Pergamon

Cement and Concrete Research, Vol. 26, No. 9, pp. 1381-1388, 1996

0008-8846/96 $15.00 + .00

PII S0008-8846(96)00121-4

USE OF GRANULATED SLAG FROM LEAD AND ZINC PROCESSING IN CONCRETE TECHNOLOGY

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(Refereed)
(Received July 21, 1995; in final form June 24, 1996)

ABSTRACT

The possibility of using granulated slags resulting from the smelting of lead and zinc in partial, or total replacement of sand in mortars and concretes, has been examined. The major components of these vitreous slags are Ca, Si, Fe and Al compounds with lead concentration of a few percent. They have suitable particle sizes for use as sand and the slag mortars and concretes studied here yielded satisfactory mechanical strengths. The extraction of lead by acid eluants might however create some problems when concretes containing these slags have to be disposed off.

Introduction

Industrial by-products can be used to advantage in cementitious materials technology. It is often possible to obtain products with superior properties at lower costs, and at the same time solve to some extent the problem of waste disposal and extracting natural materials from quarries (1-4).

Traditionally, slags from iron process metallurgy have found wide application whereas those resulting from the smelting of non-ferrous metals such as copper, lead, nickel, etc. are only just beginning to be used on a limited scale (5-16). Generally the latter are highly vitreous CaO-Fe_2O_3-SiO_2 systems.

Because of the environmental hazard created by lead, it would be particularly significant if slag from lead smelting could be rendered inert by using it in the manufacture of concrete. The pollution caused by this metal, attributable in part to the dumping of slags, is the cause for much concern in the vicinity of metallurgical plants (17).

Two possible uses of this type of slag are suggested in the literature:

-as a pozzolanic admixture to cement, after fine grinding (over 4000-5000 cm^2/g Blaine (1);
-as a substitute for sand, taking advantage of the fact that their particle sizes are generally very similar to the fine fraction of aggregates used in concrete manufacture (18).

Here the latter possibility has been examined, using slags produced by the Kivcet SS (lead smelting) and Imperial Smelting (mainly zinc, to a lesser extent lead) plants on the industrial area at Portovesme in Sardinia (Italy) (total output 130,000 tonnes of lead for year; 60,000 tonnes for years of Imperial Smelting slag; 70,000 tonnes for year of Kivcet slag) (19).

The mechanical and microstructural effects of replacing sand with slag have been studied in mortars and concretes.

Finally elution tests have been conducted for the purpose of evaluating the polluting potential of as received slag as well as cementitious materials containing slags in the event of their being dumped after the demolition of buildings.

Experimental

Kivcet (K) and Imperial Smelting (IS) slags were used as received from granulation plants. Mineral composition (using XRD) and chemical composition (using AAS and plasma techniques) were determined together with grain size distribution and porosity (MIP up to 400 MPa). A Portland type CEN ENV 197 class 42.5 cement was used for preparing the mortars and concretes. A class F fly ash, obtained from the combustion of a South African coal was added to some mixes.

Mortars were prepared with water/cement ratio of 0.50 (by mass) using either normal sand (aggregate/cement=3) or slag as a replacement on the sand. In the latter case an equivalent mass of sand was substituted (K and IS) or an equivalent volume (Kv and ISv) to allow for the difference in specific gravity.

Test specimens measuring $4 \times 4 \times 16$ cm were prepared and aged for up to 12 months. Composition of concrete used in the tests is shown in Table 1. Cubic test specimens with 16 cm side were manufactured and tests were conducted after 28 days.

Elution tests were performed on the as received slag as well as on sample of concrete crushed to 10 mm. 100g of material were added to 1600 cm^3 distilled water or an acetic acid solution with pH=5 (kept constant in the test) or a saturated calcium hydroxide solution and placed in a agitator (20 cm high, 12 cm diameter cylinder with double propellers, 120 revs at minute) for 24 hours at 20°C (20). Metal content of eluates was determined using the plasma technique (ICP-OES).

