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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

Comprehen-
sion 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

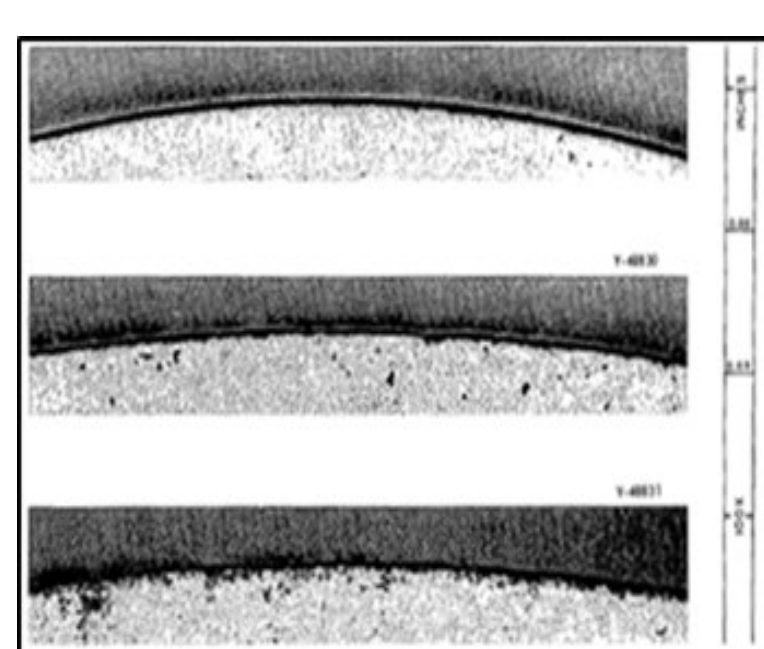
Simulation of
hydrodynamics
in real
dissolvers

1 Numerous equilibriums in nitric medium

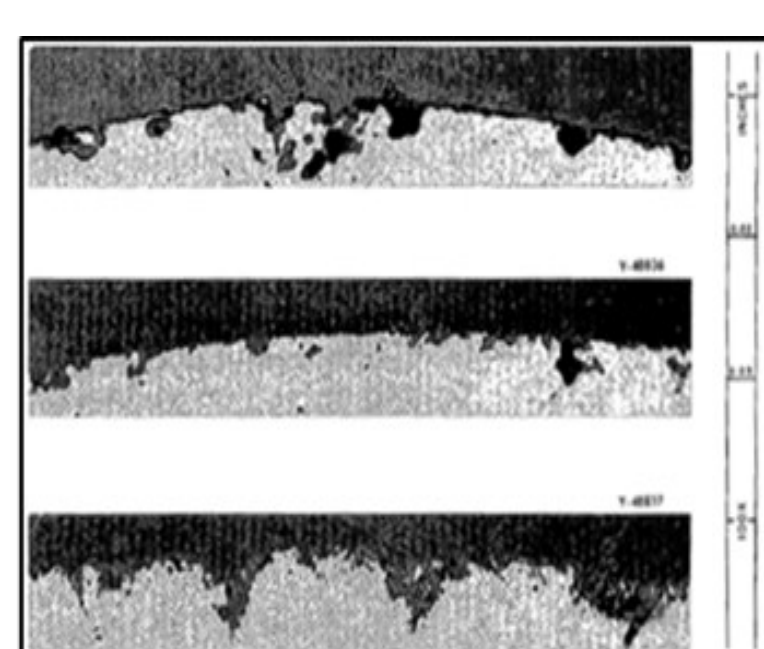
- Balanced equation depend on temperature and acid concentration,
- Numerous equilibriums in nitric acid.

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.

