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ABSTRACT: This paper presents a cement hydration model over time using the CEMDATA thermodynamic database and a series of discrete solid phases (DSP) to represent calcium silicate hydrate (C-S-H) as a ternary (CSH-3T) and quaternary (CSHQ) solid solution.

C-S-H in cement is amorphous and poorly crystalline with a range of molar Ca/Si ratios = 0.6-1.7 and displays strongly incongruent dissolution behaviour where the release of calcium into solution is several orders of magnitude greater than silicon. It is therefore important that any cement hydration model provides a credible account of this behaviour.

C-S-H has been described in the CEMDATA thermodynamic database as a number of binary, ternary and quaternary solid solutions using different end-members with differing levels of complexity. While solid solutions can be included in most modern geochemical software programs, it often leads to a significant increase in computation time.

This paper presents how the two of the more complex C-S-H solid solutions, CSH-3T and CSHQ, available in the CEMDATA database, can be represented by DSP to model cement hydration over time using the PHREEQC geochemical software. By using DSP in place of solid solutions, analysis time is much improved with no loss in accuracy in producing stable phase assemblages and reasonable predictions of pH over time.

KEY WORDS: solid solutions; discrete solid phases; C-S-H; cement; hydration.

1 INTRODUCTION

Solid solutions are homogeneous crystalline structures where one or more atom types or molecules can be partly or wholly substituted on specific lattice sites by moieties of equivalent charge. If the host and substituting moieties are chemically similar, the formation of an ideal solid solution is possible, however, as is usually the case, differences are sufficiently large to cause the formation of a non-ideal solid solution, which can be readily confirmed by the appearance of a miscibility gap [1, 2]. Solid solutions are of great importance in cement chemistry where they can be used to describe the strongly incongruent dissolution behaviour of calcium-silicate-hydrate (C-S-H) gel [3, 4], substitution of SiO_4^{4-} and $4OH^-$ in hydrogarnets [5], and substitution of cationic Al^{3+} and Fe^{3+} and anionic $2OH^-$, 2Cl–, SO_4^{2-}, and CO_3^{2-} components in AFt and AFm minerals [6-8].

If the thermodynamic properties of the unsubstituted, pure end-members are known, it is possible to calculate a series of DSP that can be used to provide a credible thermodynamic model of cement hydration. Work by [9] and [10] demonstrates that DSP can be derived for any ideal or non-ideal solid solution. For example, [10] developed a DSP C-S-H gel solubility model based on two binary non-ideal solid solutions that yielded satisfactory predictions of pH, Ca and Si concentrations for molar Ca/Si (C/S) ratios from 0 to 2.7, the occurrence of portlandite at C/S > 1.65, amorphous silica at C/S < 0.55, and congruent dissolution at C/S = 0.85.

In the current paper, DSP have been derived for the CSH3T (three end-member) and CSHQ (four end member) C-S-H gel solubility models [3], and used to predict ordinary Portland cement (OPC) hydration as a function of time using the CEMDATA thermodynamic database [11] and the PHREEQC geochemical code [12].

2 DERIVATION OF DSP FROM CEMDATA SOLID SOLUTION END-MEMBERS

The first step in deriving a series of DSP is defining the pure end-members and their thermodynamic properties in terms of Gibbs free energy (G, J/mol), enthalpy (H, J/mol), entropy (S, J/K/mol), heat capacity (Cp, J/K/mol) and molar volume (V, cm^3/mol) (see Table 1) [11]. These thermodynamic properties can then be used calculate the solubility constant, log K and its variation with temperature for dissolution reactions of each end-member (Table 2). As shown, the end-members are listed in order of increasing solubility and the analytical expressions describe the variation of log K as a function of temperature (in Kelvin) where a, c and d are calculated as functions of enthalpy (Δ_rH, J/mol), entropy (Δ_rS, J/K/mol) and heat capacity (Δ_rC_p, J/K/mol) of reaction [13] , b, e and $f = 0$ and T is temperature.

$$\log K = a + b\cdot T + c/T + d\cdot\log_{10}(T) + e\cdot T^{-2} + f\cdot T^2 \qquad (1)$$

Each of the end-members shown in Table 2 and their respective analytical expressions are written directly into PHREEQC to suit its data input syntax.

Next, appropriate mole fractions are chosen to discretize the solid solutions and create the series of DSP. In the current paper, mole fraction increments of 0.2 were used to describe the three end-members in the CSH3T model in terms of X_i, X_j & X_k and four end-members in the CSHQ model in terms of X_l, X_m, X_n and X_o), where the sum of the mole fractions in each solid solution must equal 1. Using these mole fractions, the

Table 1 Thermodynamic properties of CSH3T, as taken from the CEMDATA database [11]. Letters assigned to each end-member are shown in parentheses.

Component	G ^{i}	H ^{i}	S ^{ii}	C_p ^{ii}	V ^{iii}
CSH3T-TobH (i)	-2561532	-2832974	152.8	231.2	84.960
CSH3T-T5C (j)	-2518659	-2782034	159.9	234.1	79.261
CSH3T-T2C (k)	-2467081	-2722410	167.0	237.0	80.558
CSHQ-TobH (l)	-1668560	-1841498	89.9	141.6	55.0
CSHQ-TobD (m)	-1570891	-1742414	121.8	166.9	48.0
CSHQ-JenH (n)	-2273986	-2506256	142.5	207.9	76.0
CSHQ-JenD (o)	-2169558	-2400704	173.4	232.8	81.0
Ca^{+2}	-552790	-543069	-56.484	-30.923	
$SiO_{2(aq)}$	-833411	-887856	41.338	44.465	
H_2O	-237183	-285881	69.923	75.361	
H^+	0	0	0	0	

^{i} J/mol. ^{ii} J/mol/K. ^{iii} cm^3/mol.

