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The use of ferro-silicate slag from ISF zinc production as a sand replacement in concrete

Caroline Morrison[a,*], Rebecca Hooper[b], Kevin Lardner[a]

[a]Building Research Establishment (BRE), Centre for Concrete Construction, Garston, Watford, WD25 9XX, UK
[b]Waste and Resources Action Programme (WRAP), UK

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Abstract

Technical studies have shown that ferro-silicate slag from the Imperial Smelting Furnace (ISF slag) production of zinc can be used as a replacement for sand in cementitious mixes. The ISF slag contains trace quantities of zinc and lead, which are known to cause retardation of concrete set. Testing of experimental concrete mixes proves this retardation affect, although the delay in set does not appear deleterious to the eventual concrete hydration. If a gelatinous layer containing lead and zinc ions is formed around the cement grains in the concrete mix, set begins when this layer is disrupted and then continues as it would as if no zinc or lead had been present. Leaching studies demonstrate that pulverized fuel ash and ground granulated blast-furnace slag have the potential to reduce the leaching of lead and zinc ions from the ISF slag, even in highly alkaline solutions.

Keywords: Zinc; Aggregate; Heavy metals; Fly ash; Granulated blast-furnace slag

1. Introduction

1.1. Background

Sustainability and resource efficiency are becoming increasingly important issues within today's construction industry and the changing attitude towards secondary materials has encouraged investigation into the use of ferro-silicate slag from the Imperial Smelting Furnace (ISF slag) production of zinc as a concrete aggregate.

In 2001, Europe was responsible for 31% of the world's zinc metal production [1], through plants in Belgium, Bulgaria, Finland, France, Germany, Italy, Macedonia, Netherlands, Norway, Poland, Romania, the Russian Federation, Spain and the UK [2]. Of the European producers with the largest annual capacity (Belgium, France, Finland, Germany, Italy, Netherlands, Norway, Spain and the UK), four manufacturers use ISF production, others use electrolytic plants [3]. The UK produces 105,000 tonnes of zinc metal per annum [3] and approximately 80,000 tonnes of ISF slag, with a further 2.5 million tonnes already stockpiled [4]. An ISF production facility in Italy produces 75,000 tonnes of zinc metal every year [3] and 60,000 tonnes of slag [5]. There are equivalent zinc production plants in France and Germany [2] each producing 100,000 tonnes of metal per annum [3], with an estimated slag production of 80,000 tonnes. The United States and Canada produce 1,142,000 tonnes of zinc per annum [2], with Canada being the world's second largest metal producer and the United States the largest consumer of zinc metal [2]. Overall, 13.2% of the world's primary refined zinc is produced using the ISF process [2], suggesting slag production of approximately 975,000 tonnes.

1.2. Physical and chemical properties

The slag is glassy and granular in nature and has a similar particle size range to sand [6], indicating that it could be used as a replacement for the sand present in cementitious mixes. However, the density of this slag (3900 kg/m^3) is higher than traditional aggregates, suggesting it may give advantages over these aggregate materials in certain applications, for example, in noise barriers. Table 1 provides

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* Corresponding author. Tel.: +44-1923-664255; fax: +44-1923-664786.

E-mail address: morrisonc@bre.co.uk (C. Morrison).

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Table 1
Compositions of ISF slags

Oxide or metal	Other ISF slags					ISF slag S1	ISF slag S2
	wt.% present						
As	–	0.05	0.02	0.05	–	–	–
Al_2O_3	5.5	8.25	7.77	8.25	7.66	–	–
CaO	3.3	13.66	14.80	13.66	15.66	11.98	14.49
Cu	0.6	0.42	0.68	0.26	0.85	–	–
Fe_2O_3	52.9	30.66	38.17	39.66	38.28	38.33	37.17
Mn_2O_3	–	–	–	–	1.13	–	–
PbO	1.4	0.61	0.76	0.61	1.02	7.39	1.46
S	–	3.55	2.92	3.55	2.84	10.26 (SO_3)	4.42 (SO_3)
SiO_2	11.3	18.13	19.69	18.13	16.12	16.30	19.83
ZnO	9.8	9.48	9.01	7.62	6.93	11.37	14.23
Ref.	[5]	[7]	[8]	[9]	[4]		

details of the chemical composition of several ISF slags [4,5,7–9] and Table 2 gives an overview of the physical properties [4,6,8,9].

