



Thermal stability and decomposition mechanisms of ettringite at $<120^{\circ}\text{C}$

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Abstract

Ettringite has been synthesised in phase-pure form and its decomposition and reformation studied as a function of water vapour pressure and temperature. Isobars at $P_{\text{H}_2\text{O}}=6, 35, 75$ and 400 mm were determined and combined with data on decomposition at the self-generated water vapour pressure achieved at $\sim 120^{\circ}\text{C}$. These data follow a well-defined curve although considerable hysteresis occurs in the temperatures for reformation, which are typically $15\text{--}20^{\circ}\text{C}$ less than the corresponding decomposition temperature at each isobar. The dehydrated product is amorphous or nearly so to X-ray powder diffraction, but still gives an electron diffraction pattern: it has a water content that is fixed or variable within narrow limits, $10\text{--}13$ H_2O per ettringite formula unit. This product is termed meta-ettringite. Recommendations are also made for the upper safe service limits for ettringite-based cements. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Ettringite is an important crystalline component of Portland cement and may constitute the principal matrix former of sulfoaluminate cements. It also occurs as a deterioration product of alkaline cements exposed to sulfate-containing waters. Its structure is well known [1,2] but its stability has been the subject of numerous studies, results of which reveal some inconsistencies.

The stability of a hydrate must be defined in terms of temperature, pressure, and activities of its components including that of water; water activities are influenced by the presence of dissolved components. The stability of ettringite in the $\text{CaO}\text{--}\text{Al}_2\text{O}_3\text{--}\text{SO}_3\text{--}\text{H}_2\text{O}$ system at water saturation has been defined by experiment and calculation [3–5]. In these studies, the activity of water was mainly fixed by dissolution of the solid components in response to self-generated solubility, but the impact of soluble alkalis was also measured. Water is especially important to ettringite stability because of the high water content of the solid, which has the constitution,

$3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 30+x\text{H}_2\text{O}$, where x is in the range 0 to 2.

Ettringite is believed to be thermally unstable at elevated temperatures. For example, it is less stable than hydrogarnet, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$, which by DTA, decomposes at $\sim 325^{\circ}\text{C}$. However, the temperature, mechanism and reaction kinetics of ettringite decomposition and reconstitution are not well known. This is for two reasons: failure in previous experiments to control all relevant variables: temperature, total pressure and partial pressure of water and also, failure to demonstrate the reversibility (or otherwise) of formation and decomposition. Several notable exceptions exist: one is in the determination of the spontaneous decomposition, which was fixed by Satava and Vepřek at $\sim 125^{\circ}\text{C}$ using differential hydrothermal analysis (DHA) [6]. Some points were obtained hydrothermally at and above 100°C by Ogawa and Roy [7]. Hall et al. [8] also determined the onset of decomposition at $114\pm 1^{\circ}\text{C}$ at a calculated water vapour pressure of 1.63 bar. Marginally less relevant but noteworthy are studies by Abo-el-Enein [9] who determined weight loss at temperatures $<100^{\circ}\text{C}$, although the water activity in the vicinity of the decomposing sample was uncontrolled. Other reports of decomposition in vacuum have been made [10,11] purporting to show that decomposition occurred in stepwise fashion. However, these steps are not encountered by dynamic methods, such as DTA.

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In the present study, a somewhat different approach was used. Phase-pure ettringite was prepared in a separate step. After characterisation, it was placed in a chamber in which temperature and water vapour pressure could be independently controlled. The sample was allowed to equilibrate isothermally and isobarically, at a total pressure of 1 bar. However, the partial water vapour pressure could be independently controlled and in this way, isobars in the range 6–400 mm water vapour pressure were determined. The sample was periodically checked by weight loss and X-ray diffraction for signs of decomposition. No decomposition was deemed to occur if, once the water content decreased to less than $30\text{H}_2\text{O}$, further loss was less than 1% per day. If no decomposition was observed within 24 h, the temperature was raised. Once decomposition was found to commence, conditions were maintained until weight loss decreased to less than 1% per day. At this point, reaction was reversed and the temperature was incrementally decreased until ettringite reformed, reformation being determined by weight gain and X-ray powder diffraction. By maintaining isobaric conditions while changing temperature, either up or down in small increments, the reversibility of reaction or lack thereof could be demonstrated.