Table 2 CSH3T and CSHQ end-member properties [11]

CSH3T-TobH (i)
$(CaO)_1(SiO_2)_{1.5}(H_2O)_{2.5} + 2H^+ = Ca^{2+} + 3.5H_2O + 1.5SiO_{2(aq)}$ log K 12.5288
analytical_expression parameters (Equation (1)) ^{i}
$a = -18.8215$, $c = 3282.489718$, $d = 8.22098$

CSH3T-T5C (j)
$((CaO)_1(SiO_2)_1(H_2O)_2)_{1.25} + 2.5H^+ = 1.25Ca^{2+} + 3.75H_2O + 1.25SiO_{2(aq)}$ log K 18.1373
analytical_expression parameters (Equation (1)) ^{i}
$a = -18.5190$, $c = 5127.78826$, $d = 7.864154$

CSH3T-T2C (k)
$((CaO)_{0.75}(SiO_2)_{0.5}(H_2O)_{1.25})_2 + 3H^+ = 1.5Ca^{2+} + 4H_2O + SiO_{2(aq)}$ log K 25.2708
analytical_expression parameters (Equation (1)) ^{i}
$a = -18.2427$, $c = 7428.082891$, $d = 7.517428$

CSHQ-TobH (l)
$(CaO)_{0.6667}(SiO_2)_1(H_2O)_{1.5} + 1.3334H^+ = 0.6667Ca^{2+} + 2.1667H_2O + SiO_{2(aq)}$; log K 8.2866
analytical_expression parameters (Equation (1)) ^{i}
$a = -12.5193$, $c = 2163.381583$, $d = 5.476331$

CSHQ-TobD (m)
$((CaO)_{1.25}(SiO_2)_1(H_2O)_{2.75})_{0.6667} + 1.66675H^+ = 0.833375Ca^{2+} + 2.6668H_2O + 0.6667SiO_{2(aq)}$; log K 13.6553
analytical_expression parameters (Equation (1)) ^{i}
$a = -10.9164$, $c = 3959.367696$, $d = 4.563888$

CSHQ-JenH (n)
$(CaO)_{1.3333}(SiO_2)_1(H_2O)_{2.1667} + 2.6666H^+ = 1.3333Ca^{2+} + 3.5H_2O + SiO_{2(aq)}$; log K 22.1794
analytical_expression parameters (Equation (1)) ^{i}
$a = -17.10947$, $c = 6470.553982$, $d = 7.107847$

CSHQ-JenD (o)
$(CaO)_{1.5}(SiO_2)_{0.6667}(H_2O)_{2.5} + 3H^+ = 1.5Ca^{+2} + 4H_2O + 0.6667SiO_2$ log K 28.730362
analytical_expression parameters (Equation (1)) ^{i}
$a = -15.5918$, $c = 8609.739692$, $d = 6.24251$

^{i} $a = (\Delta_r S - \Delta_r C_p \cdot (1 + LN(298.15))) / (R \cdot LN(10))$, $b = 0$, $c = (298.15 \cdot \Delta_r C_p - \Delta_r H) / (R \cdot LN(10))$, $d = \Delta_r Cp / R$, $e = 0$, and $f = 0$, where R is the gas constant (8.31451 J/mol/K).

solid phase composition (CaO, SiO_2, H_2O), aqueous reaction components (H+, Ca^{+2}, H_2O, $SiO_{2(aq)}$), mass (g/mol) and volume (cm^3/mol) are determined for each DSP based on the original end-members. The solubility constant is determined for each DSP in the CSH3T and CSHQ models using Equations 2 and 3 respectively.

$$K_{CSH3T} = (K_i \cdot X_i)^{Xi} \cdot (K_j \cdot X_j)^{Xj} \cdot (K_k \cdot X_k)^{Xk} \qquad (2)$$

$$K_{CSHQ} = (K_l \cdot X_l)^{Xl} \cdot (K_m \cdot X_m)^{Xm} \cdot (K_n \cdot X_n)^{Xn} \cdot (K_o \cdot X_o)^{Xo} \qquad (3)$$

Dissolution reactions and solubility products for the DSP for CSH3T and CSHQ models can be calculated on a spreadsheet and suitably formatted such that the user simply needs to copy and paste directly into the PHREEQC input file. Table 3 and Table 4 shows the resulting DSP for the CSH3T and CSHQ models, respectively.

At this point, the PHREEQC input file is completed and modelling of OPC hydration can begin accounting of the kinetic dissolution of the clinker phases as a function of time [14], oversaturation of the precipitating hydrate phases during the first 12 hours of hydration [15] and the release and uptake of alkali metals (K and Na) by the C-S-H gel [16]. To aid computing time, all input data is defined in an Excel spreadsheet first and pasted directly into PHREEQC.

3 THERMODYNAMIC MODELLING

3.1 *OPC Clinker Rate Equations*

The oxide compositions of the OPC CEM I cement are shown in Table 5. A normative calculation was undertaken to convert the oxide proportions into the cement clinker phases shown in Table 5. Gypsum is assumed to exist here rather than anhydrite.

The dissolution of the four clinker phases alite (Ca_3SiO_5, C_3S), belite (Ca_2SiO_4, C_2S), aluminate ($Ca_3Al_2O_6$, C_3A), and aluminoferrite ($Ca_4Al_2Fe_2O_{10}$, C_4AF) is described by empirical rate equations proposed by Parrot and Killoh [14] and modified by Lothenbach *et al* [17] which represents the mechanisms of nucleation and growth, diffusion and formation of a hydration shell. The controlling rate (R_t) is the lowest value from Equations (4-6) for any specified hydration time (t) in days. A & A_0 in Equation (4) represent the Blaine fineness and reference surface area (385m^2/kg) respectively. Changes in temperature are accounted for by Equation (7) where T and T_0 are the curing temperature (K) and reference temperature of 293.15 K, respectively. Changes in relative humidity (*RH)* and water/cement (w/c ratio) is accounted for by Equation (8) and Equation (9) respectively where H is a constant and α_{tot} is the total degree of hydration of all four clinker phases. The fraction of clinker hydrated at each time step is given by $\alpha_t = \alpha_t - 1 + \Delta t \cdot R_{t-1}$.Writing Equation (4-9) into PHREEQC proceeds with variable time-steps with only 47 steps required to predict the dissolution of the clinker phases for a simulated 1,000 days of hydration. The constants $K^{1\text{-}3}$, $N^{1,3}$ H, and E_a^m) can be found in [17].

3.2 *Dissolution of Oxides Dissolved in OPC Clinker*

The model input predefines the molar amounts of the oxide components (K_2O, Na_2O, MgO &, and SO_3) dissolved in the OPC clinker phases (C_3S, C_2S, C_3A &, and C_4AF) using the compositions and method described by [18]. The oxide components therefore proportional to the dissolution of the OPC clinker phases as described above.

