

**Re-determination of CoSO₄-Li₂SO₄-H₂O ternary system by
Discontinuous Isoperibolic Thermal Analysis (DITA)**

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Cobalt sulfate and lithium sulfate are two of the main compounds obtained from the recycling of Lithium-ion batteries (LiB). Acid leaching is used to extract metals from the used batteries, but these methods require: i) high quantity of solvent and ii) expensive costs for neutralizing the acid. Multiple alternative recycling methods have been unsuccessfully proposed up to now [1]. In the *Thermosalt* project, we aim at improving previous methods (or developing alternative methods) for recycling LiB after leaching through a deep knowledge of the physico-chemical properties of these saline solutions (brines) and a better understanding of their chemical behavior. The approach adopted in this project combines thermodynamic modeling, based on the Pitzer model [2], and multi-instrumental experimental data acquisition.

During this study, solubilities and triphasic/biphasic phase boundaries have been determined by Discontinuous Isoperibolic Thermal Analysis (DITA) [3], an isoplethal method developed in the SMS laboratory of Rouen, based on Isoplethic Thermal Analysis (ITA) developed in Lyon [4]. This method is particularly accurate for determining extreme solubilities (low soluble compounds or high soluble compounds) and overpasses classical issues encountered in gravimetric methods (such as phase transformation, hygroscopicity of the solid phases, etc.). The combination of this thermal analysis with other characterization techniques (ICP-AES, XRD analyses) helped at re-determining the salt-solution equilibrium (SLE) isotherm at 25°C and determining new SLE isotherms at other temperatures (35°C and 50°C). In the frame of the *Thermosalt* project, all these experimental data will contribute to the calibration of the Pitzer model, *i.e.* the determination of the specific interaction parameters between solutes, to finally develop a reliable thermodynamic model for the CoSO₄-Li₂SO₄-H₂O system.

[1] C.M. Costa, J.C. Barbosa, R. Gonçalves, H. Castro, F.J.D. Campo, S. Lanceros-Méndez (2021): Recycling and Environmental Issues of Lithium-Ion Batteries: Advances, Challenges and Opportunities. *Energy Storage Mater.*, 37, 433–465.

[2] K.S. Pitzer (1991): Activity Coefficients in Electrolyte Solutions, 2nd ed (Boca Raton: CRC Press).

[3] P. Marchand, L. Lefebvre, L. Courvoisier, G. Perez, J-J. Cournioux and G. Coquerel (2001): Discontinuous Isoperibolic Thermal Analysis (DITA) (Applied to Organic Components), *J. Phys IV France*, 11, Pr10-115 – Pr10-122.

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[4] E. Labarthe, A-J. Bougrine, H. Delalu, J. Berthet and J-J. Counieux (2009): Equilibrium study between condensed phases by isoplethic thermal analysis when a miscibility gap is observed, *J. Therm. Anal Cal.*, 2009, 95(1), pp 135-139.

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