Estimation of standard molar entropy of cement hydrates and
 clinker minerals

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9 ABSTRACT

- 10 It is not straightforward to experimentally measure the standard molar
- 11 entropy of cement hydrates or clinker minerals. This is further compounded
- 12 by the controversies surrounding the entropy values reported in established
- 13 thermodynamic datasets for cements. The purpose of this study is to
- 14 assess the reliability of standard entropies compiled in those datasets. To
- this end, a simple but robust method is used in which the standard entropy
- 16 of an inorganic solid is correlated to its formula unit volume via a linear
- 17 equation. The results of this analysis show that the standard entropies
- 18 and/or molar volumes (and in cases solubility products) of the following
- 19 phases deserve closer scrutiny: meta-ettringite phases;
- 20 magnesium/aluminium layered double hydroxide solid solutions; almost all
- 21 iron-bearing monosulfate and hydrogarnet phases; and several calcium
- 22 silicate hydrate solid solution end-members. In addition, this study reports
- 23 the provisional estimates for the standard entropies of minerals ternesite
- 24 and ye'elimite.
- 25 *Keywords:* Thermodynamic, Standard entropy, Cement
- 26

27 **1. Introduction**

Thermodynamics has long been crucial to materials science, with the field of 28 cement being no exception. The past two decades have seen more uses of 29 30 thermodynamics in studying cements, but the key advancements include the equilibrium calculations of cement clinkering [1,2] and of the hydration of 31 cements which occur at much lower temperatures [3,4]. Progress has been 32 made at pace with respect to the latter where the interest lies in predicting 33 the phase assemblage of hydrating cements at standard pressure but over 34 a wide range of temperatures from 10 to 100 °C. In most studies, cements 35 36 are not the only reacting solids in the system, but they coexist with inorganic 37 salts, natural minerals and/or industrial by-products of various chemical 38 compositions. Overall, it is fairly complex to model these materials in reactions with water. This is in part due to the lack of thermodynamic data 39 Cement oxide notations used in this paper are: A=Al₂O₃; C=CaO; F=Fe₂O₃; H=H₂O; M=MgO; S=SiO₂; c=CO₂; s=SO₃ * Corresponding authors Email addresses: sam.ghazizadeh@sheffield.ac.uk (S. Ghazizadeh),

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a given cement system, in particular when constituents other than Portland
cement are present, or at temperatures other than 25 °C. The accuracy of
some of the existing data is also open to question, which further complicates
the problem.

45 To perform the equilibrium calculations of hydration, the common practice is to use available software packages (such as GEMS [5,6] or PHREEQC [7]) 46 coupled with thermodynamic databases developed specifically for cements. 47 Thermodynamic properties of several cement hydrates and clinker minerals, 48 49 especially as relates to Portland cement (and its blends) and alkali-activated materials, are compiled into two major datasets; Cemdata [3,8,9] and 50 Thermoddem [10,11]. These databases report the value of Gibbs free energy 51 of formation, enthalpy of formation, entropy, heat capacity, molar volume and 52 equilibrium solubility products for substances and reactions pertaining to 53 cements. All reported data are for the standard temperature and pressure of 54 55 298.15 K and 1 bar albeit the heat capacities are given as a function of temperature, valid up to 100 °C. The accuracy of reported data is essential 56 57 to performing reliable thermodynamic calculations.

58 The complete thermodynamic properties of a material can be constructed by 59 combining experimentally obtained entropy, enthalpy and heat capacity data. 60 Amongst these parameters, entropy at a reference temperature (for example at 298.15 K for standard entropy) is difficult to measure. To experimentally 61 62 derive the standard entropy of a material, the third law of thermodynamics needs to be followed; that is, to measure the isobaric heat capacity (C_p) over 63 a range of temperatures (T) from near 0 K to above 298.15 K, and then 64 integrate the C_p/T function with respect to T from 0 K to 298.15 K. This 65 method is hardly ever used in the cement literature to derive the standard 66 67 entropy of cement hydrates, possibly because (i) the experimental setup 68 required for the direct determination of heat capacity to near absolute 0 is not 69 widely available, and (ii) it is difficult to prepare cement hydrates (and their selected end-members) in a sufficiently pure form so that to enable precise 70 measurements. The alternative approach commonly used is to measure the 71 72 equilibrium solubility product of hydrates at multiple temperatures, then to fit the standard entropy term within the so-called three-term approximation 73 equation to the measured solubility data (for more detail, see [12] or Section 74 3 of this paper). The entropy value that gives the best fit to the measured 75 76 solubility data is deemed to be the one representing the hydrate in question.

The three-term approximation method may lead to inaccurate entropy values if it happens that the measured solubility products are missing, incorrect (or subject to significant uncertainty), or somehow fail to represent the hydrates studied. No matter how meticulously experiments are performed, there exists a possibility that the measured solubility product represents a condition in which the solution is not in equilibrium with respect to the hydrate, but rather is influenced by one or more remnant precursor materials and/or metastable
phases. Unfortunately, the accuracy of entropy data obtained to date via this
method is rarely assessed using independent techniques (although a few
exceptions exist, *e.g.* [13]). Therefore, an issue arises regarding whether the
standard entropies and equilibrium solubility data of substances reported in
established thermodynamic databases for cements are accurate and reliable
– and this poses a significant challenge.

Given the paucity of experimental entropy data, and the labour-intensive and
complex processes involved in obtaining and assessing them, it would be
very valuable to estimate the standard entropy using methods that have solid
thermodynamic grounds but are independent of the experimental procedures
used so far.

The purpose of this study is to examine the accuracy of standard entropies of cement hydrates and clinker minerals given in *Cemdata18*[3]. This dataset is chosen as it contains more hydrates than *Thermoddem* [10,11]; however, discrepancies between the two are also discussed.

In what follows, we first present a description of various methods to estimate standard entropy. Then, a simple method is employed and compared against the published entropy data. The method is also used to derive the standard entropy of ye'elimite and ternesite. These are clinker minerals that have been under rigorous investigation recently due to their potential environmental and economic benefits [14]; however, their standard entropy is still unknown.

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106 **2. Estimation of standard entropy**

107 Methods to find estimates of standard entropy are numerous, with some dating back to as early as the 1920s. Their use is also relatively familiar in 108 the field of cement science. For instance, in 1985, Babushkin et al. [15], who 109 for the first time compiled a relatively comprehensive thermodynamic dataset 110 for cement substances, adopted a few of those methods. It is not our 111 intention to comprehensively review all such methods in detail, but the key 112 methods that have already been applied to cements or have the potential to 113 be used in the future, are discussed here. 114

By far the most widely used type of method to estimate the standard entropy of inorganic minerals and hydrates consists of a mathematical relationship in which the standard molar entropy of a compound is related to [15–19]:

- 118(i)the sum of the standard molar entropies of the constituent119oxides and hydroxides, or
- 120(ii)a weighted sum of the standard molar entropies and standard121molar volumes of the constituent oxides and hydroxides, or
 - (iii) only the standard molar volume of the solid in question.

