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Dissolution viewed as a process

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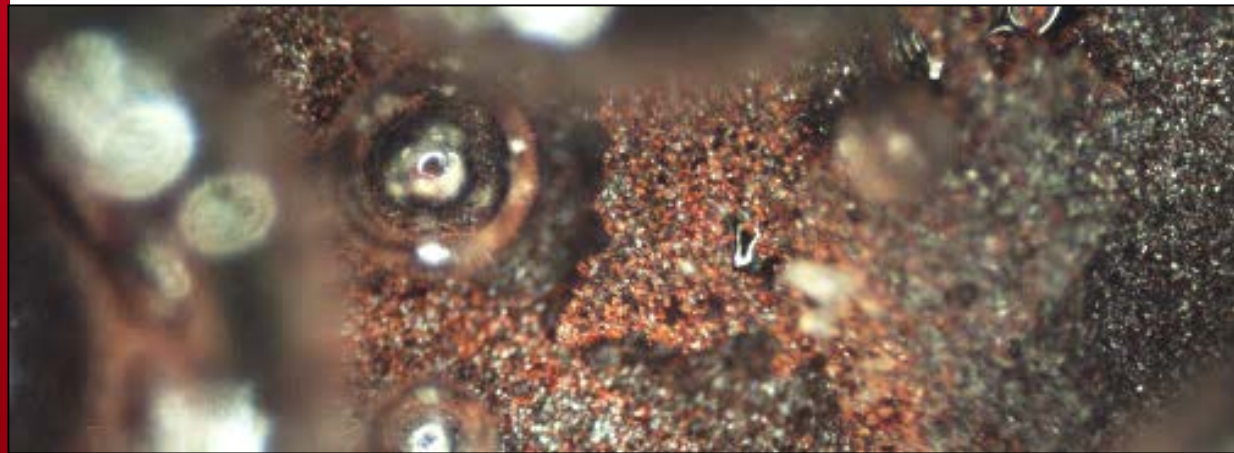
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DE LA RECHERCHE À L'INDUSTRIE

cea

DISSOLUTION VIEWED AS A PROCESS



Speaker: Alastair MAGNALDO

www.cea.fr

ENVIREE MEETING – 22ND OCTOBER 2015

Thank you for coming !

I do not know the level of all the people present, so I will talk-show on « *what happens in dissolution processes* », bringing general ideas as they come without being specific !

Part I - General discussion on Reaction – Transport - Accumulation

Part II – Focus on how to formulate the reaction part

Part III – A quick example of a more complicated process

Part IV – Back to accumulation and neo-formed solids

PART I - GENERAL DISCUSSION ON REACTION – TRANSPORT - ACCUMULATION

The global chemistry

- Chemical species and their chemical reactions
- Kinetics and reaction products

Accumulation

- Reaction products accumulate
 - Reaction consumes reagents
Induce Secondary Reactions;
 - Catalysis
 - (Re)-Precipitation...
 - Gas nucleation
- = a variable set of reactions

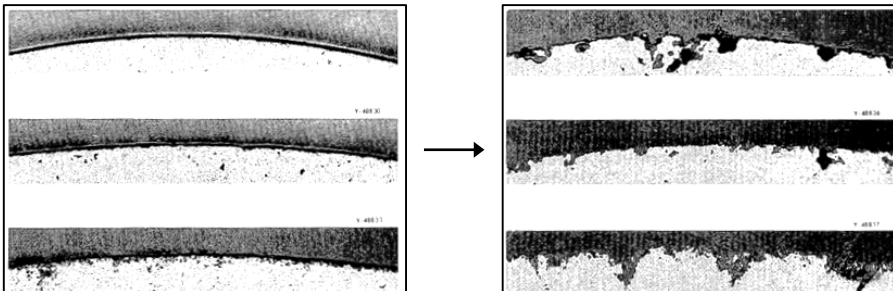


The solid

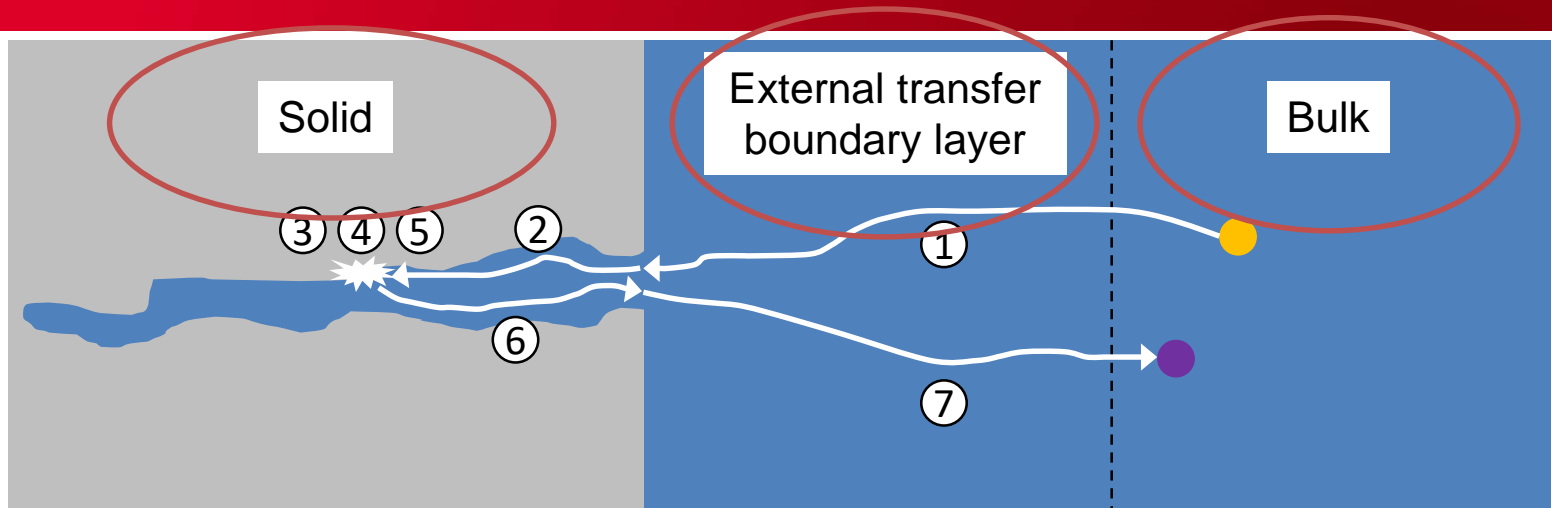
- The reactive solid is hard to de
- In permanent fast evolution

Transport

- Chemical species are produced locally.
- Transport decides where products accumulate



SOLID-LIQUID REACTION MECHANISMS



- Constituting the factors of a diffusion reaction are in this picture:

- ④ : reaction products are produced locally, and can attain very high levels
- ② : diffusion of reagents in the pores
- ③ : eventual adsorption of reagents on the solid

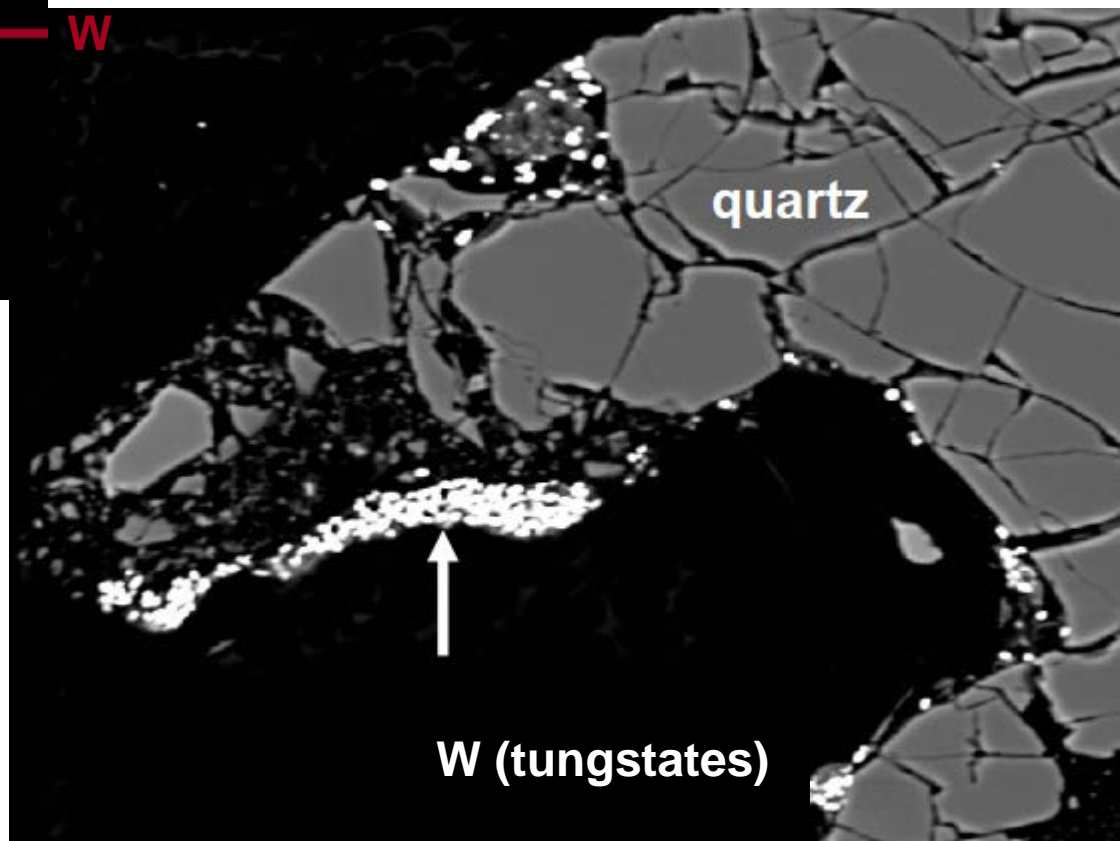
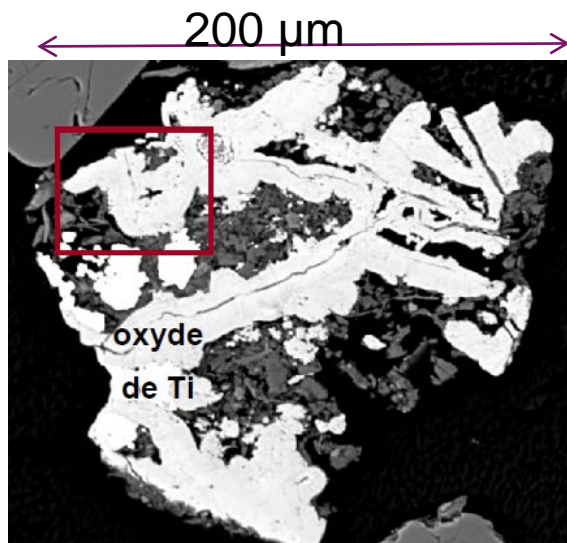
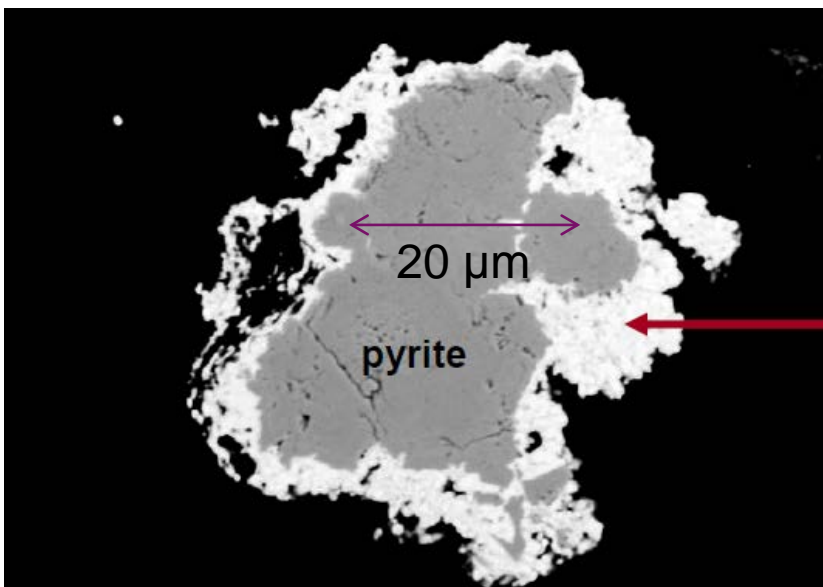
- Accumulation is present

