

Relationship between crystallinity and stability of ettringite
73x47mm (150 x 150 DPI)

1 Thermal stability of ettringite exposed to
2 atmosphere: implications for the uptake of
3 harmful ions by cement

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12 KEYWORDS: ettringite, thermal behavior, decomposition kinetics, calorimetry,

13 thermo-XRD.

14

15 ABSTRACT: The decomposition behavior of ettringite, $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$, at
16 different temperatures was studied by means of isothermal XRD experiments, in which the
17 evolution of the solid is monitored as a function of time. The experiments were performed
18 at 40, 50, 55, and 60 °C for a natural ettringite specimen. The experimental data were used
19 to construct a Temperature-Transformation-Time (TTT) diagram. Such a diagram enables
20 the prediction of the reaction pathways during the transformation process. The
21 decomposition behavior was also studied under non-isothermal conditions using
22 thermogravimetry and differential scanning calorimetry, and the obtained results were
23 correlated with the results of the XRD study. Finally, the transformation kinetics and the
24 activation energy ($E_a = 246.1 \text{ kJ}\cdot\text{mol}^{-1}$) of the reaction were estimated using the so-called
25 “time to a given fraction” method. The temperature at which the initial transformation stage
26 occurs (lower than 50°C) indicates that ettringite cannot be considered a suitable host phase
27 for the immobilization of radionuclides and other harmful elements, as is frequently
28 proposed in the literature.

29

30 INTRODUCTION

31 Ettringite occurs in natural alkaline environments that are associated with silicates,
32 calcite and phosphates.¹⁻² Ettringite is a rare mineral, being neither ubiquitous nor
33 abundant. However, a non-natural analog of ettringite forms via hydration of calcium
34 aluminates³ when gypsum is added during the early hydration of Portland cements, which
35 explains the environmental relevance given to this mineral. Portland and modified Portland
36 cements are useful matrices for the immobilization and storage of contaminants contained

37 in various forms of hazardous wastes⁴⁻⁶ ettringite is frequently assumed to play a key role in
38 these immobilization processes. After the pioneering work of Bannister et al.⁷, the crystal
39 structure of ettringite has been the subject of numerous detailed studies^{3,8-10} Hartman and
40 Berliner⁸, using time-of-flight neutron powder diffraction techniques, refined the structure
41 of ettringite in the $P31c$ space group with $a \approx 1.116$ nm and $c \approx 2.135$ nm (at 10K). The
42 calculated heavy atom positions are essentially the same as those obtained in previous
43 investigations, but in addition this study provides the precise hydrogen atom positions,
44 revealing the arrangement of the hydrogen bonding network in the structure. Moreover, a
45 comparative study on the crystal structure of wet and dried ettringite reveals that the
46 amount of structural water, the point symmetry of sulfate and the hydrogen bond network
47 are analogous in both cases¹¹. Although ettringite is typically described by the general
48 formula $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$, the exact water content varies because it can include
49 adsorbed water in addition to structural water.³ The basic structural framework consists of
50 alternating calcium and aluminum coordination polyhedra, i.e., $\text{Ca}(\text{OH})_4(\text{H}_2\text{O})_4$ and
51 $\text{Al}(\text{OH})_6$, that form ‘columns’ parallel to the c -axis. Water molecules and sulfate tetrahedra
52 occupy the wide channels located between these columns and are connected by an
53 extensive network of hydrogen bonds, which are responsible for the structural stability. Due
54 to these features, the ettringite structure is flexible enough to accommodate foreign cations
55 and oxyanions.

56 Ettringite is usually considered a remarkable host phase for the sequestration of
57 radionuclides¹² and other harmful ions. The crystal structure of ettringite favors the
58 substitution of SO_4^{2-} by other oxyanions, such as chromate, arsenate, selenate, selenite,
59 vanadate, molybdate, and stannate.¹³⁻¹⁸ Moreover, the substitution of Ca^{2+} by divalent

60 cations (Pb^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , etc.) at the M^{2+} site is largely known.¹⁹ Such availability for
61 ionic substitution suggests that ettringite-based solid-solution formation can be one of the
62 most effective mechanisms for immobilization of toxic cations and oxyanions in cements.
63 Cement maintains a high buffering reserve of alkalinity⁴, which reduces the solubility of the
64 ettringite host phase and hence the ‘solubility’ of the foreign substituting ions.

65 The best scenario for immobilization of pollutant ions by co-crystallization is to have a
66 low solubility related to a robust controlling phase.^{12,20,21} The question is whether ettringite
67 can be considered a ‘robust’ phase or not. In fact, the thermal stability of ettringite appears
68 to be quite limited. The mechanism of decomposition of ettringite has been the subject of a
69 number of studies²²⁻²⁶, but some important aspects are still under discussion. In the
70 presence of liquid water, the stability limit of ettringite is clearly established to be ~ 120
71 $^{\circ}\text{C}$ ²². However, ettringite is thermally unstable at much lower temperatures in contact with
72 the atmosphere, particularly at low water vapor pressures, when water is present mainly as
73 ‘crystal water’. During the decomposition process, there appears to be a simultaneous loss
74 of hydroxyls and water molecules from the structure⁸, which eventually leads to a product
75 that is amorphous to X-rays, although the existence of metaettringite (a partially
76 dehydroxylated product that still yields an electron diffraction pattern) has been reported.²³

77 Although the structural changes occurring during the decomposition of ettringite are
78 reasonably well established, it is not clear whether ettringite may decompose over the
79 temperature-time range relevant to the performance of ettringite-based products in warm
80 service environments.²² Concrete service temperatures can exceed 40°C in near-surface
81 scenarios where severe insolation occurs, or in deep hot mines and nuclear waste
82 repositories, where temperatures can attain values higher than 50°C as a consequence of

83 both the geothermal gradient and the heat generated by high-level nuclear wastes.²⁷⁻³⁰ For
84 instance, Blanco-Martín³¹ modelled the evolution of the temperature in a deep disposal in
85 salt rocks and they assessed temperatures above 60°C after few days of the radionuclides
86 emplacement and peaks of temperature above 180°C after about 1 year in different
87 locations of the disposal. Clearly, all the previous results indicate that the thermal stability
88 of ettringite is limited, but its decomposition kinetics at different temperatures is actually
89 not very well known.

