2022-09-12

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Recommended Citation

Shaji, N., Holmes, N., & Tyrer, M. (2022). Modelling the hydrating behaviour of fly-ash in blended cements using thermodynamics. Technological University Dublin. DOI: 10.21427/N1C6-KT17

Modelling the hydrating behaviour of fly-ash in blended cements using thermodynamics

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Keywords: hydration, fly-ash, thermodynamics, modelling, PHREEQC

ABSTRACT

This paper presents a new method to thermodynamically model the hydration behaviour of fly-ash (FA) blended cements by deriving individual phase descriptions depending on the proportion of FA in the blended cement. The predicted hydrated phase assemblage, pore solution chemistries and pH over 1,000 days of hydration and with increasing FA proportions are presented.

The thermodynamic data for the FA phases are derived using oxide proportions and mineral compositions are copied directly into the PHREEQC input file. The FA phases take account of all minerals to give a more accurate description of its behaviour during hydration. The calcium aluminosilicate hydrate (C-A-S-H) gel model consists of several Discrete Solid Phases (DSPs) derived from the quinary solid solution end-members in the cemdata18 database [1]. This method has been used previously by the authors to give reliable and computationally efficient results when modelling OPC hydration and extended here for C-A-S-H, accounting for its strongly incongruent dissolution.

A number of blended cements with FA contents ranging from 0-35% (in 5% steps) were simulated. As the amount of FA in the blended cement increases, the results show a destabilization of calcium hydroxide at higher replacement levels, more hydrotalcite than OPC, the formation of strätlingite and AFm & AFt phases like monosulfate/monocarbonate and ettringite respectively. The dissolution of Portland cement is modelled using a well-known empirical approach. FA dissolution is modelled using an approach taken from the literature that gave good correlations with experimental data.

DERIVATION OF DSP FROM CEMDATA SOLID SOLUTION END-MEMBERS

To derive a series of Discrete Solid Phases (DSPs), 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) must be known to calculate the solubility constant, log K and its variation with temperature (T) for dissolution reactions of each end-member. Equation 1 is used to calculate the solubility constant where a, c and d are calculated as functions of enthalpy (ΔrH, J/mol), entropy (ΔrS, J/K/mol) and heat capacity (ΔrCp, J/K/mol) of reaction, b, e and f = 0 and T is temperature.

$$\log K = a + b \cdot T + c/T + d \cdot \log10(T) + e \cdot T^{-2} + f \cdot T^{2} \quad (1)$$

Appropriate mole fractions (0.2 here) are chosen to discretize the solid solutions and create the series of DSP in terms of Xi, Xj, Xk, Xo & Xn and five end-members in the C-A-S-H where the sum of the mole fractions in each solid solution must equal 1. Using these mole fractions, the 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. Dissolution reactions and solubility products for the 54 DSP C-A-S-H models here can be calculated on a spreadsheet to be copied and pasted directly into the PHREEQC input file.

DERIVATION OF INDIVIDUAL FA PHASES

Individual phases for the FA depending on the proportion in the blended cements are derived using a normative calculation and the mineral proportions in the glass. Using the cement and FA described in Table 1 with a FA content of 35%, the reactive phase (FA glass) and inactive (FA_Glass_inert) phase is given below. Here, quartz, mematite and mullite are assumed to be inert so given a saturated index (SI) of -999 and only to dissolve (not precipitate) [2].

FA_Glass: (SiO2)8.79(Al2O3)2.278(Fe2O3)0.4363(CaO)1.3227(MgO)0.627(SO3) 0.0477(K2O)0.1789 (Na2O)0.1165(H2O)2.3636 = + 8.79 SiO2 + 4.556 AlO2- + 0.8726 FeO2- + 1.3227 Ca+2 + 0.627 Mg+2 + 0.0477 SO4-2 + 0.3578 K+ + 0.233 Na+ + 1.0338 H+ + 1.8467 H2O ; log_k 999 ; Vm 430.0366
FA_Glass_inert: SiO2)8.79(Al2O3)2.278(Fe2O3)0.4363(CaO)1.3227(MgO)0.627(SO3) 0.0477(K2O)0.1789(Na2O)0.1165(H2O)2.3636 = + 8.79 SiO2 + 4.556 AlO2- + 0.8726 FeO2- + 1.3227 Ca+2 + 0.627 Mg+2 + 0.0477 SO4-2 + 0.3578 K+ + 0.233 Na+ + 1.0338 H+ + 1.8467 H2O ; log_k -999.00 ; Vm 430.0366

Table 1 CEM I (52.5N) and fly-ash oxide proportions for a 65:35 blend [3]

