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Effect of TEA on fly ash solubility and early age strength of mortar

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ABSTRACT

The investigations focused on the dissolution behaviour of fly ash in alkaline solution and the effect of triethanolamine (TEA) addition. TEA is known as a grinding aid in cement production and is an Al and Fe chelating agent. To determine the effect of TEA on the dissolution behaviour of fly ash constituents, fly ash was mixed with a KOH solution at pH 13 and different dosages of TEA. Samples were taken after different times and analysed by ICP-OES. The effect of TEA on the heat evolution rates of fly ash cement pastes was investigated using isothermal calorimetry. Strength tests were also conducted to investigate the effect of TEA on plain Portland cement and fly ash/cement mortars. TEA was found to increase the dissolution rate of Al, Ca and Fe from fly ash. A slight, but reproducible, effect on heat evolution rates and an increase in early age strength was observed for fly ash cements.

1. Introduction

The partial replacement of Portland cement clinker with supplementary cementitious materials such as fly ash lowers the energy required for concrete production and thus the emission of CO_2. Fly ash also has a positive effect on the permeability of concrete and thus the durability of structural components [1]. However, a disadvantage of using fly ash as a cement substitute is its slow pozzolanic reaction which lowers early strength [2–5]. The consumption of $Ca(OH)_2$ places a limit on the maximum amount of fly ash which can be used without endangering the passivity of the steel reinforcement.

An increase in the early strength of concrete made with cement blends containing fly ash without sacrificing improved long-term durability is of obvious economic importance. Thus ways of enhancing the activity of fly ash have been considered. Besides the effect of the fineness [6–8], different kinds of additives including alkali sulphates and alkanolamines [4,9–11] have been investigated. Several oxicarbon acids are known in glass chemistry for their ability to break up the siliceous network of glass structures [12]. Therefore, these substances are thought to accelerate the dissolution of fly ash and thus the pozzolanic reaction. In particular, triethanolamine (TEA, $C_6H_{15}NO_3$), an alkanolamine used as a grinding aid in cement production, is thought to accelerate the hydration process of Portland cement [9,11,13]. Magistri et al. [10] studied the effect of grinding aids based on alkanolamines on Portland cement hydration using XRD and observed more rapid formation of C-S-H. Gartner et al. [9] observed an increased iron solubility due to the chelating potential of TEA so more iron reacted to form mono and trisulfates. Depending on the chemical composition of the Portland cement, TEA addition was observed to produce a gain in mortar strength in some cases. Lee et al. [4] noted accelerated hydration of fly ash cements due to TEA addition but did not consider whether the hydration of Portland cement or fly ash is affected by TEA. Lee et al. [4] observed that overdosage of TEA leads to a decrease in strength.

Owing to its aluminium chelating potential, TEA was found by Spencer et al. [14] and Palmer et al. [15] to be able to extract aluminium phases from sludge. In analytic chemistry, complexometric titration is a standard procedure to quantify cations where unwanted Al and Fe ions are masked by the formation of stable complexes with TEA.

The effect of TEA on the dissolution behaviour of fly ash in the pore solution of fresh concrete and subsequent hydration and strength is unknown. In the present work, the effect of TEA addition on the solubility of fly ash in alkaline TEA solutions was studied. The effect of TEA addition on heat evolution for Portland cement/fly ash pastes and the strength development of Portland cement/fly ash binders in mortar were investigated.

2. Materials and methods

2.1. Materials

Two siliceous fly ashes conforming to EN 450 and a Portland cement CEM I 42.5R were chosen for the investigations. The cement and fly ashes were analysed by XRF and XRD using the Rietveld refinement. The chemical and mineralogical compositions are given in Tables 1–3. Fly ash 2, which has lower alkali content than fly ash 1, was used for isothermal calorimetry and mortar tests.

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Table 1
Mineralogical and chemical composition of CEM I 42.5 R.

Mineralogical composition [wt.%]									
Alite	Belite	Tricalcium-aluminate	Brown-millerite	Anhydrite	Hemihydrate	Calcite	CaO	MgO	K_2SO_4
71.3	1.6	4.1	11.2	2.2	1.0	4.2	1.9	1.2	1.4

Chemical composition [wt.-%]											
LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	MnO	SO_3	K_2O	Na_2O	P_2O_5
3.4	19.2	4.18	2.54	63.9	1.59	0.17	0.032	3.05	1.19	0.16	0.21

Table 2
Mineralogical and chemical composition of fly ash 1.

