Pergamon

Cement and Concrete Research 30 (2000) 1375–1379

CEMENT AND CONCRETE RESEARCH

Sodium silicate-based alkali-activated slag mortars
Part II. The retarding effect of additions of sodium chloride or malic acid

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Received 13 June 1999; accepted 29 June 2000

Abstract

In this paper we investigate the hydration of alkali-activated slag cements in the presence of heavy contamination with chloride (up to 13% by weight as NaCl with respect to slag). Reference samples were made by activating slag with sodium silicate solution. Companion samples in which a high level of sodium chloride was added to the mix water were found, based on strength development and calorimetry, to be severely retarded. When the known retarder malic acid was also added to the mixes, the mix that also contained sodium chloride showed no significant heat development in the first 10 days. Pore expression experiments indicated that the bulk of the chloride remained dissolved in the pore solution. XRD indicated that no new crystalline hydrates were formed when NaCl was added to the system. In the systems with added malic acid or sodium chloride, the same calorimetry peaks were observed, albeit retarded, but with similar integrated heat outputs, suggesting that the basic mechanism of hydration was not altered by the retarding additions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Alkali-activated cement; Granulated blast-furnace slag; Acceleration; Retardation; Calorimetry

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1. Introduction

Alkali-activated slag cements have been used in Eastern Europe, Scandinavia and China and are discussed in two extensive reviews [1,2]. Sodium silicate-activated systems can give particularly high strengths, and have been reviewed and investigated recently by Wang et al. [3–5]. The formulation described here is based on that work, but developed further [6,7] and modified with malic acid retarder [7] to produce a workable concrete. In this paper, as part of a wider study of the corrosion of steel reinforcement in these systems [8], we investigate the effects of casting these cements in the presence of high levels of sodium chloride in the mix water. The development of hydration was assessed by measuring the compressive strength of mortars, by image analysis to measure the extent of reaction of the anhydrous slag, and at early age by calorimetry and set time measurements. Pore solution was expressed under applied pressure to investigate the interaction of the chloride ions with the cement paste.

2. Experimental

Mortar samples were prepared using a typical UK ground granulated blast furnace slag (Appleby Group, Scunthorpe) activated with 1.5 M $Na_2Si_2O_5$ solution at a ratio of 500 ml solution/1 kg slag. Malic acid was added to some mixes as a retarder [7], at a level of 0.5 wt.% malic acid/slag. Additions of malic acid or sodium chloride were dissolved in the activator solution prior to mixing. Concentrations are given as % by mass with respect to mass of slag. A silica sand was used to make mortars, with a narrow size distribution to aid the image analysis, and with a ratio of 2.33:1 sand/slag. Samples were cured at 20°C and stored in plastic bags in a chamber at $>95\%$ relative humidity. Full details of the materials used, sample preparation, scanning electron microscopy and image analysis are described elsewhere [6,9]. To measure the extent of reaction by image analysis the proportion of area of unreacted slag was compared with that expected given the initial composition of the mix. At least 20 images were acquired, selected at random from the microstructure to avoid bias, and the results averaged. A heating shutdown meant that the samples were stored at a lower temperature (but $>5°C$) from about 10 to about 21 days. Compressive strengths were measured on 16-mm

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PII: S0008-8846(00)00356-2

cubes cut from 16 × 16 × 160 mm cast mortar prisms. Isothermal calorimetry was performed at 20°C over the first 10 days using a Wexham Developments calorimeter, on separate samples mixed without aggregate. Set times were obtained using a Vicat needle; the pastes were not adjusted to standard consistency first, but measured at the fixed solution to solid ratio given above.

3. Results

3.1. Set time and compressive strength

Compressive strength measurements (Table 1) indicate that the addition of 8% NaCl to the mix significantly retards the strength development of these systems, with the system containing 8% NaCl being too weak to demould at 1 day (it was demoulded instead at 3 days). Calorimetry indicates that the strengths for samples with both malic acid retarder and NaCl added would have been too low to be worth measuring. This was confirmed by qualitative observations of small samples prepared for studying the extent of reaction of the slag. The system with retarder will be discussed in detail elsewhere [7]. For the control, the 28-day strengths were lower than expected in comparison with previous studies [6] because of the heating shutdown that occurred during this time.

