for 24 h, followed by grinding to a granule size of 2 mm for 12 h were necessary. The weight loss occurring during these treatments has been evaluated to be about 35 wt% due to mainly moisture and to the iron and glasses scraps remained as residue on the 2 mm sieve (10 Mesh). Ceramic tiles containing 5, 10 and 20 wt% of the solid residues were prepared and characterised. From the preliminary results an in-depth study was performed for the grate ash only.

2.2. Ceramic samples preparation

Cylindrical samples of 4 × 0.5 cm were prepared by:

- mixing 5, 10 and 20 wt% of the incinerator solid waste raw materials and the porcelain stoneware ceramic body;
- humidifying with distilled water at 6 wt% of the dry solid;
- cold uniaxial pressing at 400 kg/cm^2.

The samples were fired in an electric laboratory gradient furnace with 6 chambers (Nannetti mod.86/S) using a heating gradient of 20°C/min at the 1140–1200°C temperature range using a regular interval of 20°C and isothermal plateau at the maximum temperature of 15 min, trying to simulate an industrial firing cycle. The samples were naturally cooled down.

2.3. Chemical analysis

The chemical composition of the waste raw materials was performed by inductively coupled plasma (ICP-Varian Liberty 200). Chemical analysis of nitrogen, carbon, hydrogen and sulphur was performed by a Carlo Erba Elemental Analyzer (Mod. EA1110). The chloride determination was carried out with a volumetric technique using a standard solution of $AgNO_3$ 0,01N and $K_2Cr_2O_7$ as colour change indicator.

2.4. Mineralogical analysis

X-ray analysis was carried out on a powder diffractometer (Philips PW 3710) with Ni-filtered Cu K_α radiation on both the solid residues and the ceramic samples. Powders of approximately 30 μm particle size in the $2\theta = 5$–$60°$ range were used. The crystalline phases were determined for comparison with tabulated data on the JCPDS files [11].

2.5. Thermal analysis

Thermal characterisation was performed on 30 mg (powder samples <38 μm in size) of both the solid residues and the ceramic samples by a Netzsch DSC 404 from 20 to 1400°C at the heating rate of 10°C/min.

2.6. Rheological measurements

The rheological behaviour of the porcelain stoneware suspensions added to the waste raw materials (5, 10, 20 wt% dry solid content) was analysed to investigate the influence on the wet-grinding step. The suspensions in industrial water 37°F (1°F = 10 mg $CaCO_3$/1) at 65 wt% solids content were milled for 10 min in a laboratory fast ball mill (500 ml) and deflocculated with typical additives used in the ceramic field: sodium silicate (SIL) and sodium tripolyphosphate (TPP) in different amounts (0.3–1.25 wt%). The tests were conducted with a Controlled Shear Rate Viscometer VT550 Haake, with a cylinder coaxial measuring system MV1, under isothermal conditions at 25°C.

3. Results and discussion

3.1. Ceramic samples preparation

The ceramic samples after firing exhibited a different appearance depending on the kind of the waste used. The most adequate behaviour was shown by the bottom ash, while the fly ashes exhibited different problems such as dimensional instability, evident porosity formation and presence of salts on the surface that made difficult the complete characterisation of the corresponding tiles.

3.2. Chemical analysis

The chemical composition of the waste raw materials, reported in Table I, underlines that the fly ash is constituted mainly of sodium and potassium oxides (calcium is also present in the electrofilter fly ash). The grate ash presents the higher SiO_2 and Al_2O_3 ratio ensuring a good compatibility with the traditional ceramic bodies.

Moreover the high percentage of sulphates detected in the fly ash with respect to the bottom ash is confirmed by the elementary analysis (Table II). In fact, in the grate ash there is a significant presence of carbon only, while in the fly ash there is a high percentage of sulphur and sulphur plus carbon in the electrofilter and sleeve filter fly ash, respectively.

