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Retardation of cement hydration caused by heavy metals present in ISF slag used as aggregate

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ABSTRACT

A study was carried out into the potential use of slag from the Imperial Smelting Furnace method of zinc production (ISF slag) as a fine aggregate in concrete. One of the main issues associated with the use of ISF slag was that zinc and lead ions are known to cause retardation of the cement setting process. The effect of various inorganic additives to attempt to offset the retardation is reported. The previously favoured explanation for the mechanism of retardation could not fully explain observations made during this and other studies. Based on evidence gathered during this work, a detailed mechanism is proposed for the retardation of setting caused by heavy metal ions such as zinc and lead, involving the conversion of a metal hydroxide to a metal hydroxy-species. This conversion reaction consumes calcium and hydroxide ions from the surrounding solution and delays their supersaturation and hence the precipitation of CSH gel and $Ca(OH)_2$.

1. Introduction

There is currently a significant drive for the construction industry to become more sustainable. In particular, the concrete sector must aim to match the performance and efficiency of the timber and steel construction sectors. Also issues surrounding the quarrying of non-renewable primary aggregates, including concerns about noise, dust, visual intrusion and damage to biodiversity, have led to the introduction of the Aggregates Levy in the UK to tax the sale of these raw materials. Although this has not priced these aggregates out of the market, it has in part encouraged the industry to look at ways in which it can become more sustainable, which has led to the investigation of potential suitable alternative materials to primary quarried aggregates.

One material that has shown promise as a fine aggregate is slag from the Imperial Smelting Furnace method of zinc production (ISF slag). Although UK production ceased in February 2003, a large stockpile of the slag material still remains on the UK site and currently ISF zinc smelting plants around the world produce just under a million tonnes of the slag annually as a by-product material [1,2].

Although the ISF slag is glassy in nature, concrete containing it as an aggregate did not suffer damage as a result of ASR, even when elevated alkali levels were used, suggesting that it is not susceptible to ASR [3]. ISF slag does, however, cause a delay in the initial setting process [1,2], even though concrete containing the slag has been shown to have increased compressive strength characteristics compared to a control concrete tested after 28 days (49.0 MPa ± 0.5 compared to 41.5 MPa ± 0.1) [3]. This is in line with results reported for other heavy metal ions which after an initial delay in the setting process have resulted in compressive strengths at 28 days that are equivalent to, if not higher than, those from control samples [4,5].

Hence the research reported here was designed to investigate the mechanism by which ISF slag retards cement hydration and to examine methods by which it might be overcome, which would then allow the use of ISF slag as an aggregate.

2. Background – retardation of set

The nucleation and growth of CSH gel determines the rate of early hydration of the alite present in Portland cement. In addition to CSH gel, crystalline portlandite, $Ca(OH)_2$, is precipitated from a supersaturated solution containing Ca^{2+} and OH^- ions. The rate at which the relevant ionic species are made available at the surfaces of the alite grains controls the rate of reaction and hence the setting time of the cement [6].

ISF slag contains both lead and zinc ions and previous research has suggested that the presence of these heavy metal ions in a

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hydrating cement/concrete mix cause retardation of set [2,4,5,7–18]. Microscopy and X-ray photoelectron spectroscopy (XPS) studies on lead nitrate added to cement as an admixture suggested that gelatinous lead (assumed to be lead hydroxide) precipitates are formed in the alkaline environment produced by the cement, which coat the surface of the cement grains and prevent their hydration [4,7]. Several further studies on both lead and zinc compounds in cement have also suggested some sort of coating mechanism to explain their results, although they often lack direct evidence for the existence of such a coating [10–16]. Direct evidence of a coating layer was presented by Asavapisit et al. [17] who examined the immobilisation of a Zn containing electroplating sludge; however in this case the sludge used directly coated the cement grains. Nestle [18] reported varying effects of Pb on hydration with the extent of retardation being greatest with PbO then $Pb(NO_3)_2$ and then Pb_3O_4. In comparison PbO_2 resulted in no retardation. The retardation seen with PbO was attributed to surface controlled dissolution of PbO but no mechanism as to how this then resulted in retardation was given.

Lead and zinc are thought to behave similarly in a cement environment, as they both form insoluble hydroxides at high pH. However, it was admitted by Tashiro [10] that it was unclear how a precipitate could so rapidly cover the hydrating clinker particles with a membrane capable of preventing further hydration, although Yousuf et al. [16] argue that the multi-layers envisaged in their charge dispersed model would form immediately on contact with water. Arliguie et al. [12] have suggested that the retarding species might not necessarily need to coat the cement grains in order to delay hydration, but that its presence may instead delay the nucleation of stable hydration products, such as calcium silicate hydrate and portlandite. The precipitation of a phase less soluble than portlandite might result in drastic retardation. This theory has also been supported by Young [19].

Arliguie et al. [20], who investigated the hydration of C_3S and C_3A in the presence of zinc, found that the zinc formed insoluble calcium hydroxy-zincate, $CaZn_2(OH)_6 \cdot 2H_2O$, before the formation of portlandite (taken as indicating the start of the hydration process) was detected. The formation of portlandite relies on the availability of both calcium and hydroxide ions in the surrounding solution. If the Ca^{2+} and OH^- ions in solution were consumed by formation of an insoluble zincate species, it would delay saturation of the surrounding solution with calcium and hydroxide ions (and thus delay the precipitation of portlandite and CSH gel) until all of the zinc had been converted to the insoluble hydroxy-zincate compound. Although Arliguie et al. [19] still claimed the involvement of some sort of coating layer as the cause of the delay, the idea of delay in the supersaturation of the solution with Ca^{2+} and OH^- ions may constitute a suitable mechanism in its own right.