2. Experimental

2.1. Ettringite preparation

Tricalcium aluminate, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, was prepared by sintering together reagent grades of CaCO_3 and Al_2O_3 in a 3:1 mole ratio. Reaction at 1450°C required several intermediate grindings and sinterings until a phase-pure product was obtained. The C_3A was mechanically mixed with reagent grade gypsum, $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$, in the ratio 0.02 mol to 0.06 mol. The powder was slurried into 1 L of distilled decarbonated water and stoppered. The reaction mix was agitated for 7 days at $\sim 20^\circ\text{C}$: X-ray diffraction revealed a single-phase ettringite product and scanning electron microscopy disclosed needles, long prisms and aggregates of parallel crystals, 1 to $10\text{ }\mu\text{m}$ long. Although this synthesis method is slow, it gave a

product free from other potential chemical contaminants. The ettringite was generally handled in an N_2 -filled glove bag to prevent carbonation.

2.2. Equilibration and data treatment

An apparatus was constructed to equilibrate solids with a known water vapour pressure and controlled temperature such that temperature and pressure could be independently varied although total pressure remained fixed at 1 bar. Fig. 1 shows the apparatus.

Two independently controlled water baths are required. In the first, initially dry N_2 is equilibrated by passing a fine stream of bubbles through several bubblers in series, to ensure complete saturation at the reference temperature. These bubblers are filled with pure H_2O and the partial pressure of water thus achieved is determined by reference to standard tables showing vapour pressure as a function of temperature. This vapour stream next passes into a second chamber, via a gently heated line to prevent condensation occurring in the transfer stage. The second chamber was normally maintained at a higher temperature than the first and is used to allow the gas steam to equilibrate with solid ettringite after which it exits by an oil-filled bubbler, used as a seal to maintain a very slight positive pressure in the apparatus. A battery-powered digital display instrument showing temperature and humidity (not shown) was placed next to the sample, visually to monitor temperature and humidity at all temperatures lower than 60°C , the upper recommended service limit of the instrument.

The instrument was further calibrated periodically by inserting a flow meter and trapping the water vapour contained in a known volume of gas in desiccant tubes filled with magnesium perchlorate. The absolute humidity, ρ , defined as the mass of water vapour in a given volume of gas at a constant temperature is given by:

$$\rho = \frac{W_2 - W_1}{V} = \frac{W_2 - W_1}{t\nu} \times 10^6$$

where ρ is absolute humidity (g/m^3), t is the time of absorption (minutes), ν is gas flow (ml/min), V the total volume of gas (m^3), and W_1 and W_2 are the weights of the

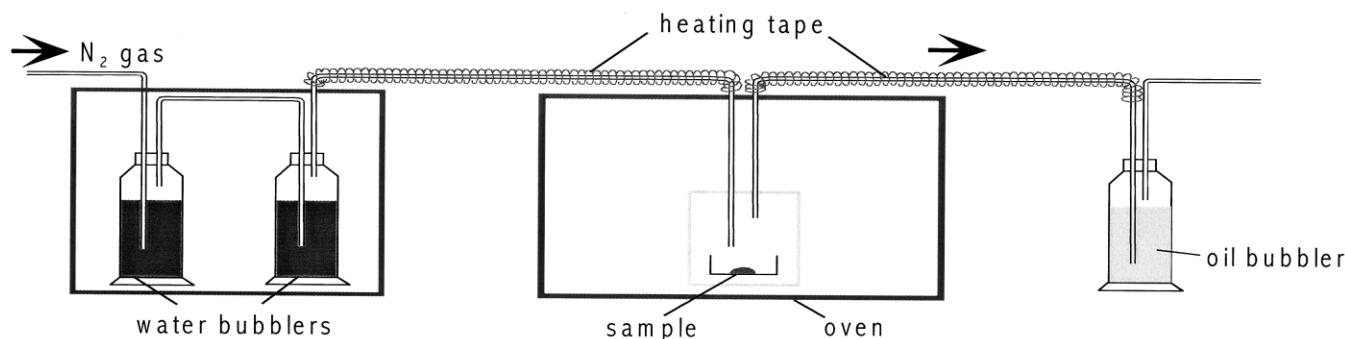


Fig. 1. Dehydration apparatus used to control $P_{\text{H}_2\text{O}}$ at selected values. Arrow shows gas flow, rectangles show temperature-controlled zone.

