Vitrification of electric arc furnace dusts

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Abstract

Electric arc furnace baghouse dust (EAFD), a waste by-product of the steelmaking process, contains the elements that are volatilized from the charge during the melting (Cr, Pb, Zn, Cu and Cd). The results of leaching tests show that the concentration of these elements exceeds the regulatory limits. Consequently, EAFD cannot be disposed of in ordinary landfill sites without stabilization of the heavy metals. In this work, the vitrification of EAFD, from both carbon and stainless steel productions, were studied. The vitrification process was selected as the inertizing process because it permits the immobilization of the hazardous elements in the glass network and represents an environmentally acceptable method for the stabilization of this waste. Glasses of various compositions were obtained by mixing EAFD with glass cullet and sand. The EAFD and the glass products were characterized by DTA, TG, X-ray analysis and by the TCLP test. The results show that the stability of the product is influenced by the glass structure, which mainly depends on the Si/O ratio. Secondary crystallization heat-treatment were carried out on some samples. The results highlighted the formation of spinel phases, which reduced the chemical durability in acid media. The possibility to recover Zn from carbon steel production EAFD was investigated and about 60–70% of metal recovery was obtained. The resulting glass show higher chemical stability than glasses obtained without metal recovery.
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1. Introduction

EAFD is generated by the electric arc steelmaking process. During melting certain elements volatilize and, after oxidation and cooling, are collected in filters. Approximately 1–2% of the charge is converted into EAFD (Zunkel, 1997). About 650–700 kt/year of EAFD are produced in USA and 1 million t/year in EU. About 200 kt/year of EAFD are generated in Italy from carbon and stainless steel production. The disposal of this waste has become a serious problem in recent years due to the fact that the greater availability of steel scrap, which represents a big part of the charge, has increased the production of steel from electric arc furnaces. Considering the current rate of growth it is expected that the world production of EAFD will reach about 5 millions t/year in 2005 (Goodwill and Schmitt, 1994). The dust contains elements such us Pb, Cr, Zn, Cd, Cu, whose solubility in leaching media exceeds the environmental regulatory limits in EU and USA.

Several treatment technologies have been developed and can be divided into two main groups: processes which recover the metals and stabilization processes. The greater part of EAFD presently is treated by a high temperature metal recovery (HTMR) process and successive condensation. This technology allows the recovery of elements with high vapor pressure, such as Zn and Pb, and produces an iron rich residue which can be recycled as part of the furnace charge. This process is efficient for the treatment of dust generated in carbon steel production when the percentage of Zn and Pb is greater than 15–20% (Zunkel, 1997; Goodwill and Schmitt, 1994). The amount of Zn and Pb contained in the dust can be increased by a direct recycling of EAFD in the furnace, if the steel quality is not influenced (Evans and Hogan, 1987; Mankins and Shields, 1996; McCrea and Pikles, 1995). Metal recovery is also accomplished by several hydrometallurgical processes. When metal recovery is not profitable a stabilization process in a cement matrix can be used (Lynn, 1988) as well as vitrification, which is acquiring importance as

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the ultimate mean for the immobilization of the heavy metals contained in the EAFD (Ionescu et al., 1995; Gress and Sarko, 1993; Ek and Schlobohm, 1993; Aota et al., 1995).

In this work results of vitrification of two different EAFD, from stainless and carbon steel respectively, are presented. By mixing glass cullet, sand and EAFD in different ratios several types of glasses were obtained and characterized. The conditions to obtain a partial recovery of Zn from carbon steel EAFD were also investigated.

2. Experimental

The EAFD studied in this work are generated in two different plants: for stainless steel (labeled **EAFD 1**) and carbon steel production (labeled **EAFD 2**) respectively. Leaching tests in 0.5 M acetic acid showed that both samples exceed the environmental regulatory limits; particularly for Cr in **EAFD 1** and for Zn in **EAFD 2**.

Dust chemical analysis was carried out by a EDXRF equipped with a 50 W Rh anode X-Ray tube. The densities was measured by a helium-displacement AccuPyc 1330 pycnometer, the particle size distribution was determined by MALVERN series 2600 laser diffraction technique and the specific surface by ASAP 2000 nitrogen porosimeter. The crystalline phases were analyzed by X-ray diffractometer (XRD), Philips 1830 utilizing a CuKα radiation. The thermal characterization of EAFD up to 1500 °C was investigated by simultaneous thermal analysis (STA), by a NETSCH STA 409 analyzer.

