Refined Ettringite Structure for Quantification of Hydration in Cement Pastes

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Abstract:

The refined new ettringite structure model [1] was employed for quantification of the ettringite formation within a 24 h period in OPC cement and in mixtures (CaO/SO_3 = 2.1) of $C\bar{S}H_{0.5}$ (calcium sulfate hemihydrate) with calcium aluminate cements. Hydration was monitored by means of in-situ XRD. Rietveld refinement of the XRD pattern of the hydrating pastes as recorded in-situ was utilised in order to acquire quantitative data regarding the dissolution of such cement phases as C_3S, C_3A, CA and $C\bar{S}H_{0.5}$ during the first 24 h of hydration. In consideration of the non-crystalline parts in the pastes – H_2O, C-S-H or aluminium hydroxyl hydrate – the quantitative data regarding the crystalline phases acquired by means of Rietveld refinement and the data regarding the amorphous phases were standardised to 100 ma.-%. The refined structure model for ettringite was verified to provide quantitative X-ray diffraction in cement pastes.

1   Introduction

Ettringite was labelled "cement bacillus" by Michaelis [2] because this mineral phase was observed in damaged concrete in the form of very small rod-shaped crystals. For this reason, the appearance of ettringite came to be constantly associated with poor concrete performance. Ettringite, however, is always be found in concrete, and in fact indicates no insufficiency in the concrete in which it is found. Ettringite-type compounds are naturally occurring minerals which also may be present in hydrated pastes from ordinary portland cement (OPC) and mixes of calcium aluminate cement (CAC) with calcium sulfate or OPC. Contrary to Michaelis's view, it is nowadays known that controlled ettringite formation results rather in unique hydraulic properties important for construction purposes: namely, very high early strength, superior sulfate resistance, lower drying shrinkage and self-drying properties. Primary formed ettringite is important in improving the workability of concrete slurry before setting

The formation of ettringite as a main hydration product can be achieved by mixing calcium aluminate oxides (CA, CA_2, $C_{12}A_7$, C_3A) with sulfate (anhydrite, hemihydrate, gypsum) and water. The phases CA, CA_2 and $C_{12}A_7$ tend to occur in CAC clinkers, whereas C_3A represents a less abundant phase in OPC clinkers compared to C_3S. In the wide range of formulations for building chemistry applications both CAC and OPC are used in sulfate containing mixtures because of their very rapid early strength.

For the investigations presented below, Rietveld refinement of the in-situ recorded XRD pattern of the hydrating pastes was utilised in order to acquire quantitative data regarding the phase composition during the first 24 h.

2   Experimental

2.1   Quantitative mineralogical phase analysis of the cements

XRD data regarding the OPC and CAC were collected using a D5000 Bragg-Brentano diffractometer with $Cu_{K\alpha}$-radiation. The samples were ground in a disc mill and sieved ($\leq$ 36 µm) in order to achieve the required grain sizes for X-ray powder diffraction. In order to guarantee representative specimen the cements were homogenised and divided by means of a laboratory sampler. Preparation for X-ray diffraction was carried out by use of the frontloading technique.

For XRD data collection for Rietveld analysis, there were used the fixed slit setup and secondary graphite monochromator. The instrumental parameters for the D5000 diffractometer are shown in Table 1.

Lattice and structural parameter refinement by Rietveld analysis with fundamental parameter approach (TOPAS Version 2.1, BRUKER AXS) was employed for crystallographic characterisation.

2.2   In-situ XRD analysis of the hydration

The phase evolution in the cement/calcium sulfate pastes, with a w/c ratio 0.325 for OPC and of 0.5 for CAC-$C\bar{S}H_{0.5}$ mix, was investigated by means of in-situ X-ray diffraction at a temperature of 23° C.

Table 1:   Measurement conditions: quantitative and in-situ XRD analysis

	Quantitative XRD-analysis (D5000)	In-situ XRD-analysis (D8)
Radiation	Cu Kα	Cu Kα
Tube voltage	40 kV	40 kV
Tube current	30 mA	30 mA
Angular range	10 - 65 °2θ	7 – 34 °2θ
Step width	0,02° 2θ	0,02° 2θ
Time per step	4 s	0,5 s
Divergence slits	0,5°/0,5° Fixed slits	0,5° Primary fixed slit
Time/range	3 h	12 min
Monochromator	Secondary graphite monochromator	Secondary Ni-Filter
Detector	Scintillation counter	Braun OED with anti scatter slit

The pastes were prepared by mixing of the samples with H_2O for 30 s by means of a stirring machine. After preparation of the pastes into a special sample holder, they were covered with a 7µm Kapton-brand X-ray film in order to create a closed saturated water vapour atmosphere in the paste. No influence of the Kapton film on preferred precipitation of ettringite at the surface of the investigated pastes could be observed. Another major advantage of the in-situ XRD is that ettringite dehydration resulting from grinding can be excluded because the sample can be investigated without further preparation. The first measurement was always started 3.5 minutes after mixing with H_2O. For each sample, 5 independent preparations were mixed and investigated by in-situ XRD. The measurement conditions for the Bruker AXS D8 equipment with a Braun PSD are shown in Table 1.