The set time results show similar trends (Table 2), with considerable retardation for addition of 8% of sodium chloride. Small additions of NaCl, however, were found to act as accelerators. The retarding effect of NaCl at 8% addition was much lower than that of malic acid at the low addition rate of $^1/_2$%.

3.2. Pore solution analyses

Pore fluid was expressed from selected samples [8], and analyses indicated that most of the chloride ions remained in solution.

3.3. Image analysis, microstructure and microanalysis — late age hydration to 3 months

Backscattered electron (BSE) images of samples without added sodium chloride (Fig. 1(a)) exhibited the expected microstructure at 3 months. In BSE images, brightness is a function of average atomic number, with porosity reducing the brightness. Thus, bright regions have a low porosity and/or a high content of oxides. The microstructure contains bright unreacted slag grains with narrow (dark) inner product rims in a featureless gel, slightly cracked in places, probably due to drying shrinkage during specimen preparation. The cracks are dark, being filled with epoxy resin, which has a lower average atomic number than the cement phases. The inner product gel is darker than the outer product, indicating that it has a lower average atomic number and/or density. The outer product gel is of uniform brightness, indicating a homogenous composition, except for the many embedded darker regions, which are inner product regions; these are relicts from fully reacted slag grains.

Table 1
Compressive strengths for 16 mm cubes

Mix	Compressive strength/MPa				
	1 day	3 days	7 days	28 days	3 months
Control	3	38	48	58	74
C + 8% NaCl	*	2	3	50	74

* Strength too low to demould samples at 1 day.

Table 2
Set times for pastes at 0.5 ml/g solution/slag ratio

Mix	Set time (h)	
	Initial	Final
C	4	5
C + 1% NaCl	2	2.5
C + 4% NaCl	3	4
C + 8% NaCl	10	12
C + M	20	22
C + M + 8% NaCl	>48	>48

C: Control; M: Malic acid (0.5%) added to mix as retarder; NaCl: percentage NaCl (by weight of slag) added to mix.

In contrast, the mix with 8% added sodium chloride (Fig. 1(b)) showed some structure within the outer product gel. The (dark) slag inner product regions are surrounded with narrow bright reaction rims, similar to those observed at early age in OPC hydration, surrounding the outside of the reacting particles. It is not possible to determine if these brighter regions contain less porosity or have a different composition to the rest of the outer product, since they are too narrow for reliable EDX microanalysis. Possibly, if they are dense, it is these rims that lead to the retardation observed for this level of addition of NaCl.

The degree of reaction measured by image analysis (Table 3) shows that more anhydrous slag remains left in the system with NaCl added than in the control mix, indicating a smaller degree of reaction. In both mixes, the distribution of unreacted slag against the interface with aggregate was similar, with a similar interfacial zone thickness (interfacial properties measured as described elsewhere [9]). In both mixes hydrates efficiently filled the region immediately adjacent to the aggregate particles.

Microanalysis of the hydrates indicated that they were similar in the two systems. In the sample with added chloride, chloride was found to be present throughout the hydrate regions, possibly with a slightly higher level in the slag inner product regions. The brighter and darker regions of the hydrate in the system with added chloride