Lieber [14,21] also noted the presence of calcium hydroxy-zincate when examining the retardation of cement hydration with zinc. However, Lieber did not make the connection between the necessary depletion of Ca^{2+} and OH^- ions from the surrounding solution as the zincate is formed and the likelihood of this then preventing the supersaturation of the solution with respect to these ions, so delaying the precipitation of CSH and portlandite. Taplin in the discussion of Lieber's paper [14] inferred that it may not be necessary for the retarding species to actually coat the cement grains, but that its mere presence could cause the retarding effect. When tin(II) chloride is present, the analogous tin compound, calcium hydroxy-stannate, $CaSn(OH)_6$, is formed [22] and retardation of setting is observed [23], similar to that witnessed with additions of zinc and lead compounds. However, when lead is present, no equivalent hydroxy-plumbate compound has been reported, even though it might be expected that zinc, tin and lead would behave similarly due to their amphoteric character and hence their ability to form hydroxy-species at high pH.

Interestingly, Lieber [14] reported that when the calcium zincate was added to cement in place of the zinc oxide used initially, cement hydration was not delayed in the same way. This suggests that it is the process of converting the initial form of zinc to the zincate (i.e. using up the available Ca^{2+} and OH^- ions that would normally form portlandite) that is the cause of the retardation, rather than the zincate itself.

3. Experimental programme

3.1. Properties of the ISF slag

The ISF slag used for this study was supplied by Britannia Zinc Ltd., who operated an ISF zinc and lead production facility based in Avonmouth, in the South West of England (this site is now closed). The slag itself is a black, granular, largely amorphous material, generally coarser in appearance than natural sand. It has a higher density than conventional aggregates, with a particle density of 3.88 Mg/m^3 compared to approximately 2.6 Mg/m^3.

The composition on an oxide basis, as measured by X-ray fluorescence (XRF), is given in Table 1. X-ray diffraction (XRD) showed the presence of inclusions of metallic iron, although the principal crystalline components detected were FeO and ZnS.

3.2. Phase analysis during setting

XRD analysis was used to follow the phase evolution during the hydration of mortar samples. As detailed in Table 2, two sets of samples were prepared and analysed – neat Portland cement (supplied by Castle Cement, Clitheroe, Lancashire) and a set of samples containing ISF slag as a fine aggregate. The mixes were designed to give a water/cement ratio of 0.6 and a cement/fine aggregate ratio of 0.4 (by volume, determined from the particle density) once water absorption, moisture content and density of the materials had been taken into consideration. The water absorption was 0.2% and the moisture content was 1.57% for the ISF slag. The water/cement ratio was set by the concrete mix design. The water/ratio of 0.6 was set following concrete trials which were designed to achieve a compressive strength, slump and wet density in

Table 1
XRF analysis of ISF slag (analysis supplied by Ceram Research)

Oxide	ISF slag
SiO_2	18.89
TiO_2	0.40
Al_2O_3	8.52
Fe_2O_3	39.15
CaO	13.92
MgO	2.05
K_2O	0.57
Na_2O	0.98
P_2O_5	0.36
Cr_2O_3	0.19
Mn_3O_4	1.12
ZrO_2	<0.02
HfO_2	<0.01
PbO	1.37
ZnO	13.95
BaO	0.66
SrO	0.07
SnO_2	0.03
CuO	0.62
CeO_2	<0.01
As_2O_3	0.36
Nb_2O_5	<0.01
NiO	<0.01
LOI	6.19
SO_3	3.77

Table 2
Details of quenched mortar mixes used for XRD analysis

Mix	Aggregate (g)	Cement (g)	Water (g)	Times quenched
Cement	0.0	70.0	42.0	2, 4, 6, 24 h, 7 and 28 d
ISF	100.0	25.6	15.4	2, 4, 6, 24, 30, 48, 51, 54, 72 h, 7 and 28 d from start of hydration

line with concrete using conventional fine aggregate. Mortar samples containing the ISF slag were mixed in polythene sample bags, sealed and stored at room temperature. Periodically, at times ranging from 2 h to 28 days, some of the sample was removed from the bag and transferred to a pestle and mortar, acetone was then stirred/ground into the sample. The acetone was allowed to evaporate, leaving a dry, granular sample, which was ground to pass a 63 µm sieve before the XRD analysis was carried out; recent work by Collier et al. [24] has shown that this acetone quenching does not cause significant deterioration in the chemical composition or microstructure of the quenched cement pastes. A Philips PW1710 Reflection Diffractometer using CuKα radiation was used with a scan from 10 to 60°2θ. The data obtained were analysed using WinX^{POW} software and the Powder Diffraction File database.

3.3. Heat evolution during hydration

A JAF Isothermal Conduction Calorimeter (ICC) was used to track the heat evolution during cement hydration. The mortar samples used (~30 g) involved the systematic replacement of Thames Valley natural river sand as a fine aggregate with ISF slag (see Table 3). The percentage of ISF given in Table 3 is the volume fraction. Both the ISF slag and the sand were ground to pass a 150 µm sieve to allow even heat distribution throughout the sample while the cement was hydrating. The cement/aggregate ratio was again 0.4. The water/cement ratio was increased for this testing compared to that used for the phase analysis, from 0.6 to 1.0; this increase in water content allowed a workable mortar to be made, despite the high surface area of the aggregates used.

Further mortars incorporating sand (40%) + ISF slag (60%), with various additives that might compensate for the delay in set, were also tested. This ratio was selected because it had been shown to cause an equivalent delay in setting (approximately 40–48 h) to the full-scale concrete mixes tested (see Section 3.4 below). During ASR related tests it was noted that NaOH appeared to prevent the delay in the setting process that was usually witnessed with the ISF slag. The equivalent molar concentration of this additive (0.00475 moles in the 30 g mixes tested) was therefore used in the calorimeter experiments as a comparison. Other potential set accelerators [25] were tested at an equivalent molar concentration to the sodium from the NaOH, so that the effectiveness of various accelerating cations could be compared. A known accelerator of concrete hydration is calcium chloride ($CaCl_2$), which is commonly used at a concentration of 2% of the mass of the cement [26]. This level was used for the calorimeter work; other additives were tested at an equivalent molar concentration (0.0015 moles in the 30 g mixes tested) to the calcium from the $CaCl_2$, so that the effectiveness of the various cations could be compared. These two molar concentrations were used as a 'high' and 'low' addition level for all of the additives tested. As indicated in Table 4, chlorides, nitrates and hydroxides of various group I and group II elements were tested as additives.