Table 3 End-members and DSP for the CSH3T model

Phase	Mole fractions			DSP dissolution reaction	log K (25ºC)	Analytical expression parameters (Eqn. 1)			Vol. cm^3/mol
	i	j	k			*a*	*c*	*d*	
CSH3T-TobH (i)	1	0	0	$(CaO)_1(SiO_2)_{1.5}(H_2O)_{2.5} + 2H^+ = Ca^{2+} + 3.5H_2O + 1.5\ SiO_{2(aq)}$	12.5288	-18.8214	3282.490	8.22098	84.960
3T-DSP$_1$	0.8	0.2	0	$(CaO)_{1.05}(SiO_2)_{1.45}(H_2O)_{2.5} + 2.1\ H^+ = 1.05\ Ca^{2+} + 3.55\ H_2O + 1.45\ SiO_{2(aq)}$	13.4332	-18.9776	3651.678	8.149126	83.820
3T-DSP$_2$	0.6	0.4	0	$(CaO)_{1.1}(SiO_2)_{1.4}(H_2O)_{2.5} + 2.2\ H^+ = 1.1\ Ca^{2+} + 3.6\ H_2O + 1.4\ SiO_{2(aq)}$	14.4799	-18.9962	4020.934	8.079203	82.680
3T-DSP$_3$	0.4	0.6	0	$(CaO)_{1.15}(SiO_2)_{1.35}(H_2O)_{2.5} + 2.3\ H^+ = 1.15\ Ca^{2+} + 3.65\ H_2O + 1.35\ SiO_{2(aq)}$	15.6016	-18.9399	4390.190	8.009281	81.540
3T-DSP$_4$	0.2	0.8	0	$(CaO)_{1.2}(SiO_2)_{1.3}(H_2O)_{2.5} + 2.4\ H^+ = 1.2\ Ca^{2+} + 3.7\ H_2O + 1.3\ SiO_{2(aq)}$	16.7983	-18.8086	4759.446	7.939358	80.400
CSH3T-T5C (j)	0	1	0	$((CaO)_1(SiO_2)_1(H_2O)_2)_{1.25} + 2.5H^+ = 1.25Ca^{2+} + 3.75H_2O + 1.25SiO_{2(aq)}$	18.1373	-18.5190	5127.790	7.864154	79.261
3T-DSP$_5$	0.8	0	0.2	$(CaO)_{1.1}(SiO_2)_{1.4}(H_2O)_{2.5} + 2.2\ H^+ = 1.1\ Ca^{2+} + 3.6\ H_2O + 1.4\ SiO_{2(aq)}$	14.8599	-18.9213	4111.716	8.079203	84.080
3T-DSP$_6$	0.6	0.2	0.2	$(CaO)_{1.15}(SiO_2)_{1.35}(H_2O)_{2.5} + 2.3\ H^+ = 1.15\ Ca^{2+} + 3.65\ H_2O + 1.35\ SiO_{2(aq)}$	15.7862	-19.0603	4480.972	8.009281	82.940
3T-DSP$_7$	0.4	0.4	0.2	$(CaO)_{1.2}(SiO_2)_{1.3}(H_2O)_{2.5} + 2.4\ H^+ = 1.2\ Ca^{2+} + 3.7\ H_2O + 1.3\ SiO_{2(aq)}$	16.8625	-19.0494	4850.228	7.939358	81.800
3T-DSP$_8$	0.2	0.6	0.2	$(CaO)_{1.25}(SiO_2)_{1.25}(H_2O)_{2.5} + 2.5\ H^+ = 1.25\ Ca^{2+} + 3.75\ H_2O + 1.25\ SiO_{2(aq)}$	18.0296	-18.9476	5219.484	7.869436	80.660
3T-DSP$_9$	0	0.8	0.2	$(CaO)_{1.3}(SiO_2)_{1.2}(H_2O)_{2.5} + 2.6\ H^+ = 1.3\ Ca^{2+} + 3.8\ H_2O + 1.2\ SiO_{2(aq)}$	19.3467	-18.6959	5588.739	7.799513	79.520
3T-DSP$_{10}$	0.6	0	0.4	$(CaO)_{1.2}(SiO_2)_{1.3}(H_2O)_{2.5} + 2.4\ H^+ = 1.2\ Ca^{2+} + 3.7\ H_2O + 1.3\ SiO_{2(aq)}$	17.3333	-18.8835	4941.009	7.939358	83.199
3T-DSP$_{11}$	0.4	0.2	0.4	$(CaO)_{1.25}(SiO_2)_{1.25}(H_2O)_{2.5} + 2.5\ H^+ = 1.25\ Ca^{2+} + 3.75\ H_2O + 1.25\ SiO_{2(aq)}$	18.2892	-18.9931	5310.26	7.869436	82.059
3T-DSP$_{12}$	0.2	0.4	0.4	$(CaO)_{1.3}(SiO_2)_{1.2}(H_2O)_{2.5} + 2.6\ H^+ = 1.3\ Ca^{2+} + 3.8\ H_2O + 1.2\ SiO_{2(aq)}$	19.4109	-18.9367	5679.52	7.799513	80.920
3T-DSP$_{13}$	0	0.6	0.4	$(CaO)_{1.35}(SiO_2)_{1.15}(H_2O)_{2.5} + 2.7\ H^+ = 1.35\ Ca^{2+} + 3.85\ H_2O + 1.15\ SiO_{2(aq)}$	20.6984	-18.7145	6048.77	7.729591	79.780
3T-DSP$_{14}$	0.4	0	0.6	$(CaO)_{1.3}(SiO_2)_{1.2}(H_2O)_{2.5} + 2.6\ H^+ = 1.3\ Ca^{2+} + 3.8\ H_2O + 1.2\ SiO_{2(aq)}$	19.8817	-18.7708	5770.30	7.799513	82.319
3T-DSP$_{15}$	0.2	0.2	0.6	$(CaO)_{1.35}(SiO_2)_{1.15}(H_2O)_{2.5} + 2.7\ H^+ = 1.35\ Ca^{2+} + 3.85\ H_2O + 1.15\ SiO_{2(aq)}$	20.8830	-18.8349	6139.55	7.729591	81.179
3T-DSP$_{16}$	0	0.4	0.6	$(CaO)_{1.4}(SiO_2)_{1.1}(H_2O)_{2.5} + 2.8\ H^+ = 1.4\ Ca^{2+} + 3.9\ H_2O + 1.1\ SiO_{2(aq)}$	22.1251	-18.6581	6508.81	7.659668	80.039
3T-DSP$_{17}$	0.2	0	0.8	$(CaO)_{1.4}(SiO_2)_{1.1}(H_2O)_{2.5} + 2.8\ H^+ = 1.4\ Ca^{2+} + 3.9\ H_2O + 1.1\ SiO_{2(aq)}$	22.5051	-18.5832	6599.59	7.659668	81.439
3T-DSP$_{18}$	0	0.2	0.8	$(CaO)_{1.45}(SiO_2)_{1.05}(H_2O)_{2.5} + 2.9\ H^+ = 1.45\ Ca^{2+} + 3.95\ H_2O + 1.05\ SiO_{2(aq)}$	23.6268	-18.5268	6968.85	7.589746	80.299
CSH3T-T2C (k)	0	0	1	$((CaO)_{0.75}(SiO_2)_{0.5}(H_2O)_{1.25})_2 + 3H^+ = 1.5Ca^{2+} + 4H_2O + SiO_{2(aq)}$	25.2708	-18.2427	7428.083	7.517428	80.558