123 The first two of these are known as *additivity methods* and take the forms 124 given by Eq. 1 or Eq. 2, respectively:

$$S_{298,j}^{\circ} = \sum_{i=1}^{x} n_i S_{298,i}^{\circ},$$
(1)

$$S_{298,j}^{\circ} - k' V_{molar,j} = \sum_{i=1}^{n} n_i (S_{298,i}^{\circ} - k' V_{molar,i}),$$
 (2)

where $S_{298,i}^{\circ}$ and $V_{molar,i}$ are the standard molar entropy and molar volume 125 of the inorganic compound of interest, n_i is the stochiometric coefficient of 126 the *i*th constituent species within this compound, $S_{298,i}^{\circ}$ and $V_{molar,i}$ are the 127 standard molar entropy and molar volume, respectively, of the constituent 128 oxide or hydroxide. k' is a constant and its value depends on the constituent 129 type and their coordination state. Holland [16] has further simplified Eq. 2, by 130 showing that k' can be approximated to 1 as $\partial S/\partial V$ at 298.15 is close to unity. 131 132 Eq. 1 has been more common than Eq. 2 in the cement literature, and has 133 previously been used, for instance, by Myers et al., to estimate the standard entropy of several end-members of the calcium (sodium) aluminosilicate 134 hydrate solid solution which can occur in Portland cement blends and alkali 135 activated cements [20,21]. 136

137 It is worth noting that the standard molar entropy of a compound is related to its heat capacity; factors that affect the latter will also affect the former (and 138 are known to be significant at temperatures near 298.15 K [17]). Considering 139 this, Eq. 2 can yield relatively smaller errors than Eq. 1, as it enables one to 140 account for factors that influence standard entropy. This includes the effect 141 142 of volume, coordination state and/or magnetic order-disorder transformation which specifically occurs in minerals with transition metals [16,17]. To correct 143 for these, different $S_{298}^{\circ} - k' V_{molar}$ can be adopted for different coordination 144 145 states, thereby also allowing for the correction of the magnetic disorder. The absence of this from Eq. 1, and its consequent influence on estimating the 146 entropy, becomes particularly evident when different polymorphs of the same 147 148 composition are to be analysed. Using Eq. 1 leads to identical standard entropies for different polymorphs, because their selected oxide or hydroxide 149 constituents are the same. However, it is not really possible for two (or more) 150 polymorphs with the same chemical composition (*i.e.* undoped) to have the 151 same standard entropy. This is due to the fact that different structures have 152 different heat capacity and thus entropy. In spite of their popularity, Eq. 1 and 153 Eq. 2 are not straightforward to use as they require very careful consideration 154 155 in the selection of the constituent oxides or hydroxides.

Using a somewhat similar principle to that embodied by Eq. 1, it has become customary in the cement literature to estimate the standard entropy of a solid by assuming a reference (usually fictive) reaction involving compounds of known entropies and with a net zero entropy ($\Delta_r S^\circ = 0$), where reactants and

products are structurally analogous to each other [10,22]. This method was 160 first proposed by Helgeson in 1978 [23]. For instance, in order to approximate 161 the standard entropy of Fe-bearing ettringite, one can write Fe-ettringite + 162 $Al_2O_3 \rightarrow Al$ -ettringite + Fe₂O₃. The shortcoming of this method (in addition to 163 those pertinent to Eq. 1) is that errors can arise and propagate if the entropies 164 of the reference compounds are already inaccurate, or if the compounds are 165 not selected carefully. This is specifically important in the case of hydrates, 166 as the binding state of water (e.g. whether it is easily removable zeolitic water 167 or structurally bound) has a significant influence on the entropy estimations. 168

169 The third type of estimation method concerns a simple relationship whereby 170 the standard entropy of an inorganic solid is directly correlated to its molar 171 volume. A seemingly rather simple form of such relationships was developed 172 by Turkdogan and Pearson [24] in 1953, which was later recommended by 173 Babushkin *et al.* in their book [15]:

$$S_{298}^{\circ} = a. V_{molar}^{n}$$
(3)

where V_{molar} is molar volume, a and n are variables and their values depend 174 on several factors such as the crystal structure, cation-anion ratio, the cation 175 176 group in the periodic table, and the nature of the anions (whether oxides, 177 silicates, sulfates or carbonates). However, Turkdogan and Pearson [24] could not systematically establish how the constants would be defined from 178 fundamental principles, mainly because they had access to an insufficient 179 body of thermodynamic data at the time. Their method was therefore proven 180 difficult to apply in estimating the entropy of material classes for which a and 181 *n* did not exist (or were not able to be fitted to existing databases). 182

Recently, Jenkins and Glasser established a new volume-based relationship
[25–27] which is much simpler than Eqs. 1-3. In their studies, the authors
found that the standard entropies of inorganic minerals and hydrates obey a
distinct relationship in which entropy is an increasing function of formula unit
volume. The general form of their relationship is presented in Eq. 4:

$$S_{298}^{\circ} = kV_m + c$$
 (4)

188 where V_m is the formula unit volume (nm³·formula-unit⁻¹), and *k* and *c* are 189 empirically determined constants. There are several ways to calculate V_m 190 [28], but the easiest is to use Eq. 5:

$$V_{\rm m} = V_{\rm molar} \times 10^{21} / N_{\rm A} \tag{5}$$

191 where V_{molar} (cm³·mol⁻¹) can be readily retrieved from most thermodynamic 192 databases (including those related to cementitious systems), and N_A is the 193 Avogadro constant (6.022 × 10²³ formula-unit·mol⁻¹). Jenkins and Glasser 194 derived Eq. 4 (which has thermodynamic basis; $\partial S/\partial V$ is constant at a given 195 pressure [25]) by the regression analysis of a standard dataset involving 196 inorganic materials with different stoichiometries. Fig. 1 shows the data used 197 in their analysis. The filled circles represent 67 inorganic ionic hydrates (*e.g.* 198 CaSO₄·2H₂O) whereas the hollow circles are 94 anhydrous minerals. From 199 these data, the authors of those studies identified that the values of the fitted 200 constants in Eq. 4 depend on whether the inorganic solids are hydrated or 201 anhydrous. Their two resulting equations are Eq. 6 and Eq. 7, providing a 202 simple means to estimate standard molar entropy (note that there are errors 203 associated with such estimates; 7.4% for Eq. 6 and 12.6% for Eq. 7 [25]).

$$S_{298}^{\circ} = 1579 V_m + 6$$
; for solid hydrates (6)
 $S_{298}^{\circ} = 1262 V_m + 13$; for anhydrous inorganic minerals (7)



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Fig. 1: Standard molar entropy versus formula unit volume, for inorganic minerals (anhydrous) and hydrated ionic solids, reproduced from the dataset given in [25].
 The dashed and solid lines are the result of regression analysis carried out by Jenkins and Glasser on each given dataset.

Following on from their earlier work, Jenkins and Glasser [26,27,29,30] have also established that the standard molar entropy of a hydrated mineral (*e.g.* $CaSO_4 \cdot 2H_2O$) is linearly correlated to that of its anhydrous counterpart (*e.g.* $CaSO_4$), via Eq. 8:

$$S_{298}^{\circ} \{X \cdot mH_2 0\} - S_{298}^{\circ} \{X\} = m\theta_{S_{298}^{\circ}}$$
(8)

213 where X denotes the anhydrous crystal, m is the number of water molecules in the hydrated crystal, and $\theta_{S^{\circ}_{208}}$ is a constant. Eq. 8 is identical to the concept 214 215 underpinning the additivity methods in Eq. 1 and Eq. 2, where entropy is seen 216 as an additive quantity of the constituents. Water is one of the constituents 217 of hydrates and so could be defined separately as a component of Eq. 1 or Eq. 2. Jenkins and Glasser investigated 83 salt pairs in [31] and determined 218 a value of $\theta_{S_{298}^{\circ}}$ = 40.9 J·K⁻¹·mol⁻¹·(H₂O molecule)⁻¹, regardless of the 219 composition of the parent salt. As an example, Fig. 2 shows the standard 220 entropy of CaSO₄·mH₂O as a function of the number (m) of water molecules 221 in its formula. The hollow circles are the standard entropies measured 222 223 experimentally, whereas the solid line represents Eq. 8. The entropy data are 224 an increasing function of water content, and Eq. 8 fits these data very well. The same has been observed for other 83 salt pairs, with correlation 225

- 226 coefficient r² being equal to 0.978 [31]. Nevertheless, the possible downside
- of Eq. 8 with a fixed constant of $\theta_{S_{298}^\circ}$ = 40.9 J·K⁻¹·mol⁻¹·(H₂O molecule)⁻¹ is
- that it only represents one state of water in the crystal structure; this will be
- discussed further in Section 3.4.