Table 3
Mortar mixes used for ICC

Mortar (% by volume)	Cement (g)	Sand aggregate (g)	ISF aggregate (g)	Water (g)	Total weight (g)
Sand control	8.5	21.5	0.0	8.5	30.0
Sand 80% + ISF 20%	8.5	17.2	6.5	8.5	32.2
Sand 60% + ISF 40%	8.5	12.9	12.9	8.5	34.3
Sand 40% + ISF 60%	8.5	8.6	19.4	8.5	36.5
Sand 20% + ISF 80%	8.5	4.3	25.8	8.5	38.6
ISF 100%	8.5	0.0	32.3	8.5	40.8

The mortars were made up in sealable polythene bags. The water was weighed into the bag, then any additive used was weighed and dissolved in the mix water. The cement and aggregates were weighed out separately and mixed together in their dry state before being added to the bag and sealed. The mortar was mixed by hand by manipulating the mortar within the bag for 1 min. The bag was then secured around a metal disc to which was fixed a small (6 × 10 mm) heater within an aluminium pot (approximately 60 mm diameter) filled with oil. This was placed inside the calorimeter pot and submerged within a water bath maintained at 20 °C. An electrical output proportional to the heat flow from the sample was generated and logged by a computer over the course of several days. Once the sample run was completed, the output was calibrated by applying a known current to the system via the heater located within the aluminium sample pot.

3.4. Temperature monitoring of ISF slag concrete

The temperature evolution in concrete samples was also followed. The technique used was similar to the embedded thermocouple method described by Bushnell-Watson and Sharp [27]. However, in the current work 150 mm cubes of concrete in insulated moulds were used, rather than small tubes of cement paste in a temperature controlled water bath. Details of the concrete mixes tested by this method and their mean compressive strengths are given in Table 5. Additionally, several additives that had been shown to be useful in overcoming the delay in set caused by the ISF slag during testing by ICC were also scaled up and tested in concrete by this method, including calcium chloride, calcium nitrate, barium chloride, magnesium chloride, magnesium nitrate and potassium hydroxide. The concentrations of the additives are given in Table 6 and correspond to those used in the ICC experiments. Low addition levels are equivalent to 0.0015 moles, while high addition levels are equivalent to 0.00475 moles.

For the tests a thermistor attached to a length of 10 mm diameter doweling was placed in the centre of an insulated 150 mm square mould and connected to an 8 bit Grant Squirrel data logger. A second thermistor was also connected to the data logger to monitor the temperature external to the mould (ambient temperature). The mould was then filled with the concrete mix and the logger set to record the temperature at intervals of 15 min, accurate to the nearest 0.5 °C, until the concrete within the mould had set.

3.5. Microstructural analysis

Mortar samples containing ISF slag or limestone control aggregate were examined by scanning electron microscopy (SEM). A

Table 4
Additives tested in association with ISF slag by ICC

Cation → Anion ↓	Li	Na	K	Mg	Ca	Sr	Ba
Cl	✓	✓	✓	✓	✓	✓	✓
NO_3	✓	✓	✓	✓	✓		
OH	✓	✓	✓		✓		

✓ Indicates that a given additive was used.

Table 5
Concrete mixes used for temperature monitoring with thermistors

Mix	Sand (control)	ISF slag
Relative density of fine aggregate (Sand or ISF slag – Mg/m^3)	2.6	3.9
Cement content (kg/m^3)	300	300
Coarse aggregate – Cheddar limestone: 20–5 mm (SSD* weight, kg/m^3)	1135	1135
Fine aggregate – sand or ISF slag: 5-0 mm (SSD* weight, kg/m^3)	757	1135
Free water/cement ratio	0.6	0.6
Mean 28 day compressive strength (MPa)	41.5 ± 0.1	49.0 ± 0.5

* SSD = Saturated, surface dry.

Table 6
Additives used in concrete for temperature monitoring experiments

Additive	Low addition (g/l)	High addition (g/l)
$MgCl_2 \cdot 6H_2O$	–	201.32
$MgNO_3 \cdot 6H_2O$	–	253.95
$CaCl_2$	–	110.53
$CaNO_3 \cdot 4H_2O$	73.03	232.89
$BaCl_2 \cdot 2H_2O$	76.32	–
KOH	–	55.26

Camscan SEM fitted with a Link Analytical EDS detector was used. This microscope was fitted with a cryo-stage enabling examination of samples that had effectively been 'frozen' in liquid nitrogen. For this part of the study the ISF slag was passed through a 300 μm sieve and a 150 μm sieve. Only the material retained on the 150 μm sieve was used in the mortar mix. This allowed better distinction between the finer cement particles and the aggregate particles under the microscope, due to their relative sizes. The mortar was mixed and stored for approximately 18 h before being quenched in liquid nitrogen. It was then placed onto the cryo-stage and the surface fractured using a sharp blade before it was transferred into the sample chamber of the SEM; the hydration of the mortar containing ISF slag was therefore frozen while it remained in the retardation phase. The control mortar was only stored for 1 h prior to quenching in liquid nitrogen to ensure that it was also in the early stages of hydration.

Transmission electron microscopy (TEM) analysis was carried out on a Philips EM420 TEM, which was also fitted with an EDS detector. Acetone quenched samples were ground by hand in a pestle and mortar and then mixed with methanol. A few drops of the mix were taken up using a disposable pipette and dropped onto a 3.05 mm diameter, 400 mesh (38 μm) copper grid covered in a thin carbon film. Once the methanol had evaporated, the sample was loaded into the TEM.

