Phase diagrams for alkali-activated slag binders

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ABSTRACT

Phase diagrams for alkali-activated slag (AAS) binders are simulated at (metastable) thermodynamic equilibrium, spanning the relevant compositional envelopes for these materials. The phase diagrams are generally consistent with experimental observations in the literature, dominated by calcium (alkali) aluminosilicate hydrate (C-(N-)A-S-H) gels and Mg-Al layered double hydroxides. Relationships between the stabilities of the predicted solid phase assemblages, pore solution compositions, and the bulk chemical composition are identified, yielding an improved understanding of AAS binder chemistry. Strätlingite is predicted at low to intermediate Si concentrations and at high Al content, while zeolites (and thus most likely also disordered alkali-aluminosilicate (hydrate) gels) tend to precipitate at higher concentrations of both Si and Al; katoite and AFm-type phases are stabilised at intermediate levels of CaO + Al_2O_3 + MgO. The application of these results in designing AAS binders can enable the phase assemblages and chemical properties of these materials to be more precisely controlled.
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1. Introduction

Alkali-activated slag (AAS) is a class of binder which is produced via the chemical reaction between an 'activator' (alkaline solution), e.g., NaOH (NH),[1] Na_2SiO_3 (NS), $Na_2Si_2O_5$ (NS$_2$), Na_2CO_3 (N$\overline{C}$), or Na_2SO_4 (N$\overline{S}$), and a metallurgical slag precursor, typically ground granulated blast furnace slag (BFS). These materials have been used in concrete infrastructure for several decades [1–3], particularly in areas where slag availability is high and a history of technical know-how exists, e.g. China and eastern Europe [2]. AAS can also be produced using other metallurgical slags that are less well utilised than BFS (e.g., phosphorus, copper, and steel slags [4]), bringing particularly high value in some specialised applications [5].

The chemistry of NH- and NS-activated slags is relatively well understood [2,6–13], with one of the key remaining questions concerning their resistance to carbonation, which is controlled to a significant extent by binder chemistry. For example, the carbonation resistance of sodium silicate-activated slag has been demonstrated to improve significantly as a function of bulk MgO content [14], although the stabilities of the Mg-Al layered double hydroxide (LDH) phases formed in these materials need to be better understood to clarify their role in the underlying chemical mechanisms of carbonation [11]. The other typical solid reaction products in these binders are poorly-crystalline calcium(-sodium) aluminosilicate hydrate (C-(N-)A-S-H) gel [6, 10] and the 'alumino-ferrite-mono' (AFm) family of Ca-Al LDH phases [8], including strätlingite [15], and sodium aluminosilicate (hydrate) (N-A-S(-H))-type gels [6,11].

Compared to binders activated by silicates or hydroxides, significantly less research effort has been devoted to N$\overline{C}$- and N$\overline{S}$-activated slag binders, and consequently a better understanding of these binders is needed to enable them to be designed for improved performance, particularly with respect to setting characteristics and long-term chemical durability [16–18]. The solid phase assemblage in N$\overline{C}$-activated slag normally contains poorly-crystalline C-(N-)A-S-H and N-A-S(-H) gels, Mg-Al LDH, and AFm-type phases predominantly intercalated with carbonate and/or hydroxide, e.g., hydrotalcite-like LDH ($M_4A\overline{C}H_9$) and calcium monocarboaluminate hydrate ($C_4A\overline{C}H_{11}$), and zeolites [16,17]. The carbonate-bearing phases typically present in these materials include calcite, aragonite and vaterite (C$\overline{C}$), gaylussite (NC$\overline{C}_2H_5$) as a transient phase at early age, and thermonatrite (N$\overline{C}$H) [16,17]. Typical solid reaction products in N$\overline{S}$-activated slag binders include ettringite ($C_6A\overline{S}_3H_{32}$), AFm intercalated with $\overline{S}$ (calcium monosulfoaluminate hydrate, $C_4A\overline{S}H_x$ with $x \approx 12$ [19]), and gypsum ($C\overline{S}H_2$), although the abundances of these phases change significantly as a function of the slag chemical composition [20].