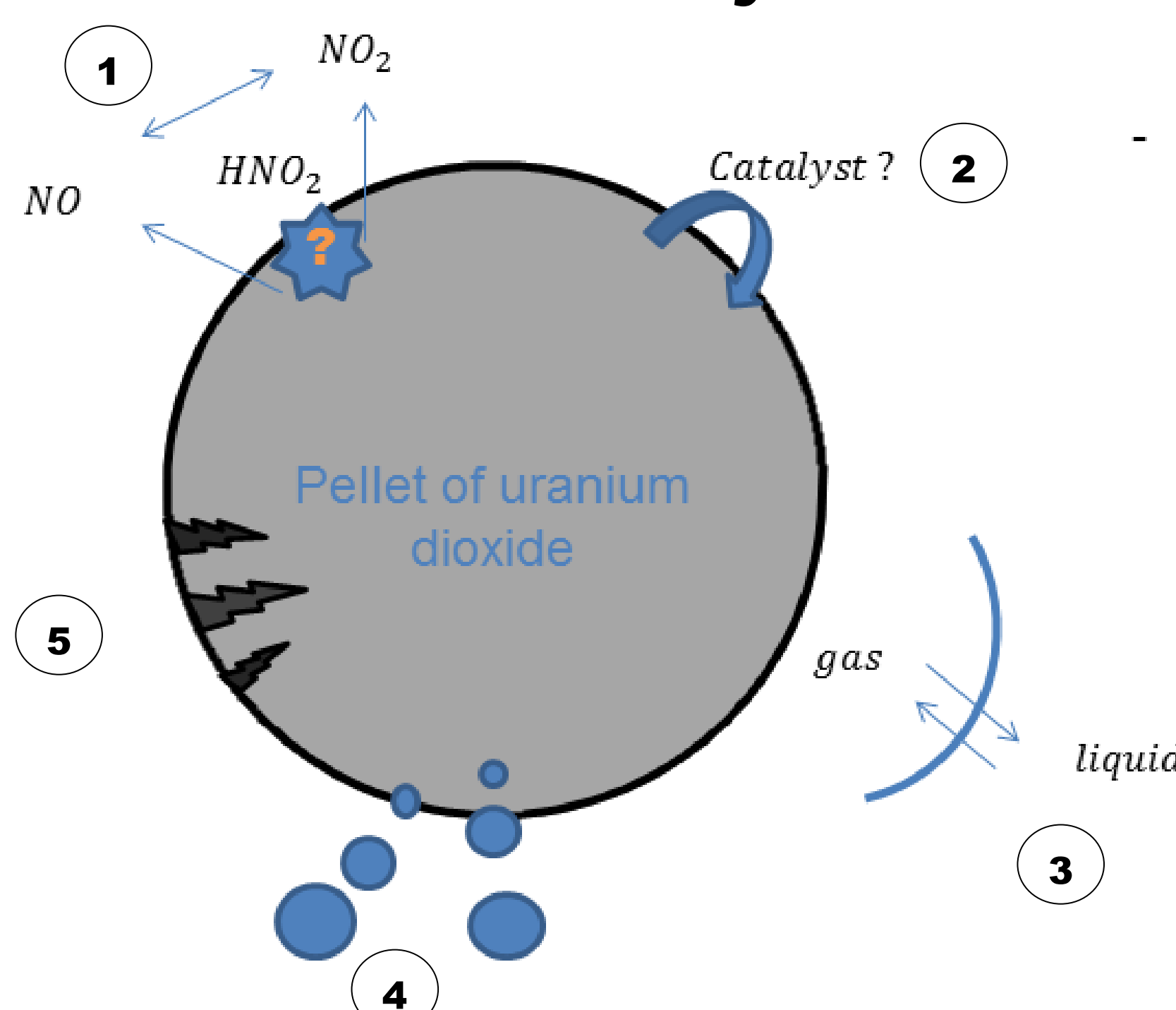


Pellet surface before dissolution [URI - 65]



Pellet surface after dissolution [URI - 65]