U-tube before and after absorption (g). The absolute humidity, ρ , is equivalent to the water vapour density. For an ideal dry gas

$$P = RT\rho$$

Water vapour has a density 0.643 that of dry N₂. That is, the water vapour density is:

$$\rho = 0.643P/RT$$

If ρ is in grams per cubic centimeter, P in millibars, $R = 2.87 \times 10^{-3}$,

$$P = 224P/T$$

and

$$P = \rho \frac{T}{224} \times 0.75$$

where P is the water vapour pressure (Torr, or mmHg), T is temperature (K), ρ is the absolute humidity (g/m³), and 0.75 is a conversion factor of pressure units, from millibars to millimeters of Hg.

The decomposition of ettringite was monitored by combined X-ray powder diffraction and weight loss. Total water content was determined by ignition in a platinum crucible at 1000°C: decomposition products are C₄A₃S̄, CaSO₄ and CaO, in agreement with reports cited in Lea [12]. The initial water content of ettringite was always close to theoretical, i.e., between 30 and 32H₂O per formula unit.

Data are depicted in terms of water loss: n is the number of water molecules associated with the anhydrous constituents, M_{AFt}^* of ettringite, mass 678.49, for 32H₂O. Thus

$$n = \frac{M_{AFt}^* G_w}{M_{H_2O}(G_s - G_w)}$$

where G_s is the sample weight, G_w is the weight loss and $M_{H_2O} = 18$.

2.3. Isobaric dehydration

Isobars were determined at $P_{H_2O} = 6, 35, 75$ and 400 mm Hg. The family of curves thus obtained are shown in Fig. 2.

