Crystal Chemistry and Microstructure of Hydrated Phases Occurring During Early OPC Hydration

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Abstract

The first hours of hydration strongly influence the properties of hardened cement stone after longer hydration periods. The addition of accelerators and retarders will reinforce this effect. The mineralogy of the OPCs and the forming hydrated phases seem to be one key to understanding early hydration mechanisms. OPCs with different additives were investigated by means of in-situ x-ray diffraction followed by Rietveld+ calculations. Heat flow calorimetry investigations complete the data sets. The results show clear evidence that the composition of the cements and the specific kind of additive applied tend to influence the crystal structure and crystal chemistry of the ettringites formed during the first hours of hydration. The quantity of ettringite and C-S-H -phase and the morphological behavior of the hydrated phases may affect hydration kinetics. The development of crystallite size of ettringite may influence the duration of the induction period of OPC hydration.

1. Introduction

The hydration of Ordinary Portland Cement (OPC) during the first hours of hydration may be reduced to two groups of reactions:
- The aluminate-sulfate reactions
- The silicate reactions

The aluminate-sulfate reactions depend on the reactivity of the tricalcium aluminate solid solution (C_3A, ss) and the sulfate carriers (derived from [1]). Where reactivity of sulfate carrier and C_3A (ss) match one another perfectly during early hydration, the reaction equation reads as follows:

$$C_3A + 3\ CaSO_4 + 32\ H_2O \rightarrow C_3A*3CaSO_4*32H_2O \text{ (ettringite, AFt) (eq. 1)}$$

Where the sulfate carrier shows higher reactivity than the C_3A (ss), the following reaction (eq. 2) takes place concurrently with ettringite formation:

$$CaSO_4 \text{ (anhydrite or bassanite)} + 2\ H_2O \rightarrow CaSO_4*2H_2O \text{ (eq. 2)}$$
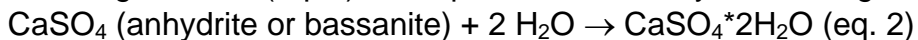
Where the C_3A (ss) shows higher reactivity than the sulfate carrier, the following reaction (eq. 3) takes place concurrently with ettringite formation:

$$C_3A + CaSO_4 + 14\ H_2O \rightarrow C_3A*CaSO_4*14H_2O \text{ (monosulfate, AFm) (eq. 3)}$$

The silicate reactions may be reduced for the first few hours of hydration to the reaction of alite (C_3S, ss). Belite will make no significant contribution to the hydration reaction during the first 24 hours of hydration. According to Fuji and Kondo [2] the ratio of CaO (C) and SiO_2 (S) for the early C-S-H phase was observed to be 1.7. The equation for the silicate reaction may therefore be written as follows:

$C_3S + 3.4\ H_2O \rightarrow C_{1.7}SH_{2.1} + 1.3\ CH$ (portlandite) (eq. 4)
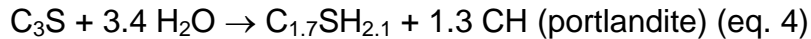
The heat evaluation of equations 1 to 4 may be calculated from the standard enthalpies of formation. The heat of hydration for equation 1 is calculated to be between 590 and 747 J/g of solid ($C_3A + CaSO_4*nH_2O$), depending on the kind of sulfate carrier. The heat of hydration calculated for equation 4 is 558 J/g of alite.

For the following X-ray diffraction (XRD) investigations a CEM I 52.5 R (European type OPC) was chosen. Calorimetric investigations on this cement and mixtures of the cement with additives were carried out by our group and have already been published [3, 4]. An isothermal heat flow calorimeter of the Erlangen Type was employed [5]. 10 g batches of the samples were mixed outside of the calorimeter for 30s in a plastic beaker with a spatula at 23°C. Water to cement (w/c) ratio for all investigations was 0.325.
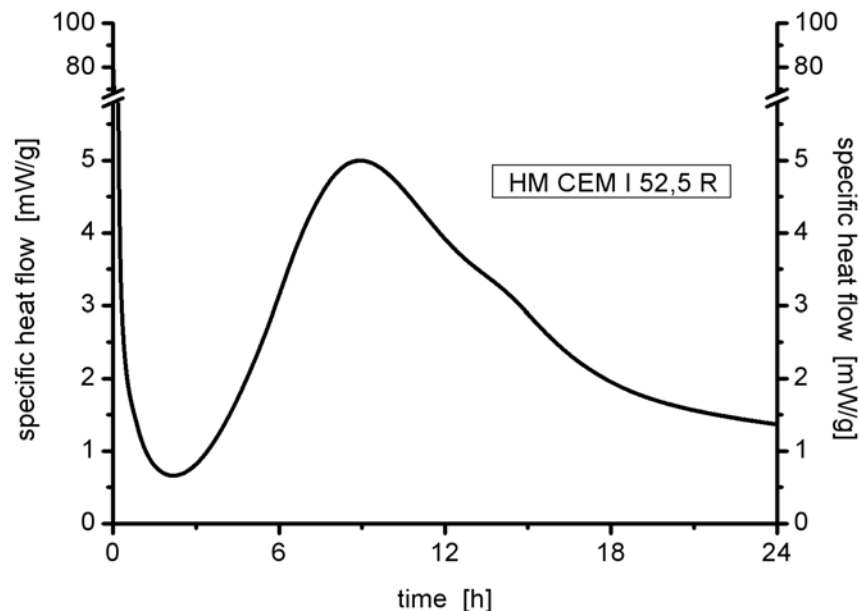

