Early age strength enhancement of blended cement systems by CaCl$_2$ and diethanol-isopropanolamine

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ABSTRACT

The enhancement of the 1 day strength of cementitious systems by a combination of calcium chloride (CaCl$_2$) and diethanol-isopropanolamine (DEIPA) was studied, particularly in blended cement systems. A combination of quantitative X-ray diffraction with Rietveld refinement (QXRD), scanning electron microscopy (SEM)/backscattered electron image analysis, thermogravimetric analysis (TGA), and isothermal calorimetry were used to investigate the mechanism of strength enhancement by the additives. The additives were found to increase the early age mortar strength by enhancing the cement hydration, with the DEIPA enhancing primarily the aluminate hydration. DEIPA also affected the morphology of portlandite which was formed as thin plates. In parallel, the calcium-to-silica ratio of the C–S–H was found to increase with the use of DEIPA, possibly because of the inclusion of microcrystalline portlandite. After 48 h DEIPA was found to directly enhance the rate of reaction of granulated blast-furnace slag and fly ash.

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1. Introduction

Calcium chloride (CaCl$_2$) has been used for many years in concrete, and is widely regarded as one of the most effective accelerators for cement, especially in cold weather. It is also the most extensively studied accelerator, with hundreds of papers published on its effects in concrete. Calcium chloride increases the rate of C–S–H formation, consequently increasing the early age strength. Calcium chloride is most active during the first day of hydration. After the first day the chloride concentration in the pore solution decreases, because chloride combines with calcium aluminate hydrates to form Friedel's salt [1]. The use of calcium chloride is known not only to change the amount of C–S–H produced, but to change its morphology. Nitrogen absorption experiments have shown that CaCl$_2$ increases the surface area of C–S–H [2]. Soft X-ray microscopy images also show that C–S–H gives a more open microstructure and products with lower bulk density [3]. However, the exact mechanism of acceleration by CaCl$_2$ is still not well understood.

When used as an accelerator in non-reinforced concrete, calcium chloride is usually added at a rate of 0.1–0.7% by mass of cement. However, in reinforced concrete the use of CaCl$_2$ is limited because of concerns about corrosion of the steel. ACI 318 specifies a maximum chloride limit in concrete of 0.06% by weight of cement to reduce the risk of corrosion (2008).

There have been many studies on triethanolamine (TEA) and triisopropanolamine (TIPA), but very few on diethanol-isopropanolamine (DEIPA). Fig. 1 shows a schematic representation of the chemical structure of DEIPA. It is useful to consider the literature regarding the mechanisms of hydration enhancement by TEA and TIPA because they are chemically related to DEIPA and may enhance the hydration of cement in a similar manner. Gartner and Myers [4] proposed enhanced iron transport as the mechanism of strength enhancement by TEA and TIPA. Ramachandran [5] showed that TEA can accelerate the formation of ettringite in pure C$_3$A–sulfate systems at very early ages (<1 h). Neubauer et al. [6] also found that TEA increased the hydration of C$_3$A and the formation of ettringite during the induction period. Other studies have shown greater enhancement of hydration when a calcium salt was used in conjunction with an alkanolamine. The combined use of TEA and calcium nitrate was first suggested in 1981 [7]. Aggoun et al. [8] recently showed that when calcium nitrate was used in combination with either TEA or TIPA, both the setting time and strength gain were accelerated for all of the cements used in the study.

A combination of CaCl$_2$ and DEIPA has been found to increase the one day strength, especially of slag cement blends. The aim of the
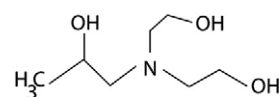

Fig. 1. Schematic representation of chemical structure of diethanol-isopropanolamine (DEIPA).

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Table 1
Cementitious materials composition.

Component	% Weight			
	HA cement	LA cement	Slag	Class F fly ash
SiO$_2$	19.1	20.48	34.32	53.89
Al$_2$O$_3$	5.13	4.72	13.99	16.59
Fe$_2$O$_3$	3.77	1.96	0.2	6.73
CaO	60.62	63.77	42.12	13.11
MgO	6.96	2.67	7.95	4.03
SO$_3$	1.29	2.98	1	0.68
Na$_2$O	0.21	0.13	0.24	0.8
K$_2$O	0.93	0.25	0.54	1.19
LOI (950 °C) (%)	1.51	2.58	0.462	0.15
Density	3.16	3.1	2.99	2.72

research presented here was to determine the mechanism of early age compressive strength enhancement, by answering the following questions:

1. Do the admixtures accelerate the degree of hydration of the cementitious (clinker + slag + fly ash + gypsum) system or change the hydration product distribution?
2. If the admixtures enhance the cement reaction, which are the cement phases most affected?
3. Do the admixtures act directly on the slag component, or accelerate the cement hydration which releases alkalis and in turn enhances the slag reaction?
4. Do the admixtures also enhance the reaction of systems containing other SCMs such as fly ash?

2. Materials

In order to elucidate question 3, a low alkali cement and a high alkali cement were chosen for this study in combination with a typical slag, and a Class F Fly Ash. The high alkali cement was made by intergrinding high alkali clinker with 4.5% gypsum in a laboratory ball mill. Commercially available cement was used for the low alkali cement. The supplementary cementing materials (SCMs) were blended with the cements in a laboratory ball mill, at a dosage of 30% replacement by mass. Table 1 shows the cement, slag and fly ash composition as determined by XRF and Table 2 shows the cement phase composition by X-ray diffraction and Rietveld analysis (QXRD).

The matrix of systems studied is shown in Table 3. When used, research grade DEIPA and CaCl$_2$ were added using a dosage by weight of cement of 0.02% and 0.06%, respectively. Potassium hydroxide was added to mix 9 to boost the potassium oxide level by 0.56% in the LA cement to study the effects of alkali content on the slag reactivity. Deionized water was used for the mixing water in all paste and mortar experiments. The pH of the mixing water and chemical admixtures when combined is shown in Table 4.

The aggregates used for the mortar strength measurements according to EN 196 [9], were natural siliceous aggregates pre-blended, weighed and packaged in plastic bags conforming to EN 196-1. The

Table 2
Cement composition as determined by QXRD.

Component	HA cement	LA cement
Alite	63.0	68.0
Belite	8.9	6.7
Aluminate	4.2	7.2
Ferrite	10.6	6.8
Periclase	8.0	1.7
Gypsum	3.2	6.4
Hemihydrate	1.2	0.6
Calcite	0	1.8
Arcanite	1.0	0

Table 3
Study experimental matrix.

Mix #	Cement	SCM	Additive	Purpose
1	HA cement	Slag	Blank	Control for high alkali cement–slag systems
2	HA cement	Slag	CaCl$_2$	Effect of CaCl$_2$ alone on high alkali cement–slag systems
3	HA cement	Slag	DEIPA	Effect of DEIPA alone on high alkali cement–slag systems
4	HA cement	Slag	DEIPA + CaCl$_2$	Synergy of DEIPA and CaCl$_2$ on increasing slag degree of hydration
5	LA cement	Slag	Blank	Effect of alkali availability and time of release on slag degree of hydration
6	LA cement	Slag	CaCl$_2$	
7	LA cement	Slag	DEIPA	
8	LA cement	Slag	DEIPA + CaCl$_2$	
9	LA cement	Slag	KOH	
10	HA cement		Blank	Comparison of effects of chemical admixture system without slag
11	HA cement		CaCl$_2$	
12	HA cement		DEIPA	
13	HA cement		DEIPA + CaCl$_2$	
14	LA cement		Blank	Comparison of effects of chemical admixture, added alkalis on system without slag
15	LA cement		CaCl$_2$	
16	LA cement		DEIPA	
17	LA cement		DEIPA + CaCl$_2$	
18	LA cement		KOH	
19	LA cement	Fly Ash	Blank	Comparison of effects of chemical admixture system with fly ash
20	LA cement	Fly Ash	CaCl$_2$	
21	LA cement	Fly Ash	DEIPA	
22	LA cement	Fly Ash	DEIPA + CaCl$_2$	

sand used for the ASTM C 109 compressive strength experiments was graded natural siliceous sand.

