

Thermodynamic study of the ternary system $\text{CoSO}_4\text{-NiSO}_4\text{-H}_2\text{O}$

NINO PATRY¹, ARNAULT LASSIN², LAURENT ANDRE^{2,3}, YOHANN CARTIGNY⁴ AND NICOLAS COUV RAT¹

¹University of Rouen Normandie

²BRGM

³ISTO

⁴Univ Rouen Normandie

Cobalt sulfate and nickel sulfate are two compounds used to produce lithium-ion batteries (LiBs), alloys or mixed crystals of $\text{Co}_x\text{Ni}_{1-x}\text{SO}_4 \cdot 6\text{H}_2\text{O}$, which have applications in photonics as UV bandpass filters [1]. While processes to recycle both compounds from scraps are already established, chemical behavior of their electrolytes in brines is still poorly described.

This study aims to investigate the chemical behavior of the $\text{CoSO}_4\text{-NiSO}_4\text{-H}_2\text{O}$ system, combining experimental and modeling approaches to improve the thermodynamic description of the system in the temperature range between 10 and 50°C. In the first step, the binary systems $\text{NiSO}_4\text{-H}_2\text{O}$ and $\text{CoSO}_4\text{-H}_2\text{O}$ were investigated in this temperature range. Then, the 25°C isothermal section of the ternary system was determined using a homemade apparatus conceived at the SMS laboratory named D.I.T.A. (Discontinuous Isoperibolic Thermal Analysis) [2]. This allowed us to determine the chemical composition of the partial solid solution $\text{Co}_x\text{Ni}_{1-x}\text{SO}_4 \cdot 6\text{H}_2\text{O}$ at 25°C.

On the modeling part, previous Pitzer descriptions of $\text{NiSO}_4\text{-H}_2\text{O}$ and $\text{CoSO}_4\text{-H}_2\text{O}$ binary systems [3,4] were combined with the experimental data acquired in this study to extend the model's applicability to the ternary system $\text{NiSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$. This model includes a thermodynamic description of the solid solution. Calculations were done with the geochemical software PhreeSCALE, which is dedicated to saline systems [5].

[1] Komornikov, V. A.; Sorokina, N. I.; Vasilyeva, N. A.; Matveeva, D. S.; Voloshin, A. E. (2024) :**Phase Formation in the $\text{NiSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$ System and Specifications in the Structures of Single Crystals of $\text{Co}_x\text{Ni}_{(2-x)}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$** . J. Phys. Chem. Solids, 185, 111706.

[2] Marchand, P.; Lefebvre, L.; Courvoisier, L.; Perez, G.; Counieux, J.-J.; Coquerel, G. (2001): **Discontinuous Isoperibolic Thermal Analysis (DITA) (Applied to Organic Components)**. J. Phys. IV, 11 (PR10), Pr10-115-Pr10-122.

[3] Kobylin, P. (2013)**Thermodynamic Modelling of Aqueous Metal Sulfate Solutions**.

[4] Vielma, T. (2021)**Thermodynamic Model for $\text{CoSO}_4(\text{Aq})$ and the Related Solid Hydrates in the Temperature Range from 270 to 374 K and at Atmospheric Pressure**. *Calphad*, 72, 102230.

[5] Lach, A.; Boulahya, F.; André, L.; Lassin, A.; Azaroual, M.; Serin, J.P.; Cézac, P. (2016) **Thermal and volumetric properties of complex aqueous electrolyte solutions using the Pitzer formalism - The PhreeSCALE code**. *Comput. & Geosci.* 92, 58–69.