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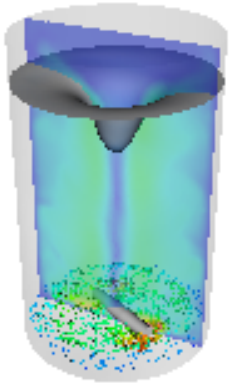
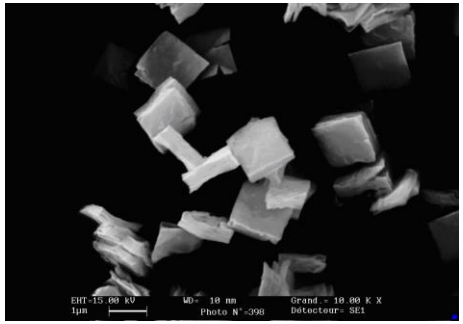
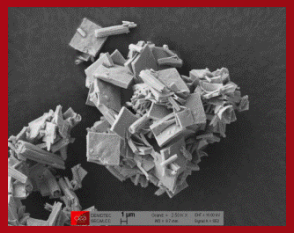




Applied thermodynamics in nuclear industry: modelling of precipitation processes

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)

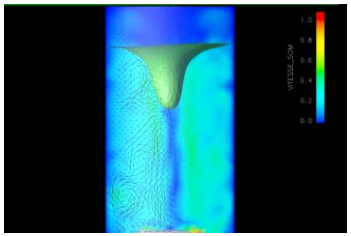


ESAT 2018, June 2018, Prague

PRECIPITATION PROCESS MODELLING

Precipitation Modelling :

Coupling Chemistry/Turbulence

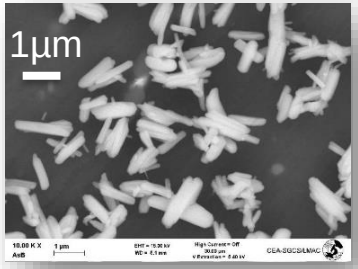


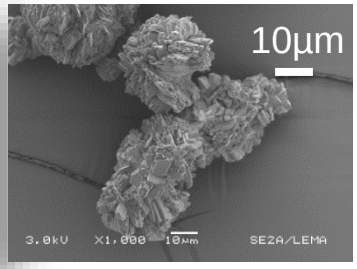
Population balance

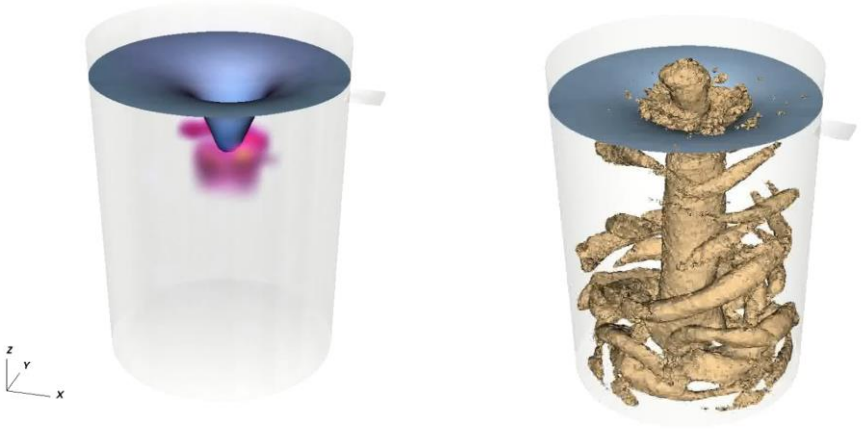
CFD simulation

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

Kinetics + **Thermodynamics**







3D LES

Calculation of Supersaturation

Objective:

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

$$\nu_+ M^{z+} + \nu_- X^{z-} \xrightarrow{H_2O} \underline{M_{\nu+}X_{\nu-}.xH_2O}$$

$$S = \left(\frac{a_{M^{z+}}^{\nu_+} \times a_{X^{z-}}^{\nu_-}}{a_{M^{z+},eq}^{\nu_+} \times a_{X^{z-},eq}^{\nu_-}} \right)^{\frac{1}{\nu_+ + \nu_-}}$$

