Non Ferrous Slag as Cementitious Material and Fine Aggregate for Concrete

By S. Monosi, P. Giretti, G. Moriconi, O.Favoni and M. Collepardi

Abstract: A non-ferrous slag from the production of metallic zinc was studied as a new ingredient for concrete. It was used in two forms: ground and un-ground material. The ground slag replaced 15% of portland cement, whereas the un-ground slag replaced 20% of the natural sand.

Five different concrete mixtures were studied, all with a water-cementitious materials ratio of 0.60:

- reference mixture with portland cement and natural aggregates;
- concrete mixture with ground non-ferrous slag replacing portland cement;
- concrete mixture with un-ground non-ferrous slag replacing sand;
- concrete mixture with ground non-ferrous slag replacing portland cement and un-ground slag replacing sand.

Additionally, for comparative purposes, a ground granulated blast-furnace slag was used to replace 15% portland cement.

The following properties were studied: compressive strength; heat development through change in temperature; and immobilisation of heavy metals of the non-ferrous slag through water-leaching tests.

- The compressive strength development of the concrete with the ground non-ferrous slag was the same as that of the corresponding concrete with ground, granulated blast-furnace slag;
- When un-ground slag was used to replace sand there was a negligible decrease in the early compressive strength;
- When both ground and un-ground non-ferrous slag were used there was a significant retardation in the development of compressive strength during the first 2 days;
- The early heat development was slightly reduced due to the portland cement replacement and the temperature peak was significantly delayed when both ground and un-ground non- ferrous slag were used;
- The leaching by water of heavy metals from the hardened specimens was negligible and then the immobilisation of zinc and lead of the slag into the cement matrix was very effective.

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INTRODUCTION

With the beginning of the twenty-first century we are entering in an era of sustainable development, since it will not be possible, in the future, to consider technological aspects only, without giving equal importance to the ecological balance in the planet earth (1).

From this point of view, cement and concrete industries can be considered to be environmentally friendly since a large amount of waste materials, such as fly ash or blast furnace slag, can be advantageously used in manufacturing cementitious products. In other words, the use of fly ash and blast-furnace slag in cement and concrete industries is helpful for both manufacturing cementitious products with improved properties (for instance durability) and for reducing the disposal of waste materials.

However, other waste materials are available, for instance from non-ferrous metallurgical industries, which should be taken into consideration as supplementary cementitious materials. Not necessarily all those waste materials can act as effective additions as fly ash or blast furnace slag do. Nevertheless, these waste materials should be studied in order to assess both their influence on the concrete properties and side effects on the environmental compatibility such as the release of dangerous emissions (2).

The purpose of the present research is to study the possible utilisation of a non-ferrous metallurgical slag from the zinc industry as an ingredient for concrete replacing cement and/or natural sand. This is an other example of reuse of waste material to bring the concrete industry into new era of sustainable development.

EXPERIMENTAL: MATERIALS AND METHODS

Cementitious Materials. Portland cement, granulated blast-furnace slag (GBFS) and non ferrous-slag (ISS) from Imperial Smelting process (metallic zinc industry) were used as cementitious materials. Table 1 shows the chemical analysis of these materials.

Both GBFS and ISS were ground to approximately the same fineness in a laboratory mill so that the percentage of retained material on the 0.180 mm sieve opening was 0.1% for both. Blended cements were manufactured by replacing 15% of portland cement with ground GBFS or ground ISS. Compressive strength of standard mortars according to European Norms (EN 197) with a *w/c* of 0.50 and sand/cement of 3 are shown in Table 2 and indicate that blended cements are as strong as portland cements at 28 days with lower strength at early curing age (2 days).

Aggregates. Natural sand and gravel were used as aggregates. For some special mixtures un-ground ISS was also used as fine aggregate to replace 20% of natural sand. Figure 1 shows the particle size grading of these three aggregates.

Concrete mixtures. Three concrete mixtures with ISS were studied, all with a water-cementitious material ratio (*w/cm*) of 0.60:

a) concrete mixture with ground ISS replacing portland cement (15%);

b) concrete mixture with un-ground ISS replacing natural sand (20%);

c) concrete mixture with ground ISS replacing portland cement (15%) and un-ground ISS replacing natural sand (20%).

