Thermodynamic study of uranium oxalate precipitation supersaturation ratio determination taking into account ideality deviation

A. Gutierrez-Chavida, M. Bertrand, G. Jouan, E. Plasari, H. Muhr, J. Nos

Thermodynamic study of uranium oxalate precipitation: supersaturation ratio determination taking into account ideality deviation

Alexandra GUTIERREZ-CHAVIDA[1], **Murielle BERTRAND[1]**, Gauthier JOUAN[1], Edouard PLASARI[2], Hervé MUHR[2] et Jérémy NOS[3]

[1]*CEA, DEN, DMRC, BP 17171Bagnols sur Cèze, France*
[2]*Reaction and Process Engineering Laboratory, University of Lorraine, France*
[3]*Orano Cycle, France*

murielle.bertrand@cea.fr

ABSTRACT

Oxalic precipitation is usually applied to process radioactive wastes or to recover actinides from a multicomponent solution. The driving force of precipitation reactions is given by supersaturation, which characterizes the deviation from the equilibrium state. Precipitation mechanisms, such as nucleation, crystal growth or agglomeration, are governed by supersaturation, which is therefore a crucial parameter to determine for process control. This work focuses on the description of a thermodynamic study of uranium (IV) oxalate precipitation in order, on the one hand, to develop a solubility model and, on the other hand, to estimate supersaturation ratio. Uranium (IV) oxalate can be precipitated by mixing an uranium (IV)-nitric acid solution and an oxalic acid solution according to the following equilibrium:

$$U(NO_3)_4 + 2\ H_2C_2O_4 \rightarrow U(C_2O_4)_2 \cdot 6H_2O + 4\ HNO_3$$
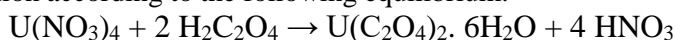
As very few information is available in the literature dealing with uranium oxalate [1], an experimental study was performed in order to determine solubilities over a wide range of conditions. The data acquisitions were carried out by dissolution of uranium oxalate powder (Fig1) in aqueous solutions with different nitric acid, oxalic acid and hydrazine nitrate concentrations at controlled temperature of 25°C and protected from light. Experimental results are of the same order of magnitude as the values of the literature in spite of experimental differences between the studies (duration of the experiment, analytical methods…). The mathematical treatment of experimental results allowed a thermodynamic model for both solubility and supersaturation ratio of uranium oxalate to be developed. The comparison between the model and the experimental data points out a good agreement as shown in the figure 2.

The thermodynamic model was then applied to compare two different approaches to determine the supersaturation ratio described in the literature: either from the free ion concentration and the ionic activity coefficient or from the total concentration of species using the mean stoichiometric activity coefficients. The comparison leads to the very interesting conclusion that both approaches are equivalent as they result in the same supersaturation values as shown in figure 3.
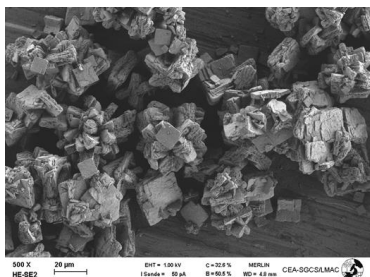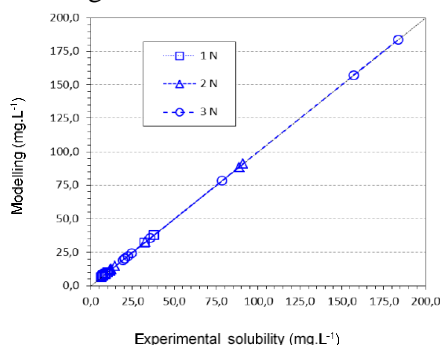
Fig1: Uranium (IV) oxalate crystals (SEM)

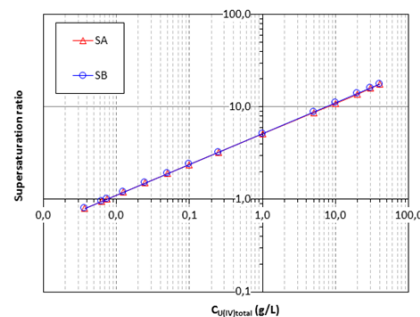Fig2: Comparison experimental/modelling

Fig3: Comparison free ions (S_B) / total concentration of species (S_A)

KEY WORDS

Uranium, oxalate, supersaturation, activity coefficients, solubility.

REFERENCES

[1]   Grinberg, A.A., Petrzhak, G.I., 1963. Supplementary data on the solubility of the oxalate of quadrivalent uranium. Radiochemistry, 5, 319-329.