Mineralogical composition [wt.%]							Physical characteristics
Amorphous	CaO	Magnesium ferrite	Hematite	Mullite	Magnetite	Quartz	Blaine fineness [m²/kg]
72.6	0.4	1.6	0.8	18.4	0.9	5.4	350

Chemical composition [wt.%]										
LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	MnO	SO_3	K_2O	Na_2O
3.3	49.27	27.27	7.26	3.04	2.23	1.05	0.09	0.84	3.76	1.35

2.2. Solubility of fly ash

Different quantities of fly ash 1 were mixed at 20 °C with 900 ml potassium hydroxide solution (0.1 mol/L, pH 13) containing 0.6, 2 and 20 g/L TEA. The fly ash/solution weight ratios (F/S) were 1/1, 1/10 and 1/100. Lower F/S ratios mean higher amounts of TEA with respect to fly ash, due to the fact that TEA dosage is related to the solution. Reference solutions were prepared without TEA. In cement production the amount of TEA does not exceed 0.05 wt.% which corresponds to concentrations of ≤1 g/L in the mixing water of a fresh paste prepared at, for example, a water/cement ratio (w/c) of 0.5.

The mixtures were rotated in sealed polyethylene flasks in a head-over laboratory agitator for periods 10, 30 min, 1, 4 and 24 h after which filtrate specimens were taken for chemical analysis with ICP-OES. This method yields the total concentration of a dissolved element independent of its chemical state. To investigate the effect of fineness, mixtures were also prepared with the same fly ash, but ground to a Blaine fineness of 490 m²/kg.

2.3. Isothermal calorimetry

An eight channel TAM Air III isothermal calorimeter was used to investigate the heat evolution rate of plain Portland cement and Portland cement blended with 25 wt.% fly ash 1 or fly ash 2. Glass ampoules (20 ml) each containing 3 g dry cementitious material were placed in the calorimeter and the injection units for each ampoule filled with amounts of water equivalent to a w/(c + f) ratio of 0.5. As well as pure water, the mixing water contained TEA at amounts equivalent to 0.01 wt.%. After a steady temperature of 20 °C had been reached, the water was injected into the ampoules and mixed inside the calorimeter with the dry material. The heat evolution rate was then measured over a period of 68 h. Repetition of the measurements showed deviations in total heat below 3% for samples of similar type. Apart from the first minutes of water addition and mixing, the heat evolution rates were essentially identical.

2.4. Mortar strength

Mortar bars ($4 \times 4 \times 16$ cm^3) were produced with cement, quartz sand and water at 1:3:0.5 by weight according to EN 196-1. The cement was replaced by 25 wt.% fly ash 1 or fly ash 2. Reference samples without fly ash were also prepared. TEA was added to the mixing water to give amounts between 0.01 and 0.2% by weight of dry cementitious material. After filling, the moulds were stored at nominally 98% RH and 20 °C (±2 °C) for 24 h before demoulding the specimens and measuring compressive strength.

3. Results and discussion

3.1. Solubility of fly ash

The addition of 0.6 g/L TEA has little effect on the dissolution of silicon and sodium (Fig. 1). However, TEA strongly enhances the amount of dissolved iron and, to a lesser extent, calcium. There is little change in the amount of dissolved aluminium.

Whereas the concentrations of iron and calcium steadily increase following water contact, the concentration of aluminium rapidly

Table 3
Mineralogical and chemical composition of fly ash 2.

Mineralogical composition [wt.%]							Physical characteristics
Amorphous	CaO	Magnesium ferrite	Hematite	Mullite	Magnetite	Quartz	Blaine fineness [m²/kg]
67.7	0.0	3.3	1.5	21.3	0.0	6.1	370

Chemical composition [wt.%]										
LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	MnO	SO_3	K_2O	Na_2O
4.8	51.6	27.8	5.1	5.25	1.7	1.45	0.1	0.56	1.23	0.41