3. Methodology

3.1. Mortar experiments

Mortar strength was measured to investigate the effects of the chemical additives on the strength development and link them to the microstructural development of the cementitious systems. The mortar strengths were measured according to EN 196 and also at the laboratories of W.R. Grace according to ASTM C 109 [10]. EN 196 specifies that the compressive strength is measured on a 40 mm by 40 mm area of each end of a 40 mm by 40 mm by 160 mm mortar prism after this has been tested in flexure, whereas the compressive strength according to ASTM C 109 is measured on 50 mm mortar cubes. EN 196 specifies a water to cementitious (w/cm) of 0.5 and an aggregate-to-cementitious ratio of 3. ASTM C 109 specifies a narrower sand gradation, a w/cm of 0.485, and an aggregate-to-cementitious ratio of 2.75. The strength values according to EN 196 are the average of 3 specimens for mixtures 1–5 and 8, and 2 specimens for the remaining mixes. The values according to ASTM C 109 are the average of 2 specimens.

Table 4
pH of mixing water and chemical admixture combinations.

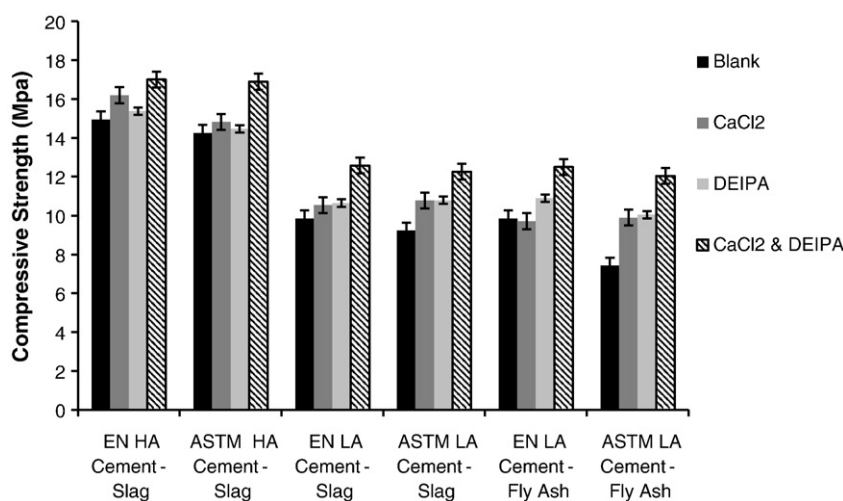| Solution	pH
Deionized water	5.5
Deionized water + 600 ppm CaCl$_2$	6.4
Deionized water + 200 ppm DEIPA	9.8
Deionized water + 600 ppm CaCl$_2$ + 200 ppm DEIPA	9.5

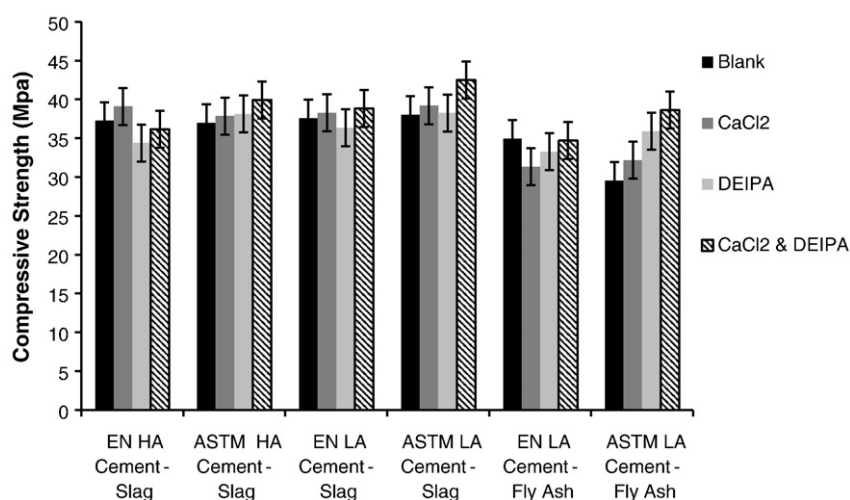**Fig. 2.** 1 Day mortar compressive strength results.

Fig. 3. 7 Day mortar compressive strength results.

3.2. Paste experiments

Most of the microstructural characterization was carried out on cement pastes, prepared to be analogous to the mortar specimens with a w/cm of 0.35[1] to quantify the effect of the chemical additives on phase and microstructural development. Quantitative XRD, SEM Image analysis, and thermogravimetric analysis were used to quantify the hydration products formed and degree of hydration of the clinker components. Isothermal calorimetry and chemical shrinkage were used to quantify the clinker and slag hydration.

Cement pastes were mixed using a laboratory mixer for 3 min at 500 rpm, followed by 2 min of rest, and finally mixed for 2 min at 2000 rpm. Samples were wet cured by adding a few milliliters of deionized water to samples 10 h after mixing.

3.2.1. Hydration stopping procedure

D-drying was used to stop hydration in samples at 24 h of age or less. D-drying works by freezing the free water in the pores below the triple point where water, ice and water vapor can coexist, and then lowering the pressure to cause sublimation of the water (direct phase change from solid to vapor). D-drying is the preferred method for stopping hydration at early ages because it is not necessary to de-mould the specimen which could cause the paste to crumble, stops hydration quicker than with solvent exchange, and does not alter the hydration products from interaction with the solvent, as can happen with some solvents such as methanol [11]. However, D-drying does have a major impact on the crystallinity of ettringite, which cannot be measured by QXRD for samples stopped in this manner. With cement pastes, it is important to use small samples, otherwise the sample may take a long time to dry, allowing the center of the sample to melt and restart hydration.

Samples for the D-drying were cast in 3.5 ml polystyrene cylinders with a diameter of 15 mm and a height of 30 mm. At the appropriate age, the samples were placed in a Dewar flask containing a mixture of isopropanol and dry ice for at least 2 h, with the sample lids remaining closed. After freezing, the samples were quickly removed from the Dewar flask, the lids removed, and the samples placed in a glass flask. The flask was then attached to a vacuum at 0.175 mbar and cooled to −55 °C. The samples were kept under vacuum for at least 24 h.