Moreover, two reference concrete mixtures, again both with a *w/cm* of 0.60, were produced for comparative purposes:

d) concrete mixtures with portland cement and natural aggregates;

e) concrete mixtures with ground GBFS replacing portland cement (15%);

Table 3 shows the composition of the five concretes where the slump level was kept in the range of 220-240mm;

Methods. Concrete specimens were compacted and cured at room temperature. The following properties were measured:

- compressive strength;

- change in temperature due to heat of hydration;

- release of heavy metals (zinc and lead) from ISS through leaching tests.

Compressive strength measurements were carried out on cube specimen (100 mm) cured at 23 °C and R.H. of 95% for a period ranging from 1 to 90 days.

Change in temperature measurements were carried out by a thermocouple into concrete specimens placed at an initial temperature of 23 °C in polystyrene formworks for at least 96 hours.

Release of heavy metals tests were determined by measuring the concentrations of zinc and lead ions in containers where 5 litres of water at 23 °C was kept in contact with each cube concrete specimens (100 mm); than the concentration of Zn and Pb in water was measured by ICP AES (Inductively Coupled Plasma Atomic Emission Spectroscopy).

RESULTS

Figure 2 shows compressive strength as a function of the curing time for the two reference mixtures, with portland cement (CEM I 52.5 R according to EN) and GBFS blended cement (CEM II/A-S 52.5 R according to EN), and for the ISS blended cement (CEM II/A-Q 52.5 R according to EN), all with natural aggregates. There is no difference between the strength of the concretes with the two blended cements with 15% of GBFS or ISS: both are slightly lower than that of the portland cement concrete. For instance, the 28-day compressive strength is 43 Mpa for the portland cement concrete, 38 Mpa for the ISS blended cement concrete and 37 Mpa for the GBFS blended cement mixture.

Figure 3 shows the compressive strength of the portland cement mixture and natural aggregate and that of the two concrete with either portland cement or ISS blended cement both with the un-ground ISS replacing 20% of natural sand. When un-ground ISS replaces the natural sand in the portland cement mixture there is a negligible decrease in the early compressive strength (Fig.3). When ISS is used as both ground cementitious material and natural sand there is a significant decrease in the early strength (no strength at all at 1-2 days) and only a slight strength decrease at later ages (7-90 days). These results can be related to the effect of the ISS slag addition on the hydration rate of portland cement.

Figures 4 and 5 (related to the thermal change caused by the heat development rate) indicate that there is a negligible retardation (in terms of the delay of thermal peak) in the early portland cement hydration when either portland cement is replaced by 15% of ground ISS (Fig.4) or natural sand is replaced by 20% of un-ground ISS (Fig.5). On the other hand, in the presence of both ground and un-ground ISS, the delay of the thermal peak from about 10 hrs to about 42 hrs (Fig.5) indicates that there is a strong retardation in the portland cement hydration. This can explain why at 1-2 days there is no strength in the presence of ISS replacing both 15% of Portland cement and 20% of natural sand (Fig.3).

The retardation, which is much lower when ISS is used to replace either portland cement (Fig.4) or natural sand (Fig.5), can be related to the effect of heavy metallic ions (such as those available in the ISS waste) on the early portland cement hydration (3).

Leaching tests for zinc and lead ions are shown in Fig 6 and 7, respectively. There is no problem in the release of zinc which is negligible, and lower than the limit of 3 mg/l in the Italian Standard (4), regardless of the use of ISS in replacing cement and/or natural sand (Fig.6).

As far as the lead is concerned, the concentration of the released metal is significantly higher in concrete mixtures containing ISS with respect to the reference mixtures with portland cement or GBFS-cement (Fig.7). However, the lead concentration is significantly lower than the limit of 50 µg/L in the Italian Standard (4). Moreover, the lead release is very low (about 5 µg/L vs. 50µg/L of the Italian Standard) when ISS is used to replace 15% of portland cement.