Figure 1: Specific heat flow of CEM I 52.5 R, w/c = 0,325 at 23°C [3]

The thermal power which is recorded is the total of aluminate-sulfate reactions and silicate reactions at any particular time. Heat-flow calorimetry cannot, however, discriminate directly between aluminate-sulfate and silicate reactions. A second method (for example in-situ XRD) has to be employed to obtain this information. Figure 1 shows the typical thermal behavior of the CEM I 52.5 R during the first 24 h of hydration. A strong reaction sets in immediately after addition of water. Heat flow reaches its

global maximum after just a few minutes during this initial period. From then on, heat flow steadily decreases down to a local minimum (induction period). Subsequently, reaction once again accelerates simultaneously with gain of strength (acceleration period). After reaching a local maximum, the heat flow again decreases slowly over a very long period (deceleration period). The dosage of additives, such as accelerators and retarders, influences hydration reactions and, subsequently, the heat evolution. Figure 2 shows the influence of calcium formate and tri-ethanol amine (TEA) on the hydration behavior of the CEM I 52.5 R [4] at 23°C and w/c = 0.325. Addition of 0.1 mass-% (ma.-%) of TEA on the dry cement clearly acts as a retarder which tends to postpone the main period of heat evolution to some later point in time. The dosage of 2.5 ma.-% calcium formate accelerates the beginning of the acceleration period.
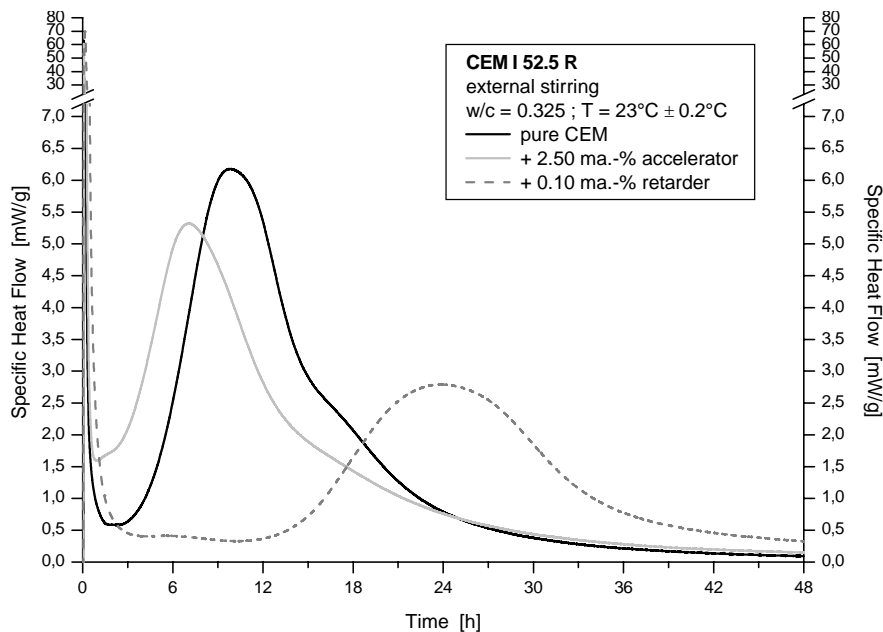

Figure 2: Specific heat flow of CEM I 52.5 R with additives, w/c = 0.325, 23°C [4]