4. Results

4.1. XRD analysis results

The XRD traces for the quenched ISF mortars are shown in Figs. 1 and 2, along with those for the raw ISF slag and for cement hydrated for an equivalent time. Fig. 1 shows the results from mortars quenched 2 h after mixing. Fig. 2 shows the trace obtained from the ISF mortar quenched after 72 h.

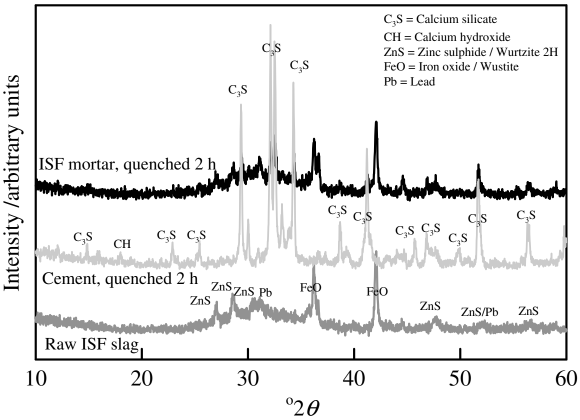

Fig. 1. XRD trace of hydrating ISF slag mortar, quenched after 2 h compared with control systems. The different XRD traces have been displaced vertically for clarity.

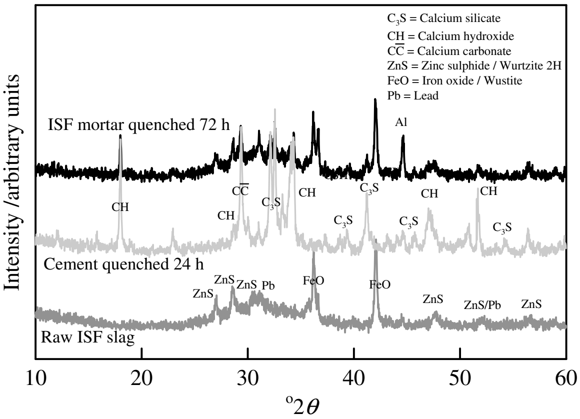

Fig. 2. XRD trace of hydrating ISF slag mortar, quenched after 72 h, compared with control systems. The different XRD traces have been displaced vertically for clarity.

The peaks corresponding to calcium hydroxide (CH) only began to appear on the ISF slag traces as small peaks after 48 h, and the strong CH peak at 18.3°2θ was not predominant on the XRD traces until after 72 h, by which time the mortar had finally hardened. This confirmed that $Ca(OH)_2$ was not produced during the retardation period caused by the inclusion of the ISF slag and therefore this phase was not responsible for the setting process.

Lieber [14] similarly failed to detect $Ca(OH)_2$ by XRD during the retardation caused by lead and zinc ions. It would appear that the lack of Ca^{2+} and OH^- ions in solution is in some way involved in the mechanism of retardation caused by the ISF slag. This ties in with the theory outlined above, that the calcium and hydroxide ions may be utilised in the conversion of a lead or zinc hydroxide species into a hydroxy-compound, thus delaying the supersaturation and precipitation of crystalline $Ca(OH)_2$ and also CSH gel, so delaying the setting and hardening of the cement.

Most peaks in the XRD traces have been attributed either to the cement or to the ISF slag. The peak at 44.6°2θ in Fig. 2, labelled Al, is due to the aluminium sample holder used. Unfortunately, the hydroxy-zincate species that has been previously reported during cement retardation by zinc [14,21] (or an equivalent hydroxy-plumbate species from lead) could not be identified by XRD in the ISF slag samples. Therefore, it cannot be conclusively shown that the conversion of lead or zinc hydroxide to their respective hydroxy-compounds is the cause of the retardation.

4.2. Isothermal conduction calorimetry

To establish a manageable delay period that could be used as a benchmark to assess the effect of any additives tested, the ISF slag was used at various replacement levels in mortars, from 20% up to 100% by volume. The calorimeter results for this are shown in Fig. 3. It is generally accepted that the setting process corresponds to a period of rapid formation of CSH and CH [28] and that setting occurs during the acceleratory period of heat evolution between the point of inflection and the main peak on the ICC curve [6,23]. Also during the temperature logging of the concrete samples it was found that additional samples prepared at the same time could not be de-moulded until the samples being logged reached temperatures towards the maximum heat output. As the level of ISF slag was increased, the onset of hydration was delayed and the maximum rate of heat evolution was reduced, which are the typical criteria indicating retardation of the set. Fig. 4 shows the total heat output over time for each of the samples, once hydration had commenced. Apart from the 20% ISF sample, which gave a much lower total heat output, the total heat outputs of all the other samples were close to that of the control (100% OPC) and lie between ~100 and 120 kJ/kg, suggesting that cement hydration had progressed to approximately the same extent in all the samples, once the retardation period had passed. The lower figure obtained for the 20% replacement level is presumed to be due to experimental error as it is out of line with all the other results.

4.3. Influence of chemical additives on retardation

The ISF replacement level of 60% selected to examine the effect of various additives gave a retardation in setting equivalent to that seen in full scale concrete mixes that contained ISF slag. Results for the additives are presented as the maximum rate of heat output against the time to the onset of rapid hydration (referred to as 'onset time' in Figs. 5 and 6), so that their effects can be clearly distinguished. Fig. 5 shows the results from the 'high' addition levels, while Fig. 6 shows the results from the 'low' addition levels. The closer the results are to the onset time of the sand control sample (including all those with an onset time of less than 16 h), the more useful the additive is in overcoming the retardation caused by the ISF slag. The higher the maximum rate of heat output, the more vigorous the reaction had been once hydration had commenced.

In both Figs. 5 and 6, additives based on group II elements (♦) appear to be generally better at overcoming the retardation than those based on group I elements (▲). The chlorides and nitrates seem to be the most effective anions in association with the group II elements, whereas the hydroxides seem to be of most benefit in association with the group I elements. However, there do not appear to be any other definite patterns in the order of effectiveness of the cations in each group and their associated anions.

