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Applied thermodynamics in nuclear industry modelling of precipitation processes

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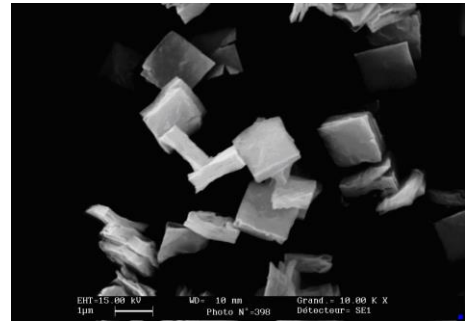
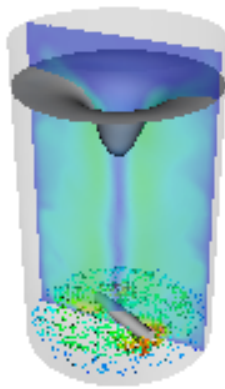
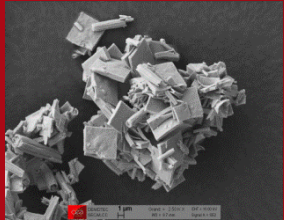
Submitted on 24 Feb 2020

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Applied thermodynamics in nuclear industry: modelling of precipitation processes

Taking account for ideality deviation in neodymium oxalate and uranium peroxide precipitation

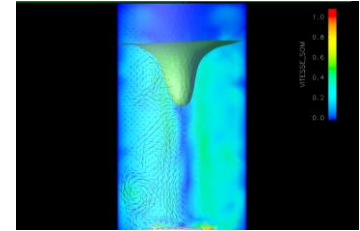
- Murielle Bertrand (CEA Marcoule)
- Sophie Lalleman, Luz-Adriana Mojica-Rodriguez, Christian Sorel, Philippe Moisy (CEA Marcoule)
- Frédéric Auger (Areva Mines)
- Edouard Plasari, Hervé Muhr (CNRS - University of Lorraine)



Precipitation Modelling : Coupling Chemistry/Turbulence

Population balance

CFD simulation

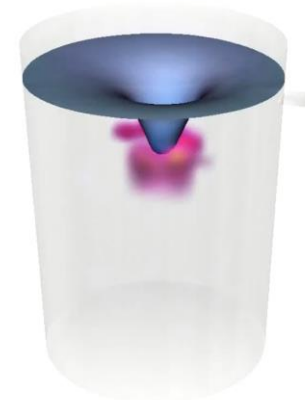
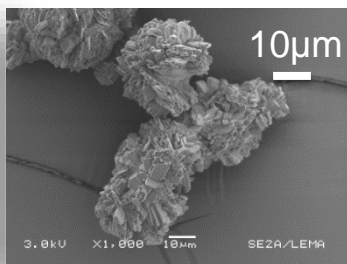
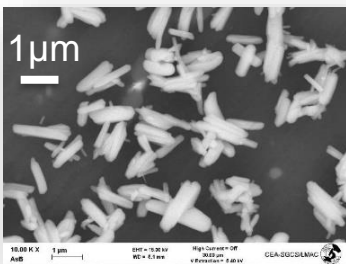


$$\frac{1}{V} \frac{\partial V\varphi(L,t)}{\partial t} + \frac{\partial G\varphi(L,t)}{\partial L} + \frac{Q_o\varphi(L,t) - Q_i\varphi_i(L,t)}{V} = R_N \delta(L)$$

Kinetics



Thermodynamics

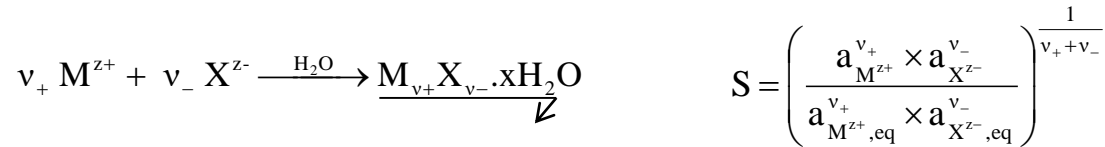


3D LES

Calculation of Supersaturation

➤ Objective:

- Calculation of the driving force = supersaturation S during the precipitation process



- In concentrated solutions involving salts and ions of high valence

➤ Coefficient activity models:

■ Physico-chemical approaches

Pitzer equations



Inconvenient ☹️ ⇒

Heavy implementation + many parameters to be adjusted

■ Empirical approaches

Bromley method or
SIT specific interaction theory



Good compromise 😊:

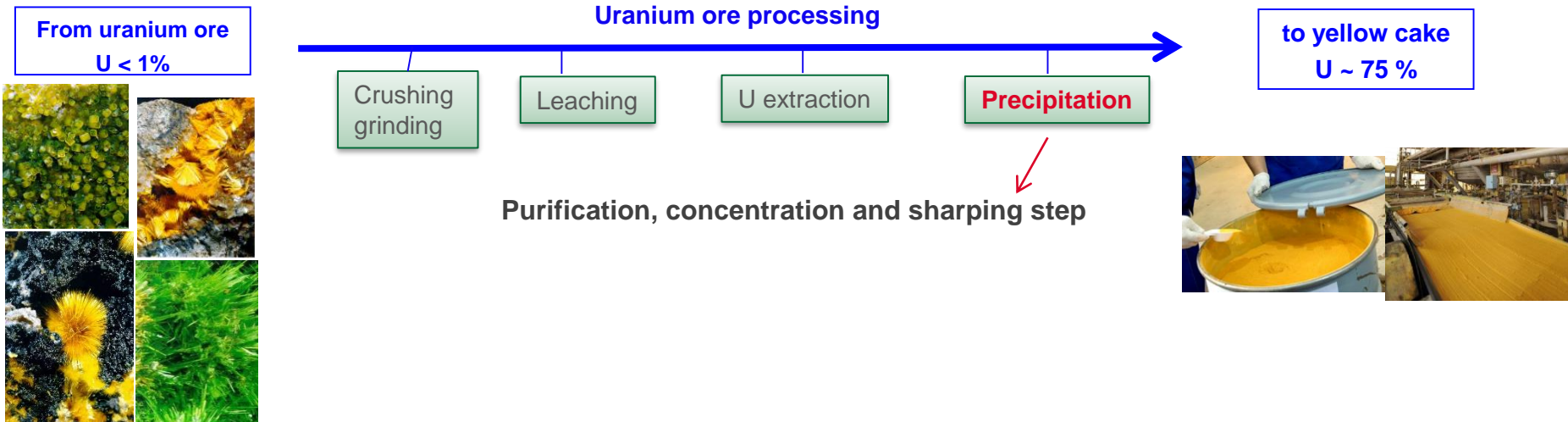
Easy-to-use / accuracy for process modelling and CFD simulations

➤ 2 examples of applications in nuclear industry:

■ Actinide / lanthanide oxalate precipitation

very low solubility \Rightarrow widely used in the Ln and An separation, analytical chemistry and treatment of high-level liquid wastes - in nitric acid medium

■ Uranium peroxide precipitation



1. Context of the study

2. Neodymium oxalate

Bromley method

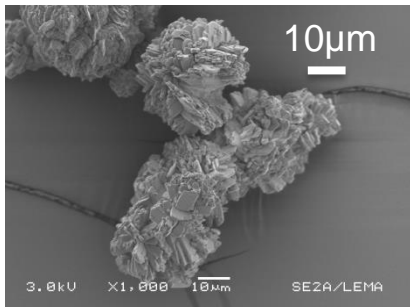
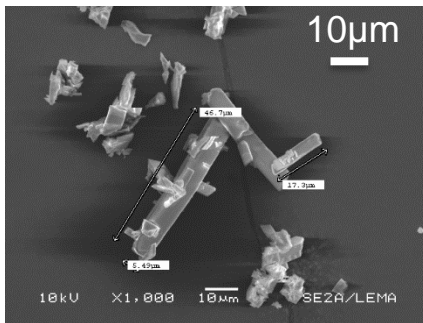
Determination of the individual contributions

