Research article

A thermodynamics-based approach for examining the suitability of cementitious formulations for solidifying and stabilizing coal-combustion wastes

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ABSTRACT

Cementitious binders are often used to immobilize industrial wastes such as residues of coal combustion. Such immobilization stabilizes wastes that contain contaminants by chemical containment, i.e., by uptake of contaminants into the cementitious reaction products. Expectedly, the release ("leachability") of contaminants is linked to: (i) the stability of the matrix (i.e., its resistance to decomposition on exposure to water), and, (ii) its porosity, which offers a pathway for the intrusion of water and egress of contaminant species. To examine the effects of the matrix chemistry on its suitability for immobilization, an equilibrium thermodynamics-based approach is demonstrated for cementitious formulations based on: ordinary portland cement (OPC), calcium aluminate cement (CAC) and alkali activated fly ash (AFA) binding agents. First, special focus is placed on computing the equilibrium phase assemblages using the bulk reactant compositions as an input. Second, the matrix's stability is assessed by simulating leaching that is controlled by progressive dissolution and precipitation of solids across a range of liquid (leachant)-to-(reaction product) solid (l/s) ratios and leachant pH's; e.g., following the LEAF 1313 and 1316 protocols. The performance of each binding formulation is evaluated based on the: (i) relative ability of the reaction products to chemically bind the contaminant(s), (ii) porosity of the matrix which correlates to its hydraulic conductivity, and, (iii) the extent of matrix degradation that follows leaching and which impact the rate and extent of release of potential contaminants. In this manner, the approach enables rapid, parametric assessment of a wide-range of stabilization solutions with due consideration of the matrix's mineralogy, porosity, and the leaching (exposure) conditions.

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1. Introduction and background

A wide variety of cementitious binders, including those based on alkali-activated fly ash (AFA) (Provis, 2009a; Shi and Fernández-Jiménez, 2006), ordinary portland cement (OPC) (Chen et al., 2009; Hills et al., 1993; Poon et al., 1985a) and calcium aluminate cement (CAC) (Navarro-Blasco et al., 2013) may be used for the immobilization (i.e., solidification and stabilization, S/S) of coal

combustion residuals (CCRs). Cementitious binders[1] provide not only physical encapsulation but also enable chemical stabilization of potential contaminants. Potential contaminants (e.g., heavy metals) can be immobilized by pathways including: (i) chemical processes that involve (co)precipitation of insoluble compounds (e.g., salts or hydroxides) of the metals (Glasser, 1997), structural incorporation (Bankowski et al., 2004; Gougar et al., 1996; Zhang, 2000) and/or surface complexation/sorption onto the solid reaction products (Van Jaarsveld et al., 1997, 1999), and, (ii) physical processes that involve encapsulation of the contaminants within a matrix of low permeability, which retards the rate of transport of contaminants to the external environment (Randall and Chattopadhyay, 2004; Roy et al., 1992).

While the matrix's mineralogy is critical to ensure good performance (Poon et al., 1985a), most often matrix compositions are identified by a trial-and-error methodology that involves varying the mixture proportions incrementally and testing the mechanical performance of the reacted solids (Ko et al., 2014). The success of this approach has been demonstrated by Kogbara et al. (2014) who studied the compressive strength, hydraulic conductivity, acid neutralization capacity and pH for a variety of formulations with varying water-to-solid and binder-to-waste ratios. While Kogbara et al. (2014) defined a range of compositions that offered acceptable performance − the time and labor intensity of the approach are substantial. Moreover, the approach is difficult to implement for highly heterogeneous wastes such as CCRs. These issues are further complicated by the fact that, so far, there doesn't exist a consensus-based protocol applicable to AFA systems which allows matching of a given activation solution (e.g., alkali hydroxides and alkali silicates) to the solid precursor (e.g., fly ash) composition (Bernal, 2016; Provis, 2017).