90 Poured and co-workers²⁴ proposed a kinetic model for ettringite decomposition from
91 isothermal and non-isothermal thermogravimetric measurements obtained at 50 °C and 0.5
92 °C/min, respectively. However, to our knowledge, a systematic thermo X-ray diffraction
93 (XRD) study has not been performed yet. In most works, XRD patterns of the
94 decomposition products are obtained *ex-situ* or are performed intermittently as the
95 temperature is increased at a given heating rate. Unfortunately, while those previous studies
96 are suitable to establish the decomposition sequence, they are unable to answer some
97 practical questions such as “How long will ettringite remain stable at 40°C in contact with
98 the atmosphere?”.

99 This work addresses the decomposition behavior of ettringite at specific temperatures
100 through isothermal XRD experiments, in which the evolution of the diffractograms is
101 monitored *in situ* as a function of time. The experiments were performed at 40, 50, 55, and
102 60°C for a natural ettringite specimen. We previously demonstrated that this natural
103 specimen was more resistant to dehydration than the typical synthetic samples, due to its
104 better crystallinity. The aim was to select the most favorable starting material from the
105 point of view of keeping stability. The experimental data were used to construct a

106 Temperature-Transformation-Time (TTT) diagram. Such a diagram allows for prediction of
107 the reaction pathways during sub-solidus phase transformations and is commonly used in
108 material and mineral sciences.³² However, to our knowledge, TTT diagrams have not been
109 applied to the decomposition processes involving solid and gas phases. The decomposition
110 behavior was also studied under non-isothermal conditions by thermogravimetry and
111 differential scanning calorimetry, and the obtained results were correlated with the results
112 of the XRD study. Finally, the transformation kinetics and the activation energy of the
113 process were estimated using the so-called “time to a given fraction” method.³²

114

115 MATERIALS AND METHODS

116 Synthetic and natural samples

117 Synthetic ettringite was obtained following a modification of the method described by
118 Perkins and Palmer³³ This procedure begins with the preparation of two reactant solutions
119 by adding 6.65g of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and 4.44 g of $\text{Ca}(\text{OH})_2$ to 100 ml and 250 ml of
120 deionized water, respectively. The two starting solutions were introduced in a glove-box
121 with a nitrogen atmosphere, in which nitrogen was bubbled through the reactant solutions
122 to avoid CO_2 contamination. After 24 hours, the reactant solutions were mixed in
123 polypropylene beakers and adjusted to pH 11.5 with the addition of 0.5 ml of NaOH (1N).
124 Next, additional deionized water (150 ml) was added to obtain 500 ml of a final solution
125 with suitable molar ratios of $\text{Ca}/\text{SO}_4 = 2$ and $\text{Ca}/\text{Al} = 3$. The mixture was stirred at 400 rpm
126 over 48 hours at 25 ± 0.5 °C and maintained statically over two weeks in nitrogen
127 atmosphere at 25°C. After the reaction period, the precipitate was separated from the
128 aqueous solution via centrifugation (6000 rpm) and subsequently filtered through 0.45 μm

129 filters. The precipitates were dried at room temperature in a desiccator to avoid
130 dehydration.

131 The natural ettringite specimen was obtained from the N'Chwaning mine in Kuruman
132 (South Africa), and consisted of single, light greenish and prismatic crystals approximately
133 8 mm in length and 3 mm in width.

134

135 **Characterization of the ettringite samples**

136 Both the synthetic and the natural samples were characterized by XRD. The natural
137 specimen was first gently crushed by hand using an agate mortar to a fine powder of
138 approximately 20 μ m in particle size, whereas the synthetic samples were analyzed as
139 obtained after being dried in a desiccator at room temperature. The diffraction patterns were
140 collected in a Philips X'Pert-PRO automatic diffractometer using CuK α radiation and
141 scanning over the 2 θ range of 5° to 60°. Indexing of the main reflections was made using
142 the crystallographic analysis tools of the computer program X'Pert HighScore Plus (©2008,
143 PANalytical B.V.). To investigate the crystallinity of the samples, the widths of some
144 selected reflections were analyzed by considering the full width at half-maximum (FWHM)
145 values. The smaller the FWHM values are, the larger the crystallite size is and the better is
146 the crystallinity.³⁴ As is widely known, the crystallite size represents the size of the
147 coherently diffracting domain and not the size of the precipitate particles. Here, the
148 crystallite size of both samples was roughly estimated using the X'Pert Plus “Scherrer
149 calculator” tool.

150 Representative individuals of the synthetic and natural samples were imaged using a
151 JEOL-6610 scanning electron microscope (SEM). The SEM is equipped with an INCA

152 Energy 350-Xmax 50 microanalysis system (EDS) with a SDD-Xmax 50 detector (INCA)
153 and an ultra-thin window, which permits the detection and semi-quantitative analysis of
154 light elements. This microanalysis system was used to estimate the chemical composition
155 (Ca, S, and Al) of both natural and synthetic samples.