- 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**

Applications

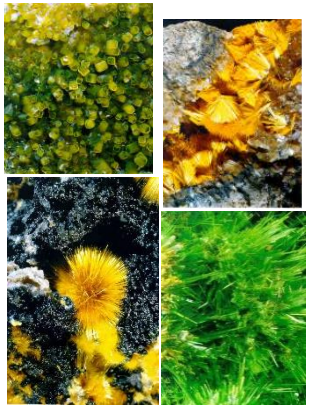
➢ **2 examples of applications in nuclear industry:**

Actinide / lanthanide oxalate precipitation

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

Uranium peroxide precipitation

From uranium ore
U < 1%



Uranium ore processing

Crushing grinding → Leaching → U extraction → **Precipitation** → **to yellow cake U ~ 75 %**

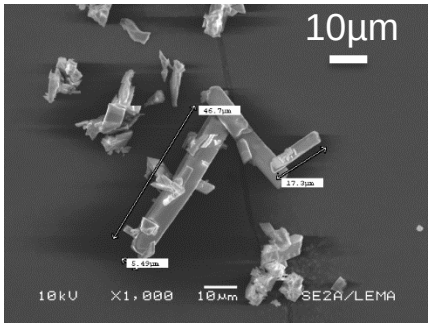
Purification, concentration and sharping step

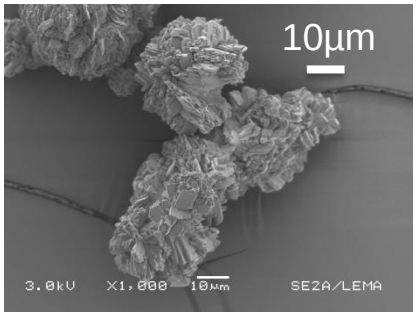
1. Context of the study

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

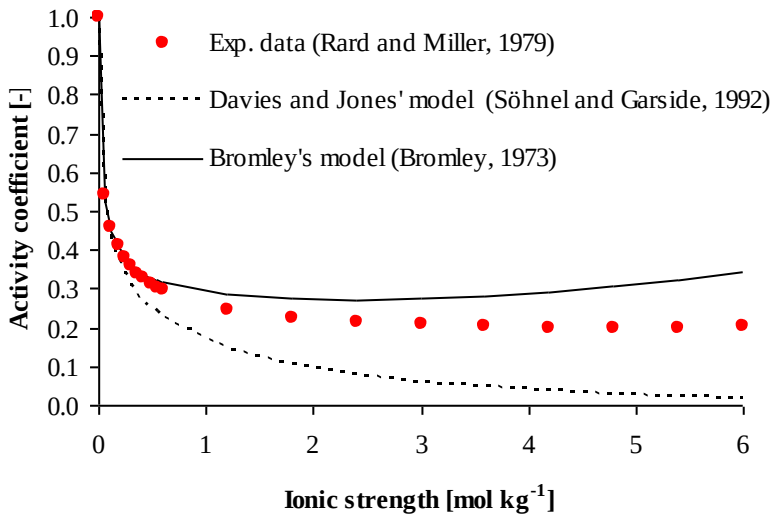
Bromley method for multicomponent systems

- Based on the contributions B_{M1X1} of every electrolytes present in solution

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

Neodymium individual contributions

- Tabulated by Bromley in 1973
- After ⇒ 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:

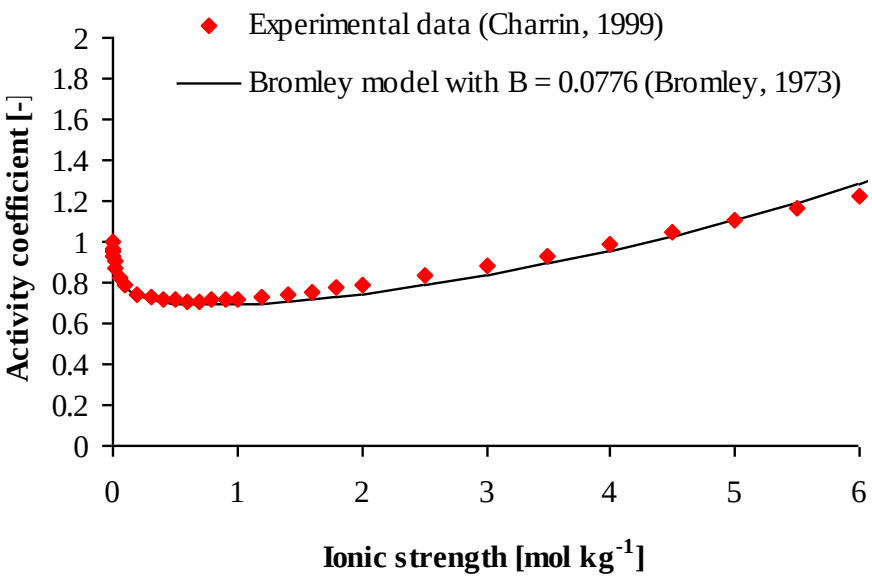
  Neodymium nitrate + Neodymium chloride

