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Thermodynamic data for cement clinkering

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Abstract

The proportions of cement clinker phases produced by the pyro-processing of a raw-material mix are often predicted through the Bogue equations, established in the 1930s; however, the Bogue approach is limited in its applicability. This presents a challenge as the cement industry is seeking innovative and more environmentally friendly cement clinker formulations and production processes. These often go beyond the limitations of the Bogue equations and more flexible approaches are required. Modern thermodynamic calculations allow this flexibility but rely on databases not freely available and often specialised for other applications. The title paper reviews the thermodynamic data for stoichiometric clinker phases and presents a new dataset. The dataset is validated, and its application demonstrated by case studies. Electronic CSV files containing the data which can be parsed for use with existing Gibbs energy minimisation solvers/software is distributed with this article as supplementary material.

Keywords: Cement; clinker; thermodynamics; dataset; compilation

Cement oxide notation

| Oxide | CaO | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | B ₂ O ₃ | K ₂ O | MgO | Na ₂ O | P ₂ O ₅ | SO ₃ | CO ₂ | TiO ₂ |
|----------|-----|------------------|--------------------------------|--------------------------------|-------------------------------|------------------|-----|-------------------|-------------------------------|-----------------|-----------------|------------------|
| Notation | C | S | A | F | B | K | M | N | P | \$ | c | T |

1 **1 Introduction**

2 Cement is the most manufactured product on earth and its production contributes
3 significantly to greenhouse gas emissions that affect our climate. Carbon dioxide (CO₂)
4 emissions from cement production account for approximately 8% of global manmade CO₂
5 emissions [1]. These emissions are mainly a result of: (1) raw-material (calcium carbonate
6 calcination) emissions, (2) direct fossil fuel emissions (pyro processing), and (3) electricity-
7 related emissions primarily from grinding. Raw-material emissions alone were estimated to
8 be 1.45 GtCO₂ in 2017 [2]. Societal pressures on the cement industry concerning its
9 environmental burden have triggered an increase in the use of alternative fuels and
10 alternative raw materials for cement manufacture [3, 4]. Environmental concerns are also
11 promoting the development of lower-calcium clinker formulations, such as calcium
12 sulfoaluminate cement clinker which contain volatile species and involve gas-solid reactions
13 not normally encountered in Portland cement (PC) clinkering [5].

14 In conventional cement manufacture, limestone is ground and mixed with specified
15 amounts of other raw materials such as siliceous clays and shales, to achieve a target
16 composition. The raw mix is pyro-processed into clinker in rotary kilns with solid
17 temperatures reaching ≈ 1500 °C. The indurated product, termed clinker, is cooled rapidly to
18 preserve, insofar as possible, the high temperature phase assemblage, which is
19 thermodynamically unstable at intermediate temperatures but preserved metastably at
20 lower temperatures due to the energy and mixing barriers. The valuable properties of
21 cement arise from this phase assemblage and its interactions with water.

22 The Bogue equation is often used to estimate clinker phase composition [6]. The calculation
23 assumes that the phase assemblage at the solidus is preserved to ambient, although certain

1 optional features enable corrections, should equilibrium not be reached during pyro
2 processing, for example failure to assimilate free lime (CaO). Input data for the Bogue
3 calculation are based on the stable coexistence of the four-phase assemblage $C_3S-C_2S-C_3A-$
4 C_4AF . Variations in temperature, kiln atmosphere, and the presence of minor components,
5 often in the order of several percent by weight total, can influence clinker development but
6 are not included in Bogue calculations and their role is best assessed by thermodynamic
7 calculations.

8 Bogue-type equations for alternative cements, e.g., calcium sulfoaluminate- based clinkers,
9 have also been developed but have proven unreliable, mainly due to the volatile nature of
10 the sulfur component causing a strong dependence of the stable phases on kiln
11 atmospheres. As process atmospheres are not included in Bogue calculations, the role of
12 complex vapour transport is also not included; however, thermodynamic calculations have
13 enabled theory and experimental data to be reconciled [7-9].

14 The thermodynamics of cement chemistry have been studied since Le Chatelier [10];
15 however, much of the literature has focused on hydration where the thermodynamic data
16 are typically valid for temperatures in the range of liquid water. Moreover, calculations
17 often must avoid following equilibrium paths as the occurrence and persistence of
18 metastable phases dominates these reactions. This contrasts with clinkering where a close
19 approach to the high temperature equilibrium is frequently attained.

20 Thermodynamic tools used for clinker equilibrium calculations include MTDData [11] and
21 FactSage [12]. The compiled databases associated with these packages are not freely
22 available but, fortunately, most stoichiometric thermodynamic data of phases related to
23 cement are recorded in the literature. Solid solution models are often used to correlate the

1 properties of complex solid phases, such as the clinker ferrite phase ($C_2(A,F)$). Melt formation
2 is desirable during clinkerisation to provide a medium/flux for reactive transport/mixing.
3 Therefore, solid and liquid solution models provide the best approach to calculating clinker
4 equilibrium; however, the data required to support calculation of solution models and of
5 solid-liquid-gas equilibria are as yet incomplete and existing models are often parametrized
6 using data derived for other industries (such as metallurgy) and cannot be directly re-
7 purposed for use in cement clinkering.

8 The utilization in cement kilns of alternative fuels and wastes that can contain or develop
9 volatile species, coupled with the development of alternative binders, present new
10 challenges. For example, the role of the kiln atmosphere in cement production becomes
11 more important; the partial pressure of gases such as CO_2 , O_2 , and SO_2 can greatly influence
12 mass transfer and reaction progression within the kiln [13-16]. This is particularly true for
13 volatile components such as calcium carbonate (Cc), calcium sulfate ($C\$,$ spurrite (C_5S_2c),
14 ye'elimite ($C_4A_3\$,$ ternesite ($C_5S_2\$,$ and many alkali chlorides, sulfates, and carbonates.

15 The title study suggests gas phase thermodynamic data that can be used to simulate process
16 atmospheres and reviews, compiles, and presents a thermodynamic database of
17 stoichiometric phases, which can be used for heat balances and limited predictive modelling
18 of clinkering. The database is evaluated and its importance, limitations, and required
19 additional developments are discussed.

1 **2 Survey of thermodynamic data for cement clinkering**

2 **2.1 Gas phase thermodynamic data**

3 The National Aeronautics and Space Administration (NASA) developed a thermodynamic
4 data-set (NASA CEA database) [17] of gaseous species and solid phases used in rocket
5 combustion calculations. It is a parameterisation of many historical collections and includes
6 extrapolation as high as 20,000K for many gas species. It forms the foundation of many
7 combustion models (e.g., GRI MECH [18]) and is suited for modelling atmospheric reactions
8 at kiln temperatures. This database also contains necessary solid and liquid thermodynamic
9 data for salts and simple oxides. As this database also contains reference data for elements
10 which have been extensively reviewed over decades, this compilation is used as the
11 reference against which database of the title study is constructed/compared.

12 **2.2 Solid and liquid phase thermodynamic data**

13 Other compilations [19-27] contain thermodynamic data for pure solid and liquid phases;
14 however, most are outdated as new material properties have been recently measured and
15 existing thermodynamic data have been re-evaluated. Babushkin and his co-authors [19]
16 were pioneers in compiling relevant thermodynamic data and their work contains
17 thermodynamic data for the major PC clinker phases. However, transcription [19]
18 introduces errors such as the heat capacity coefficients for C_3A , which differ from those in
19 the original [28]; and have been propagated into other compilations [29]. Indeed, the
20 authors of the title paper believe that the current limited success in applying free-energy
21 minimisation techniques to clinker calculations may have its roots in similar error
22 propagation.

