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3b – Uranium mining

In the processing of uranium ores, uranium is recovered from mill leach solutions and is transported to a processing plant. A solid uranium concentrate, called "yellow cake" due to its color and its doughy texture, is produced by precipitation and drying. It contains around 75% of uranium. The "yellow cake" is packaged and put into barrels, then sent to conversion facilities for further chemical processing.

Among the different existing precipitation devices, the continuous precipitation with hydrogen peroxide in a fluidized bed reactor leads to high-quality solid particles. The precipitation is achieved at pH ~ 3 by mixing hydrogen peroxide and uranyl sulfate solutions, according to the following equation:

$$UO_2SO_4 + H_2O_2 + 4H_2O \leftrightarrow UO_4 \cdot 4H_2O + H_2SO_4$$
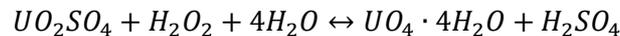
Solid particles must fulfill specific requirements, in particular concerning the size. Thus, the control of the crystal growth becomes a key parameter during the uranium peroxide precipitation. Moreover, the solubility product, K_s, is required to calculate the driving force on which the kinetic law depends. For the uranium peroxide precipitation, the supersaturation ratio, S, is linked to the activities of the uranyl and peroxide ion as:

$$S = \sqrt{\frac{a(UO_2^{2+})\, a(O_2^{2-})}{K_s}}$$

with:

$$K_s = a(UO_2^{2+})_{eq}\, a(O_2^{2-})_{eq}$$

where $a(UO_2^{2+})_{eq}$ and $a(O_2^{2-})_{eq}$ are the uranyl ion activity and the peroxide ion activity at equilibrium.

The uranyl ion activity is obtain as the product of the uranyl activity coefficient and the uranyl free concentration, which are calculated from the Specific Interaction Theory and total concentration balance, respectively. Considering the experimental data of the dissociation

constants of hydrogen peroxide and knowing that it is not very dissociated in solution, the expression of the supersaturation ratio becomes:

$$S = \sqrt{\frac{\gamma_{UO_2^{2+}}[UO_2^{2+}][H_2O_2]}{a(H^+)^2} \frac{K_{A3}K_{A4}}{K_S}}$$

where K_{A3} and K_{A4} are the dissociation constants of hydrogen peroxide and $a(H^+) = 10^{-pH}$.

In order to calculate the supersaturation ratio, the ratio $\frac{K_{A3}K_{A4}}{K_S}$ is determined from the speciation study by a regression technique.

Once the thermodynamic law is established, the kinetic laws can be determined for modelling the precipitation processes.
Dealing with the crystal growth rate, an experimental study is carried out in a glass baffled batch reactor equipped with a marine propeller in batch conditions. It is found that the crystal growth is linearly dependent on the supersaturation. Furthermore, the mechanism which governs the uranium peroxide growth is the dislocation mechanism. Finally, crystal growth kinetics is independent from the impeller speed.
The kinetic laws for the primary nucleation are identified using a specific apparatus patented by the French Atomic Energy Commission and AREVA. As the primary nucleation occurs very rapidly, this apparatus allows the reagent mixing state at molecular scale to be controlled. It has been shown to achieve very efficient micromixing, inferior to the millisecond, with a high degree of precision and reproducibility. The homogeneous and heterogeneous nucleation rates are expressed as the classical theory proposed by Volmer and Weber:
Agglomeration kernel is experimentally determined form continuous experimental runs and the mathematical treatment of experimental crystal size distributions.

All the information obtained by this study will be used for modelling the precipitation of uranium peroxide in a fluidized bed reactor.