



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 $\text{Ca}(\text{OH})_2$.

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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 ($49.0 \text{ MPa} \pm 0.5$ compared to $41.5 \text{ MPa} \pm 0.1$) [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, $\text{Ca}(\text{OH})_2$, 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 $\text{Pb}(\text{NO}_3)_2$ 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, $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$, 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, $\text{CaSn}(\text{OH})_6$, 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

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