1 Haas Jr et al. published a thermodynamic data compilation [20] which has proven very
2 useful [30]. Data for many of the species involved in cement clinkering are compiled;
3 however, it contains a number of errors as some of the expressions given do not agree with
4 the sample data (where available) or with reference points; e.g., data for H_2O , $\text{AlO}(\text{OH})$, and
5 Si. The readily available portable digital scan of this benchmark compilation [20] also seems
6 to have a missing negative sign in the enthalpy constant (a_2) for CAS. There are
7 uncertainties in the data validity regions, for example; the reported valid temperature
8 ranges for C_3AS_3 differ between the provided functions and the calculated tables. The data
9 for polymorphs of C_2S are differentiated in this compilation; however, hatrurite and other
10 polymorphs of C_3S (the major phase in Portland cement) are undifferentiated probably
11 because the data available either at that time (or now) are not known.

12 A thermodynamic data compilation by Kelley [26] contains data for cement phases not
13 included in Ref. [19]. Most of Kelley's data [26] are taken from experiments carried out by
14 the United States Bureau of Mines; however, numerous misprints occur (e.g. in the data for
15 C_2P) and unnecessary numerical rounding was introduced in equation coefficients which
16 significantly affects the accuracy of any subsequent calculations carried out using their
17 expressions. Data extracted from [26] are best reviewed after checking with the source.

18 NIST has tabulated reference thermodynamic properties [25] at standard conditions of
19 298.15 K and 1 bar for numerous species relevant to cement clinkering. This publication also
20 corrects some previous experimental measurements, such as the heats of formation of
21 calcium aluminates [31] by preferring data from Huber and Holley [32] who also re-
22 evaluated the heat of formation of CaO . This tabulation is used as the main source for
23 reference data in the title study, but one notable exception is the standard heat of

1 formation for CA_2 . Contradictory experimental values for the heat of formation of CA_2 are
2 presented [25, 27, 33, 34]. The database presented in the title study was used to reproduce
3 the phase diagram of the C – A binary system [35] and the best fit data of Petaev [34] is
4 selected.

5 Hillert et al. [36] encountered difficulties when performing equilibrium calculations for the
6 C–S binary system using available literature data and therefore reassessed the data for
7 rankinite; these data [36] are adopted in the title study in preference to those of Haas Jr et
8 al. [20].

9 More recent data-sets that contain thermodynamic data for species related to cement
10 clinkering were developed by Holland and Powell [21, 37]. These datasets are internally
11 consistent but do not contain data for the major cement clinker phases.

12 **2.3 The calcium alumino-ferrite phase**

13 The calcium alumino-ferrite ($C_2(A, F)$) composition found in cement clinkers should be
14 modelled thermodynamically as a solid solution as the A/F ratio varies. Moreover, and
15 owing to fractionation during cooling, the ferrite is often compositionally zoned. Babushkin
16 et al. [19] presented thermodynamic data for C_4AF ; however, the sources cited for their data
17 is not readily available and could not be checked. The standard enthalpy of formation of
18 C_4AF has been derived by Thorvaldson et al. [38] and Zhu et al. [39] derived its Gibbs energy
19 data over wide temperature range.

20 A significant typographical error related to the CF phase discovered in the literature is a typo
21 of 10^{-5} instead of 10^5 in Ref. [40] for the heat content of CF (crystal). Apart from the heat of
22 formation of C_6A_2F available in Refs. [41, 42], the authors are unaware of other

1 stoichiometric thermodynamic data for calcium aluminoferrites. As this study does not
2 consider solid solution models, assuming that C_4AF is the stable ferrite solid solution under
3 clinker processing conditions allows a single dataset to be used up to the eutectic; 1338 °C^a
4 for PC clinker [43] and 1275 °C^a for calcium sulfoaluminate clinker [44].

5 **3 Compiled thermodynamic data set**

6 The thermodynamic data set presented here have slightly different reference pressures (1
7 bar or 1 atm) but they all have the same reference temperature (298.15 K) and reference
8 state, i.e., the enthalpy of formation of the elements at the standard temperature and
9 pressure is zero for O₂, Si, H₂, Al, Ca, Fe, etc. No corrections are made for the differences
10 between reference pressures; however, all the gas data are at the same reference pressure,
11 1 atm. In addition, no accommodation is made for changes in the temperature standard or
12 isotopic composition. Reference elemental data used in the source literature have been
13 reviewed but generally no adjustment was needed. Formula weights for unit conversion
14 were estimated using the CIAAW^b isotopic abundances [45] along with the AME2012 atomic
15 mass evaluation [46, 47].

16 The thermodynamic model assumes ideal gases and incompressible solid phases. This allows
17 the thermodynamic data to be fit using a heat capacity polynomial,

18
$$C_{p,\alpha}(T) = \sum_i C_{i,\alpha} T^i,$$

^a These reported temperatures should only be used as guides and the actual clinker melting temperatures will vary depending mainly on iron, alumina, and alkali content of the mix.

^b Isotopic abundances were taken from the table given by CIAAW. This data was scraped on 29/07/2015.
<https://www.ciaaw.org/isotopic-abundances.htm>

1 where $C_{p,\alpha}$ is the temperature-dependent heat capacity of a pure component α and $C_{i,\alpha}$ is a
 2 fitting constant for the i^{th} power of temperature. Varying powers appear depending on the
 3 source data set with as many as nine terms for NASA CEA data. Two additional fitting
 4 constants for the entropy, s_{α}^0 , and enthalpy, h_{α}^0 , allow the chemical potential at standard
 5 conditions in pure phases, μ_{α}^0 , to be fit as follows,

$$6 \quad \mu_{\alpha}^0(T) = C_{-1,\alpha}(\ln T + 1) - C_{0,\alpha} T(1 - \ln T) + h_{\alpha}^0 - T s_{\alpha}^0 + \sum_{i \neq -1,0} \frac{C_{i,\alpha}}{i(i+1)} T^{i+1}.$$

7 To model pressure and mixing effects in gas phases, the ideal gas approximation is used,

$$8 \quad \mu_{\alpha}(T, \{x_{\alpha}\}^{N_s}) = \mu_{\alpha}^0(T) + R T (\ln (p/p_0) + \ln x_{\alpha}) \quad (\text{for an ideal gas}),$$

9 where p is the system pressure, p_0 is the reference pressure at which the heat capacity data
 10 was collected, and x_{α} is the mole fraction of species α . For incompressible phases, such as
 11 liquids and solids, the following model is used,

$$12 \quad \mu_{\alpha}(T, \{x_{\alpha}\}^{N_s}) = \mu_{\alpha}^0(T) + v_{\alpha}(p - p_0) + R T \ln x_{\alpha} \quad (\text{for an incompressible solid/liquid}),$$

13 where v_{α} is the species molar volume which is assumed to be zero for this iteration of the
 14 database. In addition, all solid phases are assumed to be pure and liquids/melts and gases
 15 are assumed to mix ideally. This is a significant approximation and thus results where melts
 16 are predicted should be treated with scepticism.