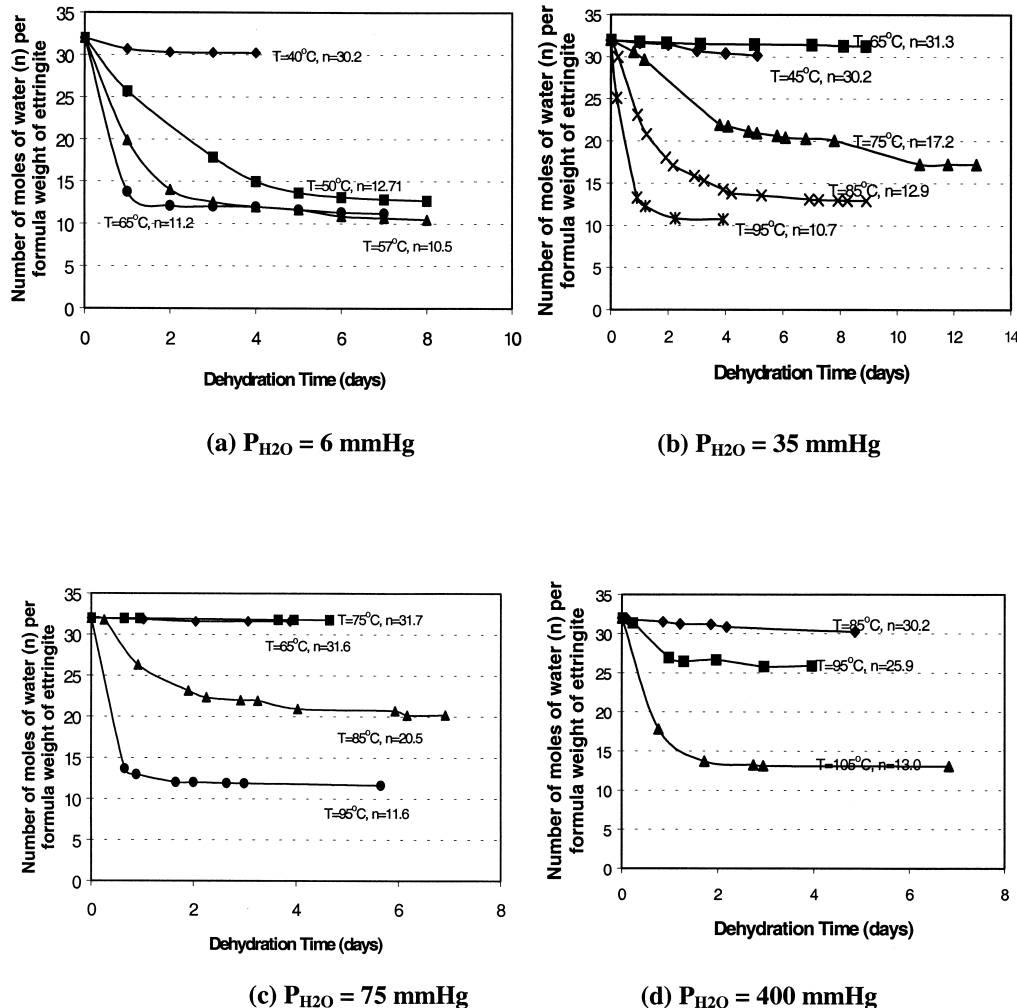


Fig. 2. Static dehydration curves for ettringite as a function of time and temperature on selected isobars.

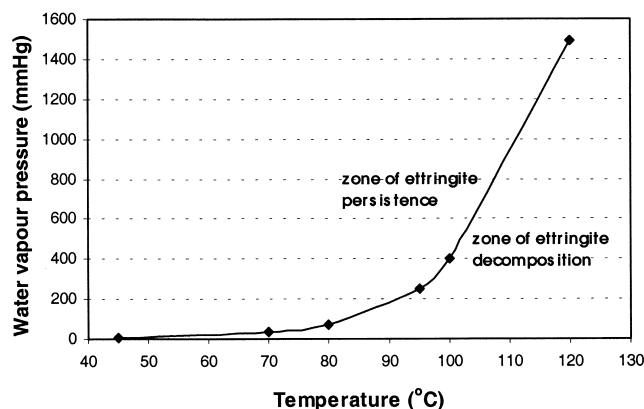


Fig. 3. Data for monotropic decomposition of ettringite showing convergence of weight loss on a product containing 10–13H₂O.

The family of curves have similar shapes. Commencing with ettringite in or near its maximum hydration state, 32H₂O, the curves show initial loss of up to two water molecules, the weight stabilising at $\sim 30\text{H}_2\text{O}$. This represents loss of zeolitic water. Although not reported here, data in a thesis [13] show water loss in this range to be rapidly reversible upon lowering temperature or increasing $P_{\text{H}_2\text{O}}$. On the other hand, once the temperature exceeds a certain critical threshold, the numerical value of which increases with increasing water vapour pressure, weight loss becomes much greater, typically on the order of a total of 18–22 H₂O molecules. X-ray powder patterns disclose that while the product at 30H₂O is crystalline, crystallinity decreases progressively as the water content decreases below 30H₂O per formula unit: see Discussion. The unit cell parameters do not change significantly ($\pm 0.1\%$) during this loss of crystallinity but, on the other hand, broadening of X-ray reflections makes it more difficult accurately to calculate their precise positions.

The family of curves obtained at successively high water vapour pressures have other noteworthy features: the progression towards higher decomposition temperatures has been noted. A steady state is also approached more rapidly

with increasing water vapour pressure and hence temperature. Reaction on one isobar, measured by rate of weight change, exhibits a more rapid approach to steady state as the temperature increases: for example, see data for 6 mm, Fig. 2, showing faster loss at 65°C than at 57°C, which, in turn, is more rapid than at 50°C. If successive isobars are compared, a steady state is attained within 1–2 days at 400 and 75 mmHg pressure but requires longer, up to 8–10 days, to attain at lower pressures. A further noteworthy feature of all isobars is that the composition of the partially dehydroxylated product phase(s) converges on a lower water state in the range 10–13 H₂O, i.e., a relatively consistent loss of about 20 water molecules per formula unit occurs in the course of transformation to an X-ray amorphous product. Occasionally the water loss is not as great; for example, the postdecomposition state converges on 26H₂O at 400 mmHg at 95°C, but the formation of an apparently amorphous product that retains 10–13H₂O is a commonly observed feature.

Fig. 3 shows changes in water content, commencing with an initial 32 mol of ettringite, as a function of temperature and H₂O pressure, at a total pressure of 1 bar. Note how reaction converges on a relatively constant water content, 10–13H₂O over a wide range of experimental conditions. The significance of this convergence is discussed subsequently.