Results and Discussion

Characteristics of the Slags. Both types of slags were essentially vitreous; gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$) and cristobalite (SiO) being the minor crystalline component of the K slag. Similarly, iron oxides have been observed in the IS slag. Table 2 shows the chemical

TABLE 1

Composition of the concretes (in Kg/m^3). In I and II the Gravel (Grav.) is Calcareous, in III it is Siliceous

	I			II			III		
	BB	KB	IB	BP	KP	IP	BFA	KFA	IFA
cem.	350	350	350	200	200	200	350	350	350
fly ash	---	---	---	---	---	---	50	50	50
water	150	150	150	160	160	160	180	180	180
sand	1000	750	750	1000	750	750	950	650	650
slag	---	250	250	---	250	250	---	250	250
grav.	950	950	950	950	950	950	950	950	950

TABLE 2

Chemical Composition of the Slags (% by Weight). Limit Concentration: Italian Act 915/82; if>0.5: Toxic; if>0.01: Very Toxic

%	SiO_2	Al_2O_3	FeO	CaO	Zn	Pb	Cu	Cd	Hg	As
slag K	18.3	5.5	26.1	15.6	14.0	3.6	0.2	0.008	<0.009	0.15
slag IS	11.3	5.5	52.9	3.3	9.8	1.4	0.6	0.001	<0.009	0.18
limit conc.	---	---	---	---	---	0.5	0.5	0.01	0.01	0.01

composition on the two slags. The major components are FeO, SiO_2, CaO and Al_2O_3, but significant amounts of metals such as zinc and lead are also present. Given the nature and content of the lead, the slag may be classed as "special" waste.

Figure 1 shows the K slag grains. Some are rounded, others polygonal as a result of conchoidal fracture caused by thermal shock induced by granulation. Some grains of the IS slag can be seen in Figure 2. They are generally less regular than the K slags.

The slags are in the form of black grains (K) also containing rusty patinas (IS). Their grain size distribution is given in Table 3 together with that of normal sand required by Italian standards(or EN196/1) for test on cements. Comparison shows considerable similarity between the particle sizes. The predominant fraction by mass is the 0.15-2 mm size range. The grains have very low porosity, on average 1% by volume for the K slag and 3% by volume for the IS slag.

Mechanical Properties of the Mortars. As the slag was to be used "in replacement of sand", first of all experiments were carried out directly on the mortars. For comparative purposes, normal sand was employed, and materials were prepared substituting all the sand with the equivalent amount, either by weight or by volume, of slag.

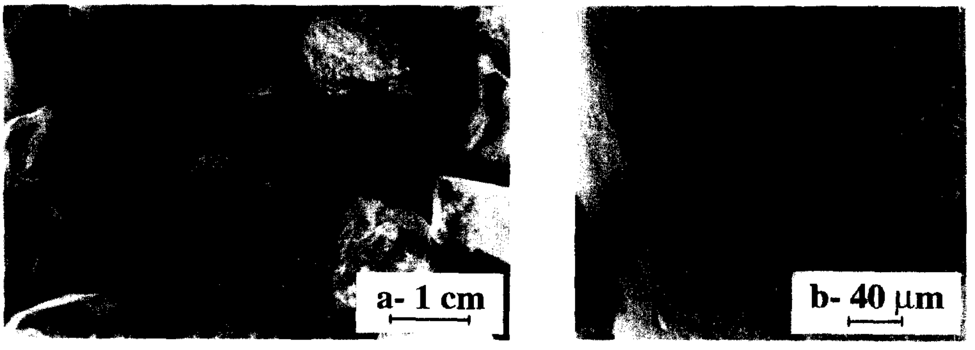

FIG. 1.
Grains of the K slag (a) and detail of the surface (b).

FIG. 2.
Grains of the IS slag.

Flexural strength (3-point) remained almost constant after a month's aging and little difference was observed between the different systems, values ranging on average from 8 to 10 MPa.

Compressive strength versus time is shown in Figure 3. While the mortars manufactured with normal sand (N) attained 50 MPa after 28 days and more than 60 MPa after 12 months aging, those containing the equivalent weight of slag in replacement of sand exhibited much poorer strengths regardless of ageing (40 and 44 MPa after 1 month, 49 and 51 MPa after 12 months, for mortars with IS and K respectively). The results of mortars containing the equivalent amount by volume were very different. Strength of the mortars containing IS slag deteriorated drastically (no more than 35 MPa after 12 months) while those containing K slags, despite initial strengths lower than the control, achieved 60 MPa after 1 month and nearly 80 MPa after 12 months.