Reaction analysis

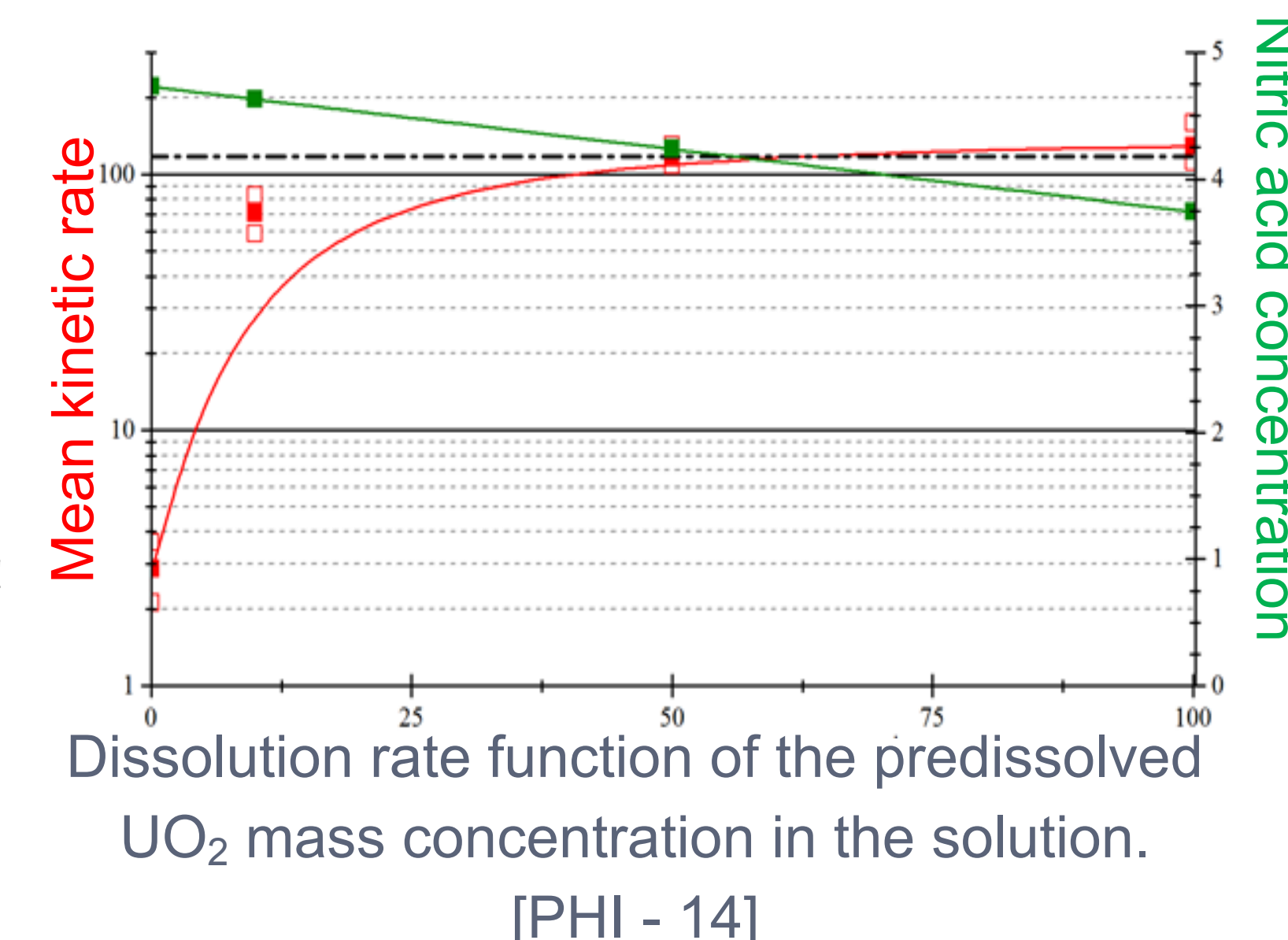


4 Triphasic reaction

- 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

Peltier

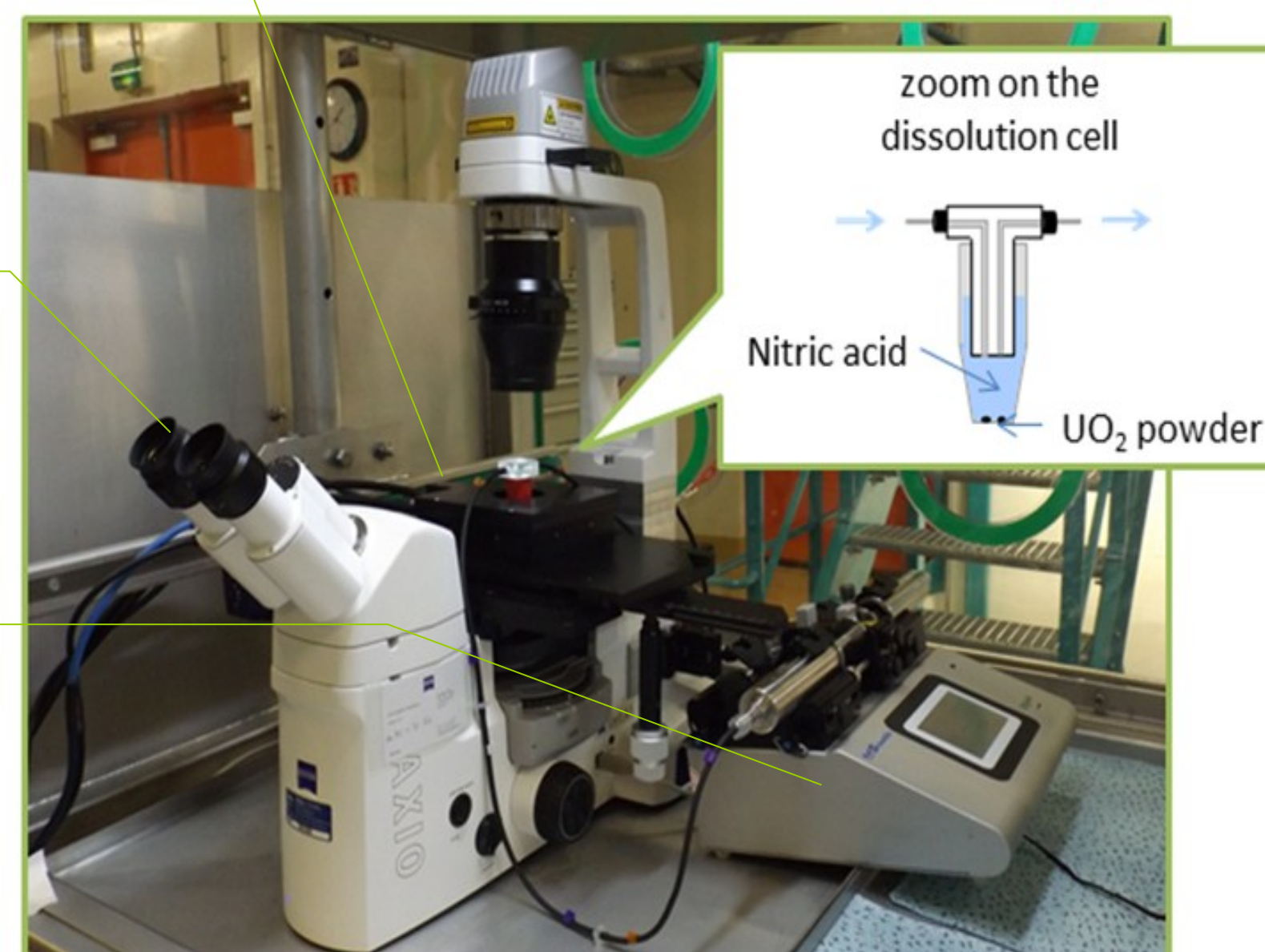