It is also very interesting to take a closer look at the heat flow during the initial period (figure 3).
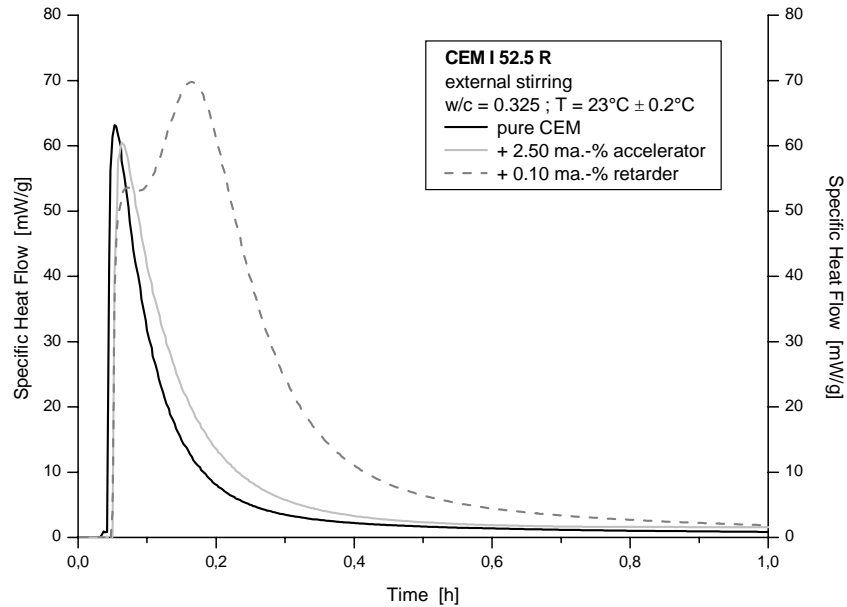
Figure 3: Early heat flow of CEM I 52.5 R with additives, w/c = 0.325, 23°C [4]

The initial heat flow of the cement with 2.5 ma.-% of calcium formate (CaFo, accelerator) seems to be similar to that of the pure cement. But by addition of the retarder (0.1 ma.-% of TEA) the initial heat flow is strongly increased. The following results can explain this behavior of the additives by means of in-situ XRD investigations followed by Rietveld refinements with quantitative approach and determination of structural information regarding ettringites.

2. Methods

The phase evolution in cement pastes prepared from CEM I 52.5 R (OPC) with a w/c ratio of 0.325 was investigated by means of in-situ X-ray diffraction at a temperature of 23° C. The samples were prepared as described in [6]:

- Mixing of 10 g of sample with water by a spatula for 30 s
- Preparation of the pastes into a special sample holder
- Covering of the pastes with a 7μm Capton foil
- Start of the first measurement after 3.5 min
- All investigations were carried out for 5 preparations

The following measurement conditions for the Bruker AXS D8 equipment with a Braun PSD were used:

Range	7 – 35° 2 theta
Step	0.02° 2 theta
Time/Step	0.3 s
Time/Range	7min 13s
Radiation	Copper Kα

Generator	30 mA, 40 kV
Divergence slit	0.2°
Time of investigation	3.5 min – 19.1 h

Quantitative phase analyses and structural refinements were carried out by constraining 5 patterns of 5 independent preparations with Topas 2.1, using an adapted fundamental parameter approach. Structural data were derived from Inorganic Crystal Structure Database (ICSD). All ICSD data were refined on basis of pure phases. Refined structural data for ettringite, which are essential for accurate quantification, were employed for Rietveld analysis [7].

Calculations for quantitative phase estimation were carried out for at least 4 defined points in time during hydration of the cement paste:

- 3.5 min (immediately after mixing with water, initial period)
- 2.5 h (induction period)
- 7.9 h (acceleration period)
- 19.1 h (deceleration period)

The amount of solid in the cement paste will be increased during hydration procedure because mixing water is bound to crystalline phases. Therefore the following calculations are necessary to describe the phase content on the basis of the whole cement paste including the mix water.

The results of the refinement obtained from Topas 2.1 were recalculated to the final phase composition using the following procedure:

1st Step:

Where no Portlandite (CH) is observed, the analysis values remain as determined. Where Portlandite proves to be present, the appropriate $C_{1.7}SH_{2.1}$ content is calculated with respect to the molar ratios in eq. 4 according to the following formula:

Content $C_{1.7}SH_{2.1}$ = content CH x 193 / (1.3 x 74)

2nd Step:

Analysis data are normalized to 100 ma.-% excluding any H_2O.

3rd Step:

Analysis data were normalized to 100 ma.-%, including crystalline-bonded and non-bonded (free) water.

Moreover, some structural data of ettringites were refined and calculated for appropriate times: lattice parameter a, lattice parameter c, isotropic crystallite size. Data were obtained by soft constraint of 5 isochronous XRD pattern.