Table 4 End-members and DSP for the CSHQ model

Phase	Mole fractions				DSP dissolution reaction	Log K (25ºC)	Analytical expression (Eqn. 1)			Vol. cm^3/mol
	l	m	n	o			*a*	*c*	*d*	
CSHQ-TobH (l)	1	0	0	0	$(CaO)_{0.6667}(SiO_2)1(H_2O)_{1.5} + 1.3334H^+ = 0.6667Ca^{2+} + 2.1667H_2O + SiO_{2(aq)}$	8.2866	-12.5193	2163.382	5.476331	55.00
Q-DSP$_1$	0.8	0.2	0	0	$(CaO)_{0.700035}(SiO_2)_{0.93334}(H_2O)_{1.566685} + 1.40007\ H^+ = 0.700035\ Ca^{2+} + 2.26672\ H_2O + 0.93334\ SiO_{2(aq)}$	9.1431	-12.4160	2522.579	5.293837	53.60
Q-DSP$_2$	0.6	0.4	0	0	$(CaO)_{0.73337}(SiO_2)_{0.86668}(H_2O)_{1.63337} + 1.46674\ H^+ = 0.73337\ Ca^{2+} + 2.36674\ H_2O + 0.86668\ SiO_{2(aq)}$	10.1418	-12.1704	2881.952	5.111348	52.20
Q-DSP$_3$	0.4	0.6	0	0	$(CaO)_{0.766705}(SiO_2)_{0.80002}(H_2O)_{1.700055} + 1.53341\ H^+ = 0.766705\ Ca^{2+} + 2.46676\ H_2O + 0.80002\ SiO_{2(aq)}$	11.2156	-11.8498	3241.324	4.928858	50.80
Q-DSP$_4$	0.2	0.8	0	0	$(CaO)_{0.80004}(SiO2)_{0.73336}(H_2O)_{1.76674} + 1.60008\ H^+ = 0.80004\ Ca^{2+} + 2.56678\ H_2O + 0.73336\ SiO_{2(aq)}$	12.3643	-11.4542	3600.697	4.746369	49.40
CSHQ-TobD (m)	0	1	0	0	$((CaO)_{1.25}(SiO_2)1(H_2O)_{2.75})_{0.6667} + 1.66675H^+ = 0.833375Ca^{2+} + 2.6668H_2O + 0.6667SiO_{2(aq)}$	13.6553	-10.9163	3959.368	4.563888	48.00
Q-DSP$_5$	0.8	0	0.2	0	$(CaO)_{0.80002}(SiO_2)_1(H_2O)_{1.63334} + 1.60004\ H^+ = 0.80002\ Ca^{2+} + 2.43336\ H_2O + SiO_{2(aq)}$	10.8479	13.6546	3024.214	5.802628	59.20
Q-DSP$_6$	0.6	0.2	0.2	0	$(CaO)_{0.833355}(SiO_2)_{0.93334}(H_2O)_{1.700025} + 1.66671\ H^+ = 0.833355\ Ca^{2+} + 2.53338\ H_2O + 0.93334\ SiO_{2(aq)}$	11.7262	-13.5294	3383.587	5.620139	57.80
Q-DSP$_7$	0.4	0.4	0.2	0	$(CaO)_{0.86669}(SiO_2)_{0.86668}(H_2O)_{1.76671} + 1.73338\ H^+ = 0.86669\ Ca^{2+} + 2.63340\ H_2O + 0.86668\ SiO_{2(aq)}$	12.7545	-13.2543	3742.959	5.437650	56.40

