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Modelling of calcium sulphate solubility in concentrated multi-component sulphate solutions

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Abstract

The chemistry of several calcium sulphate systems was successfully modelled in multi-component acid-containing sulphate solutions using the mixed solvent electrolyte (MSE) model for calculating the mean activity coefficients of the electrolyte species. The modelling involved the fitting of binary mean activity, heat capacity and solubility data, as well as ternary solubility data. The developed model was shown to accurately predict the solubility of calcium sulphate from 25 to 95 °C in simulated zinc sulphate processing solutions containing $MgSO_4$, $MnSO_4$, $Fe_2(SO_4)_3$, Na_2SO_4, $(NH_4)_2SO_4$ and H_2SO_4. The addition of H_2SO_4 results in a significant increase in the calcium sulphate solubility compared to that in water. By increasing the acid concentration, gypsum, which is a metastable phase above 40 °C, dehydrates to anhydrite, and the conversion results in a decrease in the solubility of calcium sulphate. In $ZnSO_4$–H_2SO_4 solutions, it was found that increasing $MgSO_4$, Na_2SO_4, $Fe_2(SO_4)_3$ and $(NH_4)_2SO_4$ concentrations do not have a pronounced effect on the solubility of calcium sulphate. From a practical perspective, the model is valuable tool for assessing calcium sulphate solubilities over abroad temperature range and for dilute to concentrated multi-component solutions.

Keywords: Calcium sulphate; Gypsum; Anhydrite; Zinc hydrometallurgy; Solubility; Chemical modelling; OLI; Hydrometallurgy

1. Introduction

Calcium sulphate occurs in three forms: dihydrate (or gypsum) (DH: $CaSO_4{\cdot}2H_2O$), hemihydrate (or bassanite) (HH: $CaSO_4{\cdot}0.5H_2O$) and anhydrite (AH: $CaSO_4$), depending on the temperature, pH and formation conditions. Calcium sulphate occurs widely in nature as gypsum and anhydrite, and is encountered in many industrial processes such as the evaporation of brines and the manufacture of phosphate fertilizer. Calcium sulphate commonly precipitates during the neutralization of free sulphuric acid or in iron removal operations where sulphates are eliminated from aqueous solutions by the addition of calcium-containing bases such as lime or limestone. Because of its relative insolubility, calcium sulphate is deposited almost everywhere calcium and sulphate occur together in aqueous solutions. The resulting scales are a major concern because they form even at low pH and can be effectively removed only by mechanical means. A recent evaluation of one process estimated that the control of calcium sulphate in that operation alone cost between \$6 and \$10 million per year [1].

Many studies have attempted to theoretically model the solubilities of the calcium sulphate compounds in water and in multi-component aqueous solutions. The solubility of calcium sulphate hydrates is equal to the sum of the molalities of the free calcium ion, Ca^{2+}, and the associated calcium sulphate neutral species, $CaSO_{4(aq)}$. Consequently, the solubility of calcium sulphate hydrates is governed by the following equilibria:

$$CaSO_4{\cdot}nH_2O(S) \leftrightarrow Ca^{2+} + SO_4{}^{2-} + nH_2O \tag{1}$$

$$Ca^{2+} + SO_4{}^{2-} \leftrightarrow CaSO_{4(aq)} \tag{2}$$

where $n = 0$, 0.5 and 2 corresponding to anhydrite, hemihydrate and dihydrate, respectively. The thermodynamic equilibrium constants for reactions (1) and (2) are:

$$\begin{aligned} K_{SP}^{0} &= (m_{ca^{2+}}\gamma_{ca^{2+}})(m_{SO_4^{2-}}\gamma_{SO_4^{2-}})(a_{water})^n \\ &= (m_{ca^{2+}})(m_{SO_4^{2-}})\gamma^2_{\pm(CaSO_4)}(a_{water})^n \end{aligned} \tag{3}$$

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$$K_a = \frac{a_{CaSO_4}}{a_{Ca^{2+}} a_{SO_4^{2-}}} \qquad (4)$$

The solubility of calcium sulphate is:

$$[Ca]_{total} = m_{Ca^{2+}} + m_{CaSO_{4(aq)}} \qquad (5)$$

where K_{SP}^0 is the solubility product, K_a the association constant of calcium sulphate neutral species, m molality (mol kg^{-1}), $\gamma_{\pm(CaSO_4)}$ the mean activity coefficient of $CaSO_4$, $\gamma_{CaSO_{4(aq)}}$ the activity coefficient of calcium sulphate neutral species and a_{water} is the activity of water. To calculate the solubility of calcium sulphate hydrates, all the above need to be determined.