CONCLUSIONS

The compressive strength of concrete mixtures with a non ferrous ground slag (from the Imperial Smelting process) replacing 15% of portland cement is slightly lower (38 vs. 43 Mpa at 28 days) than that of the reference mixture. The strength reduction is very close to that of concrete with ground blast-furnace slag replacing 15% Portland cement.

The strength reduction is negligible when the non- ferrous un-ground slag is used to replace 20% of sand. However the combined used of both ground and un-ground slag significantly reduces the early strength (1-2days). This effect is related to the retardation of the portland cement hydration measured through the delay in the thermal peak due to the heat development.

The retardation can be related to the effect of metallic ions, such as those (Zn, Pb, etc) present in the non-ferrous slag, on the portland cement hydration.

There is no substantial problem for the release of Zn and Pb from concretes when the ground non-ferrous slag replaces 15% of portland cement. With the use of both ground and un-ground non-ferrous slag to replace portland cement (15%) and natural sand (20%), the release of Pb is higher (32mg/L) but lower than the limit of 50 mg/L of the Italian Standard.

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(3) M. Collepardi "Water Reducers/Retarders", Chapter 3, Concrete Admixtures Handbook, Editor: V. S. Ramachandran, Noyes Publications, pp. 116-210.

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Table 1 - Composition of the ISS non-ferrous slag from Imperial Smelting process

Constituents	Percentage
FeO	29.85
CaO	15.37
SiO2	14.65
Al_2O_3	5.43
MgO	1.30
K_2O	1.11
Na_2O	0.86
Zn	4.77
Pb	2.03
C	0.66
Cu	0.55
SO_4^{2-}	0.39
MnO	0.43
TiO_2	0.19
PO_4^{3-}	0.18
B	0.08
SrO	0.04
Cl^-	0.04

Table 2 Compressive strength of mortars with Portland and blended cements according to the EN/197 European Norms

Cement type (EN/197)	Composition (%)			Compressive Strength (MPa)		Strength class (EN/197)
	Portland	GBFS	ISS	2 days	28 days	
CEM I	100	-	-	42	60	52.5R
CEM II / A-S	85	15	-	35	61	52.5R
CEM II / Q-S	85	-	15	32	59	52.5R

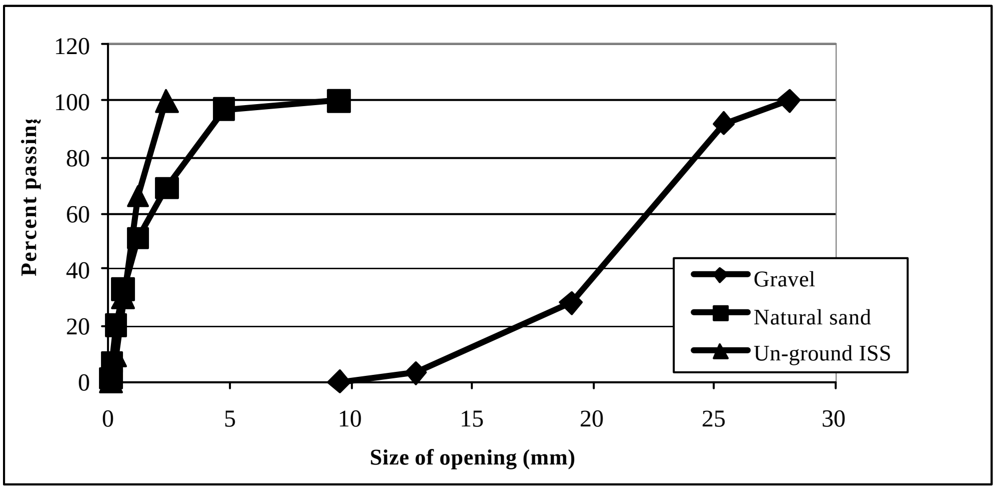


Fig. 1 - Particle size grading of the natural aggregates (sand and gravel) and un-ground ISS.

