Influence of the calcium sulphate source on the hydration mechanism of Portland cement–calcium sulfoaluminate clinker–calcium sulphate binders

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Article history:
Received 25 June 2010
Received in revised form 7 March 2011
Accepted 9 March 2011
Available online 17 March 2011

Keywords:
Calcium sulfoaluminate cement
Calcium sulphate
Pore solution
X-ray amorphous hydrates
Ternary binders

Abstract

Two different binders composed of Portland cement, calcium sulfoaluminate clinker and calcium sulphate were studied from early hydration to 28 days, one containing gypsum and one containing anhydrite at equimolar CaSO4 amount. Sodium gluconate was used as retarder to obtain a sufficient fluidity to cast the samples. Solids were analyzed by X-ray diffraction, scanning electron microscopy and thermogravimetric analysis and quantified by Rietveld refinement, while pore solutions were measured by ion chromatography. Thermodynamic modelling was used to model the hydration process of the ternary binders. This combined study allowed a precise understanding of the hydration process over time and the determination of the composition of the crystalline and of the X-ray amorphous hydrates present in the binders, which cannot be determined by conventional methods. Results show that the hydration mechanisms are similar in presence of gypsum or anhydrite, the difference being in the kinetics of reactions due to the slower dissolution of anhydrite compared to gypsum in the presence of sodium gluconate. The hydration starts with the formation of ettringite and of some X-ray amorphous hydrates. In the anhydrite-bearing system, the ettringite-forming reaction is stronger delayed by the addition of the retarder compared to the gypsum-bearing system. This stronger delay results in the formation of a significant amount of X-ray amorphous hydrates. The hydrates amorphous fraction is composed of different phases and its chemical composition is changing over time. During early hydration, it is mainly composed of aluminium hydroxide and strätlingite, while in the anhydrite-bearing system it can additionally contain some monosulphoaluminate. At later ages, the aluminium hydroxide content decreases and additional monosulphoaluminate and a C-S-H type phase are formed.

1. Introduction

Mortars based on ordinary Portland cement (OPC), calcium sulfoaluminate clinker (CSA) and calcium sulphate can achieve fast setting, rapid hardening and high early strength[1–4], which cannot be reached using OPC-based mortars alone. For those reasons, mortars based on ternary binders represent an interesting alternative for the production of dry-mix mortars. Due to the above mentioned properties, these mortars allow a reduction of working time on the construction sites. Besides this technological advantage, the production of CSA clinker has attracted new interest as it generates lower CO2 emissions than OPC due to a lower burning temperature in the kiln, a lower CO2-release from the raw materials (lower calcium carbonate content), and is easy to grind.

The data provided in the literature on the hydration of ternary binders based on OPC, CSA clinker and calcium sulphate, or on similar binders based on laboratory synthesized materials are rare[3–5]. In a previous paper, ternary blends with various OPC/CSA clinker/anhydrite mass ratios were studied, with variable anhydrite contents from 8/3/0.5 to 8/3/1.25, and variable OPC contents from 5/3/1 to 8/3/1[4]. On the one hand, it was observed that the assemblage of hydrate phases present in the binders after some weeks is not strongly dependent on the changes in the starting ternary composition, and includes ettringite, monosulphoaluminate, hydroxy-AFm (C4AHx with x = 13–19 depending on relative humidity), hemicarbonate, strätlingite and a C-S-H type phase (cement notation will be used throughout the text with A: Al2O3, C: CaO, F: Fe2O3, H: H2O, M: MgO, S: SiO2, T: TiO2). Some amorphous/micro-crystalline AH3 had formed at early age and was later partially consumed during hydroxy-AFm- or monosulphoaluminate-forming reactions. On the other hand, the changes in the
starting ternary composition strongly influenced the ettringite to monosulphoaluminate mass ratio.

The modification of the hydration process of OPC or CSA by different quantities or sources of calcium sulphate, such as gypsum, hemihydrate or anhydrite, is well known. In OPC the type and content of calcium sulphate is optimized considering the amount and the reactivity of the aluminate phase (C₃A), in order to form ettringite during early hydration [6]. In pure CSA cements, the hydrate assemblage is not strongly influenced by the amount and type of calcium sulphate added. Ettringite and monosulphoaluminate are formed due to the reaction of ye’elimite (C₄A₃S) with the calcium sulphate source. However, the amount of added calcium sulphate strongly modifies the ettringite to monosulphoaluminate mass ratio and the water demand to complete full hydration [7–9]. The amount of ettringite is affected by the reactivity of calcium sulphate (solubility and speed of dissolution) at early ages [8]. In ternary binders, the reactivity and speed of dissolution of the calcium sulphate is a key factor for the formation of ettringite or monosulphoaluminate during early hydration [5]. If the reactivity of the calcium sulphate is too low, monosulphoaluminate might form instead of ettringite.