Comparison of sections of fracture of the control mortar (N) with that containing the equivalent volume of K slag, after 12 months aging, confirms these results (Figures 4 and 5). In the first case the fracture generally proceeds due to detachment of the binding phase of the sand. In the second case the fracture usually concerns the slag particles and the paste-aggregate bond, one of the weak points of cementitious materials is clearly reinforced.

TABLE 3

Particle Sizes of Normal Sand and as Received Slags (% by Weight)

dimension Φ mm	standard sand %	Kivcet slag %	Imper. Smel. slag %
> 3.15	0	1	2
3.15 - 2	0	14	5
2 - 1	35	49	24
1 - 0.5	34	27	36
0.5 - 0.15	21	8	30
0.15-0.08	10	1	2
< 0.08	0	0	1

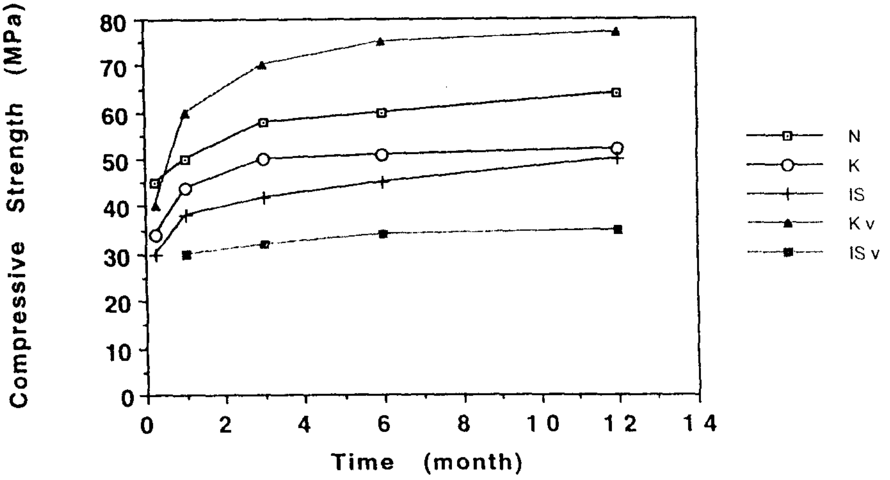

FIG. 3.
Compressive strength of slag mortars (average over 3 measurements).

After a month the pore volume of the different systems was 15-16 % and diminished steadily to reach 10-12 % after one year's aging.

Mechanical Properties of the Concretes. Three series of concretes were prepared so that a broad range of compositions and properties could be tested. In each series one concrete was prepared using normal sand (B) and another two where the sand was partially replaced with K or IS slag. Series I contained 350 Kg/m^3 cement and had water/cement ratio of 0.43. Series II ad lower cement content (200 Kg/m^3) and high water/cement ratio (0.80). In series III, 50 Kg/m^3 type F fly ash was added to the mix with 350 Kg/m^3 cement and water/cement of 0.52. In addition, in the latter series the calcareous coarse aggregate was replaced with a siliceous one.

Table 4 shows the compressive strength and porosity of the different concretes after one month. It clearly emerges that the partial replacement of sand with the amounts of slag tested here does not modify significantly the mechanical properties of the concretes.

FIG. 4.
Section of fracture in mortar N after 12 months aging.

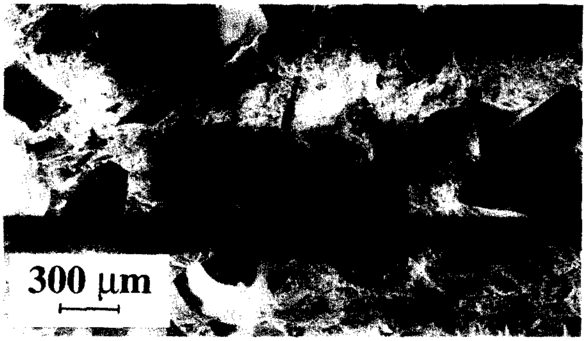

FIG. 5.
Section of fracture in mortar Kv after 12 months aging.

Polluting Potential of Concretes in Landfill. The partial replacement of sand with slag in concretes is both economically and ecologically convenient. However, the issue of waste disposal of this type of concrete when buildings are demolished needs to be addressed. Precipitations, or acqueous solutions produced by others wastes in the landfill might elute but the harmful metals contained in slag which could, for example, seep into the groundwater system.