3. Uranium peroxide

Specific interaction theory

Determination of the specific interaction coefficients

4. Conclusions



- 2 -

Neodymium oxalate precipitation The Bromley method

Bromley model

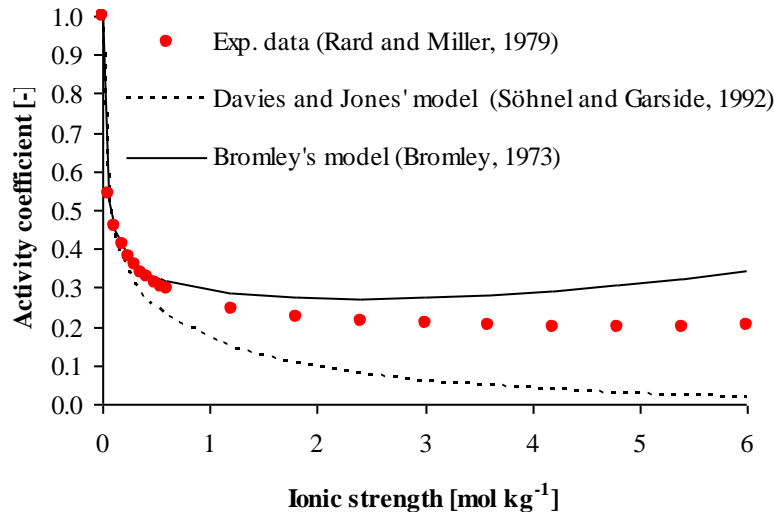
➤ Bromley method for multicomponent systems

- Based on the contributions $B_{M_1X_1}$ of every electrolytes present in solution

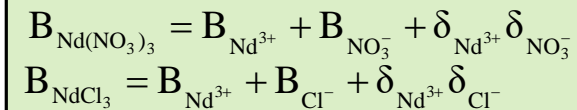
$$B_{M_1X_1} = B_+ + B_- + \delta_+ \delta_-$$

➤ Neodymium individual contributions

- Tabulated by Bromley in 1973
- After \Rightarrow New experimental binary data published later for neodymium nitrate and chloride

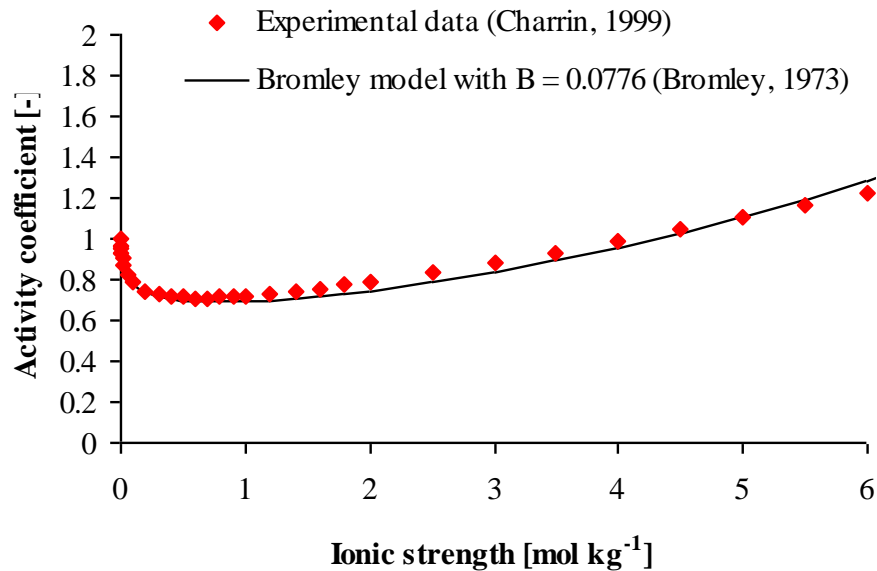


- ✓ The Bromley model not in good agreement
- ✓ Determination of new values for neodymium contributions (B_+, δ_+) using tow salts:
Neodymium nitrate + Neodymium chloride