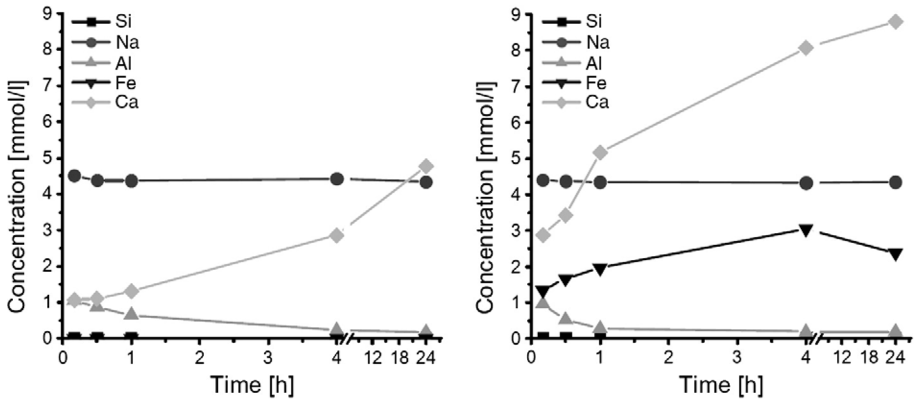

Fig. 1. Dissolution of fly ash components at F/S = 1/10 without (left) and with 0.6 g/L TEA addition (right).

reaches a maximum and then decreases at a similar rate indicating that the concentrations of Al, Fe and Ca are governed by reaction kinetics.

As expected, higher amounts of TEA have no effect on the concentration of sodium (Fig. 2). Even at 20 g/L TEA, only a small amount of additional silicon dissolves. The addition of more than 0.6 g/L TEA does not proportionally increase the concentration of aluminium and iron. The highest concentration of calcium is obtained with 20 g/L TEA.

The effect of F/S ratio on the dissolution behaviour of aluminium and iron with and without 2.0 g/L TEA addition is shown in Fig. 3. In all cases the maximum aluminium concentration is reached at the beginning; lower concentrations occurring at lower F/S ratios owing to dilution. Additional investigations revealed that a high aluminium concentration is already reached after 3 min and is significantly increased by the addition of TEA. Analysis of the solid material with XRD revealed the precipitation of ettringite which obviously removes aluminium from the solution. The concentration of aluminium after 24 h was slightly increased by using lower F/S ratios.

Contrary to aluminium, the amount of dissolved iron steadily increases over 24 h when TEA is added (Fig. 3). Without TEA there is no significant amount of dissolved iron. Therefore it appears that stable TEA/iron complexes are formed. However, for the lowest TEA to fly ash ratio (2.0 g/L TEA, F/S-ratio = 1/1), the concentration of iron decreases having reached a maximum value after 1 h. This behaviour may be explained by an insufficient amount of TEA to keep the iron in solution. In this case iron may also precipitate as AFt, as described by [9]. Grinding the fly ash resulted in increased iron concentrations.

The initial amount of dissolved calcium increases due to the addition of TEA and the use of less solution in the mixture, Fig. 4. At F/S ratios of 1/10 and 1/100, the amount of calcium steadily increases which is explained by the time-dependent release of calcium from fly ash. The simultaneous reduction in aluminium concentration is explained by the solubility behaviour of ettringite. At higher F/S ratios the high initial amount of calcium decreases owing to ettringite precipitation. Grinding the fly ash results in increased calcium concentrations and correspondingly, as expected from the ettringite solubility equilibrium, less aluminium in solution.

Adding TEA has no effect on the amount of dissolved sodium (Fig. 4). The results of F/S ratios of 1/1, 1/10 and 1/100 are comparable to each other and differ by a factor 10, respectively, owing to the effect of dilution.

An increase in the amount of TEA causes more silicon to dissolve. The concentration of silicon also depends on the F/S ratio—particularly at low values (Fig. 5). Precipitation also affects the amount of dissolved silicon.

Fig. 5 shows the evolution of the dissolved ions for 2.0 g/L TEA and a F/S ratio of 1/100 where precipitation effects are relatively small. The sulphate concentration is highest and corresponds to the dissolution of almost all the sulphate content of the fly ash.

3.2. Heat flow

The heat evolution rates shown in Fig. 6 are averages over three measurements for each cement fly ash blend and two measurements with plain Portland cement samples, respectively. Additional measurements for a w/(c + f) ratio of 0.6 with and without 0.01 wt.% TEA showed similar dependencies.