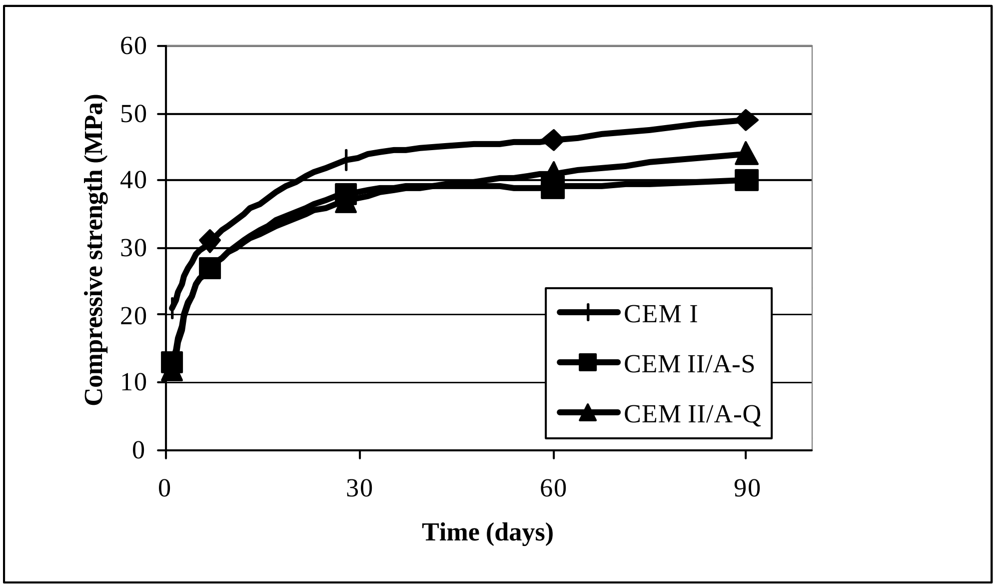


Fig. 2 - Compressive strength of concrete mixtures with CEM I (portland cement), CEM II/A-S (15% ground GBFS) and CEM II/A-Q (15% ground ISS), all with natural aggregates.

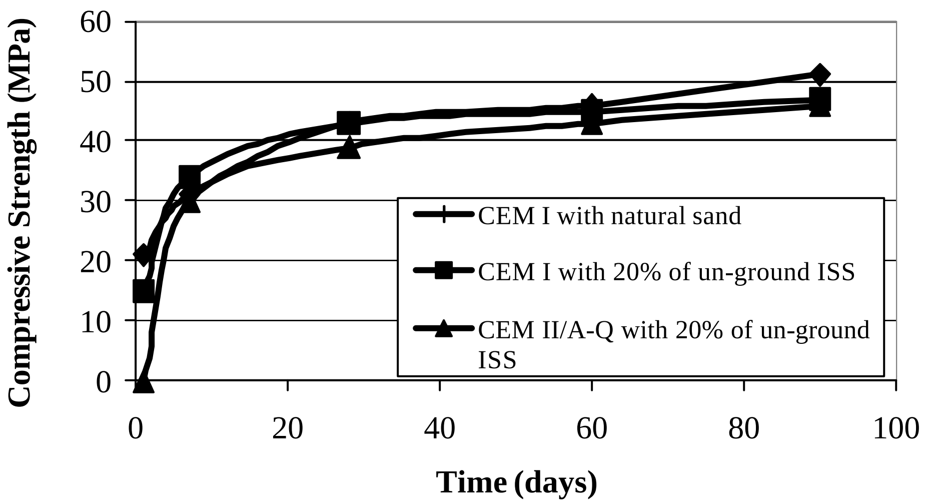


Fig. 3 - Compressive strength of concrete mixtures with CEM I and natural sand or CEM I and CEM II/A-Q (15% ground ISS) with 20% of un-ground ISS replacing sand.

