Studies of phase relations and AFm solid solution formations in the system CaO-Al₂O₃-CaCl₂-CaCrO₄-H₂O

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A B S T R A C T

The Friedel’s salt (Cl-AFm) as a major hydration phase in chlorinated cement-based materials plays an important role in the immobilization of chromate through ion exchange with chloride. To study the solid solutions of \( \text{Ca}_4[\text{Al(OH)}_6]_2\text{CrO}_4\cdot\text{nH}_2\text{O} \) (CrO₄-AFm) and the composition of coexisting aqueous phase, AFm phases containing Cl⁻ and CrO₂⁻ 4 were synthesized and characterized with XRD, SEM, FTIR, FAAS and ion chromatography (IC).

Based on the determined total solubility of products and ion concentrations in solution, a solid solution-aqueous solution (SSAS) model of a binary mixing with Cl-AFm and CrO₄-AFm phases was established to predict aqueous solubility of \( \text{Ca}_4[\text{Al(OH)}_6]_2[(\text{CrO}_4)x(\text{Cl})_{2-2x}][\text{nH}_2\text{O}] \) as a function of total Cl/Cr ratio in solid solution system. The solubility constant \((K)\) of pure Cl-AFm is 27.09 and its free energy of formation \((\Delta G_f)\) is −7047.80 kJ mol⁻¹ at 27 °C. \( K \) of pure CrO₄-AFm is 29.07 and its \( \Delta G_f \) is −8238.66 kJ mol⁻¹ at 27 °C. Both the experimental and modeled data showed that the formation of solid solutions between Cl-AFm and CrO₄-AFm could greatly lower the chromate concentration in aqueous solution. Therefore, this study suggested that (Cl, CrO₄)-AFm compounds could efficiently immobilize the trace metal CrO₄²⁻ in cement-stabilized wastes.

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1. Introduction

Chromate is a common heavy metal oxyanion contaminant in blast furnace slag, wastes of stainless steel production and other waste mixtures (Das et al., 2014). As a cement-based binder, ordinary Portland cement (OPC) has been widely used to immobilize heavy metal in materials and wastes (Chen et al., 2009; Chrysochoou and Dermatas, 2006). However, chromate, as a highly mobile and acutely toxic oxyanion in alkaline environment (Leisinger et al., 2014), could easily leach out into the aqueous phase from the hydrated OPC pastes (Park et al., 2006; Van der Sloop, 2002).

Recently, other materials, such as fly ash (FA), blast furnace slag (BFS) and metakaolin (MK), has become increasingly popular in treatment of heavy metal waste due to the financial and environmental viewpoints (Arellano Aguilar et al., 2010), as well as their improved concrete microstructure and binding capabilities to heavy metal ions (Fernández Pereira et al., 2009; Luna Galiano et al., 2011). The Friedel’s salt is stable from 0 °C up to 200 °C and transforms from a monoclinic low-temperature form (α) to a rhombohedral high-temperature form (β) at around 35 °C (Balonis, 2010). The compound belongs to Alumino-Ferrite-mono (AFm) family or a more general category of compounds called Lamellar Double Hydroxides (LDH). The structure of AFm phase is composed of layers, ideally with a charged unit \([\text{Ca}_2\text{Al(OH)}_6\cdot\text{nH}_2\text{O}]^n\), which can bind free-chloride ions into the interlayers, and thus possess better ion exchange capacity within this layer structure (Birnbaum-Yauri and Glasser, 1998; Elakneswaran et al., 2009). Many reported studies showed that (Deng and Qian, 2008; Qian et al., 2008, 2009; Shao et al., 2013) chloride-bearing materials had a wide application prospect in heavy metal oxyanion contaminant treatment due to the formation of Friedel’s salt.

