

The effect of free lime on the hydration kinetics and rheology of cement mortar

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Abstract

The effect of free lime on the hydration kinetics and rheology of cement mortar was investigated by the addition of CaO “fresh” and “aged” to a portland cement with and without fly ash. The rheology of fresh cement mortar was measured using the Rheomixer, a novel rheometer that mixes and measures rheology in a single operation. The cement hydration kinetics was monitored using an isothermal conduction calorimeter. The effect of added free lime on the pore solution was measured on parallel samples. The results indicate that free lime can have substantial effect on the cement hydration kinetics while the effect on rheology measured on fresh cement mortar was less. However, the reactivity of free lime is sensitive to ageing.

1. Introduction

The introduction of carbon dioxide taxes in Europe has accelerated the development of low clinker blended cements. A common performance issue with fly ash blended cements is longer setting times in concrete and mortar compared to mixtures with straight portland cement, especially during the winter season. The free lime (CaO) content of cement is known to influence the setting time [1] and could potentially be used to offset the longer setting times caused by increased clinker substitution. This paper presents results on the use of elevated levels of free lime (burned lime) as a setting time accelerator in an experimental blended fly ash cement and the corresponding effect on hydration kinetics and rheology in mortar with different concrete admixtures.

1.2 Equipment and methods used in this study

Rheomixer

The Rheomixer is a novel rheometer that mixes and measures rheology of mortar in one operation. It logs the torque (T) values at various rotation velocity (N). As cement based particle suspensions are non-Newtonian fluid, the simplest relation between torque (or stresses) and rotation velocity (or shear rate) is the linear with an intercept at the torque axes. This is often named Bingham behavior of the mortar or concrete. Generally, with few exceptions, mortar and concrete can be characterized

as Bingham materials [2]. The relation between the torque, T and velocity, N is, Eq.1:

$$T = G + H \cdot N \dots \dots \dots (1)$$

Where the G and H values [2,3] are the intercept on the torque axes and the “slope of the line”, respectively. These two parameters are also called Tattersall values and will be here named:

- G-yield or G-yield value [Nm]
- H-viscosity or H-viscosity value [Nm·s]

There is a linear relation between the G-yield value and H-viscosity to the (Bingham parameters) yield value and plastic viscosity, respectively, Eq.2:

$$\tau = \tau_0 + \mu \cdot \dot{\gamma} \dots \dots \dots (2)$$

Where:

- τ = shear stress [Pa]
- τ_0 = yield value [Pa]
- μ = plastic viscosity [Pa·s]
- $\dot{\gamma}$ = shear rate [1/s]

The new equipment is based on similar principle as for the Tattersall two-point test where an impeller is rotating in the testing material [3].



Fig. 1. The Rheomixer including 10” Tablet PC for data processing.

Isothermal conduction calorimeter

A novel isothermal calorimeter designed to test relatively large samples of mortar or even concrete was used for testing of mortar at 20 C. The calorimeter is a prototype manufactured by Thermometric AB in Sweden, based on a design by Lars Wadso [4]. The calorimeter was kept at

constant temperature in a portable thermostat manufactured by Sable Systems, Las Vegas, U.S.

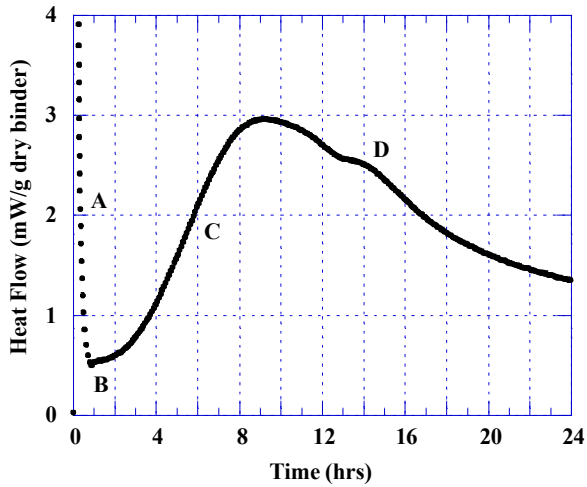


Fig. 2: Example of normal hydration of an ASTM Type II portland cement, water-to-cement ratio of 0.45.