The standard deviations (sd) for the quantitative data of the in-situ Rietveld refinements after the above given calculation steps are summarized in Table 1. These values are only valid for this CEM I 52.5 R under the described conditions.

Table 1: Estimated standard deviations for in-situ XRD quantification

Phase	sd in ma.-%
ettringite	0.6
portlandite	0.8
$C_{1.7}SH_{2.1}$	1.6
C_3A	0.6
anhydrite	0.5
alite	2.1
belite	1.7

3. Results

3.1 Cement characterization

Both the cement and the clinker were chemically analyzed. Table 2 summarizes the chemical composition of the OPC and the related clinker.

Table 2: Chemical analysis the used CEM I 52.5 R and its related clinker

	CEM I 52.5 R [ma.-%]	Clinker [ma.-%]	sd [ma.-%]
CaO	65.3	68.0	0.3
SiO_2	22.2	23.2	0.3
Al_2O_3	3.9	4.0	0.2
Fe_2O_3	1.35	1.41	0.1
Na_2O	0.12	0.13	0.03
K_2O	0.67	0.50	0.03
MgO	0.61	0.65	0.15
Mn_2O_3	0.04	0.04	0.02
TiO_2	0.11	0.10	0.02
SrO	0.17	0.16	0.02
P_2O_5	0.16	0.17	0.03
SO_3	3.77	0.17	0.2
L.O.I.	1.1	0.46	0.1
Σ	**99.5**	**99.0**	

Oxides were analyzed by Atomic Absorption Spectroscopy, SO_3 by nephelometry and P_2O_5 by colorimetry

The selected CEM I 52.5 R was analyzed by calibrated Rietveld refinement. The cubic and orthorhombic C_3A content was calculated from calibrated Rietveld refinement of XRD pattern on the basis of the residue of the salicylic-methanol extraction. Table 3 summarizes the phase analysis data of the CEM I 52.5 R.

Table 3: Rietveld analysis of the selected OPC

Phase	ma.-%	OPC CEM I 52.5 R	recalculated paste
alite	66.7		52.7
belite	13.7		10.8
$C_3A_{(cubic)}$ (ss)	6.0		7.5
$C_3A_{(orthorhombic)}$(ss)	3.5		
C_4AF (ss)	2.0	< determination limit	
periclase	0.2	< determination limit	
CaO	0.1	< detection limit	
anhydrite	5.7		4.5
bassanite	0.8	< determination limit	
gypsum	0.3	< determination limit	
calcite	0.9	< determination limit	
quartz	0.1	< determination limit	
water	-		24.5

The Rietveld analysis gives a total of 9.5 ma-% of C_3A for both cubic and orthorhombic modifications. Ferrite, periclase, bassanite, gypsum, calcite and quartz contents are below the determination limit (limit for quantitative conclusion). CaO (free lime) is below the detection limit (limit for qualitative conclusion). In order to minimize uncertainties, none of the phases which lay below detection and determination limits were quantified in the following investigations. Therefore, the phase content was recalculated to a paste composition of alite, belite, C_3A, anhydrite and water (total 100 ma.-%, Table 3 right column). The stability and accuracy of the quantitative analysis was increased by implementing only cubic C_3A in the following Rietveld refinements [8].

3.2 Quantitative phase analysis

Figures 4 to 6 show the quantitative phase composition of cement pastes at defined times. The column at 0 h gives in each case the phase composition of the cement for all phases above the determination limit and water added to w/c = 0.325 which complies with 24.5 ma.-%. At 0 h, water has not yet been in contact with the cement. Immediately after mixing with water at 0.07h, we already observe a presence of 7.9 ma.-% ettringite in the cement paste of the pure cement without additives (figure 4). C_3A (ss) and sulfate carrier content are decreased. Change in alite content appears to be insignificant. During the next 2.5 h (induction period) the phase composition is subject to only marginal changes. After 8.09 h (acceleration period) the main reaction has started, with newly formed ettringite, portlandite and subsequent C-S-H phase. Alite content as well as anhydrite and