17 Table I presents the phases considered in this work whose thermodynamic data have been
 18 taken from a single source. The thermodynamic data taken from Haas Jr et al. [20] were
 19 compared with the tables of calculated data (also contained within Ref. [20]) and some
 20 enthalpy constants have been corrected where necessary (see Table I for details). Table II
 21 presents the thermodynamic data taken from Haas Jr et al. [20] but including the

1 corrections made which go beyond a simple enthalpy correction. Table III presents the
2 thermodynamic data and its source for phases whose data have been compiled and fitted
3 from separate sources for the title study. Table IV presents data for CA_2 , CA_6 , and A_3S_2 taken
4 from separate single sources, and are not compatible with the format of Table III. Where
5 reference values for species are not provided by Haas Jr et al. [20], they are calculated from
6 the provided tabulated data in [20]. The thermodynamic data taken from the NASA CEA and
7 Holland and Powell databases are not presented in the title paper and are readily available
8 online.

9 Thorvaldson et al. [38] derived the standard enthalpy of formation of C_4AF and Zhu et al.
10 [39] presented its Gibbs energy over the temperature range 298 – 2000 °C. Coupling this
11 information [39] with the readily available thermodynamic data of the oxides, a new set of
12 thermodynamic data for C_4AF is derived and presented in this work (see Table III). The C_4AF
13 data derived in the title paper is preferred over the data by Babushkin [19]. This is justified
14 by the observation in Ref. [13] where clinker equilibrium calculations using the Babushkin
15 data predict that C_4AF is never stable, which is contradictory to well-known experimental
16 observations [35]; C_4AF is stable using the data in the title study.

17 Data for some boron-containing phases are provided in Table III; these were initially
18 compiled due to industrial interest in making boron-containing calcium sulfoaluminate
19 cement; however, these values should be used cautiously as no simulations or validations
20 including these phases have been conducted in the course of the title study.

21

22

1 Table I: Species considered in the title study whose thermodynamic data were taken from a single source. Values displayed
 2 between vertical bars (| |) represent the number of polymorphs available in the database.

| Ref. | Phase | Species |
|------|----------------|--|
| | <i>Liquids</i> | H ₂ O, MgCO ₃ , KAlO ₂ , Na ₂ CO ₃ , Na ₂ O, K ₂ O, Na ₂ SO ₄ , K ₂ CO ₃ , K ₂ SO ₄ , K ₂ Si ₂ O ₅ , K ₂ SiO ₃ , MgSiO ₃ , CaSO ₄ , CaCO ₃ , B ₂ O ₃ |
| [17] | <i>Solids</i> | CaCO ₃ , Mg ₂ SiO ₄ , Fe ₂ O ₃ 2 , MgCO ₃ , KAlO ₂ , Na ₂ CO ₃ 3 , Na ₂ O 3 , NaAlO ₂ 2 , K ₂ O 3 , Na ₂ SO ₄ 3 , K ₂ CO ₃ 2 , K ₂ SO ₄ 2 , MgO, K ₂ Si ₂ O ₅ 3 , K ₂ SiO ₃ , MgSiO ₃ 3 , CaSO ₄ 2 , MgTiO ₃ , Mg ₂ TiO ₄ , MgTi ₂ O ₅ , Ti ₃ O ₅ 2 , TiO ₂ , TiO 3 , Ti ₂ O ₃ 2 , Ti ₄ O ₇ , B ₂ O ₃ |
| [20] | <i>Solids</i> | AlO(OH) ^a 2 , Al(OH) ₃ , CaAl ₂ SiO ₆ , CaAl ₂ Si ₂ O ₈ , CaAl ₂ Si ₃ O ₁₀ (OH) ₂ ^a , CaAl ₂ SiO ₇ , Ca ₃ Al ₂ Si ₃ O ₁₂ , Al ₂ Si ₄ O ₁₀ (OH) ₂ , Al ₂ Si ₂ O ₅ (OH) ₄ 3 , Al ₂ O ₃ , Al ₂ SiO ₅ 3 , Ca ₂ Al ₃ Si ₃ O ₁₂ ^a , CaAl ₄ Si ₂ O ₁₀ (OH) ₂ ^a , CaO, CaSiO ₃ 2 , Ca ₂ SiO ₄ 4 , Ca ₃ SiO ₅ , SiO ₂ 2 |
| | <i>Liquids</i> | NaAlSi ₃ O ₈ , CaAl ₂ Si ₂ O ₈ , CaMgSi ₂ O ₆ , Mg ₂ Si ₂ O ₆ , Fe ₂ SiO ₄ , Mg ₂ SiO ₄ , KAlSi ₃ O ₈ , Al ₂ SiO ₅ |
| [21] | <i>Solids</i> | Ca ₅ Si ₂ CO ₁₁ , CaMgC ₂ O ₆ , Ca ₅ Si ₂ C ₂ O ₁₃ , NaAlSi ₃ O ₈ 2 , CaMgSi ₂ O ₆ , Mg ₂ Si ₂ O ₆ , KAlSi ₃ O ₈ , NaAlSi ₂ O ₆ , Fe ₂ SiO ₄ , Fe ₂ Si ₂ O ₆ |
| [34] | <i>Solids</i> | CaAl ₁₂ O ₁₉ , CaAl ₄ O ₇ |
| [48] | <i>Solid</i> | Al ₆ Si ₂ O ₁₃ |
| [36] | <i>Solid</i> | Ca ₃ Si ₂ O ₇ |

3 ^a denotes species whose enthalpy constants have been corrected.

Table II: Thermodynamic data (including corrections) adapted from Ref. [20]. T_{min} and T_{mix} show the temperature range over which the data is valid. Units of C_p are in $J\ mol^{-1}\ K^{-1}$. This table is provided in comma-separated values (CSV) format in the supplementary material (S1).