Fig. 2 shows an example of hydrating Portland cement in the absence of admixture, a water-to-cement ratio of 0.45, monitored at 20 °C by an isothermal conduction calorimeter. Portland cement mixed with water initially displays a strong exotherm (A) caused by rapid dissolution and initial hydration of mainly the aluminates phase. If sufficient calcium sulfate is available in solution, the hydration rate rapidly decreases (B) as aluminates react with calcium and sulfate to form ettringite like phases. After some time the strength generating alite hydration takes off, which results in a broad exotherm. Set usually occurs at the steepest part of the alite exotherm (C). The alite and aluminates hydration continue in parallel until the mixture runs out of soluble sulfate, indicated by the “sulfate depletion” peak (D) [5].

2. Experimental

2.1 Materials

A low alkali portland cement conforming to CEN CEM I and ASTM Type I was used “as is”, and interblended with quick lime (CaO) and an ASTM Type F fly ash.

Free lime was prepared as freshly burned CaO and cooled to room temperature in a desiccator. It was either blended with the cement immediately before mortar testing or two months prior to mortar testing.

A commercially available polycarboxylic acid (PCE) high range water reducer with no co-additives was used as dispersing agent, Table 1.

2.2 Mortar Mixtures

Mortars were prepared by adding dry materials gently into water previously added to the Rheomixer. Mixing and rheology testing commenced immediately after loading, Fig. 3. The mixing part can be divided into three regimes: The first one account for the time interval of 30 seconds and consists of three 10s cycles of alternating forward and reverse rotations of the impeller at a speed of +/- 1.5 revolutions per seconds (rps). The second regime consists of alternating rotations of short cycles (2s) for the next 120s. In this regime a constant rotation speed is maintained for each mix at 5 rps. The third regime account for the last 55s where a constant unidirectional speed of 1.5 rps is maintained. After the mixing process is completed the mortar is left at rest for several minutes during which at least three measurements on the rheological parameters G-yield value and H-viscosity are measured.

Table 1, Mortar mixtures

Mix no.	w/c	Cem. Type	Cement (g)	Water (g)	Sand (g)	CaO	PCE	Note
1	0,5	Cem I	582	291	1350			
2	0,5	Cem I	582	291	1350			+1,7% CaO aged
3	0,5	Cem I	582	291	1350	1,70%		
4	0,42	Cem I	643	270	1350		0,10%	
5	0,42	Cem I	643	270	1350		0,10%	+1,7% CaO aged
6	0,42	Cem I	643	270	1350	1,70%	0,10%	
7	0,50	35% FA	570	285	1350			
8	0,50	35% FA	570	285	1350	1,70%		
9	0,42	35% FA	657	276	1350		0,10%	
10	0,42	35% FA	657	276	1350	1,70%	0,10%	