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Fig. 2: Standard molar entropy of $CaSO_4 \cdot mH_2O$ as a function of the number of

formula water. Data points are retrieved from [31]. Solid line is the estimation of

standard entropy based on Eq. 8 where $\theta_{S_{298}^\circ} = 40.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}\cdot(\text{H}_2\text{O molecule})^{-1}$.

Compared to Eq. 1 and Eq. 2, Jenkins and Glasser's method is easy to apply 234 and has already been used for a variety of problems [30]. The only parameter 235 required in their approach is the formula unit volume, leading to calculations 236 237 which are simple to execute. However, this simplicity comes at a price. Eq. 4 238 compromises the accuracy of predicted standard entropy, compared to Eq. 2 where additional $S_{298}^{\circ} - k' V_{molar}$ terms could be incorporated (if necessary) 239 to correct for the factors that affect standard entropy [16,17]. An example 240 241 where Eq. 4 falls short is with respect to the standard entropies of minerals 242 larnite and calcium olivine (which are the β and γ polymorphs of Ca₂SiO₄, respectively). The standard molar entropies of these materials, as measured 243 experimentally, are 127.61 J·mol⁻¹·K⁻¹ and 120.5 J·mol⁻¹·K⁻¹, respectively; 244 however, their formula unit volumes are 0.085 nm³ formula-unit⁻¹ and 0.098 245 nm³ formula-unit⁻¹ (see data in supporting information of [25]). Eq. 4 would 246 predict a lower entropy for larnite based on its lower formula unit volume, but 247 the reverse is true. The aluminosilicate minerals and alusite and sillimanite 248 (both polymorphs of Al₂SiO₅) also show this type of inverted relationship (see 249 250 supporting data given in [25]). Nonetheless, such cases are rare; generally, 251 the differences in standard entropies caused by factors other than change of molar volume are small [16,17]. 252

Equations 6-8 can be useful in the thermodynamics of cement hydrates and clinker minerals. The application of these equations is twofold: (i) to assess the reliability of standard entropies already acquired via experiments, or (ii) to estimate standard entropies (even if provisionally) when it is difficult to measure them directly. Either way, errors associated with the use of Eq. 6-8 are small, based on the statistical estimates of uncertainties given in [25] fora wide range of mineral phases.

Equation 8 can also play an important role in estimating standard entropies of hydrates with different water contents, especially when the entropy value of a specific hydration level is required (and when molar volume is not known to high precision, preventing the use of Eq. 6). It has occurred in the past that studies derived the standard entropy of a hydrate with specific water content, but then struggled to compare their findings with other datasets (see *e.g.* [13]).

In the following sections, we take the standard entropies of cement hydrates 267 268 and clinker minerals in [3], and plot them against their corresponding formula 269 unit volumes. Therein, Eq. 6 or Eq. 7 is also plotted for comparison. Where the relationship between the standard entropy and formula unit volume falls 270 significantly away from the lines defined by Eq. 6 or Eq. 7, it is possible that 271 272 errors are associated with one or both of these parameters, and the possible reasons for such errors are therefore explored. Discussions are also included 273 when discrepancies are found between Cemdata18 [3] and Thermoddem 274 275 [10,11] datasets.

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277 3. Cement hydrates

278 3.1 AFt phases

The standard molar entropies and formula unit volumes of all AFt hydrates listed in [3] are shown in Fig. 3. The solid line represents Eq. 6, which is applicable to hydrous phases. The main observation from Fig. 3 is that there are only two data points which are not described accurately by Eq. 6: the ettringite hydrates with $13H_2O$ and $9H_2O$ water contents. The reason for this is as follows.

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286 3.1.1 meta-ettringite

287 The standard entropies of these phases were originally derived by Baquerizo et al. [32], by examining how ettringite ($C_6As_3H_{32}$) decomposes or reforms as 288 relative humidity and temperature change. Those authors made an 289 290 interesting observation, consistent with an earlier study by Zhou and Glasser [33], that $C_6As_3H_{32}$ loses water as relative humidity reduces, thereby 291 transforming to $C_6As_3H_{13}$ or $C_6As_3H_9$ (these phases are generally referred to 292 293 as meta-ettringite). However, once they are exposed to increased levels of relative humidity, ettringite reforms, but following a pattern which is distinct 294 295 from that of decomposition. This pattern is shown in Fig. 4.

296 Unfortunately, this behaviour of ettringite made it difficult for Baquerizo et al.

[32] to derive the exact standard entropies of $C_6As_3H_{13}$ or $C_6As_3H_9$. To better

appreciate why, their method is briefly discussed here.



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Fig. 3: Standard molar entropy (from [3]) plotted against formula unit volume, for AFt hydrates. Formula unit volumes were calculated using Eq. 5 and the molar

302 volumes tabulated for these phases in Table 1 of [3]. The solid line is Eq. 6.



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Fig. 4: Stability of ettringite as a function of relative humidity and temperature, for reactions given in Eq. 9 and Eq. 10 as defined in the text; data are from [32]. The dots represent the data obtained experimentally, whereas the solid and dashed curves result from the thermodynamic model developed in [32]. The true thermodynamic equilibrium for $C_6As_3H_{13}$ is believed to be somewhere within the hysteresis loop (not shown here, but an estimate of the zero-hysteresis line was made by Baquerizo *et al.* in their article [32]).

To calculate the standard entropy of $C_6As_3H_{13}$, the authors of [32] followed reactions given in Eq. 9 and Eq. 10:

$$C_6As_3H_{13} + 17H_2O \rightarrow C_6As_3H_{30}$$
 (9)

$$C_6 A s_3 H_{30} \to C_6 A s_3 H_{13} + 17 H_2 O \tag{10}$$

and determined the equilibrium relative humidity at different temperatures for

these reactions. Thereafter, the equilibrium points, shown in Fig. 4, were

entered into the van't Hoff equation (Eq. 11) to calculate $\Delta_r H^{\circ}$:

$$\frac{\partial(\ln K_{eq})}{\partial(1/T)} = \frac{-\Delta_r H^{\circ}}{R}$$
(11)

where K_{eq} is the equilibrium constant, *R* is the gas constant (8.31451 J·mol⁻ ¹·K⁻¹) and *T* is the temperature in Kelvin. The Gibbs free energy ($\Delta_r G^\circ$) of the reactions was then calculated using Eq. 12:

$$\Delta_{\rm r} G^{\circ} = -RT \ln K_{\rm eq} \tag{12}$$

and $\Delta_r S^\circ$ was subsequently obtained via Eq.13:

$$\Delta_{\rm r} {\rm G}^{\circ} = \Delta_{\rm r} {\rm H}^{\circ} - {\rm T} \Delta_{\rm r} {\rm S}^{\circ} \tag{13}$$

The standard entropy of $C_6As_3H_{13}$ could then be simply calculated using the standard entropies of water and $C_6As_3H_{30}$. A similar procedure was also used to calculate the standard entropy of $C_6As_3H_9$ but considering the reaction in Eq. 14:

$$C_6As_3H_{13} \rightarrow C_6As_3H_9 + 4H_2O$$
 (14)

324 Taking C₆As₃H₁₃ as an example, since the formation and decomposition of 325 this phase follow two different patterns (as seen in Fig. 4), the calculations 326 via Eqs. 11-13 would lead to two different quantities of standard entropy for 327 $C_6As_3H_{13}$; that is 710.6 J·K⁻¹·mol⁻¹ for Eq. 9 and 1960 J·K⁻¹·mol⁻¹ for Eq. 10. The key question is which entropy value should be taken as the standard 328 entropy of $C_6As_3H_{13}$ – in principle the answer is that neither of these should 329 be, as neither Eq. 9 nor Eq. 10 represents the true equilibrium conditions with 330 331 respect to $C_6As_3H_{13}$ formation. The same argument applies to $C_6As_3H_9$.