- ⑤ : eventual desorption of products
- ⑥ : at the scale of the pores and cracks,
- ② : diffusion of products in the pores,
- ⑦ : external transport of reagents through the boundary layer
- ③ : at the scale of the bulk liquid

- Mainly Two kinds of controlling phenomena:

- Chemical reaction controlled dissolution
- Diffusion controlled dissolution

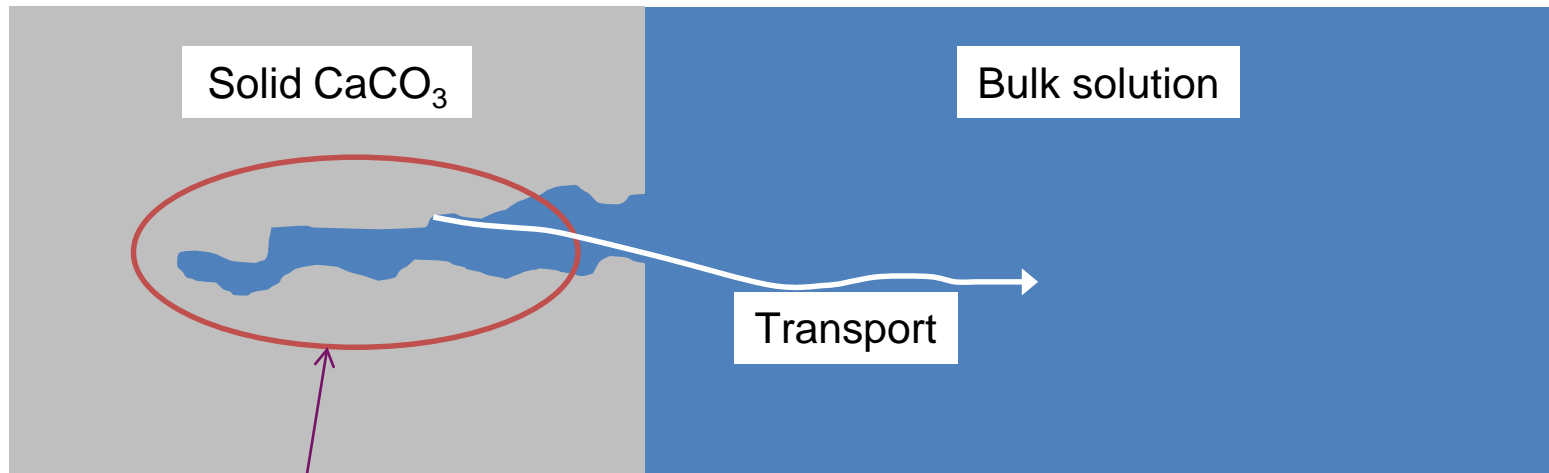
REAL SAMPLES



Global reaction



Solid \nearrow Soluble complex \nearrow Dissolved gas \nwarrow



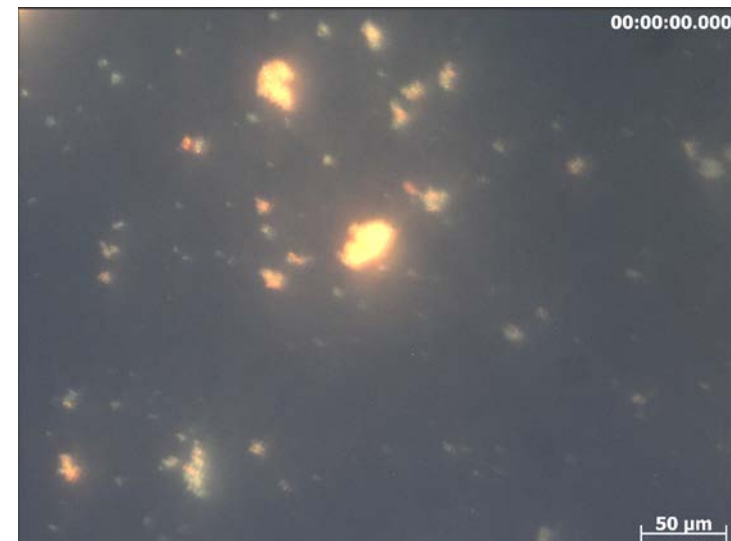
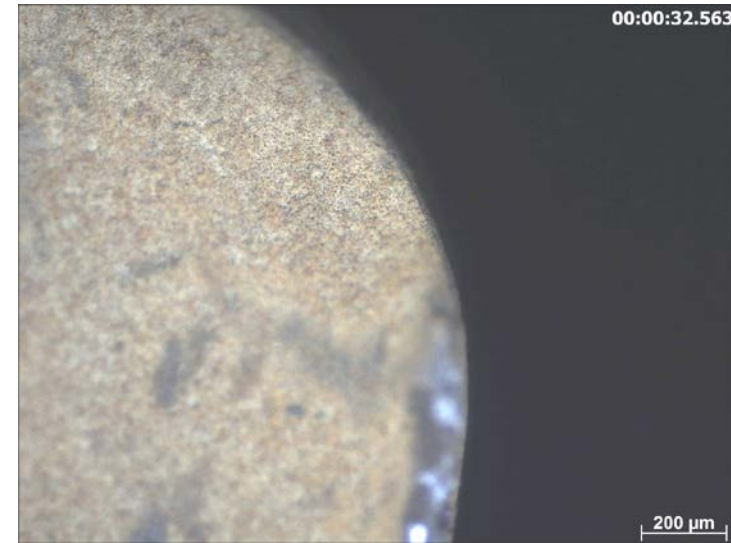
- Accumulation of reaction products
- Depletion of reagent
- Accumulation of competitive impurities

Solid CaSO₄ precipitation at limit of solubility

CO₂ gas nucleation

CaSO₄ → very insoluble Ca(OH)₂

- Observation of the dissolution of a sintered UO_2 pellet
- Here the effect of accumulation introduces a secondary catalyzed reaction
- Dissolves according to very different time scales:
 - Pellet crumbles apart within ~ 20 min; **STRONG ACCUMULATION**
 - Dislodged particles dissolve slowly within ~ 24 h; **NO ACCUMULATION**



- But always bear in mind that for a cost effective process, we want:
 - the smallest ratio of reagent over solid (high solid concentration)
 - fast global chemical kinetics in order to limit hold-up (or size of plant)

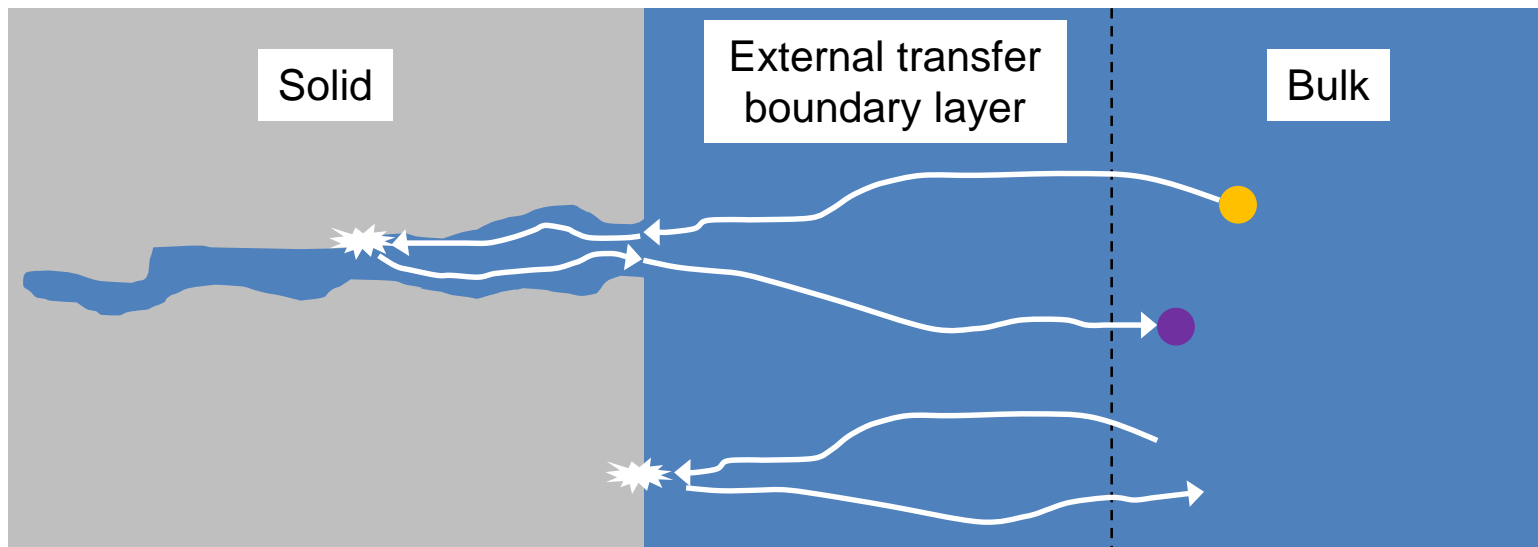


Both ask for high accumulation



The problems induced by accumulation of all products and at all scales will generally be a good indicator of the feasibility and economical viability of a dissolution process