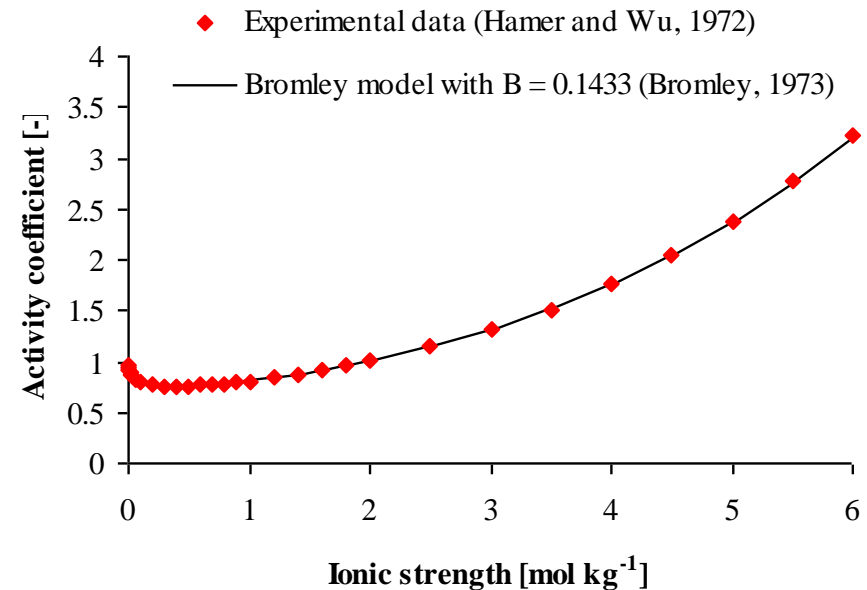


1st STEP: Validation of the Bromley individual contributions for NO_3^- and Cl^- from experimental data of HNO_3 and HCl

HNO_3



HCl



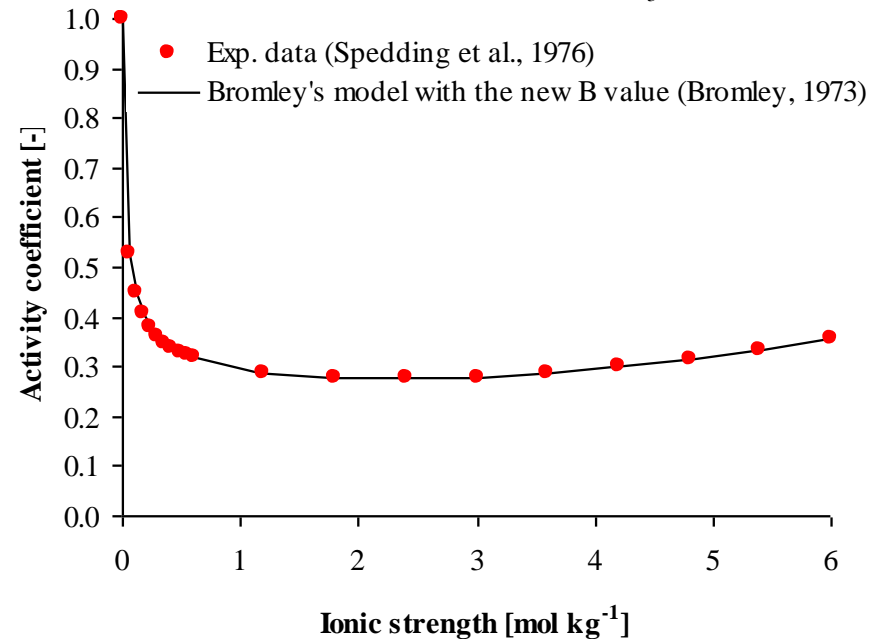
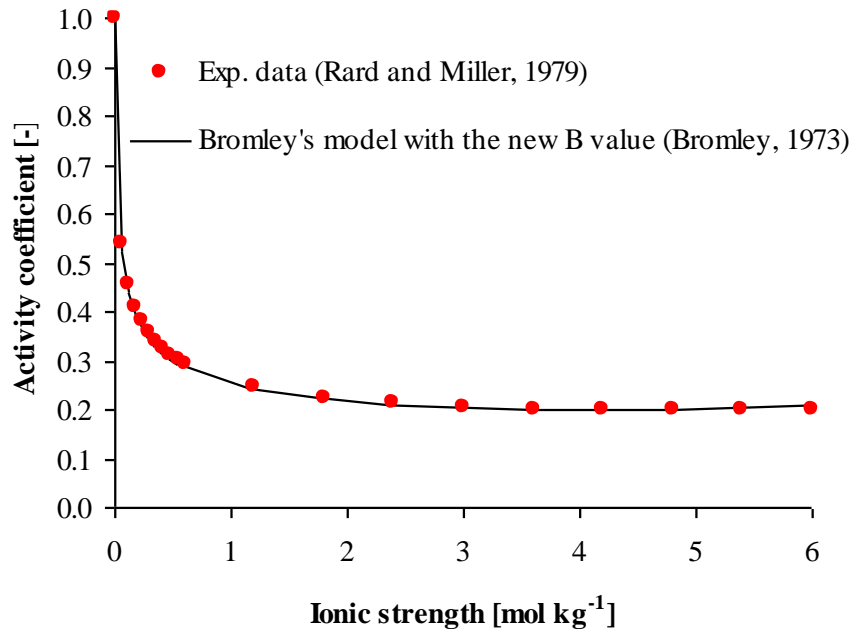
Very good agreement between exp. data and the Bromley model combined with the contributions of HNO_3 and HCl