NaOH has been previously noted as an accelerator in concrete. It is thought to work by reacting with gypsum ($CaSO_4 \cdot 2H_2O$) during the initial hydration, resulting in formation of Na_2SO_4 and $Ca(OH)_2$ [28–31]:

$$CaSO_4 \cdot 2H_2O + 2NaOH \rightarrow Na_2SO_4 + Ca(OH)_2 + 2H_2O$$

Gypsum is used as a retarder in Portland cement to prevent the flash set that can be caused by the hydration of tricalcium aluminate (C3A). If some of the gypsum is used up by the reaction with NaOH, the hydration of C3A may occur more quickly than usual, thus shortening the retardation period. However, in the context of the proposed mechanism based on the conversion of metal hydroxides to calcium hydroxy-species, the increased concentration of Ca+ and OH− ions resulting from the reaction of NaOH with CaSO4 may also be beneficial in overcoming the delay.

Lithium, sodium and potassium are all more reactive than calcium, so an equivalent reaction might be expected with all of these group I hydroxides. The calorimetry results for the group I hydroxides seem to support this. The only group II hydroxide tested was $Ca(OH)_2$, which reduced the delay experienced with the ISF slag, presumably due to the presence of additional Ca^{2+} and OH^- in solution.

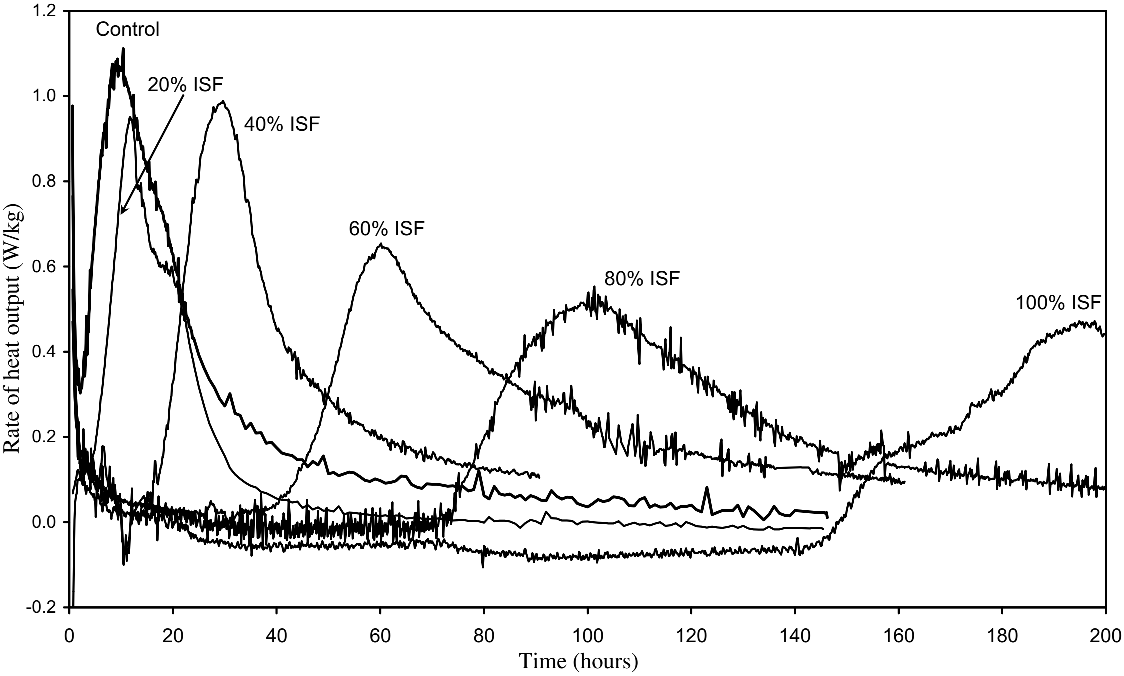

Fig. 3. Rate of heat output against time by hydrating mortar samples containing ISF slag as measured by ICC.

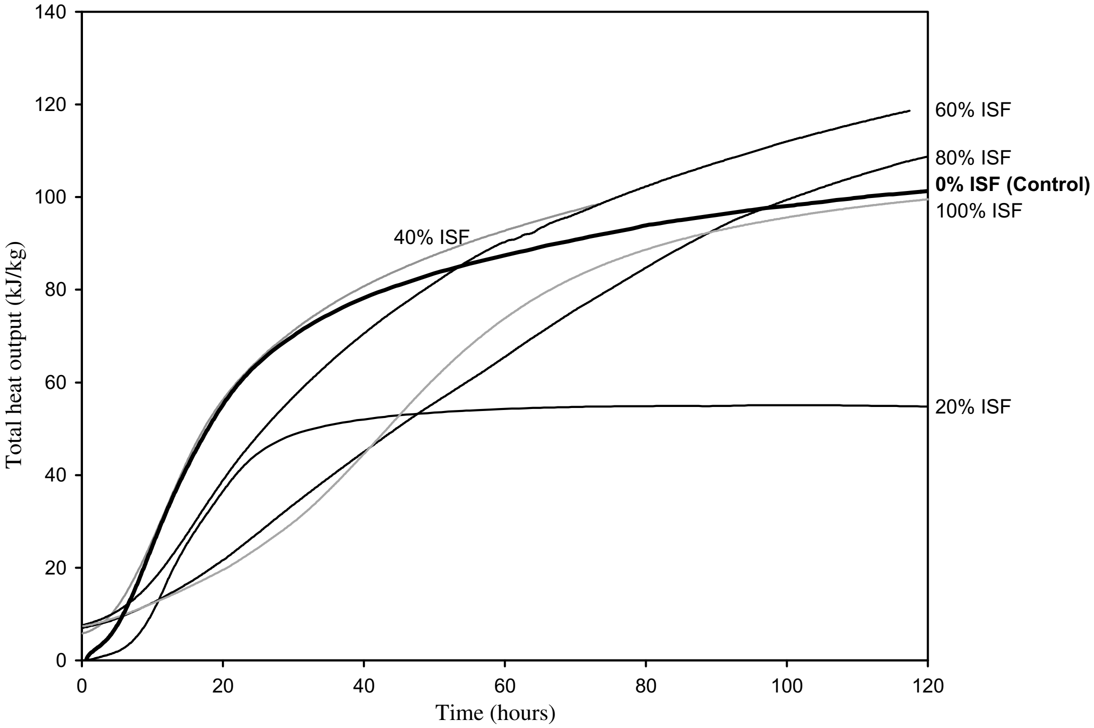

Fig. 4. Total heat output of samples shown in Fig. 3, once hydration has commenced.