However, there are unsolved issues despite the available data on the hydration mechanism of ternary binders. On the one hand, an important fraction of X-ray amorphous hydrates are present in the binders and their composition is still a matter of debate. AH₃ and a C-S-H type phase are assumed to be part of it, while it could also contain other hydrates not detectable using the X-ray diffraction technique or thermogravimetry (due to overlaps). On the other hand, a previous study showed that the use of an organic retarder is needed to obtain a sufficient workability, and that citric acid efficiently retards the early hydration reactions, such as the ettringite formation, in anhydrite-bearing ternary binders [3,4]. However, the impact of the addition of an organic retarder to CSA-bearing ternary binders based on different calcium sulphate sources has never been described in the literature.

In order to study these topics, two ternary binders based on OPC, CSA clinker and gypsum or anhydrite were examined in the presence of sodium gluconate (NaCa(H₂O)₂). To obtain the quantitative composition of the solid phase, the hydrated binders were studied by X-ray diffraction (XRD)/Rietveld refinement and thermogravimetric analysis (TGA). The liquid phase was studied by ion chromatography (IC), pH and total organic carbon measurements in order to follow the chemical evolution of the pore solution over time and to evaluate the adsorption of the gluconate on the cement particles or hydrate phases. Based on the obtained analytical data, thermodynamic modelling was used to calculate the effective saturation indices and to simulate the evolution of the solid and liquid phases over time. These thermodynamic calculations coupled to analytical data allowed a better understanding of the hydration mechanism and of the nature of the hydrates amorphous fraction present in the ternary binders.

2. Materials

The chemical and mineralogical compositions of the raw materials can be found in Table 1. The chemical composition was measured by X-ray fluorescence (XRF), except for sulphur which was determined with a Leico® apparatus. Free lime content was measured according to Franke [10]. The mineralogical composition was determined from the X-ray diffraction (XRD) patterns using Rietveld refinement. The OPC used was an OPC CEM I 52.5 R containing 3.5% anhydrite and 0.9% hemihydrate. Its free lime content was measured to be 0.25% and its Blaine fineness at 5030 cm²/g. The CSA clinker used contained 62.8% ye’elimite (C₄A₃S) and was characterized by CA and Cₐ₂ present as minor hydraulic components, 8.1% and 3.1% respectively. It had a Blaine fineness of 4180 cm²/g. Both calcium sulphates used were technical products. The gypsum contained some anhydrite (3.3%) and the anhydrite some SiO₂ (1.1%). To determine the amount of alkali sulphates in the OPC and in the CSA clinker (K₂SO₄ and Na₂SO₄ in Table 1), 5 g of cement or clinker were stirred in 50 ml of deionised water for 5 min. Solution was then filtered and Na and K concentrations in solution were measured by ion chromatography. The selected ternary gypsum- and anhydrite-bearing formulations (TER-G, TER-A) were chosen to have the same total SO₄ content (Table 1).

3. Methods

All the experiments were performed at 20 °C and at a water to cement ratio of 0.42. For each sample, 900 g of cement were mixed with 378 g of deionised water according to the EN 196-3 standard. The pastes were cast in 500 ml polyethylene (PE) bottles, and stored in a thermostatic water bath. The increase of temperature during the first hours of hydration was measured for TER-G in the centre of the bottle to check whether the temperature increase was relevant. The temperature reached about 23.5 °C after 3 h, and then quickly decreased to about 20.0 °C. The conditions were nearly isothermal. The pore solutions were extracted after 1 h, 5 h 30, 15 h 30, 1 day, 7 days and 28 days. Unset samples were pressure filtered to separate the solid and liquid phases (TER-G at 1 h, TER-A at 1 h and 5 h 30), while the hardened samples were treated with the steel die method to extract the pore solutions [11]. A maximum pressure of 250 N/mm² was used to extract the pore solutions from hardened pastes.

