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Hydration study of slag-blended cement based on thermodynamic considerations

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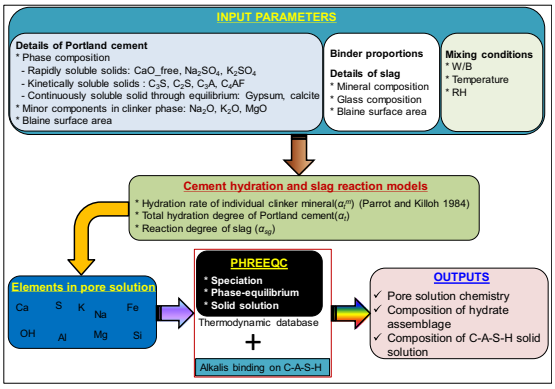
HIGHLIGHTS

- An integrated model coupling PHREEQC and Excel® was developed for hydration in Portland and slag-blended cements.
- Comparison of the simulated results with experimental data validates the proposed model.
- C-A-S-H solid solution model is important in predicting the hydration products.

GRAPHICAL ABSTRACT



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ABSTRACT

Thermodynamic calculations, using the geochemical code PHREEQC coupled with empirical equations for kinetics of cement hydration and slag reaction, were carried out to predict the compositions of the hydrate assemblage and pore solutions of hydrating Portland cement and cement blended with slag and the blended cement containing limestone. The predicted compositions of hydration products and element concentrations in pore solutions compared well with experimental data reported in literature. The calculation results showed the varying Ca/Si and Al/Si ratios of calcium aluminosilicate hydrate (C-A-S-H)[1] in the hydration products due to hydration and slag addition. Limitations on the equation for reaction of slag and the importance of a C-A-S-H solid solution model in prediction of hydration products are discussed.

1. Introduction

A partial replacement of Portland cement (PC) by supplementary cementitious materials (SCMs) or innovative low-carbon cement-based materials can substantially reduce CO_2 emissions associated with PC production [1]. Several studies have focused on developing SCMs from a variety of waste and by-product materials, in addition to common SCMs such as fly ash, ground granulated blast-furnace slag, and silica fume [2]. Further, novel cement systems/concrete are being developed through alkaline activation of aluminosilicates or innovative uses of waste materials [3]. Some of these novel cements are in use on a limited scale in some parts of the world; however, their short- and long-term performance as compared to conventional PC needs to be established

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[1] Cement chemistry shorthand notations: A = Al_2O_3, C = CaO, S = SiO_2, and H = H_2O.

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for their large-scale application [1]. More investigation on the properties and performance of SCMs or novel cements is necessary for their successful usage as partial or complete replacement of PC in concrete.

Knowledge of hydrating cement and the cementitious behaviour and pozzolanic characteristics of SCMs are important for better understanding of the properties and performance of the materials in concrete. It is also essential in terms of materials selection for concrete and for predicting properties and the durability and structural performance of concrete. The properties of hydrated PC and blended cement can be determined by laboratory experiments. However, it is difficult to depend entirely on experimental methods to determine the properties owing to the variety of SCMs used and the time it takes to perform these experiments. On the other hand, thermodynamic or mathematical models significantly reduce the reliance on laboratory experiments and help to predict hydration processes and materials properties.

Thermodynamic models in cementitious systems would make it possible to predict the composition of the hydrate assemblage and the aqueous phase composition based on information about the starting materials. Rothstein [4] studied the saturation indexes of solid phases in hydrating PC during the first 28 days of hydration using thermodynamic analysis of the element concentrations and compared the calculated saturation indexes with the supersaturation of phases found in previous work. Lothenbach and associates [5–12] made significant contributions to the thermodynamic calculations for cementitious materials to better understand cement hydration processes. Their work facilitated prediction of the composition of solid and liquid phases during hydration as a function of hydration time and simulation of the phase changes in cementitious materials in contact with ionic solutions. A thermodynamic model developed using the Gibbs free energy minimisation program GEMS-PSI (available at http://gems.web.psi.ch/) coupled with kinetic equations for the dissolution of clinker minerals successfully predicted the solid-phase assemblage and pore solution composition of hydrated PC [7] and PC-containing limestone [7,9]. The model was extended to allow calculations in the temperature range of 0–100 °C [10]; it was also applied to various cements [8] and mineral admixtures [5,12]. In addition to thermodynamic models, several hydration models in cementitious materials have been proposed to simulate the hydration reaction of cement and slag and also to predict the evolution of hydration products [13–14]. It is recognised that a partial or complete replacement of PC with slag reduces the Ca/Si ratio of calcium silicate hydrate (C-S-H) and also forms calcium aluminosilicate hydrate (C-A-S-H) [2,15–16]. The incorporation of aluminium in C-S-H of PC has also been reported in previous studies [2,16]. However, details of these aspects have not yet been taken into account in existing models for predicting the composition of the hydrate assemblage and pore solution chemistry. A model that includes Al incorporation and various Ca/Si ratios of C-S-H is thus important for better prediction of the solid products and aqueous phase compositions formed in PC and slag-blended systems.