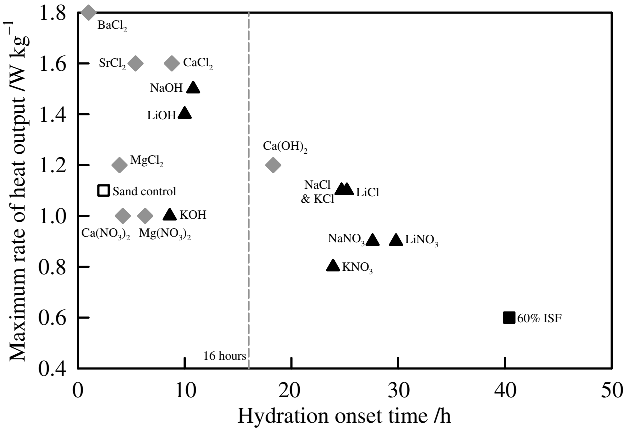

Fig. 5. Effect of high concentrations of the various additives on the maximum rate of heat output and the onset time for hydration of mortars containing ISF slag.

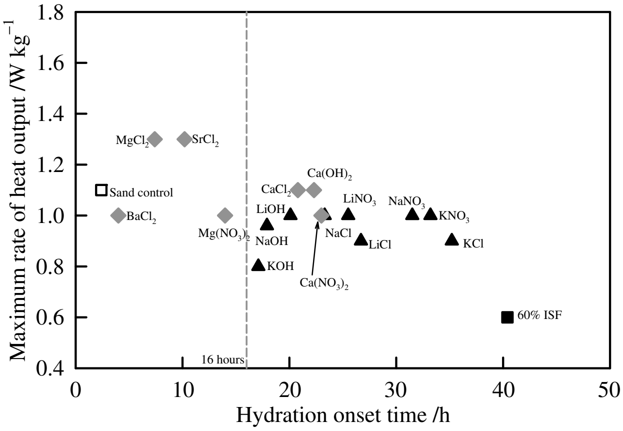

Fig. 6. Effect of low concentrations of the on the maximum rate of heat output and the onset time for hydration of mortars containing ISF slag.

Species giving more soluble calcium compounds (Cl^-, NO_3^-) seem to have a greater effect on reducing the retardation. $CaCl_2$ and other chlorides are known to act as accelerators in concrete. The chloride ions displace the OH^- ions that would normally be present in solution, causing a premature saturation of the solution with OH^- ions, which combine with calcium ions in solution to form $Ca(OH)_2$, hence speeding up the hydration reaction [32].

One reason that the group I chlorides may not perform as well as the group II chlorides is because the molar concentrations of the chlorides added were not equivalent. The additions were made at equivalent molar cation rather than anion concentrations, to compare the relative behaviour of the group I and group II elements, hence there will have been twice the molar concentration of chloride ions with the group II additions. Potassium and lithium chlorides show moderate improvement at high addition levels compared to the low addition levels. However, there is relatively little difference in the onset time with NaCl at the two concentrations.

The chlorides of the other group II metals tested appeared to be more effective than $CaCl_2$. This may be related to their relative solubilities. At room temperature, the order of solubility of the group II chlorides is $Ba < Sr < Mg < Ca$ [33]. Although the order of efficiency of the ions as accelerators does not exactly follow this pattern, barium is certainly the most effective and calcium the least effective at both addition levels. The reason why the least soluble ions are most effective is unclear. The nitrates may undergo a similar type of reaction, since the results obtained with them, when compared to the equivalent chlorides, were often of a similar order. However, a reliable pattern is again not apparent.

In general, the common influence of all of the additives considered seems to be to increase the concentration of hydroxide ions in

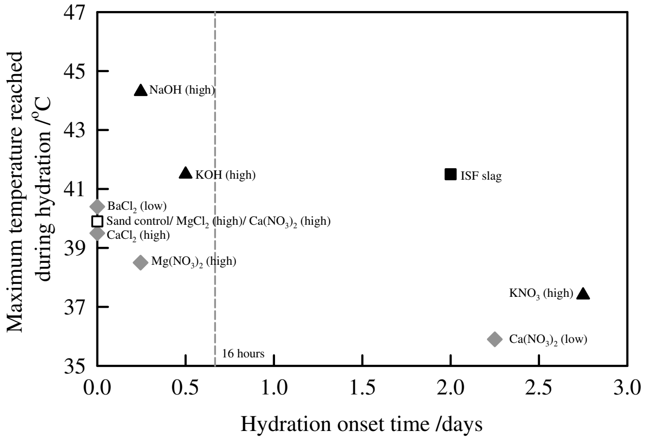

Fig. 7. Influence of various additives on the setting behaviour of ISF slag concrete.

solution. Calcium ions are provided by the cement as it hydrates (or other group II cations may reduce the need for calcium by reacting with the retarding species in its place), which allows the supersaturation and precipitation of $Ca(OH)_2$ and CSH gel to occur more quickly and so reduce the retardation experienced.

4.4. Temperature monitoring of setting concrete – effect of chemical additives

The effect of several chemical additives (at either high or low addition levels) on the retardation of ISF concrete, as determined by monitoring the temperature of the concrete with an embedded thermocouple, is shown in Fig. 7. The results are presented as the maximum temperature recorded plotted against the time to the onset of hydration.