With a syringe equipped with a Nylon filter 0.45 μm, 4.5 ml of the liquid phase of each sample were immediately collected and placed into separate vessels. In the first PE-vessel 1 ml of solution was diluted (1:10) with Milli-Q water for ion chromatography. The second PE-vessel was filled with 3 ml of solution to determine the pH value. A 35 ml glass vessel was filled with 0.35 ml of pore solution and diluted (1:10) with Milli-Q water for total organic carbon (TOC) measurement. To determine the pH value, a Knick SE pH/Pt1000 electrode was used. In order to minimize the alkali error, fresh KOH solutions with known concentration were measured (0.001 mol/l to 1 mol/l). The obtained values were correlated to the calculated ones, considering the temperature during measurement (~ 23 °C) and the ionic strength of the KOH solutions. The total concentrations of Al, Ca, Na, K, Si and S were determined using ion chromatography (Dionex ICS-3000). The total organic content (TOC) of the pore solution samples was measured using a Sievers 5310C.

Heat flow curves were obtained by isothermal calorimetry with a Thermometric TAM Air instrument calibrated at 600 mW, in order to obtain an overview of the hydration kinetics of the two ternary binders. For the analysis, about 3.4 g of paste were mixed inside the apparatus using the admix amouple [12].

X-ray diffraction (XRD) and thermogravimetry (TGA) were used to determine the mineralogical composition of the solid phase. Prior to the analyses, hydration was stopped by plunging the samples 1 h in about 50 ml isopropanol and rinsing twice with diethyl ether. Samples were subsequently dried in a desiccator for about 12 h at room temperature. Prior to XRD and TGA, cement was ground to a grain size <63 μm for the analysis. The thermogravimetric analyses were done with a Mettler Toledo TGA/SDTA851e, where about 10 mg of sample were placed in an open vessel under N₂ atmosphere, heating up 20 °C/min up to 980 °C.

XRD data were collected using a PANalytical X’Pert Pro MPD diffractometer in a θ–2θ configuration using incident beam monochromator employing the Cu Kα radiation (λ = 1.54 Å) with a fixed divergence slit 1° and a rotating sample stage. The samples were
scanned between 5° and 80° with the Xcelerator detector. The anhydrous OPC was analyzed according to the protocol presented by Le Saout et al. [13] with the X’celerator detector. The phases used for the Rietveld refinement of the CSA clinker and the EDX analyses during which major and minor elements were semi-quantitatively measured (Ca, Al, Si, S, Fe, Mg, Ti, Na, K, Zn and Cr).

A mass balance calculation was used to determine the CaO, Al₂O₃, SO₃ and SiO₂ contents of the X-ray amorphous fraction of the hydrated pastes. In the one hand, the contents of the various oxides in the whole system were calculated using the chemical composition of the OPC, the CSA clinker and the calcium sulphates. In the other hand, the contents of the various oxides in the crystalline phases (anhydrous and hydrates) and their increase or decrease observed by Rietveld refinement were considered. Chemical composition of C₃S, C₃A₇S, CA, C₂AS and CT were measured by EDX on the anhydrous clinkers, while the chemical composition of the anhydrite and gypsum were known. For C₃A, C₃S and C₃AF, values were taken from Taylor [22]. For calcite, quartz, spinel (MA), ettringite and portlandite, oxides contents were calculated from their theoretical stoichiometry, the two lasts being too small to be separately measured by EDX. Finally, the chemical composition of all the crystalline solids was deduced from the total composition of the system for each oxide, giving the composition of the amorphous fraction for this oxide.

In order to carry out the thermodynamic calculations, the geochemical GEMS-PSI software was used linked to the cement-specific CEMDATA database [23–27]. Thermodynamic modelling was used to calculate the saturation indices of the various hydrate phases which could potentially form in the hydrating binder, using TGA results, so that the results were referred to the mass of anhydrous materials. The total could therefore be >100 wt.% (at w/c = 0.42, maximum is 142 wt.% representing 100 g of dry cement mixed with 42 g of water if all the water is incorporated in the system). The final result was then normalized to 100% (g/100 g paste). With this data representation, the “real” decrease or increase of the various phases can be observed. The error from the Rietveld refinement ranges between 5% and 20% for the clinker phases, while for the calcium sulphates it can go up to 40%