In this study, chemical thermodynamic calculations were carried out to predict the solid-phase assemblages and pore solution composition of hydrating PC and slag as a function of hydration time. An integrated model that coupled PHREEQC [17–18] with empirical expressions for dissolution of clinker minerals and reactions of slag was developed, in which, the reactions among solids, aqueous solutions, and solid solutions were considered simultaneously at each hydration time step. Various calculation features built into PHREEQC including phase-equilibrium, speciation, and solid solutions, allowed the performance of a variety of geochemical calculations at higher ionic strengths as well, using an incorporated Pitzer model [19]. A solid solution that consists of various C-S-H and C-A-S-H gels as end-members was considered to account for the changing Ca/Si ratio and aluminium uptake in the gels [15,20]. The results of thermodynamic calculations in terms of solid-phase composition and concentration of elements in the pore solution were compared with the experimental data in literature for hydrating PC, cement blended with slag, and blended cement containing limestone.

2. Model description

2.1. Thermodynamic model

In this study, a phase-equilibrium module in PHREEQC was employed to carry out thermodynamic equilibrium calculations [17–18]. When a pure phase is no longer in equilibrium with a solution, it will dissolve or precipitate. The equilibrium reactions are expressed by the mass-action equation as

$$K_p = \prod_i (\gamma_i c_i)^{n_{i,p}} \tag{1}$$

where K_p is the thermodynamic equilibrium constant for phase p, γ_i is the activity coefficient of ion i (−), c_i is the concentration of ion i (mol/L), and $n_{i,p}$ is the stoichiometric coefficient of ion i in phase p (−). The thermodynamic equilibrium constant, K_p, at a given temperature T (K) can be expressed as

$$K_p = \exp\left(-\frac{\Delta_r G_T^0}{RT}\right) \tag{2}$$

where $\Delta_r G_T^0$ is the standard Gibbs energy of reaction at temperature T and R is the universal gas constant (8.31451 J/(mol K)). The standard Gibbs energy of reaction is expressed as

$$\Delta_r G_T^0 = \sum \Delta_f G_{T,products}^0 - \sum \Delta_f G_{T,reactants}^0 \tag{3}$$

where $\Delta_f G_T^0$ is the Gibbs free energy of formation for a species at a given temperature T. The equilibrium constant ($logK_p$) and the standard heats of reaction ($\Delta_r H^0$), which is used in the Van't Hoff equation (Appelo and Postma, 2009) to determine temperature dependence of the equilibrium constant, for the dissolution reactions of phases used in the simulation are tabulated in Table 1. The name of the phase (defined by dissolution reaction, $logK_p$, and $\Delta_r H^0$, as given in Table 1), the specified saturation index (which has a value of zero for equilibrium), and the amount of the phase were the input parameters for the phase-equilibrium module in PHREEQC.

2.2. Cement hydration model

In this study, the cement hydration model proposed by Parrot and Killoh [21] was used to estimate the hydration degree of each cement clinker mineral as a function of time. The model is described in detail elsewhere [7,9,21]; the main equations are briefly described here. Parrot and Killoh [21] derived a set of empirical equations to describe the hydration rate, R_t^m, of an individual clinker mineral m at time t ($m = C_3S$, C_2S, C_3A, C_4AF):

Nucleation and growth

$$R_{t,1}^m = \frac{K_1}{N_1}[1-\alpha_t^m]\{-\ln(1-\alpha_t^m)\}^{(1-N_1)} \tag{4}$$

Diffusion

$$R_{t,2}^m = \frac{K_2(1-\alpha_t^m)^{2/3}}{1-(1-\alpha_t^m)^{1/3}} \tag{5}$$

Hydration shell formation

$$R_{t,3}^m = K_3(1-\alpha_t^m)^{N_3} \tag{6}$$