Different batches were prepared by mixing **EAFD 1** or **EAFD 2** with glass cullet and sand. Melting was carried out by a super Kantal-kiln at temperatures ranging from 1450 to 1500 °C for 1–2 h using alumina crucibles, followed by quenching in water and steel mould. In **EAFD 2** batches, different amount of carbon (from 0 to 10%) were added in order to enhance the zinc vaporization during a preliminary heat treatment at 1200 °C for 5 h in air or nitrogen atmospheres.

Glasses were characterized by EDXRF, XRD and STA and the chemical durability by leaching in acid acetic 0.5 M (TCLP).

3. Results and discussion

3.1. Dust characterization

The chemical compositions of the EAFD are shown in Table 1 together with the composition of the glass cullet. Besides Fe oxides, **EAFD 1** is characterized by the presence of Cr and Ca oxides while **EAFD 2** by

Table 1
Chemical composition (wt.%) of **EAFD 1**, **EAFD 2** and glass cullet

	EAFD 1	EAFD 2	Glass-cullet
SiO_2	4.4	5.94	72.53
Al_2O_3	1.48	0.65	0.51
Cr_2O_3	15.85	1.12	–
Fe_2O_3	24.28	52.82	0.11
CaO	20.69	7.50	8.89
MgO	9.6	5.21	3.95
MnO	5.05	5.33	–
ZnO	7.57	13.80	–
CuO	0.41	0.18	–
Na_2O	6.62	0.91	13.81
K_2O	1.76	1.01	0.20
NiO	1.8	0.08	–
PbO	0.49	0.48	–

ZnO. XRD analysis showed that in **EAFD 1** the major crystalline phases are the magnetite–chromite spinel, the calcium carbonate and ZnO. In **EAFD 2** sample magnetite and ZnO are the major phases with traces of FeS.

The particle size is very fine. Laser diffraction analyses show that **EAFD 1** and **EAFD 2** have 34 and 65% of particle size less than 10 μm, respectively; the specific surface resulted as 4.36 ± 0.10 m^2/g for **EAFD 1** and 4.82 ± 0.10 m^2/g for **EAFD 2**. Densities are 3.740 ± 0.002 and 4.257 ± 0.002 g/cm^3, respectively.

TG-DTA up to 1000 °C highlighted that weight loss for **EAFD 1** is about 6%, due to $CaCO_3$ decomposition (600–800 °C), while is about 2% for **EAFD 2**. Above this temperature, weight losses are also observed due to the volatilization of Pb and Zn, accompanied by an endothermic effect in the DTA trace. This effect is more evident in **EAFD 2** trace because of the higher zinc content. Similar results are reported by other authors (Aota et al., 1995).