Q-DSP$_8$	0.2	0.6	0.2	0	$(CaO)_{0.900025}(SiO_2)_{0.80002}(H_2O)_{1.833395} + 1.80005\ H^+ = 0.900025\ Ca^{2+} + 2.73342\ H_2O + 0.80002\ SiO_{2(aq)}$	13.8737	-12.8882	4102.332	5.255160	55.00
Q-DSP$_9$	0	0.8	0.2	0	$(CaO)_{0.93336}(SiO_2)_{0.73336}(H_2O)_{1.90008} + 1.86672\ H^+ = 0.93336\ Ca^{2+} + 2.83344\ H_2O + 0.73336\ SiO_{2(aq)}$	15.1428	-12.3723	4461.705	5.072671	53.60
Q-DSP$_{10}$	0.6	0	0.4	0	$(CaO)_{0.93334}(SiO_2)_1(H_2O)_{1.76668} + 1.86668\ H^+ = 0.93334\ Ca^{2+} + 2.70002\ H_2O + SiO_{2(aq)}$	13.5514	-14.6476	3885.222	6.128930	63.40
Q-DSP$_{11}$	0.4	0.2	0.4	0	$(CaO)_{0.966675}(SiO_2)_{0.93334}(H_2O)_{1.833365} + 1.93335\ H^+ = 0.966675\ Ca^{2+} + 2.80004\ H_2O + 0.93334\ SiO_{2(aq)}$	14.4593	-14.4929	4244.594	5.946441	62.00
Q-DSP$_{12}$	0.2	0.4	0.4	0	$(CaO)_{1.00001}(SiO_2)_{0.86668}(H_2O)_{1.90005} + 2.00002\ H^+ = 1.00001\ Ca^{2+} + 2.90006\ H_2O + 0.86668\ SiO_{2(aq)}$	15.5330	-14.1723	4603.967	5.763952	60.60
Q-DSP$_{13}$	0	0.6	0.4	0	$(CaO)_{1.033345}(SiO_2)_{0.80002}(H_2O)_{1.966735} + 2.06669\ H^+ = 1.033345\ Ca^{2+} + 3.00008\ H_2O + 0.80002\ SiO_{2(aq)}$	16.7726	-13.6858	4963.340	5.581462	59.20
Q-DSP$_{14}$	0.4	0	0.6	0	$(CaO)_{1.06666}(SiO_2)_1(H_2O)_{1.90002} + 2.13332\ H^+ = 1.06666\ Ca^{2+} + 2.96668\ H_2O + SiO_{2(aq)}$	16.3300	-15.5656	4746.229	6.455232	67.60
Q-DSP$_{15}$	0.2	0.2	0.6	0	$(CaO)_{1.099995}(SiO_2)_{0.93334}(H_2O)_{1.966705} + 2.19999\ H^+ = 1.099995\ Ca^{2+} + 3.0667\ H_2O + 0.93334\ SiO_{2(aq)}$	17.2833	-15.3655	5105.602	6.272743	66.20
Q-DSP$_{16}$	0	0.4	0.6	0	$(CaO)_{1.13333}(SiO_2)_{0.86668}(H_2O)_{2.03339} + 2.26666\ H^+ = 1.13333\ Ca^{2+} + 3.16672\ H_2O + 0.86668\ SiO_{2(aq)}$	18.4774	-14.9245	5464.975	6.090254	64.80
Q-DSP$_{17}$	0.2	0	0.8	0	$(CaO)_{1.19998}(SiO_2)_1(H_2O)_{2.03336} + 2.39996\ H^+ = 1.19998\ Ca^{2+} + 3.23334\ H_2O + SiO_{2(aq)}$	19.1835	-16.4087	5607.237	6.781534	71.80
Q-DSP$_{18}$	0	0.2	0.8	0	$(CaO)_{1.233315}(SiO_2)_{0.93334}(H_2O)_{2.100045} + 2.46663\ H^+ = 1.233315\ Ca^{2+} + 3.33336\ H_2O + 0.93334\ SiO_{2(aq)}$	20.2572	-16.0881	5966.610	6.599045	70.40
CSHQ-JenH (n)	0	0	1	0	$(CaO)_{1.3333}(SiO_2)_1(H_2O)_{2.1667} + 2.6666H^+ = 1.3333Ca^{2+} + 3.5H_2O + SiO_{2(aq)}$	22.1793	-17.1094	6470.554	7.107847	76.00
Q-DSP$_{19}$	0	0.8	0.2	0	$(CaO)_{0.93336}(SiO_2)_{0.73336}(H_2O)_{1.90008} + 1.86672\ H+ = 0.93336\ Ca^{2+} + 2.83344\ H_2O + 0.73336\ SiO_{2(aq)}$	15.1428	-12.3723	4461.705	5.072671	53.60
Q-DSP$_{20}$	0	0.6	0.4	0	$(CaO)_{1.033345}(SiO_2)_{0.80002}(H_2O)_{1.966735} + 2.06669\ H+ = 1.033345\ Ca^{2+} + 3.00008\ H_2O + 0.80002\ SiO_{2(aq)}$	16.7726	-13.6858	4963.340	5.581462	59.20
Q-DSP$_{21}$	0	0.4	0.6	0	$(CaO)_{1.13333}(SiO_2)_{0.86668}(H_2O)_{2.03339} + 2.26666\ H^+ = 1.13333\ Ca^{2+} + 3.16672\ H_2O + 0.86668\ SiO_2$	18.4774	-14.9245	5464.975	6.090254	64.80
Q-DSP$_{22}$	0	0.2	0.8	0	$(CaO)_{1.233315}(SiO_2)_{0.93334}(H_2O)_{2.100045} + 2.46663\ H^+ = 1.233315\ Ca^{2+} + 3.33336\ H_2O + 0.93334\ SiO_{2(aq)}$	20.2572	-16.0881	5966.610	6.599045	70.40
Q-DSP$_{23}$	0	0.8	0	0.2	$(CaO)_{0.9667}(SiO_2)_{0.6667}(H_2O)_{1.96674} + 1.9334\ H^+ = 0.9667\ Ca^{2+} + 2.93344\ H_2O + 0.6667\ SiO_{2(aq)}$	16.4530	-12.0687	4.890.00	4.899604	54.60
Q-DSP$_{24}$	0	0.6	0.2	0.2	$(CaO)_{1.066685}(SiO_2)_{0.73336}(H_2O)_{2.033395} + 2.13337\ H^+ = 1.066685\ Ca^{2+} + 3.10008\ H_2O + 0.73336\ SiO_{2(aq)}$	17.9624	-13.5027	5391.63	5.408395	60.20
Q-DSP$_{25}$	0	0.4	0.4	0.2	$(CaO)_{1.16667}(SiO_2)_{0.80002}(H_2O)_{2.10005} + 2.33334\ H^+ = 1.16667\ Ca^{2+} + 3.26672\ H_2O + 0.80002\ SiO_{2(aq)}$	19.6218	-14.7868	5893.27	5.917186	65.80
Q-DSP$_{26}$	0	0.2	0.6	0.2	$(CaO)_{1.266655}(SiO_2)_{0.86668}(H_2O)_{2.166705} + 2.53331\ H^+ = 1.266655\ Ca^{2+} + 3.43336\ H_2O + 0.86668\ SiO_{2(aq)}$	21.3720	-15.9800	6394.90	6.425978	71.40
Q-DSP$_{27}$	0	0	0.8	0.2	$(CaO)_{1.36664}(SiO_2)_{0.93334}(H_2O)_{2.23336} + 2.73328\ H^+ = 1.36664\ Ca^{2+} + 3.6\ H_2O + 0.93334\ SiO_{2(aq)}$	23.2722	-17.0232	6896.54	6.934769	77.00
Q-DSP$_{28}$	0	0.6	0	0.4	$(CaO)_{1.100025}(SiO_2)_{0.6667}(H_2O)_{2.100055} + 2.20005\ H^+ = 1.100025\ Ca^{2+} + 3.20008\ H_2O + 0.6667\ SiO_{2(aq)}$	19.3930	-13.0788	5819.93	5.235327	61.20
Q-DSP$_{29}$	0	0.4	0.2	0.4	$(CaO)_{1.20001}(SiO_2)_{0.73336}(H_2O)_{2.16671} + 2.40002\ H^+ = 1.20001\ Ca^{2+} + 3.36672\ H_2O + 0.73336\ SiO_{2(aq)}$	20.9320	-14.4832	6321.57	5.744119	66.80
Q-DSP$_{30}$	0	0.2	0.4	0.4	$(CaO)_{1.299995}(SiO_2)_{0.80002}(H_2O)_{2.233365} + 2.59999\ H+ = 1.299995\ Ca^{2+} + 3.53336\ H_2O + 0.80002\ SiO_{2(aq)}$	22.6368	-15.7219	6823.20	6.252910	72.40
Q-DSP$_{31}$	0	0	0.6	0.4	$(CaO)_{1.39998}(SiO_2)_{0.86668}(H_2O)_{2.30002} + 2.79996\ H^+ = 1.39998\ Ca^{2+} + 3.7\ H_2O + 0.86668\ SiO_{2(aq)}$	24.5074	-16.7946	7324.84	6.761701	78.00
Q-DSP$_{32}$	0	0.4	0	0.6	$(CaO)_{1.23335}(SiO_2)_{0.6667}(H_2O)_{2.23337} + 2.4667\ H^+ = 1.23335\ Ca^{2+} + 3.46672\ H_2O + 0.6667\ SiO_{2(aq)}$	22.4081	-14.0138	6749.87	5.571051	67.80
Q-DSP$_{33}$	0	0.2	0.2	0.6	$(CaO)_{1.333335}(SiO_2)_{0.73336}(H_2O)_{2.300025} + 2.66667\ H^+ = 1.333335\ Ca^{2+} + 3.63336\ H_2O + 0.73336\ SiO_{2(aq)}$	23.9924	-15.3729	7251.50	6.079843	73.40
Q-DSP$_{34}$	0	0	0.4	0.6	$(CaO)_{1.43332}(SiO_2)_{0.80002}(H_2O)2.36668 + 2.86664\ H^+ = 1.43332\ Ca^{2+} + 3.8\ H_2O + 0.80002\ SiO_{2(aq)}$	25.8177	-16.4911	7753.14	6.588634	79.00
Q-DSP$_{35}$	0	0.2	0	0.8	$(CaO)_{1.366675}(SiO_2)_{0.6667}(H_2O)_{2.366685} + 2.73335\ H^+ = 1.366675\ Ca^{2+} + 3.73336\ H_2O + 0.6667\ SiO_{2(aq)}$	25.4980	-14.8740	7679.80	5.906775	74.40
Q-DSP$_{36}$	0	0	0.2	0.8	$(CaO)_{1.46666}(SiO_2)_{0.73336}(H_2O)_{2.43334} + 2.93332\ H^+ = 1.46666\ Ca^{2+} + 3.9\ H_2O + 0.73336\ SiO_{2(aq)}$	27.2028	-16.1126	8181.43	6.415566	80.00
CSHQ-JenD (o)	0	0	0	1	$(CaO)_{1.5}(SiO_2)_{0.6667}(H_2O)_{2.5} + 3H^+ = 1.5Ca^{2+} + 4H_2O + 0.6667SiO_{2(aq)}$	28.7304	-15.5918	8609.740	6.24251	81.00