C₃A (ss) content are reduced at the same time. After 19.1 h the reaction has progressed. An ettringite content of 17.7 ma.-% has been attained. The silicate reaction produces at the same time a total of 27.0 ma.-% C-S-H and portlandite. Anhydrite was close to the detection limit. Finally, 4.7 ma.-% C₃A (ss) is present. Belite content remains unchanged throughout the 24 h of hydration.
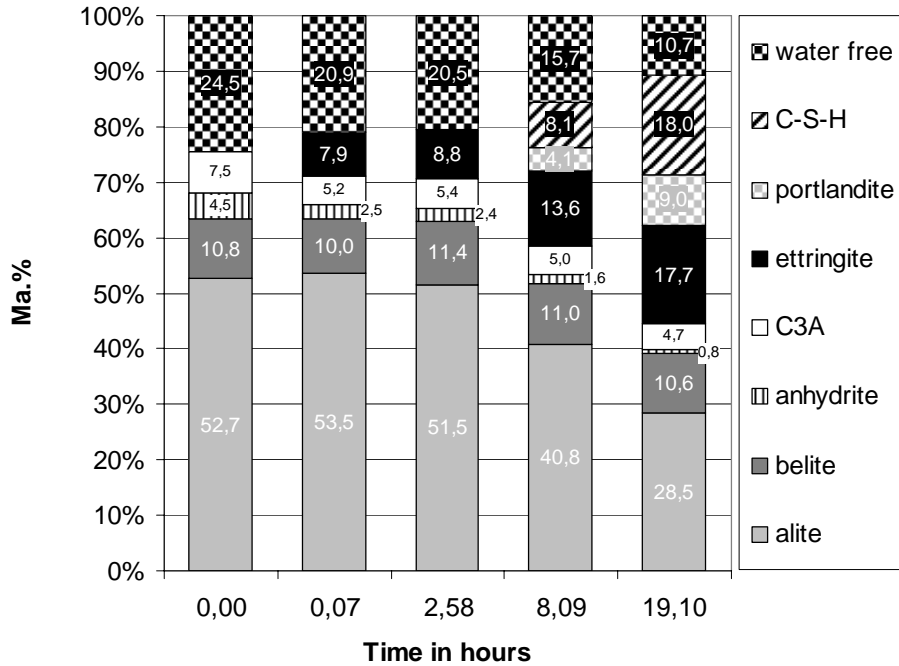

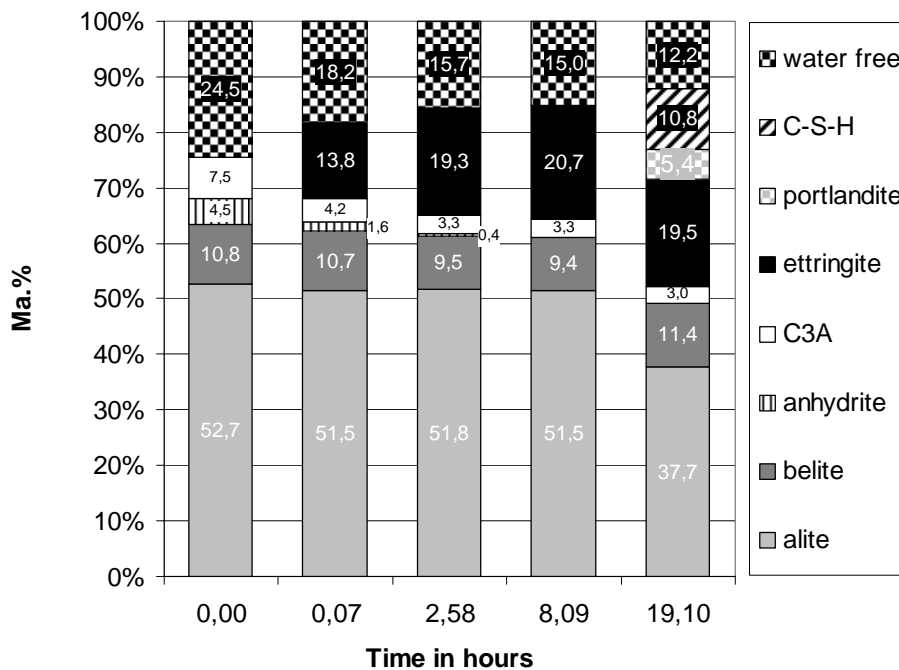Figure 4: Quantitative phase evolution for OPC without additive (23°C)

Figure 5: Quantitative phase evolution for OPC with 0.1 ma.-% TEA (23°C)

The cement paste with dosage of 0.1 ma.-% TEA displays a different behavior (figure 5). Immediately upon mixing with water, the ettringite content attains 13.8 ma.-%. Anhydrite content is strongly reduced, falling to 1.6 ma.-%. Up to the 8.9 h point, no significant alite reaction can be observed. The ettringite content increases between 0.07 and 2.58 h. At 8.09 h, anhydrite has been used up. Ettringite content attains 20.7 ma.-% after 8.09 h. Silicate reaction begins between 8.09 and 19.1 h. After 19.1 h portlandite and C-S-H are present.