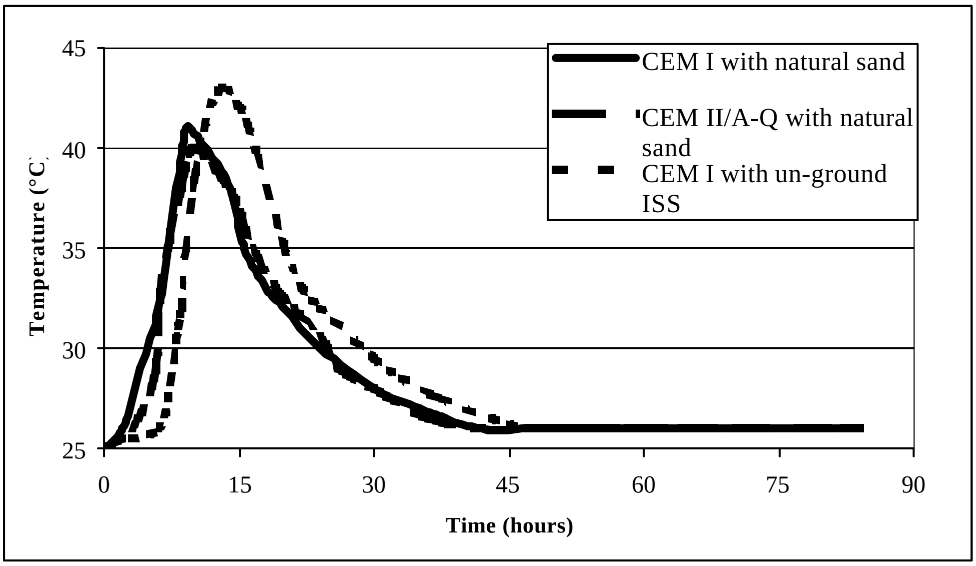


Fig. 4 - Heat development rate of concrete mixtures with CEM I or CEM II/A-Q (15% ground ISS) both with natural sand and CEM I with 20% of un-ground ISS replacing natural sand.