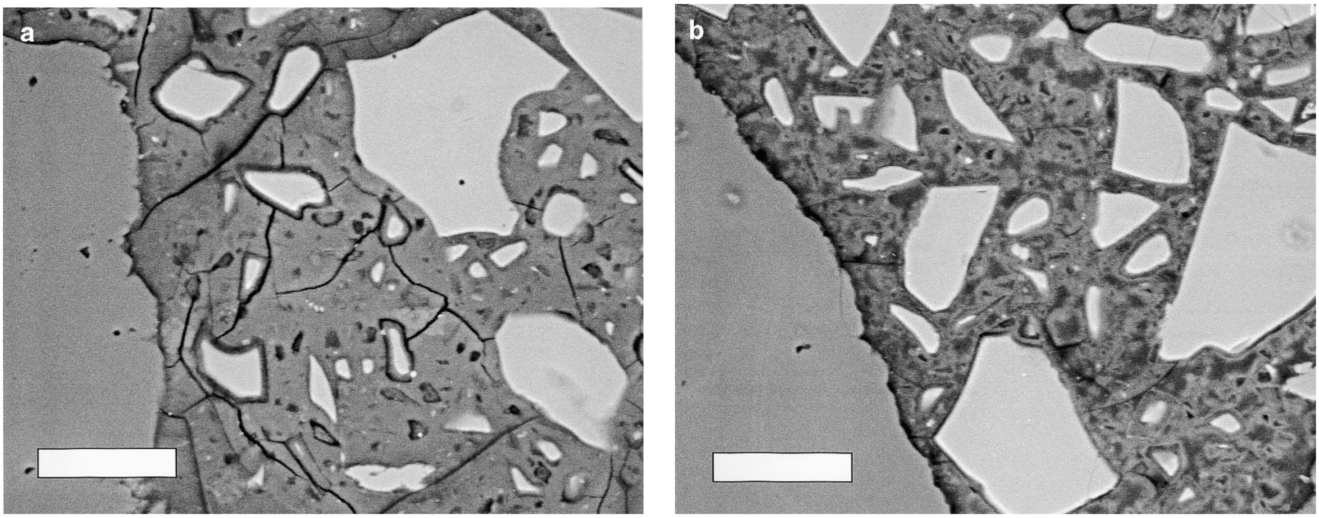

Fig. 1. Microstructure of the systems without malic acid, after 3 months hydration with (a) 0% or (b) 8% added NaCl. Markers are 20 μm.

were too finely intermixed to obtain distinct analyses. No simple compositional correlations were found.

3.4. X-ray diffraction

Powder X-ray diffraction (Fig. 2) did not show formation of any new crystalline phases, although at the highest levels of NaCl addition some crystalline NaCl was observed. No significant peaks are seen in the region 8–13° 2θ as would be expected for AFm compounds or for Friedel's salt. At the highest levels of NaCl addition, the reflections for CSH were sharper, perhaps indicating that the CSH present became slightly less disordered with increasing additions of NaCl.

3.5. Calorimetry — early age hydration

In the absence of NaCl, alkali activated slag hydrates in two observable stages [6] (Fig. 3). There is an initial heat evolution peak at around 3 h coinciding with set due to the gellation of the sodium silicate, followed by a second peak at about 40 h due to bulk hydration of the slag. The peak due to heat of absorption of liquid on the slag surface is lost during the time required to bring the calorimeter to steady state after mixing and assembly.

Table 3
Image analysis results for pastes at 0.5 ml/g solution/slag ratio after 3 months hydration

Mix	Anhydrous (%)	Reaction (%)
C	20.5 (1.3)	50 (3.2)
C + 8% NaCl	24.5 (0.8)	40 (2.0)

Results are the average from approximately 30 images per sample, with a pixel size of 0.6 μm, and with 512 × 480 pixel images. Figures in brackets indicate standard errors. Anhydrous: area percentage of anhydrous material, measured from BSE images in the SEM. Reaction: reaction percentage, assuming that the initial paste contained 41 area % of anhydrous material, as calculated from the solution/slag ratio and density. C: control (without malic acid retarder). 8% NaCl: 8% NaCl (by weight of slag) added to mix.

Addition of sodium chloride or malic acid was found to retard the two main peaks significantly as shown in Figs. 3 and 4 and Table 4. When both the retarder malic acid and sodium chloride are present the peaks are further retarded, indeed to the point where the total heat output at 10 days is reduced nearly to zero. This experiment was repeated a number of times in different calorimeter cells to confirm the validity of the result.