$$B_{Nd(NO_3)_3} = B_{Nd^{3+}} + B_{NO_3^-} + \delta_{Nd^{3+}}\delta_{NO_3^-}$$
$$B_{NdCl_3} = B_{Nd^{3+}} + B_{Cl^-} + \delta_{Nd^{3+}}\delta_{Cl^-}$$

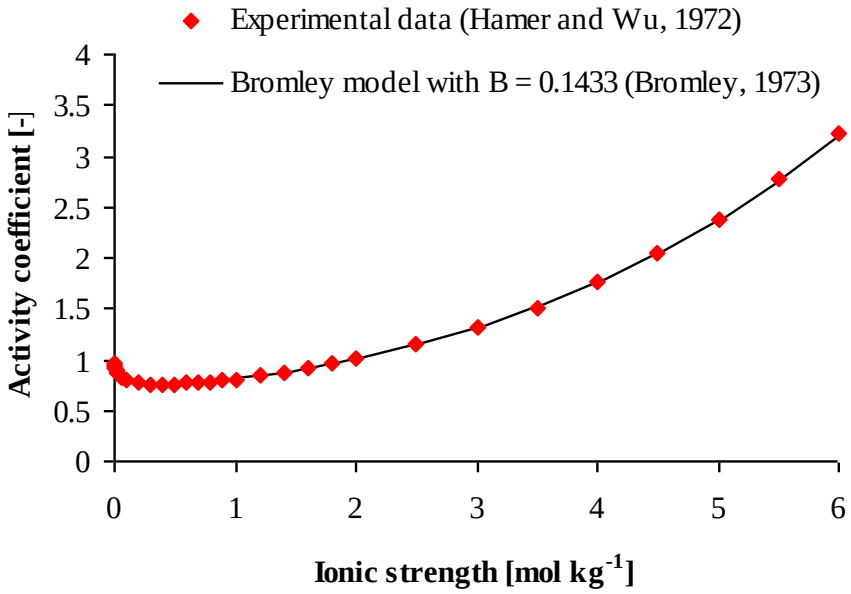
New contributions of Nd^{3+} in the Bromley model

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

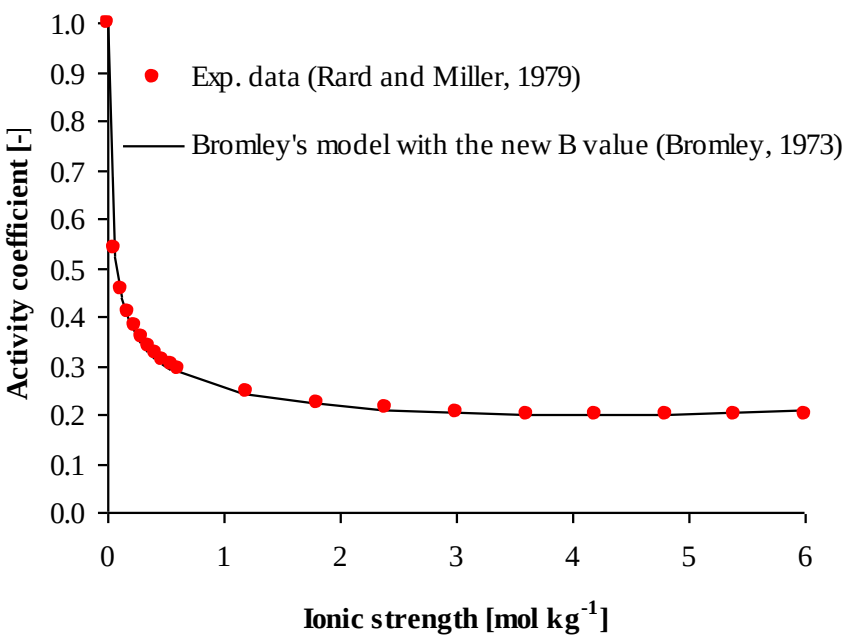
[1] Rard J.A. and Miller D.G, 1979. J. Chem. Eng. Data 24, 348-353