Figure 6 displays the phase composition with the dosage of 2.5 ma.-% calcium formate (CaFo). As usual, hydration begins with the aluminate reaction producing ettringite immediately upon mixing with water. After 2.58 h, aluminate reaction has progressed and silicate reaction has begun. Portlandite and C-S-H were present at 2.58 h. After 8.09 h, aluminate-sulfate reaction was finished, with a final ettringite content of 16.4 ma.-%. Silicate reaction progressed strongly, with a total of C-S-H and portlandite of 38.2 ma.-% after 19.1 h.
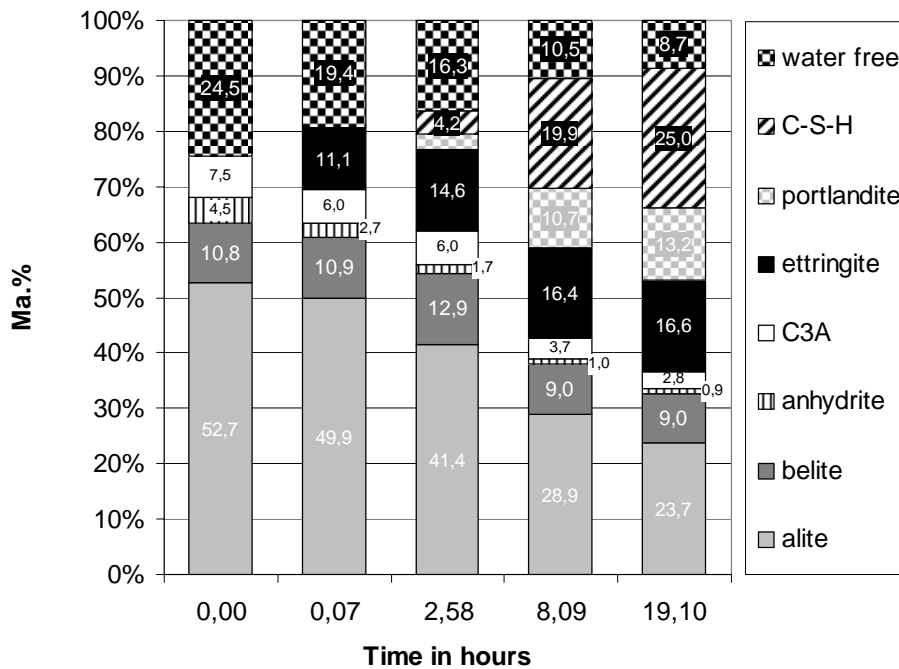

Figure 6: Quantitative phase evolution for OPC with 2.5 ma.-% CaFo (23°C)

3.3. Structural data of ettringites

Lattice parameters of ettringites were evaluated during hydration of the cement pastes. Cement pastes containing pure OPC and OPC with 2.5 ma.-% CaFo display similar behavior. Lattice parameter a_0 increases very strongly during the first hours of hydration, especially during the induction period (figure 7). After 19.1 h, all cement pastes display lattice parameters a_0 at 11.205 +/- 0.01 Å. Lattice parameter a_0 of ettringites from the ce-

ment paste with 0.1 ma.-% TEA displays no change within the uncertainty of the measurements during hydration from 0 up to 19.1 h.
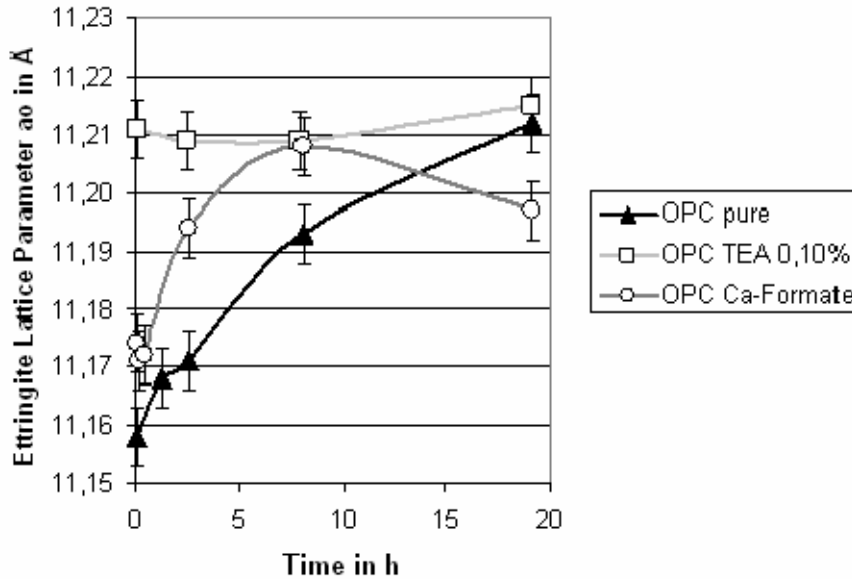