In light of Fig. 3 and the procedure outlined above, it becomes clear that the entropies of $C_6As_3H_{13}$ and $C_6As_3H_9$ derived by Baquerizo *et al.* [32] should have been expected to depart far from their equilibrium values.

According to Eq. 6, the standard entropies of C₆As₃H₁₃ and C₆As₃H₉ phases 335 should be close to 1079.7 J·K⁻¹·mol⁻¹ and 953.4 J·K⁻¹·mol⁻¹, respectively. 336 337 Interestingly, Baguerizo et al. did attempt to find a zero-hysteresis curve for Eq. 9 and Eq. 10 which might represent the true equilibrium. They used the 338 curve to calculate an alternative standard entropy for C₆As₃H₁₃ and found it 339 to be 1132.5 J·K⁻¹·mol⁻¹. This is in fact quite close to the value of 1079.7 J·K⁻¹ 340 ¹·mol⁻¹ estimated from the volume-based method here. This is an important 341 outcome, as it indirectly confirms the validity of the zero-hysteresis approach 342 343 chosen by Baquerizo et al. [32] in order to define the equilibrium properties of meta-ettringite. Nevertheless, for reasons not discussed in [3], the zero 344 345 hysteresis data are currently not included in Cemdata18.

346 3.1.2 tricarboaluminate

According to Fig. 3, it also seems that the data point for $C_6Ac_3H_{32}$ lies slightly above Eq. 6. Although the difference seems small on the scale of the graph, it is around 150 J·K⁻¹·mol⁻¹, which is significant and beyond the uncertainty level of Eq. 6 [25]. It is known that $C_6Ac_3H_{32}$ is metastable with respect to 351 C_4AcH_{11} ; thus, studies have paid less attention to the thermodynamic 352 properties of $C_6Ac_3H_{32}$ [9,10]. For instance, *Thermoddem* includes no 353 thermodynamic data for this phase. Nevertheless, Matschei *et al.* [22] 354 estimated the standard entropy of $C_6Ac_3H_{32}$, which is used in [3], by 355 employing the reference reaction in Eq. 15:

$$C_6Ac_3H_{32} + 3Cc \rightarrow C_6As_3H_{32} + 3Cs$$
 (15)

where $\Delta_r S^{\circ}$ is assumed to be zero and the standard entropies of C₆As₃H₃₂, 356 Cc and Cs are 1900 J·K⁻¹·mol⁻¹, 93 J·K⁻¹·mol⁻¹ and 107 J·K⁻¹·mol⁻¹, 357 respectively. This led to a standard entropy of 1858 $J \cdot K^{-1} \cdot mol^{-1}$ for C₆Ac₃H₃₂. 358 A possible reason for the observed discrepancy might reside in the value of 359 molar volume given for this phase in [3] being inconsistent with the hydration 360 level of 32H₂O. That molar volume was calculated by Thomas et al. [22] using 361 the unit cell parameters given in Taylor's book [34]. To test this hypothesis, 362 we use Eq. 15 but replace C₆Ac₃H₃₂ and C₆As₃H₃₂ by their 30H₂O water 363 content counterparts. Taking 1792.4 J.K⁻¹.mol⁻¹ as the standard entropy of 364 $C_6As_3H_{30}$ (reported in [3] for this phase), the standard entropy of $C_6Ac_3H_{30}$ 365 would be 1750.4 J·K⁻¹·mol⁻¹ which is closer to the estimate from Eq. 6 (1709.7 366 J·K⁻¹·mol⁻¹). Nevertheless, the exact reason for the observed inconsistency 367 368 is not easy to identify at this stage, as the water contents of carbonate AFt phases are still subject to some uncertainty. 369

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371 *3.1.3 thaumasite*

372 Another hydrate that is worthwhile to discuss here is thaumasite. Two values have been reported for the standard entropy of thaumasite, but they differ by 373 about 40 J·K⁻¹·mol⁻¹. Cemdata [3] reports 897.1 J·K⁻¹·mol⁻¹, whereas Blanc 374 et al. gave 941.5 J·K⁻¹·mol⁻¹ [10] although the molar volumes are identical in 375 both compilations. The former value, shown in Fig. 3, agrees well with Eq. 6, 376 and it was originally calculated by Matschei et al. [35] using the solubility 377 378 products of phase-pure thaumasite measured at several temperatures. On the other hand, Blanc et al. [10] approximated the entropy following the 379 method used by Schmidt *et al.* [36], assuming a fictive reaction with $\Delta_r S^\circ = 0$ 380 involving seven compounds of known entropies (including amorphous SiO₂). 381 However, as discussed earlier, the assumption of $\Delta_r S^\circ = 0$ should be used with 382 high caution, as this method is susceptible to errors propagation depending 383 on the type and number of compounds chosen. The reference reaction 384 proposed by Schmidt et al. [36] is rather long with an unusually high number 385 of compounds, making it even more prone to errors. Since the value obtained 386 by Matschei et al. [35] is more consistent with Eq. 6, it seems reasonable to 387 infer that their value is more accurate, compared to that proposed in 388 Thermoddem [10]. 389

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391 3.2 Layered double hydroxides: AFm phases and hydrotalcite

Figure 5 shows the extent to which the standard molar entropies and formula unit volumes of AFm phases included in *Cemdata* [3] can be described by Eq. 6. All phases appear to match the linear trend, although slight deviations from Eq. 6 can be seen. All data points of C_4AH_n lie above Eq. 6 with some of the entropy values exceeding Eq. 6 by as much as 100 J·K⁻¹·mol⁻¹. Some of the M_xAH_n phases seem to have been underestimated, compared to Eq. 6.



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Fig. 5: Standard molar entropy versus formula unit volume of several AFm
hydrates and M_xAH_n phases. Entropies are from [3]. Formula unit volumes were
calculated using Eq. 5, using the molar volumes tabulated for these phases in
Tables 1 and 3 of [3]. The solid line represents Eq. 6. Subscript *n* denotes water
content, and *x* is the M/A ratio; here *x* can be 4, 6 or 8.

405 3.2.1 C₄AH_n

With respect to C_4AH_n phases, Lothenbach *et al.* [37] calculated the standard entropy of C_4AH_{19} using the solubility product of this phase reported in the literature. To do this, the authors fitted a three-term approximation to the temperature dependence of the solubility product, Eq. 16, using experimental solubility data:

$$\log K_{\rm T} = 0.4343 {\rm R}^{-1} ({\rm A}_0 - {\rm A}_2 {\rm T}^{-1} + {\rm A}_3 {\rm lnT}), \tag{16}$$

411 where K_T is the solubility product at temperature *T*, and A_0 , A_2 and A_3 are;

$$A_{0} = \Delta_{r} S_{298}^{\circ} - \Delta_{r} C_{p_{298}}^{\circ} (1 + \ln T_{0})$$
(17)

$$A_{2} = \Delta_{r} H_{298}^{\circ} - \Delta_{r} C_{p_{298}}^{\circ} T_{0}$$
(18)

$$A_{3} = \Delta_{r} C_{p_{298}}^{\circ}$$
(19)

412 where T_0 is 298.15 K, and $\Delta_r S_{298}^{\circ}$, $\Delta_r C_{p_{298}}^{\circ}$ and $\Delta_r H_{298}^{\circ}$ represent the change 413 of entropy, heat capacity and enthalpy of reaction, respectively, at standard 414 temperature of 298.15 K. Considering Eq. 20 which represents the formation 415 of C₄AH₁₉, the standard entropy of C₄AH₁₉ can be deduced by fitting Eq. 16 416 to the measured solubility products. $\begin{array}{c} C_4 A H_{19} \rightarrow 4 C a^{2^+} + 2 A I (OH)_{4^-} + 6 O H^- + 12 H_2 O, \eqno(20) \\ \end{array}$