## Table 1

<table>
<thead>
<tr>
<th>OPC (wt.%)</th>
<th>CSA (wt.%)</th>
<th>CSH₂ (wt.%)</th>
<th>C (wt.%)</th>
<th>OPC (wt.%)</th>
<th>CSA (wt.%)</th>
<th>CSH₂ (wt.%)</th>
<th>C (wt.%)</th>
<th>TER-G (g)</th>
<th>TER-A (g)</th>
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Mineralogical composition determined by XRD/Rietveld refinement. Chemical analyses by XRF, except for SO₃ measured with a Leco® apparatus. CaO (free) determined according to Franke [10]. Loss on ignition (L.O.I) measured until 950 °C; - Na₂O and K₂O contents measured by SEM/EDX are 0.39 ± 0.24 wt.% and 0.6 ± 0.2 wt.% in C₃S, 0.15 ± 0.02 wt.% and 0.8 ± 0.3 wt.% in CA₂ and 0.24 ± 0.01 wt.% and 0.2 ± 0.1 wt.% in CA. K₂O content of C₃AH₃ was measured at 0.6 ± 0.3 wt.%.

## Table 2

ICSD codes used for the Rietveld refinement.

<table>
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<tr>
<th>Phases</th>
<th>Formulae</th>
<th>Crystal system</th>
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<th>References</th>
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</table>
the composition of the pore solutions. This shows when and which hydrates were in equilibrium with the pore solution, thus being able to precipitate. When the pore solution is undersaturated with respect to a certain solid, it is not formed. Thermodynamic calculations were also carried out to model the hydration processes of the two studied ternary binders over time. The following modelling strategy was applied: (i) The chemical compositions of the two dry-mixed cements were used as input, (ii) the dissolution kinetics determined from XRD/Rietveld refinement for C₃S, C₂S, C₃AF, C₄A, C₄A₃S, CA, CaCO₃, CSH₂ and CS were fitted using polynomial equations, while K₂SO₄, Na₂SO₄, hemihydrate, free MgO and free lime were allowed to dissolve instantaneously and spinel (MA), quartz, perovskite (CT), gehlenite (C₂AS) were considered to be inert (based on the XRD data), and (iii) the thermodynamic equilibria for the solid phases involved in the hydration process were calculated by GEMS considering the given empirical dissolution kinetics mentioned above. As no dissolution kinetics could be provided for CA₂ by the Rietveld refinement due to its low amount (<1 wt.%) in the ternary blends and to peak overlap, the dissolution of CA was used to model the CA₂ decrease (the same empirical equation was used). Free MgO was allowed to dissolve instantaneously due to its very low concentration in the two ternary binders (<0.06 wt.%), which did not strongly influence the modelled hydration process.

4. Results and discussion

In the absence of an organic retarder TER-G and TER-A set within some minutes. However, in the presence of sodium gluconate, TER-A is more retarded than TER-G. This is clearly visible on the heat flow calorimetric curves (Fig. 1). TER-G heat flow curve shows two peaks, the first one has a maximum heat flow around 30 min and the second one around 3 h. In TER-A two similar peaks are observed and delayed. The first peak has a maximum heat flow

![Graph showing heat flow curves for TER-G and TER-A](image)

**Fig. 1.** Heat flow curves obtained by isothermal calorimetry on the gypsum-bearing (TER-G) and on the anhydrite-bearing (TER-A) systems during the first 24 h of hydration.

![Graph showing evolution of solid phase composition](image)

**Fig. 2.** Evolution of the solid phase composition over time deduced from X-ray diffraction, Rietveld refinement and thermogravimetry for the gypsum-bearing (TER-G) and the anhydrite-bearing (TER-A) systems: (a and b) consumption of clinker phases and calcium sulphates, (c and d) formation of hydrate phases. AFt = ettringite, Amorphous = X-ray amorphous hydrates, CA = monocalcium aluminate, CA₁ = aluminate, CA₁F = ferrite, CA₃S = ye'elimite, CH = portlandite, C₃S = alite, C₅S = belite, C₆ = anhydrite, CSH₂ = gypsum. The amount of solid is presented as g/100 g of paste in order to avoid artefacts due to “dilution” effects (see methods description above).
around 1 h 30 and the second one around 7 h. However, the second peak seems to be composed of several convoluted peaks (shoulders at 6 h and 10 h), suggesting a more complex hydration evolution than TER-G at early ages with the formation and conversion of hydrates. The following paragraphs will always refer to the retarded mixes.