From these preliminary data, the grate ash seems to be the most suitable waste material for the mixing with a ceramic body, as appears evident from the chemical composition of the porcelain stoneware ceramic body considered in this work (Table III). The high SiO_2 and

TABLE I Chemical analysis (wt%) of the main oxides in the waste raw materials

Oxide	Grate ash	Electrofilter fly ash	Sleeve filter fly ash
SiO_2	40–50	10–20	0.5–1
Al_2O_3	8–10	10–12	0.3–0.4
CaO	18–20	18–20	1.0–1.5
MgO	2–2.5	2–2.5	0.1–0.2
Na_2O	4–5	6–7	45–47
K_2O	1–1.5	8–10	2.5–3.0
Fe_2O_3	3–4	3–4	0.1–0.5
SO_4^{--}	1–1.5	7–7.5	5–5.5
Cl^{-a}	0.040 ppm	1.976 ppm	2.587 ppm

[a] Titration with $AgNO_3$ 0.01N.

TABLE II Light elements analysis (wt%) performed on the waste raw materials

Element	Grate ash	Electro filter fly ash	Sleeve filter fly ash
N	0.03	0.06	0.04
C	1.69	0.59	6.63
H	0.15	0.06	0.05
S	0.63	2.75	1.85

TABLE III Chemical analysis (oxides in wt%) of the porcelain stoneware ceramic body used

Oxides	Wt%
SiO_2	67.46
Al_2O_3	19.38
Na_2O	2.81
K_2O	1.44
CaO	0.90
MgO	0.66
Fe_2O_3	0.62
TiO_2	0.56
LOI (950°C)	6.98
Total	100.81

Al_2O_3 wt% content present in the kaolinitic clay minerals ensures the refractoriness and leads to the development of a high amount of mullite ($3Al_2O_3 \cdot 2SiO_2$) in the firing step, which is responsible of the elevated mechanical properties.

3.3. Mineralogical analysis

The X-ray diffraction patterns of the waste raw materials under investigation are given in Fig. 1. In the grate ash the main constituent is quartz (SiO_2, file 33-1161), followed by calcite ($CaCO_3$, file 5-586), anhydrite ($CaSO_4$, file 37-1496), ghelenite ($Ca_2Al_2SiO_7$, file 35-755), kyanite (Al_2SiO_5, file 11-46) and enstatite ($MgSiO_3$, file 22-714; 19-769). In the electrofilter fly ash the crystalline phases identified are mainly halite (NaCl, file 5-628) and sylvite (KCl, file 41-1476), followed by anhydrite and ghelenite. The sleeve filter fly ash is constituted by halite only. These mineralogical data further confirm the grate ash to be the more adequate for the mixing with the ceramic body.

The crystalline phases present in the porcelain stoneware body after firing are quartz and mullite ($Al_6Si_2O_{13}$, file 15-776) as shown in Fig. 2. The introduction of the grate ash into the ceramic body (the only waste material that appears to be compatible with the porcelain stoneware) causes the development of a new phase, named anorthite ($CaAl_2Si_2O_6$, file 20-20), in agreement with other studies on traditional ceramic bodies added with waste materials containing calcium compounds [12], and with the phase diagram of the ternary $CaO\text{-}Al_2O_3\text{-}SiO_2$ system [13]. The formation of the anorthite phase decreases the amount of mullite, since the reaction between silica, alumina and calcium compounds to obtain the anorthite phase occurs at lower temperatures with respect to the characteristic temperature for mullite formation, as Fig. 2 shows. In Fig. 2 an increase of the amount of anorthitic crystalline phase is observed, as expected by increasing the grate ash amount in the ceramic body.