The shown effects on the dissolution by using TEA were observed by isothermal calorimetry too. Although there was only a little effect, the results are reproducible. In agreement with the investigations of Gartner and Myers [9], the induction period was

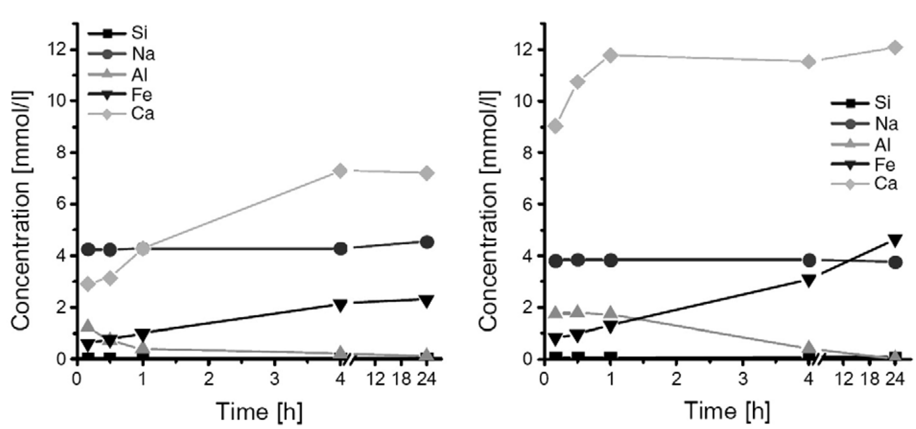

Fig. 2. Dissolution of fly ash components at F/S = 1/10 with 2.0 g/L (left) and 20.0 g/L (right) TEA addition.

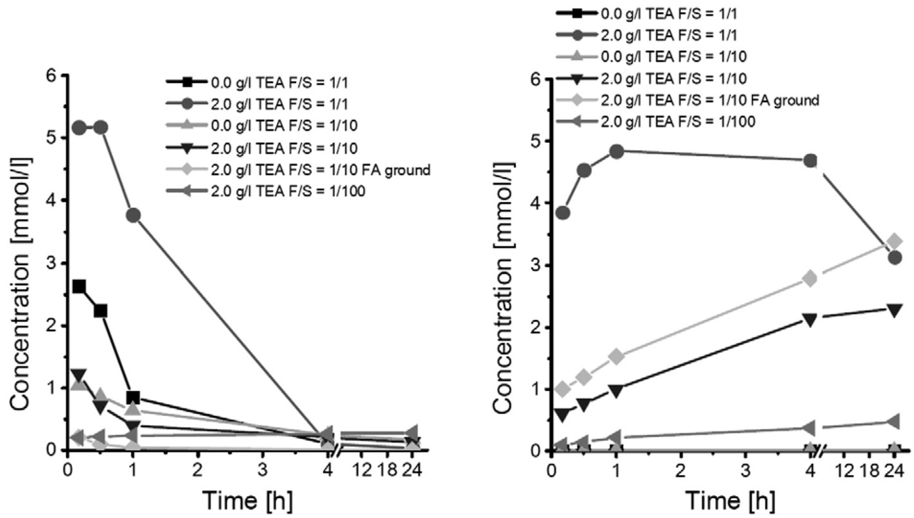

Fig. 3. Dissolution of aluminium (left) and iron (right) out of fly ash in KOH solution at different fly ash to solution ratios (F/S) and TEA dosages.

prolonged due to the addition of TEA. Moreover, TEA results in higher heat evolution rates as shown by the slightly higher slope and the higher maximum of the mixtures with TEA compared to mixtures without TEA. TEA affects the hydration of both plain Portland cement and cement fly ash blends.

Although the heat evolution rate showed a higher peak with TEA, the total heat of hydration is not significantly affected by the addition of TEA (Fig. 7). A slight increase of total heat due to TEA addition was only observed when using the cement fly ash blends. This effect was reproducible for both fly ashes.