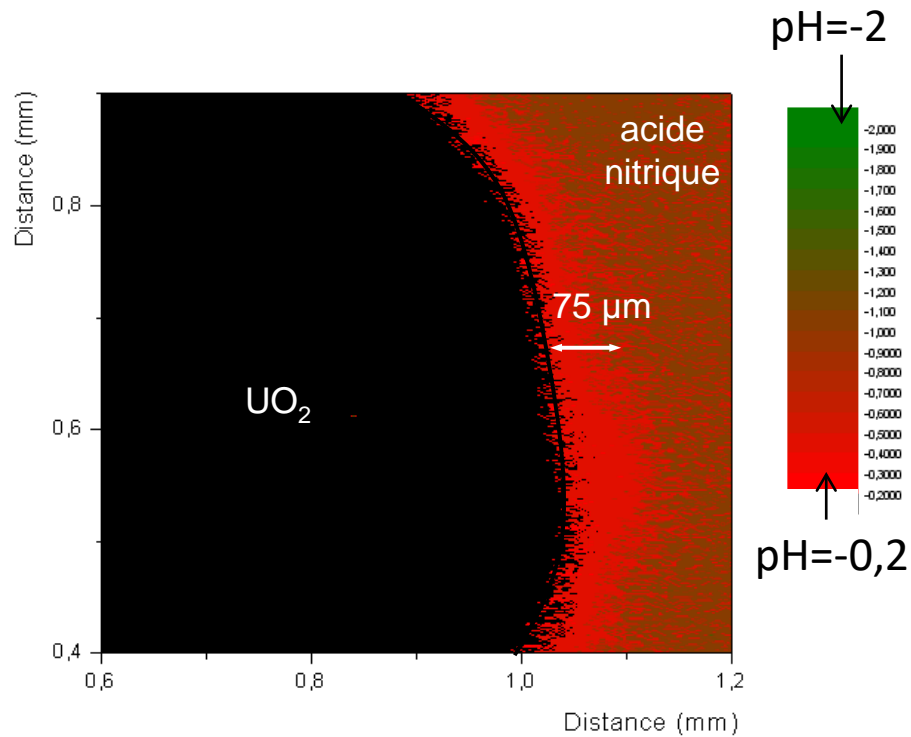
SO WHO CONTROLS THE GLOBAL REACTION ?



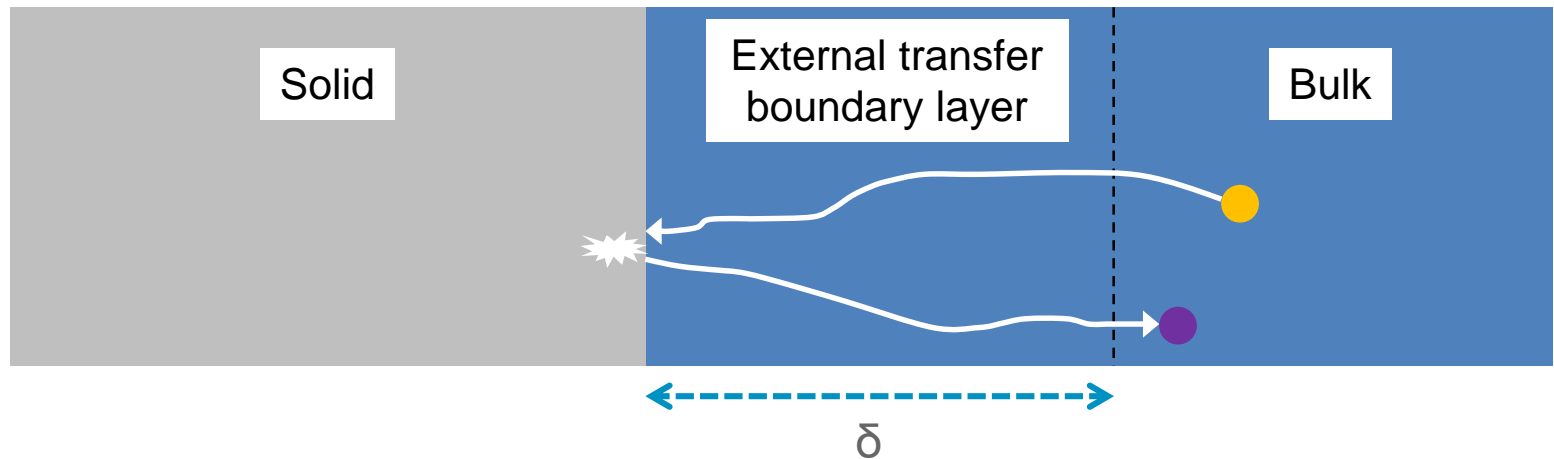
With chaining mechanisms, the slowest controls the global rate

With parallel mechanisms the fastest controls the global rate

SO WHO CONTROLS THE GLOBAL REACTION ?



EXTERNAL TRANSPORT IN MORE DETAIL



① $N_{diff} = k_D(c_{bulk} - c_{surface})$ Is the flux density of matter in $\text{mol.s}^{-1}.\text{m}^{-2}$
 k_D is the matter transfer conductance in m.s^{-1}

② k_D depends on the thickness of the boundary layer, δ , as $k_D = \frac{D}{\delta}$

③ Obviously, hydrodynamics determine the boundary layer thickness. Many correlations (unproven - experimentally determined) give the Sherwood number, for example :

$$Sh = \frac{k_D \phi_{particule}}{D} = 2 + 1.8 \times Re^{1/2} Sc^{1/3} \text{ (Ranz-Levenspiel for small particles)}$$

δ ranges from 10 to 100's of μm .

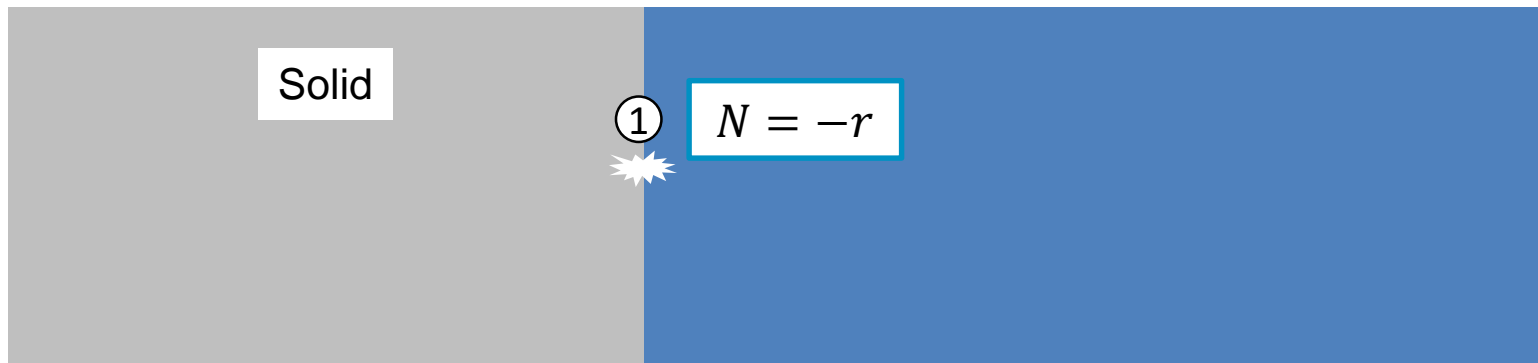
Inertia/viscous forces

mass diffusivity/quantity of mvt diffusivity

Implications :

- Bad hydrodynamics (thick boundary layer) usually control the reaction, but,
- dissolution of very small particles is not diffusion controlled, meaning that
- the end part of complete dissolution is always chemically controlled

PART II – A FOCUS ON « REACTION »



①

$$N_{reaction} = -r$$

is the reaction flux density of matter in $\text{mol.s}^{-1}.\text{m}^{-2}$
which can be converted into a speed in m.s^{-1}

$$N_{reaction} = -r(T^{\circ}, c_{surface}, \dots)$$

So who said « difficult » ? A working equilibrium is $N_{reaction} = -r = N_{diff} !!$

