

## Phase Behavior and Thermodynamic Solubility Constants for Novel Nickel Sulfate Phases Formed Under Secondary Coolant Hideout Conditions

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Inorganic ions such as aqueous sulfate and sodium enter the secondary coolant loops of nuclear reactors through condenser leaks where they can participate in “hideout” reactions under steam generator deposits. These hideout reaction products are largely uncharacterized because the solids redissolve in the secondary coolant upon cooling. In this study, three nickel – sulfate hideout phases were isolated by an *in situ* filtration technique at reaction temperatures between 200-250 °C, and aqueous sodium to sulfate ratios between 0.5 to 2.0. These solid phases are Ni<sub>3</sub>(OH)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O, trinickel dihydroxide bis(sulfate(VI)) dihydrate; Na<sub>2</sub>SO<sub>4</sub>·NiSO<sub>4</sub>·4H<sub>2</sub>O – nickel blödite; and NaHSO<sub>4</sub>·Ni<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O, nickel natrochalcite. Ni<sub>3</sub>(OH)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O was found to be a metastable phase at 225 °C, converting to nickel blödite as the temperature was raised to 250 °C, and not reappearing upon cooling back to 225 °C. Stirred pressure vessel experiments were used to determine thermodynamic solubility constants the three solid phases in equilibrium with an excess of nickel oxide, NiO, consistent with the Meissner activity coefficient model. Solubility constants were determined for Ni<sub>3</sub>(OH)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O at 225 °C, nickel blödite at 225 and 250 °C, and nickel natrochalcite at 300 °C. These equilibrium constants, and corresponding standard Gibbs energies and enthalpies of reaction, will be incorporated into databases aimed at modelling sulfate and reduced-sulfur water chemistry that may play a role in the stress-corrosion cracking of boiler tube alloys under steam generator operating conditions.