156

157 **Thermal study: Thermogravimetry, DSC and Thermo-XRD**

158 Thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses were
159 performed with the ettringite samples (~20 mg of initial mass) using a Mettler Toledo
160 TGA/SDTA 851 thermal analyzer. All measurements were performed between 298 and
161 1273 K at a heating rate of 10 K·min⁻¹ in a dynamic atmosphere, using a nitrogen flow rate
162 of 50 ml/min. The temperature and weight precision of the apparatus were ± 0.25 K and ± 1
163 µg, respectively. A Pfeiffer Vacuum ThermoStar™ GSD301T mass spectrometer was used
164 to analyze the gas phases released during the TG study. The masses 18 (H₂O) and 44 (CO₂)
165 were tested by using a detector C-SEM, operating at 1400 V, with a time constant of 0.5 s.

166 The samples were also analyzed via Differential Scanning Calorimetry (DSC) using a
167 Mettler Toledo DCS 822e apparatus to determine the temperatures and enthalpies of
168 dehydration. Heat-flow measurements were performed in the temperature range of 298-900
169 K under a flow of N₂ gas at a heating rate of 10 K·min⁻¹. The initial mass of each sample
170 was ~6 mg. Before characterizing the samples, the equipment was operated using indium
171 and zinc standards to calibrate the temperature and heat flow. The temperature precision of
172 the equipment was ± 0.2 K, and the reproducibility was ± 0.1 K.

173 The evolution of both the natural and the synthetic sample with increasing temperature
174 was studied via *in situ* thermo-XRD using CuK α radiation on a PANalytical X'Pert Pro

175 powder diffractometer equipped with a PIXcel solid-state detector and a high temperature
176 chamber (Anton Paar HTK 1200 N). Diffractograms were collected over a $5 < 2\theta < 40^\circ$
177 range with a step size of 0.013° . All measurements were performed in static air atmosphere
178 by collecting the diffraction patterns at fixed temperatures (typically at 25°C increments)
179 between 25°C and 250°C . The heating rate between two consecutive scans was $5 \text{ K}\cdot\text{min}^{-1}$.

180

181 **Isothermal XRD experiments**

182 The decomposition behavior of the natural specimen was studied via *in-situ* XRD
183 isothermal experiments using the PANalytical X'Pert Pro powder diffractometer previously
184 described. The sample was placed in a holder, which was introduced in a closed oven
185 chamber (Anton Paar HTK 1200N) at ambient conditions ($25 \pm 2^\circ\text{C}$, relative humidity 60-
186 70%) and then brought to prefixed temperatures (40°C , 50°C , 55°C or 60°C). The heating
187 rate was $10 \text{ K}\cdot\text{min}^{-1}$, and once the temperature was reached, the sample was maintained at
188 isothermal conditions. The powder patterns in each isothermal series were collected in a
189 static air atmosphere at regular intervals of 5 min (during the first two hours), 1 hour
190 (during the first day) and 6 hours (from the second day). All the diffraction patterns were
191 scanned in the range of $8^\circ < 2\theta < 30^\circ$ with a step size of 0.001° . Every run was
192 duplicated, and the results were found to be reproducible. The decomposition of ettringite
193 with increasing time was checked by evaluating the peak area (A) in counts per second
194 (cps) of the first reflection (100) by using X'Pert Viewer. The transformation extent was
195 established from the ratio A_t/A_0 , where A_0 and A_t correspond to peak areas at the beginning
196 of the experiment ($t = 0$) and at a given time (t), respectively.

197

198 **RESULTS AND DISCUSSION**

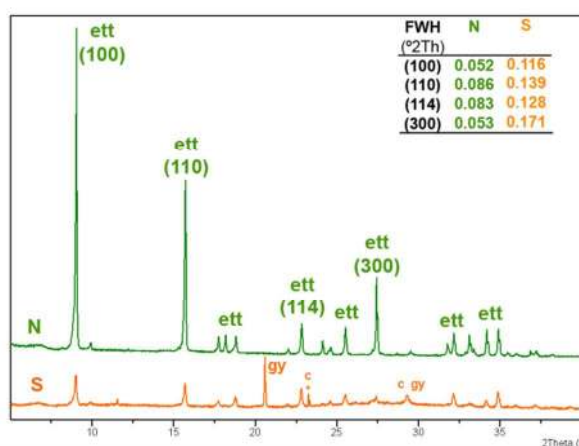
199 **Characterization of the synthetic sample and the natural ettringite**

200 Figure 1 shows the powder XRD patterns obtained for both the natural and the synthetic
201 sample before the thermal treatment. As expected, both diffractograms fit the reference
202 pattern of ettringite (PDF 00-041-1451; spatial group $P31c$). The main reflections can be
203 indexed as 100, 110, 104, and 114 (with d -spacings of ~ 9.72 , 5.61, 4.69, and 3.87 Å,
204 respectively). In the case of the synthetic sample, other minor reflections appear, with d -
205 spacings of ~ 7.63 and 4.28 Å, which can be assigned to the main reflections of gypsum
206 (020 and 021 respectively). Atkins³⁵ also reported the gypsum impurities in their synthetic
207 samples of ettringite. As can be observed, a broad reflection also appears at $2\theta \sim 29.22^\circ$,
208 which can be assigned to a combination of the main reflection of calcite (104) and the
209 third most important reflection of gypsum (041) that typically occur at $2\theta \sim 29.45$ and
210 29.11° , respectively. The occurrence of carbonate phases can be explained by the effect of
211 CO_2 atmospheric²³ during handling of the samples but also by trace amounts of calcite in the
212 reactant (CaOH) used in the synthesis of ettringite.