$$R_t = \frac{K^1}{N^1}(1-\alpha_t)\big(-ln(1-\alpha_t)\big)^{(1-N^1)} \cdot \frac{A}{A_0} \cdot f(T) \cdot f(RH) \cdot f(\frac{w}{c}) \tag{4}$$

$$f(T) = exp\left[\frac{E_a^m}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{7}$$

$$R_t = \frac{K^2(1-\alpha_t)^{\frac{2}{3}}}{1-(1-\alpha_t)^{\frac{1}{3}}} \cdot f(T) \cdot f(RH) \cdot f(\frac{w}{c}) \tag{5}$$

$$f(RH) = \left(\frac{RH - 0.55}{0.45}\right)^4 \tag{8}$$

$$R_t = K^3(1-\alpha_t)^{N^3} \cdot f(T) \cdot f(RH) \cdot f(\frac{w}{c}) \tag{6}$$

$$f(\frac{w}{c}) = (1 + 3.333\cdot(H\cdot\frac{w}{c} - \alpha_{tot}))^4;\ \text{for } \alpha_{tot} > H \cdot \frac{w}{c} \tag{9}$$

Table 5 Cement oxide and clinker phase proportions

Oxide proportions (wt.%)		Phase composition	
		Phase	g/100g
SiO_2	20.19	C_3S	46.90
Al_2O_3	4.79	C_2S	20.93
Fe_2O_3	2.86	C_3A	7.64
CaO	62.50	C_4AF	8.47
MgO	1.68	Calcite	4.62
Na_2O	0.63	Gypsum	4.19
K_2O	0.16	K_2SO_4	0.26
CaO (free)	1.50	Lime	1.46
CO_2	2.09	Na_2SO_4	0.63
SO_3	2.49	K_2O	0.02
Periclase	0.50	Na_2O	0.34
Blaine fineness (m^2/kg)	419	MgO	1.63
Loss in ignition	2.72	SO_3	2.42

Table 6 n values and saturation indices (S.I. = 0.15·n)

Phase	**Composition**	**N**	**S.I. < 12hrs**
Brucite	$Mg(OH)_2$	3	0.45
Ettringite	$Ca_6(Al(OH)_6)_2(SO_4)_3(H_2O)_{26}$	15	2.25
Gypsum	$CaSO_4(H_2O)_2$	2	0.30
Portlandite	$Ca(OH)_2$	3	0.45
Syngenite	$K_2Ca(SO_4)_2(H_2O)$	5	0.75

CSH3T	***n***	**SI**	**CSHQ**	***n***	**SI**
TobH	3.00	0.45	*TobH*	2.00	0.30
3T-DSP_1	3.15	0.47	Q-DSP_1	2.10	0.32
3T-DSP_2	3.30	0.50	Q-DSP_2	2.20	0.33
3T-DSP_3	3.45	0.52	Q-DSP_3	2.30	0.35
3T-DSP_4	3.60	0.54	Q-DSP_4	2.40	0.36
T5C	3.75	0.56	*TobD*	2.50	0.38
3T-DSP_5	3.30	0.49	Q-DSP_5	2.40	0.36
3T-DSP_6	3.45	0.52	Q-DSP_6	2.50	0.38
3T-DSP_7	3.60	0.54	Q-DSP_7	2.60	0.39
3T-DSP_8	3.75	0.56	Q-DSP_8	2.70	0.41
3T-DSP_9	3.90	0.58	Q-DSP_9	2.80	0.42
3T-DSP_{10}	3.60	0.54	Q-DSP_{10}	2.80	0.42
3T-DSP_{11}	3.75	0.56	Q-DSP_{11}	2.90	0.44
3T-DSP_{12}	3.90	0.59	Q-DSP_{12}	3.00	0.45
3T-DSP_{13}	4.05	0.61	Q-DSP_{13}	3.10	0.47
3T-DSP_{14}	3.90	0.58	Q-DSP_{14}	3.20	0.48
3T-DSP_{15}	4.05	0.61	Q-DSP_{15}	3.30	0.49
3T-DSP_{16}	4.20	0.63	Q-DSP_{16}	3.40	0.51
3T-DSP_{17}	4.20	0.63	Q-DSP_{17}	3.60	0.54
3T-DSP_{18}	4.35	0.65	Q-DSP_{18}	3.70	0.55
T2C	4.50	0.68	*JenH*	4.00	0.60
			Q-DSP_{19}	2.80	0.42
			Q-DSP_{20}	3.10	0.47
			Q-DSP_{21}	3.40	0.51
			Q-DSP_{22}	3.70	0.55
			Q-DSP_{23}	2.90	0.44
			Q-DSP_{24}	3.20	0.48
			Q-DSP_{25}	3.50	0.53
			Q-DSP_{26}	3.80	0.57
			Q-DSP_{27}	4.10	0.61
			Q-DSP_{28}	3.30	0.50
			Q-DSP_{29}	3.60	0.54
			Q-DSP_{30}	3.90	0.58
			Q-DSP_{31}	4.20	0.63
			Q-DSP_{32}	3.70	0.56
			Q-DSP_{33}	4.00	0.60
			Q-DSP_{34}	4.30	0.64
			Q-DSP_{35}	4.10	0.62
			Q-DSP_{36}	4.40	0.66
			JenD	4.50	0.68