Microscopically, ettringite crystals retain their original shape and dehydrate to pseudomorphs. Electron diffraction discloses retention of some crystallinity although the same product is amorphous to X-ray powder diffraction, using copper K alpha radiation. Because the product containing 10–13H₂O is crystalline by electron diffraction but not by X-ray powder diffractometry, we term it “meta-ettringite.” Preliminary interpretation of the electron diffraction patterns supports this explanation: these patterns and the characterisation of meta-ettringite will be discussed in a subsequent paper.

The onset of ettringite decomposition as a function of temperature and water vapour pressure is shown in Fig. 4. Points marked with a solid diamond were obtained in the

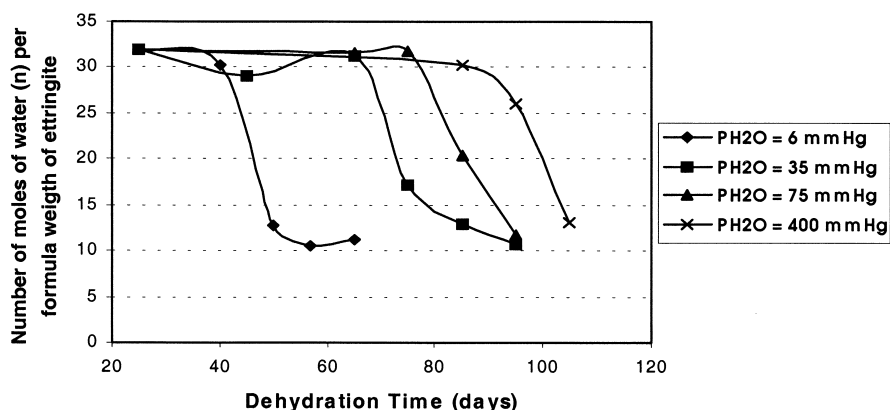


Fig. 4. Data for the monotropic decomposition.

course of the study. Although all the points can be made to line on a single curve, a difference in decomposition mechanism occurs; in the title study, decomposition to meta-ettringite occurred except at $\sim 114^\circ\text{C}$, at which temperature a mixture of amorphous and crystalline products were obtained: Hall et al. [8] obtained all crystalline products of decomposition: sulfate AFm and calcium sulfate hemihydrate. Because of the apparent difference in the mineralogical nature of the decomposition products, implying a change in mechanism, we attempted to reproduce this point. A sample of ettringite was placed in a sealed tube together with a little water and the tube heated to progressively higher temperatures for ~ 24 h at each isotherm. No decomposition occurred at 114°C but complete decomposition to a mixture of gypsum and hemihydrate, together with amorphous material, occurred at 120°C . Upon stepwise reduction of temperature to 115°C , some reformation of ettringite occurred together with hemihydrate, while nearly complete reformation of

ettringite occurred at 110°C . We thus fix the reversible formation and decomposition of ettringite at $117.5 \pm 2.5^\circ\text{C}$: This temperature corresponds to a water vapour pressure of 1372 mmHg. This pressure is of course for pure H_2O and is uncorrected for the solubility of ettringite components. Thus we essentially confirm Hall et al.'s decomposition temperature within $\pm 3^\circ\text{C}$ and additionally demonstrate that reaction is reversible. But we do not find AFm amongst the decomposition products. The occurrence of mixtures of hemihydrate and gypsum are also suspected of being an artefact: partial hydration of hemihydrate may have occurred during cooling.

The decomposition curves thus far presented at < 1 bar total pressure represent a monotropic reaction, i.e., reaction has been determined in only one direction. As such, the determinations may not represent a true equilibrium. Therefore reversibility was tested on successive isobars by taking the decomposition product, meta-ettringite, and lowering the temperature until (i) weight gain commenced, even-