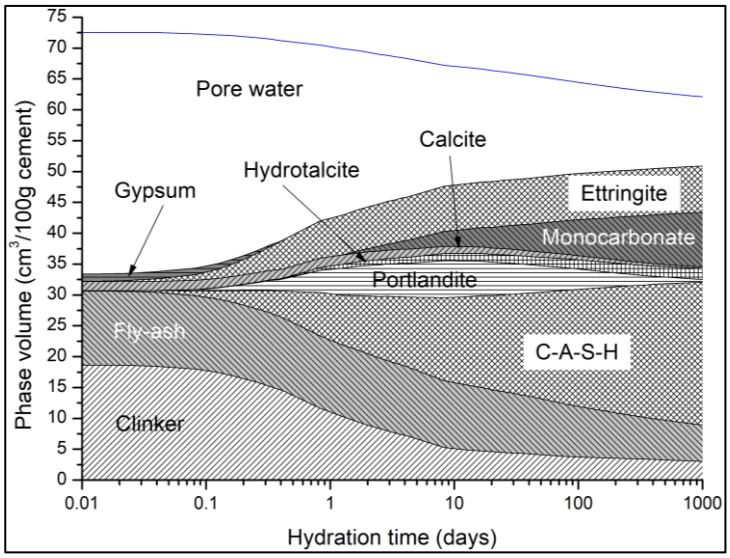
Oxide proportions (g/100g cement)				**XRD-Rietveld analysis**	
CEM I 52.5		**Fly-ash** [3]		**Fly-ash (g/100g)** [3]	
SiO_2	19.04	SiO	50.0	Quartz	12.3
Al_2O_3	5.01	Al_2O_3	23.9	Calcite	0.4
Fe_2O_3	2.83	Fe_2O_3	6.0	Hematite	0.6
CaO	63.4	CaO	6.3	Anhydrite	0.4
MgO	2.31	MgO	2.1	Mullite	18.3
Na_2O	0.28	Na_2O	0.6	Amorphous	68.0
K_2O	0.54	K_2O	1.4		
CaO free	1.71	CaO free	-		
CO_2	1.32	CO_2	-		
SO_3	2.65	SO_3	0.4		
Periclase	1.00	Periclase	-		
Fineness (m^2/kg)	386	450			

At this point, the PHREEQC input file is completed and modelling of a blended Portland : FA cement hydration can begin accounting for the kinetic dissolution of the clinker phases as a function of time, oversaturation of the precipitating hydrates from 0-12hrs and the release and uptake of alkalis by the C-A-S-H gel [HOLMES]. To model the reaction of the fly ash as a function of time, Equation 3 from the literature [3] was written into the spreadsheet, where α_{FA} is the degree of fly-ash hydration and *t* is time in days.

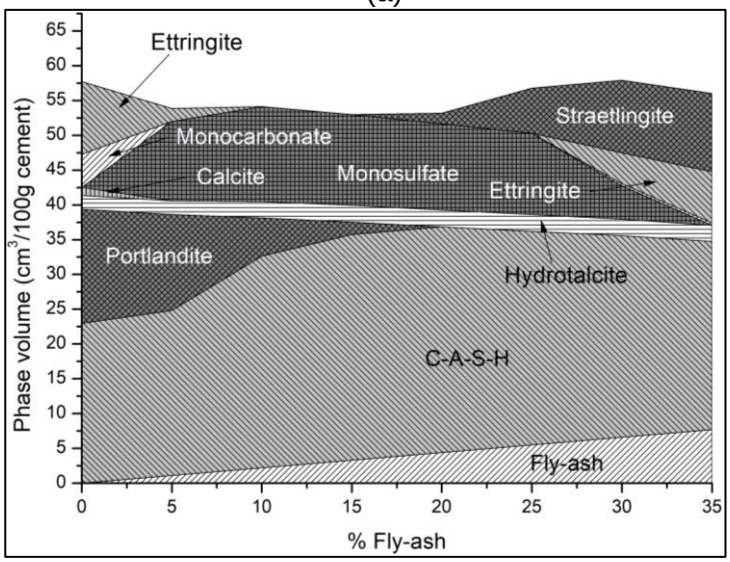
$$\alpha_{FA} = -15 + 10\ ln(t + 4.5) \quad (3)$$

OUTPUT

The phase assemblages for (a) over 1,000 days of hydration for a 35% FA replacement level and (b) 0-35% in 5% steps are shown in Figure 1. AS may be shown, portlandite is depleting with time and increasing FA proportions as expected.



(a)



(b)

Figure 1 Phase assemblages for (a) 35% FA replacement and (b) 0-35% FA

Acknowledgment: The authors would like to express appreciation for the support of the TU Dublin Business Partners Part-time Fee Award.

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