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Dissolution of uranium dioxide in nitric medium, towards a macroscopic model of reactors

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Introduction

Dissolution plays an important part at the head of many industrial processes. It is a key step for the **recycling of rare metals** and also **uranium dioxide**, mainly present in spent nuclear fuel. However, **heterogeneous reactions** are particularly **complex** in those cases as they are **triphasics** and **catalyzed by one of their products**.

Dissolvers could be optimised with a good knowledge of the physico-chemistry implied in this kind of reactions. Hence, this work focuses on developing a model of the reactor including all the characteristics of the dissolution and their effects on the kinetics.

Our approach

Caption :
Well advanced
Ongoing
Next episode

Comprehension of phenomena involved in the dissolution

1 Numerous equilibriums in nitric medium

- Balanced equation depend on temperature and acid concentration,
- Numerous equilibriums in nitric acid.

5 Heterogenous attack of the solid

- Increase in the specific surface at the beginning of the reaction,
- Greater activity in the pits created during dissolution.

Pellet surface before dissolution [URI - 65] Pellet surface after dissolution [URI - 65]

Reaction analysis

4 Triphasic reaction

- Solid – liquid reaction,
- Product of the reaction are gases.

2 Auto-catalyzed reaction

- One of the product accelerates the reaction,
- The mechanism is not yet identified.

Mean kinetic rate vs Dissolution rate function of the predissolved UO₂ mass concentration in the solution. [PHI - 14]

3 Gas-liquid exchanges

- Catalyst could be related to the gases emitted.

Kinetic study without influence of heat transfer and mass transport

Kinetic study

- Peltier** → no temperature gradient in the dissolution cell.
- Microscope** to follow the projected surface of the particles.
- Syringue pump** → renewal of nitric acid. → No concentration Gradient.

zoom on the dissolution cell

Nitric acid UO₂ powder

Kinetic study diagram: $A_p(t + \Delta t) - A_p(t) \approx -P(t) \Delta l = -P(t) v_{app} \Delta t$

A_p : projected area of the particle
 P : perimeter of the particle
 v_{app} : apparent kinetic rate

Evolution of equivalent radius
Concentration : 8 mol.l⁻¹ Temperature : 65°C

Equivalent radius, normed by the initial value vs Time (min)

The dissolution rate is very slow at the beginning. **Why ?**

- Oxidation layer ?
- Evolution of the specific surface ?
- Catalyst in the pores ?

Model for the local kinetic rate

Solid - liquid reaction kinetic

Modeling

Limitant kinetic step ?
3, 4, 5 : reaction is under kinetic control,
1, 2, 6, 7 : reaction is under diffusion control.

Different scales of accumulation for the catalyst
- Bulk liquid,
- Boundary layer,
- Pores and cracks.

Reaction rate

The global reaction rate (v) is the addition of the kinetics of non catalysed reaction (nc) and catalysed (c) one.

$$v = v_{nc} + v_c$$

$$= k_{nc} C_S^{n_1} + k_c C_S^{n_2} C_{cat}^p$$

n_1 order for nitric acid (nc)
 n_2 order for nitric acid (c)
 p order for catalyst

Arrhenius law

$$k = A \times \exp\left(\frac{-E_a}{RT}\right)$$

Range of temperature : 50 - 70 °C
Activation energy : 18,6 kJ.mol⁻¹

Diffusion rate v_{diff} ,

$$v_{diff,i} = k_{d,i} (C_{i,b} - C_{i,s})$$

$k_{d,i}$: diffusion coefficient of specie i
 $C_{i,b}$: Bulk concentration
 $C_{i,s}$: Surface concentration

Local kinetic rate [mol.m⁻².s⁻¹] vs $X = [HNO_3]_{local} / [HNO_3]_{initial}$

Evolution of kinetic rate (yellow curve)
Diffusion flux (purple curve)

UO₂ pellet equilibrium point
UO₂ particles equilibrium point

Application of the kinetic model to ideal reactors

Simulation of hydrodynamics in real dissolvers

Comparison with experimental results

Application of the model to more elaborated reactors

- Recycling of nitric acid
- Recombination of gas

Conclusions and perspectives

Such a **multiscale** model for the dissolution kinetic will enable to :

- **optimize** actual dissolvers,
- **develop innovative reactors** for recycling of metals or spent nuclear fuel.