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Expansive properties of ettringite in a mixture of calcium aluminate cement, Portland cement and β-calcium sulfate hemihydrate

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Abstract

The hydration of a paste consisting of 25 wt.% calcium aluminate cement, 12.5 wt.% Portland cement, 12.5 wt.% β-calcium sulfate hemihydrate and 50 wt.% water was studied at 20°C and 100% relative humidity, using in-situ synchrotron X-ray powder diffraction, isothermal conduction calorimetry and dilatometric measurements. Initially, gypsum and ettringite form, while hemihydrate is consumed (0–45 min). Ettringite then continues forming at the expense of gypsum. When gypsum is depleted after 2 h and 45 min, aluminate-AFm starts forming, while the amount of ettringite stays constant up to 7 h. The first peak in the heat rate curve includes contributions from mechanical mixing, initial wetting and dissolution plus the formation of ettringite and gypsum, the second maximum involves the replacement of gypsum by ettringite, and the third corresponds to the formation of aluminate-AFm. The replacement of gypsum by ettringite is accompanied by an average linear expansion of 0.7%. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Hydration; Calorimetry; X-ray diffraction; Expansion; Ettringite

1. Introduction

A hydrating paste of Portland cement in contact with unsaturated air will exhibit a decrease in volume caused by a combination of chemical and physical processes. The difference in absolute volume between the resulting hydration products and the unhydrated cement plus reacting water is called the chemical shrinkage [1]. The phenomenon of external volume reduction of cement paste, mortar and concrete caused by chemical shrinkage is referred to as autogenous shrinkage, and does not include loss or ingress of substances to the system, nor temperature variations or application of an external force [1]. The difference between chemical shrinkage and autogenous shrinkage is the volume occupied by the pores that form in the solid matrix. The hydration consumes water from the pores, and will thus lead to a structure with gas-filled voids. A similar result is the consequence of drying, when the water in the pores evaporates to the surroundings. The formation of the gas-filled voids add a set of physical phenomena that might contribute to the shrinkage, including effects that causes the pores to collapse, capillary stress and change in surface free energy, and movement of water in the structure [2].

The shrinkage can be compensated by inclusion of other cementitious materials, which form voluminous hydrates. Blends of calcium aluminate-rich materials, calcium sulfates and water are known to produce ettringite, a hydrate that may form long needles. The expansive effect of ettringite formation from the addition of calcium sulfates and materials rich in phases, like CA, $C_4A_3\bar{S}$ or C_3A, has been utilised to compensate shrinkage in Portland-cement-based special cements [3].

Mixtures of ordinary Portland cement and calcium aluminate cement, e.g., Ciment Fondu with CA as dominating cementitious phase, exhibit short setting times compared to pastes of the two end-member cements [4]. The addition of a sulfate-rich phase, i.e., calcium sulfate, gives the possibility to obtain cement systems with rapid setting, high early strength and shrinkage compensating properties. A mixture of Portland cement, calcium aluminate cement and calcium sulfate has been described earlier, by dilatation measurements and in-situ synchrotron X-ray diffraction, to form ettringite, and have expansive properties [5]. The aim of the present article has been the continued study of this type of mixture, with an emphasis on using cements of the same age and on having the same relative humidity and temperature,

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during the different experiments. An additional set of experiments has been performed, where the hydration heat has been registered by isothermal calorimetry. Connecting the reaction heat to the phase formation will make it possible to perform a larger number of experiments due to the calorimeter's simpler experimental procedure and better availability compared to the synchrotron beamline.

2. Experimental

The major phases of the utilised calcium aluminate cement were CA, C_4AF and $C_{12}A_7$. Blends of 50% by weight of calcium aluminate cement, 25% of ordinary Portland cement, and 25% of β-calcium sulfate hemihydrate were examined. A water to binder weight ratio of unity was utilised, and pure deionised water was used to mix the pastes. The dilatation of the paste was measured, the phase formation during hydration was studied by synchrotron X-ray powder diffraction, and the hydration heat was registered with an isothermal calorimeter. All the cementitious raw materials were commercially available products. The experiments were performed during a time period of 2 weeks using the same batches of cement, in order to ensure identical reactivity and behaviour of the cement blend in all measurements. The experiments were performed at a relative humidity of 100% and at room temperature.