2.3 Rietveld refinement of the XRD data

Quantitative phase analyses and lattice parameter refinements were carried out during the first 24 h of hydration, using Topas 2.1 with a suitable fundamental parameter approach. Structural data for the refinement project were derived from the ICSD structural database (FIZ, Karlsruhe) [3] and were refined on the basis of the dry cements.

For the refinement of the resulting crystalline hydrate, namely ettringite a new structural data set, which included the hydrogen positions in the structure model [1], was employed. The model was derived from two different existing structure models. In the first published ettringite structure, proposed by Moore & Taylor [4], none of the 128 positions for H are given in the unit cell, which results in reduced scattering power in combination with reduced ettringite density for the use of this model (ρ= 1.676 g/cm^3 for the Moore & Taylor model compared to ρ= 1.774 g/cm^3 for the new model). For precise quantification of ettringite containing 45.9 ma.% H_2O in samples together with anhydrous phases, the contribution of H-atoms on scattering power and cell mass are indispensable. Especially for low diffraction angles (0 to 0.2 $\sin\theta/\lambda$) the use of wrong scattering power tends to result in erroneous quantification results for ettringite and therefore consequently for all other phases. In dependence to the applied scattering factors for all ions – which may be related to the Rietveld software - the quantification of CAC-C$\bar{\text{S}}$H$_{0.5}$ pastes could lead to results which show a maximal relative error up to 15 % in ettringite content in the pastes.

The revised structure model is based on the data of Moore and Taylor, supplemented by the H-positions determined by Berliner [5] on the basis of a neutron diffraction structural investigation. The accuracy of the ettringite structure model was checked for quantitative analyses by calculating calibration mixtures with zircon as internal standard [1]. Zircon was chosen because there exists a good comparability between its mass absorption coefficient of 80.56 cm^2/g and the mass absorption coefficients of the other phases occurring in cements, dry mortar mixes or pastes of these.

Displayed in Figures 1 and 2 are the observed data, the calculated data and the difference plots of pure ettringite, refined with the structure data of

Moore & Taylor [4] and with the revised ettringite structural data [1]. Introduction of hydrogen positions into the structure, and refinement of these positions, resulted in an excellent fit, especially in the interesting low 2θ area (8-12 °2θ), as compared with Figure 2.

The difference plot in Figure 1 is leading to lower results of ettringite when the model is employed for refinement of the ettringite quantities. In case of the refinement of the pastes this misfit is even more enhanced and quantification of ettringite is always lower than for the revised ettringite model (Figure 2).
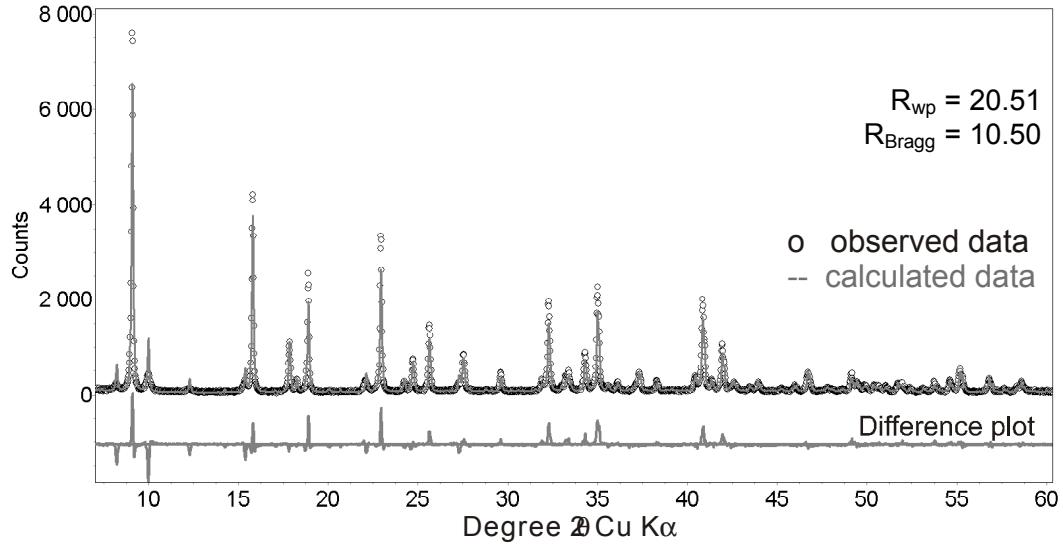