[1] Rard J.A. and Miller D.G, 1979. J. Chem. Eng. Data 24, 348-353

[2] Spedding et al., 1976. J. chem. Eng. Data 21, 341-360.

New contributions of Nd^{3+} in the Bromley model

2nd STEP: Determination of the salt contributions and adjustment of the Bromley contributions for Nd^{3+}



Very good agreement between exp. data and the Bromley model with the new contributions of $\text{Nd}(\text{NO}_3)_3$ et NdCl_3



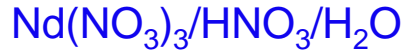
$$B_{\text{Nd}^{3+}} = 0.0321 \text{ and } \delta_{\text{Nd}^{3+}} = 0.163$$

$$B_{\text{Nd}^{3+}} = 0.035 \text{ and } \delta_{\text{Nd}^{3+}} = 0.27$$

Bromley's values

Application of the Bromley model to ternary mixtures

- These new contributions ⇒ application to ternary solutions



- Measurements of water activity a_w in ternary mixtures

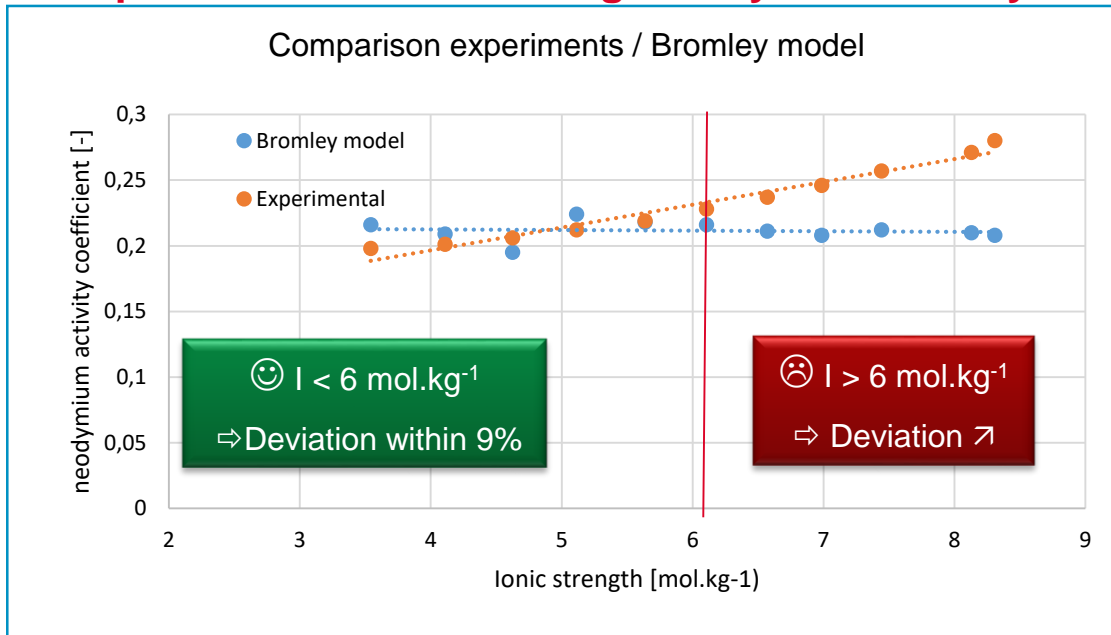
■ Using the concept of simple solutions and Mikulin equation*:

$$a_w \Rightarrow \text{activity coefficients } \gamma_{\text{Nd}(\text{NO}_3)}^{\text{mixture}}$$

- Comparison with the values given by the Bromley method