Elution tests in water and in acetic acid solutions at pH=5 were thus conducted on the as received slags as well on the slag concretes. The waters circulating in landfills are sometimes slightly acid (their pH ranges in fact between 5.3 and 8.5) (22). Elution of slags was also tested in a saturated lime solution, aimed at simulating the behaviour in a strongly alkaline environment, typical of concretes.

The highest concentrations of metals in the slag eluates concerned lead and zinc, as can be seen from the data given in Table 5. K slag is decisively more stable than IS slag in both acid and alkaline environments. However, the Pb content is high enough to warrant classifying the as received K slag as "special, toxic or dangerous" waste (for example in Italy: Act 915/82, art.4).

The as received K slag yields, in the acetic acid eluate, 0.45 ppm Pb. This figure is much lower than that observed for the K slag concretes (3.0, 4.5 and 6.6 for KB, KP and KFA respectively; Table 6). As the Pb concentrations of the other concrete components are totally negligible, this finding may be attributable to the destabilization of the slag in an alkaline environment. In fact in the saturated lime solution the slag released as much as 12 ppm Pb.

The higher pore volume (and hence permeability) of the concretes of series III and especially of series II, accounts for their greater ability to release Pb than the concretes of series I.

TABLE 4

Compressive Strength (c.s.; MPa) and Porosity (p.;% by Volume) of the Concretes

	I			II			III		
	BB	KB	IB	BP	KP	IP	BFA	KFA	IFA
c.s.	55	58	56	20	21	18	43	44	42
p.		ì10			ì20			ì13	

TABLE 5

Concentration of the Elements Eluted out of the as Received Slags

	Kivcet in water	Kivcet in acet. acid	Kivcet in sat. lime	Imper. in water	Imper. in acet. acid	Imper. in sat. lime
Pb, ppm	0.14	0.45	12.0	0.15	228.0	115.0
Zn, ppm	1.7	24.0	0.8	0.52	30.0	1.2

As<0.5; Hg<0.001; Cd<0.03; Cr<0.05; Cr(VI)<0.02; Cu<0.1 ppm

Conclusions

1. The partial or total replacement of sand with granulated slag from the Kivcet and Imperial Smelting plants having the composition examined here is feasible, provided that the mix design does not impair the mechanical strengths of the concrete.
2. The possibility of using these slags as received, with no need for preliminary treatment, is a major economic advantage for concrete industries operating in the vicinity of metallurgical plants and largely solves the problem of their disposal.
3. When designing a material however due consideration should be given to its environmental impact in the event of its being used for landfill. The life of a concrete does not cease with the demolition of the building. Tests carried out on the concrete used here suggest that, despite having a strong neutralizing potential on acid waters, the material releases significant amounts of lead when kept at pH=5. This implies in any case the need to dispose of the material in environments where such acidity cannot be attained by the elution waters.

TABLE 6

Concentration of the Elements Eluted out of the Concretes

	Pb, ppm		Zn, ppm		Cu, ppm		Cr, ppm	
	in water	in acet. acid	in water	in acet. acid	in water	in acet. acid	in water	in acet. acid
BB	< 0.10	0.30	< 0.05	0.80	< 0.10	< 0.10	< 0.10	< 0.10
KB	< 0.10	3.00	< 0.05	60.0	< 0.10	0.12	< 0.10	< 0.10
IB	0.15	9.00	< 0.05	15.0	< 0.10	0.25	< 0.10	0.12
BP	< 0.10	1.10	< 0.05	7.80	< 0.10	< 0.10	< 0.10	0.12
KP	< 0.01	4.50	< 0.05	90.0	< 0.10	0.25	< 0.01	0.12
IP	0.15	10.0	< 0.05	20.0	< 0.10	0.20	< 0.01	0.12
BFA	< 0.10	< 0.15	< 0.05	< 0.20	< 0.10	< 0.10	< 0.10	< 0.10
KFA	< 0.10	6.60	< 0.05	95.0	< 0.10	< 0.10	< 0.10	< 0.10
IFA	< 0.10	5.70	< 0.05	45.2	< 0.10	< 0.10	< 0.10	< 0.10

As<0.5; Hg<0.001; Cd<0.03; Cr(VI)<0.02 ppm

Acknowledgements

This work has been financially supported in part by the Italian Ministry for Universities and Scientific and Technological Research (MURST; "40%" fund) and by Calcestruzzi S.p.A. Ravenna. The authors alone are responsible for the views expressed in this paper.

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