→ no temperature gradient in the dissolution cell.

Microscope

to follow the projected surface of the particles.

Syringue pump

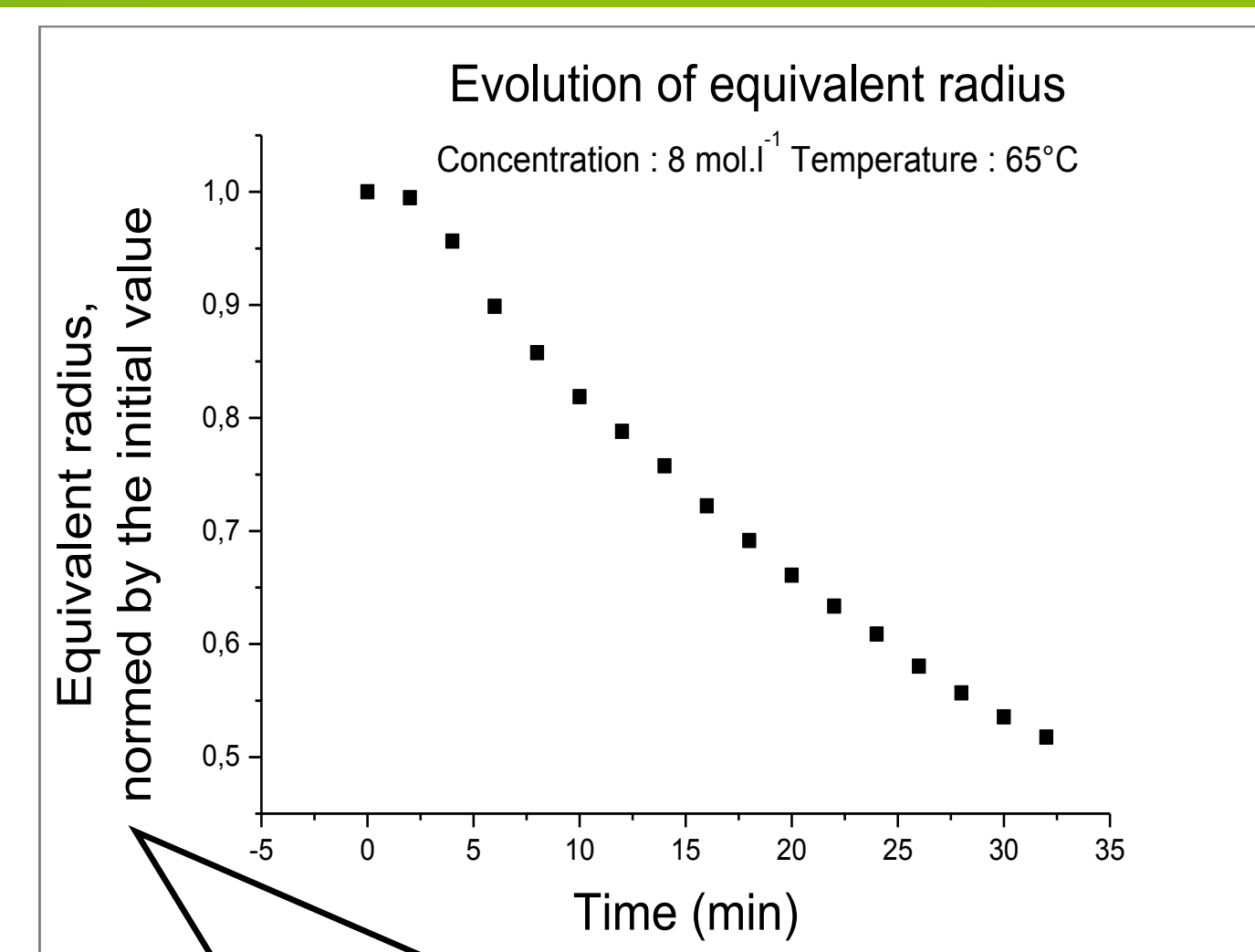
→ renewal of nitric acid.
→ No concentration Gradient.