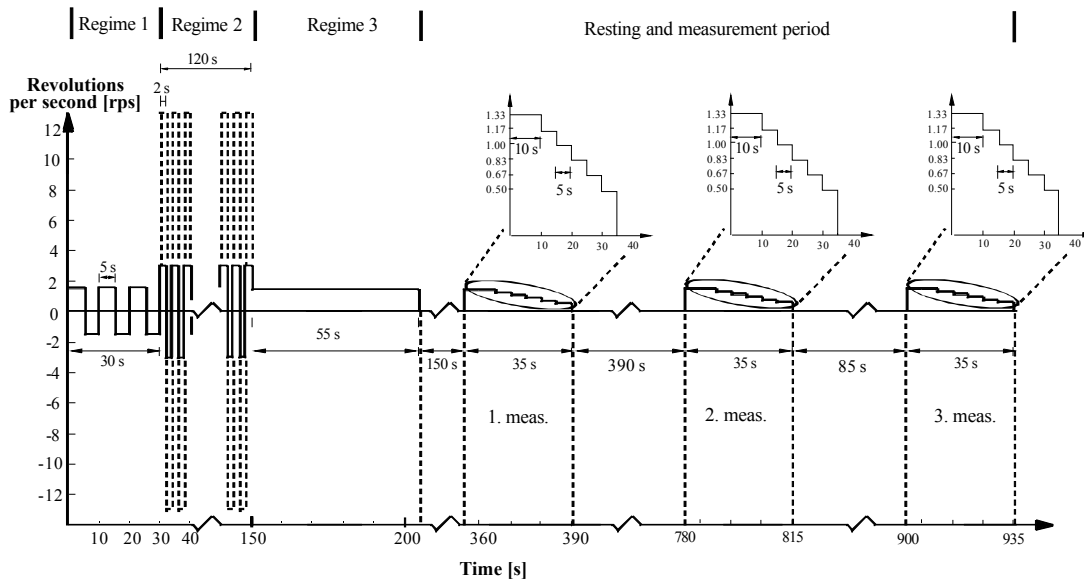


Fig 3. Rheomixer mixing and testing sequence. The mixing is carried out in regimes 1-3 whereof the variable mixing speed is executed in regime 2.

An environmental temperature of 22 +/- 1°C was maintained during the tests. If used, the chemical admixture was added with the mixing water. The volume of each mixture was kept constant or 1.0 liter (not including air). The volume of sand was constant in all mixtures. The mixture proportions are given in Table 1.

All mixtures were prepared and tested in the Rheomixer during the first hour of hydration. After 70 minutes hydration, approximately 50 g of mortar (the exact mass was recorded for each mix) was removed from the Rheomixer and placed in the isothermal calorimeter at 20°C. Since all mixtures were prepared externally, non-isothermal conditions exist in the beginning of each calorimetry test. A set of eight duplicate blank mixtures were prepared and tested for the purpose of measuring the time needed for the results to converge, Fig. 4. The result was used as an estimate of the time required to reach isothermal conditions in the calorimeter, e.g. approximately 60 minutes was needed to reach isothermal conditions after placing a 50 g mortar sample in the calorimeter.

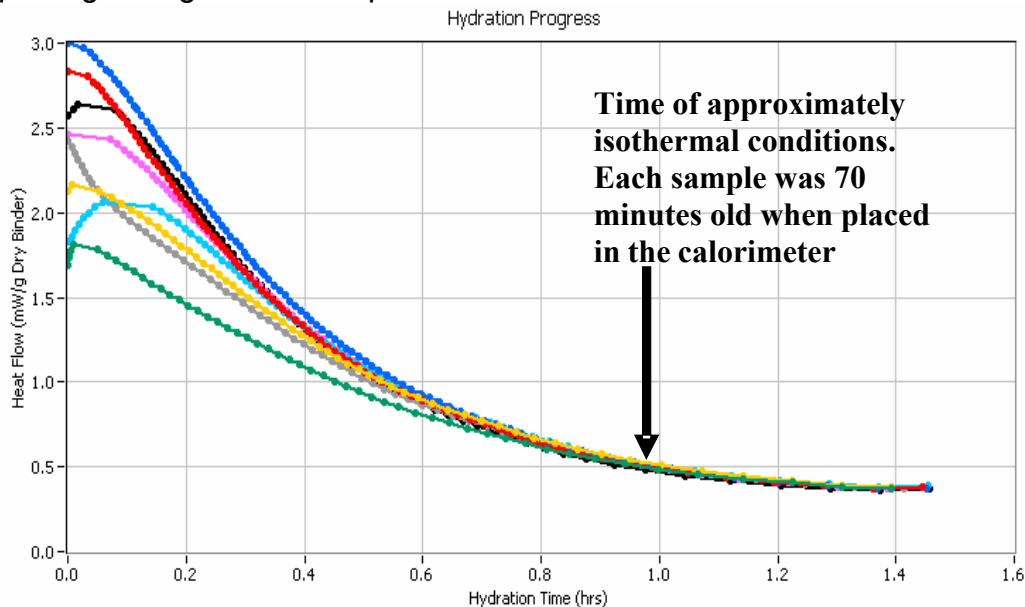


Fig. 4. Estimation of the time needed for isothermal conditions. 8 duplicate 50 g mortar samples w/c 0.50 placed in the calorimeter after mixing and rheology testing in the Rheomixer.