3.2. Vitrification and products characterization

Using **EAFD 1** and glass cullet in the ratios 25/75, 40/60 and 50/50 three batches were prepared. The compositions, labeled as **G1–25**, **G1–40**, **G1–50** are reported in Table 2. After melting, the chemical stability of the as quenched frit was tested by the TCLP. The results are presented in Table 3 while in Fig. 1, the concentrations of Cu, Al, Pb and Zn are plotted as a function of the percentage of **EAFD 1** in the batch. In Fig. 2, the Si concentration in the leaching solution is plotted as function of the SiO_2 percentage in the glass. It is evident that **G1–25**, **G1–40** are stable glasses while **G1–50** shows solubility in 0.5 M acid acetic. The chemical stability is influenced by the glass structure which mainly depends on the Si/O ratio. When this ratio is less than 0.33 there are no conditions for the formation of a continuos Si–O–Si network and the
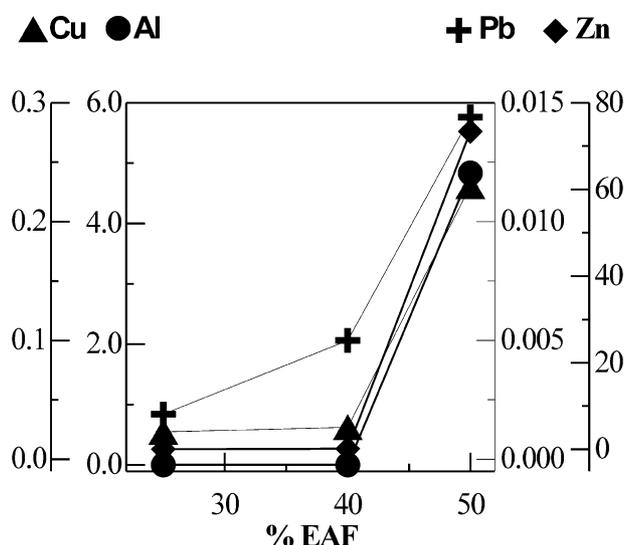
Fig. 1. Cu, Al, Pb and Zn concentration (mg/l) in the leaching test solution as a function of wt.% **EAFD 1** in the batch.
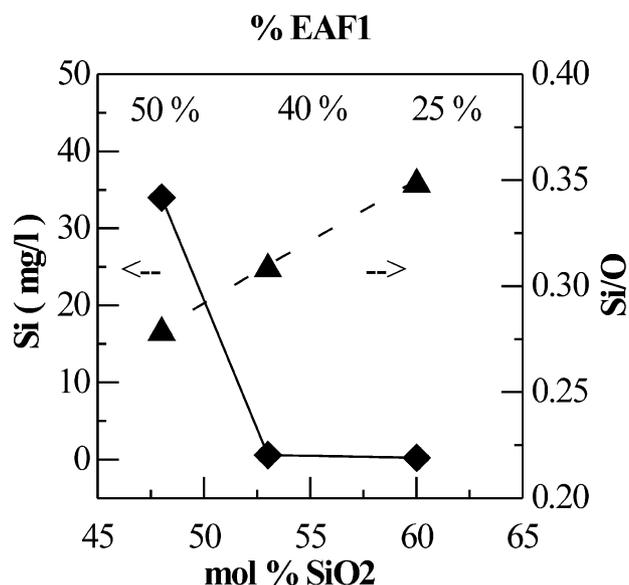

Fig. 2. Si concentration (mg/l) in the leaching test solution and Si/O ratio as a function of SiO_2 mol% in batch and wt.% **EAFD** 1 in the batch.

resulting glass structure is not chemically stable (Appen, 1974). The Si/O ratio for the **G1–25**, **G1–40**, **G1–50** glasses are reported in Table 2 and in Fig. 2.

With the aim of maximizing the **EAFD 1** content in the glass, part of the glass cullet was replaced by sand. Using 45% of **EAFD 1**, 27.5% of glass cullet and 27.5% of sand, the glass labeled **G1–45** was obtained. The melting temperature was increased up to 1500 °C for 2 h due to the higher silica percentage. The results of **G1–45** leaching test are also reported in Table 3. The chemical stability of this glass is very high and comparable with the low EAFD content composition **G1–25**.

Another aspect influencing the chemical durability of an amorphous material is crystallization. In commercial glass-ceramics, crystallization usually improves the chemical durability (Strnad, 1986) due to the formation of stable crystal phases and an increasing of SiO_2 content in the residual glass. However, in particular systems,

such as $Li_2O.SiO_2$, the crystal phase has lower stability than the parent glass. In our previous work (Pisciella et al., 2001), the chemical durability of Jarosite iron-rich glasses and glass-ceramics was investigated. In that case the chemical durability of the crystallized product depended on the ratio between the magnetite and pyroxene crystal phases. When pyroxene was the major phase, crystallization increased the chemical durability in both acid and basic conditions, while when the magnetite/pyroxene ratio was near one no improvements was noticed.

In EAFD-1 glasses the influence of the crystallization on the chemical durability was investigated using the **G1–50** composition, which showed the highest crystallization tendency. The crystallization heat-treatment was carried out for 2 h at 650 °C. The XRD spectra reports 7–10% of cromite–spinel phase in parent glass. It must be pointed out that the term glass is improperly used, because, due to the high Cr, Zn and Fe content, EAFD compositions have a high tendency to crystallize even in drastic quenching conditions. The glass-cera-