In this study, a thermodynamic model was established to predict aqueous solubility of \( \text{Ca}_4[\text{Al(OH)}_6]_2[(\text{CrO}_4)x(\text{Cl})_{2-2x}][\text{nH}_2\text{O}] \) as a function of the Cl/Cr ratio according to the solid solution-aqueous solution (SSAS) model of a binary mixing with \( \text{Ca}_4[\text{Al(OH)}_6]_2\cdot\text{nH}_2\text{O} \) (abbreviated as Cl-AFm) and \( \text{Ca}_4[\text{Al(OH)}_6]_2\cdot\text{CrO}_4\cdot\text{nH}_2\text{O} \) (abbreviated as CrO₄-AFm) phases. These results would...
be very helpful in the potential modeling of Friedel’s salt in order to control the trace components of CrO2-.

2. Material and methods

2.1. Materials

Chemicals (CaO, NaCl and Na2CrO4·4H2O) used in solid solutions were at least analytically pure. NaAlO2 was chemically pure. All experiments were carried out in a glove box under a N2 atmosphere (O2, CO2 < 2 ppm) to prevent possible CO2 contamination. Ultrapure water was used to prepare solutions and to rinse. All polyethylene bottles, tubes and glassware were washed in acid solution (0.3 M HNO3) for at least 24 h and rinsed with ultrapure water three times.

2.2. Synthesis of solid phases

Solid solution phases \( \text{Ca}_4\text{Al(OH)}_6\text{Cl}_2\text{·}_x \) \( x \) \( n \) \text{H}_2\text{O} were synthesized according to the following.

Stoichiometric amounts of CaO (4 mmol), NaAlO2 (2 mmol), Na2CrO4·4H2O and NaCl (4·2x mmol in total) were added to ultrapure water (500 ml) to obtain solid solution phases with different chromate mole fractions \( x = \frac{[\text{CrO}_4^{2-}]}{[\text{CrO}_4^{2-}]+[\text{Cl}^-]} \) of 0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1. Samples were named as CrX (CrO4- was pure Friedel’s salt \( \text{Ca}_4\text{Al(OH)}_6\text{Cl}_2\text{·}n\text{H}_2\text{O} \) and Cr10 was pure CrO4- Afm \( \text{Ca}_4\text{Al(OH)}_6\text{Cl}_2\text{·}n\text{H}_2\text{O} \)).

All mixtures were equilibrated for 30 days in sealed 1 L HDEP bottles at 27 °C on a rotary shaker at 125 rpm. The samples were then centrifuged for 20 min at 4000 rpm. The supernatant was separated and filtered with a 0.45 μm membrane filter and stored at 4 °C. A quadruple Plus Pt 1000 electrode form Metrohm was used to measure pH of the liquid phase. Dissolved concentrations of Ca, Al and Cr were determined with ICP-AES and dissolved concentrations of Cl were determined with IC. The solid phases were washed with absolute ethyl alcohol and stored in desiccator (35%RH) over silica gel and soda lime and for one weeks then characterized with XRD, FTIR, SEM, ICP-AES and IC. The ICP-AES and IC were tested after solid samples were dissolved with HNO3.

2.3. Thermodynamic modeling

In the solid solution-aqueous solution (SSAS) equilibrium model, solubilities of the pure end-members \( \text{Ca}_4\text{Al(OH)}_6\text{Cl}_2\text{·}n\text{H}_2\text{O} \) and \( \text{Ca}_4\text{Al(OH)}_6\text{CrO}_4\text{·}n\text{H}_2\text{O} \) can be determined according to the following mass action laws (Glynn and Reardon, 1990).

\[ \text{Ca}_4\text{Al(OH)}_6\text{Cl}_2\text{·}n\text{H}_2\text{O} = [\text{Ca}^{2+}]^4 [\text{Al(OH)}_4^-]^2 [\text{Cl}^-]^2 = K_{\text{Cl}} \]

\[ \text{Ca}_4\text{Al(OH)}_6\text{CrO}_4\text{·}n\text{H}_2\text{O} = [\text{Ca}^{2+}]^4 [\text{Al(OH)}_4^-]^2 [\text{OH}^-]^4 [\text{CrO}_4^{2-}] = K_{\text{Cr}} \]