Variable-impedance hygrometer
AW Center™ (Novasina)



* Charrin et al., 1999. Radiochim. Acta 86, 143-149.

* Kappenstein et al., 2000. Phys. Chem. Chem. Phys. 2, 2725-2730

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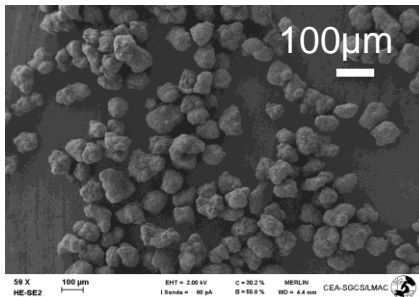
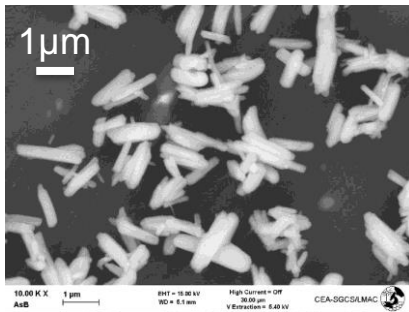
Determination of the individual contributions

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- 3 -

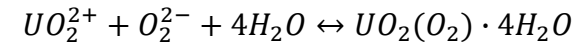
Uranium Peroxide precipitation SIT

Specific Interaction Theory SIT

➤ Precipitation in sulphuric media

$UO_2SO_4 / H_2SO_4 / Na_2SO_4 / H_2O_2 / H_2O$

- Bromley method not adapted: sulphuric acid partially dissociated
- + no data for hydrogen peroxide



$$S = \sqrt{\frac{a_{UO_2^{2+}} a_{O_2^{2-}}}{a_{UO_2^{2+},eq} a_{O_2^{2-},eq}}}$$

➤ Specific Interaction Theory* **

- Based on specific interaction coefficients between ions of opposite charge

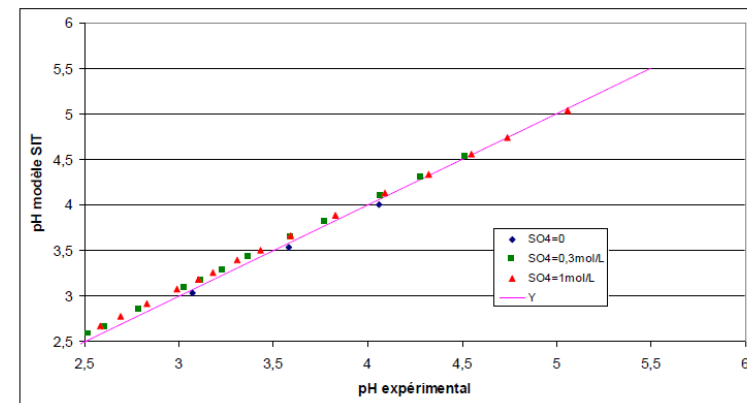
$$\log \gamma_i = -z_i^2 \frac{a\sqrt{I}}{1 + b_{i,j}\sqrt{I}} + \sum_j \varepsilon(i, j)m_j$$