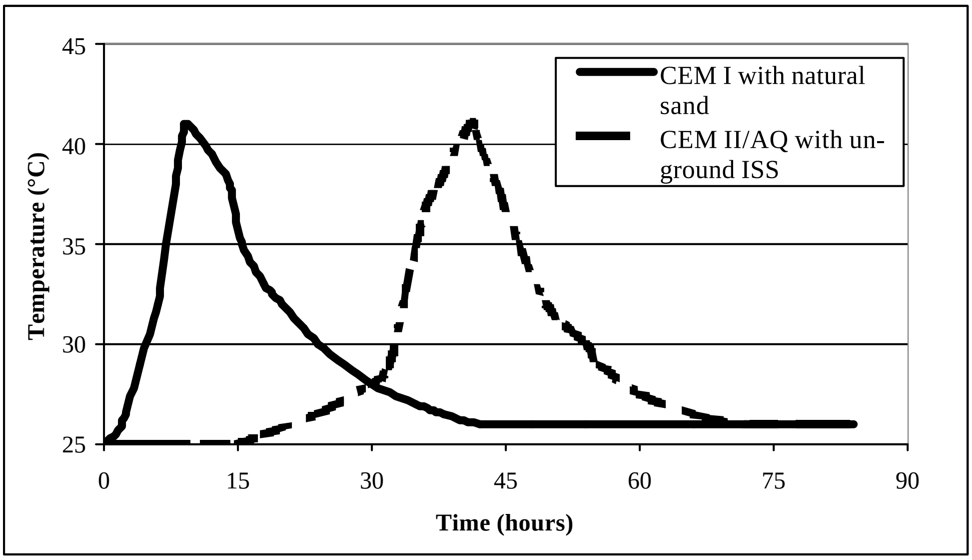
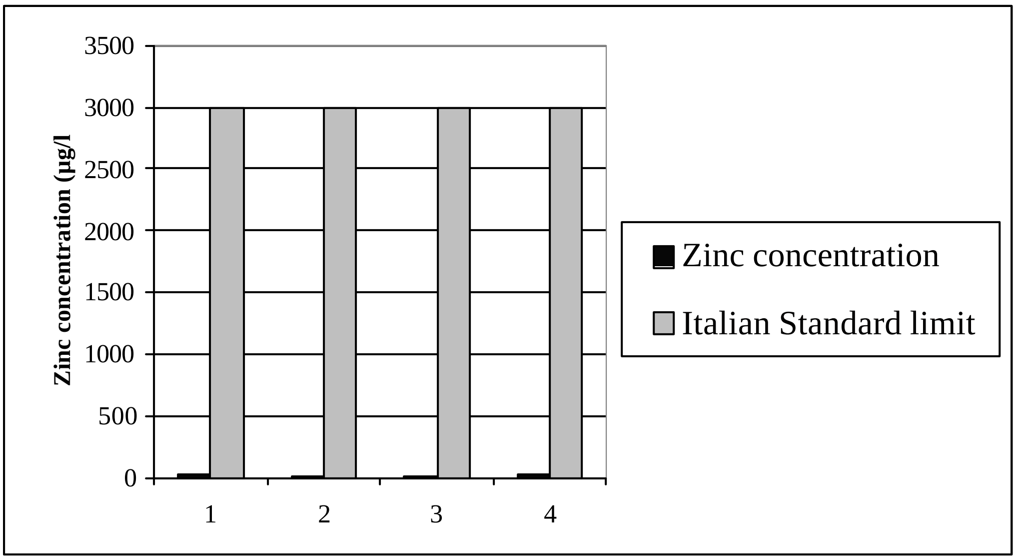
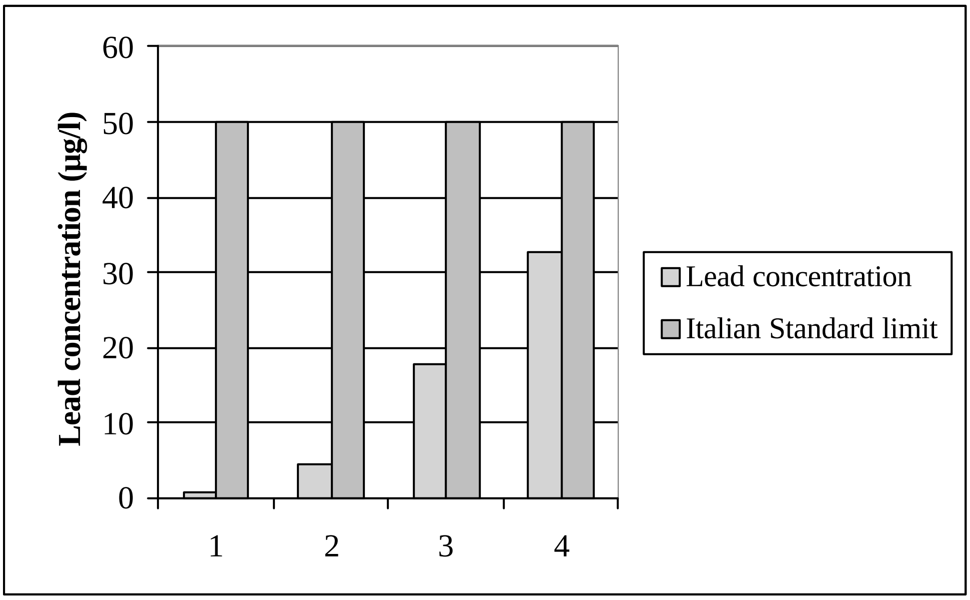


Fig. 5 - Heat development rate of concrete mixtures with CEM I and natural sand or CEM II/A-Q (15% ground ISS) and 20% of un-ground ISS.



1: CEM I and natural sand
2: CEM II/A-Q and natural sand
3: CEM I and un-ground ISS (20% replacing natural sand)
4: CEM II/A-Q and un-ground ISS (20% replacing natural sand)

Fig. 6 - Release of zinc from concrete mixtures vs. Italian Standard limits (3000 µg/l).



1: CEM I and natural sand
2: CEM II/A-Q and natural sand
3: CEM I and un-ground ISS (20% replacing natural sand)
4: CEM II/A-Q and un-ground ISS (20% replacing natural sand)

Fig. 7 - Release of lead from concrete mixtures vs. Italian Standard limits (50 µg/l).