



Thermodynamic model for acidic Ni(II) sulfate from solubility data



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ABSTRACT

Acidic nickel sulfate solutions are generated in a large scale in the hydro- and pyrometallurgical industries. They are also produced in many industrial processes from nickel refining to surface finishing of metals by electroplating. Acid mine drainage has long been a significant environmental problem in coal and metal mining. The demand of recycling and reuse of materials has increased significantly especially in EU. Dumping a neutralized deposit is not an option any more. Thus, several techniques of recycling and reuse of sulfuric acid and/or metal sulfates from the side streams are needed.

When developing alternative solutions, a better understanding of the thermodynamic behavior of NiSO₄–H₂SO₄–H₂O system is needed. In this study a thermodynamic model of this system has been developed in order to yield a thermodynamically consistent set of values for the solubility of nickel sulfate in a wide temperature and concentration range. The current model presents the experimental data available with a good accuracy and consistently up to 90 °C, and sulfuric acid concentrations up to 10 mol/kg. The model also predicts well the solubility measurements available in dilute up to 1.55 mol/kg sulfuric acid solutions at 200–250 °C.

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1. Introduction

The water–nickel sulfate–sulfuric acid system has been studied in the literature due to its key importance in many hydrometallurgical processes, which typically operate at temperatures between 50 and 300 °C. Hydrometallurgical processes such as stainless steel pickling acid regeneration, lateritic nickel hydrometallurgy, nickel refining as well as acid mine drainage from tailings ponds need internally consistent thermodynamic databases to improve, develop and deeper understand the systems and phenomena in the aqueous process solutions and environments.

In aqueous sulfuric acid solutions, nickel sulfate forms hydrates with 1, 2, 4, 5, 6 (α and β), and 7 molecules of crystalline water, with the chemical names for the stable phases dwornickite (1), nickel hexahydrate (β -6), retgersite (α -6) and morenosite (7), respectively [1,2]. Thermodynamics of the H₂O–NiSO₄–H₂SO₄ system have been modeled earlier by Reardon [3] using the Pitzer model. Pitzer parameters used in Reardon's model have also been reviewed critically in this work.

Reardon assessed the NiSO₄–H₂SO₄–H₂O system using the Harvie's modification [4,5] of the Pitzer model for the determination of activity coefficients over a temperature range from 0 to

70 °C in the ternary system and from 0 to 100 °C for the binary NiSO₄–H₂O [3 and references therein]. The solubility data in H₂O were used together with activity of water and enthalpy of solution data to generate the temperature dependent equations for the solubility products (K_{sp}) for hexahydrate, retgersite and morenosite, which were used with the ternary solubility data to generate Pitzer parameters for the NiSO₄–H₂SO₄–H₂O system. Reardon did an iterative regression analysis on the ternary system with the concentration limit of the experimental data of H₂SO₄ 6 mol/kg. Reardon assessed Pitzer parameters for nickel sulfate and sulfuric acid and used second dissociation constant K_2 from Pitzer et al. [6]. Reardon [3] model is lacking NiSO₄·H₂O(s) phase and that is why it cannot be used at higher temperatures of nickel refining [7] where NiSO₄·H₂O(s) is the only stable solid phase. This model also exhibits poor extrapolating behavior of higher sulfuric acid concentrations.

Liu and Papangelakis [8] modeled the chemistry of high temperature aqueous processing systems. Thermodynamic properties of aqueous species were calculated with Helgeson–Kirkham–Flowers (HKF) model [9] as well as with Density model [10]. Nonidealities were treated through the Bromley–Zemaitis ion interaction method [11]. Liu and Papangelakis [8] used experimental data from Marshall et al. [12] for comparison. They used two equilibrium constant parameters, solid NiSO₄·H₂O(s) and NiHSO₄⁺(aq) species, to fit the data.

The new improved thermodynamic models of the binary systems NiSO₄–H₂O and H₂SO₄–H₂O have been published in separate papers [13,14] by the authors. In the NiSO₄–H₂O paper

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dwornickite, hexahydrate, retgersite and morenosite were found to be stable phases with the peritectic transition temperatures at 28.4, 54.0 and 91.5 °C, respectively. Adding sulfuric acid to the system will decrease this temperature due to lowering the activity of water so that there is a peritectic point with different compositions at each temperature from 0–91.5 °C. The NiSO₄–H₂O system was successfully assessed from –3 to 220 °C from pure water up to solubility limit of nickel sulfate 4.73 mol/kg. The H₂SO₄–H₂O system has been assessed by Sippola [14] with experimental EMF cell and osmotic coefficient data only, and it is valid up to 6.1 mol/kg and over a temperature interval of 0–55 °C. Sippola [14] found out that four different K₂ equations for the dissociation of HSO₄[–] are equally suitable for presenting the H₂SO₄–H₂O system. The K₂ equation of Matsushima and Okuwaki [15] was chosen in this work since it has been found out by the authors to be able to describe the H₂SO₄–FeSO₄–H₂O system well [16].