The rate of heat evolution was normalized to the dry content of binder, e.g. mW/g dry binder.

2.3 Paste mixtures for Pore water extraction and analysis

Separate tests with cement paste w/c 0.50 were prepared in order to evaluate the effect of free lime on the calcium concentration in porewater. The cement paste was mixed at room temperature for 120 seconds and the porewater was extracted at different hydration times using vacuum filtration. The extracted porewater was immediately acidified using 1.0 M nitric acid to pH 1 to prevent precipitation followed by analysis for Calcium and Sulfur content by atomic adsorption spectroscopy.

3. Results

The effects of adding freshly burned CaO cooled to room temperature on the rheology, hydration kinetics and selected pore water ions are shown in Fig. 5-11. For the calorimetry results, note that all mixtures were 70 minutes old at time zero. The first 60 minutes calorimetry data omitted due to non-isothermal conditions.

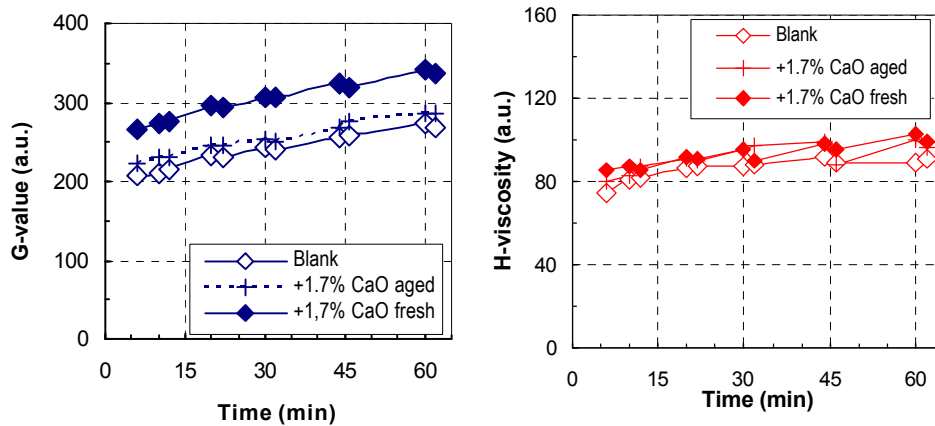


Fig. 5. Effect of free lime on the relative yield value and viscosity as function of time (CEM I, w/c 0.50, no chemical admixture).

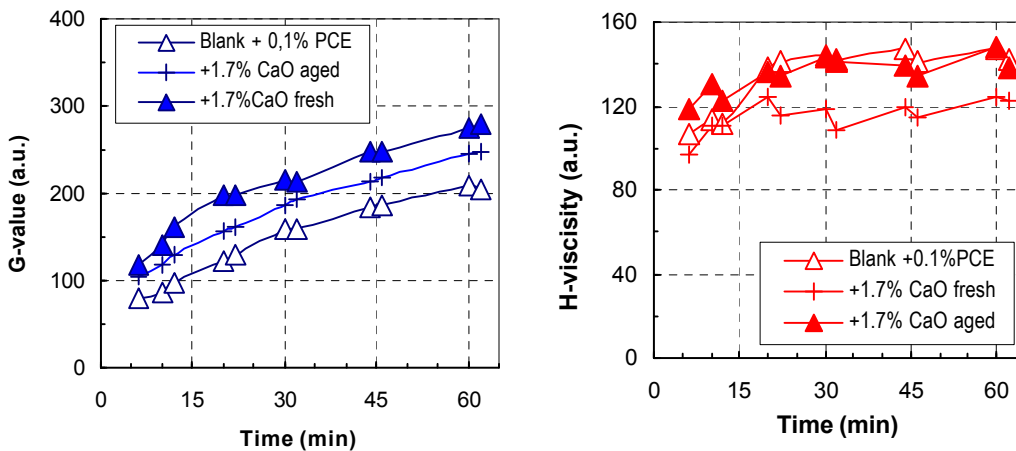


Fig. 6. Effect of free lime, both aged in cement and added fresh on the G- and H-value as function of time (CEM I, w/c 0.42, PCE 0.1%).