Solvent exchange with isopropanol was used to stop hydration in samples at ages later than 1 day. Samples for these later ages were cast in 50 ml polystyrene cylinders with a 35 mm inside diameter and 70 mm in height. At the appropriate age, the samples were removed from the container and saw cut into slices 2–5 mm thick. Ethanol was

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[1] The w/cm ratio is lower in pastes due to the higher level of water in the interfacial transition zone in mortars. Use of the w/cm in pastes as mortars would result in high levels of bleeding in the pastes.
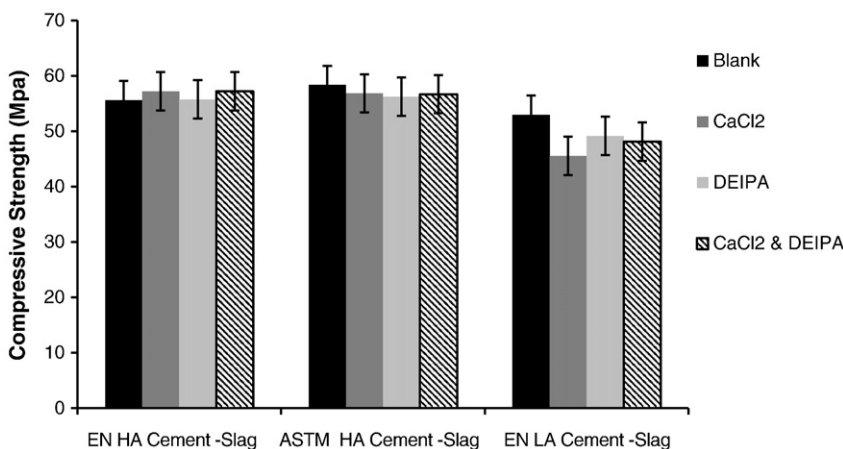
Fig. 4. 28 Day mortar compressive strength results.

used as a lubricating agent during cutting. After cutting, the samples were immersed in isopropanol for 7 days. After removal from the isopropanol, the sample was placed in a vacuum for at least 24 h to dry, and then weighed to determine the sample free water content.

3.2.2. Quantitative X-ray diffraction

Quantitative X-ray diffraction was used to study the phase development and measure the degree of hydration of the cement phases and the total cement degree of hydration. Freeze dried samples were used for QXRD at an age of 24 h or earlier. For samples at ages later than 24 h, an extra slice of hardened cement paste was sawn at the same time as the samples used for solvent exchange. Immediately after cutting and washing the sample with ethanol it was analyzed by QXRD. The samples for QXRD older than 24 h were not dried as the drying will affect the ettringite crystallinity. Rutile was used as an external standard for quantification of the sample amorphous content.

3.2.3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was used to quantify the portlandite content of the systems studied. TGA is the most accurate method for quantifying the portlandite content. As a complimentary method to QXRD for quantifying portlandite, TGA can serve as a check on the accuracy of the QXRD measurements. Samples, from which the free water had been removed by D-drying or solvent exchange were heated from 30 °C to 950 °C at 10 °C/min in a nitrogen environment. The mass losses for portlandite and calcium carbonate were quantified by the tangent method.

3.2.4. SEM BSE image analysis

Quantitative analysis of SEM images was carried out on polished cement paste sections. Care was taken to minimize the damage to alite grains during polishing due to difference in hardness between the clinker and slag grains. The percent area (equivalent to% volume) of anhydrous clinker, slag, portlandite, C–S–H, and porosity were quantified by the automatic SEM image analysis.

3.2.5. Isothermal calorimetry

An 8 channel isothermal calorimeter (Thermometrics TAMair) was used to quantify the kinetics of cement hydration with and without the chemical admixtures. Water, with the same heat capacity as the sample, was used for the reference sample. The isothermal calorimetry experiments were run for 10 days to track the early hydration of the cementitious systems.

4. Results and discussion

4.1. Strength development

The mortar strengths at 24 h and 7 days according to EN 196 and ASTM C 109 are shown in Figs. 2 and 3. The strengths at 28 days for the EN 196-1 method are shown in Fig. 4. The combination of DEIPA and $CaCl_2$ enhanced the 1-day compressive strengths of the HA cement and slag blend by 14–19% (2.1–2.6 MPa), the LA cement and slag blend by 28–33% (2.8–3.1 MPa), and the LA cement and Class F Fly Ash blend by 28–62% (2.6–4.7 MPa). The admixtures however, did not significantly affect the 7 day or 28 day compressive strengths despite
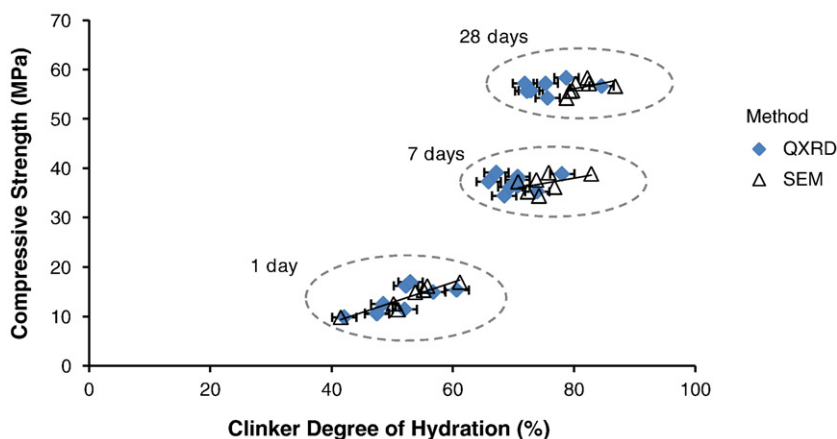

Fig. 5. HA cement–slag blends and LA cement–slag blends compressive strength at 1 day, 7 days, and 28 days vs. clinker degree of hydration as measured by QXRD or SEM/BSE image analysis. Trend lines shown are for clinker degree of hydration as measured by SEM/BSE image analysis. Trend lines shown are for clinker degree of hydration as measured by SEM/BSE image analysis.
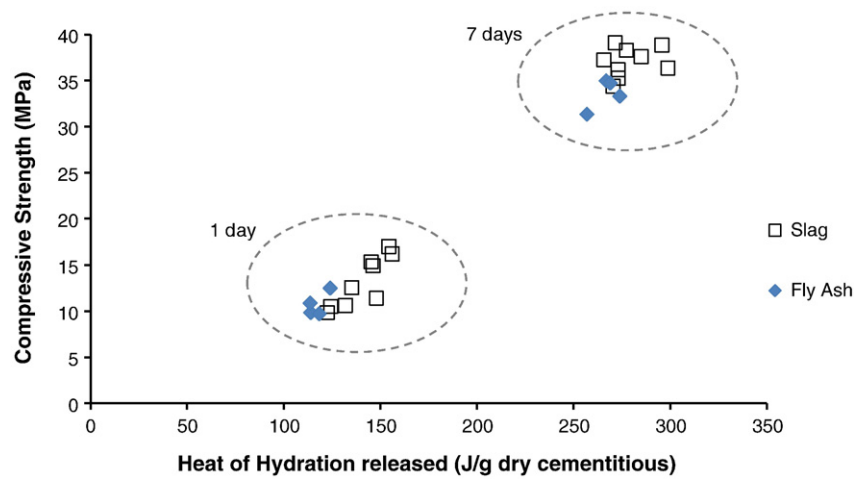
Fig. 6. Compressive strength vs. heat of hydration released in isothermal calorimetry (J/g dry cementitious) for all mixtures at 1 day or 7 days containing slag or fly ash.

higher measured degrees of hydration. Similar trends were seen for the mortar mixtures without SCMs at 1 and 7 days as measured according to ASTM C 109.