4.1. Solid phase composition

In TER-G, the Rietveld refinement analysis reveals that within the first hour only the rapid soluble phases of the OPC are dissolved such as the soluble alkalis (K$_2$SO$_4$ and Na$_2$SO$_4$), free lime (CaO$_f$) and hemihydrate. Only little C$_3$S dissolves within these first hours (Fig. 2a and c), and continues to dissolve until later ages. According to the Rietveld result, almost no or very little C$_4$A$_3$S seems to dissolve within the first hour (considering an error of 20% for C$_4$A$_3$S). The period between 1 h and 5 h 30 is characterized by a strong decrease in the C$_4$A$_3$S content and the complete consumption of the gypsum (C$_3$S$_2$H$_2$). This leads to the massive formation of ettringite (AFt) due to the reaction (i) C$_4$A$_3$S + 2CH$_2$ + 34H $\rightarrow$ C$_3$A·3C·SH$_2$ + 2AH$_3$, and of some X-ray amorphous hydrates (Fig. 2c). From 5 h 30 to 7 days, C$_4$A$_3$S is dissolving in the absence of gypsum. The AFt content stays constant, while the amount of X-ray amorphous hydrates strongly increases. The period beyond 7 days is characterized by a decrease of the AFt content, while some X-ray amorphous hydrates are still formed.

The hydrate phases observed in the derivative TGA curves for TER-G (Fig. 3a) are partly in agreement with the XRD results, including AFt and some X-ray amorphous hydrates, while monosulphoaluminate is additionally found in the TGA curves at hydration times of 7 and 28 days due to the reaction (ii) C$_4$A$_3$S + 18H $\rightarrow$ C$_3$A·CS·H$_3$ + 2AH$_3$. A little amount of CH seems to be present in the samples at 7 day and 28 day. The formation of AFt starts within the first hour. In order to be able to form AFt, it is obvious that some C$_4$A$_3$S or C$_4$A had dissolved at that time, in contrast to what was shown by Rietveld refinement. This discrepancy is due to the uncertainty of the Rietveld refinement method, which could be around ±2 g for 10 g of C$_4$A$_3$S (difference between C$_4$A$_3$S in the dry mix and the corresponding Rietveld result for the same sample). Even if the presence of some X-ray amorphous hydrates is deduced from the derivative TGA curves, their nature cannot be precisely determined using this method. The corresponding broad and flat peak ranges between 200 °C and 400 °C and could therefore be related to the presence of some AH$_3$, which would be in agreement with the AFt-forming reaction (i) mentioned above. However, AH$_3$ is probably not the only phase responsible for this signal. Moreover some additional peaks related to some X-ray amorphous hydrates (e.g. a C-S-H type phase) could be present at temperatures <200 °C overlapping with AFt and/or monosulphoaluminate.

More information can be gained from a mass balance calculation based on the XRD data to estimate the CaO, Al$_2$O$_3$, SO$_3$ and SiO$_2$ contents in the hydrates amorphous fraction, and its elemental molar ratios (Fig. 4a and c). In TER-G at 1 h, about 12% of the total Al$_2$O$_3$ of the system and no or little SiO$_2$ or SO$_3$ are present in the amorphous fraction. This confirms that some AH$_3$ forms in TER-G within the first hour. Beyond 1 h, some SiO$_2$ and SO$_3$ are contained in the amorphous fraction, showing that AFm-type phases or a C-S-H type phase could be present in it. The decrease over time of the calculated AI to Si molar ratio in the amorphous fraction is in agreement with the consumption of AH$_3$ and the formation of a C-S-H type phase during late hydration reactions observed in similar ternary binders [4].

In TER-A the kinetics of clinker dissolution and hydrate phases formation is different to the one of TER-G, except for the rapid dissolution of the alkali sulphates (K$_2$SO$_4$ and Na$_2$SO$_4$), free lime (CaO$_f$) and hemihydrate during very early hydration. Until 5 h 30, C$_3$S is the main phase to react and the volume of the X-ray amorphous fraction increases (Fig. 2d and e). As for TER-G, C$_3$S continuously dissolves in the investigated samples over time. The massive consumption of C$_4$A$_3$S and anhydrite occurs later compared to TER-G, between 5 h 30 and 1 d, leading to the massive formation of AFt (Fig. 2d) via the reaction (i) C$_4$A$_3$S + 2C$_3$S + 38H $\rightarrow$ C$_3$A·3C·SH$_2$ + 2AH$_3$. The decrease of the AFt content starts beyond 1 day and is coupled to the formation of some X-ray amorphous hydrates. Some CH is present in TER-A at 7 day and 28 day (Fig. 2d). From the Rietveld refinement analysis, less AFt and more amorphous hydrates and CH form in TER-A compared to TER-G.