Table 2
Chemical composition (wt.%) of the investigated glasses

	G1–25	G1–40	G1–50	G1–45	G2–45	G2–50
SiO_2	56.15	46.12	39.4	50.57	46.9	45.82
Al_2O_3	0.73	0.88	0.99	0.84	0.44	0.37
Cr_2O_3	3.79	6.15	7.74	6.9	0.48	0.58
Fe_2O_3	5.89	9.48	11.87	10.62	25.65	29.52
CaO	11.71	13.47	14.64	11.48	6.48	6.44
MgO	5.3	6.14	6.7	5.3	3.9	2.89
MnO	1.32	1.96	2.46	2.23	2.52	2.85
ZnO	1.81	2.94	3.69	3.32	6.52	2.81
CuO	0.1	0.16	0.2	0.18	0.58	0.07
Na_2O	12.07	11.01	10.31	6.76	5.73	4.50
K_2O	0.57	0.81	0.96	0.84	0.74	0.30
NiO	0.43	0.7	0.88	0.79	0.03	0.03
PbO	0.12	0.19	0.24	0.22	0.22	0.02
Si/O	0.35	0.30	0.27	0.33	0.32	0.31

Table 3
TCLP leaching test results for the **EAFD 1** glasses (mg/l)

Elements	G1–25	G1–40	G1–45	G1–50	GC1–50	Italian limits
Si	0.23	0.6	0.14	33.9	37.7	–
Cr	<0.01	<0.01	<0.01	<0.01	6.90	2
Al	<0.01	<0.01	<0.01	4.84	10.73	1
Ni	<0.01	<0.01	<0.01	0.62	1.93	2
Pb	<0.01	<0.01	<0.01	0.01	0.01	0.2
Cu	0.02	0.04	<0.01	0.23	0.23	0.1
Zn	0.09	0.19	0.12	73.4	109.9	0.5

mics, labeled as **GC1–50**, show 30–35% cromite–magnetite spinels and 20–25% pyroxene.

The results of the chemical stability test are reported in Table 3 and show that the values for Zn, Al and particularly for Cr are higher than the parent glass (see Table 3). The better chemical behavior of the parent glass can be explained by assuming that the spinels are dispersed and enclosed in the amorphous matrix so that the leaching test results can be attributed to the solubility of the glassy phase. After the crystallization, the chemical behavior is influenced by the low stability of the spinels in the acid leaching medium. The Si concentration in the solution is similar for the glass and glass ceramics, so it can be assumed that the solubility of the residual glass after crystallization is similar to the parent glass.

3.3. Recovery of Zn from carbon steel

Glass labeled **G2–45** was obtained by mixing 45% EAFD2, 35% glass cullet and 20% sand. The composition is reported in Table 2. The XRD spectrum shows that 6–9% magnetite spinel is formed in the parent frit.

DTA traces (Fig. 3) present a very intensive crystallization peak at about 720 °C and two melting endo-effects—1125 and 1180 °C. The XRD spectrum of crystallized frit, (2 h at 700 °C) shows 33–36% spinel and 22–26% pyroxene phases.

The **G2–45** glass has a 0.32 Si/O ratio. The leaching test results confirmed that the glass network is chemically stable. Table 4 reports the TCLP results for the parent frit, as well as the results after crystallization (**GC2–45**).

In order to obtain reducing conditions in the batch, different percentages of carbon, ranging from 0 to 10%, were added to EAFD 2. In these tests, 50% EAFD was mixed with 33% glass cullet and 18% sand. The batches were heated in air or nitrogen atmospheres for 5 h at 1200 °C, followed by melting in Al_2O_3 crucibles at 1500 °C for 2 h in air.