The thermodynamic equilibrium in the pseudo binary system can be described with the following appropriate mass action expressions,

\[ [\text{Ca}^{2+}]^4 [\text{Al(OH)}_4^-]^2 [\text{OH}^-]^4 [\text{Cl}^-]^2 = K_{\text{CaCl}} = K_{\text{CrCl}} \gamma_{\text{Cl}} \]

where, \( K_{\text{Cl}} \) are the pure end-member soluble products, \( a_{\text{CaCl}} \) and \( a_{\text{CrCl}} \) are the activities of Cl-AFm and CrO4-AFm components in the \( \text{Ca}_4\text{Al(OH)}_6\text{Cl}_2\text{·}n\text{H}_2\text{O} \) solid solution, \( \gamma_{\text{Cl}} \) and \( \gamma_{\text{Cr}} \) are the mole fractions of Cl-AFm and CrO4-AFm components in the solid solution, and \( \gamma_{\text{Cl}} \) and \( \gamma_{\text{Cr}} \) are the solid phase activity coefficients.

Eq. (2) and Eq. (3) showed the equivalence of chemical potentials of the solid and aqueous phase components in an equilibrium system.

In order to describe the aqueous solubility of binary systems, Lippmann (Lippmann, 1977, 1982b, 1980, 1982a) introduced a new expression, named \( \Sigma \Pi \) or the “total solubility of products”. In (Cl, CrO4)-Afm system, it can be defined as:

\[ \Sigma \Pi = [\text{Ca}^{2+}]^4 [\text{Al(OH)}_4^-]^2 [\text{OH}^-]^4 \left( \frac{[\text{Cl}^-]^2}{[\text{CrO}_4^{2-}]} \right) \]

At thermodynamic equilibrium, the definition of \( \Sigma \Pi \) can be substituted through the combination of Eq. (1) and Eq. (2).

\[ \Sigma \Pi_{eq} = K_{\text{Cr}} \gamma_{\text{Cl}} \gamma_{\text{Cr}} + K_{\text{Cr}} \gamma_{\text{Cl}} \gamma_{\text{Cr}} \]

The \( \Sigma \Pi_{eq} \) in Eq. (6) can be calculated from individual activities of components in the solid phase at thermodynamic equilibrium. This family of points is the solidus curve of Lippmann phase diagram. Alternatively, \( \Sigma \Pi_{eq} \) can be calculated from activities of components in aqueous phase. The activity fractions of (Cl, CrO4)-Afm system are defined as the following.

\[ \chi_{\text{Cl}} = \frac{[\text{Cl}^-]^2}{[\text{CrO}_4^{2-}]} \]

\[ \chi_{\text{Cr}} = \frac{[\text{CrO}_4^{2-}]}{[\text{CrO}_4^{2-}]} \]

When Eq. (7) and Eq. (8) are introduced into Eq. (6), the Lippmann phase diagram is

\[ \Sigma \Pi_{eq} = 1 \left( \frac{\chi_{\text{Cl}}}{K_{\text{Cr}}} + \frac{\chi_{\text{Cr}}}{K_{\text{Cl}}} \right) \]

A Lippmann diagram is a plot of a solidus curve as a function of the solid chromate mole fractions (Eq. (6)), and a solutus curve as a function of the chromate activity fractions in solution (Eq. (9)). With the total solubility of products \( \Sigma \Pi \), Eq. (9) can be used to predict the solubility of a solid solution at thermodynamics equilibrium (Prieto, 2009).

The distribution coefficient, \( D \), is given from the Berthelot-Nernst distribution law.

\[ D = \frac{\chi_{\text{Cl}} / \chi_{\text{Cr}}}{[\text{Cl}^-]^2 / [\text{CrO}_4^{2-}]} = K_{\text{Cr}} \gamma_{\text{Cr}} / K_{\text{Cr}} \gamma_{\text{Cl}} \]

Substituting the definitions of the solid-phase activity in the Guggenheim excess free-energy fitting parameters \( (a_0 \) and \( a_1 ) \), we have.

\[ D = \frac{K_{\text{Cr}}}{K_{\text{Cl}}} \exp \left\{ 2 \chi_{\text{Cl}} - 1 \right\} a_0 + \left[ 6 \chi_{\text{Cl}} - 3 \right] a_1 \]