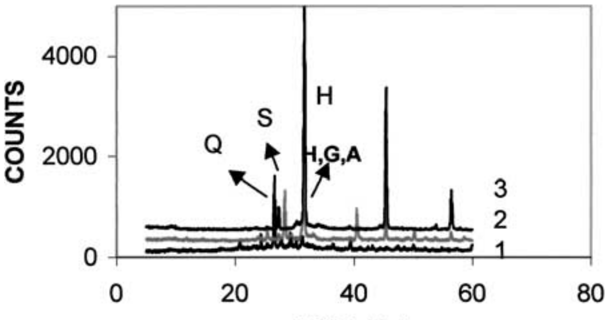

Figure 1 XRD patterns of (1) grate ash, (2) electrofilter and (3) sleeves filter fly ash (H = halite, S = sylvite, G = ghelenite, A = anhydrite, Q = Quarz).

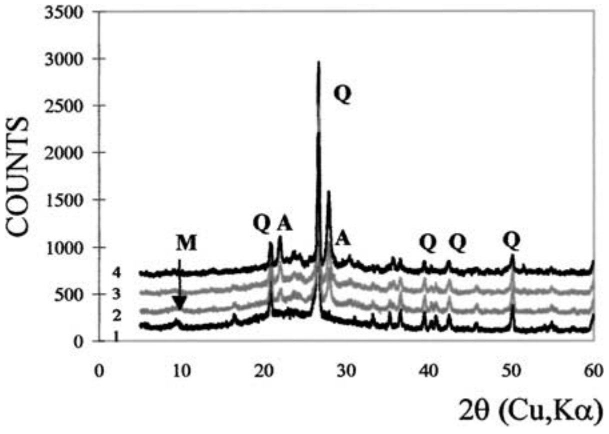

Figure 2 X-ray diffraction spectra of the powdered ceramic products fired at 1180°C containing (1) 0, (2) 5, (3) 10 and (4) 20 wt% of grate ash, respectively (M = mullite, Q = quarz and A = anorthite).

3.4. Thermal analysis

The DTA curves of the waste raw materials (Fig. 3) show a common exothermic event in the 350–550°C temperature range, which is particularly evident in the sleeve filter fly ash, corresponding to the oxidation phenomena of carbon and sulfur, in agreement with the elementary analysis. In the grate ash, the endothermic

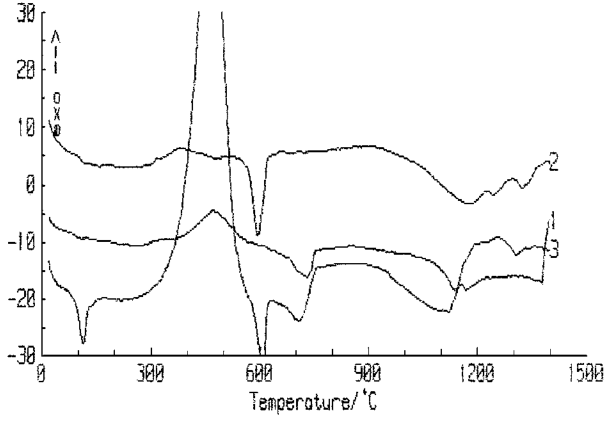

Figure 3 DTA runs of the waste raw materials considered: grate ash (1), electrofilter (2) and sleeves filter (3) fly ash.

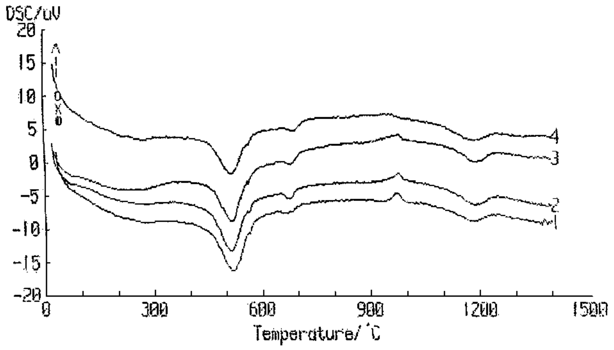

Figure 4 DTA curves of the porcelain stoneware body without (1) and containing (2) 5, (3) 10 and (4) 20 wt% of grate ash.

calcite decomposition occurs around 730°C and finally over 1100°C the raw material melts. The considerable presence of chlorides in the fly ash is detected as an endothermic peak of volatilisation near 600°C.