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

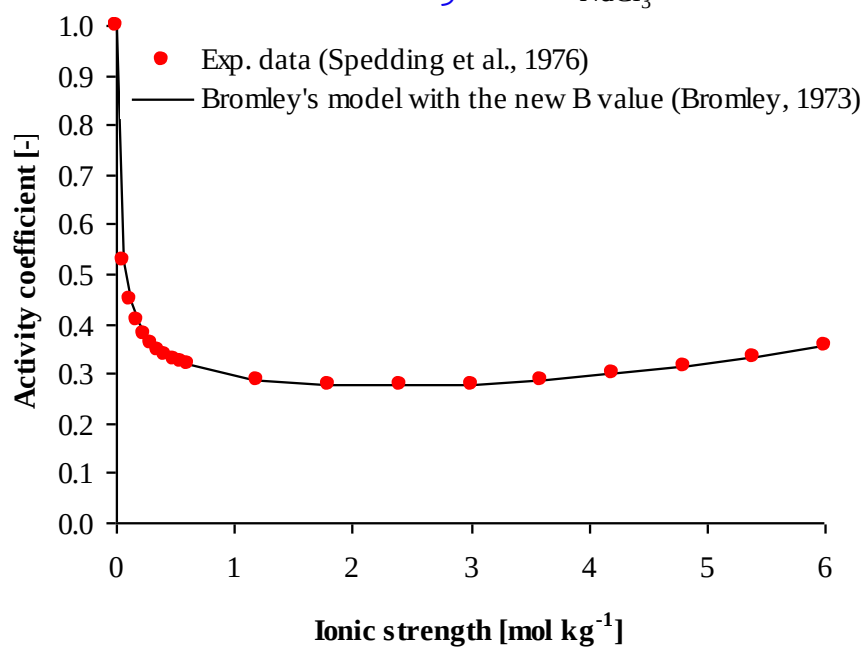
New contributions of Nd^{3+} in the Bromley model

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

$Nd(NO_3)_3$ => $B_{Nd(NO_3)_3} = 0.0511$



$NdCl_3$=> $B_{NdCl_3} = 0.0855$



Very good agreement between exp. data and the Bromley model with the new contributions of $Nd(NO_3)_3$ et $NdCl_3$

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

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

Bromley's values

Lalleman, Bertrand, Plasari, Sorel, Moisy, Chemical Engineering Science 77 (2012) 189-195

Application of the Bromley model to ternary mixtures

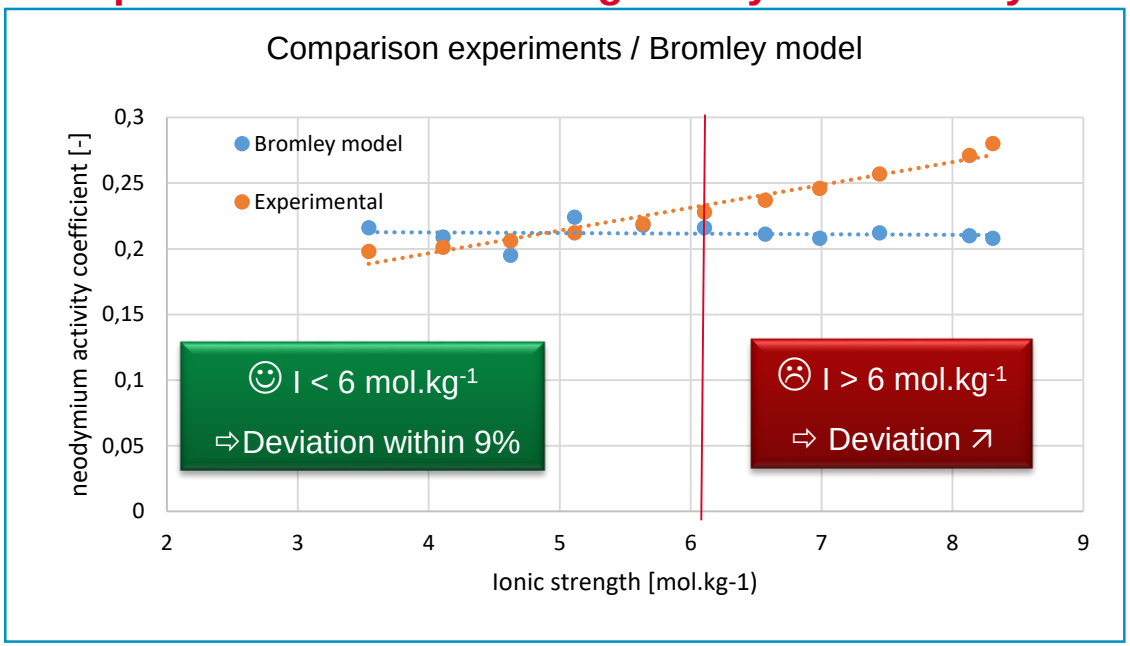
- **These new contributions ⇒ application to ternary solutions**