Figure 1: Difference plot from Rietveld refinement with TOPAS 2.1 for synthetic ettringite refined with ettringite structure data of Moore & Taylor
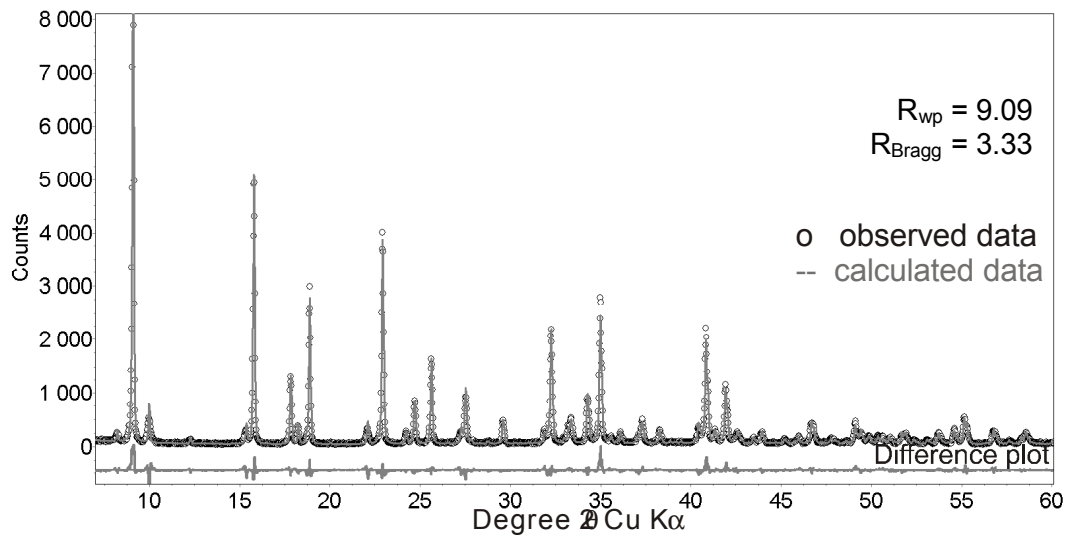

Figure 2: Difference plot from Rietveld refinement with TOPAS 2.1 for synthetic ettringite refined with revised ettringite structure data

3 Mineralogical characterisation of the materials used

3.1 Quantitative phase analysis of the cements

A clinker specific Rietveld quantification method was developed by mixing of synthetic phases with compositions determined by means of the technical clinker. With this calibration, the values of quantitative phase analysis can be assumed to be true values. Table 2 shows the average values as determined for Fe-free CAC and Table 3 the data for the OPC together with the employed structure models from ICSD [3].

Table 2: Quantitative phase analysis of the Fe-free calcium aluminate cement (CAC) and the used structural data sets

Phase	Average [ma.%]	ICSD-number
CA	60.3	260
CA_2	33.5	27264
A	6.2	63647

Table 3: Quantitative phase analysis of the selected OPC and the used structural data sets

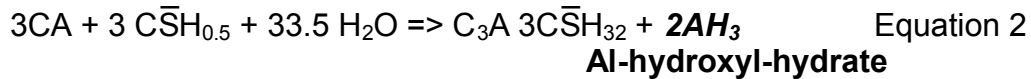| Phase	Average [ma.%]	ICSD-number
C_3S	70.6	64759
C_2S	11.7	963
$C_3A_{(cubic)}$	6.0	1841
$C_3A_{(orthorhombic)}$	3.5	1880
C_4AF	2.0*	9197
MgO	0.21*	9863
CaO	0.11*	28905
anhydrite	3.8	15876
bassanite	0.8*	69060
gypsum	0.34*	2059
calcite	0.86*	18166
quartz	0.13*	26429

* < determination limit

3.2 Quantitative phase analysis of the pastes

The refinement project for the pastes was extended to the hydrate phases as these occurred. In case of OPC paste quantification, portlandite and ettringite structure data were included in the refinement method for the cement phases (Table 3). For quantification of the CAC-$C\bar{S}H_{0.5}$ mix (CaO/SO$_3$ = 2.1), ettringite and gypsum structure data were used in addition to the calcium aluminium cement phases (Table 2). After Rietveld re-

finement, which leads to phase composition of 100 ma.%, the amorphous phases have to be calculated from the correlating crystalline hydrates. For OPC hydration, the C-S-H content was derived from the portlandite content according to equation 1. Due to Fuji and Kondo [6] the ratio of C/S for the early occurring C-S-H phase was observed to be 1.7. Therefore the equation for the silicate reaction may be written as follows:

$$C_3S + 3.4\ H_2O \rightarrow \underset{\textbf{C-S-H}}{\boldsymbol{C_{1.7}SH_{2.1}}} + 1.3\ CH \qquad\qquad \text{Equation 1}$$
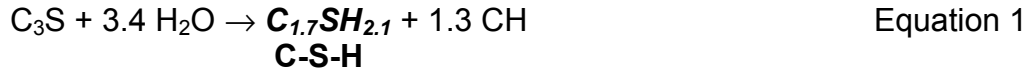
The aluminium-hydroxyl-hydrate content can be generated from the refined ettringite value according to Equation 2:

$$3CA + 3\ C\overline{S}H_{0.5} + 33.5\ H_2O => C_3A\ 3C\overline{S}H_{32} + \underset{\textbf{Al-hydroxyl-hydrate}}{\boldsymbol{2AH_3}} \qquad \text{Equation 2}$$

Only after standardisation of all phases in the pastes – including H_2O-content – up to 100 ma.% can the quantifications during hydration be compared, at any point of time, with each other. The standardisation procedure requires several steps and results finally, in values for crystalline phases, amorphous phases and non-structurally-bound H_2O (free water) which amount in total to 100 ma.% [7, p. 65].

- The crystalline phase composition was refined with Rietveld analysis.
- According to the determined ettringite content the content of aluminium-hydroxyl-hydrate ($AH_3 = 0.25\cdot$ettringite) was calculated.
- From that values the chemical composition without H_2O was calculated and simultaneously the values for bound H_2O in the hydrate phases was calculated by subtraction from $(100 + n)$ ma.%.
- Then standardisation onto the anhydrous content of the phases in the paste related to the start mix was calculated (100 ma.% anhydrous + 50 ma.% H_2O for w/c = 0.5).
- For all hydrates (ettringite, gypsum, bassanite, AH_3) the bound H_2O was calculated from the ratio of molar weights (e.g. for ettringite the factor 1.849 was applied)
- From the difference of the H_2O-content in the start mix and the bound H_2O in hydrate phases the not crystalline bound H_2O related to 100 ma.% cement + 50 ma.% H_2O was determined.
- In consideration of the H_2O in the hydrate phases and the addition of not dissolved cement phases this must result together with the not bound H_2O to 150 ma. %.
- Standardisation of all phases down to 100 ma. % was performed in the final calculation step.
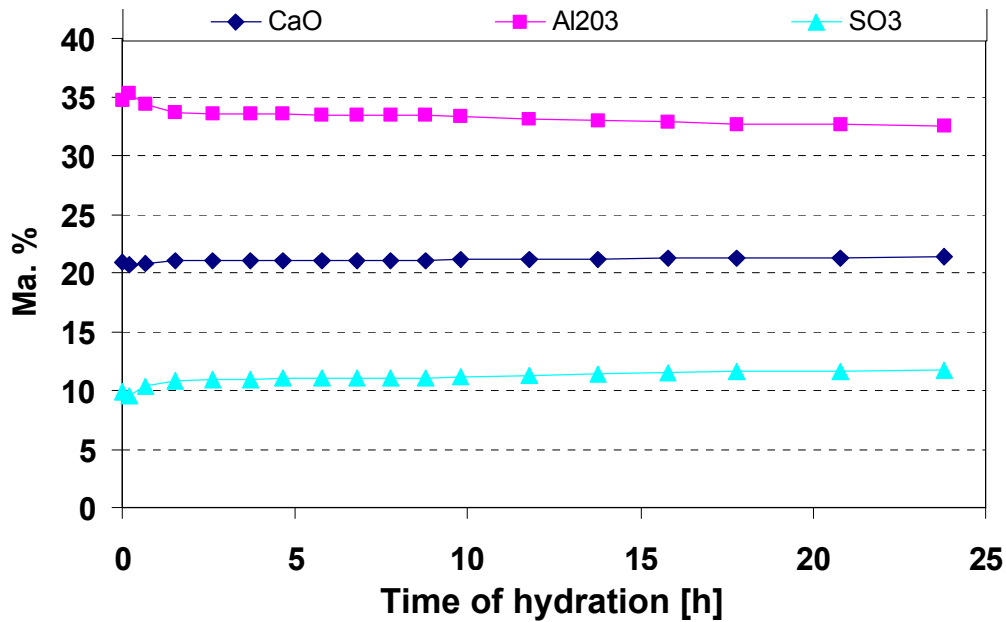
Figure 3: Chemical composition in the CAC-C$\overline{S}$H$_{0.5}$-mix with 0.2 ma.% Li$_2$CO$_3$ with 0.2 ma.% tartaric acid (standardised for w/s=0.5) calculated from the mass fractions and compositions of all phases at the different hydration times

On the basis of control calculations of the overall values for CaO, SO$_3$ and Al$_2$O$_3$ during 24 h from the mass fraction of the standardised phase compositions (Figure 3), there was determined an absolute error of 2 ma.% for ettringite, CA, C$\overline{S}$H$_{0.5}$ and CA$_2$. The absolute error for the minor phases gypsum and corundum is lower: namely, 0.5-1.0 ma.%. These errors are the estimated maximal errors, given by the chemical composition. But statistical errors from 5 independent preparations are much lower: namely, 0.2-1.0 ma.% for all phases.