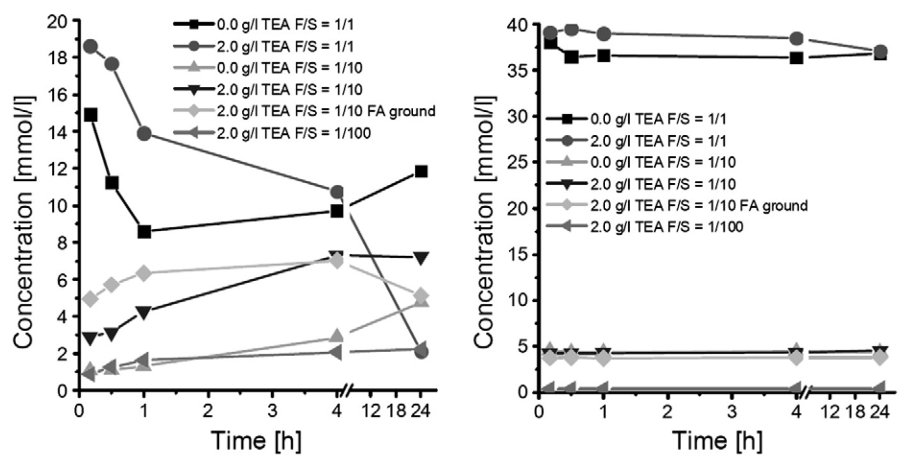

Fig. 4. Dissolution of calcium (left) and sodium (right) out of fly ash in KOH solution at different fly ash to solution ratios (F/S).

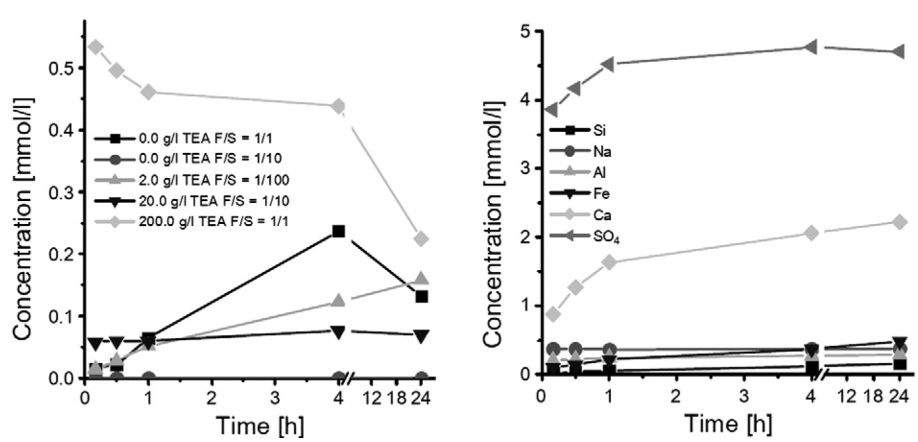

Fig. 5. Dissolution of silicon (left) out of fly ash in KOH solution at different fly ash to solution ratios (F/S) and dissolution of fly ash components for 2.0 g/L TEA addition at F/S = 1/100 (right).

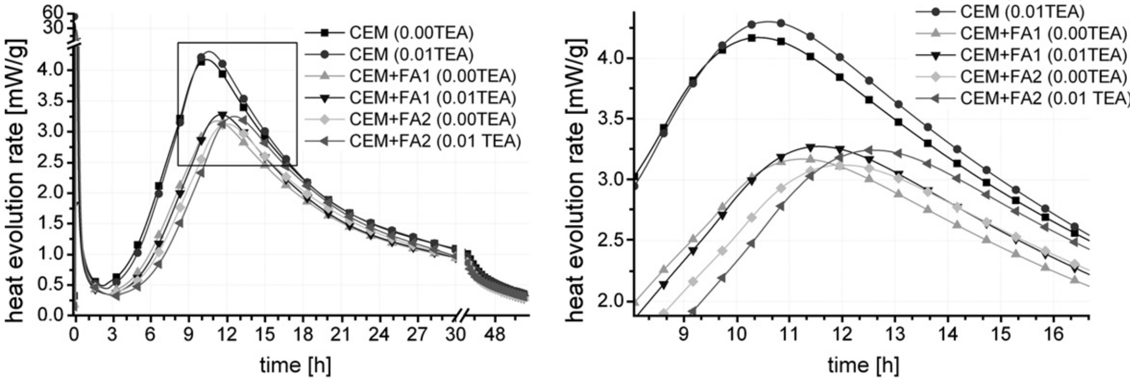

Fig. 6. Heat evolution rates of cement pastes with w/(c + f) = 0.5 and different additions of TEA [wt.%] (left: complete measurement, right: detail).