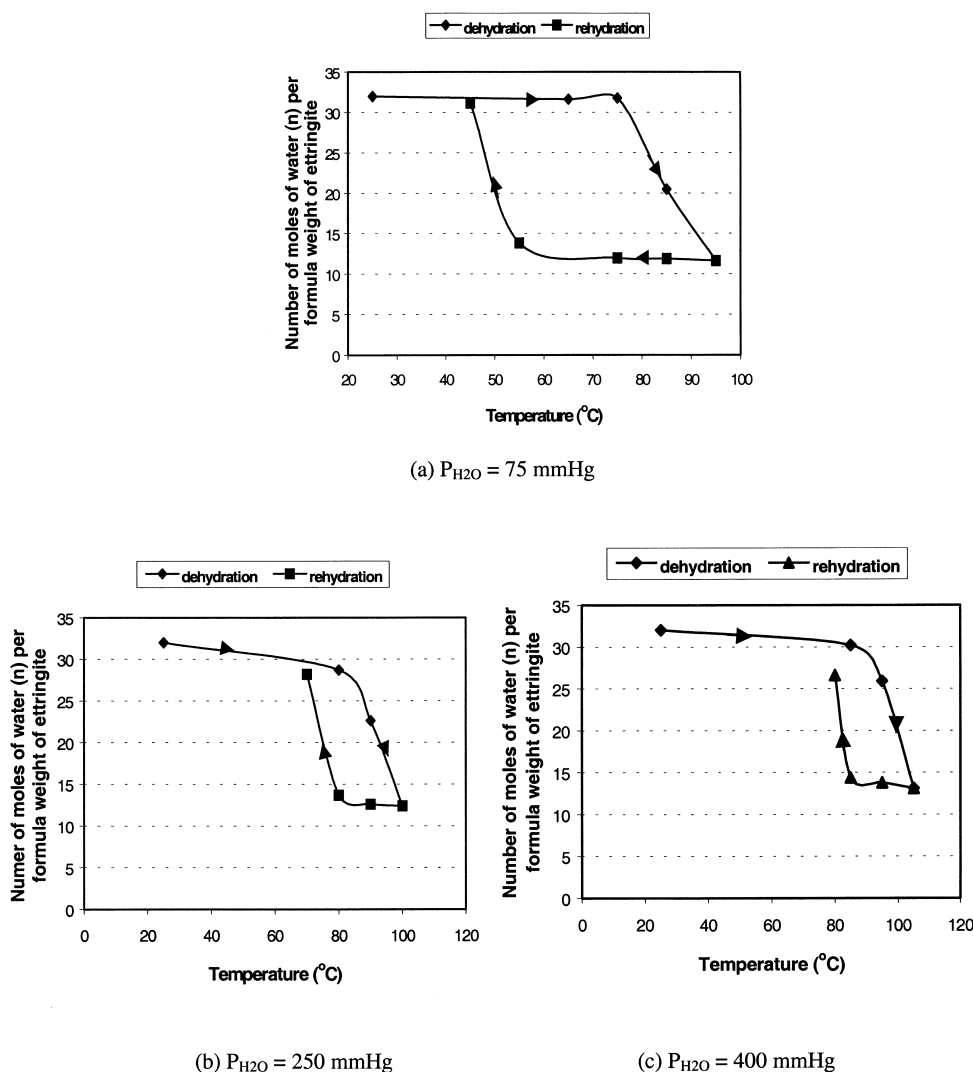


Fig. 5. Reversibility of ettringite decomposition and reformation on selected isobars.

tually achieving full rehydration and (ii) supplementary X-ray characterisation disclosed that ettringite reformed. Reaction at 6 mm pressure was too slow to achieve rehydration within 6 weeks, but Fig. 5 shows that reversibility could be achieved at 75, 250 and 400 mm water vapour pressure. The criterion for isothermal weight gain was, as before, that it had to exceed more than 1% per 24 h at each isothermal halt: if it did not, the temperature was incrementally reduced to a lower isotherm. The identity of products forming during weight gain was monitored by powder X-ray patterns. It was noticeable that although the main product of rehydration was ettringite, some gypsum persisted during reformation experiments.