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[1] Cement chemistry notation is used throughout the paper: C = CaO; S = SiO$_2$; A = Al$_2$O$_3$; N = Na$_2$O; M = MgO; $\overline{C}$ = CO$_2$; $\overline{S}$ = SO$_3$; H = H$_2$O.

Recent research has substantially advanced the degree of confidence in which the solid phase assemblages of AAS binders can be accurately predicted under (metastable) thermodynamic equilibrium conditions. Notably, the CNASH_ss thermodynamic model [21], containing the first explicit descriptions of Al and alkali uptake in C-S-H-type phases, describes the volumetric properties of C-(N-)A-S-H gel in AAS binders, and was validated against a large set of solubility data in the CaO-(Na_2O,Al_2O_3)-SiO_2-H_2O systems, C-(A-)S-H gel chemical compositions, and NH- and NS-activated slag pore solution chemistry. The CNASH_ss thermodynamic model was later applied to simulate the chemistry of NS- and N$\bar{\text{C}}$-activated slag binders [11,22]; simulation of the former system showed a relatively lower stability of ettringite than existing thermodynamic modelling work [23], in closer agreement with the experimental literature, and that zeolite-type phases are also potentially stable in these systems. An ideal solid solution model for Mg-Al LDH intercalated with OH^- (hereafter termed MA-OH-LDH) was also developed, again providing a significant advancement over earlier work [24, 25], which has further improved the utility of thermodynamic modelling to predict AAS binder chemistry.

In this paper, the solid phase assemblages in NS-, NS$_2$-, N$\bar{\text{C}}$- and N$\bar{\text{S}}$-activated slag binders are predicted by thermodynamic modelling, and presented as phase diagrams in the CaO-Al_2O_3-MgO pseudo-ternary system at fixed contents of SiO_2, sulfur, and Na_2O, extending from recently published phase diagrams for NH-AS [11]. These phase diagrams are compared to experimental results to assess the reliability of the simulations, to gain insight into kinetic and other thermodynamic effects not captured by the modelling performed, and to improve the current understanding of AAS binder chemistry across a wide range of activator chemistries.

2. Methods

Phase diagrams for NS-, NS$_2$-, N$\bar{\text{C}}$-, and N$\bar{\text{S}}$-activated slag binders were generated using simulated slag precursors with 30 wt% and 40 wt% SiO_2, and 2 wt% SO_3 equivalent as H_2S (i.e., specified as S^{2-} and H^+), to approximate the typical chemical composition of BFS [26,27]. The remainders of the chemical compositions of the slag precursors were varied within the CaO-Al_2O_3-MgO pseudo-ternary system to span the range of chemistries that are relevant to AAS-based binders: $0.5 \leq CaO \leq 1$, $0 \leq Al_2O_3 \leq 0.5$ and $0 \leq MgO \leq 0.5$ (on a molar basis), on the basis of the sum of CaO + Al_2O_3 + MgO being normalised to 1 (i.e., at fixed contents of SiO_2 and SO_3 equivalent, which are thus omitted from the pseudo-ternary diagrams). Fe was excluded from the simulations, consistent with the identification of its passivated state as entrained metallic particles in BFS [28], and with sulfur in the slag represented as sulfide. Therefore, the simulations are most relevant to AAS synthesised using BFS and less to those produced using non-ferrous slags, e.g., Cu slag (typically having compositions in the CaO-FeO-Fe_2O_3-SiO_2 system). A slag reaction extent of 60% was specified, which lies in the normal range measured for AAS binders after 180 days of reaction [6,7,14,17]. Therefore, simulations were carried out using 100 g slag, 60 g of which is 'reactive' and comprised of CaO, Al_2O_3, MgO, SiO_2, S^{2-}, and H^+ (for charge balance), and 40 g of which is 'unreactive'. A water to binder (solids + anhydrous activator component) mass ratio (w/b) of 0.4 was used, which is typical for AAS binders. A dosage of 8 g activator per 100 g slag was specified except for the $Na_2O \cdot 2SiO_2$ (NS$_2$) activator, which was added at a dose of 4 g Na_2O per 100 g slag.