| Species | Polymorph | $h(298.15K)$ (J/mol) | T_{min} (K) | T_{max} (K) | $C_{-2,\alpha}$ | h_{α}^0 | $C_{-0.5,\alpha}$ | s_{α}^0 | $C_{0,\alpha}$ | $C_{1,\alpha} \times 10^3$ | $C_{2,\alpha} \times 10^5$ |
|--|---------------------|-------------------------|------------------|------------------|-----------------|----------------|-------------------|----------------|----------------|----------------------------|----------------------------|
| A | Corundum | -1675711 | 200 | 1800 | 0 | 17321 | -2465.18 | -1550.92 | 233.004 | -19.5913 | 0.94441 |
| 0.5×AH | Diaspore | -999456 | 200 | 800 | 243069 | 15671.57 | -1730.02 | -1021.486 | 150.556 | 0 | 0 |
| | Boehmite | -990420 | 200 | 800 | 777111 | 30456.1 | -2592.74 | -1426.36 | 206.903 | 0 | 0 |
| 0.5×AH ₃ | Gibbsite | -1293334 | 200 | 800 | 661704.4 | 25824.3 | -2667.64 | -1513.072 | 220.8509 | 30.06455 | 0 |
| AS | Kyanite | -2594270 | 200 | 1800 | 0 | 23795.1 | -3557.46 | -2234.89 | 336.114 | -12.98 | 0 |
| | Andalusite | -2590270 | 200 | 1800 | 2287510 | 87578.7 | -6754.36 | -3712.02 | 543.227 | -103.545 | 6.68935 |
| | Sillimanite | -2587774 | 200 | 1800 | 0 | 16676.2 | -3164.868 | -2050.871 | 313.4705 | -9.47081 | 0 |
| AS ₂ H ₂ | Dickite | -4118475 | 200 | 1000 | 3804450 | 137944.8 | -11195.31 | -6190.732 | 908.3598 | -105.6632 | 0 |
| | Halloysite | -4101028 | 200 | 1000 | 1936712 | 84151.4 | -8729.481 | -5153.86 | 772.3004 | -72.58844 | 0 |
| | Kaolinite | -4119800 | 200 | 1000 | 1491950 | 73551.4 | -8278.64 | -4973.66 | 749.175 | -67.7102 | 0 |
| AS ₄ H | Pyrophyllite | -5642023 | 200 | 1000 | 6069358 | 231127 | -17742.85 | -9850.236 | 1454.512 | -396.0932 | 39.71889 |
| C | Lime | -635094 | 200 | 1800 | -255577 | -7058 | -431.99 | -420.068 | 71.6851 | -3.08248 | 0.223862 |
| CS | Wollastonite | -1634766 | 200 | 1800 | 0 | 3025.9 | -1729.6 | -1212.413 | 192.7733 | -9.115107 | 0.4413189 |
| | Cyclo-wollastonite | -1627614 | 200 | 1800 | -9739.076 | -2474.4 | -1372.368 | -1024.504 | 167.2547 | -0.3621589 | 0 |
| C ₂ S | gamma | -2316534 | 200 | 1150 | -2360066 | -73871.8 | 1656.378 | 239.1441 | 0 | 106.5862 | -8.150119 |
| | alphaprime | -2309710 | 950 | 1750 | 0 | -48354.4 | 0 | -805.6381 | 161.6203 | 0 | 1.8897 |
| | alpha | -2317614 | 1650 | 1800 | 0 | -59510 | 0 | -1052.325 | 199.6 | 0 | 0 |
| | beta | -2306697 | 200 | 1000 | 0 | -2120.9 | -2094.286 | -1538.485 | 249.689 | 0 | 0 |
| C ₃ S | | -2933130 | 200 | 1800 | -65259.72 | -4046 | -2766.085 | -2053.31 | 333.9197 | -2.325287 | 0 |
| CAS | Ca-Al Clinopyroxene | -3298900 | 298.15 | 2000 | -2720240 | -29896.3 | -2185.82 | -1966.33 | 322.848 | 0 | 0 |
| CAS ₂ | Anorthite | -4227800 | 200 | 1800 | 3185910 | 110301 | -9449.81 | -5358.32 | 800.971 | -146.45 | 10.5663 |
| C ₂ AS | Gehlenite | -3981700 | 200 | 1800 | 1510470 | 51954.3 | -6274.33 | -3822.22 | 588.351 | -67.1533 | 3.89086 |
| C ₃ AS ₃ | Grossular | -6636300 | 200 | 1600 | 1770800 | 90229.2 | -10707.7 | -6532.38 | 985.362 | -96.6435 | 3.35314 |
| C ₂ AS ₃ H | Prehnite | -6193631 | 298.15 | 1250 | 2755226 | 96995.98 | -10560.51 | -6270.704 | 946.022 | -57.53272 | 0 |
| 0.5×C ₄ A ₃ S ₆ H | Zoisite | -6891117 | 200 | 1250 | 0 | 34330.83 | -8148.754 | -5391.475 | 834.6223 | -19.84469 | 0 |
| CA ₂ S ₂ H | Margarite | -6239610 | 200 | 1250 | 0 | 46846.6 | -8427.438 | -5406.581 | 826.504 | -25.14555 | 0 |
| S | alpha | -910699 | 200 | 844 | 0 | 1058 | -777.338 | -529.232 | 83.2101 | 10.9962 | 0 |
| | Beta | -911268 | 844 | 1800 | 0 | -18010.85 | 0 | -300.994 | 58.9107 | 5.0208 | 0 |

Table III: The sources and thermodynamic data of species included in the title study. Where a symbol follows the species, this denotes whether the species is a liquid (L) or it denotes the polymorph of the crystal phase (α , β , or γ); where no symbol follows the species, this implies the species is a crystal with no polymorphism. The range in which the data are valid are represented by T_{min} and T_{max} . Units of C_p are in $J\ mol^{-1}\ K^{-1}$. This table is provided in comma-separated values (CSV) format in the supplementary material (S2).

| Species | $s(298.15K)$ (J/mol/K) | Ref | $h(298.15K)$ (J/mol) | Ref | $C_{0,\alpha}$ | $2C_{1,\alpha}$ $\times 10^3$ | $-C_{-2,\alpha}$ $\times 10^{-5}$ | h_α^0 | T_{min} (K) | T_{max} (K) | $s(T_{min})$ (J/mol/K) | Ref. |
|---|---------------------------|------|-------------------------|------|----------------|----------------------------------|--------------------------------------|--------------|------------------|------------------|---------------------------|------|
| C ₁₂ A ₇ α | 1046.8 | [25] | -19430000 | [25] | 1263.40064 | 137.026 | 231.3752 | -466478.34 | 298 | 1310 | | [28] |
| C ₁₂ A ₇ β | 1046.8 | [25] | -19430000 | [25] | 956.12768 | 205.93648 | 0 | -164544.17 | 1310 | 1700 | 2022.5456 | [28] |
| C ₂ B (L) | 145.1 | [25] | -2734410 | [25] | 285.3488 | 0 | 0 | -70082 | 1585 | 1900 | 410.032 | [49] |
| C ₂ B α | 145.1 | [25] | -2734410 | [25] | 183.05 | 24.058 | 44.72696 | -71717.94 | 298 | 804 | | [49] |
| C ₂ B β | 145.1 | [25] | -2734410 | [25] | 218.78136 | 5.0208 | 0 | -77960.47 | 804 | 1585 | 190.12096 | [49] |
| C ₂ F | 188.78 | [25] | -2139280 | [25] | 247.86016 | 0 | 48.86912 | -90290.72 | 298 | 1750 | | [40] |
| C ₂ F (L) | 188.78 | [25] | -2139280 | [25] | 310.4528 | 0 | 0 | -45940.32 | 1750 | 1850 | 497.51944 | [40] |
| C ₃ A | 205.9 | [25] | -3587800 | [25] | 260.57952 | 9.58136 | 50.24984 | -95399.38 | 298 | 1800 | | [28] |
| C ₃ B | 183.7 | [25] | -3429080 | [25] | 236.14496 | 21.79864 | 54.47568 | -90730.04 | 298 | 1760 | | [49] |
| C ₃ B (L) | 183.7 | [25] | -3429080 | [25] | 393.296 | 0 | 0 | -148113.6 | 1760 | 1900 | 538.0624 | [49] |
| C ₃ S ₂ | 210.37 | [36] | -3951761 | [36] | 251.375 | 29.491 | 48.262 | -93756 | 293 | 2500 | | [36] |
| C ₄ AF | 427.28 | [39] | -5076016 | [38] | 374.42616 | 36.4008 | 0 | -114871.2 | 298 | 1863 | | [19] |
| CA | 114.22 | [25] | -2326300 | [25] | 150.624 | 12.46832 | 33.30464 | -57186.91 | 298 | 1800 | | [28] |
| CB | 104.85 | [25] | -2030960 | [25] | 129.78768 | 20.41792 | 33.76488 | -51835.58 | 298 | 1435 | | [49] |
| CB (L) | 104.85 | [25] | -2030960 | [25] | 258.1528 | 0 | 0 | -117695.92 | 1435 | 1700 | 283.80072 | [49] |
| CB ₂ | 134.7 | [25] | -3360250 | [25] | 214.80656 | 40.08272 | 71.79744 | -91688.18 | 298 | 1260 | | [49] |
| CB ₂ (L) | 134.7 | [25] | -3360250 | [25] | 444.7592 | 0 | 0 | -198907.36 | 1260 | 1800 | 438.52504 | [49] |
| CF | 145.35 | [25] | -1520340 | [25] | 164.93328 | 9.95792 | 15.31344 | -55203.7 | 298 | 1510 | | [40] |
| CF (L) | 145.35 | [25] | -1520340 | [25] | 229.7016 | 0 | 0 | -21045.52 | 1510 | 1800 | 355.34712 | [40] |
| CT α | 93.64 | [25] | -1660600 | [25] | 127.48648 | 2.84512 | 27.99096 | -47651.58 | 298 | 1530 | | [50] |
| CT β | 93.64 | [25] | -1660600 | [25] | 134.01352 | 0 | 0 | -46848.25 | 1530 | 1800 | 202.2964 | [50] |
| CTS | 129.2 | [25] | -2603300 | [25] | 177.35976 | 11.58968 | 40.29192 | -67425.16 | 298 | 1670 | | [51] |
| CTS (L) | 129.2 | [25] | -2603300 | [25] | 279.4912 | 0 | 0 | -79454.16 | 1670 | 1811 | 389.65592 | [51] |
| FS | 145.2 | [25] | -1479900 | [25] | 152.75784 | 19.58112 | 28.0328 | -56689.02 | 298 | 1490 | | [52] |
| FS (L) | 145.2 | [25] | -1479900 | [25] | 240.58 | 0 | 0 | -50015.54 | 1490 | 1724 | 339.15504 | [52] |
| FT | 105.86 | [53] | -1246400 | [27] | 116.60808 | 9.12112 | 20.053912 | -42304.42 | 298 | 1640 | | [50] |
| FT (L) | 105.86 | [53] | -1246400 | [27] | 199.1584 | 0 | 0 | -61262.13 | 1640 | 1800 | 267.65048 | [50] |
| M ₂ S | 95.14 | [25] | -2174000.12 | [25] | 149.82904 | 13.68168 | 35.64768 | -57843.8 | 298 | 1808 | | [52] |