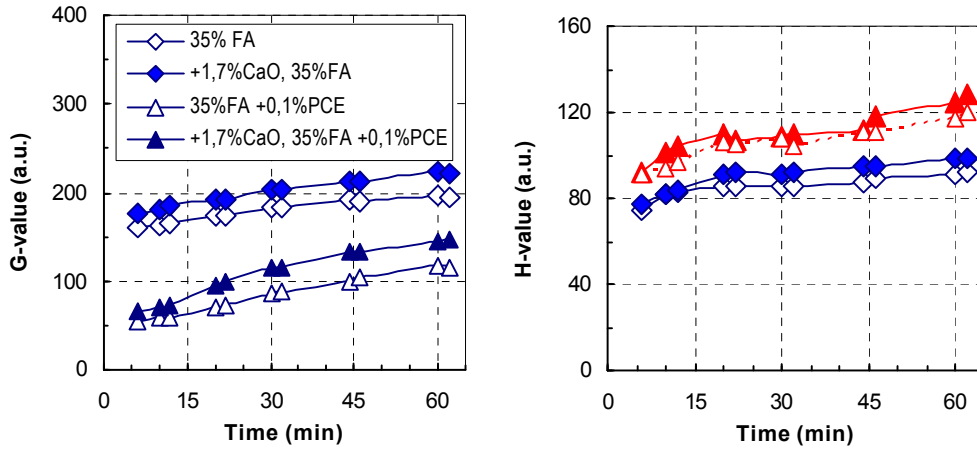
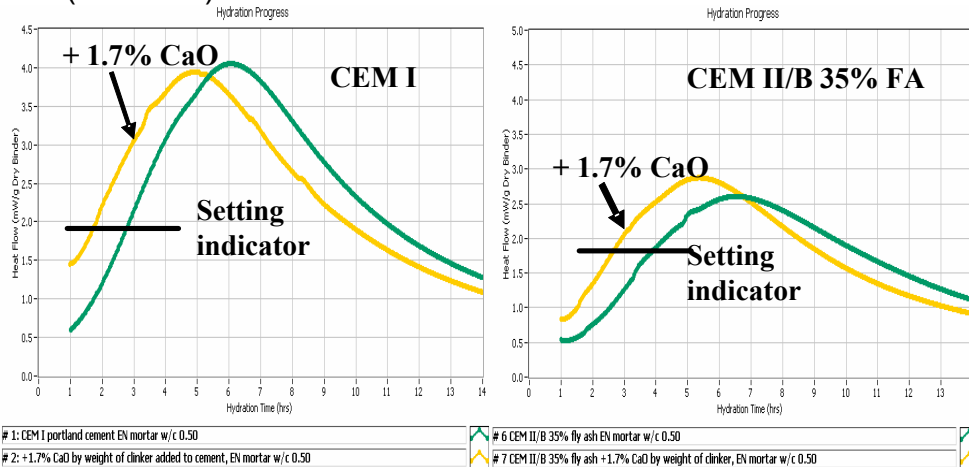


Fig. 7. Effect of added fresh free lime in cement (CEM II/B, 35% fly ash) on the G- and H-value as function of time in mixes without (w/c: 0.5) and with (w/c: 0.42) 0.1% PCE.



1: CEM I portland cement EN mortar w/c 0.50
 # 2: +1.7% CaO by weight of clinker added to cement, EN mortar w/c 0.50
 # 6 CEM II/B 35% fly ash EN mortar w/c 0.50
 # 7 CEM II/B 35% fly ash +1.7% CaO by weight of clinker, EN mortar w/c 0.50

Fig. 8. Effect of added free lime on cement hydration kinetics tested at 20 C, EN mortar without chemical admixture – Left: CEM I portland cement, w/c 0.50. Right: CEM II/B, 35% fly ash, w/c 0.50.