3. Discussion

Ettringite is an attractive material with which to form low-cost cements and to use as alternatives to gypsum-based materials. It is much less soluble than gypsum, hence more resistant to wetting and drying, and can achieve significantly higher compressive strengths. Because of its high water content, it has an apparently high specific heat for decomposition and is usefully incorporated into sacrificial fire-resistant solids. However, a possible disadvantage is that it may decompose under extremes of normal, ambient conditions. To assess the possibility of decomposition in different environments, data reported in the course of the present study have been combined into a composite diagram, Fig. 6, which can be used to determine the likely performance of ettringite-based compositions. Because considerable hysteresis occurs between decomposition and reformation of ettringite, the family of formation and decomposition curves divide water vapour pressure–temperature space into three regions. At the left of the diagram, ettringite is both stable and persistent: if decomposed to meta-ettringite, ettringite will spontaneously reform in this region. To the right of the diagram, ettringite is not stable and, once decomposed, cannot reform spontaneously. Between these two regions lies a pressure–temperature space bounded by the hysteresis loop defined by two P – T curves, one for ettringite formation and the other for decomposition. Within this P – T space, ettringite, formed in a previous stage, will not undergo significant decomposition but once decomposed, will not reform spontaneously. Prudence suggests that the recommended area of performance, defined by ettringite stability, should be limited to the left-hand region of Fig. 6. Thus, for example, it would be prudent not to exceed 70°C at 200 mm H₂O pressure, (corresponding to 86% rh), even though at this pressure (or humidity) ettringite will not actively decompose until 94°C. As more is learned about the relationships between crystallite size and perfection and the resulting resistance to decomposition, it may be possible to extend these safe limits, particularly if they are exceeded only briefly, or in dense compacts whose decomposition is, in part, controlled by the rate of water migration.

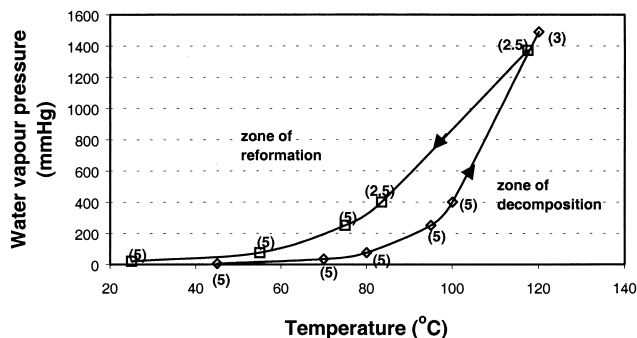


Fig. 6. Curves of ettringite decomposition at various P_{H_2O} for the decomposition and formation reactions. Numbers marked along curves indicate the uncertainties in temperature (°C), of data points. Equations of best fit for formation and decomposition are $\ln P = 1.89 + 0.047T$ and $\ln P = -1.61 + 0.075T$, respectively.

An important conclusion of the present study is that over most of the temperature–humidity range of interest to the performance of ettringite-based products in warm service environments, broadly defined as less than 100°C, ettringite will decompose to a product containing much water, typically 10 to 13 H₂O per formula weight of ettringite. Thermal analysis at typical heating rates, 2–20°C/min, fails to disclose the existence of this stepwise mode of decomposition, illustrating the value of static or semistatic methods.

Data obtained by electron diffraction show that the product of decomposition containing 10–13H₂O is meta-ettringite. Despite similarities in water content to an AFm phase, the CaO:Al₂O₃:SO₃ ratios are characteristic of ettringite as are the electron diffractions. Important differences emerge about the decomposition mechanism as a function of temperature: meta-ettringite characteristically forms in the range 50–100°C as a consequence of reducing water vapour pressure below the limits shown in Fig. 6, whereas at higher temperatures, crystalline products are obtained. Thus at 110–114°C, decomposition occurs by a heterogeneous mechanism, yielding a mixture of gypsum and hemihydrate and amorphous materials: perhaps also AFm. At the other extreme, at very low water vapour pressures (6 mm), meta-ettringite is the initial product of decomposition but upon standing it slowly and spontaneously crystallises to sulfate AFm. However, the excess of sulfate over the AFm composition, known from stoichiometry to be present, remains amorphous to X-ray diffraction. Differences in the nature of the product(s) obtained as a function of temperature in the range 50–115°C and water vapour pressures in the range 6–400 mm suggest that (i) the diagram, Fig. 6, is not a true P – T phase diagram, although it approximates to one, because of the nonreversibility of reaction and (ii) it is inappropriate to do a full kinetic analysis of the data, since both homogeneous and inhomogeneous mechanisms operate even within this rather narrow range of temperatures and pressures.