The hydrate phases observed in the derivative TGA curves of TER-A are partly in agreement with the XRD results (Fig. 3b), including AFt and some X-ray amorphous hydrates, while monosulphoaluminate is additionally found in the TGA curves. As previously mentioned, the composition of the hydrates amorphous fraction cannot be gained from the derivative TGA curves. However, the mass balance calculation shows that some CaO, Al$_2$O$_3$, SO$_3$ and SiO$_2$ are present in the amorphous fraction from the early hydration period (Fig. 4b). It could therefore contain some monosulphoaluminate and other AFm-type phases or a C-S-H type phase. The mass balance calculations showed that the composition of the hydrates amorphous fraction in TER-A is slightly modified within the first hours of hydration, compared to TER-G where it is more significantly changed with a strong decrease of the Al to Si ratio (Fig. 4c and d).
4.2. Liquid composition

All results obtained from the chemical analyses of the extracted pore solutions, including elemental compositions, pH and total organic carbon measurements, are presented in Table 3. In pore solutions from TER-G and TER-A, Na and K continuously increase over time (Fig. 5a and b). They are released by the alkali sulphates (Na$_2$SO$_4$ and K$_2$SO$_4$) and sodium gluconate (only Na) at the early beginning and later by the dissolution of the clinker phases [11,22,28,29], such as C$_3$S and C$_3$A from the OPC or C$_4$A$_3$S, CA$_2$ or CA from the CSA clinker (see Na$_2$O and K$_2$O contents measured in these phases by SEM/EDX; footnote of Table 1).

In order to be able to evaluate an eventual alkali uptake by the hydrate phases, the discrepancy between the calculated and the measured contents of alkalis in the pore solution was determined (Fig. 6), taking into account only the measured dissolution of the clinkers, of the easily soluble alkali sulphates and of the sodium gluconate. The calculated and measured curves generally evolve in a parallel way, showing that alkalis are hardly incorporated into hydrate phases and that their increase in solution is mainly related to their release from the clinker phases and to the decrease of the pore solution volume over time. In TER-G the calculated values tend to be overestimated between 1 h and 5 h 30, when AFt and some X-ray amorphous hydrates are formed. Some small

<table>
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<th>Sample</th>
<th>Time (days)</th>
<th>pH</th>
<th>Al (mmol/l)</th>
<th>Na (mmol/l)</th>
<th>K (mmol/l)</th>
<th>Ca (mmol/l)</th>
<th>Si (mmol/l)</th>
<th>S (mmol/l)</th>
<th>OH (mmol/l)</th>
<th>TOC (mmol/l)</th>
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<td>6.5</td>
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TOC: total organic carbon, n.e.: not sufficient pore solution to perform measurement.
quantities of alkalis could therefore be sorbed by one or more of these phases. According to Andac and Glasser [30], some K can be sorbed by hydrates during the hydration of CSA cements beyond 3 days when monosulphoaluminate and strätlingite are formed. Moreover, strätlingite was clearly identified to be a K-binding phase in CSA cements [29]. Other literature data obtained on synthetic gels, such as C-S-H, C-A-S-H or M-S-H, showed that Na and K can be sorbed by these gels [31–34].

The Ca and S concentrations tend to decrease over time in the pore solutions of TER-G and TER-A (Fig. 5). They are released by the dissolution of C₄A₃S, of the calcium sulphates, and Ca is additionally released during free lime and OPC clinker dissolution. As soon as they are released in solution, they are consumed to form the AFt and some X-ray amorphous hydrates. Some SEM/EDX analyses showed that the hydrates amorphous fraction contains some Ca, which was confirmed by the mass balance calculations on the solid phases.

The Al concentration in the solutions stays constant in TER-G and TER-A (Fig. 5). It is balanced by the C₄A₃S dissolution, and the formation of AFt and of some Al-bearing amorphous hydrates. The dissolved Si concentration in TER-G continuously increases until 7 days (Fig. 5a). It is released by the dissolution of C₅S/C₃S and is incorporated in the hydrates amorphous fraction (Fig. 4a). Between 7 and 28 days, the dissolved Si concentration is rather constant (Fig. 5a). This could be due to the formation of some Si-bearing phases in the amorphous fraction, such a C-S-H type phase or an AFm-type phase. The evolution of the Si contents in pore solutions from TER-A is similar to the one observed in TER-G.