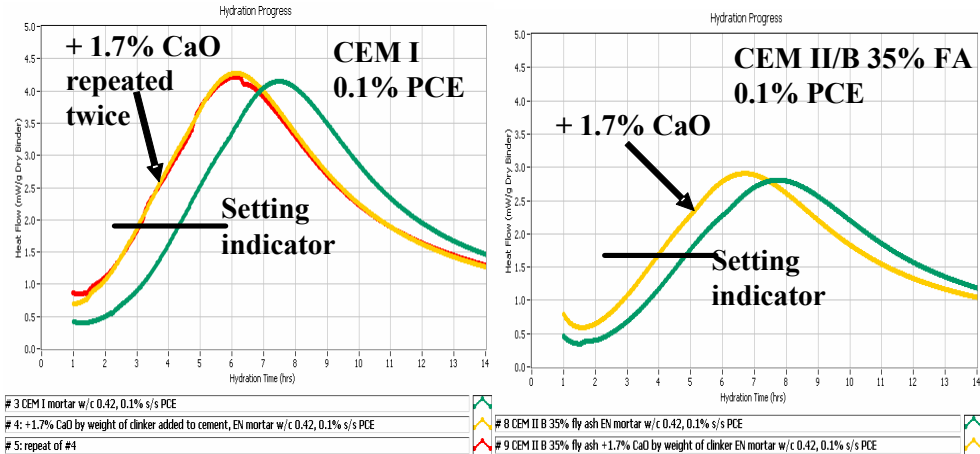


Fig. 9. Effect of added free lime on cement hydration kinetics tested at 20 C, EN mortar with 0.1% s/s PCE added with mix water – Left: CEM I portland cement, w/c 0.50. Right: CEM II/B, 35% fly ash, w/c 0.42.

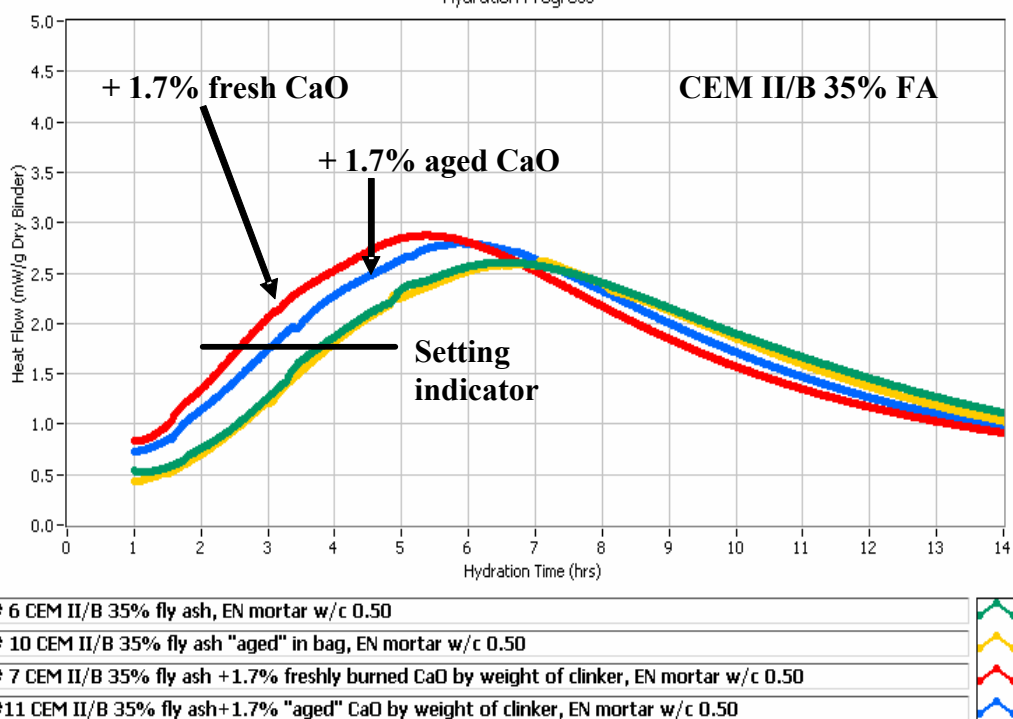


Fig. 10. Effect of ageing of free lime on cement hydration kinetics tested at 20 C, EN mortar without chemical admixture –CEM II/B, 35% fly ash, w/c 0.50.