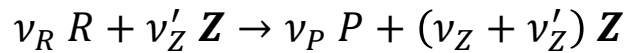
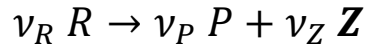
See the following example with accumulation and catalysis:

$$N_{diff} = k_D(c_{bulk} - c_{surface})$$

$$N_{reaction} = -r = N_{diff} !!$$

A COMPLICATED CASE MADE SIMPLE

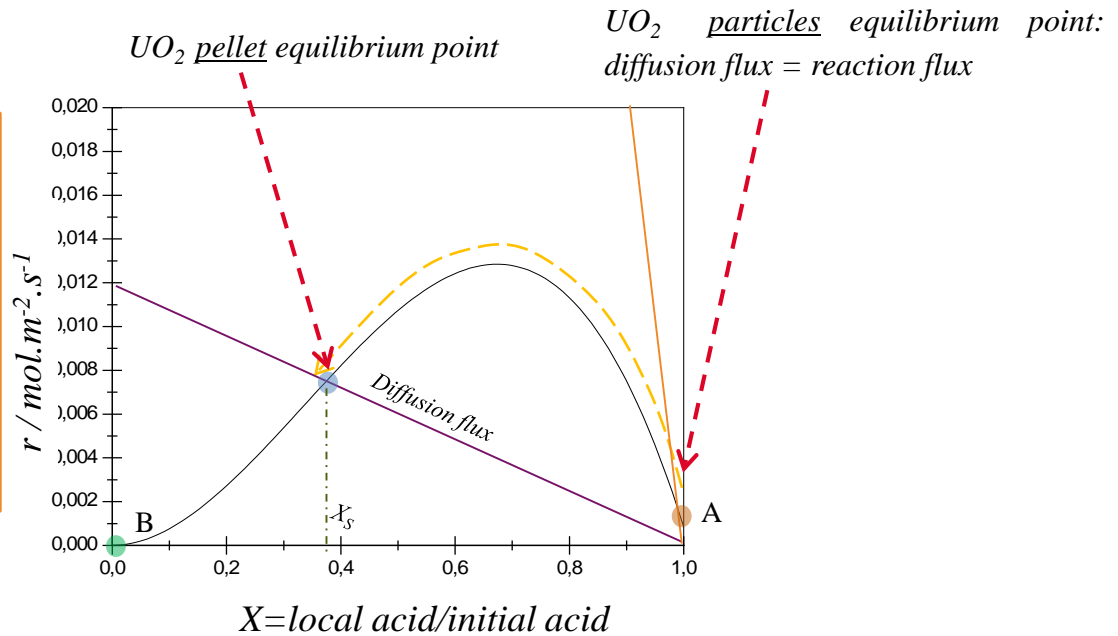
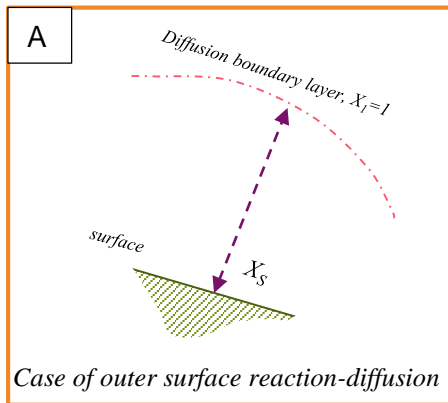
- Autocatalysis consists of 2 parallel reactions – initiation – catalysis



$$r \propto \frac{v}{v_0} = X^{n_1} + \omega X^{n_2} (1 - X)^p$$

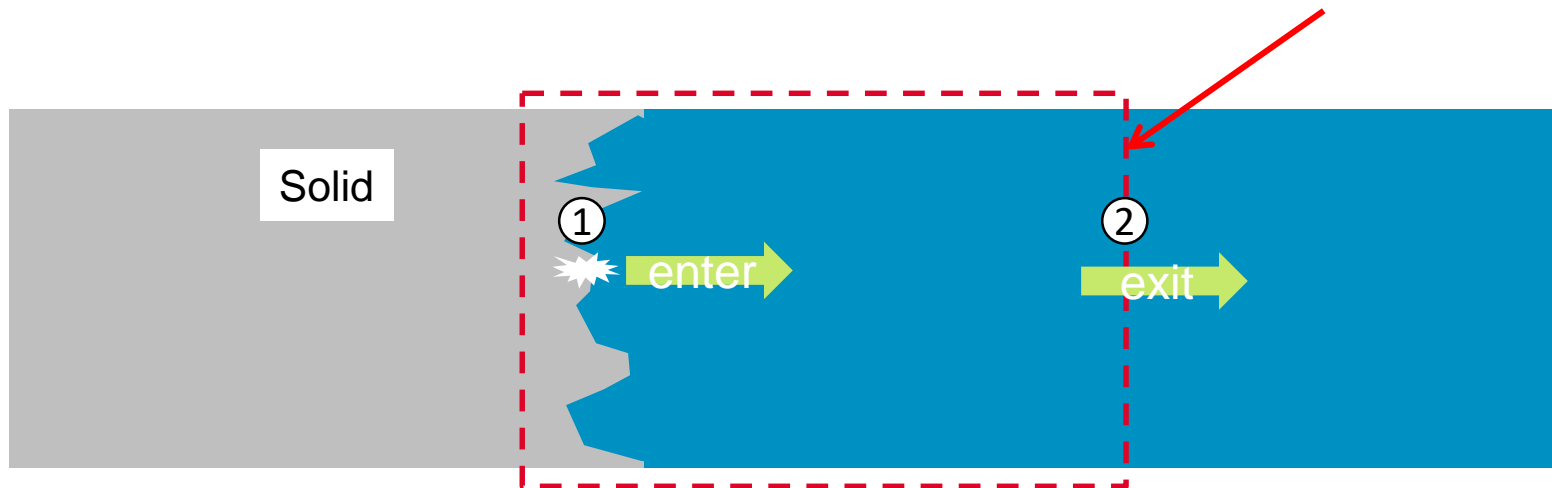
$$X = \frac{\text{local acid concentration}}{\text{initial bulk concentration}}$$

Case A:



YOU DIDN'T GET AWAY WITH IT !!!

- ① $N_{reaction} = -r$ is the reaction flux **density** of matter in $\text{mol.s}^{-1}.\text{m}^{-2}$
- $n_{reaction} = N_{reaction} \times S_{reaction}$ is the reaction flux
- $S_{reaction}$ is the reactive surface
- ② $n_{diff} = N_{diff} \times S_{any\ surface\ as\ long\ as\ a\ vectoriel\ product\ is\ considered}$
and can be for ex. a "geometrical enveloppe" of the surface



$$-r \times S_{reaction} = k_D(c_{bulk} - c_{surface}) \times S_{geo} \quad \text{is the real relation}$$

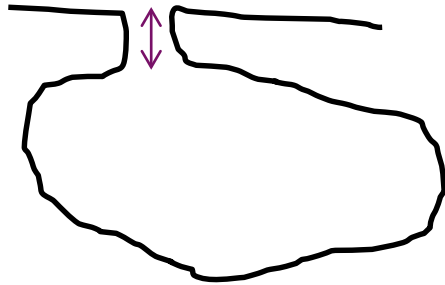
WHAT IS THE REACTIVE DISSOLUTION SURFACE $S_{reaction}$?

- It's impossible to measure "per se" except in some exceptional cases,

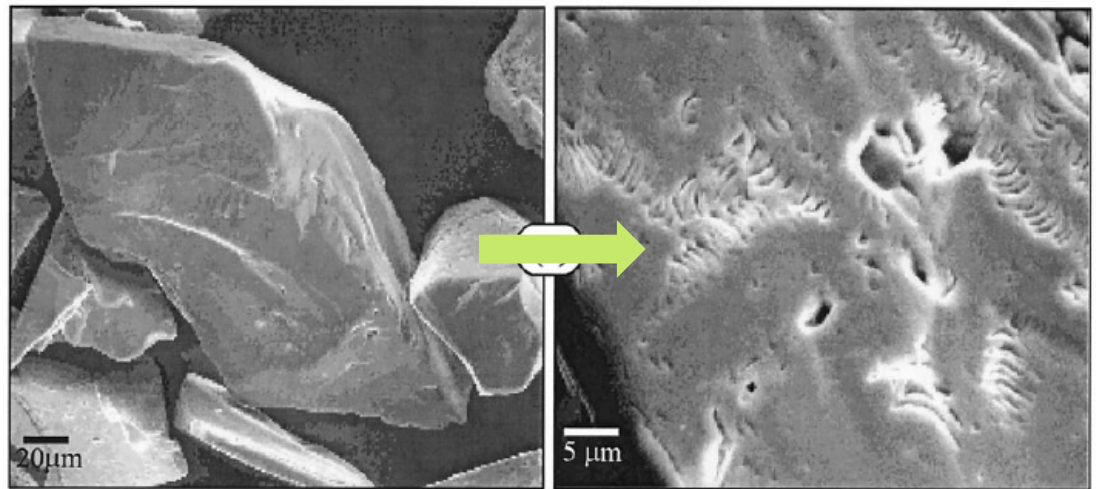
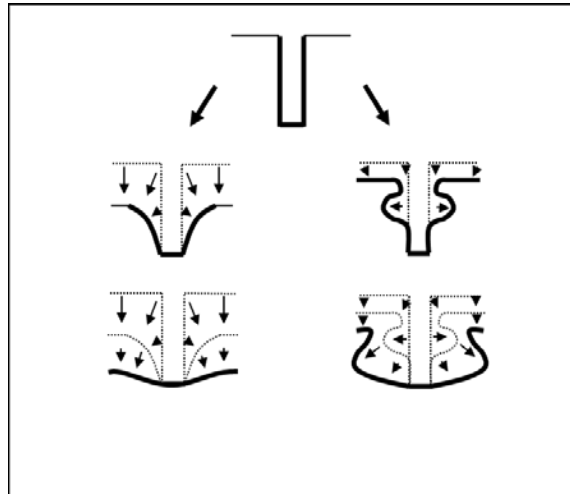
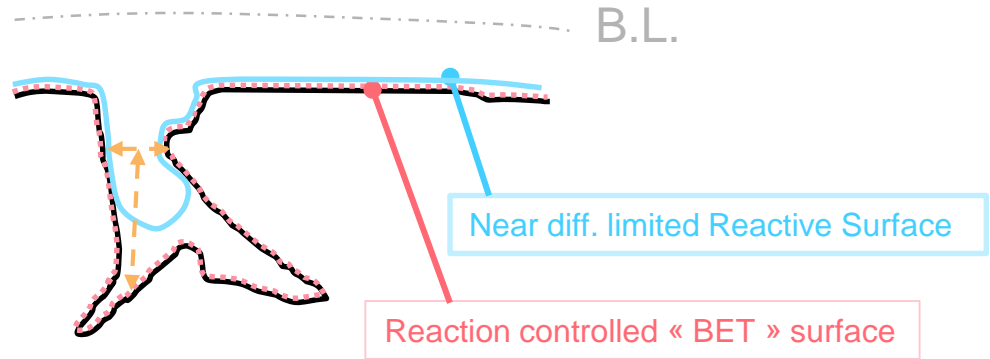
- It's **reaction dependant !!!**

slow reaction kinetics = more surface involved

- Bottleneck effects



- Strong time variability

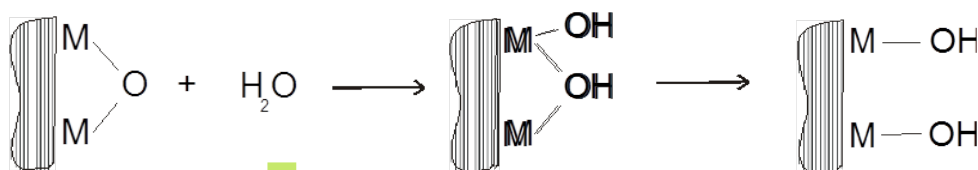


Gauthier et al.