Figure 7: Lattice parameter a_o of ettringites during hydration

Lattice parameter c_o of ettringites from pure cement paste and cement paste with CaFo is enlarged (21.61 – 21.63 Å) immediately upon contact with water (figure 8). During the induction and acceleration periods, there is a strong decrease of lattice parameter c_o in both pastes. Paste with 0.1 ma.-% TEA displays, once again, no significant change of lattice parameter c_o during hydration time.
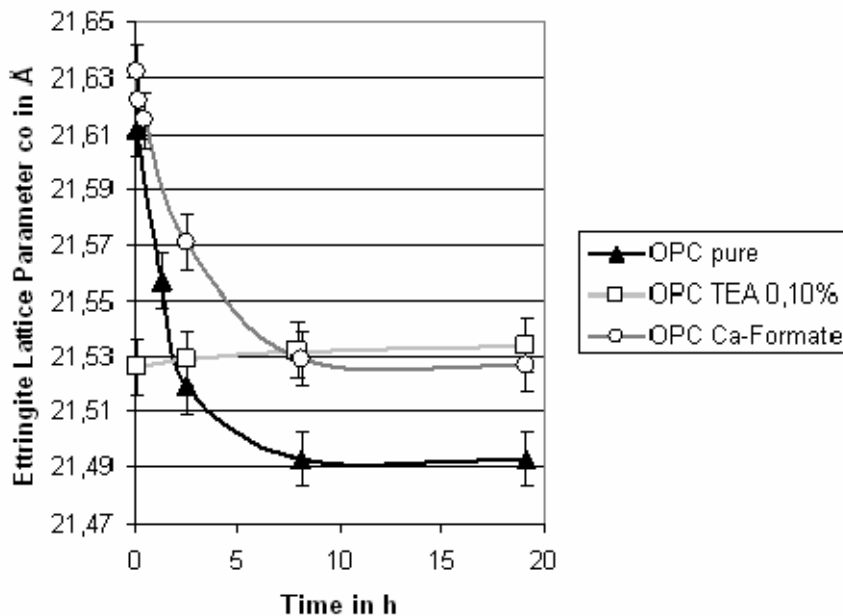

Figure 8: Lattice parameter c_o of ettringites during hydration

The crystallite sizes of ettringites in the 3 different pastes are illustrated in figure 9. Pure cement paste displayed a strong increase in crystallite size during the induction period (up to 2.58 h). Cement paste with 2.5 ma.-% CaFo exhibited an even faster increase in crystallite sizes at very early points in the hydration process. Again, the behavior of cement paste with 0.1 ma.-% TEA appeared quite different. There was no increase in crystallite size during the induction period.
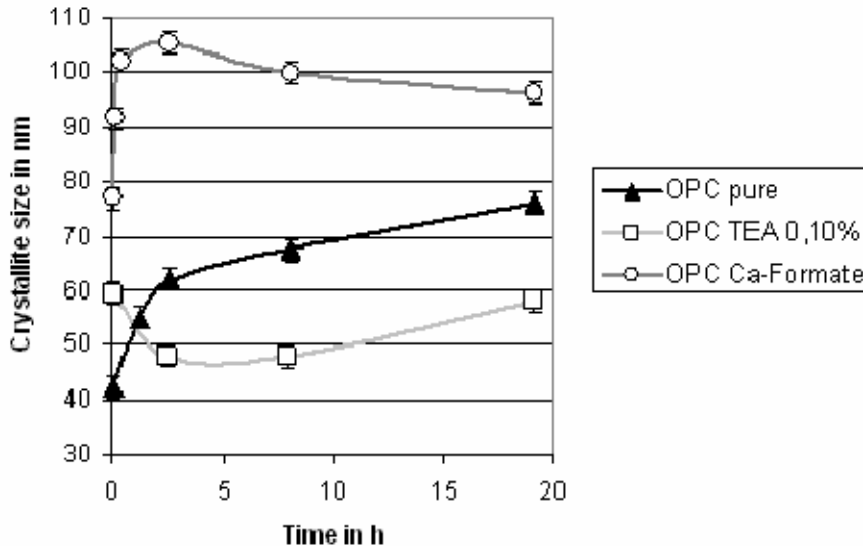