It can be seen that the additives that were most successful during the calorimetry testing described above (reducing the delay to less than 16 h) were equally successful here. However, those that had previously brought about a moderate reduction to the delay (to between 16 and 24 h) were less effective when scaled up into the concrete mix. This time period must represent a critical crossover area between the two techniques used. Additives that reduced the delay to within 16 h in the calorimetry testing were similarly successful in the concrete tests, while any that did not reduce the delay to less than 16 h in the calorimetry test could not overcome the retardation caused by the ISF slag in concrete within a manageable timeframe. Variations in the concentrations used might be able to overcome this, but these observations emphasise the need for representative testing, rather than reliance on small-scale testing.

Of all the chemical additives tested in concrete, it was found that $BaCl_2$ was able to be used successfully at the 'low' addition level. From the calorimetry results, low additions of $MgCl_2$, $SrCl_2$ and $MgNO_3$ also reduced the retardation of mortars to within 16 h, hence might be expected to work as effectively in concrete made with ISF slag. Factors that are likely to dictate the choice of additive used include their relative cost, their effect on the workability of the concrete, and its long term strength gain and durability.

4.5. Microstructural analysis

Secondary electron images of a mortar mix that is retarded reveal spherical ISF slag particles protruding from regions of cement, as shown in Fig. 8. The slag particles do not appear to have been attacked or degraded in any way.

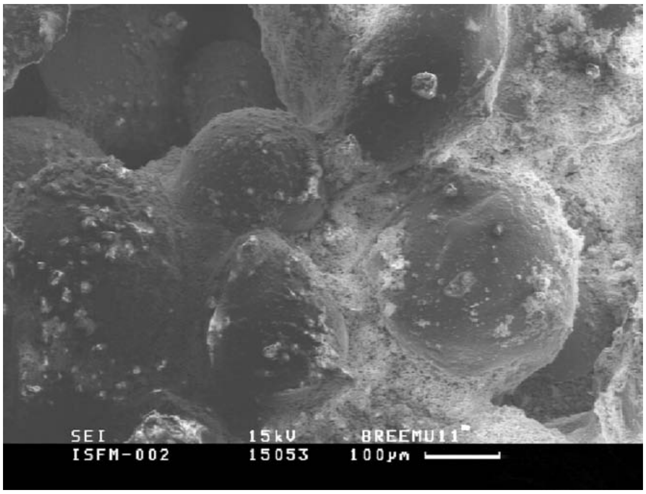

Fig. 8. Secondary electron image of ISF slag particles within a mortar mix containing ISF slag after 18 h.

Closer examination of the cement grains showed that they did not appear to have hydrated particularly, even after a period of 18 h. In Fig. 9, distinct cement particles can still be distinguished (e.g. A and B in Fig. 9). EDS analysis showed no presence of any metal ions on the surface of these cement grains implying that they were not being coated by layers of gelatinous lead or zinc compounds.

When cement and ISF mortar samples were quenched during their hydration period and examined by TEM, no evidence of any apparent coating of the cement grains was observed around the particles. Fig. 10 shows the TEM images and selected area diffraction patterns that were obtained from the quenched ISF mortar sample (A) and a quenched cement sample for comparison (B). The amorphous ring patterns from each quenched sample are very similar, suggesting that the rings must primarily arise from the cement. No lead or zinc could be detected around the cement particles by EDS analysis. There was therefore no evidence to suggest that any lead or zinc-containing amorphous coating was present around the cement grains to prevent their hydration.

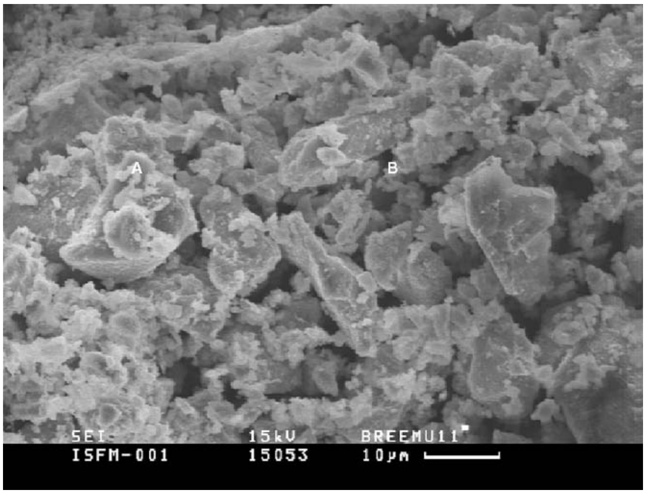

Fig. 9. Secondary electron image of cement grains within a mortar mix containing ISF slag after 18 h.

