



Impact of water activity on the stability of ettringite



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ABSTRACT

The stability of ettringite as function of temperature and water vapour pressure was studied on synthetic samples using X-ray diffraction, thermogravimetric analysis, sorption balance measurements and different calorimetry techniques. Crystalline ettringite has a water content per mol of Al_2O_3 , n , varying from 30 to 32 H_2O , while the amorphous product formed on drying it, metaettringite, has only 9 to 13 H_2O . Very large hysteresis was observed during the desorption and absorption cycles. The total enthalpy values associated with the decomposition and reformation of ettringite were consistent and similar. During rehydration, different absorption stages were identified and quantified with sorption calorimetry. Due to the hysteresis it was not possible to model the absorption/desorption behaviour using the enthalpies determined by calorimetry, so the values calculated with the van't Hoff equation were used. The area of performance of ettringite-based systems recommended in this work has been extended compared to previously reported data.

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1. Introduction

Ettringite is a rare mineral in nature, but a common product occurring during the hydration of Portland cements. It is also the main hydration product of special binders such as calcium sulfoaluminate cements and calcium aluminate cements blended with calcium sulphates. The formation of ettringite at early ages is associated with the use of added sulphates to avoid flash set, but its formation at later ages, due to external sulphate attack or delayed ettringite formation, can cause degradation of concrete structures [1–3].

The structure of ettringite has been widely studied in the past. Moore and Taylor first reported its crystal structure [4,5], and since then, other techniques such as neutron diffraction [6] and time-of-flight neutron diffraction analysis [7] have been used to precisely determine the location of the atoms within the structure, especially the hydrogen atoms. Ettringite has a structure based on columns and channels. The columns, with the empirical formula $[\text{Ca}_3\text{Al}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]^{3+}$, run parallel to the c axis and are composed of $\text{Al}(\text{OH})_6$ octahedra alternating with triangular groups of edge-sharing CaO_8 polyhedra, with which they share OH^- [8]. Each Ca atom is also coordinated by four H_2O molecules, which form the cylindrical surface of the column. Between the columns are channels containing sulphate and zeolitic water [8]. The structural formula of ettringite is $[\text{Ca}_6\text{Al}_2(\text{OH})_{12} \cdot 24\text{H}_2\text{O}]^{6+} [3(\text{SO}_4) \cdot 2\text{H}_2\text{O}]^{6-}$ (or $\text{C}_6\text{A}\hat{\text{S}}_3\text{H}_{32}$ in cement notation¹), where the first bracket corresponds to the columns and the second to the channels.

The thermal stability of ettringite has also been extensively studied. Hall et al. [9] showed that, in the presence of water, ettringite rapidly decomposes into monosulfoaluminate and bassanite at 114 °C. In unsaturated conditions, i.e., at water vapour pressures below saturation, different dehydration and/or decomposition processes have been reported.

As an individual solid phase, ettringite ideally contains 32 H_2O molecules, from which 30 are fixed in the columns and 2 H_2O of zeolitic water more loosely bound in the channels [10]. There are some reports of ettringite containing up to 6 H_2O of zeolitic water, giving a final water content of $n = 36$ [11]. Nevertheless, most researchers agree on a maximum value of $n = 32$. Renaudin et al. [12] reported that the water content of ettringite in a wet sample and in a sample dried at 35% RH is very similar and that there is no higher water modification of this structure. The removal of the two interchannel H_2O molecules takes place with reducing relative humidity (RH) without significant change of the structure-related properties, such as unit cell size and crystallinity [13]. Nevertheless, part of these 2 water molecules might be adsorbed on the surface of the crystals or in crystal defects. For this reason, an accurate quantification of the interchannel water is rather difficult. Below $n = 30$ ettringite is known to undergo a series of structural changes. Skoblinskaya et al. [10,14] described the decomposition of ettringite from 30 to 6 H_2O in two stages: (1) the loss of 12 H_2O bound to the Ca atoms until $n = 18$ H_2O , was said to keep the same structure as crystalline ettringite, but with marked decrease of the a lattice parameter (which is related to the inter-columnar distance), although diffraction line broadening during drying may have affected an accurate determination of lattice parameters, and (2) the loss of the remaining 12 H_2O , bound to the Ca atoms, was more complex, requiring very low water vapour pressures to reach $n = 10$ and high

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¹ Cement notation: C = CaO , A = Al_2O_3 , S = SiO_2 , $\hat{\text{C}}$ = CO_2 , $\hat{\text{S}}$ = SO_3 , H = H_2O .

temperatures (up to 180 °C) to reach $n = 6$. The final decomposition product was said to be amorphous.

Detailed work by Zhou and Glasser [15] described the stability of ettringite as function of water vapour pressure (P_{H_2O}) and temperature. At a low P_{H_2O} (whose value decreased with decreasing temperature), water content drops below $n = 30$ H₂O to a minimum value of 10 H₂O, and the crystallinity decreased progressively. No distinction between different dehydration stages was made, although the decomposition product, termed metaettringite, was said to have a variable water content from 10 to 13 H₂O and to be amorphous, or nearly so, to X-ray diffraction. An important outcome of this study was the determination of the reversibility of the decomposition process, which takes place with a marked hysteresis. The reformation of ettringite occurred at relatively high P_{H_2O} at every temperature, which according to the authors might be due to condensation of water on crystal defects and surfaces that initiate the nucleation of ettringite. Nevertheless, no further explanation was given to describe the hysteric behaviour. This reversibility from an amorphous product to a crystalline one was also observed by Clark et al. [16] on ettringite subjected to high pressure. In a subsequent work, Zhou et al. [13] demonstrated that metaettringite shows electron diffraction patterns similar to those of ettringite, with a marked decrease of the a lattice parameter and small change in c , which suggests that the columns $[Ca_3Al(OH)_6]^{3+}$ are preserved but move closer together.