← Specific interaction coefficient

➤ 1st step: Validation of the specific interaction coefficients of ions: SO_4^{2-} , HSO_4^- and H^+

- Comparison between experimental pH and pH calculated using SIT in ternary systems $H_2SO_4 - Na_2SO_4 - H_2O$

Very good agreement between experimental pH and SIT



*T. Vercouter, B. Amekraz, C. Moulin, E. Giffaut and P. Vitorge, Inorg. Chem., 2005, 44, 7570–7581 Bromley L.A., 1973. AIChE J. 19, 313-320

**R. M. Cigala, F. Crea, C. De Stefano, G. Lando, D. Milea and S. Sammartano, Geochim. Cosmochim. Acta, 2012, 87, 1–20

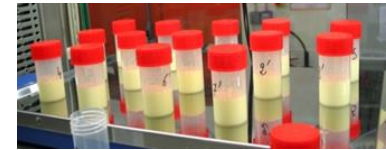
Determination of specific interaction coefficients

➤ 2nd step: determination of the specific interaction coefficients of other ions

■ from experimental data of uranium peroxide solubility (ICP-AES and ICP-MS)

■ And by application of the SIT hypothesis:

- Commutative function $\varepsilon(i,j) = \varepsilon(j,i)$
- Independent from I
- $\varepsilon(i,j) = 0$ for ions of same charge
- For unknown coefficients \Rightarrow analogies between ions of same charge



Determination of a set of values for SI coefficients:

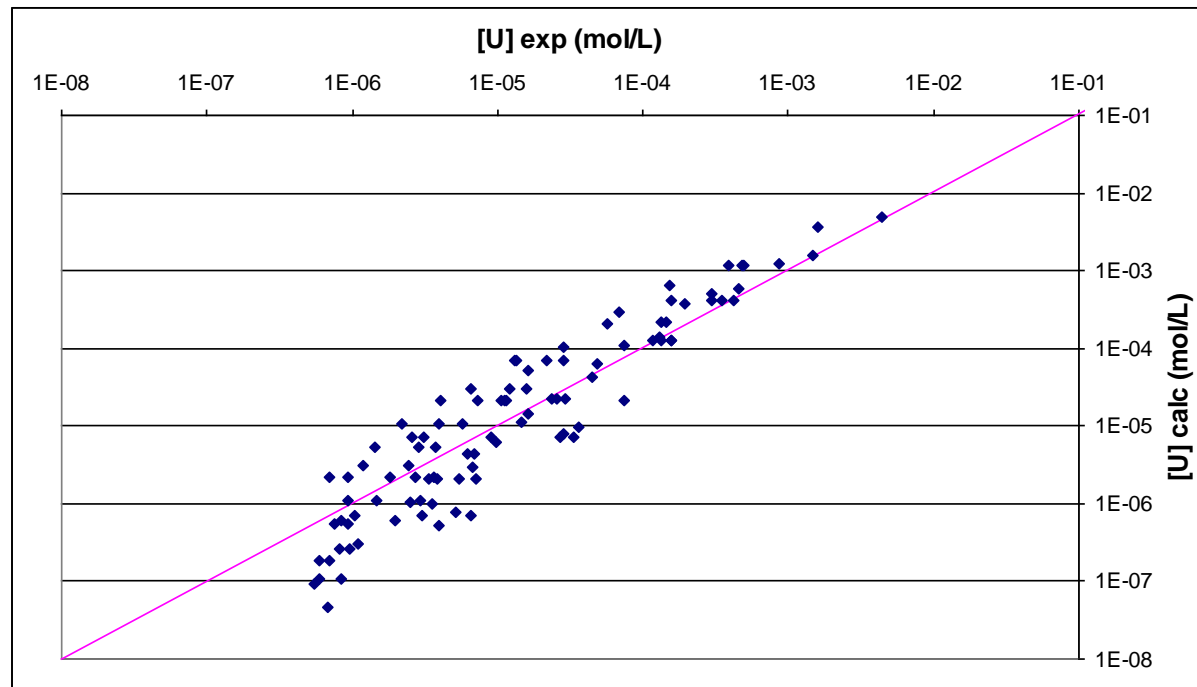
- **blue**: from the literature
- **green**: by analogy
- **red**: optimised values from experimental data