The DTA thermograms of the porcelain stoneware body containing grate ash (Fig. 4) underline the good compatibility between this waste and the ceramic body used. Increasing the waste content lowers both the endothermic peak at about 530°C, corresponding to the dehydroxilation of the clay kaolinitic materials present in the ceramic body [14], and the exothermic peak at about 980°C due to the mullite phase formation.

3.5. Rheological analysis

The control of the rheological behaviour of porcelain stoneware suspensions mixed with the solid wastes is especially important since these are unusual additions to the ceramic body. In order to evaluate the effect on the porcelain stoneware wet-grinding process, rheological measurements were carried out on the suspensions prepared as described in Section 2.6.

The sleeve and electrofilter fly ash resulted no suitable from a rheological point of view to be added to the ceramic body due to the high amount of chloride compounds soluble causing an important increase of the viscosity values.

For the suspensions containing grate ash at different percentages all the systems have a no Newtonian behaviour (the viscosity is not constant at a given temperature and pressure in this case, but varies with the shear rate and shear stress applied); therefore only "apparent viscosity" values may be determined [15].

The rheological behaviour is plastic and presents time dependence. The yield stress (τ_0) and plastic viscosity (η_p) were obtained by Bingham model. Fig. 5 shows the deflocculation curves obtained using TPP as deflocculating agent, while the SIL was inefficient deflocculant in these conditions. The results highlight that the apparent viscosity values increase as a function of the grate ash amount added to the ceramic body. As it is evident from the Fig. 5 the amount of the TPP introduced to obtain the minimum of the curve increases from 0.75% to 1.00% for suspensions with 5 and 20 wt% of grate ash, respectively. The data obtained have demonstrated the compatibility of the bottom ash addition (up to 20 wt%) with the porcelain stoneware wet-grinding process, allowing to exclude incidental problems during dispersion in water, because in this conditions the apparent viscosity values are not higher than the limit of the industrial workability (200 mPa · s).

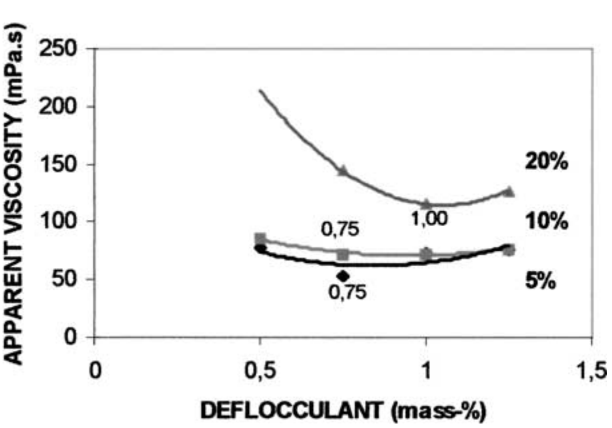

Figure 5 Deflocculation curves for porcelain stoneware suspensions containing different amounts of grate ash (5, 10, 20 wt%) and using TPP as deflocculating agent.

4. Conclusions

The potential recycle of solid residues from municipal wastes incineration in the ceramic manufacture seems to be limited to the grate ash. The high chloride and organic content of the electrofilter and sleeve filter fly ash is a problem for both the industrial plant (corrosive phenomena) and the final product (bubbles, pores, black core...) and therefore these wastes are incompatible with the ceramic body. Tiles containing up to 20 wt% of grate ash into a porcelain stoneware body and fired using a laboratory thermal cycle simulating the industrial conditions show a good mineralogical, thermal and rheological compatibility with the pure porcelain stoneware product. An in-depth study on the mechanical and aesthetical properties of the waste-containing tiles will be useful to evaluate whether or not it is possible the reutilization of the grate ash into a porcelain stoneware body.

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