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 dioxyde**, 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 physiso-chemistry implied in this kind of reactions. Hence, this work focuses on developing a model of the reactor including all the caracteristics of the dissolution and their effects on the kinetics.

Our approach

Caption :
Well advanced
Ongoing
Next episode

- Comprehension of phenomena involved in the dissolution
- Kinetic study without influence of heat transfer and mass transport
- Model for the local kinetic rate
- Application of the kinetic model to ideal reactors

Reaction analysis

(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]

Pellet of uranium dioxide

NO_2
NO
HNO_2
Catalyst ?
gas
liquid

(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 / Nitric acid concentration

Dissolution rate function of the predissolved UO_2 mass concentration in the solution. [PHI - 14]

(3) Gas-liquid exchanges
- Catalyst could be related to the gases emited.

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
UO_2 powder

$$A_p(t + \Delta t) - A_p(t) \approx - P(t)\,\Delta l = - P(t)\,v_{app}\,\Delta t$$

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
Time (min)

The dissolution rate si very slow at the begining. **Why ?**
- Oxidation layer ?
- Evolution of the specific surface ?
- Catalyst in the pores ?

Modeling

Solid - liquid reaction kinetic

Solid | External transfer boundary layer | Bulk reactions

1 and 7 - diffusion of reactants and products in the diffusion layer.
2 and 6 - diffusion inside the pores.
3 and 5 - adsorption of reactants and desorption of products.
4 - chemical reaction.

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

UO_2 *pellet* equilibrium point
UO_2 *particles* equilibrium point
Local kinetic rate [mol.m^{-2}.s^{-1}]
Evolution of kinetic rate
Diffusion flux
X_s
$X=[HNO_3]_{local} / [HNO_3]_{initial}$

Conclusions and perspectives

- 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

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.

References
[PHI - 14] P. Marc, *Etude de réactions hétérogènes autocatalytiques. Application à la dissolution du dioxyde d'uranium.* Thèse de l'université de Lorraine, 17 décembre 2014.
[URI - 65] A. L. Uriarte & R. H. Rainey, « Dissolution of high-density UO_2, PuO_2, and UO_2-PuO_2 pellets in inorganic acids », *Document technique ORNL*, Réf. ORNL-3695, avril 1965.

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