213

214 In summary, ettringite was found to be the only phase present in the natural sample,
215 whereas a mixture of ettringite with minor amounts of gypsum, calcite and monocarbonate
216 was identified in the synthetic sample. The initial experimental setup was designed to reach
217 a pH value of 11.5, for which ettringite is the most stable phase. However, during aging (48
218 hours), the pH decreases until values close to 10.7 are reached, at which point ettringite and
219 gypsum can co-precipitate.¹⁴ The presence of gypsum may hence be a result of the
220 compositional evolution of the parent solution during the experiment. These results can be

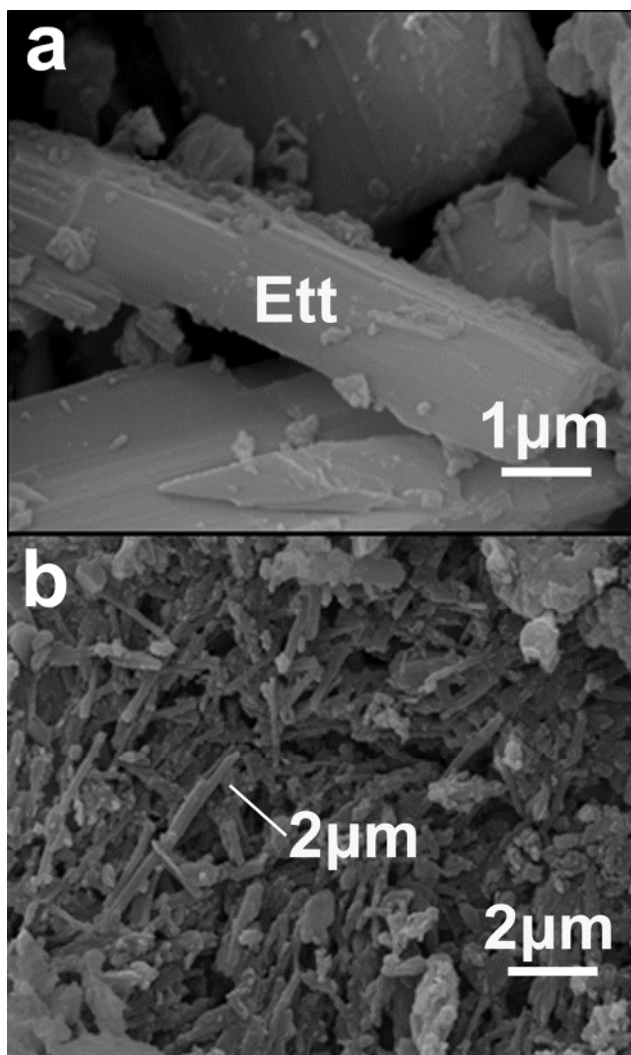
221 predicted by inputting the concentration and pH of the parent solution into geochemical
222 codes, such as PHREEQC³⁶ or GEMS.³⁷ Using PHREEQC with the WATEQ4F database
223 and the solubility data of Perkins and Palmer³³, the saturation index (SI) with respect to
224 ettringite takes a value of ~19.9, which is therefore the most likely phase to precipitate. The
225 parent solution was also supersaturated with respect to gypsum (SI = 0.78 > 0) and other
226 metastable solid phases (monosulfate, portlandite, gibbsite, hydrogarnet), but only gypsum,
227 calcite and monocarbonate were identified in the diffractograms.



228
229 **Figure 1.** Powder XRD patterns of the natural (N) and synthetic (S) samples. Ettringite
230 (ett) is the main phase in both samples, while gypsum (g), calcite (c) and monocarbonate
231 (*) were identified as minor phases in the precipitate. FWHM values indicate (see inset)
232 that the natural sample is more crystalline than the synthetic.

233
234 Secondary electron images show the elongated, prismatic habit of the ettringite crystals in
235 both the natural and the synthetic sample (Figure 2). Although the habit is similar in both
236 cases, the crystal sizes are clearly different. The crystals obtained by precipitation were
237 found to be significantly smaller (~5µm long) than the natural ones (~8mm long). Semi-

238 quantitative EDS microanalyses of both the natural and the synthetic sample confirm that
239 the mean Ca/S and Ca/Al atomic ratios are close to 3 and 2 respectively, which agree with
240 the ettringite stoichiometry. The natural specimen appeared to be relatively pure since the
241 presence of foreign elements was not detected via EDS-microanalyses.
242



243

244 **Figure 2.** SEM images showing the elongated crystal habit of ettringite in the natural (a)
245 and the synthetic (b) samples.

246

247 In the case of the natural sample, the refined unit cell parameters ($a = 11.2530 \text{ \AA}$ and $c =$
248 21.6436 \AA) are quite similar to those reported in the reference pattern ($a = 11.2240 \text{ \AA}$ and c
249 $= 21.4080 \text{ \AA}$). However, the cell parameters calculated for the synthetic sample ($a =$
250 11.2514 \AA and $c = 22.6788 \text{ \AA}$), exhibit some differences. While the a -axis parameter is
251 slightly smaller, the c -axis parameter is clearly larger. These results indicate that the
252 columns of Ca-Al polyhedra along the c -axis³ are slightly longer for the synthetic sample
253 than for both the natural specimen and the reference pattern. Significant differences
254 between the crystals in this study and the synthesized ($a = 11.66881 \text{ \AA}$ and $c = 21.5366 \text{ \AA}$)
255 by Hartman⁸ were also observed. Both the crystal size and the crystal-chemistry appear to
256 be influenced by the crystallization conditions of the precipitation experiments, which
257 obviously differ from the typical conditions of ettringite formation in natural environments.