1.3. Control of leaching of lead and zinc ions

The retardation of concrete setting in the presence of lead and zinc ions is well documented [10–14]. However, very little is published concerning the mechanisms of, or methods, to overcome this retardation. Since little was known about the impact of the lead and zinc leached from the ISF slag when included in cementitious mixes, an experimental programme to examine the retardation of set in concrete was initiated.

A review of waste processing literature [15–25] was undertaken to suggest any mechanisms to remove lead and zinc ions from wastewater and industrial effluent that could be transferred to cementitious applications and thus control the potential retardation. The review highlighted the successful ion exchange of lead from contaminated wastewater with fly ash (from power plants and the incineration of municipal waste) and slag (assumed to be blastfurnace slag) [15,16]. Since pulverized fuel ash (PFA) and ground granulated blast-furnace slag (GGBS) are common cement additions in the UK [26,27], an experimental programme to test their impact on the leaching of lead and zinc from ISF slag was devised.

These two experimental programmes have recently concluded with positive results. Experimentation was carried out on two different ISF slags that reflect variations in the UK production process (S1 and S2), the compositions of these ISF slags are given in Table 1.

Table 2
Physical properties of ISF slags

% Mass passing through sieve					
Sieve size/mm	BS 882: 1992 [6]				ISF slag
	Overall limits	Coarse sand	Medium sand	Fine sand	
5.00	89–100	–	–	–	100
2.36	60–100	60–100	65–100	80–100	98
1.18	30–100	30–90	45–100	70–100	86
0.60	15–100	15–54	25–80	55–100	49
0.30	5–70	5–40	5–48	5–70	11
	Sand	ISF slag			
Approximate specific gravity	2.59	3.88			
Ref.	[9]				
Approximate % water absorption	2.7	0.2			

2. Experimental programme

2.1. Details of concrete set experiments

Temperature monitoring of setting concrete samples was carried out on mixes containing the ISF slags to assess their impact on concrete set. Table 3 gives details of the concrete mixes that were cast for this study. Temperature monitors (thermistors) were cast into the concrete and data loggers were used to record temperature changes over time. An increase in temperature of the mix shows reaction/hydration of the cement in the concrete.

2.2. Results of concrete set experiments

Fig. 1 shows the temperature changes during the setting of a control mix and the test mixes containing the ISF slags. All mixes reach approximately the same maximum temperature (37 ± 2 °C), however, the mixes containing the ISF slags show a delay in achieving this maximum temperature, although the temperature change profiles are very similar. This suggests that the hydration reaction occurs to the same extent in each mix, but that the ISF slags retard the onset of hydration.

Table 3
Experimental concrete mix details

	Control mix	% ISF slag as volumetric replacement for sand fraction	
		50%	100%
Cement content (kg/m^3)	270	270	270
Coarse siltstone aggregate 20–10 mm (kg/m^3)	663	663	663
Coarse siltstone aggregate 10–5 mm (kg/m^3)	82	82	82
Sand limestone aggregate 5–0 mm (kg/m^3)	998	498	–
Sand ISF slag aggregate 5–0 mm (kg/m^3)	–	667	1333
Free water (kg/m^3)	200	200	200
Free water/cement ratio (kg/m^3)	0.74	0.74	0.74
Target wet density (kg/m^3)	2210	2550	2550
Actual wet density (kg/m^3)	2410	2625	2820