421 A reason for the discrepancy observed between Eq. 6 and the C₄AH₁₉ data 422 point in Fig. 5 could be that the solubility data gathered from the literature by Lothenbach et al. [37] were inaccurate or misleading. It is important to note 423 424 that C₄AH₁₉ is metastable with respect to C₃AH₆ and CH at 20 °C and higher 425 temperatures. Although the authors of [37] were careful of this phenomenon and chose solubility data of samples that had been reacted for more than 10 426 months at temperatures below 20 °C, it might have still been the case that 427 the very old samples had started to decompose to C₃AH₆ and CH or were 428 429 subject to carbonation. It follows that fitting Eq. 12 to those data would have led to propagation of errors. If so, these errors would also have carried over 430 into the entropy data for C_4AH_{11} and/or C_4AH_{13} , which were calculated from 431 that of C₄AH₁₉ by Baguerizo et al. [38] using the same method they used for 432 ettringite (as outlined in Section 3.1) but with reactions Eq. 21 and Eq. 22 433 434 instead:

$$C_4 A H_{11} + 2 H_2 O \to C_4 A H_{13}$$
 (21)

$$C_4AH_{13} + 6H_2O \rightarrow C_4AH_{19}$$
 (22)

Alternatively, the standard heat capacity of C_4AH_{19} might be the origin of error since heat capacity is a key parameter involved in the fitting equations (*i.e.* Eq. 18 and Eq. 19). Nevertheless, it is difficult to verify this hypothesis without newly measured heat capacity data.

- 439
- 440 3.2.2 M_xAH_n

441 Regarding the M_xAH_n solid solutions, Myers *et al.* [21] estimated the standard 442 entropies of M_4AH_{10} , M_6AH_{12} and M_8AH_{14} by adjusting the standard entropy 443 of $Mg_{0.74}AI_{0.26}(OH)_2(CO_3)_{0.13} \cdot 0.39H_2O$ using the additivity method (Eq. 1), with 444 $Mg(OH)_2$ and $MgCO_3$ as constituents. For example, Eq. 23 shows how to 445 build up the standard entropy of M_4AH_{10} :

$$S_{M_{4}AH_{10}}^{\circ} = 2\left(\frac{1}{0.26}S_{Mg_{0.74}Al_{0.26}(OH)_{2}(CO_{3})_{0.13}\cdot0.39H_{2}O} - 0.5S_{MgCO_{3}}^{\circ} - 0.346S_{Mg(OH)_{2}}^{\circ}\right)$$
(23)

446 Equation 6 almost fits the standard entropy of M_4AH_{10} , as shown in Fig. 5, 447 but this is not the case for M_6AH_{12} and M_8AH_{14} . There could be two reasons 448 for this; either the molar volumes for these two phases are not accurately 449 reported in the datasets used [3,21], or errors in the standard entropies of 450 compounds used in Eq. 23 have led to the underestimation of entropy. 451 The first could be unlikely. The molar volumes reported for M_xAH_n in [3,21] were based on the theoretical estimations according to the model outlined by 452 Richardson in [39,40]. Richardson's model is based on a set of experimental 453 data and is carefully formulated by taking into account how the crystal lattice 454 parameters change when a fraction of trivalent cations replaces divalent 455 456 cations in M_xAH_n . Therefore, this leaves little doubt that the molar volumes calculated by Myers et al. [21] according to Richardson's model are relatively 457 458 accurate.

459 The errors arising from the value of standard entropies used in Eq. 23 could also be improbable. The standard entropies of magnesium carbonate and 460 hydroxide are known to high precision, and Myers et al. [21] adopted the 461 standard entropy of Mg_{0.74}Al_{0.26}(OH)₂(CO₃)_{0.13}·0.39H₂O from [41] where the 462 authors determined entropy by using the third law and low-temperature heat 463 capacity measurements. Although it is not easy to verify the accuracy of their 464 heat capacity data, it is sensible to assume that the derived standard entropy 465 for this phase is sufficiently reliable, in particular that the standard entropy 466 and volume of M_4AH_{10} is in agreement with Eq. 6. 467

In spite of the above, the observed inconsistencies could be due to the choice of compounds used in Eq. 23. To test this hypothesis, the standard entropies of M_xAH_n is recalculated here but with a different fictive reaction than that in Eq. 23. To that end, it is useful to revisit the chemical formula and structural constituents of layered double hydroxides, as given in Eq. 24:

$$\left[\mathsf{M}_{(1-x')}^{2+}\mathsf{M}_{x'}^{3+}(\mathsf{OH})_{2}\right](\mathsf{A}^{n'-})_{\frac{x'}{n'}}\cdot m'\mathsf{H}_{2}\mathsf{O}$$
(24)

where M^{2+} and M^{3+} are divalent and trivalent cations. If the ratio of cations 473 $(M^{2+}/M^{3+})=Q$, then x'=1/(1+Q). $A^{n'-}$ is the anion (e.g. OH⁻) in the interlayer 474 region and m' is the number of water molecules per cation. Hence, for one 475 main layer of M₈AH₁₄; Q=4, x'=1/5, n'=1 and m'=3/10. The structure of the 476 cation layer in M_xAH_n phases consists of a series of edge-sharing octahedra 477 where cations M^{2+} and M^{3+} are distributed with a particular order depending 478 on the x' value. A portion of hydroxyl groups are part of octahedra, with the 479 rest being in the form of hydroxyl ions in the interlayer region to balance the 480 extra electrostatic charge resulting from M^{2+} substitution by M^{3+} . With this 481 in mind, it might make more sense to write the standard entropy of M_xAH_n in 482 Eq. 23 as an additive quantity of Mg(OH)₂, Al(OH)₃ and H₂O entropies, as in 483 principle these hydroxides and water are the main constituents of M_xAH_n. In 484 485 this way, the estimated entropy could be more consistent with M_xAH_n crystal 486 structure. Therefore, for M₈AH₁₄ for which the highest discrepancy was 487 observed in Fig. 5, one may write:

$$S_{M_8AH_{14}}^{\circ} = 2x' S_{Mg(OH)_2}^{\circ} + 2S_{Al(OH)_3}^{\circ} + 3S_{H_2O}^{\circ}; x'=4$$
(25)

488 where the standard entropies of Mg(OH)₂, Al(OH)₃ and H₂O are assumed to 489 be $63.1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, 140 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (taken from Table 1 in [21]) and 69.92 490 $J \cdot K^{-1} \cdot mol^{-1}$ (Table D1 in [3]). This gives $S^{\circ}_{M_8AH_{14}}$ =994.65 $J \cdot K^{-1} \cdot mol^{-1}$ which is 491 close to the estimation from Eq. 6; *i.e.* 1034.9 $J \cdot K^{-1} \cdot mol^{-1}$.

492 An important issue worth discussing regarding Eq. 25 is the choice of entropy value for AI(OH)₃. The standard entropy value used above for this hydroxide 493 is for the so-called microcrystalline Al(OH)₃. This phase is less crystalline 494 than gibbsite and so has a higher standard entropy [42]. It turns out that in 495 order to reach the same value of entropy for M₄AH₁₀ as Eq. 23 (and to ensure 496 497 that the M₄AH₁₀ data point matches Eq. 6 with the molar volume calculated in [21]), $S^{\circ}_{Al(OH)_3}$ in Eq. 25 should be adjusted to that of gibbsite (*i.e.* 70 J·K⁻ 498 ¹·mol⁻¹ [22]). This gives $S_{M_4AH_{10}}^{\circ}$ = 602.2 J·K⁻¹·mol⁻¹ which is near 549 J·K⁻¹ 499 ¹·mol⁻¹ estimated with Eq. 23. Blanc et al. [10] also estimates an intermediate 500 value of 552 J·K⁻¹·mol⁻¹ using similar compounds as those in Eq. 23 although 501 they make no estimates for higher x' values, and so it is not possible to make 502 direct comparison for those phases. The fact that $\dot{S_{Al(OH)_3}}$ value needs to be 503 changed depending on x' might well be due to the change of AI^{3+} state in the 504 505 crystal structure of M₄AH₁₀ compared to M₈AH₁₄; this could be an interesting area of future research. 506

507 These findings and the variation of estimations from different fictive reactions 508 prove that the *additivity method* is sensitive to the selection of constituents 509 and that in cases this may lead to inconsistent estimations. To avoid these, 510 it would be useful if future studies measure the standard entropy of M_xAH_n 511 phases using the third law and heat-capacity measurements.