2.1. Dilatometry

The binder and water were mixed with a blender for 2 min, and the paste was filled in a 250-mm long mould with a square cross-section measuring 25 mm × 25 mm. The sides and ends of the mould consisted of square brass bars (25 mm × 25 mm). One of the long sides and one of the short end bars were secured to the bottom plate of aluminium, while the top was open. This arrangement allowed the paste to expand in all three directions. The long sides and the bottom of the mould were covered with LD polyethylene film. Adding a few drops of water on the sides of the mould and covering the top of the mould with plastic film ensured a relative humidity of 100%. Condensed water on the inside of the film at the end of the experiments showed that the humidity did not go below 100%. The movement of the nonsecured brass bar at one of the short ends of the mould was registered by an inductive displacement transducer (output sensitivity 0.16 V/mm), and the data was logged automatically by a computer through an A/D-card with 12 bits resolution. Four moulds could be monitored in parallel.

2.2. In-situ X-ray diffraction

The phase formation during hydration was followed by synchrotron X-ray powder diffraction. Two consecutive experiments were performed to study the reproducibility of the technique. The cement blend and water were mixed manually, and the paste was drawn into a glass capillary (Glas, 0.70 mm outer diameter, 0.01 mm wall thickness) using a syringe (Codan) fitted with a piece of silicone rubber tubing. The diffraction data on the hydrating samples were collected on beamline I711 at MAX-lab in Lund, using monochromatised radiation of wavelength 1.52225 Å. The X-ray measurements were undertaken using a Bruker system with a SMART 1000 CCD detector. Data collection was performed using the software SMART and each new X-ray spectrum was collected for a period of 3 min. The detector had been shifted in order to make the incoming beam hit the edge of the detector, and thus obtain reflections in a wider 2θ region. The detector was covered with aluminium foil to decrease the background radiation. The two-dimensional ring pattern from the detector was transformed to a one-dimensional spectrum using the software GADDS. The total time for the data collection was between 7 and 8 h in both experiments. The capillary with paste could only be rotated 180° during one data collection due to software limitations. The systematic variation in the amount of paste in the beam thus lead to two sets of data from each experiment. The data evaluation utilised the peaks corresponding to the interplanar spacings, $d = 6.0$ Å for calcium sulfate hemihydrate, $d = 7.59$ and 4.28 Å for gypsum, $d = 9.72$ and 3.87 Å for ettringite, and $d = 10.70$ Å for C_2AH_8. The calculation of intensities from the X-ray spectra was performed as previously described [5] using a software routine developed in Matlab 5.1 (The MathWorks, Natick, MA, USA). There was little variation in the results between the two hydrations or between the two partial data sets due to the limited rotation. The diffracted intensities were corrected for an exponential loss in intensity of the primary beam with time.

2.3. Calorimetry

The cement blend (2.0 g) was put in a 10-ml glass ampoule (Scantec). A rubber stopper closed the ampoule, and thus ensured a relative humidity of 100% in the gas phase during the subsequent hydrations. Two steel capillaries were fitted through the stopper. The capillary in the middle of the stopper contained a mixer made from a thin steel tube. The other capillary was used when adding water to the cement blend. The ampoule was put in the calorimeter. After a baseline was obtained, 2.0-ml water, equilibrated to room temperature outside the calorimeter, was added to the cement under mixing using a Codan 2-ml syringe with a 30-cm long steel capillary glued to the inside of the needle. The calorimeter was a six-channel heat conduction calorimeter with a heat sink consisting of a large piece of aluminium, and temperature stability was achieved by 50-mm mineral fiber insulation. The sensitivity of each channel was approximately 0.07 V/W. The heat production rate of the hydration reactions was measured with semiconductor thermocouple plates (Peltier plates), and registered automatically every minute using the data software Pico.

In a heat conduction calorimeter, the energy change from the ongoing reaction is immediately corrected for by a heat flow to or from the calorimeter, thus, no heat accumulation occurs in the sample. As a result, the measured quantity is the heat production rate, i.e., the thermal power P [W = J/s], as a function of time. The total energy change from the reaction, the total heat evolved Q [J], is the integral of the thermal power ($P = \mathrm{d}Q/\mathrm{d}t$).

3. Results and discussion

3.1. Dilatation

The external dilatation measured in the present case does not correspond to an autogeneous length change according to the strict definition [1], since the paste is not completely sealed off from the atmosphere. The open type of system used here is nevertheless of relevance from a practical point of view.