| | | | | | | | | | | | | |
|------------------|--------|------|-------------|------|-----------|----------|----------|-----------|------|------|-----------|------|
| M ₂ T | 109.33 | [25] | -2165200 | [25] | 150.45664 | 17.86568 | 28.82776 | -56115.81 | 298 | 1800 | | [54] |
| MA | 80.63 | [25] | -2299900.03 | [25] | 153.9712 | 13.3888 | 40.91952 | -60822.81 | 298 | 1800 | | [28] |
| MF α | 123.8 | [25] | -1428400 | [25] | 88.11504 | 93.26136 | 0 | -34564.02 | 298 | 665 | | [40] |
| MF β | 123.8 | [25] | -1428400 | [25] | 189.9536 | 0 | 0 | -61044.56 | 665 | 1230 | 139.36904 | [40] |
| MF γ | 123.8 | [25] | -1428400 | [25] | 107.40328 | 28.40936 | 0 | -1033.45 | 1230 | 1800 | 257.35784 | [40] |
| MT | 74.56 | [25] | -1572800 | [25] | 118.36536 | 6.86176 | 27.32152 | -45065.86 | 298 | 1800 | | [50] |
| MT ₂ | 127.28 | [25] | -2509600 | [25] | 170.20512 | 19.2464 | 30.7524 | -62772.55 | 298 | 1800 | | [54] |
| NT (L) | 121.67 | [25] | -1591199.89 | [25] | 196.2296 | 0 | 0 | -16484.96 | 1303 | 1600 | 290.5788 | [55] |
| NT α | 121.67 | [25] | -1591199.89 | [25] | 105.35312 | 43.34624 | 0 | -35266.94 | 298 | 560 | | [55] |
| NT β | 121.67 | [25] | -1591199.89 | [25] | 108.5748 | 35.564 | 0 | -32969.92 | 560 | 1303 | 92.08984 | [55] |

Table IV: Revised thermodynamic data for CA₂, CA₆, and A₃S₂. The temperature range over which the data are valid are represented by T_{min} and T_{max}. Units of Cp are in J mol⁻¹ K⁻¹. This table is provided in comma-separated values (CSV) format in the supplementary material (S3)

| Species | $s(298.15K)$ (J/mol/K) | $h(298.15K)$ (J/mol) | $C_{0,\alpha}$ | $C_{-0.5,\alpha}$ | $C_{-2,\alpha}$ $\times 10^{-7}$ | $C_{-3,\alpha}$ $\times 10^{-9}$ | $C_{1,\alpha} \times 10^2$ | $C_{2,\alpha} \times 10^5$ | T_{min} (K) | T_{max} (K) | Ref |
|-------------------------------|---------------------------|-------------------------|----------------|-------------------|-------------------------------------|-------------------------------------|----------------------------|----------------------------|------------------|------------------|------|
| A ₃ S ₂ | 254.3872 | -6848057 | 853.677 | -9818.19377 | 0.547237701 | 0 | 0.64178016 | -1.92257126 | 298 | 2000 | [48] |
| CA ₂ | 172 | -4007000 | 310.64 | -395.88 | -1.4152 | 1.6974 | 1.04 | 0 | 200 | 2000 | [34] |
| CA ₆ | 391.7 | -10715000 | 818.02 | -579.13 | -3.8774 | 4.3798 | 1.846 | 0 | 200 | 2000 | [34] |

1 Together, these tabulations make up a thermodynamic database for cement clinkering
2 equilibrium calculations.

3 **4 Validation**

4 In order to calculate the clinker products resulting from a particular raw feedstock and
5 processing environment we consider equilibrium where the temperature and pressure are
6 equal among all phases and the entropy is at a maximum using the solver described by Hanein
7 et al. [13]. For fixed pressure and temperature, the Gibbs energy $G = \sum_{\alpha} N_{\alpha} \mu_{\alpha}$ is minimised
8 until the difference between iterations is less than 0.001% by mass for each component. The
9 IPOPT package is used to provide the minimisation [56].

10 **4.1 Clinker mineral composition**

11 The thermodynamic data are first validated here against thermodynamic clinkering calculations
12 carried out by Hökfors et al. [57] where the equilibrium calculations were performed at 1360 °C
13 followed by Scheil cooling ^c; the raw meal composition was: 77.36% CaCO₃, 13.73% SiO₂, 2.93%
14 Al₂O₃, 1.843% Fe₂O₃, 1.83% MgO, 0.85% K₂O, 0.14% Na₂O, 1.08% SO₃, 0.153% TiO₂, 0.06% Cl,
15 0.02% P₂O₅, and 0.01% ZnO (by mass). This same raw meal and temperature were used in the
16 title study to calculate equilibrium; but, P₂O₅, ZnO, and Cl were neglected owing to insufficient
17 thermodynamic data. The initial atmospheric composition is air and the input mass of air are
18 assumed to be 1 g per gram of raw meal. The results are compared to those calculated by
19 Hökfors et al. [57] and to the original Bogue calculations, Table V.

^c Scheil cooling is a constrained equilibrium approach, used in metallurgy for the redistribution of phases in a melt during cooling. The approach assumes that once a component has partitioned from the liquid to the solid phase, it does not undergo further reaction.