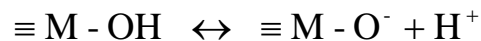
WHAT IS THE REACTIVE DISSOLUTION SURFACE $S_{reaction}$?

- More importantly, the elementary crystal domains do not react in the same manner,
- as is the case of crystals; dissolution speed depend on crystal **habit**.

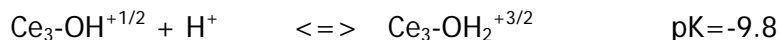
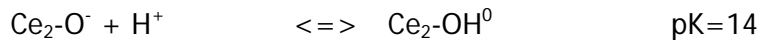
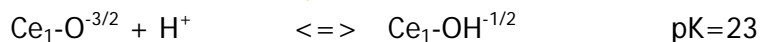
Disclaimer: case of metal oxide and multisite surface complexation and charge distribution model, maybe wrong but who cares... the principle is OK



Hydroxylation



Protonation – deprotonation of surface sites



Taking into account of crystal habit by introducing a formal charge by dividing the charge of M by the coordination number. For cerine, cristal faces 100, 111 and 110 have different charges and acido-basic reactions

- Some crystal faces are more reactive, others probably inactive !
- Proportion of active faces increase and decrease as dissolution progresses.

HOW DO WE DEAL WITH THESE ISSUES ?

- Literature shows that although we do try... but we can't deal with these issues
- In practice for a *solid particle* we use Noyes and Whitney equation (1897), far from saturation:

$$\frac{dm}{dt} = -r \times S_{reaction} = -k \times S_{geo}$$

Reaction flux density

Disclaimer: spherical particles, 1 reagent etc..

Dissolution constant, or **ignorance factor** !
englobing everything we don't know, and very often in literature:

- doesn't vary with time
- doesn't vary with the kinetics
- doesn't vary with the particles' diameter etc..

And basically says that

$S_{reaction} \text{ always } \propto S_{geo}$!

$$\left\{ \begin{array}{l} \frac{dR}{dt} = -k_0 \cdot r \\ \frac{dC_{sol}}{dt} = \frac{4\pi}{V} \cdot k_D \cdot R^2 \cdot (C_{surf} - C_{sol}) \\ k_D \cdot (C_{sol} - C_{surf}) = \gamma \cdot r \end{array} \right.$$

Yields the usual « always the same » set of equations:

- 1) *Reaction*
- 2) *What diffuses is accumulated in volume*
- 3) *What reacts is diffused*

IF WE LOOK CLOSER AT REACTION LIMITED DISSOLUTION...

$$\frac{dm}{dt} = -r \times S_{reaction} \xrightarrow{\text{yields}} \frac{dR}{dt} = -r \times \frac{S_{reaction}}{S_{geo}} = v \quad \text{is a dissolution speed in m/second}$$

- R (for ex. radius of an equivalent object of same mass), like m (mass) are perfectly defined, just as S_{geo}
- No surface measurement is more, or less, pertinent than any other as long as no link with $S_{reaction}$ is demonstrated. Which is NOT the case of BET measurements.

So

- What is the « good » yardstick for measuring a dissolving surface ? One answer; fractal description !

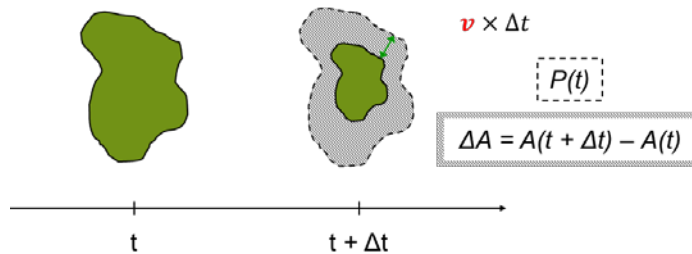
$$-r \times \frac{S_{reaction}}{S_{geo}} = v$$

Needs a fractal description !

Allows fractal description

A fractal description of a surface relies on self-similarity: the length of a perimeter depends on the length of the yardstick

- A and P the projected surface and perimeter



$$P(R) = R^{D_{line}}$$

$$v = \frac{dA}{dt} \times \frac{1}{P(R)} = \frac{\pi}{k_1} \frac{dR}{dt} R^{1-D_{line}}$$

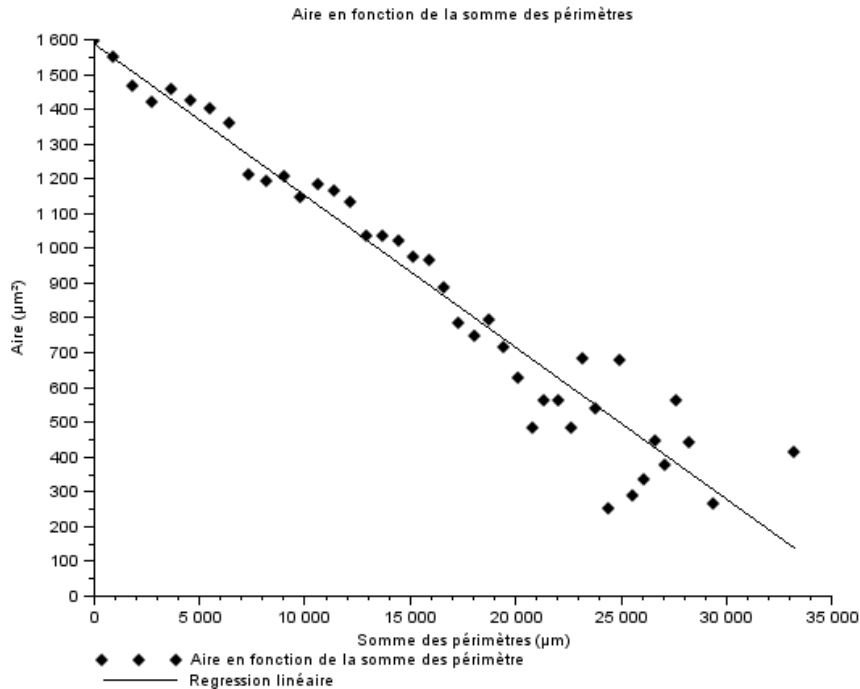
$$D_{surface} = D_{line} + 1!$$

$$\frac{dR}{dt} = -k' \times R^{D_r-2}$$

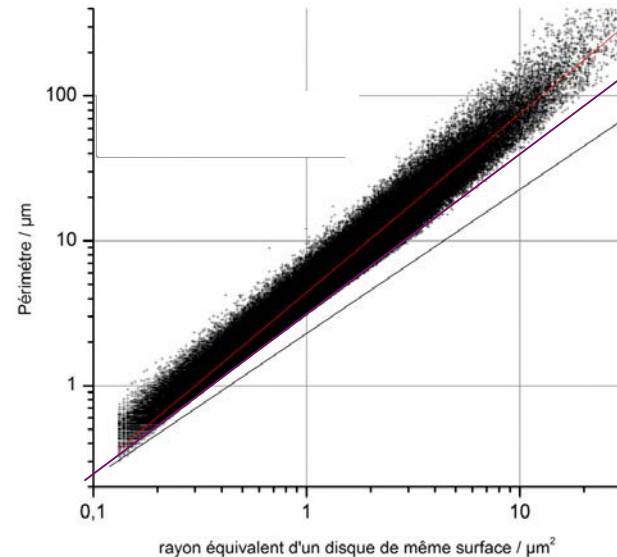
D_r fractal dimension of reactive surface

$$v = -\beta r^{D_r-D_{surface}}$$

■ We have $v...$



■ We have D_{line} by MEB observations of the projected surface on millions of particules



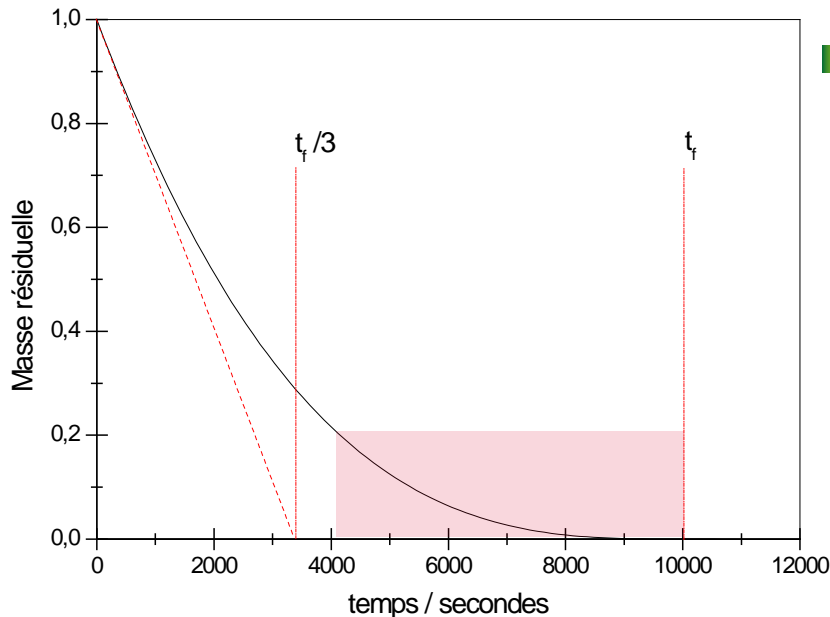
we extract $D_R...$ hopefully

■ $D_R = D_{surface}$ all the way through the dissolution means we have an homogenous distribution of dissolution sites on the surface

- Diffusion or reaction limited kinetics
- Small particules are always chemically controlled
- We want fast processes with high chemical reaction kinetics to the limit of diffusion control
- Most processes are simply modeled by reaction-diffusion-accumulation relations