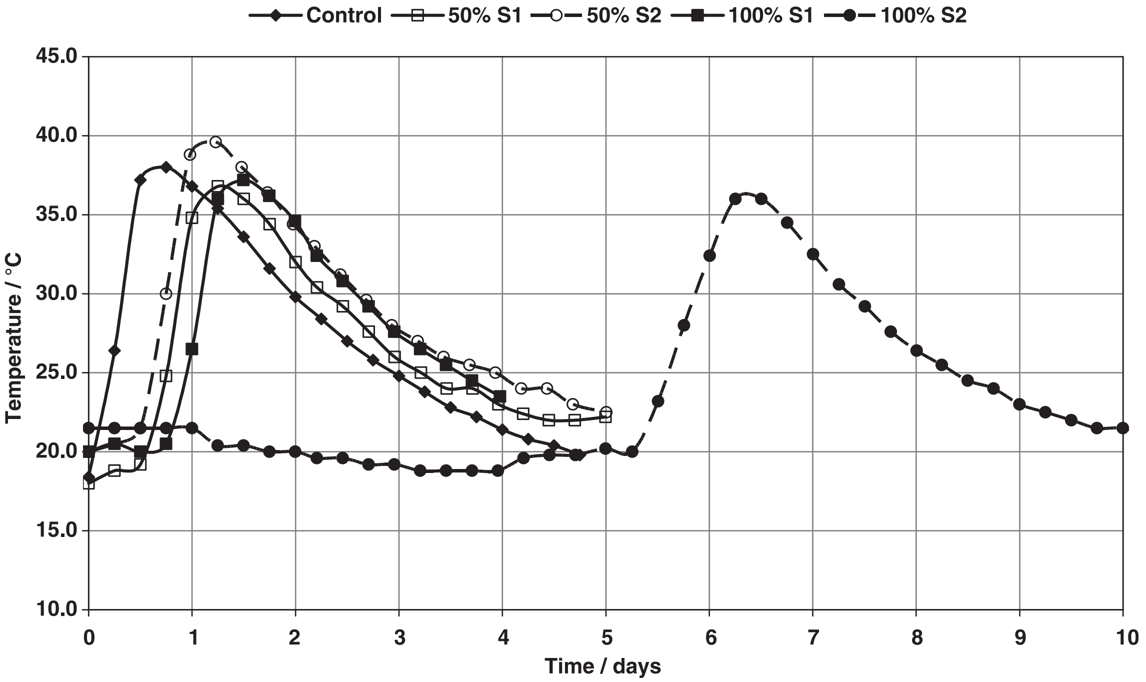

Fig. 1. Temperature profiles of setting concrete.

This conclusion is supported by 28-day compressive strength measurements of mortar mixes, which show little variation in average strength of mixes containing the ISF slag compared to a control (see Table 4). This concurs with the results of Atzeni et al. [5], who found that the partial replacement of sand with ISF slag in concrete was not significantly detrimental to the compressive strength of the concrete after 1 month.

2.3. Details of leaching experiments

Leaching experiments were carried out to determine the levels of zinc and lead released from the slags in various solutions. PFA, in combination with calcium oxide solution, was also tested to assess the behaviour of PFA at high alkali levels.

Table 4
A 28-day compressive strength of mortars containing ISF slag

	Control mix	% ISF slag as volumetric replacement for sand fraction	
		50%	100%
Cement content (kg/m^3)	510	510	510
Sand flint (chert) aggregate 5–0 mm (kg/m^3)	1530	765	–
Sand ISF slag aggregate 5–0 mm (kg/m^3)	–	1130	2260
Free water (kg/m^3)	270	295	275
Free water/cement ratio (kg/m^3)	0.53	0.58	0.54
Average 28-day compressive strength (N/mm^2)	40.2	39.0	33.8

Twenty-five grams of each ISF slag were added to 100 ml of the test solution and then shaken for a period of 24 h. The samples were then filtered and the solutions were tested for the presence of zinc and lead ions by atomic absorption spectroscopy.

2.4. Results of leaching experiments

Leaching experiments provided evidence that more lead is leached from the slags than zinc, although elementally zinc is more abundant, suggesting the lead is more accessible for leaching than zinc. Table 5 shows the experimental results for the leaching of lead and zinc ions into the test solutions.