1 Table V: A comparison of clinker equilibrium calculations between results from this work, literature, and Bogue calculations (all
 2 in wt. %). (C-A-F) represents the sum of all calcium aluminate ferrite solid solutions reported by Hökfors et al. [57]

| Phase | Equilibrium [57] | Scheil cooled [57] | Bogue calculations* | Title study |
|-------------------------------------|------------------|--------------------|---------------------|-------------|
| C ₃ S | 72.3 | 72.3 | 75.2 (80.3) | 76 |
| C ₂ S (stoichiometric) | - | - | 2.9 (3.1) | 3.4 |
| C ₂ S (solid solution) | 3.5 | 6.2 | - | - |
| (C-A-F) | 0 | 14.5 | - | - |
| C ₃ A | - | - | 7 (7.5) | 7.2 |
| C ₄ AF | - | - | 8.5 (9.1) | 8.6 |
| M | 2.3 | 3 | - | 2.8 |
| CT | - | - | - | 0.4 |
| Na ₂ SO ₄ (L) | - | - | - | 0.1 |
| K ₂ SO ₄ (L) | - | - | - | 1.4 |
| CaO | 1.3 | 2 | - | 0 |
| Salt melt | 0.8 | 1.3 | - | - |
| Oxide melt | 19.7 | 0 | - | - |

* Values in parenthesis are normalised to 100%

3

4 Direct comparison of the results of the present study with those of Hökfors et al. [57] and the
 5 Bogue calculation are complicated by a number of factors. Several versions of Bogue exist
 6 differing in assumptions although all are based on phase relations at the solidus temperature.
 7 But different assumptions can be made about the course of cooling and its impact on phase
 8 development. For example, Hökfors et al. [57] defines two states, 1) a high temperature state
 9 “equilibrium” consisting of solid phase(s) and melt, and 2) an assumption about cooling (Scheil
 10 cooling) where melt crystallises without reaction with previously formed crystals.

11 It is known that “melt” invariably crystallises under industrial conditions, giving rise to belite,
 12 ferrite and aluminate, etc; these cumulate with crystal totals formed above the solidus. This
 13 condition accords most closely with Scheil cooling which allows additional belite to form (see
 14 Table V).

1 What can be concluded is that the Bogue results, derived from experiment, and those of the
2 title study, derived from first principals using thermodynamic data are in accord. The Bogue
3 weight percentage calculations do not initially add up to 100%; this is due to the raw meal
4 containing species which are not accounted for in the general four-phase (C_3S , C_2S , C_3A , C_4AF)
5 Bogue assumption. Although calculations presented here do not take into account solid
6 solutions, the final clinker products can still be deduced assuming that there are no significant
7 phase changes during rapid cooling other than polymorphic transformations which are
8 isochemical. This holds true for pure compounds but in solid solutions exsolution may occur
9 upon cooling. The predicted formation of alkali sulfates is justified as clinkers are well known to
10 contain alkali sulfates [58]. The agreement between the predictions appears to validate the use
11 of a purely stoichiometric thermodynamic approach for traditional clinkering.

12 The Bogue equations capture the output of the thermodynamic calculations as indeed they
13 should; however, thermodynamic simulations can be taken beyond the limitations of the Bogue
14 equations and examples are given below.

15 **4.2 Phase evolution during clinkering**

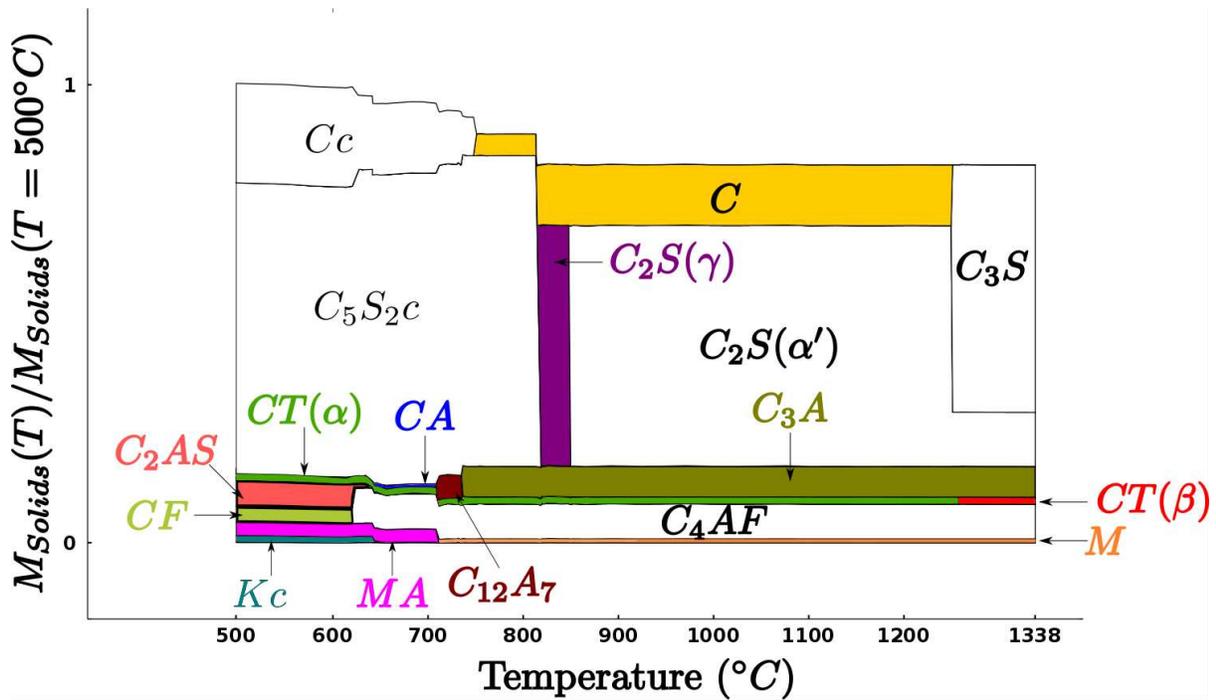
16 A Portland cement clinker composition, taken from Ref. [35], is: 67.0% CaO, 22.0% SiO₂, 5.0%
17 Al₂O₃, 3.0% Fe₂O₃, 1.0% MgO, 1.0% K₂O, and 1.0% TiO₂ by mass. Calculations are performed to
18 show the equilibrium evolution of phases during heating and contrast this with observations.

19 The reactions at lower temperature are sensitive to process atmosphere and the composition
20 during clinkering depends on the partial pressures of oxygen and carbon dioxide. For this
21 calculation example, the atmosphere was assumed to have been generated from the

1 combustion of methane (natural gas) in 15% excess air. It was also assumed that 50% of the CO₂
2 released by the process arises from calcination of limestone and 50% from the combustion of
3 fuel. Thus, the atmospheric composition input to calculation per gram raw meal is calculated as
4 follows: 0.01g O₂, 0.98 g N₂, 0.22 g CO₂, and 0.18 g H₂O. The clinker solid phases at equilibrium
5 for the temperature range 500 – 1338 °C are presented in Fig. 1. The simulations are truncated
6 at the expected solidus, 1338 °C [43]. Mass loss in Fig. 1 is due to mass transfer from solid to
7 gas phase thus, explaining the disappearance of the alkali at the higher temperatures.

