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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 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 developping 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

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**

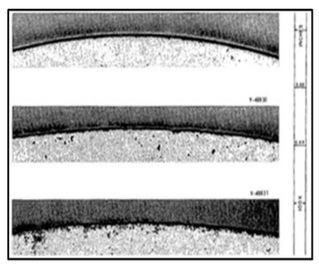
Reaction analysis

1 Numerous equilibriums in nitric medium

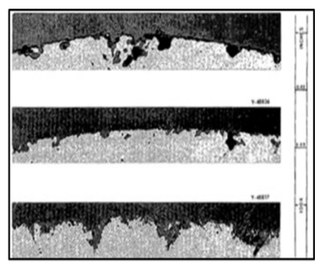
- Balanced equation depend on temperature and acid concentration,
- Numerous equilibriums in nitric acid.

5 Heterogenous attack of the solid

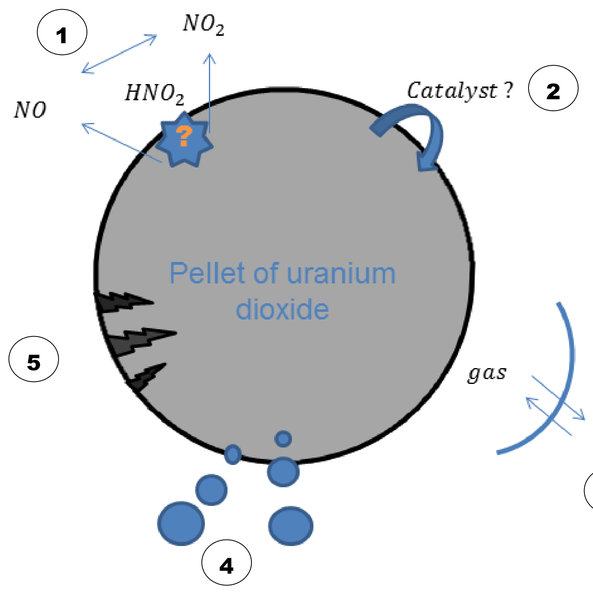
- Increase in the specific surface at the beginning of the reaction,
- Greater activity in the pits created during dissolution.



Pellet surface before dissolution [URI - 65]



Pellet surface after dissolution [URI - 65]

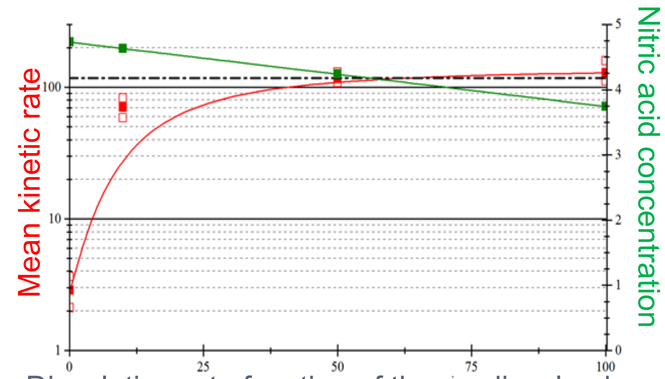


4 Triphasic reaction

- 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.



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

3 Gas-liquid exchanges

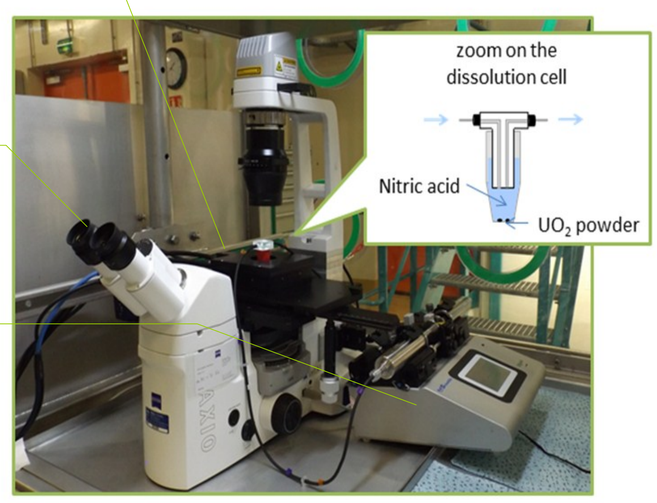
- Catalyst could be related to the gases emited.