Although the rate of heat evolution and the time at which it was evolved were sensitive to the presence of NaCl and/or malic acid retarder, the total heat evolved in each stage was not affected in those cases where it could

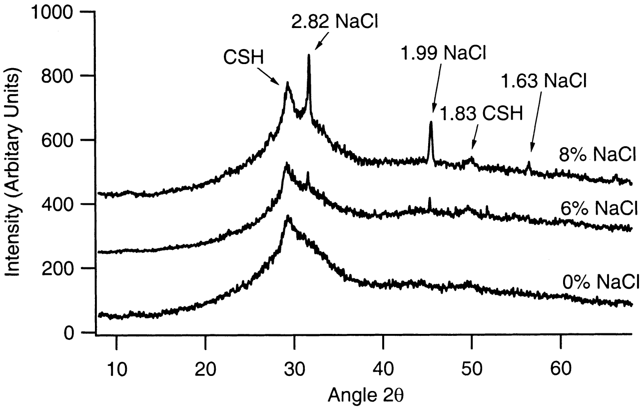

Fig. 2. Powder XRD spectra for three pastes hydrated for 28 days with various additions of NaCl. All three mixes contained 0.5% (by weight of slag) malic acid retarder. Assigned peaks are annotated with the d-spacing in Å.

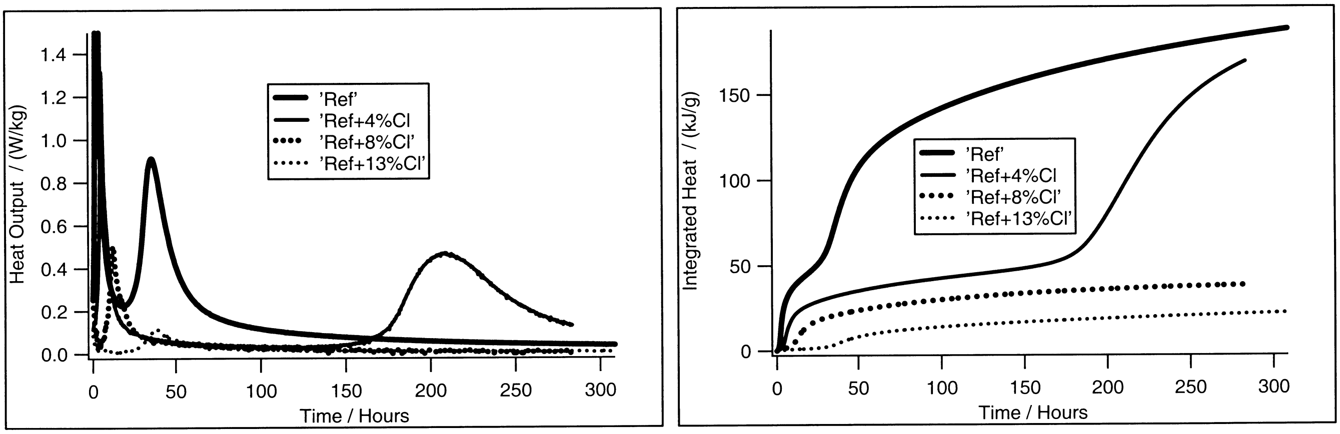

Fig. 3. Isothermal Calorimetry of reference alkali-activated slag mix, without retarder, and with various additions of sodium chloride up to 13% by weight of slag (a saturated solution). (a) Rate of heat evolution, and (b) integral heat output.