4   Results of the quantitative phase analysis (Rietveld results after standardisation to 100 ma.%)

4.1   Hydration of OPC (CEM I at w/c 0.325)

Hydration of CEM I (low iron) mixed with deionised H$_2$O was quantified by Rietveld refinement and standardised for the non-crystalline phases C-S-H and free H$_2$O. The diagram below (Figure 4) shows the course of phase evolution in relation to hydration time.
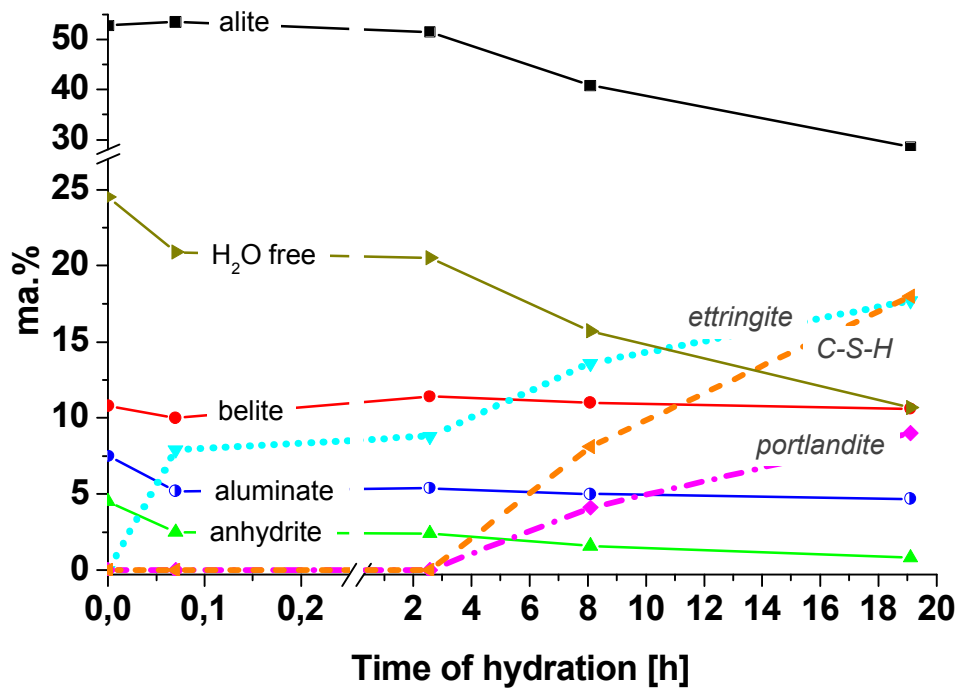
Figure 4: Standardised quantities of the investigated CEM I with H_2O and its hydration products (ettringite, portlandite and C-S-H phase) during 20 h of hydration for w/s=0.5 at 23 °C.

Ettringite is formed instantly upon addition of water, as shown in Figure 2, and at 0.07 h there could already be measured a level of 7.9 ma.% in the pastes. There is no significant change in phase composition up to 2.58 h. Within the time range of 2.58 h and the next quantification at 8.09 h, the OPC typical induction must be finished and further hydration can be observed in the paste. The ettringite content continues to increase up to 17.7 ma.% at 19.1 h. Alite, on the other hand, decreases from 52.8 to, finally, 28.5 ma.%. The other hydration products – namely, portlandite with C-S-H - were found at 8.09 h and had increased, by 19.09 h, to values of 9.0 and 18.0 ma.% respectively.

4.2 Hydration of CAC-C$\bar{S}H_{0.5}$ mix (CaO/SO$_3$ = 2.1) at w/c 0.5

Reactions of the mix CAC-C$\bar{S}H_{0.5}$ at w/s=0.5 are dominated by the dissolution of the main phase CA together with C$\bar{S}H_{0.5}$ and the formation of ettringite (Equation 2) and very small quantities of gypsum. All phases of the CAC, together with C$\bar{S}H_{0.5}$, ettringite, gypsum and the calculated phases Al-hydroxyl-hydrate and free H_2O, are plotted in Figures 3 to 5. The diagrams below show the course of phase evolution without additive