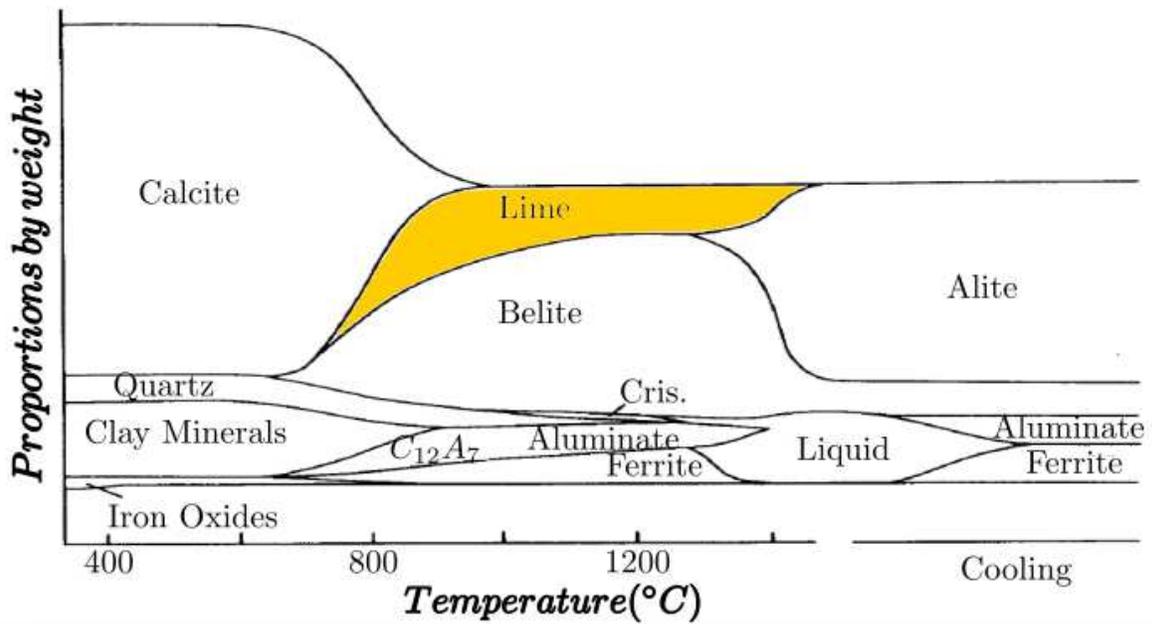
8 Equilibrium calculations were performed at intervals of 2°C and this generates a stepped
9 appearance. In reality, these transitions are smooth owing to kinetic effects. Due to the lack of
10 kinetics/dynamics in the model, real transitions will often depart from predictions based on
11 equilibrium.

12 Actual observations in modern kilns are complicated by the two stages used; decarbonisation
13 reactions are essentially complete in the suspension preheater and subsequently, the reaction
14 is finished in the rotary kiln where sampling points are limited. The sequence of observed phase
15 changes is shown in Fig. 2, which is an often-reproduced textbook diagram [35] and relates to
16 older single stage operation. While still broadly applicable to modern practice, important
17 differences may occur with the suspension preheater operating at different CO₂ partial
18 pressures than the kiln.



1

2 Figure 1: The equilibrium cumulative mass distribution of the solid and liquid phases (relative to the total mass at $T = 500\text{ }^{\circ}\text{C}$)
 3 calculated for PC clinker production over the temperature range $500 - 1338\text{ }^{\circ}\text{C}$. Observed mass loss is due to mass transfer to
 4 the gas phase at calculated equilibrium.



5

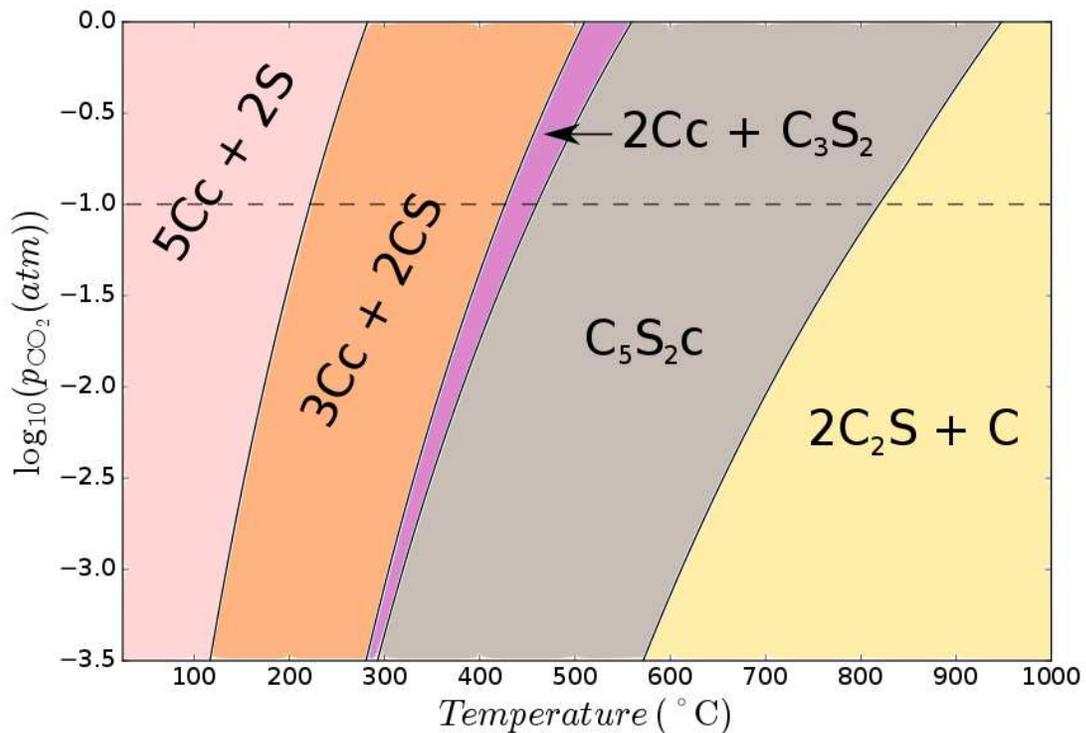
6 Figure 2: Qualitative representation of expected phase variations during PC clinkering. Adapted from Ref. [35].

1 If we contrast the practical observation with equilibrium, spurrite (C_5S_2C) is predicted but does
2 not appear except in small quantities and its occurrence is often confined to slow moving meal
3 adhering to the kiln walls or forming rings in single-stage kilns [59-62]. Thus, the equilibrium
4 model developed here reproduces only in part the qualitative phase chemistry with deviations
5 especially apparent at lower temperatures, <1000 °C. If radical changes in clinkering are made,
6 as for example if fluidised bed combustion were used, the course of mineral formation during
7 clinkering could change radically from that of the “observed” model, Fig 2.

8 Zhang et al. [63] report the experimentally calculated heat of formation from the elements at
9 298.15 K of spurrite to be -5845.5 ± 10.9 kJ/mol (oxide melt solution calorimetry); this is in
10 agreement with the value calculated (-5847.08 kJ/mol) from the Holland and Powell database
11 [21] and used for calculations in the title study . Also, the entropy of spurrite at 298.15K and 1
12 bar reported by Holland and Powell (332.0 kJmol⁻¹K⁻¹) agrees with that reported by Robie and
13 Hemingway [23] (331.0 kJmol⁻¹K⁻¹).

14 The decomposition temperature of spurrite is reported to be between 750 – 917 °C depending
15 on CO₂ partial pressure [59, 61] and the literature experimental observations are in accord with
16 the decomposition temperatures shown in Fig 3. Bolio-Arceo and Glasser [59] observed the
17 formation of spurrite at 900 °C in a tube furnace with a CO₂ partial pressure of 0.89–0.95 atm;
18 this is also in agreement with calculated spurrite stability. Spurrite decomposition temperature
19 measurements by Glasser [60] give temperatures of spurrite to be 790 ± 5 °C and 912 ± 5 °C at
20 CO₂ partial pressures of 0.08 atm and 1 atm respectively; these values are in near agreement
21 although slightly lower than those of the title study at 805 °C and 945 °C respectively.

1 The remarkable thermal stability of spurrite contrasted with its apparent failure to appear in
 2 normal clinkering, have led to additional calculations of its stability; results are shown in Fig 3.
 3 Temperature and CO₂ partial pressure are the key variables. Fig. 3 shows only the composition
 4 of the individual solid phases with the result that the bulk composition is not constant. The
 5 slope of the boundary curves show how progressive decarbonisation occurs as temperature
 6 and CO₂ pressure change.