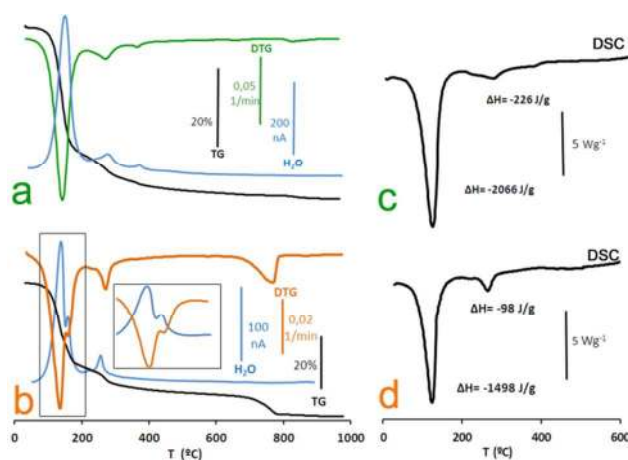
258 All the reflections were found to display smaller broadening and higher intensity in the
259 natural sample than in the synthetic one (Figure 1). Inspection of the FWHM data indicates
260 that the most intense 100 reflection is the most narrow (0.053 and $0.116^\circ 2\theta$ for the
261 natural sample and the synthetic, respectively). In a polycrystalline sample, a variety of
262 microstructural phenomena exist that lead to anomalous diffraction effects.³⁸ Peak
263 broadening can be caused by a small crystallite size, the presence of crystal defects, lattice
264 strain, or compositional heterogeneities.^{39,40} Because ettringite is a stoichiometric phase, the
265 broadening differences between both samples cannot be attributed to compositional
266 heterogeneity. Based on the FWHM of the 100 reflections, the crystallite size can be
267 estimated to be 126 nm and 69 nm for the natural and the synthetic sample, respectively.
268 However, polycrystalline material usually contains other imperfections that can also
269 produce broadening effects.⁴¹ Unfortunately, determining the precise contribution of each

270 of the microstructural factors to the observed broadening is not straightforward.⁴² In the
271 case of ettringite, synthetic crystals are usually obtained at a high supersaturation and can
272 be expected to incorporate a higher concentration of defects than natural crystals. Such is
273 the case here, where the precipitation-aging experiments were performed under conditions
274 that appear to affect the crystallinity (Figure 1), crystal habit and crystal size (Figure 2).

275

276 **Dehydration behavior of ettringite**

277 Although some thermal studies have been performed on natural ettringite⁴³, most
278 research was performed using synthetic samples.^{23, 25, 26} A comparison between the thermal
279 behavior of synthetic solids and natural specimens of higher crystallinity can provide
280 further insight into this matter. With this aim, Figure 3 displays the thermogravimetric (TG)
281 and derivative thermogravimetric (DTG) curves obtained for the natural (Figure 3a)
282 specimen and the synthetic sample (Figure 3b). Mass spectrometry analyses of the amount
283 of H₂O released from both samples at increasing temperatures are also shown. No
284 significant quantities of CO₂ were detected in the released gases. Overall, the combination
285 of these three curves (TG, DTG and H₂O) indicates that the weight loss observed in both
286 the natural and the synthetic sample is due to the release of water molecules and/or
287 hydroxyl groups.



288

289 **Figure 3.** TG curves (black), DTG curves (green and orange) and H₂O (blue) depicting
 290 the release from natural (a) and synthetic (b) samples. DSC curves for natural (c) and
 291 synthetic (d) samples as a function of temperature.

292

293 Although the TG curves obtained for both samples exhibit a similar profile, a detailed study
 294 of the DTG curves indicates that differences exist between natural and synthetic sample.
 295 The natural sample undergoes a higher (45.5%) total weight loss than the synthetic one
 296 (40.50%) at the end of the TG analyses (1000°C). Some features of the DTG curves, such
 297 as the temperature corresponding to the maximum weight-loss rate, also indicate
 298 differences in the dehydration behavior of both samples. The natural sample dehydrated in
 299 two separated stages (Figure 3a). The first stage occurs between 25-190°C, with a total loss
 300 of ~33%, equivalent to 23 water molecules. The maximum weight-loss rate occurs at
 301 ~138°C, corresponding to the release of ~16 water molecules from the sample. The second
 302 stage (190-300 °C) involves a loss of ~4.5%, which corresponds to a release of ~3 water
 303 molecules at a maximum rate at ~274°C. After the second stage, both the TG and DTG
 304 curves (Figure 3a) show a progressive weight loss (~7.5%) until the end of the experiment

305 (1000°C). In the case of the synthetic sample, a double-step dehydration event occurs in the
306 first stage, with a total loss of ~ 27% (~ 19 water molecules) between 25-190°C. The DTG
307 curve shows a maximum rate of weight loss at ~130 °C and a shoulder at ~155 °C. The
308 shoulder could be explained by the presence of gypsum, which also dehydrates in two
309 steps: The initial formation of bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) is closely followed by a second
310 step, in which dehydration proceeds to completion, with anhydrite ($\alpha\text{-CaSO}_4$) being the
311 final anhydrous phase.⁴⁴ Here, the combined dehydration of gypsum and ettringite could
312 explain the DTG behavior of the synthetic sample during the first stage. Dehydration of the
313 ettringite component continues between 190-300 °C, with a maximum rate at ~ 269 °C and
314 a total weight loss of ~ 5.6%. At the end of the second stage, the synthetic sample
315 undergoes a total weight loss of ~32.6%. After complete dehydration, a new weight loss
316 occurs between 650 and 800 °C (Figure 3b), which can correspond to the decomposition of
317 calcite identified by DRX (Figure 1).