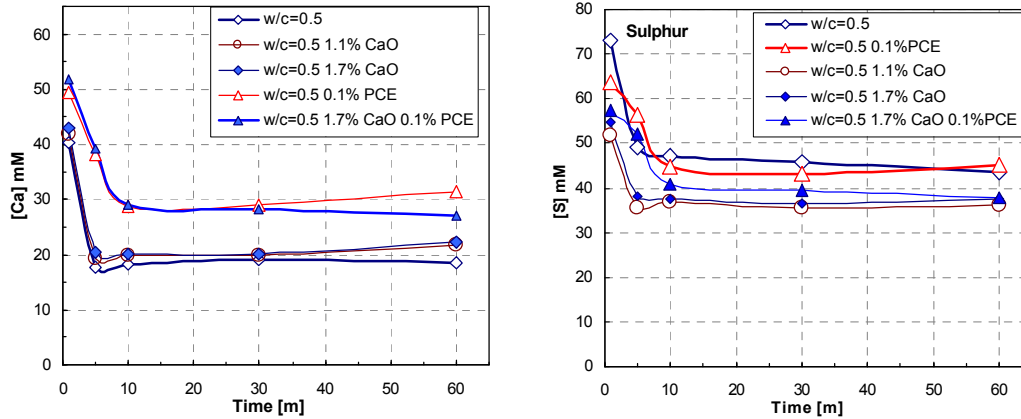


Fig. 11. Calcium and sulfate (measured as sulfur) concentration in extracted porewater.

4. Discussion

4.1 Rheology by Rheomixer

Addition of 1,7% freshly burned CaO cooled to room temperature influenced the rheology more than if the same amount of CaO was added and allowed to age in the cement for 2 months. However, the effect of adding fresh free lime is small compared to the effect of changing the w/c-ratio. The effect of addition of fresh 1.7% CaO to the cement increased the yield-value approximately 80 a.u. or approximately 50 Pa, Fig. 5. The measured increase in the yield value corresponds to a change in w/c ratio of approximately 0.01.

A similar trend was observed in the mixes containing 0.1% PCE (w/c: 0.42), Fig. 6. The fresh CaO increased the relative yield value approximately 80 a.u. while the aged CaO increased the relative yield value approximately 40 a.u. However, the rate of change in the rheological parameters was relatively unaffected by the addition of CaO.

The effect of addition of fresh CaO to the blended cement with 35% fly ash was smaller compared to the CEM I portland cement, ~25 Pa, Fig. 7. This is expected, as the clinker fraction of the cement is smaller. It is noteworthy that the change in G-yield-value as a function of time (e.g. “workability loss”) is significantly smaller in the mixes containing FA. The influence on the addition of fresh free lime on the H-viscosity is insignificant.

4.2 Hydration kinetics by isothermal calorimetry

The calorimetry results indicated as strong accelerating effect of added free lime on the onset of the alite hydration peak, or approx. 1 hr shorter setting time. The free lime content could be adjusted by intergrinding quicklime if not feasible by adjusting the clinkering process. However, the accelerating effect was reduced with ageing of the free lime.

4.3 Porewater composition

The addition of free lime did not significantly affect the concentration of calcium in the extracted porewater. The results indicate that the free lime addition accelerates cement hydration probably by increased nucleation without changing the amount of calcium in solution. Therefore, the measured effect of free lime addition on rheology is primarily due to the effect on cement hydration and not due to a change in calcium ion concentration. The effect of free lime addition on the ionic strength is probably also minor.

5. Conclusion

The results obtained indicate the possibility of shortening the setting time of blended fly ash cement by means of increasing the free lime content without detrimental effects on rheology of mortar or concrete. However, the benefit of the added free lime is sensitive to cement ageing.

6. References

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