	ε (kg.mol ⁻¹)		
	UO ₂ ²⁺	Na ⁺	H ⁺
SO ₄ ²⁻	0,12	-0,12 ± 0,06 → -0,18	0 → 0,046
HSO ₄ ⁻	0,46 ± 0,03 → 0,46	-0,01 ± 0,02 → -0,03	-0,01 ± 0,02 → -0,01
UO ₂ (SO ₄) ₂ ²⁻	0,12	-0,12 ± 0,06 → -0,18	-0,12 ± 0,06 → -0,12
UO ₂ (SO ₄) ₃ ⁴⁻	0,24	-0,06	-0,24

* Bromley L.A., 1973. AIChE J. 19, 313-320

Determination of specific interaction coefficients

- Comparison between experimental and calculated solubilities over a wide range of operating conditions



Good agreement
higher deviations at low sulphate concentrations ⇨
very low solubilities ⇨ high analytical uncertainties

Conclusion and outlooks

- **For precipitation process modelling \Rightarrow development of thermodynamic models to calculate the supersaturation taking into account the nonideality of the solutions**
- **On the basis of simple empirical methods**
- **Advantage \Rightarrow easy to use and accurate**
- **Application \Rightarrow Experiments**
 - New individual contributions of the neodymium ion for the Bromley model
 - New specific interaction coefficients for SIT
- **Comparison between experiments and models \Rightarrow a good agreement**



These methods can be applied to many other systems provided

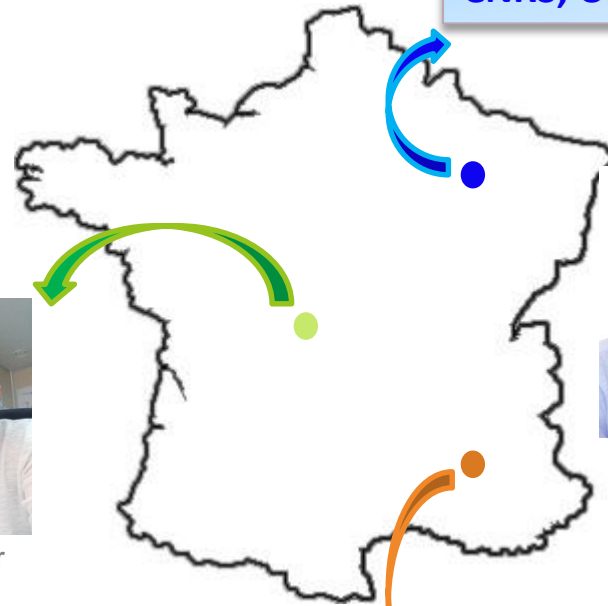
- the binary data of 2 salts are known for the Bromley model
- solubility measurements can be performed for SIT

Scientific team

Reaction and Process Engineering Laboratory
CNRS, University of Lorraine



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Pf E. Plasari



AREVA Mines
Bessines site
Uranium extraction



F. Auger



French Atomic Energy Commission
Marcoule facility
Nuclear fuel reprocessing and waste processing



Dr Luz Mojica-Rodriguez
Dr M. Bertrand



**Thank you for
your attention !**