  $Nd(NO_3)_3/HNO_3/H_2O$

- **Measurements of water activity a_W in ternary mixtures**
  - Using the concept of simple solutions and Mikulin equation*:

    a_W ⇒ activity coefficients $\gamma_{Nd(NO3)}^{mixture}$

- **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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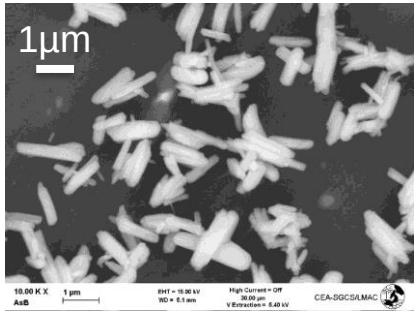
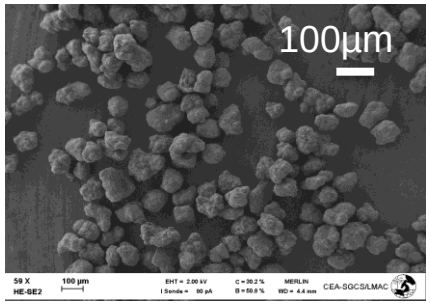




- 3 -
Uranium Peroxide precipitation
SIT

Specific Interaction Theory SIT

Precipitation in sulphuric media

$$UO_2^{2+} + O_2^{2-} + 4H_2O \leftrightarrow UO_2(O_2)\cdot 4H_2O$$

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

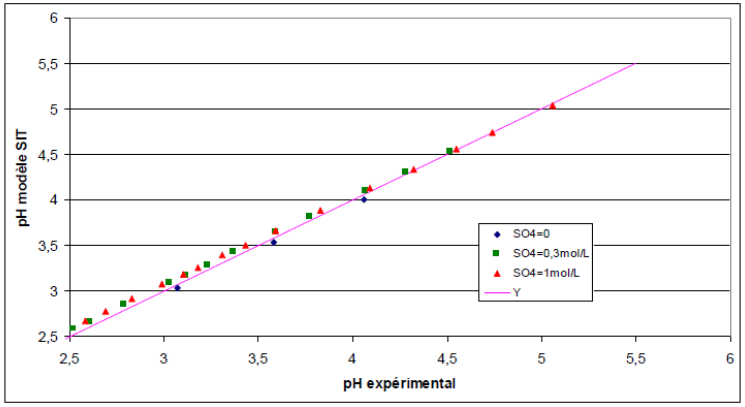
$$\log\gamma_i = -z_i^2 \frac{a\sqrt{I}}{1+b_{i,j}\sqrt{I}} + \sum_j \varepsilon(i,j) m_j$$

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, 7570–7581Bromley 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 ⇨ analogies between ions of same charge

Determination of a set of values for SI coefficients:

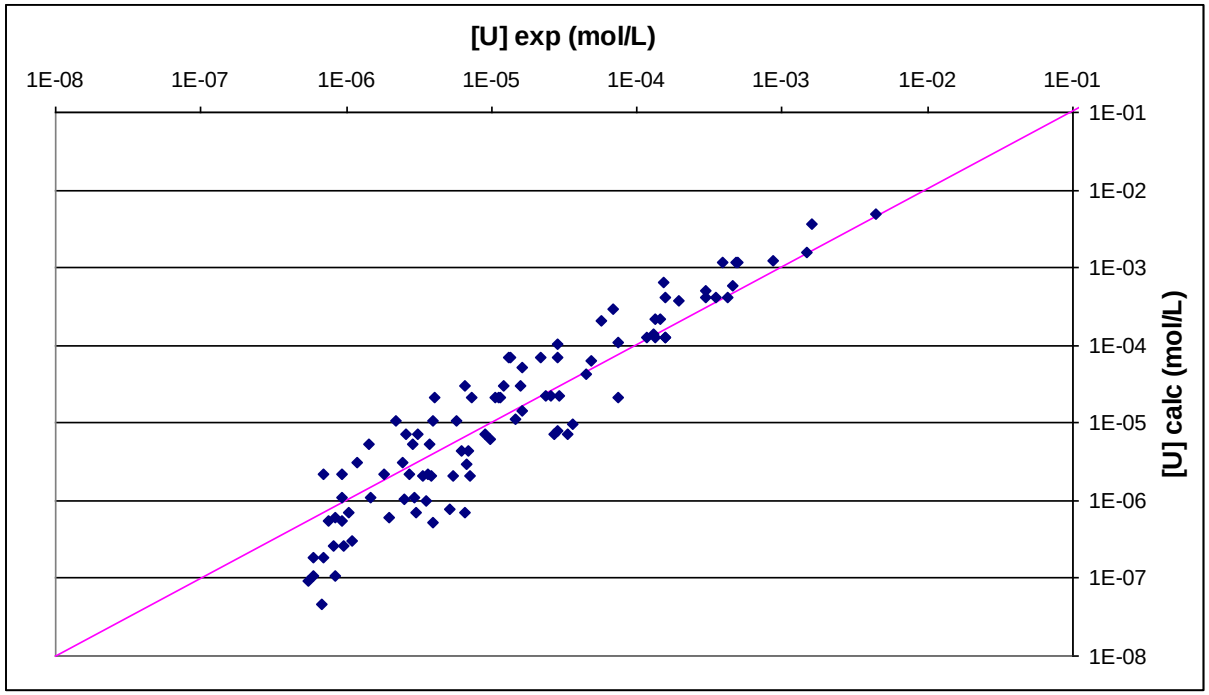
- **blue:** from the literature
- **green**: by analogy
- **red:** optimised values from experimental data

	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 ⇒ development of thermodynamic models to calculate the supersaturation taking into account the nonideality of the solutions**

- **On the basis of simple empirical methods**

- **Advantage ⇒ easy to use and accurate**
- **Application ⇒ Experiments**
  - New individual contributions of the neodymium ion for the Bromley model
  - New specific interaction coefficients for SIT

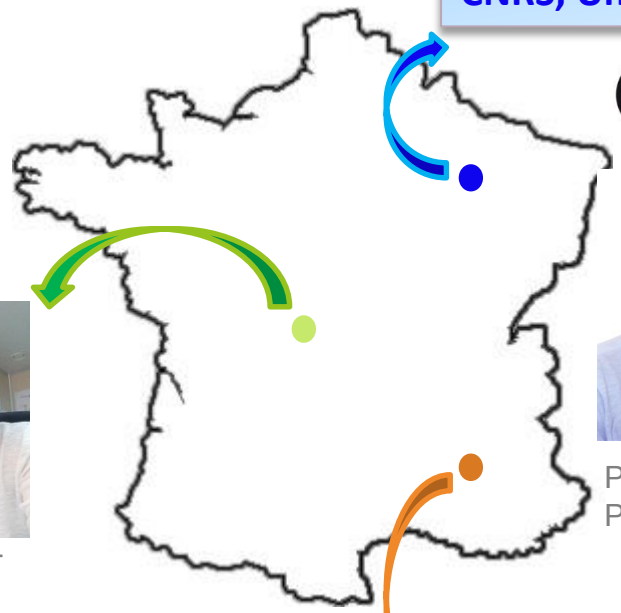
- **Comparison between experiments and models ⇒ a good agreement**

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

AREVA Mines
Bessines site
Uranium extraction

F. Auger



Reaction and Process Engineering Laboratory
CNRS, University of Lorraine

UNIVERSITÉ DE LORRAINE

Pf H. Muhr
Pf E. Plasari

Dr Luz Mojica-Rodriguez
Dr M. Bertrand

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

Thank you for your attention !