512

513 3.3 Fe-bearing phases

The standard molar entropies of all iron-bearing phases included in [3] are presented in Fig. 6, along with their formula unit volumes. Somewhat surprisingly, the data points of only two of these ten phases are in reasonable agreement with Eq. 6; these are Fe-ettringite ($C_6Fs_3H_{32}$) and C_4FH_{13} .



518

Fig. 6: Standard molar entropy versus formula unit volume of several Fe-bearing
hydrates. Entropies are from [3]. Formula unit volumes were calculated using Eq. 5
and the molar volumes tabulated for these phases in Table 1 of [3]. The solid line
represents Eq. 6.

523 Möschner *et al.* [43] estimated the standard entropy of Fe-ettringite using Eq. 524 26 and the assumption that $\Delta_r S^\circ = 0$ for this reaction:

$$C_6Fs_3H_{32} + A \rightarrow C_6As_3H_{32} + F$$
 (26)

where the major hydrate with a similar structure to Fe-ettringite is Al-ettringite
which was shown earlier (Fig. 3) to be well described by Eq. 6. Therefore, it
comes as no surprise that Fe-ettringite is also consistent with Eq. 6.

The data point shown for C₄FH₁₃ in Fig. 6 lies slightly below the prediction of 528 Eq. 6. Dilnesa et al. [44] derived the standard entropy of this phase by fitting 529 Eq. 12 to its solubility products measured experimentally at temperatures of 530 20 and 50 °C. The use of Eq. 12 has caused the underestimation of the 531 standard entropy by about 100 J·K⁻¹·mol⁻¹. Two factors could have been at 532 the origin of this discrepancy, which is worthy of discussion although less 533 marked than in the case of some of the other Fe-bearing hydrates. First, the 534 authors of [44] measured the solubility product of C₄FH₁₃ at 20 °C for samples 535 which were left to react for one or two years; however, in the case of the 50 536 °C samples, they were kept for seven days only which might have been 537 538 insufficient for reaching equilibrium conditions. Second, some uncertainty 539 could be associated with the fitting of Eq. 12 to the measured data since only two temperatures were studied. 540

The rest of the data points shown in Fig. 6 are related to several AFm and 541 hydrogarnet phases, containing Fe³⁺ isomorphously substituted for Al³⁺. As 542 for C₄FH₁₃, the entropy of these phases were all derived experimentally by 543 Dilnesa et al. via Eq. 16 and solubility measurements [44-47]. There are no 544 other data reported for these hydrates to allow for direct comparison between 545 studies, except for C₄FsH₁₂. Dilnesa et al. [46] derived the standard entropy 546 547 of C₄FsH₁₂ and found it to be 1430 J·K⁻¹·mol⁻¹. This value lies markedly above 548 Eq. 6 (provided that there are no errors associated with the molar volume of this phase reported in [3], but this should be unlikely as the molar volume reported for C₄FsH₁₂ is quite close to that of C₄AsH₁₂). This value disagrees with 833 J·K⁻¹·mol⁻¹ that was estimated theoretically by Blanc *et al.* [10] using a reference reaction based on isomorphous Fe/Al substitution into C₄AsH₁₂ and the assumption that $\Delta_r S^\circ = 0$. Their estimated value is much closer to the prediction of Eq. 6 (*i.e.* 842.4 J·K⁻¹·mol⁻¹).

It is difficult at this stage to identify the exact cause of large discrepancies 555 between the Eq. 6 trend and the studies of Dilnesa et al., and this certainly 556 requires further experimental investigation. Since Dilnesa et al. relied on 557 solubility data to calculate the standard entropy, there may be uncertainty in 558 559 the solubility products measured for these phases, e.g. some influence of 560 unreacted C₂F which was employed as the starting material but persisted in 561 the samples after a long reaction time. This is an important finding and needs 562 attention, especially as commonly-used cements (such as Portland cement) 563 may contain more quantities of iron-bearing phases in the future [48].

It should be mentioned that the presence of iron in minerals causes magnetic disorder, which is known to affect the heat capacity and so standard entropy. However, the extent of such changes is expected to be in the order of few entropy units only [16,17], but the discrepancies observed in Fig. 6 are as high as 600 J·K⁻¹·mol⁻¹. Therefore, it is highly unlikely that the magnetic effect of iron is the reason why the entropy data for iron-bearing phases are so deviated from Eq. 6.

571

572 3.4 Hydrates with varying water content

573 From the preceding discussion, it is clear that the estimation of the standard 574 entropies of hydrates with varying water content has in many cases been 575 problematic. Here, we employ Eq. 8, which was originally developed for ionic 576 hydrates only, to examine whether it is suitable to apply it to cement-related hydrates. However, the key issue that needs attention is the state of water 577 molecules in hydrated crystals. Overall, the bonding state of water with the 578 crystal lattice constituents can affect the lattice vibration modes and hence 579 580 the standard heat capacity and entropy of the crystal. In general, water can 581 occur in three forms in cement hydrates: (i) crystal water, in which water is in 582 the form of OH; (ii) coordination water, in which water molecules are bound 583 to the constituents of the lattice; or (iii) zeolitic water, in which water molecules are not bound to the lattice, but fill in the vacancies only. In the 584 original derivation of Eq. 8, the constant m refers to the coordination water 585 only, given that the hydrates studied by Jenkins and Glasser [31] contained 586 this form of water in their structures. With respect to the thermodynamic 587 modelling of cements, hydrates involving in reactions whereby crystal water 588 589 is removed are not of interest, as dehydroxylation to such an extent would 590 transform the hydrate to a completely different compound. Therefore, we

591 propose that it suffices to use Eq. 8 as long as the change of water content 592 concerns the coordination (and zeolitic) water state.

Fig. 7 compares points calculated using Eq. 8, in which the value of $\theta_{S_{non}^{\circ}}$ is 593 40.9 J·K⁻¹·mol⁻¹·(H₂O molecule)⁻¹ [31], against the gradient of standard 594 entropies (as a function of water content) for several AFt, AFm and 595 596 hydrogarnet phases: C_6AsH_m , C_4AsH_m , C_2ASH_m (or $C_4A(AS_2)H_m$), C_4AH_m and C₄Ac_{0.5}H_m where η in Fig. 7 denotes the number of water molecules in 597 coordination and zeolitic states. All gradients are presented as a function of 598 η , which was calculated by subtracting the number of bound hydroxyl groups 599 in the hydrate structure from the total number m of water molecules in the 600 formula of each crystal. The number of bound hydroxyls for C₆AsH_m, C₄AsH_m, 601 $C_4A(AS_2)H_m$, C_4AH_m and $C_4Ac_{0.5}H_m$ are 6, 6, 5, 7, and 7 respectively, 602 603 according to the structures described in [32,38,49]. All standard entropies 604 used in Fig. 7 are based on experimental derivations and fit the entropy-605 volume relationship in Fig. 3 or Fig. 5. The standard entropies of C₆As₃H₉ and C₆As₃H₁₃ derived experimentally in [32] are not shown in Fig. 7, as they 606 are for non-equilibrium conditions. 607

11 can be seen from Fig. 7 that all calculated gradients follow Eq. 8 although there are slight deviations from the linear trend. This could be due to the possible errors in the correlation of entropy data from one hydration state to another, but the striking observation is that if the value of m is correctly selected based on crystal chemistry, it is possible to predict and/or compare the standard entropies at different hydration levels. Our finding here further reinforces the estimation method proposed by Jenkins and Glasser [29,31].