The ZnO percentage in glasses are summarized in Table 5. The results showed that with 10% carbon addition in nitrogen atmosphere about 60% of Zn may be recovered from the batch before melting step. The composition of the glass, with 7% carbon addition, is reported in Table 2 as **G2–50**. The XRD spectrum
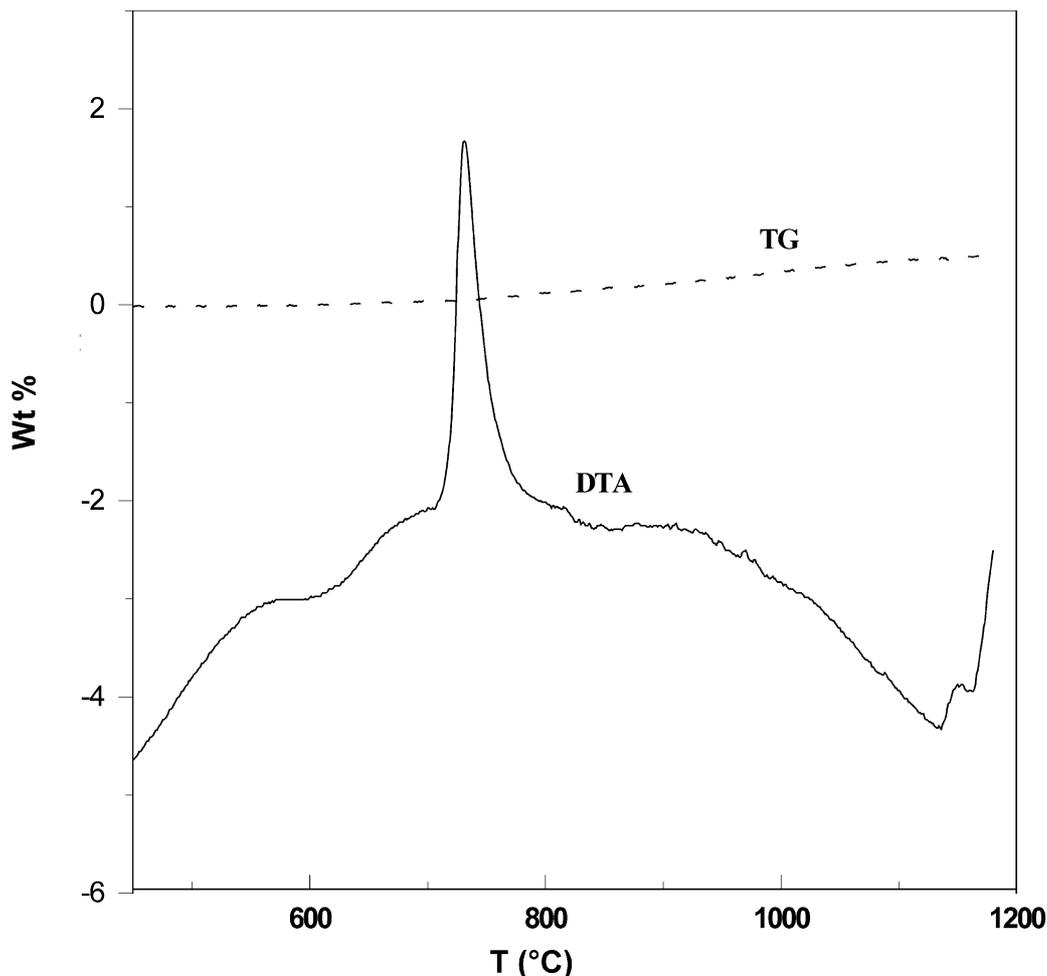

Fig. 3. DTA-TG trace of **G2–45** composition.

Table 4
TCLP leaching test results for the **EAFD 2** glasses (mg/l)

	G2–45	GC2–45	G2–50	GC2–50
Cr	0.06	<0.01	0.04	0.03
Pb	0.01	0.13	<0.01	<0.01
Zn	0.38	12.36	0.18	6.06

Table 5
The ZnO concentration in the resulting glasses as function of the C addition and atmosphere (air or nitrogen)

	wt.% Carbon in the batch				
	0	2	5	7	10
Air atmosphere (ZnO%)	6.47	6.41	6.39	6.27	6.1
Nitrogen atmosphere (ZnO%)	6.21	5.78	4.95	2.81	2.41

shows that 8–10% magnetite spinel is formed in the parent frit; after crystallization (**GC2–50**) the spectrum shows 35–39% spinel and 20–24% pyroxene phases.

The TCLP test, reported in Table 4, highlighted that the metal recovery has a positive effect on the chemical stability notwithstanding a 50% EAFD2 in the batch. After crystallization the chemical durability decreases, which confirm the results obtained with **G1–50** composition.

4. Conclusions

The results demonstrated the role played by the silica network on the glass chemical resistance. When the Si/O ratio is below 0.33 no stable glass was obtained and high concentration of heavy metals are found in the solution.

When crystallization takes place the chemical durability decreases due to the low chemical stability of Fe, Cr, Zn spinels.

Zinc evaporation from carbon steel EAFD batches allows to obtain a more stable glass and eventually recover a valuable zinc portion. Best results were obtained by operating on nitrogen atmosphere and with 10% of carbon addition to the batch.

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