$$A_p(t + \Delta t) - A_p(t) \approx -P(t) \Delta l$$

$$= -P(t) v_{app} \Delta t$$

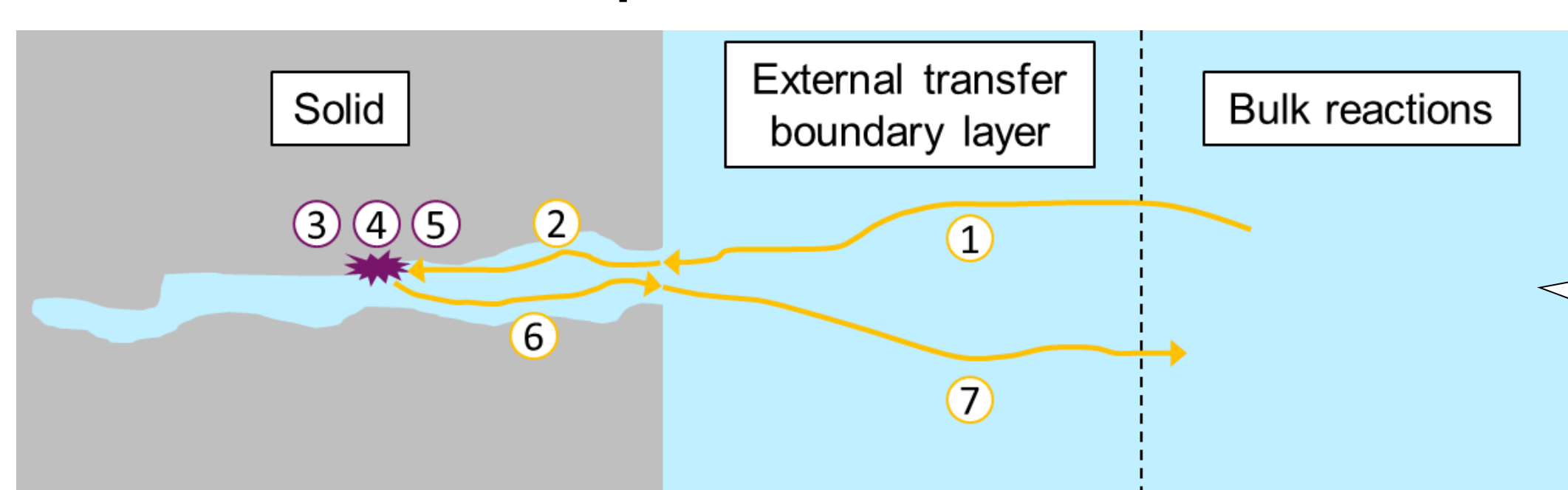
A_p : projected area of the particle
 P : perimeter of the particle
 v_{app} : apparent kinetic rate



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

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

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 - adsorption of reactants and desorption of products.
- 4 - chemical reaction.