Fig. 5 shows the correlation between the mortar compressive strengths according to EN 196-1 with the degree of hydration of the clinker component from QXRD or SEM/BSE image analysis. The trend lines shown in Fig. 5 are for the clinker degree of hydration as measured by SEM/BSE image analysis. The clinker degree of hydration is used for comparison instead of cement degree of hydration because the gypsum is a dark color in SEM/BSE image analysis and not easily quantified. Fig. 6 shows the compressive strength determined according to EN 196-1 vs. the cumulative heat released in isothermal calorimetry for all mixtures containing slag and for the LA cement–fly ash blend. Table 5 shows the compressive strength measurements by both standard methods used along with the measured degree of cement and slag hydration using QXRD and SEM/BSE image analysis. The increased degree of hydration of the clinker component by SEM correlates well with the strength increase for the systems with the chemical additives at 1 day. The degree of hydration as measured by isothermal calorimetry was the best indicator of the compressive strength gain at one day because it is the most accurate method for measuring early age hydration, although similar trends (not shown) were found for the porosity as measured by evaporable water and SEM/BSE image analysis. Additionally, any change in the slag or fly ash rate of hydration will be directly measured in the isothermal calorimetry. The strength clearly increases with age as the hydration progresses. At 7 and 28 days, there appears to be very little impact of the admixtures on strength despite some measurable differences in degree of hydration. It is interesting to note the relationship between strength and degree of hydration at each age. During the first day, it is the total degree of hydration and consequently the total porosity that determines the strength. As the degree of hydration increases, similar strengths are seen for the different mixtures even though the degree of hydration is different, indicating that the overall porosity is less important at these ages.

As seen in Fig. 6, the relationship between heat released in isothermal calorimetry and compressive strength for the mixtures containing fly ash at 1 and 7 days follows the same trend as the mixtures made with slag. The mixtures containing slag show a higher amount of heat released and compressive strength than the mixtures with fly ash.

4.2. Effect on different cement phases

There was a small increase in the isothermal calorimetry peaks associated with the hydration of the aluminate phases, as seen in Fig. 7 for the LA cement and Fig. 8 for the HA cement. The DEIPA shows a larger increase in the aluminate peaks of the LA cement because of the higher aluminate content in the LA cement. Additionally, the use of $CaCl_2$

Table 5
1 Day compressive strength, cement degree of hydration, and slag degree of hydration as measured by different methods for the cement–slag systems studied.

| Cementitious system			1 Day compressive strength		1 Day cement degree of hydration		1 Day slag degree of hydration
Cement	SCM	Chemical admixtures	EPFL-EN 196	W.R. Grace ASTM C 109	QXRD (%)	SEM (%)	SEM (%)
HA cement	–	Blank	–	22.7	56	–	–
HA cement	–	$CaCl_2$	–	25.1	59	–	–
HA cement	–	DEIPA	–	24.5	60	–	–
HA cement	–	$CaCl_2$ and DEIPA	–	26.6	60	–	–
HA cement	Slag	Blank	14.9	14.3	59	57	13
HA cement	Slag	$CaCl_2$	16.2	14.8	55	58	18
HA cement	Slag	DEIPA	15.4	14.5	63	58	20
HA cement	Slag	$CaCl_2$ and DEIPA	17.0	16.9	55	64	14
LA cement	Slag	Blank	9.8	9.2	48	42	13
LA cement	Slag	$CaCl_2$	10.5	10.8	53	–	–
LA cement	Slag	DEIPA	10.6	10.8	54	–	–
LA cement	Slag	$CaCl_2$ and DEIPA	12.6	12.3	54	54	14
LA cement	Slag	KOH	11.4	–	57	55	21
LA cement	–	Blank	–	15.3	55	–	–
LA cement	–	$CaCl_2$	–	17.4	60	–	–
LA cement	–	DEIPA	–	16.5	59	–	–
LA cement	–	$CaCl_2$ and DEIPA	–	19.1	63	–	–
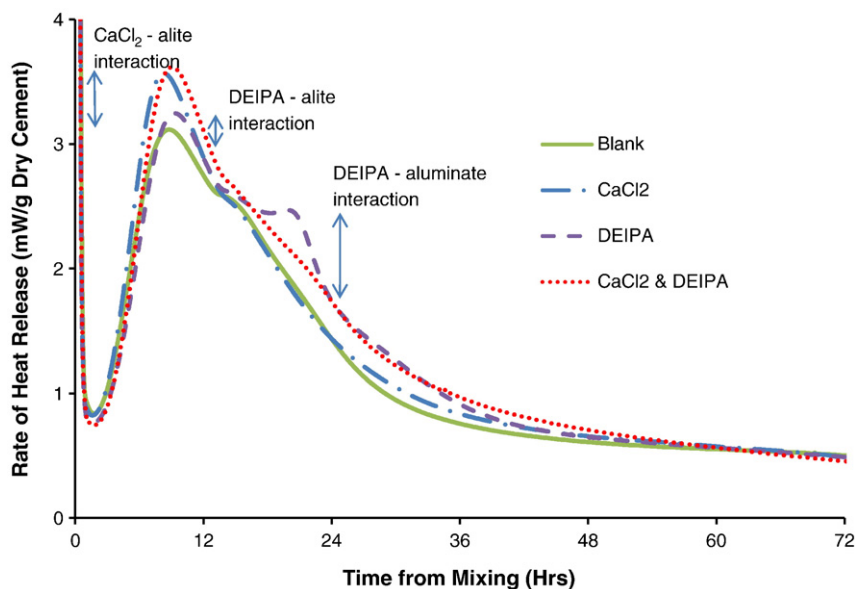
Fig. 7. LA cement and slag isothermal calorimetry.

increases the alite peak in Figs. 7 and 8. QXRD was carried out on the LA cement–slag blend with and without the chemical additives to investigate any differences in the consumption of C_3A or C3S during the first day. Hydration was stopped for these experiments every 2 h between 4 and 24 h of age by D-drying. Fig. 9 shows the a) C_3A, b) C_3S, and c) C_4AF content as determined by QXRD for the LA cement–slag blend during the first day. The differences in the C_3A, C_3S, and C_4AF content from the use of the chemicals were smaller than the accuracy achievable by QXRD, although the aluminate content tended to be lower when DEIPA is used. The level of addition of the chemical additive in this study was much lower than that used by Neubauer et al. or Ramachandran, making any changes in C_3A reaction more difficult to detect.

4.3. Microstructural changes induced by additives

The examination of the samples in the SEM did not indicate any significant microstructural changes due to the presence of the admixtures except for the morphology of portlandite, which changed dramatically in the presence of DEIPA. The portlandite crystals changed from being large masses to thin plates with the addition of DEIPA. The

change in the portlandite morphology occurred at a very early age as this difference was already noticeable in samples at 10 h of hydration as shown in Fig. 10a and b. A slight decrease in the portlandite content measured by TGA after 1 day of hydration for the samples with DEIPA compared to the references without was also noticed in this study for both cements with slag, and is shown for the LA cement and slag system in Fig. 11. The same slight decrease was also noticed in the QXRD measurements for LA cement and for both cements containing slag. Fig. 12 shows the portlandite content as measured by QXRD vs. the cement degree of hydration as measured by QXRD for the LA cement without slag, which removes the effects of kinetics and allows for a better comparison. Since these samples shown in Fig. 12 do not contain any SCMs, the decrease in measureable portlandite content for the same amount of cement reacted is more apparent when DEIPA is used.