The evolution of the OH⁻ concentration in solution is negatively correlated to the S concentration and positively correlated to the Na and K concentrations, as the charge balance of the solution is maintained. For that reason OH⁻ generally increases over time in both TER-G and TER-A (Fig. 5). During early hydration pH values are lower than 12.6, being similar to pH values observed in the pore solutions of CSA cements [29]. At later ages they range between 13 and 14, being similar to pH values observed in pore solutions of OPC [11,26,28,35].

The measurement of the total organic carbon concentration in solution reveals that in TER-G, the percentage of adsorbed organic
carbon reaches about 85% after 1 h and then stays constant (Fig. 7). This means that 15% of the added gluconate stay in the pore solution until 28 days, whereas 85% are adsorbed. In TER-A, it is below 50% until 5 h 30 and then increases to about 83% and stays constant. From Fig. 2, it can be deduced that the samples, where the percentage of adsorbed organic carbon is higher than 80%, are those containing relevant amounts of Aft and/or gypsum (TER-G at 1 h). According to literature data, Aft in natural or synthesized pore solutions can adsorb high amounts of negatively charged polycarboxylate-based superplasticizers [36–39]. As the gluconate used in the present study is also negatively charged, it could adsorb on Aft surfaces. According to Zingg et al. [39–40] the number of submicron particles, which are mainly Aft in OPC, is much higher in cement paste at early age than in unhydrated cement. Therefore the high specific surface area of Aft could be available for the gluconate to adsorb, and could explain the high percentage of adsorbed organic carbon observed in TER-G at 1 h. In TER-A within the first hours, lower amounts of organic carbon are adsorbed, about 50%, while Aft is not present in the pastes. In that case, the gluconate could adsorb on another phase having a strongly positive zeta potential in pore solution such as e.g. an Afm-type phase [36,38], which could be present in the hydrates amorphous fraction of TER-A at early age as shown by the mass balance calculations (Fig. 4b).

4.3. Thermodynamic modelling

4.3.1. Saturation indices

The effective saturation index shows which hydrates are in equilibrium with the pore solution (saturation index = 0), or are oversaturated (saturation index > 0), thus being able to precipitate. When the pore solution is undersaturated with respect to a certain solid (saturation index < 0), this latter is not formed but may dissolve if present. The calculations show that three hydrate phases are oversaturated with respect to the pore solutions of TER-G or TER-A at any hydration time (Fig. 8), Aft, monosulphoaluminate and strätlingite (C2ASH8). Gibbsite (crystalline AH3), which is oversaturated during early hydration, becomes undersaturated at later ages. Gypsum is always undersaturated. C-S-H and CH are oversaturated with respect to the pore solutions only at later ages.

The model predicts the formation of crystalline AH3. This discrepancy between the model and the analytical data is due to the fact that the solubility product of AH3 is strongly dependent on its crystallinity. At about 20 °C the amorphous AH3 has a solubility product around 10^{-1.99} [41], the micro-crystalline AH3 around 10^{-0.22} [42,43], and the crystalline AH3 (gibbsite) around 10^{-0.06} [44]. In that case, the modelling program favours the formation of the component with the lowest solubility product, respectively gibbsite (according to the Ostwald step rule). Therefore in cement systems, amorphous or micro-crystalline AH3 could form during early hydration and could be progressively recrystallized to more crystalline AH3.

The calculation of the saturation indices allows a better estimation of the composition of the hydrates amorphous fraction present in TER-G and TER-A. In TER-G until 1 day, this component should be mainly composed of AH3 and could contain some additional strätlingite (C2ASH8), explaining the Si content deduced from the mass balance calculations (Fig. 4a). At later ages, while the AH3 content in the amorphous fraction decreases, a C-S-H type phase can be formed. This could easily explain the calculated decrease of the Al to Si ratio over time (Fig. 4a). Some monosulphoaluminate could also form, as the Si content in the amorphous fraction increases at later ages (Fig. 4a). A similar scenario can be drawn for TER-A. However in that case, some strätlingite and some monosulphoaluminate could also form in the amorphous fraction within the first hour of hydration (Fig. 4b).