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

Modeling

Limitant kinetic step ?

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

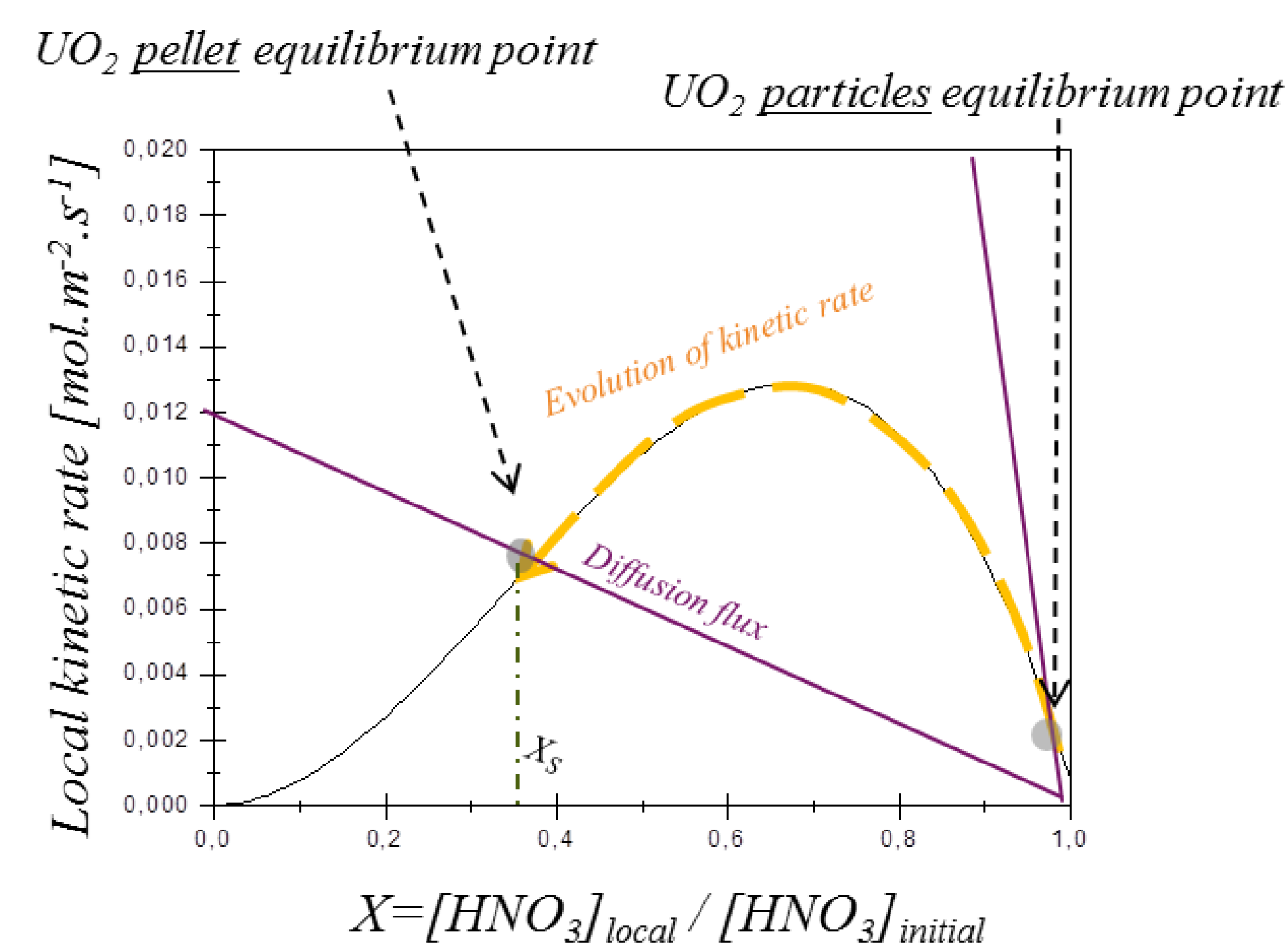
Different scales of accumulation for the catalyst

- Bulk liquid,
- Boundary layer,
- Pores and cracks.

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



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.