Analysis of the C–S–H composition of the cement–slag blends by many EDX points showed that the C–S–H has a slightly higher calcium-to-silica ratio when DEIPA was used. Fig. 13 shows the alumina-to-calcium ratio vs. the silica-to-calcium ratio for the HA cement–slag blends with and without DEIPA with the trend to the C–S–H composition shown for each system. The higher calcium content in the C–S–
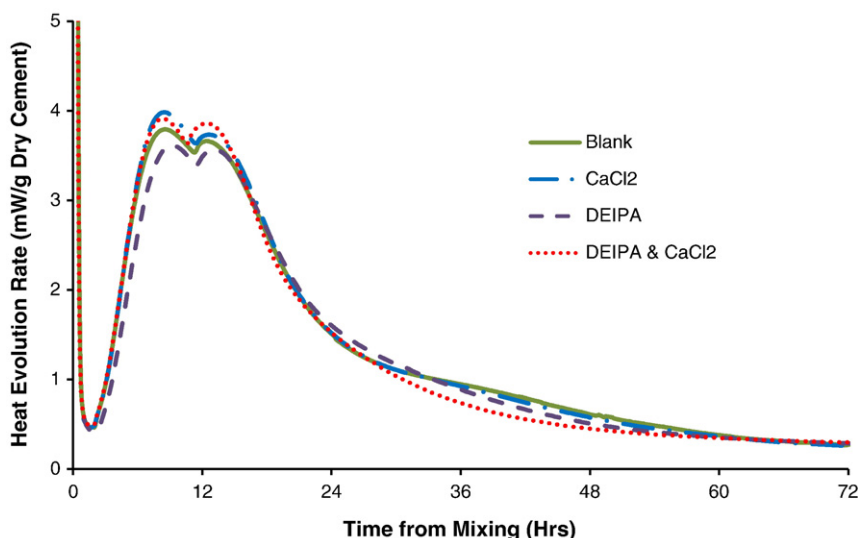

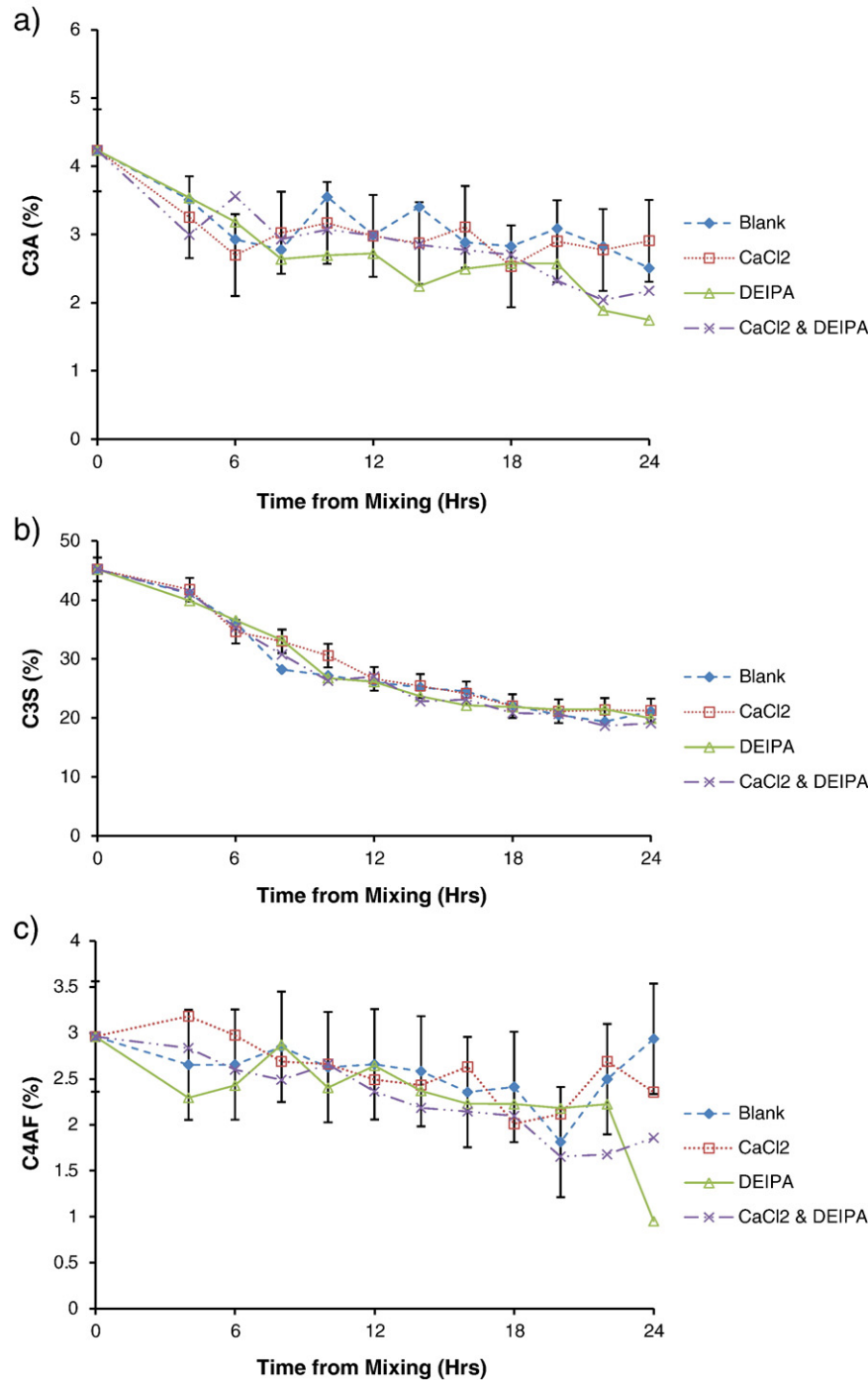**Fig. 8.** HA cement and slag isothermal calorimetry.

Fig. 9. a) C_3A, b) C_3S, and c) Ferrite content with time for the LA cement–slag blend.

H could account for a decrease of 0.9–1.3% of the portlandite content, which is very similar to the decrease in portlandite content measured by TGA and QXRD. Ramachandran [12] found a decrease in the amount of portlandite in hydrated C_3S pastes treated with TEA at the same degree of hydration as the control paste, suggesting that DEIPA and TEA have a similar mechanism of hydration enhancement of alite after 1 day. This increase in measured calcium-to-silica ratio could be because of either an increase in the calcium in C–S–H or an increase in micro-crystalline portlandite intermixed with C–S–H.

A previous study has shown that the portlandite morphology is also affected by the presence of aluminate in the cement [13]. There may be a link between the enhanced aluminate reaction with the use of DEIPA which is shown in the isothermal calorimetry and the inhibition of calcium hydroxide growth on the 0001 faces. As long as there is space available for the portlandite crystals to grow anisotropically in hexagonal plates, the portlandite content was the same with and without DEIPA. After 1 day when the space available for anisotropic growth becomes limited, the portlandite crystals are forced to either thicken or form new crystals. As the organic additive makes it more difficult for the plates to thicken, portlandite may be forced to precipitate as micro-crystals intermixed with the C–S–H.