318 The fact that the water molecules in ettringite occupy structural positions with different
319 crystal-chemical roles³ determines both the hydrogen bonding architecture and the
320 homogenous distribution of the positive charges, which could favor a sequential release of
321 the water molecules with increasing temperature. These crystallographic features would
322 explain the different stages of weight loss observed in the TG/DTG experiments.^{25,45,46}
323 However, there is no evidence to exclude a more complex behavior involving the
324 simultaneous loss of hydroxyl groups and water molecules.²⁶ The results of the DSC
325 experiments do not clarify this matter. As seen in Figures 3c and 3d, the DSC curves show
326 two main exothermic intervals below 300°C. In the case of the synthetic sample, the DSC
327 curve shows a double peak in the first interval. The enthalpy ΔH (J/g) and T (°C) of the

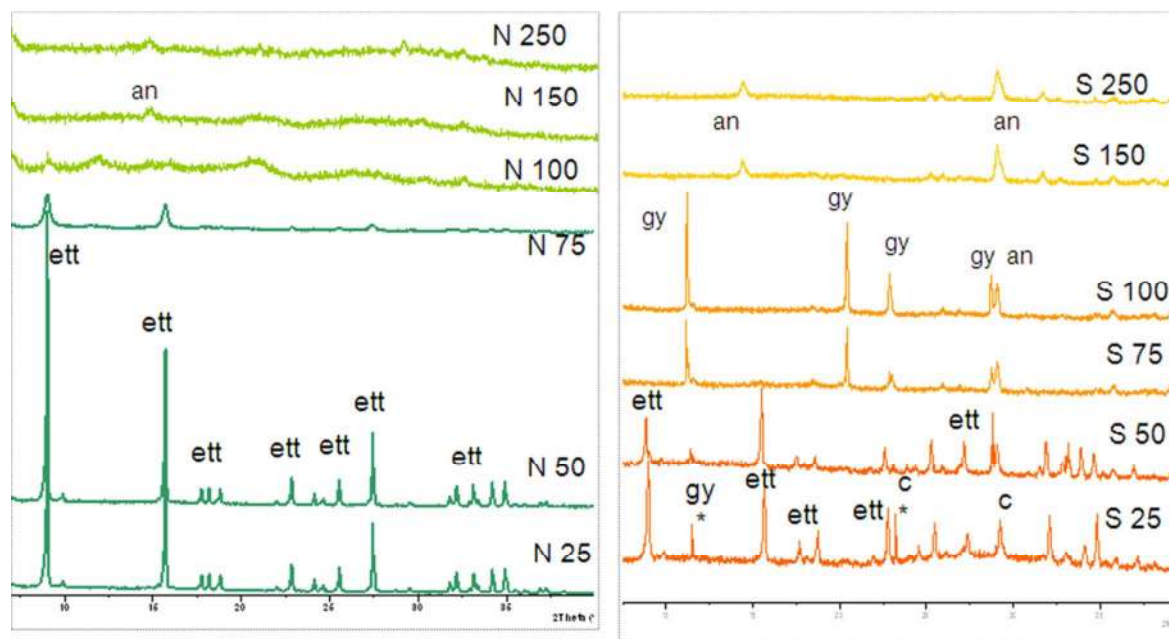
328 exothermic peaks for each interval are displayed in the graphs. Note that the peak minima
329 in both intervals are less pronounced for the natural sample than for the synthetic one.
330 These results are in good agreement with the TG/DTG study and clearly support the idea
331 that the two exothermic peaks observed in the natural sample are related to the two stages
332 of dehydration/decomposition. In the case of the synthetic sample, the DSC curves confirm
333 the double-step behavior in the first temperature range (25-190°C), which is attributed to
334 the presence of gypsum. Consequently, establishing the nature of the phases resulting from
335 the dehydration process requires complementary structural data.

336

337 **Thermal evolution of the XRD patterns**

338 Figure 4a displays a series of diffractograms obtained for the natural sample with
339 increasing temperature obtained via thermo-XRD experiments. The most important
340 reflections (100, 110, and 114) of ettringite are found to be fully preserved in the
341 diffractograms obtained up to 50°C and can be clearly identified below 100°C (Figure 4a).
342 Nevertheless, the reflections become less intense and undergo a progressive increase of
343 FWHM values, which indicates a decreasing degree of crystallinity with increasing
344 temperature (see Table 1). The thermal degradation of ettringite is generally considered to
345 represent the transition to an amorphous phase.²⁶ Although this new phase appears to be
346 amorphous according to the XRD results, it shows signs of crystallinity via electron
347 diffraction.²³ Such a new phase was termed meta-ettringite because it retains the columnar
348 structure of ettringite along the *c*-axis. The mechanism of collapse of ettringite to meta-
349 ettringite involves the loss of water molecules and possibly a rotation of individual cationic
350 columns, which results in the loss of crystallinity typical of meta-ettringite²² at

351 temperatures approximately 115°C. Figure 4a shows that ettringite reflections are no longer
 352 recognized in the diffractograms obtained above 100°C.



353

354 **Figure 4.** Selected powder XRD patterns obtained during thermal treatment of (a) natural
 355 (N) and (b) synthetic samples (S). The numbers indicate the temperature in °C. The
 356 reflections are labelled as ettringite (ett), calcite (c), monocarbonate (*), gypsum (gy) and
 357 anhydrite (an).