Greater concentrations of lead and zinc ions were leached from S1 than from S2, which might be anticipated from the compositional analysis (Table 1). Leaching is greater at the

Table 5
Leaching of lead and zinc from ISF slag into test solutions

Solution	S1			S2		
	pH	Average leached (mg/l)		pH	Average leached (mg/l)	
		Lead	Zinc		Lead	Zinc
Control—deionised water	9.7	116.00	0.02	8.5	117.00	0.39
pH 13 buffer solution	13.4	1493.00	15.04	13.4	337.00	23.47
Saturated calcium oxide (CaO) solution	11.8	572.00	2.02	11.9	286.00	2.04
Saturated CaO solution and PFA	9.8	229.00	1.88	9.7	236.00	1.89
PFA and deionised water	10.3	3.13	0.03	9.3	0.21	0.00
GGBS and deionised water	10.0	4.19	0.00	8.9	0.22	0.00

high pH anticipated in cementitious mixes (pH 12–13) than at a lower pH associated with water (pH 7–8). There is a reduction in leaching in calcium oxide solution when compared to the pH 13 buffer solution and further reduction with calcium oxide in combination with PFA, which is indicative of a binding effect. Very low levels of ions were leached from the slags into solutions of PFA and GGBS.

3. Discussion of results

Thomas et al. [11] suggest that, within cementitious mixes, metal ions such as lead and zinc form a gelatinous layer around the cement grains, which prevents cement hydration from occurring. Water diffusing through this gelatinous layer finally reacts to form hydrated cement. Such a diffusion controlled reaction mechanism would imply that the rate of hydration of the cement should be slowed in the presence of lead and zinc. However, Fig. 1 indicates that hydration is prevented for a time, but that when it occurs the reaction temperature profiles are almost identical to mixes without these ions present. This suggests that once water has penetrated to the cement grain, the gelatinous layer is completely disrupted and hydration can take place unhindered.

The longest delay in cement hydration is seen with the complete replacement of the sand with the slag S2, although there are generally less lead and zinc ions leached from this slag than from S1. This suggests that the retardation period is not directly connected to the concentration of ions present but to the ratio in which these ions are present. This ratio may affect the chemical composition of the gelatinous layer formed, which in turn affects the layers' permeability to water, and hence, the delay in the onset of cement hydration.

This mechanism of retardation, by the formation of a permeable gelatinous layer, implies that the ability of PFA and GGBS to "mop-up" ions from the mix water may prevent the formation of a gelatinous layer, and hence, eliminate the retardation of set.

Reduction in ion availability will not only be beneficial in reducing the potential for delayed set but could also minimise the probability of detrimental in-service leaching of ions into the surrounding environment. Additionally, the inclusion of PFA and GGBS, specified measures in the control of alkali–silica reaction (ASR) [29–31], could eliminate any concerns about the glassy nature of the aggregate and its susceptibility to ASR [32].

4. Conclusions

The initial programme of experiments discussed in this paper was designed to test whether:

- the replacement of sand in concrete mixes with ferrosilicate slag from the ISF production of zinc (ISF slag) would cause a retardation of concrete set.
- leaching of metal ions from the ISF slags could be controlled through the use of PFA and GGBS.

The results demonstrate that inclusion of the ISF slag in concrete mixes does indeed delay the set of concrete. If a gelatinous layer containing lead and zinc ions, proposed by previous authors, is formed around the cement grains in the concrete mix, set begins when this layer is disrupted and then continues as it would as if no zinc or lead had been present. The length of retardation of set is not directly connected to the quantities of zinc or lead ions leached from the ISF slag, indicating that it may be the ratio of these ions that controls the retardation.

As expected, the leaching of lead and zinc ions is substantially increased in high pH solutions. However, the combination of ISF slag and PFA or GGBS reduces this leaching, even in highly alkaline solutions containing PFA.

Further work is underway to test the impact of PFA and GGBS upon the retardation of set in concrete mixes and to quantify the leaching of lead and zinc ions from experimental concrete mixes containing ISF slag, in addition to determining the alkali–silica reactivity of such concrete.

5. Uncited reference

[28]

Acknowledgements

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