7

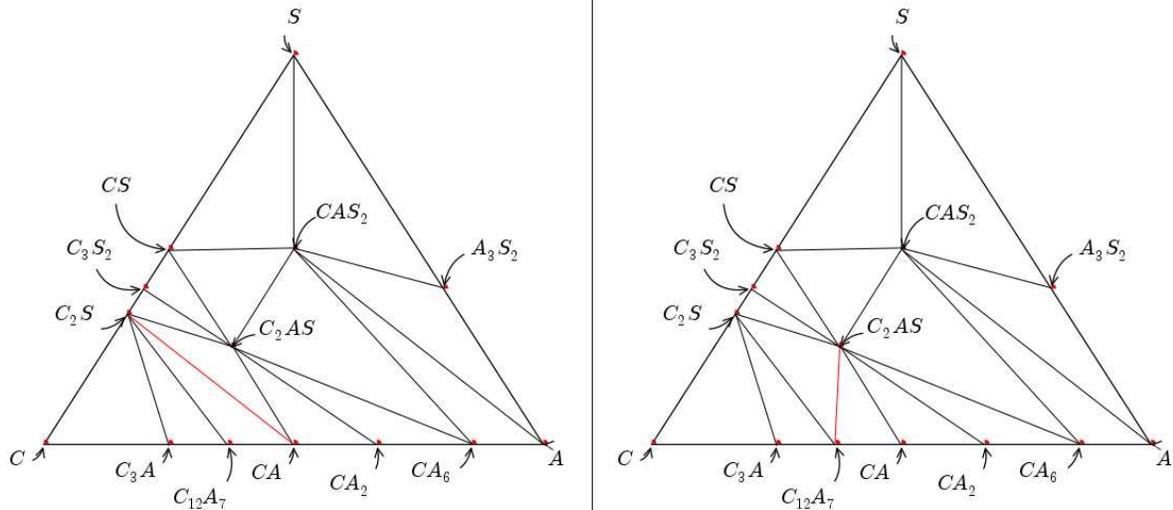
8 *Figure 3: Spurrite stability between 30 - 1000° C as a function of partial pressure of CO₂. The grey broken line denotes where the*
 9 *CO₂ partial pressure is 0.1 atm (~10% by volume); the CO₂ pressure during cement manufacture is usually above this line.*

10 During cement manufacture, incoming air and raw materials have a low CO₂ partial pressure
 11 but in zones where calcium carbonate decomposition occurs, and in contact with combustion
 12 gas from fossil fuels, the CO₂ pressure rises. Combustion atmospheres nominally have ≈ 4 – 13%
 13 CO₂ (depending on fuel) but, decomposition of calcium carbonate in the suspension heater may

1 increase CO₂ concentrations locally to ≈40%. The grey broken line in Fig. 3 shows the
2 conventional CO₂ pressure in the kiln (10%v or 0.1 atm); the CO₂ pressure is normally at or
3 above this isobar. The curvature of the field boundaries shows the upper temperature limit of
4 stability of spurrite which is enhanced in CO₂-rich atmospheres as may occur in as oxyfuel
5 combustion [64, 65] which typically generate atmospheres rich in CO₂.

6 **4.3 The CaO-Al₂O₃-SiO₂ at subsolidus temperatures**

7 Data for some important phases in the CaO-Al₂O₃-SiO₂ system are yet to be validated. The
8 model of the title study has been used to reproduce the isothermal phase diagrams [35, 66] for
9 the C-A-S system up to 1250 °C. The calculated phase compatibility of the C-A-S system is
10 temperature dependent. Fig. 4 shows how the calculations for the interval: 1000 °C – 1100 °C
11 (left) differs from the calculation for 1150 °C - 1250 °C (right). These diagrams are largely in
12 agreement with the literature [35, 66] except for some minor discrepancies (see red lines in Fig.
13 4). However, Sahu and Majling [66] report the phase compatibility agrees with Fig. 4 (left) for
14 the temperature range 1000 – 1200 °C. Another discrepancy is with the experimental results
15 observed in Ref. [15] where the phase compatibility at 1250 °C agrees with Fig. 4 (left) rather
16 than Fig. 4 (right) for 1250°C. It is of course possible that some substitution occurs in the
17 relevant solids and influences the observed coexistences but the free energy difference
18 between phases approaches zero so any error in the numerical values of the free energy will
19 strongly influence the calculation. It is clear that better data are needed.



1

2 *Figure 4: Ternary phase diagrams (mole) of the C-A-S system produced from the database compiled in the title paper. The*
 3 *diagram on the left is produced at temperatures of 1000° C, 1050° C, and 1100° C. The diagram on the right is produced at*
 4 *temperatures of 1150 °C, 1200 °C, and 1250 °C. Above 1250 °C, alite (C₃S) is stabilised.*

5 5 Discussion and future work

6 An improved database for calculation of thermodynamic functions of cement systems is
 7 presented and application examples are given. Nevertheless, some knowledge gaps remain,
 8 and predictions made from thermodynamic model may need experimental verification before
 9 being accepted; however, calculation certainly reduces the amount of experimental work
 10 needed. The next steps are to extend the database and to deal with solid solution formation as
 11 well as melting and freezing processes; this will include the dependence of the Al/Fe ratio in the
 12 ferrite phase on temperature. These tasks are not trivial, models often need approximations
 13 when dealing with solution phases, solid or liquid, and in its present state, the database will not
 14 predict element fractionation between phases or the existence of metastable transitions such
 15 as formation of beta belite during cooling.

1 The developed model does include the process atmosphere and enable calculation of gas-solid
2 reactions; the calculation of spurrite stability is an example of how. The development of novel
3 cements, such as calcium sulfoaluminates can be driven by thermodynamic calculations
4 showing, for example, conditions under which ye'elimite is stable [67]. The feasibility of making
5 calcium sulfoaluminate was piloted by thermodynamic calculation before trials were made [7,
6 9, 68]. Likewise the conditions for ternesite formation were delineated by calculation [8].
7 Additionally, the database/model has been used to predict compatibility regions for formation
8 of alite-calcium sulfoaluminate clinkers [14]. Thermodynamic data for ye'elimite and ternesite
9 are not included in the compilation of the title study as they are still being developed; however,
10 current available data can be found in Refs. [8, 67, 69-71].

11 Future work will also need to focus on thermodynamic data relevant to assessing the role of
12 minor components such as Mg, Ti, F, Cl, Zn, P, Na, K, Sr, and Br which will affect relative free
13 energies and stabilities; for example, as shown by the mineralisation, stabilisation, and lower
14 formation temperature of alite [72].

15 **6 Conclusion**

16 A high-temperature thermodynamic dataset for cement clinkering equilibrium calculations is
17 reviewed, compiled, and presented; the dataset is also validated through a series of case
18 studies. The dataset and model can be used to calculate heat balances and conduct limited
19 predictive modelling. The information presented here is beneficial to develop novel cement
20 formulations and production processes; equally, it will find use by cement producers looking to
21 optimise production and for quality control.

1 The data is provided in electronic format as downloadable supplementary material with this
2 article (S1, S2, and S3). This database will be updated over time, but this study can serve as a
3 benchmark of thermodynamic data for cement clinkering.

4 **8 Additional information**

5 This work began as part of a PhD project; further information related to the development of
6 this dataset can be found in the published thesis available online [73]. The database presented
7 here is the initial cement thermodynamic data parsed in SimCem along with other
8 thermodynamic data which can be found at www.SimCem.com.

9 **9 Acknowledgements**

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