615

616 **Fig. 7:** Gradient of standard entropies (based on the definition in Eq. 8) as a 617 function of the number η of molecular (coordination or zeolitic) waters per formula 618 unit, shown for several AFt, AFm and hydrogarnet phases. The entropy values of 619 C₆As₃H₉ and C₆As₃H₁₃ are not included here, as they are for non-equilibrium 620 conditions.

621

622

623 3.5 Silicate hydrate solid solutions

Figure 8 shows the standard molar entropies and formula unit volumes of solid solution models used in [3] to describe some of the alkali-earth silicate hydrates forming during the hydration of Portland and other cements. It is immediately evident that many of the data points are not well described by Eq. 6.

The data points for CSH-II are inconsistent with Eq. 6. The standard entropy of the CSH-II model originates from [9] where the authors used solubility data to calculate entropy, and estimated $\pm 50 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ uncertainty in their values; this is, to a degree, consistent with the observations from Fig. 8.

All ECSH-1 and ECSH-2 phases from [50,51] are well described by Eq. 6, 633 634 except for C_{0.83}SH_{1.83}, CS_{0.6}H_{1.1} and SrSH₂. The standard entropy data for 635 these phases were developed in [50,51] where the authors used the additivity method of Eq. 1 (with constituents being in the form of oxide and water) and 636 molar volumes were derived using gram-formula masses and an assumed 637 638 dry bulk density; any of which could be the source of the discrepancy of these data from Eq. 6. It should be noted that the accurate determination of water 639 contents and molar volumes of specific hydrous silicates is complex and still 640 641 prone to significant uncertainty.

For CSHQ, CNASH and CSH3T models of silicate hydrates, there are points 642 643 that are far below Eq. 6. The reasons for these are also not easy to identify, 644 as both the standard entropies and molar volumes were estimated in the reference studies [20,52]; these are the end-members of thermodynamic 645 models for complex solid solutions, and so in general they were not actually 646 synthesised as pure phases in any of those studies. If the source of error is 647 648 the molar volume of any given end-member, then this needs immediate attention as the change of volume as a result of formation or decomposition 649 of silicate hydrates can influence the porosity and durability of cementitious 650 materials containing these hydrates. 651



652

Fig. 8: Standard molar entropy versus formula unit volume of a variety of alkali-653 earth silicate hydrate solid solutions. Entropies were retrieved from [3], but they 654 were originally calculated in [9], [20], [51], [50], [52], and [53]. Formula unit volumes 655 were calculated using Eq. 5 and the molar volumes given in Table 1 of [3]. The 656 657 solid line represents Eq. 6.

3.5 Zeolites 658

659 For zeolites included in Cemdata18 [3], which are zeolite P(Ca), natrolite, chabazite, zeolite X(Na) and zeolite Y(Na), all appear to be well described 660 by Eq. 6 apart from zeolite P(Ca) (see Fig. 9), which is somewhat 661 controversial. In the Thermoddem database, the standard entropy of zeolite 662 P(Ca) is 397 J.K⁻¹.mol⁻¹ which is much closer to Eq. 6 (407 J.K⁻¹.mol⁻¹ with 663 V_{molar}=153 cm³.mol⁻¹), compared to 779 J.K⁻¹.mol⁻¹ in Cemdata18 which was 664 derived originally by Lothenbach et al. in [54]. In both cases, the authors used 665 the solubility product at various temperatures to calculate the standard 666 entropy, and there is a clear difference between the solubility data measured 667 by Lothenbach et al. in [54] and those reported by Blanc et al. [55]. Therefore, 668 it is reasonable to suggest that the origin of the discrepancy lies in the 669 670 measured solubility data.



671

- Fig. 9: Standard molar entropy versus formula unit volume of several zeolites. 672 673 Entropies and the molar volumes are from [3]. Formula unit volumes were 674
 - calculated using Eq. 5. The solid line represents Eq. 6.

675 4. Clinker minerals

676 Figure 10 shows the standard molar entropies of clinker minerals (given in [3]) as a function of their formula unit volumes. The dashed line represents 677 Eq. 7, which evidently fits the entropy and volume data very well. This finding 678 was somewhat expected, as the entropy data of most of the clinker minerals 679 come from the same standard database as was used by Jenkins and Glasser 680 681 [25] to develop their equation. As highlighted earlier, caution must be taken when Eq. 7 is used for modelling different polymorphs of the same mineral, 682 as it is possible that standard entropy is not an increasing function of formula 683 684 unit volume; an example of this was given in Section 2. Nevertheless, Eq. 7 is useful to provisionally estimate the standard entropy of some of the clinker 685 minerals for which thermodynamic data are scarce, such as ve'elimite and 686 ternesite. 687



688

Fig. 10: Standard molar entropy versus formula unit volume of clinker minerals.
Entropies are from [3]. Formula unit volumes were calculated using Eq. 5 and the
molar volumes tabulated for the clinker minerals in Table 1 of [3]. The dashed line
represents Eq. 7. Note that it is unclear in [3] what polymorphs these minerals are,
and as a result this detail is missing here.

694

695 4.1 Standard entropy of ye'elimite and ternesite

Entropy data for ye'elimite and ternesite are scarce in the literature. Hanein *et al.* [2,56,57] derived entropy data of these minerals at high temperatures
from existing vapour pressure measurements, but there is not sufficient data
to accurately extrapolate these down to 298.15 K. Eq. 7 can be helpful here.
The standard entropies of different polymorphs of ye'elimite and ternesite are
estimated and shown in Table 1, using Eq. 7 and their unit cell volumes from
[58–60]. Unit cell volume was converted to formula unit volume via Eq. 27:

$$V_{\rm m} = \frac{V_{cell}}{1000 \,\mathrm{Z}} \tag{27}$$

- where V_{cell} is unit cell volume in Å³ and Z is the number of formula units within the crystallographic unit cell. The estimated entropy values in Table 1 should be verified with careful experimental techniques in the future, but these data can serve as provisional estimates. We attempted to test the accuracy of the entropy value for ye'elimite (see Appendix A for more detail), and it appears
- to be in reasonable agreement with Table 1.
- **Table 1:** Estimated standard molar entropy of orthorhombic ye'elimite (Pcc2) and
 cubic ye'elimite (I43m) and ternesite using Eq. 7

	1				
Crystal name	V _{cell}	Ζ	Reference	Vm	S° ₂₉₈
(symmetry group)	(A^3)		study	(nm ³)	(J·K⁻¹·mol⁻¹)
					estimated
Ye'elimite (Pcc2)	1557.78	4	[58]	0.389	504.5
Ye'elimite (I43m)	789.55	2	[60]	0.394	511.2
Ternesite (Pnma)	1075.12	4	[59]	0.268	352.2

711

712 **5. Conclusions**

Methods to estimate the standard entropy of cement hydrates or clinker 713 minerals are useful for the purpose of thermodynamic modelling, especially 714 to assess the quality of existing entropy data obtained via experiments. This 715 study employed a simple mathematical relationship, established by Jenkins 716 and Glasser [25], to examine the accuracy of standard entropies and molar 717 volumes of cement related substances listed in established thermodynamic 718 719 datasets for cements. The relationship used here relates the standard molar entropy of an inorganic solid to its formula unit volume via a linear equation 720 with known constants. 721

In general, the standard entropies and molar volumes of many cement
hydrates were found to be consistent with Jenkin and Glasser's relationship.
The exceptions to this were:

- 725 two ettringite-group phases with water contents of 9 and $13H_2O$
- 726 magnesium/aluminium layered double hydroxide solid solutions
- almost all Fe-bearing monosulfate and hydrogarnet phases, and
- several calcium silicate hydrate end-members.