Fig. 1 shows a representative dilatation curve for the system. The change in length per unit length is displayed as a function of time. An initial expansion of 0.5‰ occurs during the first half-hour, followed by a period without any length change. After approximately 1 h, the paste starts to expand further. This expansion continues until about 4 h after the start of the experiment, and the total expansion reaches an average value of 7.5‰. The spread in the total expansion is around ±15% in six measurements, but there is only a minor variation of ±9 min between the hydration curves at the time when the expansion occurs. The total time period during which the major expansion takes place is almost the same as obtained earlier [5], but the expansion is slightly larger in the present experiments.

Similar expansive properties have also been observed in type K cement, which is usually based on a blend of Portland cement, calcium sulfate and a clinker containing the calcium sulfoaluminate $C_4A_3\bar{S}$ [6]. In type K cement, the expansion takes place over a period of days instead of hours, and the total expansion reaches 1% or more.

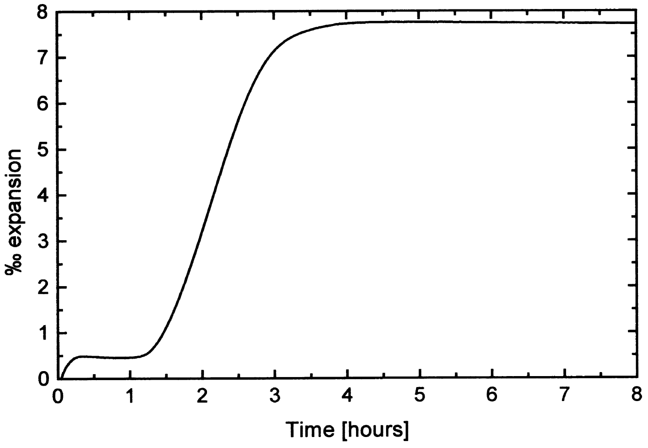

Fig. 1. The linear dilatation of the paste during the first 8 h of hydration.

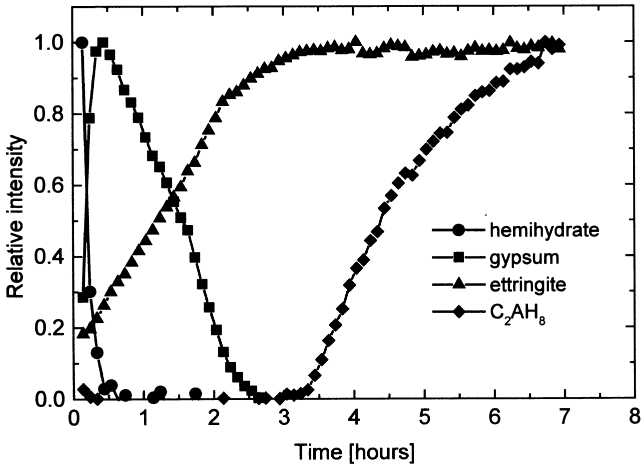

Fig. 2. The relative intensities of the identified phases as determined by synchrotron X-ray powder diffraction.

3.2. Phase formation

The following crystalline hydrates were identified by comparison with the powder diffraction reference files [7]: hemihydrate, $CaSO_4 \cdot 0.5H_2O$ (no. 36-0527); gypsum, $CaSO_4 \cdot 2H_2O$ (36-0432); ettringite, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ (41-1451); and C_2AH_8, $2CaO \cdot Al_2O_3 \cdot 8H_2O$ (11-0205). Fig. 2 shows the relative intensities of hemihydrate, gypsum, ettringite and C_2AH_8 as a function of time. During the first half-hour, the hemihydrate reacts with water to form gypsum. The formation of ettringite starts within 10 min after the addition of water. When all the hemihydrate is consumed, the maximum amount of gypsum is present, then the continued ettringite formation consumes the gypsum. An ettringite network thus replaces the solid network of gypsum. About 3 h after the start of the experiment, all the gypsum, and thus the sulfate, is consumed, and the amount of ettringite reaches its maximum level. The calcium aluminate cement continues to react with water, and C_2AH_8 (aluminate-AFm) starts to form. Mass balance calculations indicates the potential presence of 35–50% by weight of ettringite, 10–25% C_2AH_8 and 15–20% unreacted water at the end of the hydration, depending on the detailed assumptions made concerning the sulfate content of the ettringite and the stoichiometry of the chemical reactions.

