



## 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.

**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.

**Kinetic study**

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

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

**Evolution of equivalent radius**  
Concentration : 8 mol.l<sup>-1</sup> Temperature : 65°C

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**

**Application of the kinetic model to ideal reactors**

**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 ( $v_{nc}$ ) and catalysed ( $v_c$ ) 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<sup>-1</sup>

**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<sup>-2</sup>.s<sup>-1</sup>]**

$X = [HNO_3]_{local} / [HNO_3]_{initial}$

**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.