(Figure 5), with the addition only of 0.2 ma.% Li_2CO_3 (Figure 6) and finally (Figure 7) with the addition of 0.2 ma.% Li_2CO_3 in combination with 0.2 ma.% tartaric acid, all at w/s=0.5.
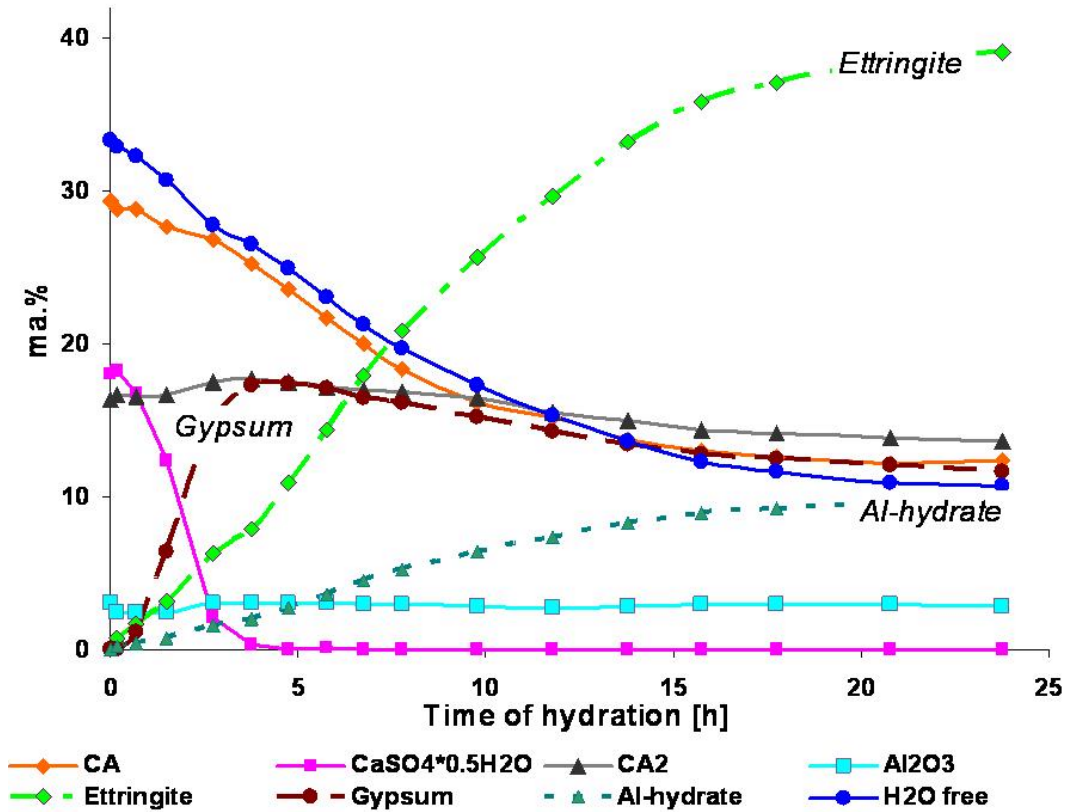

Figure 5: Standardised quantities of the investigated CAC-C$\overline{S}$H$_{0.5}$ mix with H_2O and its hydration products (ettringite, Al-hydroxyl-hydrate and gypsum) during 24 h of hydration without additive for w/s=0.5 at 23 °C.