729 The entropy data for some of these phases were derived in previous studies by measuring the solubility products at different temperatures and fitting the 730 731 three-term approximation equation of solubility product to those measured 732 solubility data. The fitting equation is a function of standard entropy, and to 733 achieve a desired fitting, the entropy term is the key parameter that needs to 734 be adjusted. In view of this, errors associated with standard entropies can imply inaccuracies in solubility product measurements. Thus, there are now 735 open questions as to whether the measured solubility products for some of 736 737 the phases listed above are reliable. This deserves closer investigation, 738 especially given that the formation or decomposition of most of these phases have important implications for modelling the dimensional stability and/or 739 740 durability of cement systems.

741 The standard entropies for clinker minerals were found to linearly correlate

to their formula unit volumes, consistent with Jenkins and Glasser's equation.

The standard entropy of clinker minerals ye'elimite and ternesite were also

estimated provisionally using the volume-based relationship.

745

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ye'elimite sample.

752

753 Appendix A.

The standard entropy of ye'elimite was experimentally derived using its heat capacity over a range of temperatures and the third law (Eq. 28).

$$S^{\circ}_{298} = \int_{0}^{298.15} \frac{Cp}{T} dt$$
 (28)

756

757 A.1 synthesis of ye'elimite

758 Ye'elimite was synthesised by sintering the stoichiometric mixture of Al₂O₃, CaSO₄ and CaCO₃ (Sigma-Aldrich, ACS reagent, \geq 99%). The reagents were 759 first mixed for five minutes using a mortar and pestle. A few drops of ethanol 760 were also added to the mix to facilitate mixing. The reagents were then left 761 in an oven set at 100 °C for 2 hours to dry. Once the required time had 762 elapsed, the dried mixture was placed into a platinum crucible and subjected 763 to heating at 1250 °C for a period of 20 minutes in a muffle furnace. 764 Thereafter, the sample was removed from the furnace and quenched at room 765 766 temperature. The sample was then homogenised using the mortar and pestle and placed again into the furnace. This process was repeated five times until 767 the resultant material was highly pure ye'elimite. To confirm the purity, X-ray 768 769 diffraction pattern of the sample was recorded over 20 ranging from 5° to 70° 770 with a step size of 0.026° using a Philips Empyrean diffractometer operated at 45 kV and 40 mA. The source of X-ray was Cu K α , and the diffractometer 771 was equipped with a Ge monochromator and a PIXcel1D detector. The 772 773 sample holder was set to rotate at 15 rpm to improve counting statistics. Fig. A.1 shows the X-ray powder diffraction pattern measured for the ye'elimite 774 775 sample. The result of Rietveld analysis (carried out using GSAS software) indicates that the sample is primarily composed of about 97% ye'elimite with 776 777 slight trace of Cs and CA.



778

Fig. A.1: Measured X-ray powder diffraction pattern of synthesised ye'elimite
(shown with dots), indicating the presence of cubic and orthorhombic polymorphs
of ye'elimite (based on [58] and [60], respectively) as well as a slight trace of Cs
(ICSD 16382) [61] and CA (ICSD 602) [62]. The ICSD database search was based
on the recommendations given in [63]. The Rietveld analysis suggests the
following composition: 87.1% orthorhombic and 9.4% cubic ye'elimite, 0.8% Cs
and 2.7% CA (wRp = 8.72).

786 A.2 heat capacity measurements of ye'elimite

787 The heat capacity of ye'elimite was measured using a differential scanning calorimeter (DSC 214 Polyma, NETZSCH) and based on ASTM E1269 [64]. 788 Measurements were conducted in duplicates on 20±0.1 mg sample placed 789 790 in a closed alumina crucible. The sample was cooled down to -170 °C using liquid nitrogen cooling, then kept at a 10-min isotherm and heated up to 30 791 792 °C at 10 K/min. Ideally, the heat capacity should have been measured from temperatures starting from near 0 K in order to ensure that the behaviour of 793 794 the material is captured at low temperatures. However, this was not possible 795 with the available resources in this study; thus, the value calculated here is expected to deviate from its true value. To assess whether deviation due to 796 797 the measurement technique occurred, the heat capacity of K₂CO₃ (ACS 798 reagent, 99%) was also measured as a control.

The measured heat capacity patterns were fitted by a combination of Debye and Einstein functions, given by Eq. 29, which are shown to well describe the heat capacity of solids at temperatures below 300 K [65,66]. The resultant fitting function was then used in Eq. 28 to calculate standard entropy. Here it is assumed that the isobaric and isochoric heat capacities are the same; *i.e.*, volume remains constant throughout the measurements. This assumption is valid in the temperature range studied in this paper [16].

$$C_{p} = mD\left(\frac{\theta_{D}}{T}\right) + nE\left(\frac{\theta_{E}}{T}\right)$$
(29)

$$D\left(\frac{\theta_{\rm D}}{\rm T}\right) = 9R\left(\frac{\rm T}{\theta_{\rm D}}\right)^3 \int_0^{\frac{\theta_{\rm D}}{\rm T}} {\rm y}^4 \frac{{\rm e}^{\rm y}}{[{\rm e}^{\rm y}-1]^2} \, {\rm d}{\rm y}$$
(30)

$$E\left(\frac{\theta_E}{T}\right) = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\frac{\Theta_E}{T}}}{\left[e^{\frac{\Theta_E}{T}} - 1\right]^2}$$
(31)

For Eqs. 29-31, *m*, *n*, θ_D and θ_E are the fitting parameters. *R* is the universal 806 gas constant and T is the temperature in Kelvin. To fit Eq. 29 to the measured 807 data, an algorithm was written in MATLAB incorporating a least-square fitting 808 function. The measured data were fitted from 120 K to 300 K. We chose this 809 range of temperatures as it was noted that the heat capacity data below 120 810 811 K were abnormal and inconsistent with those known for K₂CO₃. As a general rule, the sum of m and n parameters obtained from the fitting process ought 812 to be equal to the number of atoms in the compound's formula [65,66]. For 813 814 example, m + n = 6 for K₂CO₃.

The measured and fitted heat capacity patterns for ye'elimite and K_2CO_3 are shown in Fig. A.2. There are no anomalies in the measured data for K_2CO_3 within the temperature range presented here; however, ye'elimite pattern exhibits a feature around 273 K, which is attributed to the presence of water in the bulk material. This feature was removed from the fitting process by ignoring the measured data between 253 K and 285 K.





Fig. A.2: Measured (dots) and fitted (lines) heat capacity patterns of synthesised
 ye'elimite and K₂CO₃.

The fitting of K₂CO₃ heat capacity data results in a standard entropy of 147.28 J.K⁻¹.mol⁻¹ for this phase, with m + n = 5.989. This value is reasonably consistent with 155.57 J.K⁻¹.mol⁻¹ known for this compound (\approx 5% deviation) [67]. In the case of ye'elimite sample, the standard entropy is found to be 432 J.K⁻¹.mol⁻¹ with m + n = 27.05 (which is close to 27 atoms in its formula). This entropy value is close to the estimates given in Table 1, further validating Eq. 7. The discrepancy (\approx 15%; Pcc2; orthorhombic) is inevitable in the case of our study because the ye'elimite sample contained impurities as well as two
polymorphs, and that the heat capacity data below 120 K were lacking from
the fitting process. In future studies, a purer sample needs be tested and
other types of calorimetry (such as relaxation calorimetry where temperature
can reach as low as near 0 K) may be employed to assess the accuracy of
estimates in Table 1.

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