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Immobilization of iron rich steel industry waste and products characterization



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ABSTRACT

The steel industry produces large amount of wastes, some of which are today used in other industrial sectors; iron oxide rich wastes are difficult to recycle and vitrification is one of the most efficient techniques to stabilize them and produce materials suitable for new applications. The waste considered in this study comes from the purification of fumes captured by hoods during agglomeration process in the sinter plant. These dusts have been vitrified on a laboratory scale by the addition of glass cullet coming from diversified harvest of municipal waste, varying the glass/dust ratio from 80:20 to 50:50. The as produced materials have been characterized by means of XRD analysis and SEM images, and leaching tests have been carried out to evaluate their chemical stability. The electrical and magnetic properties of these iron rich materials have been evaluated too. The resistivity of the samples produced with 45% and 50% of waste are 20 and $1.5 \times 10^3 \Omega$ m respectively, considerably lower than the common soda-lime glass resistivity value ($10^{12} \Omega$ m). Moreover the materials show a ferromagnetic behaviour; the Curie Temperature of the materials lies in the range from T=395 °C to T=533 °C, confirming the presence of magnetite/maghemite phases.

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Introduction

Management of industrial waste is an important issue in the European Community which enforces regulations requiring waste to be treated and recycled. Two of the most popular methods for stabilization and neutralization are the incorporation of the waste in a solid matrix [1-3] and its eventual vitrification [4-11]. Vitrification of the iron rich wastes from steel industry processes converts them into dense glass-like materials which can be used as new raw materials for different types of industries. This process could allow to limit the use of landfills for waste disposal, following the aim of European Directive 2008/98: to apply as a priority order the waste management hierarchy. The waste considered in this

study comes from the purification of fumes captured by hoods during agglomeration process. These wastes are fine dust and they are currently considered dangerous and, after a specific treatment, disposed as "hazardous wastes". Dust from the steel industry contains large quantities of iron oxide and other metal oxide, therefore a suitable treatment to immobilize these metal is necessary. Vitrification is one of the most efficient techniques to incorporate heavy metals into the amorphous structure of glass and, at the same time, toxic organic compounds decompose when high temperatures (such as 1300°C) are reached. This method leaves, however, vitreous products that could require disposal. Although these products are chemically inert, it is important to evaluate chemical durability since they contain a large amount of potentially hazardous elements. Combinations of fine dust from steel industry and glass cullet were vitrified on a laboratory scale; the batch compositions were defined with the objective of stabilizing the highest quantity of waste and recycling the glass or glass-ceramic products in the construction industry.

Moreover, considering the high amount of iron oxides present in the analysed fine dust, electrical and magnetic proprieties of the produced glasses have been evaluated too. The possibility to

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Table 1	
Compositions of glass cullet and ESP fine dust.	

	Glass cullet (%)	ESP (%)
SiO ₂	71.41	6.78
Fe ₂ O ₃	0.33	75.57
Na ₂ O	13.04	0.18
CaO	10.23	9.33
Al_2O_3	1.98	1.39
MgO	2.16	2.22
K ₂ O	0.86	1.44
MnO	1	0.82

 Table 3

 Theoretical composition of the produced glasses.

	G20 (%)	G30 (%)	G40 (%)	G45 (%)	G50 (%)
SiO ₂	58.48	52.02	45.56	42.32	39.09
Fe ₂ O ₃	15.38	22.90	30.43	34.19	37.95
Na ₂ O	10.47	9.18	7.89	7.25	6.61
CaO	10.05	9.96	9.87	9.82	9.78
Al_2O_3	1.86	1.80	1.74	1.71	1.68
MgO	2.17	2.18	2.18	2.18	2.19
K ₂ O	0.98	1.04	1.09	1.12	1.15
MnO	0.16	0.25	0.33	0.37	0.41

exploit the functional properties of these materials in addition to the structural ones, paves the way to new massive smart application, as pointed out in a recent paper on iron-containing glass originated from the mixture of blast furnace slag and flue dust [12]. Electrical and magnetic properties have also great potential to be exploited in the production systems of glasses.