Without any additive, there is observed a steady increase in ettringite formation which continues up to the hydration time of 15 h and then begins slightly to decline (Figure 6). Ettringite formation is probably not completed at 24 h but is still continuing - although the overall quantity of 41 ma.% was indeed already attained after 24 h. Simultaneously with the process of the formation of ettringite there occurred a process of dissolution of CA and C$\overline{S}$H$_{0.5}$. Within the same time-period, 17 ma.% of the CA was dissolved. Calcium sulfate hydrate (C$\overline{S}$H$_{0.5}$) was, as per Equation 2, completely dissolved after 5 h. But the CA dissolution rate v_{CA} was lower than the C$\overline{S}$H$_{0.5}$ dissolution rate $v_{C\overline{S}H}$ and gypsum was precipitated at the same time. After 5 h this gypsum was partly consumed for additional ettringite formation. After 24 h of hydration without additives, there was determined a gypsum content of 11.6 ma.%. The CAC phases CA_2 and A (corundum) were not affected by hydration. There was no decrease in CA_2 content - a finding significant with respect to the absolute error of the quantification method for CA_2.
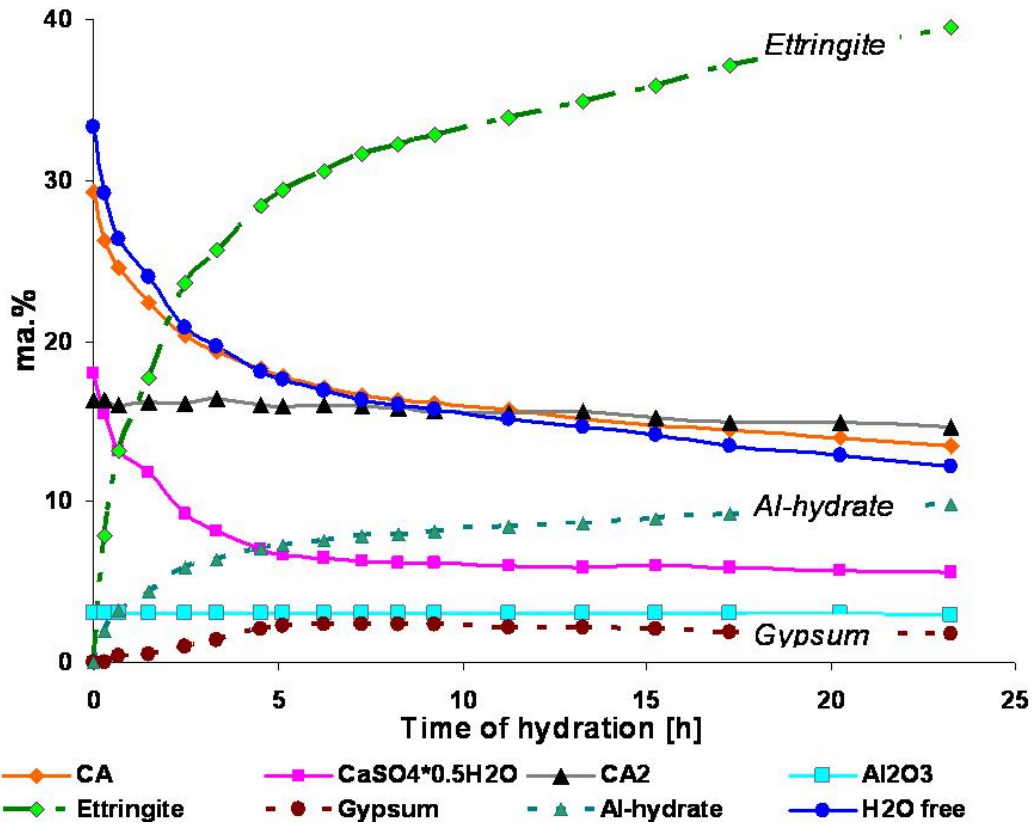
Figure 6: Standardised quantities of the investigated CAC-C$\overline{S}$H$_{0.5}$ mix with 0.2 ma.% Li$_2$CO$_3$ dissolved in H$_2$O and its hydration products (ettringite, Al-hydroxyl-hydrate and gypsum) during 24 h of hydration for w/s=0.5 at 23 °C.

Ettringite formation with 0.2 ma.% Li$_2$CO$_3$ was characterised by a high increase in the standardised quantities within 0 to 5 h, this curve later declining somewhat (Figure 7). An average quantity of 38 ma.% ettringite was formed and within 24 h of hydration 15 ma.% of CA were dissolved. Where Li$_2$CO$_3$ was present, the C$\overline{S}$H$_{0.5}$ content was diminished after 5 h, but not completely dissolved, as had been the case where Li$_2$CO$_3$ had not been present at all. The maximum determined gypsum content was low: namely, 2.3 ma.%. This is a clear indication that the CA dissolution rate v$_{CA}$ was almost coincided with the C$\overline{S}$H$_{0.5}$ dissolution rate v$_{C\overline{S}H}$. The very comparable course of dissolution of both phases is shown in Figure 7. Here again, there was no change in CA$_2$ and A (corundum) from the CAC during the first 24 h of hydration. The slight decrease in CA$_2$ content from 16.3 ma,% to 15.0 ma.% is not significant with respect to the estimated absolute error for CA$_2$ quantification.