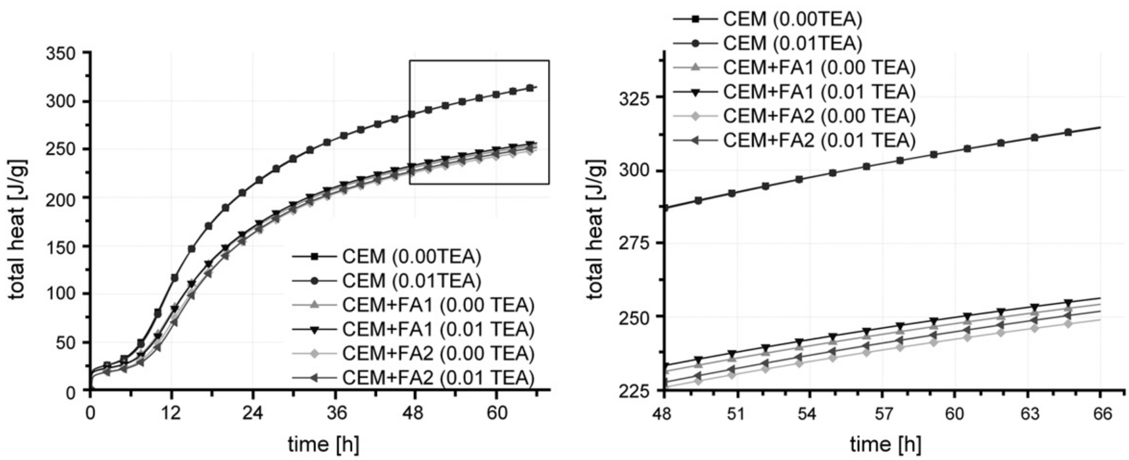

Fig. 7. Total heat of cement pastes with w/(c + f) = 0.5 and different additions of TEA [wt.%] (left: complete measurement, right: detail).

3.3. Mortar tests

The early age strength of mortar made with plain Portland cement, without fly ash, showed no significant effect of TEA addition between 0.01 and 0.2 wt.% (Fig. 8). However, the addition of TEA resulted in higher strengths at 1 day for mortar containing fly ash (25 wt.% cement replacement) at dosages up to 0.04 wt.%. This effect was observed with both fly ashes. In all cases, the strength of mortar made with plain Portland cement was higher. Since TEA has little effect on the early strength of plain Portland cement mortar, the increased strength of fly ash cement mortar is attributed to the action of TEA on fly ash.

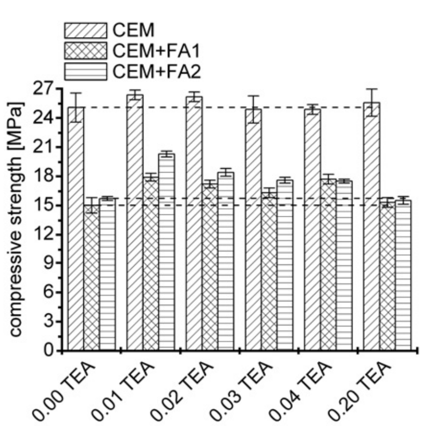

Fig. 8. One day compressive strength of plain Portland cement and cement fly ash blends with and without different additions of TEA [wt.%].

4. Conclusions

Investigations of the leaching behaviour of fly ash in an alkaline solution (KOH, pH 13) with or without TEA addition showed two limiting factors. The first limit on concentration is the dissolvable amount of the ions in the fly ash. This is the case for highly soluble Na where concentration is not affected by TEA addition and the fly ash/solution weight (F/S) ratio simply determines the degree of dilution. Secondly, the concentrations of less soluble ions such as Ca, Al, Fe and Si are controlled by their dissolution behaviour. TEA addition leads to higher amounts of dissolved Al and Fe owing to complexation. The amount of Ca also increases. In general, the concentration of Fe, Al, Ca and Si in the mixing water of Portland cement fly ash blends containing TEA is controlled by dissolution kinetics, precipitation according to the solubility equilibrium (e.g. AFt) and dilution depending on the F/S ratio. As opposed to Fe, the highest Al concentrations are reached shortly after contact with water.

Isothermal calorimetry showed a prolonged induction period and increased maximum heat evolution rates for Portland cement and fly ash cement blends due to the addition of TEA. TEA addition to fly ash/cement pastes resulted in a slightly higher total release of hydration heat. These results were verified by the strength tests. The early age strength of mortar made with fly ash/cement is increased by the addition of TEA owing to its action on the fly ash. This is probably due to the complexation of fly ash components and thus higher availability for the hydration. The present investigations have shown that some organic additives are able to increase the solubility of fly ash in fresh concrete and increase strength. In order to achieve a higher degree of fly ash activation compared with TEA, higher alkanolamines and several oxicarbon acids will be considered in future.

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