4.4. Slag reactivity

The heat release from the presence of slag was calculated by subtracting the heat released when slag is used from the heat released
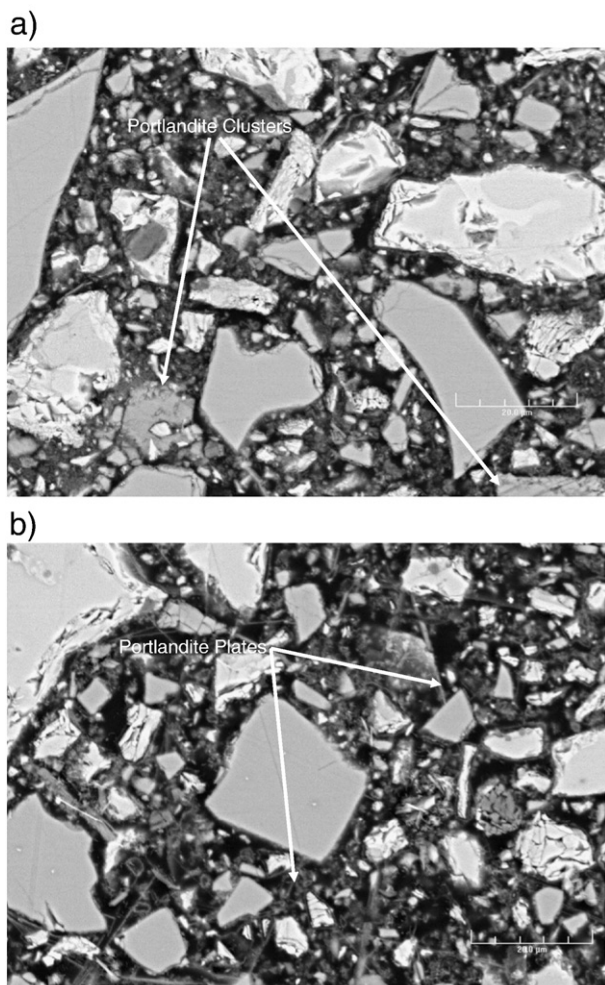
Fig. 10. SEM/BSE micrographs at 10 h of hydration for HA cement and slag with a) CaCl$_2$ and b) CaCl$_2$ and DEIPA.

for the cement reaction without slag, normalized by the mass of dry cement. Fig. 14 shows the heat that is from the presence of slag, this includes the impact of the slag on the reaction of the clinker components, due to the extra space available for hydration and slag grains acting as nucleation sites, as well as the reaction of the slag

itself. The difference in heat released was then normalized to the mass of dry slag and is shown for LA cement in Fig. 15 and for HA cement in Fig. 16. During the first 24 h, the method captures mainly the effect of the slag on the cement hydration. After the first 24 h, the increased heat of hydration is mainly from slag reaction. A more complete description of the method and possible errors is given by Kocaba [14].

The degree of slag reaction as measured by SEM/BSE image analysis, as shown in Fig. 17 for the HA cement blended system, confirms the increase in the slag degree of reaction shown by isothermal calorimetry when DEIPA was used. CaCl$_2$ increases slightly the slag rate of reaction as seen in Figs. 15 and 16. This is probably due to the increased rate of cement reaction and the release of alkalis which can slightly enhance the slag hydration. DEIPA however shows a very different effect on the slag hydration. During the first 24 h there is a slight reduction in heat released in the systems containing slag with DEIPA. At later ages however, there is a large increase in the amount of heat released indicating a very significant increase in the degree of slag hydration from the use of DEIPA. The enhanced slag reaction with DEIPA is seen sooner with the LA cement (24 h) than with the HA cement (130 h). This is because the increase in slag reaction due to alkalis in the HA cement overshadows the increased reaction of the slag by DEIPA at earlier ages.

Fig. 18 shows the heat of reaction due to slag for both of the cements and the LA cement with added KOH all without admixtures. The added alkalis sharply increase the heat of reaction due to the presence of slag during the first 24 h. This is because the added alkalis are added already in solution instead of slowly released as in the case of alkalis from cement. After the first 24 h, when most of the alkalis have been released from the cement, the heat due to slag reaction with HA cement is similar to that of the boosted alkalis. Fig. 19 shows the influence of the slag on the heat of hydration for both cements set to zero at 24 h to focus only on the increase in slag reaction. The influence of alkalis on the slag hydration is to accelerate the rate of hydration during the first few days. DEIPA on the other hand, increases greatly the slag rate of reaction after 24 h, suggesting that DEIPA works directly on the slag.

4.5. Fly ash reactivity

The fly ash heat of hydration was calculated from isothermal calorimetry in the same manner as with slag, and is shown in Fig. 20. The use of CaCl$_2$ increases the rate of reaction slightly of the fly ash, probably from the increased rate of reaction of the cement which releases alkalis faster, in turn speeding up the reaction of the fly ash. DEIPA enhances
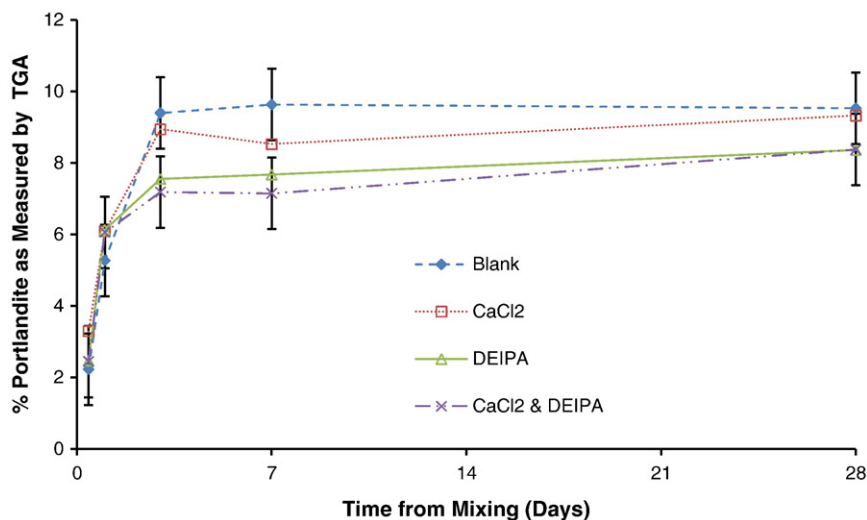

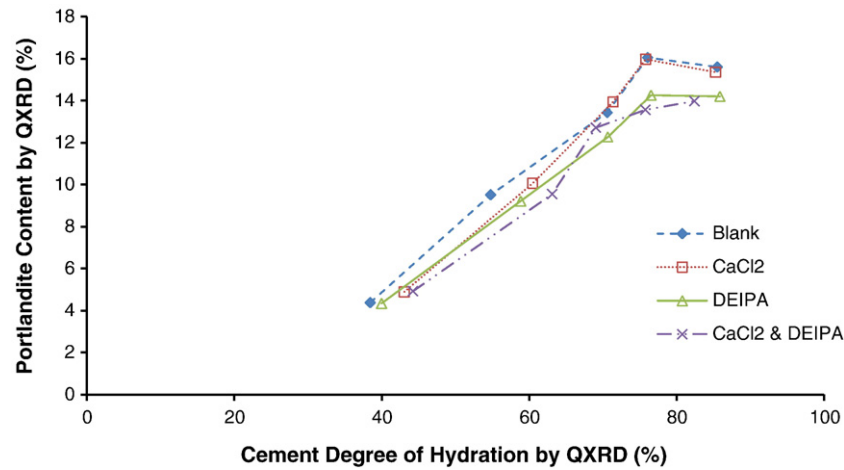Fig. 11. % Portlandite content for LA cement–slag blend as measured by TGA.