The aim of this study is to compile and reassess the experimental observations of the system NiSO₄–H₂O–H₂SO₄ at 0–90 °C and H₂SO₄ concentration range up to 10 mol/kg and test the thermodynamic description for the system up to 250 °C to validate our previous NiSO₄–H₂O and H₂SO₄–H₂O binary models [13,14] with this ternary system. All experimental data used in the modeling were taken from the literature. The resulting thermodynamic model was obtained using the thermodynamic equilibrium package software MTDATA[®] (<http://www.mtdata-software.com>), which uses global Gibbs energy minimization routine and includes the Pitzer activity coefficient model for the excess Gibbs energy of the aqueous solutions. The CALPHAD (CALculation of PHase Diagrams) method [17] was used in the modeling, to ensure internal consistency of the thermodynamic database.

2. Modeling the aqueous solutions

The Pitzer model is one of the most used activity coefficient models for aqueous solutions. The original approach assumes that the aqueous solution consists only of ions, and no ion complexes are formed. Details of the Pitzer model used are available in [18–20]. Later, Harvie and Weare [4] and Harvie et al. [5] included unsymmetrical electrostatic mixing terms in their modification of the Pitzer model, which has been shown to improve the fit in multicomponent systems. The values for the internal constant parameters of the Harvie's modification of the Pitzer equation used in this work are shown in Table 1. All the necessary Pitzer model equations, variables and parameters have been explained in our previous paper [21].

2.1. Thermodynamic functions

The consistent concentration unit in aqueous solutions is molality of NiSO₄ and H₂SO₄ (mol/kg of water), which is used throughout this paper. The temperature dependency equation in MTDATA[®] for heat capacity of a species has the following form:

$$C_p = A + B \left(\frac{T}{K} \right) + C \left(\frac{T}{K} \right)^2 + D \left(\frac{T}{K} \right)^{-2} \quad (1)$$

Table 1
Internal parameters ($b=1.2$) of the Pitzer model used in this work.

Parameter	1-1, 1-2, 1-3 and 1-4 electrolyte	2-2 electrolyte
$\alpha_1(\text{kg/mol})^{1/2}$	2.0	1.4
$\alpha_2(\text{kg/mol})^{1/2}$	–	12

and thus Gibbs energy has a temperature dependent form

$$G(T) = A_G + B_G \left(\frac{T}{K} \right) + C_G \left(\frac{T}{K} \right) \ln \left(\frac{T}{K} \right) + D_G \left(\frac{T}{K} \right)^2 + E_G \left(\frac{T}{K} \right)^3 + F_G \left(\frac{T}{K} \right)^{-1} \quad (2)$$

The general temperature dependency available in MTDATA[®] for the Pitzer equation parameter (p) is

$$p = A_{\text{Pitz}} + B_{\text{Pitz}} \left(\frac{T}{K} \right) + C_{\text{Pitz}} \left(\frac{T}{K} \right) \ln \left(\frac{T}{K} \right) + D_{\text{Pitz}} \left(\frac{T}{K} \right)^2 + E_{\text{Pitz}} \left(\frac{T}{K} \right)^3 + F_{\text{Pitz}} \left(\frac{T}{K} \right)^{-1} \quad (3)$$

3. Experimental observations

3.1. Solubility data

Solubility measurements have been made at temperatures ranging from 0 to 90 °C and 200–350 °C [22–31,12]. The solubilities have been reviewed by Linke and Seidell [32], Marshall et al. [12] measured solubilities at 200–350 °C. According to Marshall et al. [12], NiSO₄·H₂O(s) is the stable phase at those temperatures.

The peritectic point, which mean the condition at which the phase transition from morenosite to retgersite, retgersite to hexahydrate or hexahydrate to dwornickite is in equilibrium with the aqueous sulfuric acid phase, has been determined experimentally at 0–75 °C [23–29,31].

3.2. Activity of water

Awakura et al. [33] measured activity of water at 25 °C and from 0 to 2.5 mol/kg of both NiSO₄ and H₂SO₄.

3.3. Enthalpy data

Przepiera et al. [34] reported results of calorimetric determination of integral enthalpies of solution at infinite dilution at 25 °C as a function of H₂SO₄ additions up to 2 mol/kg. No enthalpy and heat capacity data were used for the ternary model in this work because the enthalpy data have not been taken into account in the modeling of the binary H₂SO₄–H₂O system [14].

4. Parameter optimization

Evaluation of the thermodynamic properties of the aqueous phase as well as the condensed nickel sulfate hydrates was carried out using the MTDATA[®] assessment module, version 4.81 and MTDATA Studio 5.03, using Harvie's modification of the Pitzer equations [(4) and (5)]. The assessment module minimizes the weighted sum of squares of errors between the measured and fitted values, according to Eq. (4). Thus, the objective function (OF) to be minimized in the optimization can be written as

$$OF = \sum_{i=1}^n W_i \left(\frac{C_i - E_i}{U_i} \right)^2 \quad (4)$$

where n is the number of properties (data items) to be reproduced, C_i and E_i are the calculated and experimental values of property i , U_i is the uncertainty associated with value E_i and W_i is the weight assigned to property (data item) i .

4.1. Experimental phase equilibrium data used in the optimization

The experimental solubility data used in the optimization at temperature range of 0–90 °C are shown in Table 2. The H₂SO₄

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