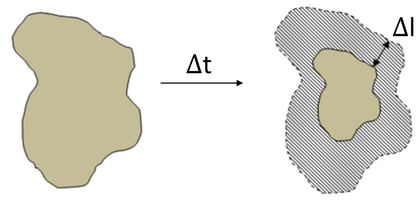
Kinetic study

Peltier
→ no temperature gradient in the dissolution cell.

Microscope
to follow the projected surface of the particles.

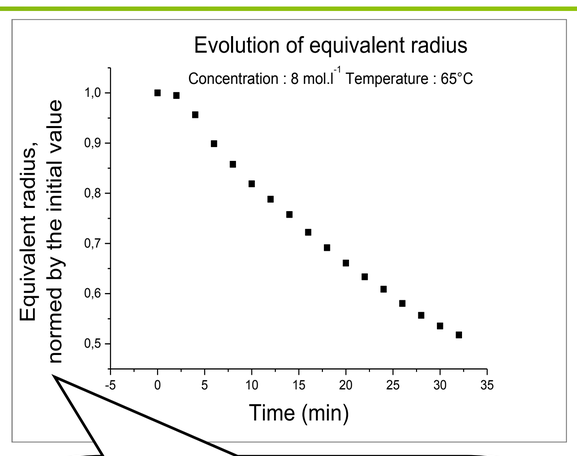
Syringue pump
→ renewal of nitric acid.
→ No concentration Gradient.





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

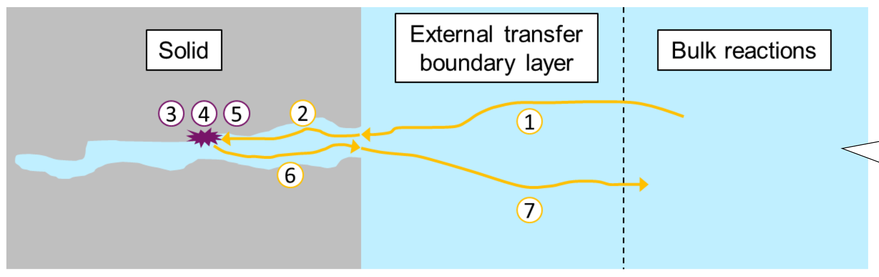
A_p: projected area of the particle
P : perimeter of the particle
v_{app} : apparent kinetic rate



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



1 and 7 - diffusion of reactants and products in the diffusion layer.
2 and 6 - diffusion inside the pores.
3 and 5 - adsoprtion 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.

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*

Reaction rate

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

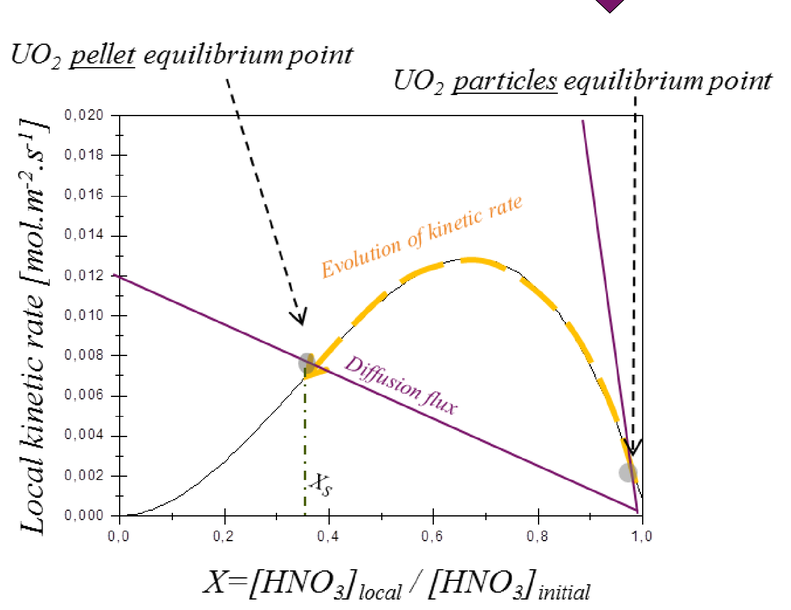
$$v = v_{nc} + v_c$$
$$= k_{nc}\,C_S^{n_1} + k_c\,C_S^{n_2}\,C_{cat}^{p}$$

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}



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.

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[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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