Fig. 12. Portlandite content as measured by QXRD (%) vs. cement degree of hydration as measured by QXRD (%) for LA cement.
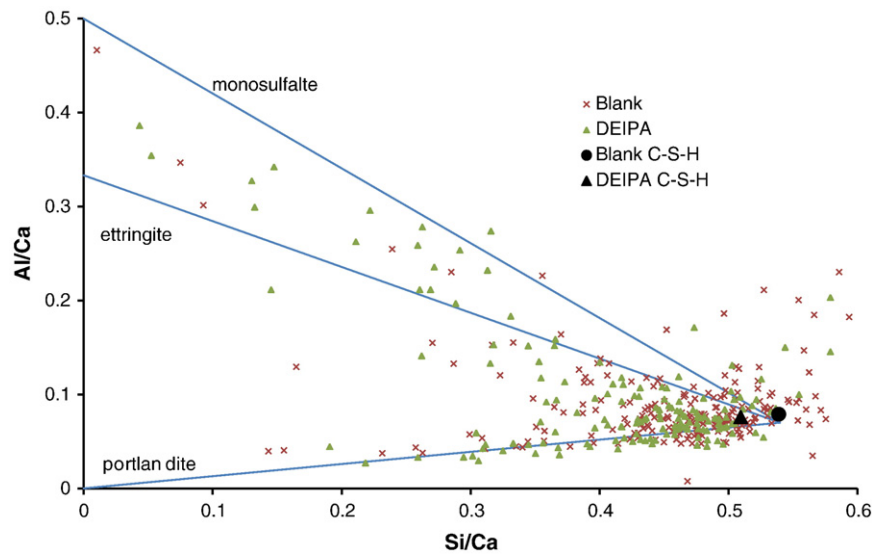

Fig. 13. EDX analysis of points from HA cement–slag blend with and without DEIPA.

the fly ash reaction at later ages much like the slag reaction. This indicates that the DEIPA could increase the hydration of supplementary cementing materials by increasing the dissolution of glasses or en-hancing the diffusion of the ions. However, more research would be needed to determine the exact mechanism of strength enhancement with fly ash, and the effect of DEIPA on different types of fly ash.

5. Discussion and conclusions

The following conclusions can be drawn from the present study on the strength enhancement of blended systems by $CaCl_2$ and DEIPA:

- The combination of DEIPA and $CaCl_2$ increases the early age strength of mortar by increasing the degree of cement reaction.
- DEIPA mainly accelerates the aluminate phases.
- DEIPA changes the portlandite morphology and precipitation. A lower portlandite content and a higher calcium-to-silica ratio in C–S–H were measured in samples with DEIPA. Anisotropic portlandite growth with DEIPA led to thin plate morphology instead of large crystal masses.
- DEIPA increases directly the hydration of slag after 48 h, possibly by either increasing the attack on the glassy phases, or enhancing the mobility of elements dissolving from the slag. Further investigation is needed to determine the exact mechanism of SCM hydration enhancement by the admixtures.

Fig. 14. Illustration of the method used to calculate the influence of slag on the heat of hydration.
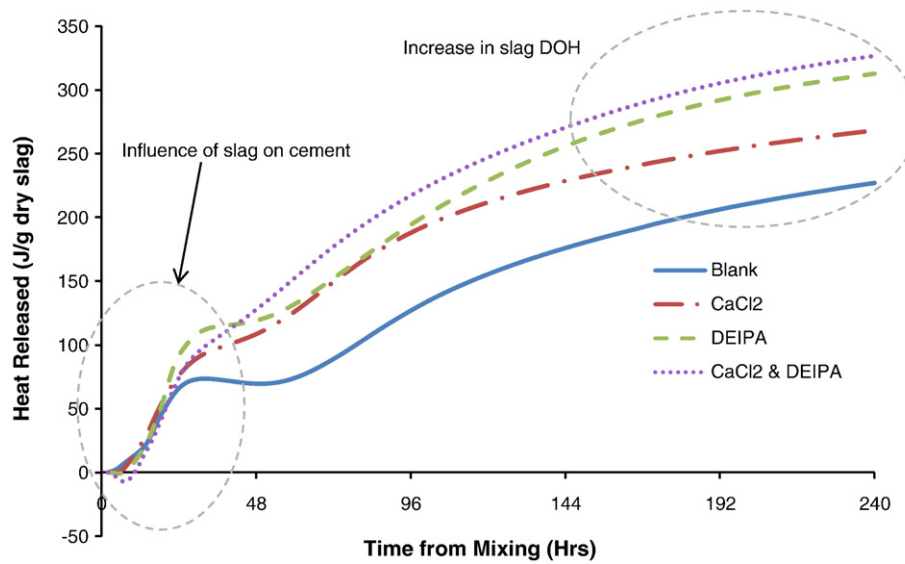
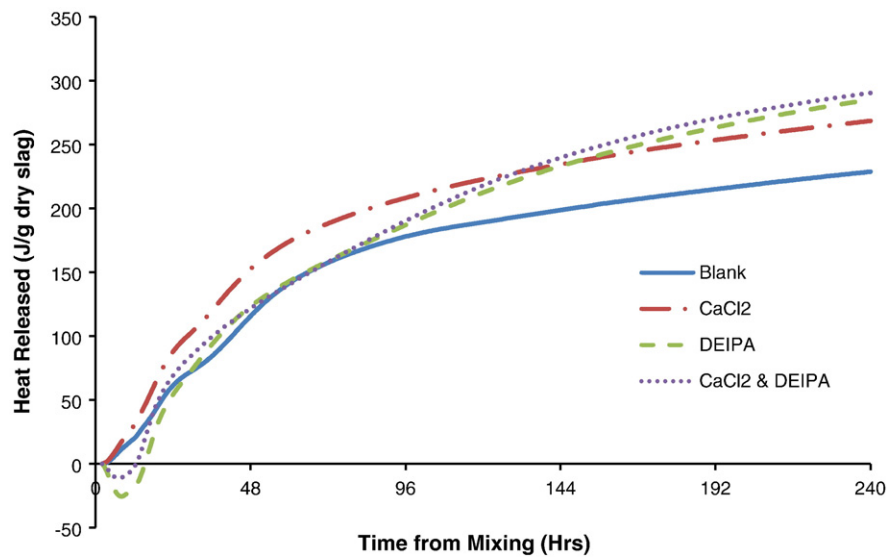Fig. 15. Influence of slag on heat of hydration for LA cement.

Fig. 16. Heat of hydration release from the use of slag and HA cement.
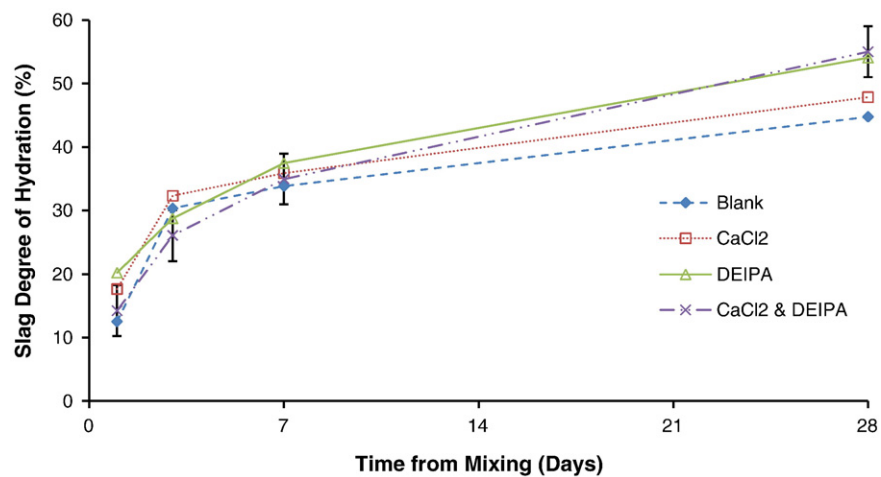