358

359 **Table 1.** Evolution of the crystallinity of ettringite during thermal treatment: broadening
 360 (FWHM) and intensities (I) obtained for the main reflections identified in ettringite.

sample	T (°C)	(001)		(110)	
		FWHM (°2Th)	I (counts)	FWHM (°2Th)	I (counts)
Natural	25	0.053	19423	0.086	9847
Natural	50	0.075	9258	0.087	9741
Natural	75	0.23	2635	0.306	788

Natural	100	0.33	42.3	0.305	42
Synthetic	25	0.152	852	0.139	1402
Synthetic	50	0.216	282	0.118	1305

361

362 Although the diffraction patterns obtained between 100°C and 250°C appear to
363 correspond to a non-crystalline material, despite the poor crystallinity, some incipient
364 reflections can be identified (Figure 4a). Thus, in the diffractograms obtained between
365 100°C and 175°C, the main reflections of gypsum (020 and 021) appear. In addition, some
366 broad reflections observed between 75°C and 250°C can be identified (Figure 4a) as
367 bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) and/or metastable γ -anhydrite (CaSO_4). Distinguishing bassanite
368 from γ -anhydrite using conventional powder XRD is complicated due to the slight
369 differences between their crystal structures.⁴⁷ The presence of gypsum, hemihydrate and/or
370 anhydrite can be explained by the reaction between water molecules, sulfate and calcium
371 ions to yield coherently diffracting domains of calcium sulfate phases within a matrix of
372 amorphous material. Previous works^{48,23} reported the formation of mixtures of gypsum,
373 hemihydrate and monosulfate (AFm) at ~ 115 °C. Here, monosulfate was not identified in
374 any of the diffractograms obtained between 25°C and 250°C. Moreover, no crystalline
375 aluminates were found, which indicates that the aluminum released from ettringite occurs
376 as an amorphous phase containing aluminum.

377 Figure 4b shows a series of diffractograms obtained at increasing temperatures for the
378 synthetic sample. Some important differences are found with respect to the series obtained
379 with the natural sample. The main reflections of ettringite only appear in diffractograms
380 obtained below 50 °C, while they were present in the natural sample up to 100°C. By
381 comparing the values of width and intensity of the main reflections (Figure 1), it is clear

382 that the synthetic ettringite undergoes an earlier decrease of crystallinity during the heating
383 process. Gypsum appears in the diffractograms obtained at temperatures below 125°C,
384 while bassanite/anhydrite reflections appear in the diffractograms obtained at higher
385 temperatures.

386 In summary, the previous results indicate that the natural specimen is more resistant to
387 dehydration than the synthetic sample. The natural sample was found to remain unaltered
388 up to 75°C; in contrast, for the synthetic sample, the ettringite reflections begin to vanish at
389 a lower temperature (>50°C). Such a different behavior can be explained by the smaller
390 crystallinity degree of the synthetic sample, which is consistent with the small particle size
391 of these precipitates. Low crystallinity is mostly due to a small crystallite size. The
392 crystallite size is the size of a coherently diffracting domain and thus does not necessarily
393 coincides with the particle size. However, tiny crystals precipitated at a high
394 supersaturation normally exhibit small coherently diffracting domains and poor
395 crystallinity. Therefore, the natural specimen appears to be the best choice to study the
396 dehydration kinetics of ettringite and its implications in the role of this mineral as
397 sequestering phase for harmful ions.

398

399 **Dehydration kinetics**

400 In-situ XRD isothermal experiments were performed different temperatures (40°C, 50°C,
401 55°C and 60°C) to determine the dehydration kinetics of ettringite. The study was focused
402 on the first stage described in the previous section and was applied to the natural specimen,
403 which was demonstrated to be a more 'robust' phase. Figure 5a shows the changes in the
404 peak area (A) of the main XRD reflection of ettringite (100) as a function of time during

405 the isothermal experiments. The peak area decreases quickly during the early hours and
406 then slowly evolves towards an asymptotic value. The trend is the same in all the
407 experiments, which indicate that the same transformation mechanism is operating at the
408 studied temperatures. A quantitative estimation of the transformation extent was
409 determined from the ratio A_t/A_0 . The time (t) to transform a fraction of ettringite (Y_{10}) of
410 approximately 10% was calculated (see inset in Figure 5b). The decrease in the peak area
411 observed in the isothermal experiments is consistent with the initial decomposition stage,
412 which involves dehydration (Figure 4) and a loss of crystallinity (Table 1). Nucleation,
413 growth and transformation of gypsum and anhydrite occur during the second stage of the
414 thermal treatment (Figure 4) and are not considered here.

415 The experimental values obtained at different temperatures for the time (t) at which the
416 fraction transformed was Y_{10} can be used to estimate the activation energy (Ea) via the
417 method of “time to given fraction”.³² This method establishes that the transformed fraction
418 (Y) and time (t) are related by a function in which the dependent variable is t instead of the
419 kinetic constant (k). Hence, the strong dependence of the “kinetic constant” procedure is
420 avoided. When the mechanism does not change over the temperature range studied, t_Y can
421 be described by the expression:

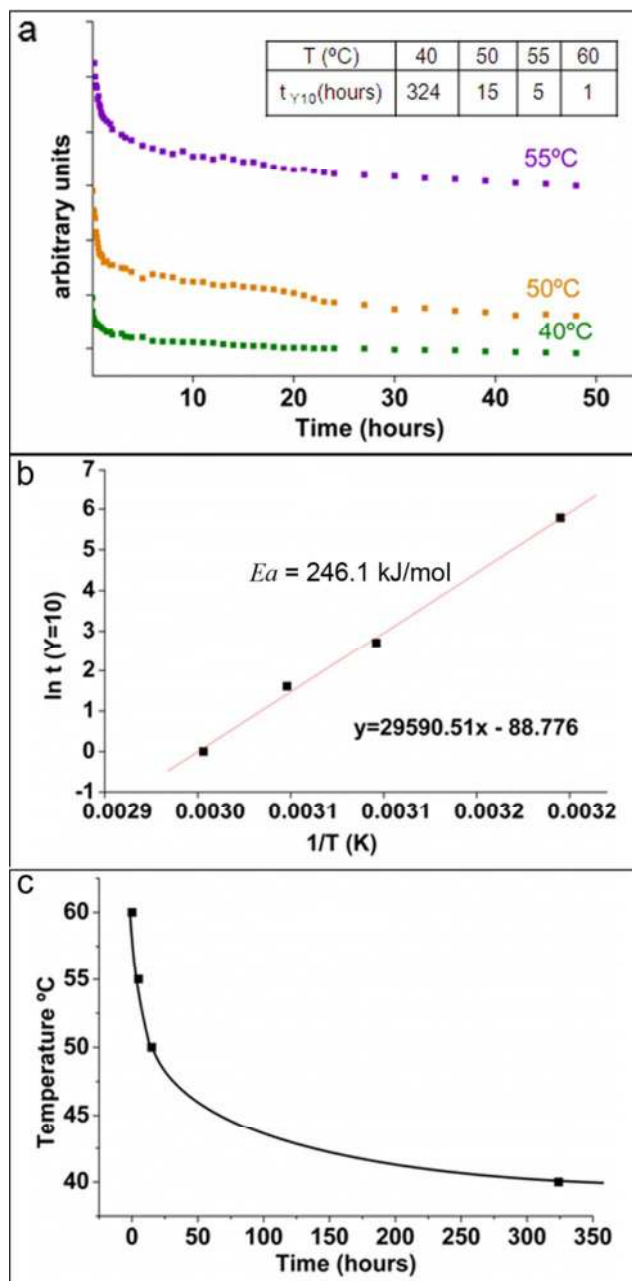
$$422 \quad t_Y = A^{-1} \cdot e^{\left(\frac{Ea}{RT}\right)},$$

423 (1)

424 Where A is a fitting constant, R the gas constant, and T the temperature in Kelvin. In
425 practice, the experimental data can be plotted as shown in Figure 5b, where $\ln t_{0.1}$ is
426 represented on the ordinate against $1/T$ on the abscissa. The slope of the straight line fitting
427 these data-points corresponds to Ea/R and the activation energy can be determined. Here, a

428 value $Ea = 246 \text{ kJ}\cdot\text{mol}^{-1}$ was obtained for the transformation of ettringite during the first
429 stage. The determination of the kinetic parameters of the complete transformation would
430 require very long experiments that are beyond the scope of the present work.

431 The progress of a transformation can also be described by a Time-Temperature-
432 Transformation (TTT) diagram⁴⁹, which indicates the time at which the transformation
433 occurs when a sample is kept under isothermal conditions.³² Figure 5c displays the TTT
434 diagram determined for the beginning of the ettringite transformation ($Y=10$). The critical
435 temperature ($T_c \approx 30^\circ\text{C}$) was estimated by running a heating and cooling cycle over a short
436 period of time, in which no phase transformation was observed below T_c . The curve
437 connecting the experimental data exhibit the typical shape of the TTT diagrams for
438 transformations with increasing temperature. At low temperatures above T_c , the
439 transformation begins after long periods of time. A further increase of temperature
440 dramatically reduces the time over which the transformation begins.



441

442 **Figure 5.** a) Variation of the peak area of the 100 reflection as a function of time during
 443 three series of isothermal experiments. b) Experimental data of the time ($\ln t_{0.1}$) for a 10%
 444 fraction of transformed ettringite versus $1/T$. The slope of the fitting straight line
 445 corresponds to E_a/R . Time (hours) to transform a fraction ($Y = 10$) of ettringite. c) TTT
 446 diagram corresponding to a fraction $Y = 0.1$ of the transformed ettringite.

447

448 **Environmental implications**

449

450 The capacity of the ettringite to immobilize contaminants is mostly related with its crystal
451 structure, which allow the substitution of sulfate by oxyanions (chromate, arsenate, or
452 selenate) and calcium by cations (lead, cadmium, cobalt). Such availability for ionic
453 substitution suggests that ettringite-based solid-solution formation can be one of the most
454 effective mechanisms for immobilization of pollutant ions in cements. Among the elements
455 immobilized by ettringite, selenium is considered to have a high priority in the field of
456 nuclear wastes due to the high toxicity of the radioisotope ^{76}Se with a half-life of
457 3.27×10^5 years⁵⁰. In fact, ^{79}Se is a critical radionuclide that might diffuse through the
458 engineering and geological barriers of repositories and hence, release from waste disposals
459 to the environment causing an increase of radiotoxicity²⁷ In that context, the study of the
460 thermal stability of ettringite is crucial to understand the evolution of the crystal structure
461 containing harmful ions and how it affects the storage environment. In the present work, the
462 results obtained by calorimetric and thermo-XRD indicate that the
463 dehydration/decomposition of ettringite occurs in two stages via the formation of poorly
464 crystalline phases identified as calcium sulfates with different degrees of hydration and an
465 amorphous phase containing aluminum. The kinetic study performed in this work is
466 focused on the first stage and, for the first time, reveals that the initial transformation stage
467 of ettringite occurs at relatively low temperature (40°C). These results indicate that
468 ettringite cannot be considered an optimum host phase for the immobilization of
469 radionuclides and other harmful elements as frequently proposed in the literature. As long

470 as decomposition of ettringite exposed to atmospheric conditions is to be expected, the risk
471 of dehydration in different long-term evolutionary scenarios deserves careful assessment.

472

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