In the case of hydration of the mix CAC-C$\overline{S}$H$_{0.5}$ with the additive combination of 0.2 ma.% Li$_2$CO$_3$ **and** 0.2 ma.% tartaric acid, there occurred a quite different curve for the phase evolution of ettringite formation (Figure 7). As late as 3.5 h after mixing, no ettringite could be observed in the paste from five independent measurements.
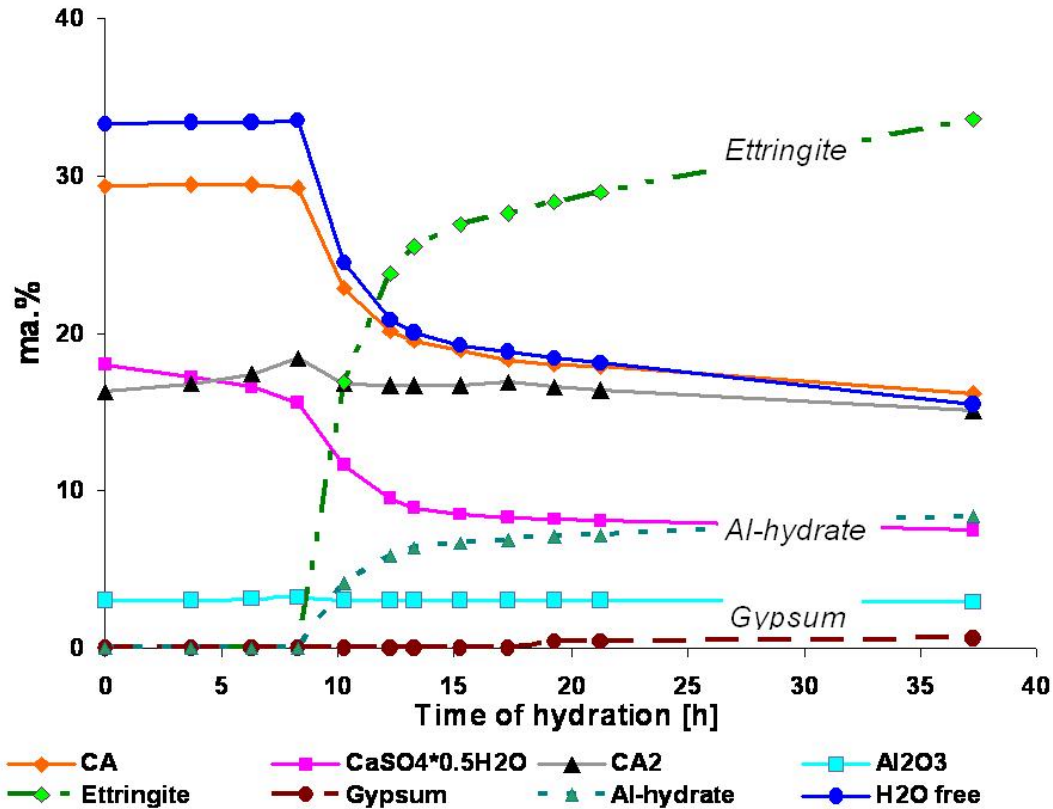
Figure 7: Standardised quantities of the investigated CAC-C$\overline{S}$H$_{0.5}$ mix with 0.2 ma.% Li$_2$CO$_3$ and 0.2 ma.% tartaric acid dissolved in H$_2$O and its hydration products (ettringite, Al-hydroxyl-hydrate and gypsum) during 24 h of hydration for w/s=0.5 at 23 °C.

But in the time-period 3.5 to 12 h ettringite began to be formed very rapidly – displaying a curve nearly as steep as that observed during the hydration of the mix without tartaric acid. This effect could be due to the addition of Li$_2$CO$_3$. After 24 h, an average quantity of ettringite was determined which was lower than that for the hydration of the CAC-C$\overline{S}$H$_{0.5}$-mix with only 0.2 ma.% Li$_2$CO$_3$ and for its hydration without additive. Consequently the lowest amount of CA and C$\overline{S}$H$_{0.5}$ were dissolved after 24 h. The gypsum content never exceeded 2.5 ma.% during early hydration – something not observed for the hydration of the CAC- C$\overline{S}$H$_{0.5}$-mix without tartaric acid. The retarding effect of tartaric acid on CA has already been described for the pure CAC [8].

5   Conclusion

The ettringite structure employed, with the H-positions in the structure model, with appropriate thermal parameters for hydrogen included and with the correct ettringite density of ρ= 1.774 g/cm^3 proves its outstanding performance during the investigation of the hydration of both OPC and CAC-C$\overline{S}$H$_{0.5}$ pastes . The results of the quantifications are of high quality

with respect to accuracy and precision. Although up to six phases were present in the OPC and the CAC- $C\bar{S}H_{0.5}$ pastes, the data are of a high degree of reproducibility.

The final results, after standardisation of C-S-H phase Al-hydroxyl-hydrate, remain dependent on the precise Rietveld quantification of portlandite and ettringite. Moreover the final results are dependent on the validity of equations 1 and 2 at early hydration age. The applied stoechiometries of C-S-H and of AH_x are determining very much their calculated quantities. In case of CAC- $C\bar{S}H_{0.5}$ pastes the sum of AH_x and not bound H2O is constant for all chosen AH_x stoechiometry. It is not reported in this study but there was observed a very clear time dependent correlation with data from heat flow calorimetry of the same pastes [9, 10].

For cement hydration, it proved possible to develop a new tool for characterising ettringite formation kinetics in pastes with different cements. We were able to monitor the influence of additives on hydration and to obtain, by means of in situ XRD investigations, quantitative data which may lead to new possibilities of interpretation.

6   Literature

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