In the hydration of Portland cements, C_3A and gypsum form ettringite. If the system contains insufficient amounts of sulfate in comparison to the equivalent amounts of calcium and aluminium to form ettringite, the remaining C_3A reacts with water and forms monosulfate (sulfate-AFm) by consumption of the ettringite [2]. The blended cement system studied here contains other calcium aluminate phases (CA, $C_{12}A_7$), it has a different chemical composition in general, and the pastes have a higher water content, than is normally the case with pure Portland cement pastes. This is probably the reason why the ettringite becomes more stable, and this prevents the ettringite from being consumed when the new, low-sulfate, AFm phase is formed. The increase in ettringite stability due to a change in chemistry has also been observed in systems of C_3A–CaO–$CaSO_4$, where the addition of $CaCO_3$ stabilises ettringite relative to monosulfate formation [8].

Hydration of C_3A in the presence of hemihydrate [9,10] shows a type of phase development similar to that reported here. The ettringite formation starts immediately after the addition of water, and continuous growth of ettringite is observed during 8–9 days, until all gypsum is consumed, but the ettringite then converts to monosulfate instead of being stable during the formation of C_2AH_8.

The phase formation in the cement paste reported here is faster than in some previously studied [5]. In the phase formation experiments reported earlier [5], the cements had been stored for several months longer than in the present experiments, and increasing age apparently reduces the reactivity of the cement blend. In the previous tests, the amount of gypsum reached its maximum level after 1 h, and the replacement of gypsum by ettringite took place during the whole experiment, which lasted slightly more than 6 h. No hydrate of AFm-type was detected at the end of the run. The CCD detector allowed the recording of higher intensities compared to the previously used position sensitive detector [5], but the resolution in 2θ was poorer.

Comparing the dilatation curve with the phase development, one can see that the major expansion takes place over the same period of time as that when the gypsum matrix is replaced by a matrix of ettringite. No specific hydration phases from Portland cement is detected. The C–S–H gel is X-ray amorphous, and thus hard to detect in this kind of experiment. CA is the major phase in calcium aluminate cement [2]. A mass balance shows that additional calcium is needed in order to form ettringite ($C_6A\bar{S}_3H_{32}$) from CA and calcium sulfate ($C\bar{S}$). No $Ca(OH)_2$ is observed, and this phase is usually crystalline enough to be detected by X-ray diffraction. It is thus reasonable to assume that calcium ions from the dissolution of Portland cement are consumed in the formation of ettringite, but the question as to what extent C–S–H gel is formed requires further study.

3.3. Heat evolution

Using the mixing procedure described in Section 2.3, the recorded heat evolution curves exhibit good reproducibility. Fig. 3 shows the thermal power, *P*, measured from the hydrating pastes and the total heat evolved, *Q*, both as a function of time. A peak in the heat liberation curve, $P=f(t)$, is registered instantly after addition of water. It flattens out after around 45 min. This corresponds in time to the formation of gypsum from hemihydrate. In addition the peak includes the heat contributions from the mechanical mixing of cement and water, initial wetting, dissolution of solid phases and early formation of ettringite. A second maximum occurs after about 1 h and 45 min and a third at about 4 h and 30 min, the second peak coinciding in time with the replacement of gypsum by ettringite and the third with the formation of C_2AH_8. This indicates a good correlation between the phase development recorded by synchrotron X-ray diffraction and the measurement of the hydration heat, despite the differences in sample size and experimental conditions. When such a correlation between phase formation and heat evolution has been established, the influence on the system of additives affecting the time dependency of the different hydration reactions can be studied by calorimetry. The less complicated experimental procedure of the calorimetric measurements and the restricted availability of synchrotron radiation means that it will be possible to perform a greater number of experiments using the calorimeter compared to the exclusive utilisation of synchrotron X-ray diffraction.

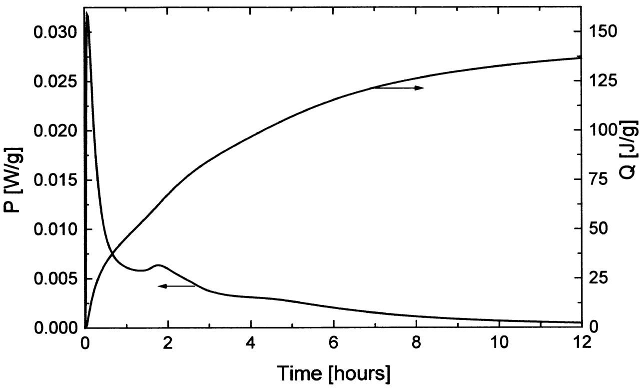

Fig. 3. The produced (*P*) and accumulated (*Q*) heat per unit weight of paste from the hydration reactions measured by isothermal calorimetry.

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