Thermodynamic simulations based on the Gibbs Free Energy Minimization (GEM) method have been extensively applied to describe phase relations, compatibilities and interactions in complex chemical environments (Bennett et al., 1992; Damidot et al., 2011; Lothenbach and Winnefeld, 2006; Lothenbach et al., 2008; Lothenbach, 2010; Myers et al., 2015b). Simulations of this nature provide descriptions of phase balances, chemical (aqueous) speciation and partitioning in a multi-component system following the principle of the minimization of the Gibbs free energy. While this method has been successfully applied to develop an understanding of the role of reactant (binder) composition on the mineralogy and mechanical performance of hydrated cementitious solids, so far it has not been applied to estimate the suitability (or lack thereof) of alkali-activated formulations for the immobilization of coal combustion residues. Herein, the GEMS method was used to ascertain the reaction product mineralogy as a function of the binder composition (e.g., for AFA, OPC, and CAC based binders) and mixture proportions so as to identify: (i) formulations that produce hydrates with the greatest potential for stabilizing heavy metals by structural incorporation, and/or, (ii) formulations which yield the lowest porosity − and diffusion coefficients − that restrict the transport of heavy metals (and other contaminants). While the equilibrium nature of the simulations makes no consideration of the reaction kinetics or evolution of pore structure as a function of leaching, the approach offers a thermodynamics-based strategy that carefully considers phase compatibility, and stability to, *a priori*, screen the suitability of any given binder composition for the immobilization of coal combustion residues.

2. Some insights into contaminant immobilization in cementitious environments

The immobilization of contaminants in cementitious environments depends both on the nature of solids present and the pH of the pore solution (Glasser, 1997; Poon et al., 1985a). While each system should be considered for its own complexity, a review of the literature suggests the following broad guidance (Ioannidis and Zouboulis, 2005; Provis, 2009a; Wieland et al., 2006):

- Cations of Cd, Co, Cu, Ni, Pb, and Zn readily precipitate insoluble (or sparingly soluble) salts at high pH (Glasser, 1997) and are therefore readily immobilized at $pH \geq 13$ (Palacios and Palomo, 2004; Phair et al., 2004; Provis, 2009a; Van Jaarsveld et al., 1997, 1999).
- Metal oxyanions such as CrO_4^{2-}, SeO_4^{2-} and AsO_4^{3-}, and metals that do not form insoluble precipitates at elevated pH are mobile in alkaline environments (Chrysochoou and Dermatas, 2006; Fernández-Jiménez et al., 2005; Provis, 2009a; Álvarez-Ayuso et al., 2008). In such cases, ionic mobility is hindered only via physical encapsulation by the cementitious matrix. Therefore, the leachability of these species is a function of the porosity of the matrix (Chrysochoou and Dermatas, 2006; Poon et al., 1985b).
- Isovalent metallic ions may substitute cations with similar charge in hydrated cement solids, e.g., Cd may partially substitutes Ca in C-S-H (Díez et al., 1997; Pomiès et al., 2001; Żak and Deja, 2015), and,
- Alumino-ferrite tri-substituent (AFt, i.e., ettringite) and alumino-ferrite monosubstituent (AFm, e.g., monosulfoaluminate) compounds may incorporate oxyanions, including CrO_4^{2-}, SeO_4^{2-} and AsO_4^{3-} and therefore may contribute to their stabilization (Bankowski et al., 2004; Gougar et al., 1996; Zhang, 2000). However, factors such as pH, temperature, presence of sulfate, carbonate and other competing anions may influence the extent/stability of such incorporations (Chrysochoou and Dermatas, 2006; Ghosh et al., 2006; Guan et al., 2009).

3. Simulation approach

3.1. Materials

The materials considered in the simulations include a representative coal combustion waste (a trona-impacted fly ash, FA), ordinary portland cement (OPC), and calcium aluminate cement (CAC) as solid precursors. The activation solutions used to compose a model geopolymer system consisted of: (a) 2-to-10 M NaOH solutions, and, (b) mixtures of 8 M NaOH + SiO_2, composed to offer a silica modulus, SiO_2/Na_2O = 0-to-2 (mole basis). The simulations were carried out at 25 °C and 1 bar, for w/b = 0.50 (water-to-binder

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[1] Cement chemistry notation is used throughout this paper. Following this notation: A = Al_2O_3, c = CO_2, C = CaO, F = Fe_2O_3, H = H_2O, M = MgO, N = Na_2O, s = SO_3, S = SiO_2.

Table 1
The simple oxide compositions of the solid precursors considered in the simulations.

Simple Oxide	OPC	CAC	Fly ash
CaO	64.66	38.54	25.72
SiO_2	21.73	5.31	31.00
Al_2O_3	4.51	52.78	17.18
Fe_2O_3	3.11	2.35	5.50
MgO	2.45	0.60	5.90
Na_2O	0.20	0.08	8.80
K_2O	0.84	0.31	0.44
SO_3	2.49	0.02	5.46
Total	100	100	100