Hartman et al. [17] reported the decomposition pathway of ettringite to involve simultaneously the loss of water and hydroxyl groups, which contradicts the sequential water loss reported by Skoblinkaya et al. [10,14]. These results are also in contrast with the suggested structure of metaettringite [13] since a loss of (OH)⁻ would produce a collapse of the columnar structure with a marked decrease of the c parameter.

In the present study, the decomposition and recrystallization of ettringite as function of RH (P_{H_2O}) and temperature was studied using the multi-method approach described by Baquerizo et al. [18], which includes the use of X-ray diffraction (XRD), thermogravimetric analysis (TGA), sorption calorimetry and sorption balance measurements. In addition, differential scanning calorimetry (DSC) and isothermal calorimetry were used to measure the enthalpies of decomposition and reformation, respectively. With this methodology, the decomposition and reformation of ettringite can be assessed in detail and the thermodynamic properties associated with these changes can be quantified. The results presented here complement previous work carried out on AFm phases [19]. In this work, the phases are denoted by an abbreviation² followed by an index which denotes the water content in moles per mol of Al₂O₃; thus, Ett32 corresponds to ettringite with 32 H₂O.

2. Experimental procedure

2.1. Preparation of ettringite

In order to produce phase-pure synthetic ettringite several precursors are required. Synthesis was done from analytical grade reagents. The main precursor in the synthesis of ettringite was tricalcium aluminate (3CaO·Al₂O₃), which was prepared from a 3:1 molar ratio of CaCO₃ and Al₂O₃ at 1400 °C. Anhydrite CaSO₄ was prepared by dehydration of gypsum in a muffle furnace at 550 °C.

Ettringite was prepared from a suspension of a 1:3 molar mixture of C₃A and CaSO₄ with a water-to-solid (w/s) ratio of 20 using double distilled CO₂ free water. The mixture was stirred with a magnetic stirrer for 3 days and then periodically agitated for 2 weeks.

Once purity has been confirmed by XRD, the solids were vacuum-filtered under a N₂ atmosphere in a glove box and then placed inside

small (open) plastic bottles, which were subsequently introduced inside hermetically sealed glass bottles containing salt solutions at the bottom in order to equilibrate the samples at different RHs [20], as shown in Table 1. Finally, the glass bottles were conditioned at 5 °C, 25 °C, 50 °C and 80 °C for different periods of time (from 1 to 30 months). The RH was periodically checked using a Testo 174H humidity probe, except in the case of aging at 80 °C, which exceeds the operation temperature of the probe.

2.2. Experimental methods

The stability of ettringite and its thermodynamic properties were investigated using the methodology developed by Baquerizo et al. [18]. In addition, DSC and isothermal calorimetry were also used. A short description of the methods follows.

XRD on samples aged at different conditions was carried out at room temperature (unless otherwise stated) with a Bruker D8 Advance diffractometer (CuK α radiation, 45 mA, 35 kV) equipped with a Super Speed detector, in the 2θ range 5–70°, with a step size and time per step of 0.02° and 0.5 s, respectively. A low background-airtight specimen holder (Bruker AXS) was used to avoid carbonation and drying during testing. Small additions of rutile were used to correct for pattern displacement due to variations in sample height. The lattice parameters were refined by a LeBail fit [21] using TOPAS 4.2 (Bruker AXS). A humidity chamber CHC plus⁺ from Anton Paar coupled to the Bruker D8 Advance diffractometer was used to run several in-situ desorption/adsorption tests. In this work, when several XRD patterns are shown in one graph, their intensities axes are not the same (unless carried out in the humidity chamber) because the samples tested were different and no spinning was possible during characterization due to the use of the airtight sample holder, which greatly influenced preferred orientation.

TGA measurements were carried out in a Mettler Toledo TGA/SDTA 851^e under N₂ flux, over the temperature range 25–1200 °C with a heating rate of 20 K/min. Measurements were done on samples dried at different temperatures and RHs and on vacuum-dried (ca. 0.2 mbar) samples as well.

The sorption balance experiments were carried out at 25 °C using a DVS Advantage system (Surface Measurement Systems, London, UK). The step method was used [22], during which the RH is kept constant for certain period of time before being increased or decreased while the mass of the sample is continuously recorded. Two measurements were carried out in order to study the isotherms between 5% and 95% RH and between ~0.1% and 95% RH. Sample masses were 10.3 and 7.5 mg, respectively.

Sorption calorimetry was carried out at 25 °C using a calorimeter capable of measuring water activity, moisture content and enthalpy of sorption on an initially dried sample during an ad/absorption process [23,24]. A pure sample was initially vacuum dried at 25 °C for 1 day before starting the test. The sample mass was 65.5 mg.

Table 1
Equilibrium RH of selected saturated salt solutions at different temperatures [20].

Salt solution	RH (%)			
	5 °C	25 °C	50 °C	80 °C
LiBr	–	–	–	5.2
Na(OH)	10.5 ^a	8.2	4.9	–
CH ₃ CO ₂ K	26 ^a	22.5	19 ^a	–
MgCl ₂	33.6	32.8	30.5	26.1
NaBr	–	–	–	51.4
Mg(NO ₃) ₂	58.9	52.9	45.4	–
NaCl	75.7	75.3	74.4	–
KCl	87.7	84.3	81.2	78.9
K ₂ SO ₄	98.5	97.3	95.8	–

^a Measured.

² Abbreviation of phases: Ett = ettringite, Met = metaettringite, Ms = monosulfoaluminate.

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