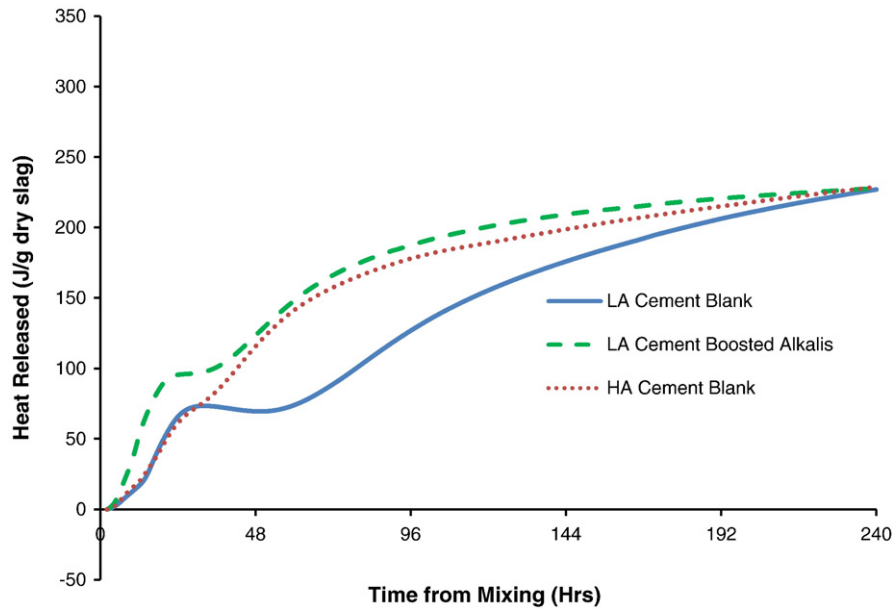Fig. 17. Increase in slag degree of hydration as measured by SEM image analysis.

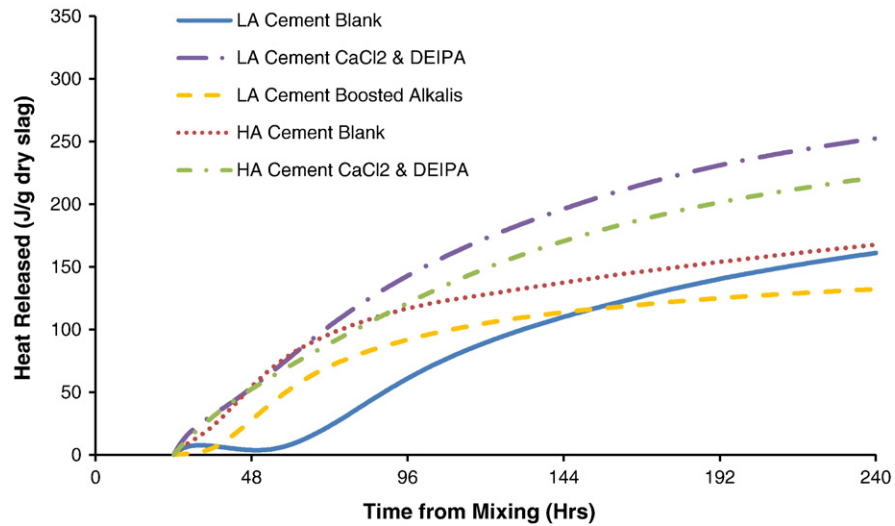**Fig. 18.** Heat of hydration release of slag and boosted alkalis on heat of hydration.

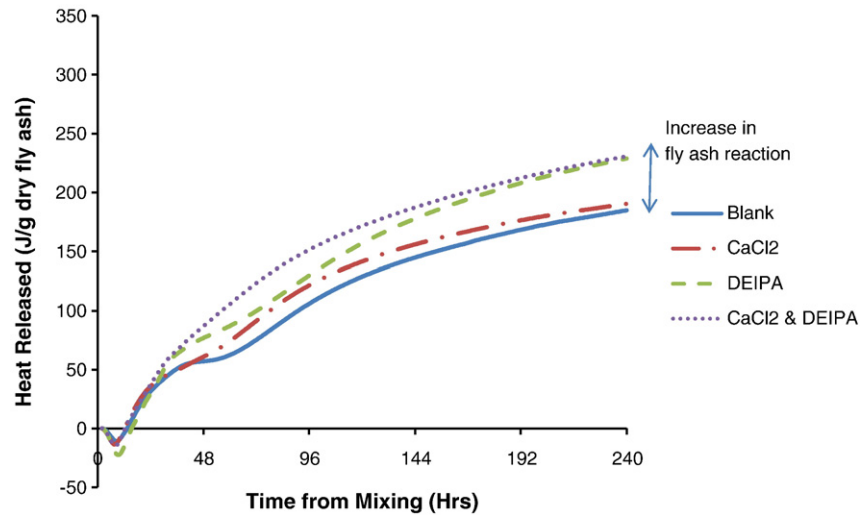**Fig. 19.** Influence of slag on heat of hydration after 24 h for both cements.

Fig. 20. Calculated fly ash heat of hydration with LA cement.

• Fly ash hydration was also enhanced after 48 h by the use of DEIPA, probably by similar mechanisms as the slag.

Acknowledgements

References

[1] S. Diamond, F. Lopez-Flores, Fate of calcium chloride dissolved in concrete mix water, J. Am. Ceram. Soc. 64 (11) (1981) 162–164 1981.
[2] M.C. Juenger, H.M. Jennings, The use of nitrogen adsorption to assess the microstructure of cement pastes, Cem. Concr. Res. 31 (6) (2001) 883–892.
[3] M.C. Juenger, P.J. Monteiro, E.M. Gartner, G.P. Denbeaux, A soft X-ray microscope investigation into the effects of calcium chloride on tricalcium silicate hydration, Cem. Concr. Res. 35 (1) (2005) 19–25.
[4] E. Gartner, D. Myers, Influence of tertiary alkanolamines on Portland cement hydration, J. Am. Ceram. Soc. 76 (6) (1993) 883–892.
[5] V.S. Ramachandran, Action of triethanolamine of the hydration of tricalcium aluminate, Cem. Concr. Res. 3 (1) (1973) 41–54.
[6] J. Neubauer, F. Goetz-Neunhoeffer, U. Holland, D. Schmitt, Crystal chemistry and microstructure of hydrated phases occuring during early OPC hydration, Proceedings of the 12th International Congress on the Chemistry of Cement, Montreal, Canada, 2007.
[7] M. Cheikh-Zouaoui, N. Chikh, S. Aggoun, R. Duval, Studies on effects of activators on properties and mechanism of hydration of Portland cement, Proceedings of the International Conference on Admixtures — Enhancing Concrete Performance, Dundee, Scotland, United Kingdon, 2005, pp. 183–190.
[8] S. Aggoun, M. Cheikh-Zouaoui, N. Chikh, R. Duval, Effect of some admixtures on the setting time and strength evolution of cement pastes at early ages, Constr. Build. Mater. 22 (2) (2008) 106–110.
[9] EN 196-1, Methods of Testing Cement — Part 1: Determination of Strength, 2005.
[10] ASTM C 109, Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens), American Society for Testing and Materials, 2007, pp. 1–9.
[11] R.F. Feldman, Diffusion measurements in cement paste by water replacement using propan-2-ol, Cem. Concr. Res. 17 (4) (1987) 602–612.
[12] V.S. Ramachandran, Influence of triethanolamine on the hydration characteristics of tricalcium silicate, J. Appl. Chem. Biotechnol. 22 (11) (1972) 1125–1138.
[13] E. Gallucci, K. Scrivener, Crystallization of calcium hydroxide in early age model and ordinary cementitious systems, Cem. Concr. Res. 37 (4) (2007) 492–501.
[14] Kocaba, Development and evaluation of methods to follow microstructural development of cementitious systems including slags, Ph.D. Thesis No. 4523, Swiss Federal Institute of Technology at Lausanne, 2009, 239 pp.