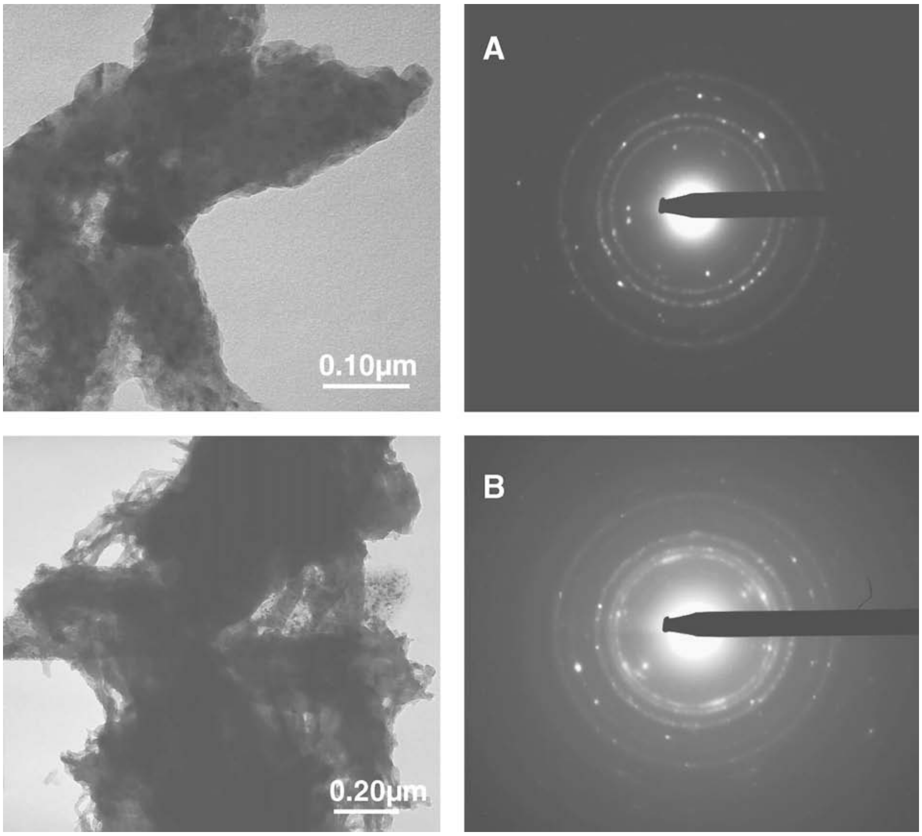

Fig. 10. TEM images and diffraction patterns from an ISF slag mortar (A) and from cement alone (B), quenched during hydration at 18 h and 12 h, respectively.

5. Discussion

As outlined in Section 1, previous workers have explained the retardation of set caused by certain heavy metal ions in concrete by the rapid formation of a gelatinous metal hydroxide layer on the surface of the cement grains, due to the highly alkaline environment within the cement mix. There was no satisfactory explanation as to why or how the hydration reaction would finally proceed after the retardation experienced and no evidence was found in the current study for the formation of such layers. This is in disagreement with some previous reports [4,8], although it should be noted that there were a number of necessary differences in experimental technique between the work reported in the literature and that conducted here. In the earlier studies, lead was added as an admixture in a controlled fashion via a soluble nitrate rather than being a part of the aggregate. Additionally, in the published TEM studies [4] it is implied that the final stages of sample dehydration were carried out in the microscope. The need to maintain a good quality vacuum in the TEM used here meant that it was necessary for all free water to have been removed before the sample was placed in the TEM. These differences might explain why such layers were seen in the work of Thomas et al. [5] and were not seen in the current work. Against this, however, in the earlier work [5] separate microscopes were used for imaging and EDS analysis, whereas in the current work the imaging and EDS analysis were carried out in the same microscope. It is therefore difficult to see how the previous study guaranteed that the same areas were imaged and subjected to EDS analysis, something which is not an issue here. Within the limits of our sample preparation we are therefore confident that there is no evidence of substantial gelatinous metal hydroxide layers on the cement particles, although thin layers only a few nanometres thick would probably have remained undetected.

Although metal hydroxide precipitates are expected to form quickly in the high alkaline environment of a cement mix, there does not appear to be any reason why they should preferentially coat the cement grains. Zinc and lead ions are amphoteric and the hydroxide precipitates would re-dissolve in an excess of hydroxide ions to form soluble zincates (ZnO_2^{2-}) and plumbates (PbO_2^{2-}) [11]. As outlined above, Lieber [14], Yousof et al. [16] and Hill [34] have reported the formation of calcium hydroxy-zincate ($CaZn_2(OH)_6 \cdot 2H_2O$) during the retardation period. This consumes both calcium and hydroxide ions, which would be removed from solution, thereby delaying the normal cement hydration process in which calcium and hydroxide ions gradually saturate the mix water until supersaturation is reached and solid $Ca(OH)_2$ is precipitated out along with the formation of CSH gel. A generalised equation for the conversion of the retarding species, M, for example Zn, Pb or Sn, would therefore be

$$M \overset{\text{in the presence of}\mathrm{OH}^{-}\text{ions}}{\longrightarrow} \mathrm{M(OH)_2}$$
$$\times \overset{\text{in the presence of excess }\mathrm{OH}_{-}\text{ and }\mathrm{Ca}^{+}\text{ions}}{\longrightarrow} \mathrm{CaM_2(OH)}_x \cdot y\mathrm{H_2O}$$

This reaction removes calcium and hydroxide ions from the surrounding solution and so prolongs the time required before calcium hydroxide would precipitate out, although the ultimate reaction of the cement would be largely unaffected by the delay. It follows that an increase in the concentration of available hydroxide ions present shortens the retardation period experienced and that the total heat of hydration for the reactions should be largely unchanged, in line with the results obtained here.

There is more circumstantial evidence to support this mechanism: calcium hydroxide was not detected in the XRD samples until after the retardation period had ceased; the aggregate/cement ratio was critical to the delay in set rather than any other factor (if diffusion of water through a gelatinous layer caused the eventual hydration of the cement, the water/cement ratio of the mix should influence the delay). Evidence for the formation of either a calcium hydroxy-zincate or plumbate species would have supported the results of this study, but neither was actually detected by XRD during testing. This may indicate that the compounds are poorly crystalline or below the limits of detection by XRD, but clearly our results are not definitive. Overall, however, we conclude that delay of set by the formation of an insoluble calcium hydroxy-zincate or plumbate is a more likely mechanism than the formation of a gelatinous layer.

6. Conclusions

- ISF slag used as a fine aggregate retards the setting of Portland cement.
- Microstructural studies showed no evidence for the formation of coatings on the cement grains.
- XRD analysis did not indicate the formation of any new compounds, but did confirm that calcium hydroxide was not precipitated until after the retardation period had ended.
- The most successful additions for overcoming the delay in setting were those containing group II cations, which promoted an increase in the concentration of hydroxide ions in solution.
- The retardation of set caused by the ISF slag is more likely to be due to the formation of calcium hydroxyl-zincate or plumbate than to formation of a gelatinous surface layer. This reaction consumes calcium and hydroxide ions from solution and delays the supersaturation and precipitation of calcium hydroxide and development of CSH gel.

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*Indicates publications under the author's previous name, now Weeks C.

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