We also note that the exact conditions of reformation of ettringite at or close to 115°C do not correspond strictly to

isobaric reaction: in order to reverse reaction, the temperature has to be decreased, in which case, the water vapour pressure is also reduced and is thus somewhat less than for the decomposition reaction. While the resulting changes in pressure are not large, they may be important to any physiochemical analysis of the data: in common with other investigators we have not been able to maintain strictly isobaric conditions at temperatures $>100^{\circ}\text{C}$. But in general, the equilibrium point at or close to 115°C does involve the persistence of liquid water, whereas points determined in the course of the present study at lower-pressure isobars involve reformation in the nominal absence of liquid water, i.e., reformation of ettringite occurs below the dew point. For example, the relative humidities corresponding to ettringite reformation at 75, 250 and 400 mm water vapour pressure are, respectively 81%, 87% and 98%. At these humidities it is likely that some condensation will occur selectively along crystal margins and at surfaces, particularly on defect-rich surfaces of the solids, thereby initiating a local through-solution nucleation mechanism leading to reformation of ettringite.

4. Summary

The physiochemical stability of ettringite has been determined by a semistatic method in which water vapour pressure and temperature can be independently controlled. Only in this way is it possible to obtain absolute stability data in a range of conditions relevant to service environments. Formation and decomposition are shown to be reversible with hysteresis. The data are used to predict safe conditions for the use of ettringite and ettringite-based cements in warm conditions, $<100^{\circ}\text{C}$, as a function of $P_{\text{H}_2\text{O}}$ (or humidity) and temperature. The decomposition reaction is unusual, inasmuch as the initial product is amorphous to X-ray powder diffraction but has a relatively constant water content, 10 to $13\text{H}_2\text{O}$, per ettringite formula unit. Electron diffraction, to be presented in a subsequent paper, suggests that the partially dehydroxylated product corresponds to meta-ettringite.

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References

- [1] H.F.W. Taylor, Crystal structure of some double hydroxide minerals, *Miner. Mag.* 39 (304) (1973) 377–389.
- [2] A.E. Moore, H.F.W. Taylor, Crystal structure of ettringite, *Acta Crystallogr.* 26B (1970) 386–393.
- [3] D. Damidot, F.P. Glasser, Prediction of AF5 stability from phase equilibria, *Proceedings of the 9th International Congress on the Chemistry of Cement National Council for Cement and Building Materials (New Delhi)* 5 (1992) 316–321.
- [4] D. Damidot, F.P. Glasser, Thermodynamic investigation of the $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaSO}_4-\text{H}_2\text{O}$ system at 50°C and 85°C , *Cem. Concr. Res.* 22 (1992) 1179–1191.
- [5] D. Damidot, F.P. Glasser, Thermodynamic investigation of the $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaSO}_4-\text{CaCl}_2-\text{H}_2\text{O}$ system and the influence of Na_2O , *Proceedings of the 10th International Congress on the Chemistry of Cement (Göteborg, Sweden)*, vol. 4, paper 4IV 066, Amarkai AB and Göteborg AB, 1997.
- [6] V. Satava, O. Veprek, Thermal decomposition of ettringite under hydrothermal conditions, *J. Am. Ceram. Soc.* 58 (7–8) (1975) 357–359.
- [7] K. Ogawa, D.M. Roy, $\text{C}_4\text{A}_3\bar{\text{S}}$ hydration ettringite, and its expansion mechanism: I. Expansion; ettringite stability, *Cem. Concr. Res.* 11 (1981) 741–750.
- [8] C. Hall, P. Barnes, A.D. Billimore, A.C. Jupe, X. Turrillas, Thermal decomposition of ettringite $\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$, *J. Chem. Soc., Faraday Trans.* 92 (12) (1996) 2125–2129.
- [9] S.A. Abo-el-enein, S. Hanafi, E.E. Hekal, Thermal and physicochemical studies on ettringite: II. Dehydration and thermal stability, *Cemento* 85 (2) (1988) 121–132.
- [10] N.N. Skobtinskaya, K.G. Krastnikov, Changes in crystal structure of ettringite on dehydration. Part 1, *Cem. Concr. Res.* 5 (4) (1975) 381–394.
- [11] N.N. Skobtinskaya, K.G. Krastnikov, Changes in crystal structure of ettringite on dehydration. Part 2, *Cem. Concr. Res.* 5 (4) (1975) 419–432.
- [12] F.M. Lea, *The Chemistry of Cement and Concrete*, third ed., Edward Arnold Publishing, London, 1970.
- [13] Q. Zhou, PhD thesis. University of Aberdeen, U.K., 2001, submitted.