Material and methods

In this work dust and glass cullet were mixed to have a new product, whose properties have been defined here. The used dust has been originated by an abatement technique for emissions from sinter plant, in particular from advanced electrostatic precipitator (ESP), the most common dry electrostatic precipitator to abate emissions. These systems work by generating an electrostatic field across the path of the dust in the air stream. The particles become negatively charged and migrate towards positively charged collection plates. In dry electrostatic precipitators, the collected material is removed by 'rappers', which periodically strike or vibrate the collection plates, dislodging the material and allowing it to fall into collection hoppers [13]; the as collected dust are named ESP fine dust. The glass cullet used in this work comes from diversified harvest of municipal wastes. Their chemical composition (obtained from the suppliers) are reported in Table 1. The glass/dust ratios have been modulated from 80:20 to 50:50 (in weight percentage) as shown in Table 2: the theoretical compositions of the produced materials are reported in Table 3.

The glasses were prepared by melting the starting powders in "fire clay" crucibles, heating rate: 2°C/min, max temperature: 1350 °C for 180 min: the melted materials were casted onto a steel mold at room temperature. The produced glass was characterized by XRD, with a Thermo ARL X'TRA X-ray diffractometer with Si-Li detector, using Co-K α radiation at 40 kV and 40 mA, step size 0.05°, scan rate 1.5°/min in the range 3-70°. In order to assess the chemical resistance of the produced glasses, they were submitted to leaching tests according to UNI EN 12457-2_2004 in distilled water and in acid solution, according to IRSA-CNR method. The samples were immersed in distilled water under shaking. The test time was fixed in 24h. At the end of the test the solution was filtered and analysed by atomic emission spectroscopy in order to quantify the metals released. For the leaching tests in acid solutions, the glasses were put in contact for 24 h with diluted acid acetic solution. The pH of the solution was kept constant to 5 by addition of diluted acetic acid 0.5 N [14] and the analyses of the liquids were carried out by means of atomic emission spectroscopy. The reported SEM images were taken by using a JEOL 6400 scanning electron microscope equipped with an Oxford

Table 2	
Glass/ESP fine dust ratio for the prepared samples (weight percentage).	

	G20 (%)	G30 (%)	G40 (%)	G45 (%)	G50 (%)
Cullet glass	80	70	60	55	50
ESP	20	30	40	45	50

Instruments Link Analytical Si(Li) Energy Dispersive System detector. The samples with the higher amount of iron were submitted to analysis in order to determine their magnetic and electrical properties. Magnetic hysteresis loops were measured at room temperature by a vibrating sample magnetometer in magnetic fields $\mu_0 H$ up to 2 T. Thermomagnetic analysis, consisting of a.c. magnetic susceptibility measurements as a function of temperature, was performed in the temperature range T=20-550 °C in suitable atmospheres (air and Ar). The electrical resistivity at room temperature was obtained by using samples having a rectangular shape with a uniform thickness. Four equally spaced and parallel Au stripes were deposited on the entire samples by vacuum evaporation to ensure low resistance contacts. The resistivity ρ was calculated by applying a fixed current (I) between the external contacts and measuring the voltage drop (V)on the internal ones to avoid possible effects due to non-ohmic contacts. The ρ values are determined by the formula $\rho = (V/I) \times (A/I)$ l) where A is the cross-sectional area of the sample and l is the distance between the two voltage contacts.

Results and discussion

Structural characterization

The first analysis performed to characterize the produced materials was the X-ray diffraction. In Fig. 1 the XRD spectra of the samples G20, G30, G40, G45 and G50 are reported (see Tables 2 and 3 for the compositions). It can be observed that G20 and G30 are completely amorphous; instead, for G40 a partial crystallization of magnetite/maghemite and hematite can be observed. G45 and G50



Fig. 1. XRD spectra of G20, G30, G40, G45 and G50 samples. The samples having the highest amount of iron oxide clearly show the crystallization of magnetite and hematite.

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