Thermodynamic Modeling and Experimental Measurement of Calcium Sulphate Solubility in Complex Aqueous Solutions

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Chemical modeling has become an important subject of research in applied thermodynamics for designing, developing, and controlling of various industrial processes. In this work, a new database was developed to accurately model the solid and aqueous phase equilibria in a number of hydrometallurgical processes using the Mixed Solvent Electrolyte (MSE) model of the OLI Systems software. The MSE model is a variant of an excess Gibbs free energy model for mixed-solvent electrolyte systems with a comprehensive treatment of chemical equilibria. The MSE model takes into account long-range electrostatic interactions obtained from a Pitzer-Debye-Hückel equation, middle-range interactions expressed by second Virial coefficient-type equation and short-range interactions obtained from the UNIQUAC model. In this work, modeling involved the fitting of binary experimental data such as mean activity, heat capacity and solubility, as well as ternary solubility data. In order to validate the predictability of the model developed, a number of experimental measurements were conducted in multicomponent mixed sulphate/chloride solutions containing $NiSO_4$, H_2SO_4, $MnSO_4$,HCl, NaCl, $MgSO_4$, and $Al_2(SO_4)_3$ at 25-95°C and 150-250°C. High temperature experimental measurements were carried out in a titanium pressure vessel equipped with a dip tube for sample withdrawal through an in-situ titanium porous filter. Low temperature experiments were performed under an atmospheric pressure inside jacketed glass reactors in which samples were taken using preheated syringes and filtration was performed using syringe filters. The solubility values obtained at high temperatures were significantly lower (~1/10) of those obtained at temperatures below 100°C. This is due to the fact that the dominant solid phase at lower temperatures ($CaSO_4 \cdot 2H_2O_{(s)}$) transforms to $CaSO_{4(s)}$ anhydrous for which the stability region is located at higher temperatures. This means that processing solutions, saturated with $CaSO_4$ at low temperatures, can reject calcium and form scale inside autoclaves resulting in lower thermal efficiencies or causing corrosion problems. The developed model accurately predicts the chemistry of calcium sulphate solid formation in the systems studied in this work. Since it is not practical to measure solubility data under all conditions of interest, the model developed and the experimental results obtained serves the purpose of assessing calcium sulphate scaling capability for a wide variety of complex aqueous industrial streams.