Marshall and Slusher [2], Tanji and Doneen [3], Zemaitis et al. [4], Demopoulos et al. [5] and Arslan and Dutt [6] proposed different methods based on different correlations for the activity coefficient that include the extended Debye–Hückel and Guggenheim–Davies expressions, as well as the Bromley, Meissner or Pitzer models to predict the solubility of calcium sulphate in various electrolyte solutions.

More recently, Adams [1] studied gypsum scale formation in a continuous sulphuric acid neutralization process. In this work, the solubility of gypsum and its scaling potential in sulphate systems were accurately modelled with the aid of the OLI software package (http://www.olisystems.com) using the mixed solvent electrolyte (MSE) [7–9] activity coefficient model for the temperature range from 25 to 90 °C. This model was capable of predicting the gypsum solubility over the indicated temperature range. However, other forms of calcium sulphate; i.e., anhydrite and hemihydrate were not taken into account in this study.

Li and Demopoulos [10] recently developed a model for the solubility of calcium sulphate in multi-component aqueous chloride solutions over the temperature range from 10 to 100 °C. The Bromley–Zemaitis activity coefficient model [11] was used, and the regression of the experimental data was carried out with the aid of the OLI software package.

Most of the previous studies focused on the solubility of gypsum at temperatures below 100 °C. Although mixed multi-component systems of sulphates are present in neutralization reactors, zinc processing solutions and pressure acid leaching circuits, no previous work had been formally undertaken to study the solubility of the three phases of calcium sulphate in such solutions. In particular, little work has been reported over a wide temperature range, and no phase transition diagram has been established among the different calcium sulphate hydrates in such complex mixed aqueous electrolytes.

In this work, the solubility of calcium sulphate systems was successfully modelled using the mixed solvent electrolyte (MSE) model [7–9]. The modelling involved the regression of binary activity, heat capacity and solubility data, as well as ternary solubility data. New interaction parameters for free calcium ions and associated calcium sulphate neutral species with other dominant species in the solution were also determined. The procedures followed were similar to those described elsewhere [12].

2. Chemical modelling

2.1. Equilibrium constant

To obtain the equilibrium constants in Eqs. (3) and (4) at temperature T and pressure P, the standard state chemical potentials of the products and reactants must be known. These data are widely available in standard thermodynamic compilations. The *HKF model*, developed by Tanger and Helgeson [13], is embedded in the OLI software to calculate the standard state thermodynamic properties at high temperatures and pressures, up to 1000 °C and 5 kbar. The general equation is as follows:

$$X_{T,P}^0 = X(T, P, a_1, a_2, a_3, a_4, c_1, c_2, \bar{\omega}) \qquad (6)$$

where X denotes a thermodynamic function such as chemical potential (μ), partial molal enthalpy (H), entropy (S), volume (V), or heat capacity (C_p), and $a_1, a_2, a_3, a_4, c_1, c_2, \bar{\omega}$ are HKF parameters.

2.2. Activity coefficient model

The activity coefficient is a parameter which accounts for the nonideality (excess properties) of electrolyte solutions, and is defined by the excess Gibbs free energy of the solution, G^E:

$$\ln\gamma_i = \left(\frac{\partial(G^E/RT)}{\partial n_i}\right)_{T,P,n_{i\neq j}} \qquad (7)$$

where n_i is the number of moles of the solution constituents (species i), and j is any other species. The pursuit of an expression for G^E to calculate γ has been ongoing for decades. Numerous models have been proposed and some of them have been incorporated into commercial software and applied in industry [12].

The more recently developed mixed solvent electrolyte (MSE) model [7–9] is capable of accurately calculating the thermodynamic properties of electrolyte solutions in water and/or organic solvent(s) over the entire concentration range from infinite dilution to pure fused salt electrolytes. The application of the MSE model within the OLI software platform for hydrometallurgical processing solutions has already proved its efficiency and accuracy in predicting the properties of multi-component solutions [12,14].

In this work, the MSE model used in the OLI software platform is employed. In the MSE model, the excess Gibbs free energy consists of three terms [8]:

$$\frac{G^E}{RT} = \frac{G^E_{LR}}{RT} + \frac{G^E_{MR}}{RT} + \frac{G^E_{SR}}{RT} \qquad (8)$$

where G^E_{LR} represents the contribution of long-range electrostatic interactions expressed by the Pitzer–Debye–Hückel equation, G^E_{SR} is the short-range contribution term resulting from molecule–molecule, molecule–ion and ion–ion interactions that is calculated by the UNIQUAC model, and G^E_{MR} accounts for the middle-range ionic interactions (i.e., ion–ion, ion–molecule) that are not included in the long-range term. The middle-range