- By the way, batch reactors are very inefficient for many reasons; reason n°1

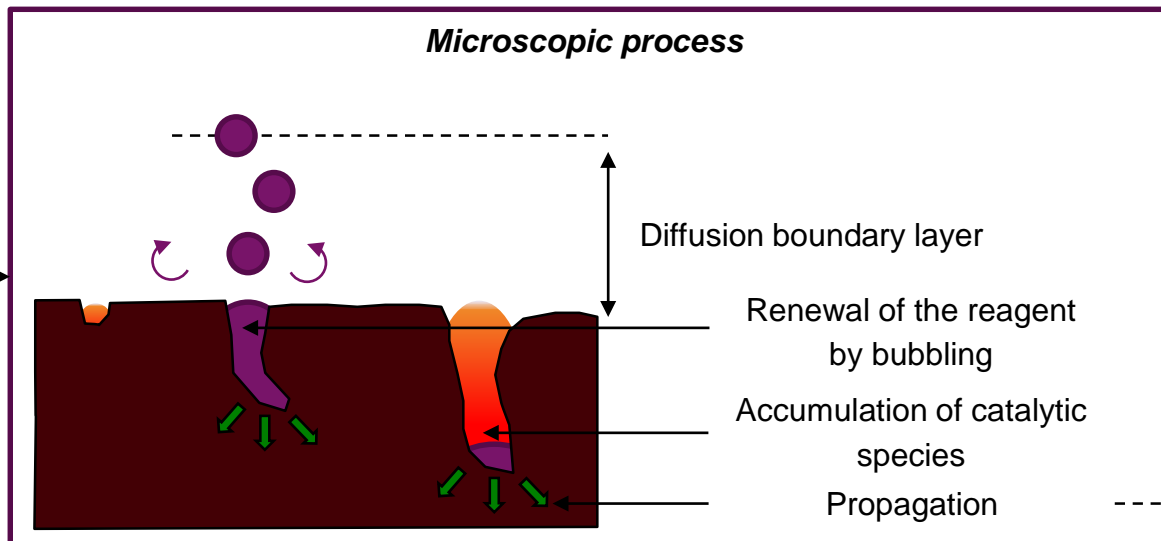
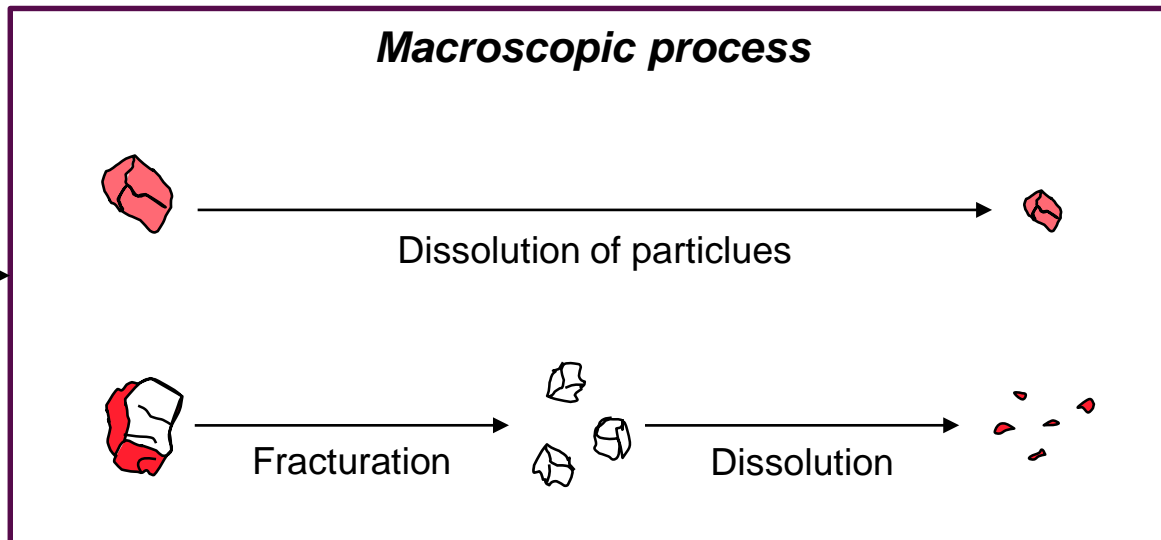


- *More than half the processe time spent to recuperate less than 20 % of the residual mass... pffff...*

PART III – A MORE COMPLICATED EXAMLPE

BUT SOME PROCESSES ARE MUCH MORE COMPLEX !

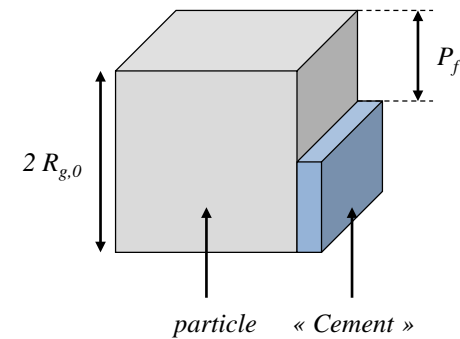
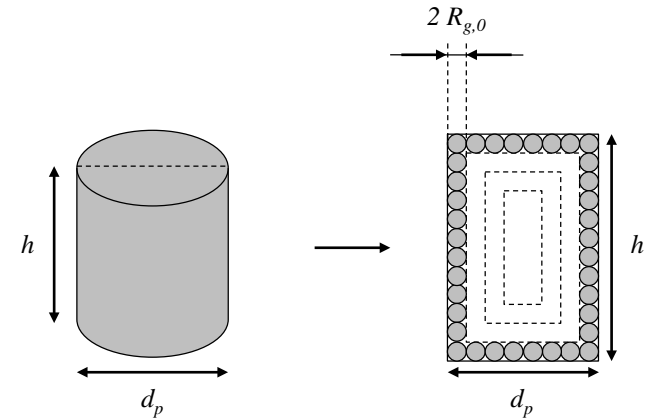
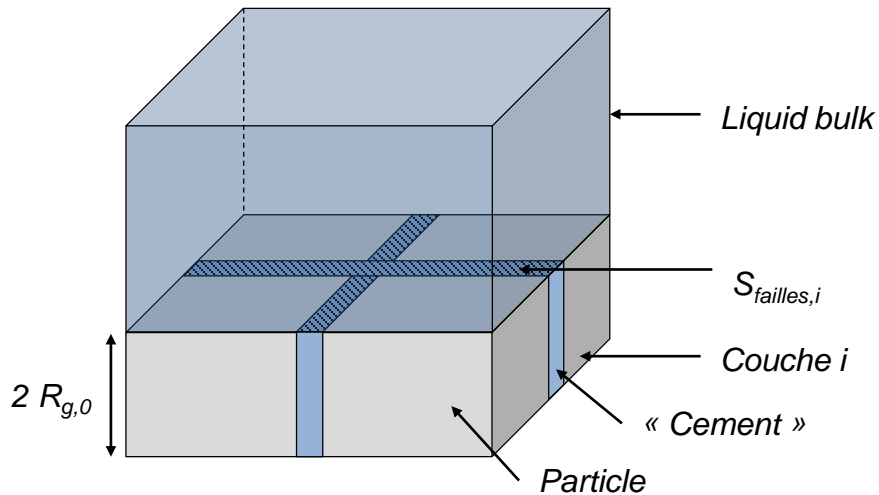
Crumbling of a chunk of material



Bulk solid is a aggregate of individuel particles:

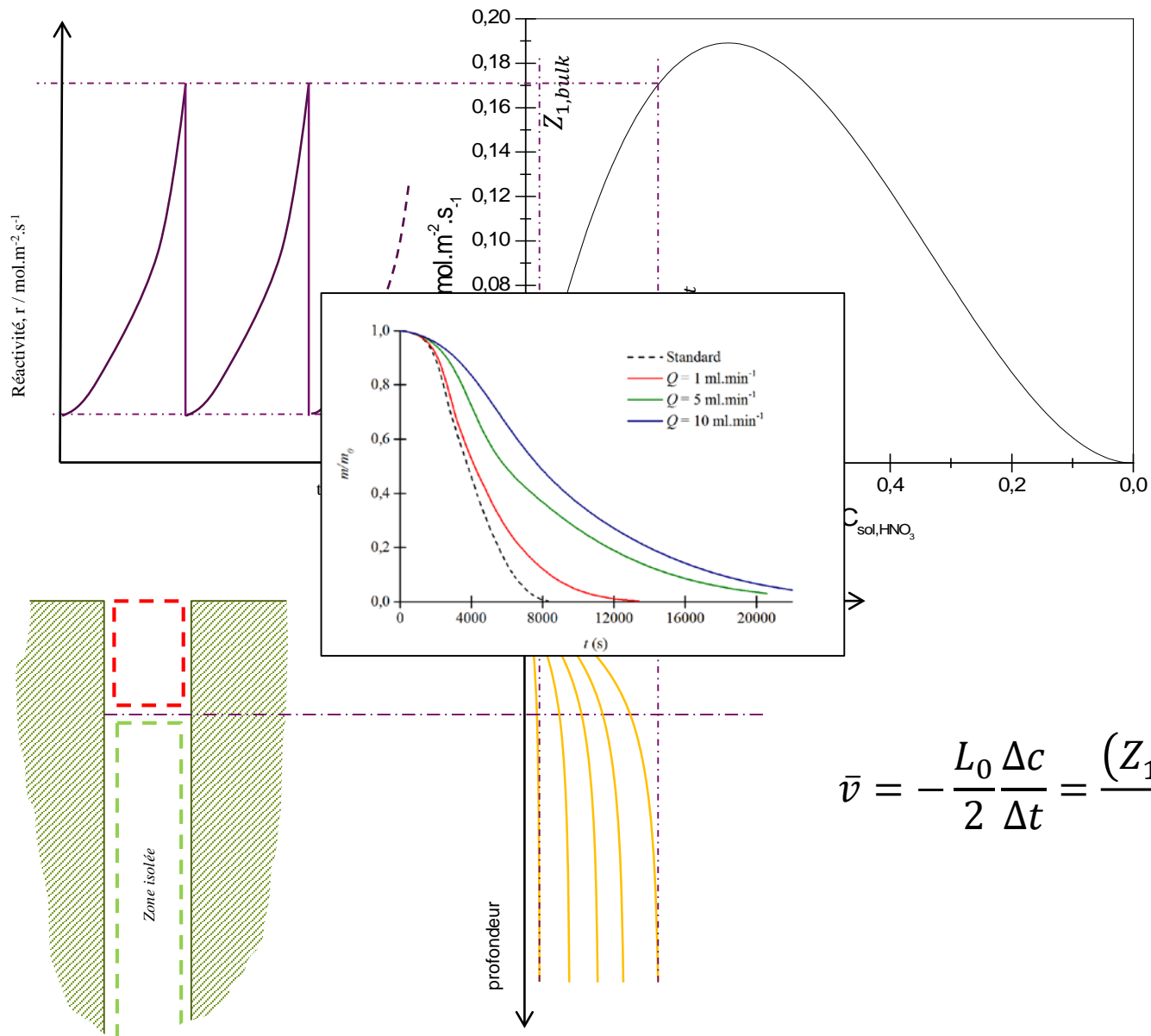
Modeling the crumbling:

- Particules held together by a dissolving « cement »
- Liberation of the particles as the cement dissolves



$$p_f(t + \Delta t) = p_f(t) + v_{UO_2} \frac{M_{UO_2}}{\rho_{UO_2}} \bar{v} \Delta t$$

DISSOLUTION IS AN OSCILATING REACTION



$$\bar{v} = -\frac{L_0 \Delta c}{2 \Delta t} = \frac{(Z_{1,bulk} - Z_{1,crit}^{III})}{\int_{Z_{1,crit}^{III}}^{Z_{1,bulk}} \frac{dZ}{r(Z)}}$$

- We want fast processes with high chemical reaction kinetics *to the limit of* diffusion control

$$-r \times S_{reaction} = k_D (c_{bulk} - c_{surface}) \times S_{geo}$$



$$c_{reagent,surface} \approx 0$$

$$c_{product,surface} \gg c_{product,bulk}$$

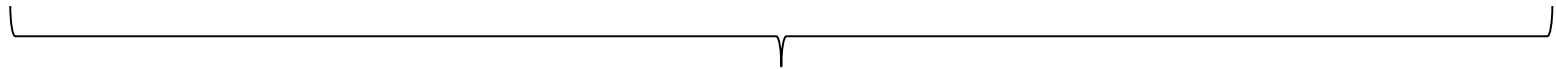


- Low acidity, low complexant concentrations



- High product concentrations
- Including undesirable elements

- + We want high solid/liquid ratio for high throughput and small facilities cost



- The best recipe for forming undesirable products leading to fouling and reagent consumption !!!



Or neo-formed products

Again : the problems induced by accumulation at every scale will generally be a good indicator of the feasibility and economical viability of a dissolution process

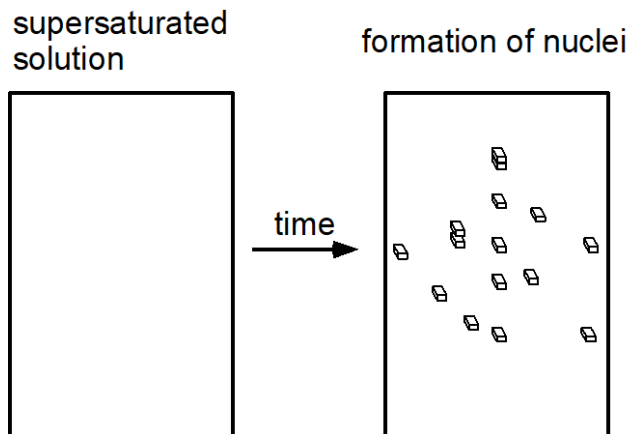
PART IV – BACK TO ACCUMULATION

Nucleation



Formation of nuclei

Transformation from liquid phase to solid does not start at the instant the process becomes possible. It needs at least one nucleus to be formed.



Nucleation = **kinetic** process with **chemical** driving force

Nucleation

primary

secondary

Not influenced by presence of same solid phase

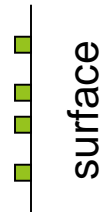
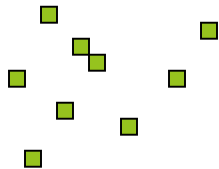
Influenced by presence of same solid phase

homogeneous

heterogeneous

No influence of foreign phase

Catalysed by presence of foreign phase



foreign particle

THE DRIVING FORCE FOR NUCLEATION

supersaturation

$$\Delta\mu = -R T \ln \left(\frac{c_+^{v+} \cdot c_-^{v-} \cdot \gamma_{\pm,c}^v}{c_{+,eq}^{v+} \cdot c_{-,eq}^{v-} \cdot \gamma_{\pm,eq}^v} \right) = -R T \ln S_c \cdot \gamma_c$$

$$S_c = \left(\frac{c_+^{v+} \cdot c_-^{v-}}{c_{+,eq}^{v+} \cdot c_{-,eq}^{v-}} \right)^{\frac{1}{v}}$$

S_c is molar concentration supersaturation ratio



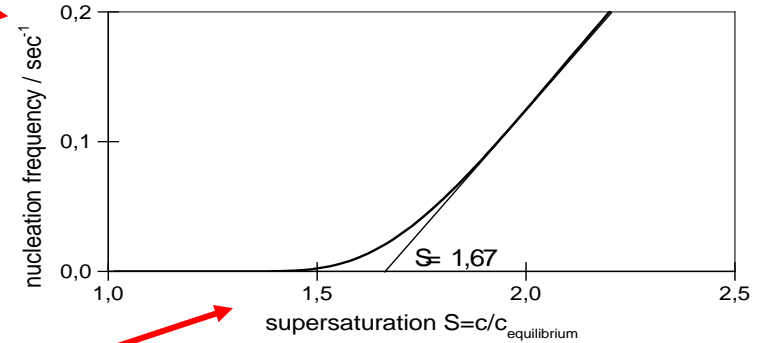
In some case for example, $S_c = [Mo]/[Mo]_{eq}$