3.3 Accessory Clinker Phases

The remaining accessory clinker phases lime (CaO), calcite ($CaCO_3$), gypsum ($CaSO_4·2H_2O$), periclase (MgO), and the alkali metal sulfates (K_2SO_4 & Na_2SO_4) are allowed to reach equilibrium with the pore solution in the first time-step and are immediately available to dissolve and contribute to the precipitation of solid hydrate phases. Due to the immediate availability of free lime, periclase and the alkali metal sulfates for example, result in the precipitation of small amounts of portlandite and gypsum.

3.4 Oversaturation

To increase the solubility of precipitating solid hydrate phases, gypsum, C-S-H gel (as DSP), portlandite, syngenite, brucite and ettringite are assigned a saturation index (SI), given by 0.15(n) (Table 6) to account for their oversaturation in the first 12 hours of hydration, where n is the number of number of charged aqueous species involved in the dissolution reaction.

3.5 Alkalis binding to the C-S-H

The distribution of the alkali elements K and Na between the pore solution and the C-S-H gel was defined by a distribution coefficient (Kd, mL/g) using values of 1.0 and 0.80 for K and Na in the CSH3T model where C-S-H gel having a Ca:Si ratio of 1.5 [19]. For the CSHQ, a Kd of 0.42 was used for both on a Ca:Si ratio of 1.8 [19].

3.6 Modelling predictions

The predicted phase assemblages using the CEMDATA database [11] and PHREEQC geochemical software [12] for the CSH3T and CSHQ models are shown in Figure 1 and Figure 2 respectively. As may be seen, thermodynamic modelling predicts the presence of C-S-H, portlandite, hydrotalcite, and ettringite, with small amounts of brucite, hydrogarnet and monocarbonate. The precipitation of monocarbonate helps to stabilize the formation of ettringite, leading to a higher volume (and compressive strength) than if monosulfate was predicted to form. This agrees well with similar observations in the literature [17].

4 DISCUSSION

The above work shows how C-S-H gel solubility can be modelled as a series of DSP, which can be derived from the CSH3T and CSHQ end-members provided in the CEMDATA database. It should be noted however, that a solid solution model is not required to model OPC hydration, which in fact only requires portlandite and a suitable C-S-H gel phase of fixed C/S = 1.6-1.8 and water/Si (H/S) molar ratios = 2.0-2.1. In the DSP model presented in [10], these values are closely matched by the CSH165 phase, which has a C/S = 1.65 and H/S = 2.1167. In the current work, the CSH3T model predicted only the precipitation of 3T-DSP_{18} to represent C-S-H gel, which with a C/S = 1.38 and H/S = 2.38 is not suitable to represent C-S-H gel in hydrated OPC. The CSH3T model should therefore only be used in cement blends where lower C/S ratios are purposefully targeted by the addition of supplementary cementitious materials (SCM). Similarly, the CSHQ model predicted that only Q-DSP_{29} would precipitate to represent C-S-H gel, which has a C/S = 1.64 and H/S = 2.95. In this case the C/S ratio is satisfactory, but the H/S ratio is too large resulting incorrect predictions of the amount of C-S-H gel, free water and pH and so too therefore the dissolution of the solid

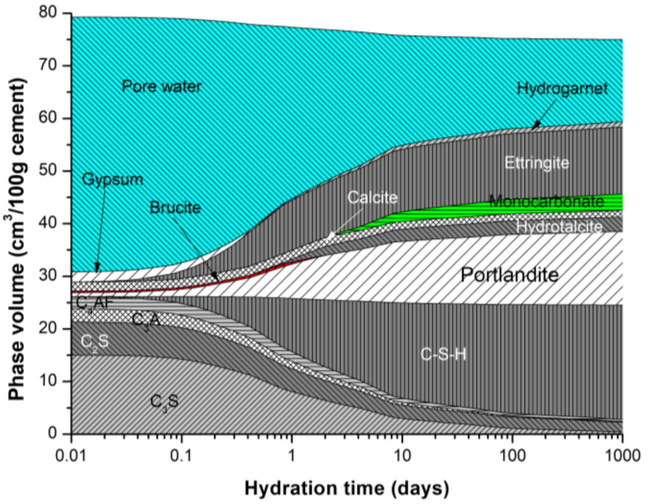

Figure 1 Phase assemblage predictions for the CSH-3T

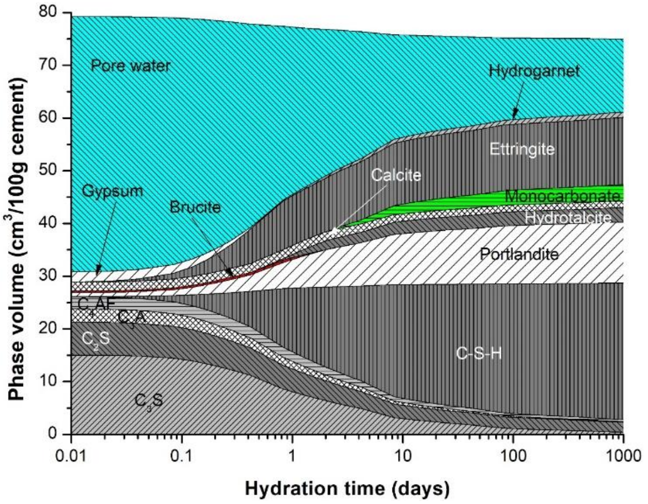

Figure 2 Phase assemblage predictions for the CSHQ

hydrate phases and the composition of the porewater.