Thermodynamic modelling was performed using the Gibbs energy minimisation software GEM-Selektor v.3 (http://gems.web.psi.ch/) [29, 30] using the thermodynamic database described in [11], which is based on an updated version of CEMDATA07 [24]. This thermodynamic database contains ideal solid solution models for C-(N-)A-S-H gel [21] and MA-OH-LDH [11]. These models are provided as Supporting Information in formats that can be directly loaded into GEMS v.3.2 and v.3.3. The thermodynamic database also contains a small subset of zeolites. These zeolites were chosen following a preliminary investigation which showed that thermodynamic modelling results obtained using these

data are consistent with experimentally determined phase assemblages of AAS binders. The thermodynamic data used to describe the zeolite phases and alkali carbonate minerals here should be treated as provisional because they were not recompiled for full internal consistency with the thermodynamic database used [11]. These data and the thermodynamic model used to describe MA-OH-LDH are based on data with generally larger uncertainty than that associated with the solubility data used to describe the other solid phases here. Therefore, the modelled stability regions for these phases should be regarded as less reliable than the others.

It should also be noted that this thermodynamic database does not contain data for magnesium-silicate-hydrate (M-S-H) phases that can stabilise in high Mg cementitious and clay-containing environments [31], which thus reduces the reliability of the Mg-rich regions of the phase diagrams modelled here. These M-S-H phases have not yet been identified in AAS binders, and data for these phases have only very recently been published [32]. Further work is needed to understand their compatibility in AAS systems (including consideration of kinetic effects). Precipitation of Si-hydrogarnet was suppressed because this phase tends not to form at ambient temperature and pressure in hydrated cementitious systems [24]. A predominantly $N_{2\,(g)}$ atmosphere was used as the gas phase in all simulations.

The Truesdell-Jones form of the extended Debye-Hückel equation (Eq. (1)) [33] and the ideal gas equation of state were used as aqueous and gaseous phase models, respectively, with the average ion size ($\dot{a}$, Å) and the parameter for common short-range interactions of charged species (b_γ, kg mol^{-1}) specified to represent NaOH-dominated solutions (3.31 Å and 0.098 kg mol^{-1}, respectively [33]).

$$\log_{10}\gamma_j = \frac{-A_\gamma z_j^2 \sqrt{I}}{1 + \dot{a}B_\gamma \sqrt{I}} + b_\gamma I + \log_{10}\frac{x_{jw}}{X_w} \tag{1}$$

The parameters γ_j and z_j in Eq. (1) are the activity coefficient and charge of the jth aqueous species, respectively; A_γ (kg$^{0.5}$ mol$^{-0.5}$) and B_γ (kg$^{0.5}$ mol$^{-0.5}$ cm^{-1}) are T,P-dependent electrostatic parameters; I is the ionic strength of the aqueous electrolyte phase (mol kg^{-1}); x_{jw} (mol) is the molar quantity of water; and X_w (mol) is the total molar amount of the aqueous phase. The activity of water is calculated from the osmotic coefficient [33], and unity activity coefficients are used for neutral dissolved species.

A step size of 0.02 normalised CaO-Al_2O_3-MgO molar composition units was used to construct the phase diagrams, i.e., (CaO, Al_2O_3, MgO) = (0.00, 1.00, 0.00), (0.02, 0.98, 0.00), (0.02, 0.96, 0.02), and so on. The masses of each stable solid phase and the chemical compositions of the aqueous solutions simulated by GEMS were transferred to Origin and plotted. Stability regions for each phase correspond to the chemical composition envelopes where they are simulated to have non-zero mass. Major, minor, and trace classifications are assigned to solid phases with masses of >40%, 5–40%, and <5% of the total simulated solid mass, respectively. The full set of modelled solid (tabulated) and aqueous (tabulated and graphical) phase data reported here are presented as Supporting Information. Additional properties of the C-(N-)A-S-H gel phases simulated using the CNASH_ss thermodynamic model, its chemical composition, density, molar volume, and mean chain length (calculated using formula for non-cross-linked C-(N-)A-S-H structures and described in [21,34]), are provided alongside those data (Supporting Information).

3. Results and discussion

3.1. Phase diagrams for NS-activated slag binders

The simulated phase diagrams for NS-activated slag binders (Fig. 1; in this graphic and other similar graphics throughout the paper, the table of compositional regions refers to both parts A and B) are dominated by C-(N-)A-S-H gel and Mg-Al LDH intercalated with