4.3.2. Hydration mechanism

The thermodynamic modelling is used to calculate the stable phase assemblage during the hydration based on the measured dissolution of the clinker phases (XRD/Rietveld refinement). The modelling reveals that the main differences between the hydration mechanisms of TER-G and TER-A occur within the first day. For that reason, the modelled compositions of the hydrated cements are presented until 7 days in Fig. 9. In TER-G, the hydration process begins with the formation of Aft and AH3 from the hydration of C3A.S, which is in agreement with the analytical data and with reaction (i) C3A.S + 2C3H54 + 4H → C3AH6.S.C3S.H32 + 2AH3. The Aft content strongly increases during the first hours, then stays more or less constant, and finally decreases at later ages. This evolution is in agreement with the Rietveld refinement results (Fig. 2c). Some C-S-H and strätlingite are also modelled to form within the first hours. As these phases are not observed by XRD, they could be present in the hydrates amorphous fraction. This would explain the increase of the Si content shown in Fig. 4a within the first hours of hydration (mass balance calculation). Later, AH3 content decreases and after 1 day monosulphoaluminate starts to form. According to the modelling, the composition of the monosulphoaluminate solid solution is close to the monosulphoaluminate end-member (C2AS12). As monosulphoaluminate is not observed by XRD (only suspected beyond 7 days), it could be present in the amorphous fraction, which is consistent with the increase of the Si content from 1 day shown in Fig. 4a. No CH was predicted to form in the modelled hydration process.

Comparing the amorphous content calculated by XRD/Rietveld refinement to the total amount of amorphous phases calculated by the modelling, respectively those being absent from the XRD patterns, strätlingite, Aft, C-S-H and monosulphoaluminate (Fig. 10), there is a good correlation between the Rietveld and the modelled results until 28 days. From this observation, we can conclude that these four phases belong to the hydrates amorphous fraction. Moreover, during early hydration of TER-G, the
monosulphoaluminate is formed as one of the X-ray amorphous hydrates, which could at later ages increase its crystallinity.

In TER-A, little AFt is predicted to form within the first hour of hydration, while the period where the higher amount of AFt is formed is between 5 h 30 and 15 h 30 (Fig. 9b), which is in agreement with the Rietveld refinement results (Fig. 2d). The AFt content decreases at later ages. Monosulphoaluminate is predicted to form earlier in TER-A than in TER-G. This is certainly related to the slower dissolution of anhydrite compared to gypsum, as observed for CSA cements [8,29]. According to the modelling, AH₃ and strätlingite are formed during early hydration in addition to monosulphoaluminate (Fig. 9b). This easily explains the observed SiO₂ and SO₃ contents in the hydrates amorphous fraction at early age (mass balance calculations; Fig. 4b). The most significant discrepancies between the Rietveld refinement results and the modelling results are the absence of CH and the high amount of

Fig. 9. Modelled hydration until 7 days of a) the gypsum-bearing system (TER-G) and b) of the anhydrite-bearing system (TER-A). Calculation made with w/c = 0.42 and 20 °C.

Results expressed as mass in g/100 g dry cement. AFt = ettringite, AH₃ = gibbsite, CA = monocalcium aluminate, CA₂ = monocalcium dialuminate, C₂A = aluminate, C₄AF = ferrite, C₆A₅S = ye'elimite, CaCO₃ = calcite, C₃S = alite, CₛS = belite, CS = anhydrite, CSH₂ = gypsum. Monosulphoaluminate is an SO₄–OH–monosulphate solid solution close to C₄ASH₁₂. Inert includes the non hydraulic phases spinel (M₆), CT, gehlenite (C₂AS) and SiO₂. C-S-H composition is a tobermorite–jennite solid solution close to the jennite endmember, except for TER-G at early age where some tobermorite-amorphous SiO₂ solid solution compositions were calculated (close to the tobermorite endmember). Hydrotalcite is present in both mixes and approximately constant at low concentrations (<0.16 g/100 g dry cement). As no CA₂ dissolution kinetics could be deduced from the Rietveld refinement, the empirical function of the CA dissolution was used to model the CA₂ decrease.
monosulphoaluminate due to the slower consumption of anhydrite compared to gypsum. At later ages, the aluminium hydroxide content in the amorphous fraction decreases and additional monosulphoaluminate and a C-S-H type phase are formed.

Acknowledgements

The authors would like to thank the innovation promotion agency (CTI) in Switzerland for its financial support (Project no. 9623.1; 3 PF PW-IW) and the Saint gobain Weber Favro research teams. Thanks are extended to L. Brunetti and A. Steffen for their experimental support in the laboratory.

References


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