Solid solution modelling encompasses all known synthetic ranges of C-S-H gels, which are in fact only needed if portlandite is lost and the Ca/Si ratio in the C-S-H gel is lowered, either by the addition of siliceous SCM or by chemical degradation in increasingly larger volumes of leachate provided by the ingress of groundwater or seawater.

5 CONCLUSIONS

The above work has derived a series of DSP to describe the incongruent dissolution of C-S-H gel from the end-members of two C-S-H gel solubility models, CSH3T and CSHQ, as provided in the CEMDATA thermodynamic database. Both DSP C-S-H gel solubility models were used to simulate the hydration of OPC with the geochemical code PHREEQC. The computational time in both cases was less than one minute with discernible loss in accuracy. While it is possible to model these end-members as sold solutions in PHREEQC, the analysis time is significantly slower. In the case of modelling OPC hydration, only one C-S-H gel phase and portlandite are required thereby making the derivation of the DSP model unnecessary. In the CSH3T model, however, the predicted C-S-H gel composition was C/S = 1.38 and H/S = 2.38, which does not match known C-S-H gel compositions in hydrated OPC. On the other hand, the CSHQ model predicted a C-S-H gel composition with a satisfactory C/S = 1.64, but the predicted H/S = 2.95 was too high. Solid solutions and the derivation of a series of DSP are a thermodynamic credible approach to model the incongruent solubility behaviour of C-S-H gel but are only required for modelling hydration of OPC with the addition of siliceous SCM or for hydrated OPC undergoing chemical attack.

REFERENCES

[1] J. Bruno, D. Bosbach, D. Kulik, and A. Navrotsky, "Chemical Thermodynamics of Solid Solutions of Interest in Nuclear Waste Management," in "Chemical Thermodynamics Vol. 10," North Holland Elsevier Science Publishers B.V., Amsterdam, The Netherlands, 2007.

[2] E. Curti, "Coprecipitation of radionuclides with calcite: estimation of partition coefficients based on a review of laboratory investigations and geochemical data," *Applied Geochemistry*, vol. 14, no. 4, pp. 433-445, 1999, doi: https://doi.org/10.1016/S0883-2927(98)00065-1.

[3] D. A. Kulik, "Improving the structural consistency of C-S-H solid solution thermodynamic models," *Cem. Concr. Res.*, vol. 41, no. 5, pp. 477-495, 2011.

[4] A. Atkinson, J. A. Hearne, and C. F. Knights, "Aqueous chemistry and thermodynamic modeling of CaO-SiO2-H2O gels," *J. Chem. Soc. Dalt. Trans.*, no. 12, pp. 2371-2379, 1989.

[5] T. Matschei, B. Lothenbach, and F. P. Glasser, "Thermodynamic properties of Portland cement hydrates in the system CaO–Al_2O_3–SiO_2–$CaSO_4$–$CaCO_3$–H_2O," *Cem. Concr. Res.*, vol. 37, no. 10, pp. 1379-1410, 2007.

[6] G. Möschner, B. Lothenbach, F. Winnefeld, A. Ulrich, R. Figi, and R. Kretzschmar, "Solid solution between Al-ettringite and Fe-ettringite ($Ca[Al_{1-x}Fe_x(OH)_6]_2(SO_4)_3.26H_2O$," *Cem. Concr. Res.*, vol. 39, no. 6, pp. 482-489, 2009.

[7] B. Z. Dilnesa *et al.*, "Iron in carbonate containing AFm phases," *Cem. Concr. Res.*, vol. 41, no. 3, pp. 311-323, 2011.

[8] M. Y. Hobbs, "Solubilities and ion exchange properties of solid solutions between the OH, Cl and CO3 end members of the monocalcium aluminate hydrates," Ph.D., Earth Sciences, University of Waterloo, Waterloo, Ontario, Canada, 2001.

[9] D. Kulik, G. D. Miron, and B. Lothenbach, "A structurally consistent CASH+ sublattice solid solution model for fully hydrated C-S-H phases: Thermodynamic basis, methods, and Ca-Si-H_2O core sub-model," *Cem. Concr. Res.*, vol. 151, p. 106585, 2022.

[10] C. S. Walker, S. Sutou, C. Oda, M. Mihara, and A. Honda, "Calcium silicate hydrate (C-S-H) gel solubility data and a discrete solid phase model at 25°C based on two binary non-ideal solid solutions," *Cem. Concr. Res.*, vol. 79, pp. 1-30, 2016.

[11] B. Lothenbach *et al.*, "Cemdata18: A chemical thermodynamic database for hydrated Portland cements and alkali-activated materials," *Cement and Concrete Research*, vol. 115, pp. 472–506, 2019.

[12] D. J. Parkhurst and C. A. J. Appelo, "Description of Input and Examples for PHREEQC Version 3 - A Computer Program for Speciation, Batch-reaction, One-dimensional Transport and Inverse Geochemical Calculations," USGS, Denver, 2013.

[13] W. Hummel, U. Berner, E. Curti, F. J. Pearson, and T. Thoenen, *Nagra / PSI Chemical Thermodynamic Database 01/01*. Florida, USA: Universal Publishers, 2002, p. 589.

[14] L. J. Parrot and D. C. Killoh, "Prediction of cement hydration," *Brit. Ceram. Proc.*, vol. 35, pp. 41-53, 1984.

[15] B. Lothenbach and F. Winnefeld, "Thermodynamic modelling of the hydration of Portland cement," *Cem. Concr. Res.*, vol. 36, no. 2, pp. 209-226, 2006.

[16] S. Y. Hong and F. P. Glasser, "Alkali binding in cement pastes Part I: The C-S-H phase," *Cem. Concr. Res.*, vol. 29, no. 12, pp. 1893-1903, 1999.

[17] B. Lothenbach, G. L. Saout, E. Gallucci, and K. Scrivener, "Influence of limestone on the hydration of Portland cements," *Cement and Concrete Research*, vol. 38, pp. 848–860, 2008.

[18] H. F. W. Taylor, *Cement Chemistry*. Thomas Telford Publishing, 1997.

[19] S. Y. Hong and F. P. Glasser, "Alkali binding in cement pastes: Part I. The C-S-H phase," *Cement and Concrete Research*, vol. 29, pp. 1893–1903, 1999.