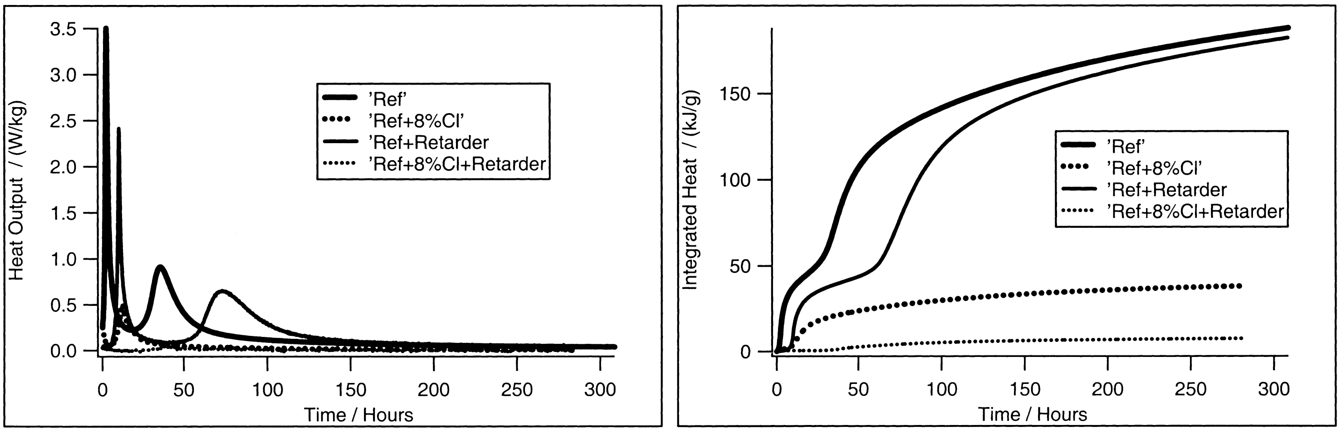

Fig. 4. Isothermal Calorimetry of reference alkali-activated slag mix, with malic acid retarder, and with additions of 8% sodium chloride by weight of slag. (a) Rate of heat evolution, and (b) integral heat output.

be measured, being approximately 40–45 kJ/g for the 1st stage, and 150+ kJ/g for the 2nd stage.

Table 4
Summary of data relating to calorimetry

	Heat at 240 h	1st peak			2nd peak[b]	
NaCl addition[a]	Integral (kJ/g)	Time (h)	Peak (mW/g)	Integral (kJ/g)	Time (h)	Peak (mW/g)
0	178	3	3.50	43	36	0.90
4	139	6	1.30	42	210	0.45
8	37	13	0.50	>37	[c]	[c]
13	20	39	0.10	>20	[c]	[c]
0 M	171	11	2.40	40	73	0.65
8 M	7	40	0.05	>7	[c]	[c]

[a] % by weight with respect to slag. M: malic acid retarder also added.

[b] The second peak is still generating heat at the end of the measuring time, so reliable integrals are not available.

[c] Not observed — either occurs later than 10 days, or not at all.

4. Discussion

In hydration of ordinary Portland cement, NaCl is known to act as an accelerator [10] at low concentrations, but as a retarder at high concentration [11]. This is also observed in the alkali-activated systems studied in this paper, NaCl was found to act as an accelerator at levels of 4% and below, but as a retarder at 8% additions, almost stopping hydration at the very highest concentrations. Malic acid was confirmed as an effective retarder, as reported elsewhere [7].

Set times were found approximately to coincide with the 1st main heat evolution peak measured by calorimetry. The main strength development peak then followed at a later age.

The compressive strength data are consistent with the observed calorimetric data, with the 0% NaCl system developing significant strength during the 1st 7 days when the 2nd calorimetry peak occurs, while the system with 8% NaCl does not have a 2nd heat peak in this time period, and does not develop significant strength until after 7 days. By 28 days, image analysis showed that the slag in both systems had hydrated significantly, though slightly less in the system with added NaCl. Similar strengths were achieved, which is consistent with normal strength development, where slow growth of hydrates gives rise to a stronger matrix for a given amount of hydrate.

The fact that the heat output for the two calorimetry peaks is largely unchanged upon addition of malic acid or NaCl retarder strongly suggests that these additions influence the rate of the gellation and hydration reactions but not their fundamental nature. This was confirmed by the similar composition of the hydration products in the systems with and without chloride. From the microanalysis no evidence was found for formation of distinct chloride-containing phases, which was consistent with the pore expression results, which showed most of the chloride remaining in solution.

5. Conclusions

(1) In alkali silicate-activated slag mortars, sodium chloride significantly retards both setting and strength development at high levels. At low addition levels, 4% or less by weight on the slag it acts as an accelerator.

(2) The integrated heat output for the two main calorimetric peaks is similar for retarded and non-retarded systems, the nature of the hydration products is similar and no new phases are seen by microanalysis or XRD. These results strongly suggests that the mechanism of hydration is not significantly altered by the presence of NaCl or malic acid.

Acknowledgments

We thank EPSRC, the Cementitious Slag Makers Association, and BNFL for support under grants GK/52201 and GR/K52218, the EPSRC for funding equipment under grant GR/L26537, and the Appleby Group and Crossfield for the supply of blast furnace slag and sodium silicates, respectively. We thank G. Fowler, Department of Civil Engineering, Imperial College, for use of and help with using the calorimetry facilities.

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