Figure 9: Isotropic crystallite size of ettringites during hydration

4. Conclusion and discussion
4.1 Pure cement paste

Calorimetric investigations of OPC reveal a typical evolution of heat during the course of investigation as displayed in figure 1. The thermal power which is released during the first 30 minutes of hydration is due mainly to the aluminate-sulfate reaction (eq. 1). The quantitative phase analysis yields an ettringite content of about 8 ma.-% for the pure cement paste immediately upon its contact with water. C_3A (ss) and anhydrite are decreasing at the same time. Alite content has not significantly shifted. No portlandite is present up to 2.58 h. During the induction period, only a small increase in ettringite content could be detected. Silicate reaction (eq. 4) with formation of portlandite begins after about 3h and aluminate-sulfate reaction also begins once again. Belite shows no significant decrease during the first 19.1 h of hydration. The heat flow during the main period is due to a combination of aluminate-sulfate and silicate reaction.

The structural data of ettringites display very interesting behavior during the first 24 h of hydration. The small a_o parameter (11.16 Å instead of 11.24 Å for pure ettringite [7]) indicates that the ettringite which is precipitated during the first minutes contains carbonate and hydroxide at sulfate positions in its crystal lattice (compare [9]). During the induction and ac-

celeration periods, carbonate and hydroxide are replaced by sulfate. Lattice parameter c_o also displays an interesting behavior. That ettringite which is precipitated immediately after the mixing with water displays large c_o parameters (21.61 instead of 21.49 Å for pure $C_3A*3CaSO_4*32H_2O$ [7]). This lattice parameter indicates that aluminum is replaced by iron in the ettringite lattice. Later, during the induction and acceleration periods, iron is replaced by aluminum. The lattice parameter c_o is continuously shortened, down to 21.49 Å, which indicates almost iron-free ettringite.

Isotropic crystallite sizes of ettringites were also determined during the whole course of hydration. The authors are aware that crystallite sizes of ettringites should be nonisotropic in a_o and c_o directions. Isotropic refinement, therefore, leads to average dimensions of crystallites which should be carefully evaluated. Crystallite sizes for ettringites from pure cement paste display an increase mainly during the induction period, in the course of which only very small amounts of ettringite are newly formed. This is evidence, together with the change in chemical composition, for a particularly marked maturation of ettringite specifically during the induction period. This maturation of ettringite could be a trigger for the start of the acceleration period.

4.2 Cement paste with TEA

The dosage of 0.1 ma.-% TEA displays a significant influence on the heat flow detected by calorimetry (figure 2 + 3). It results in a strong heat flow during the initial period. Quantitative phase analysis reveals a massive ettringite precipitation immediately upon contact with water. The ettringite content is up to 6 +/- 0.6 ma.-% higher than in the pure cement paste. After 2.58 h, the ettringite content has increased to 19.3 +/- 0.6 ma.-%, which is comparable to pure cement paste after 19.1 h. At the same time, C_3A (ss) and anhydrite content sharply decrease. Alite is not significantly dissolved; no portlandite could be detected up to 8.09 h. Aluminate-sulfate reaction is intensively accelerated during the induction period by the dosage of 0.1 ma.-% TEA. This observation agrees well with the findings published in [10].

Structural data of ettringites show only small differences during the first 24h of hydration. Chemical composition of ettringite seems to be quite constant during 19.1 h of hydration.

Furthermore, crystallinity does not display any change when we compare early precipitated ettringite with ettringite that is formed only later. There is no maturation effect, as this is observed, for example, in the case of pure cement paste. The huge amount of ettringite which does not mature might well go to block surfaces, resulting in a strong retarding effect. Silicate reaction begins quite late, after more than 8.09 h of hydration. On the other hand, we have to bear in mind that the iron may be complexed by TEA.

4.3 Cement paste with calcium formate

The dosage of 2.5 ma.-% calcium formate does not influence the heat flow during the initial period as strongly as does 0.1 ma.-% TEA (figure 3). Quantitative phase analysis shows that ettringite formation during the initial period is less strongly accelerated than it is by TEA.
Refined structural data of ettringite display a strong increase in crystallite size during the first hour of hydration. The change in chemical composition determined from lattice parameters is comparable to ettringites in pure cement paste. Overall, there seems to be a stronger maturation effect on ettringites with the dosage of 2.5 ma.-% calcium formate. This fast and strong maturation of ettringites might be one factor which goes to make calcium formate a highly efficient accelerator. At the same time, the influence of calcium formate on the formation of portlandite, which tends here to occur at an earlier point in time, has to be discussed.

5. References

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