Nucleation frequency = 1/induction period

$$R_N = A_N \exp\left(-\frac{B_N}{(\ln S)^2}\right)$$

$$B_N = \frac{16\pi\Omega^2\gamma^3}{3(kT)^3}$$

is characteristic of the **solid**,
mainly, **interfacial** energy

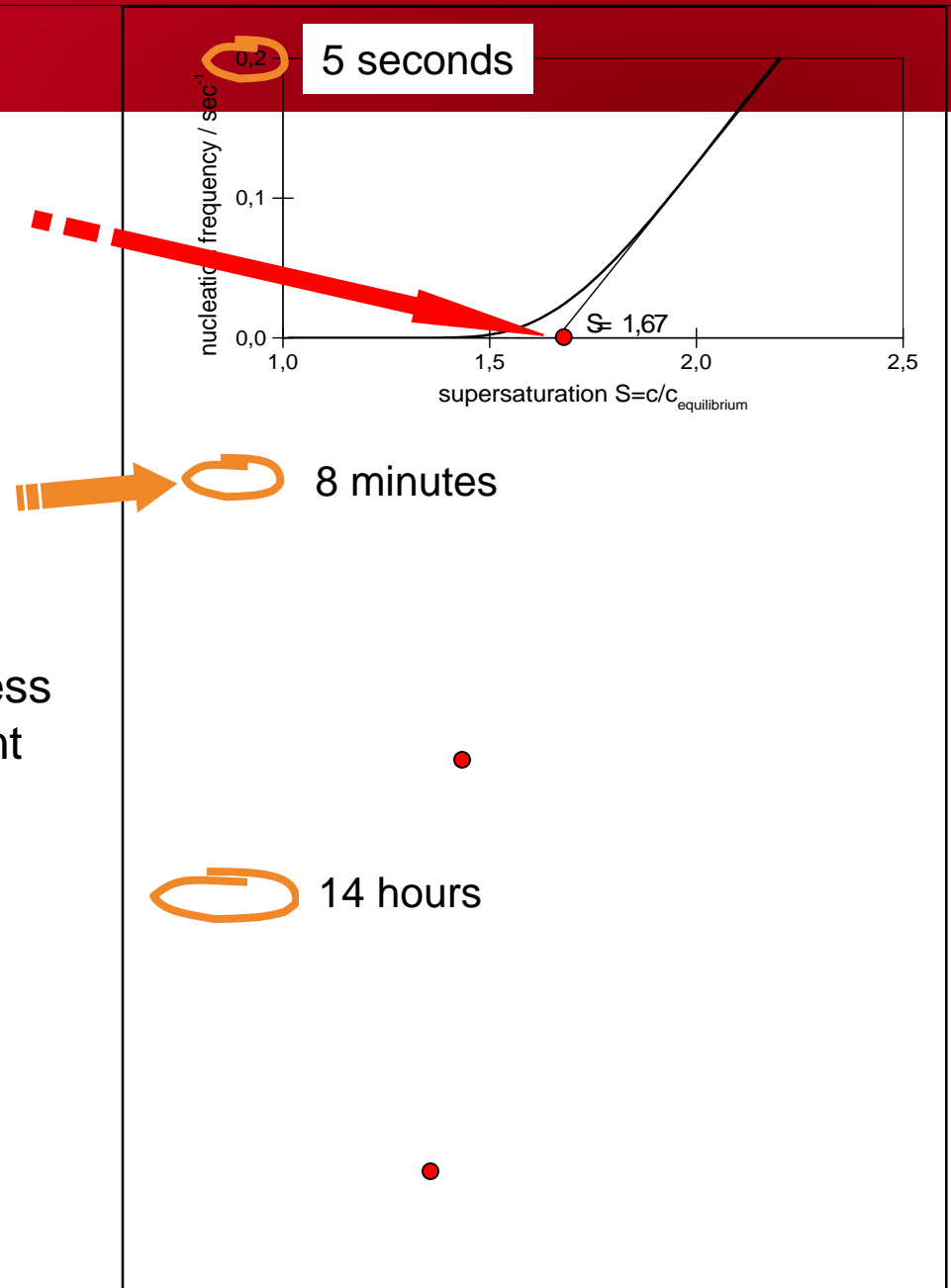


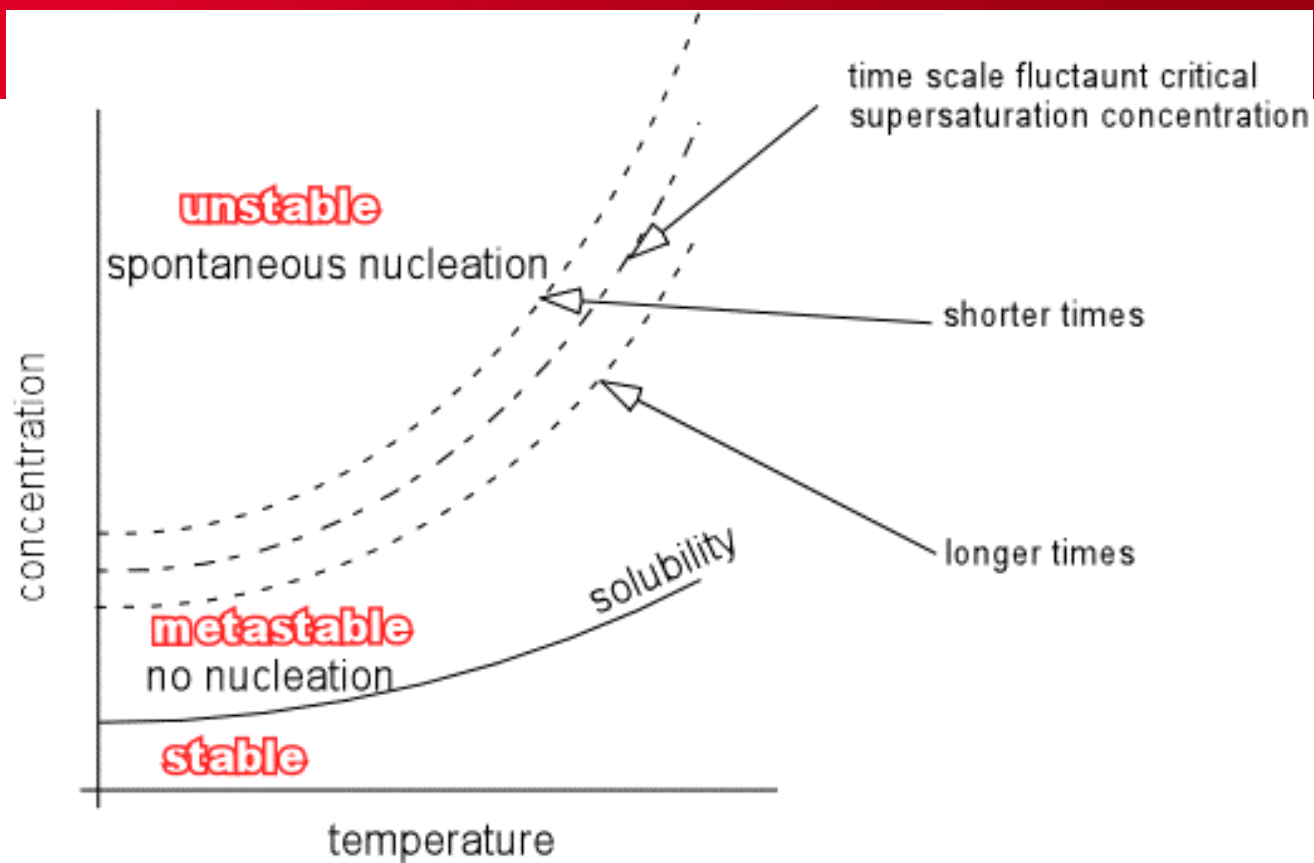
critical supersaturation

is dependant on the

observation time scale

In the case of the dissolver, a slow process induces higher neo-formed solid content





critical supersaturation
concentration defines a time dependant frontier

but

above solubility, crystal growth persists :
only a clean dissolver will not foul

SO WHAT CAN PRECIPITATE ?

Exemple of a nitric acid media

Plethora of cations



Na, Fe, Cs, K, Ba, Sr, Zr, Ce etc...

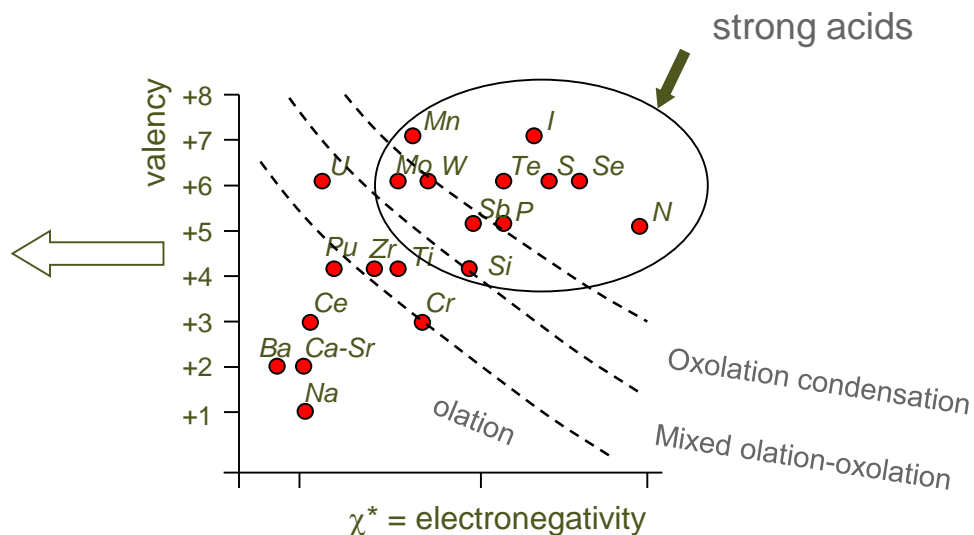
Few neutral or anionic candidates
other than NO_3^-



Sufficiently acid species = species without hydroxo ligand

Rule of the thumb

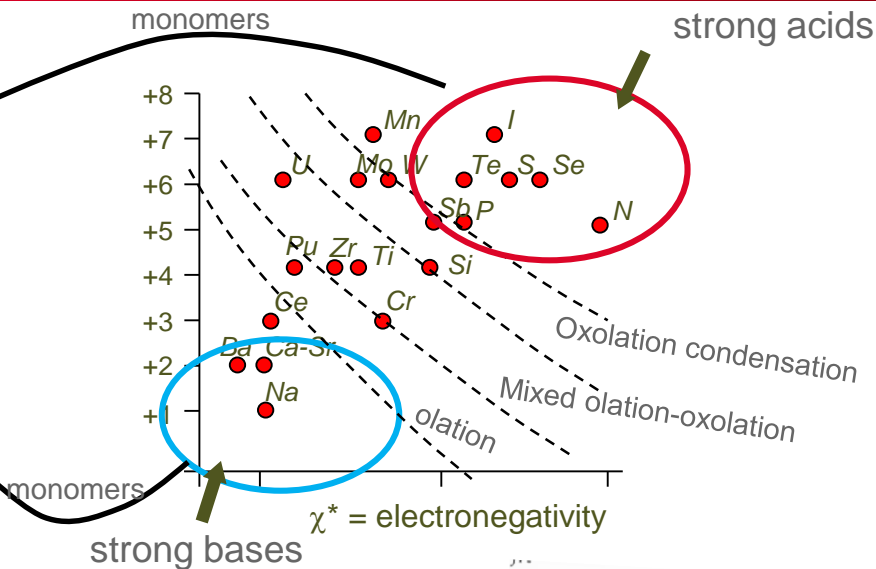
Few candidates for making
neutral species... so usually
always the same ones
But very complex chemistries...



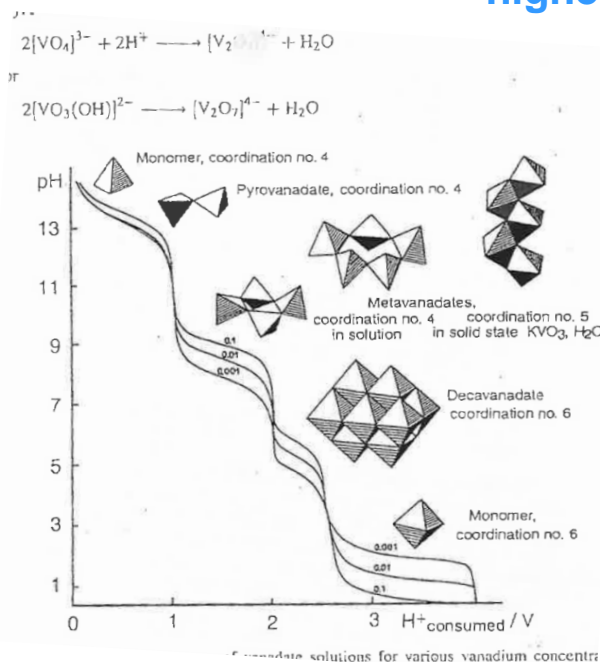
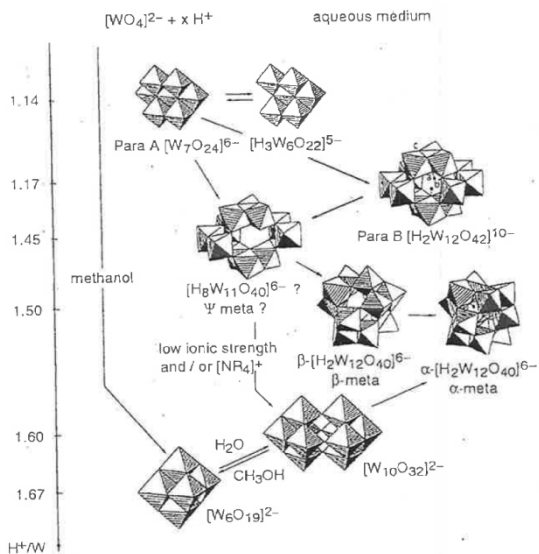
N, P, W, Si, Mo, V but also Te, Sb, Se, etc..

RULE OF THE THUMB CHEMISTRY

Rapid and « simple »
précipitation as salts; $(Ba,Sr)(NO_3)_2$
 $Al(NO_3)_3$ or $Ca(SO_4)$



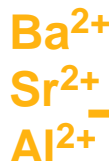
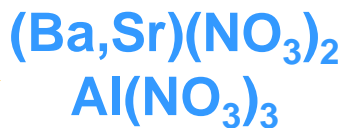
Slow condensation in
mild acidities –
decondensation in
higher acidities



LES ESPÈCES D'INTÉRÊT



Précipitation rapide



Comportement « prévisible » ?
Ks + activités



Composés phosphatés



Oxolations lentes +
changements
de coordination

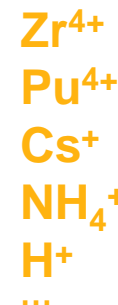
Polyanions : 2 à 36

Hétéropoly molybdates,
Dont structure de Keggin :
 $(\text{P(V)}, \text{Zr(IV)})\text{Mo}_{12}\text{O}_{40}^{n-}$

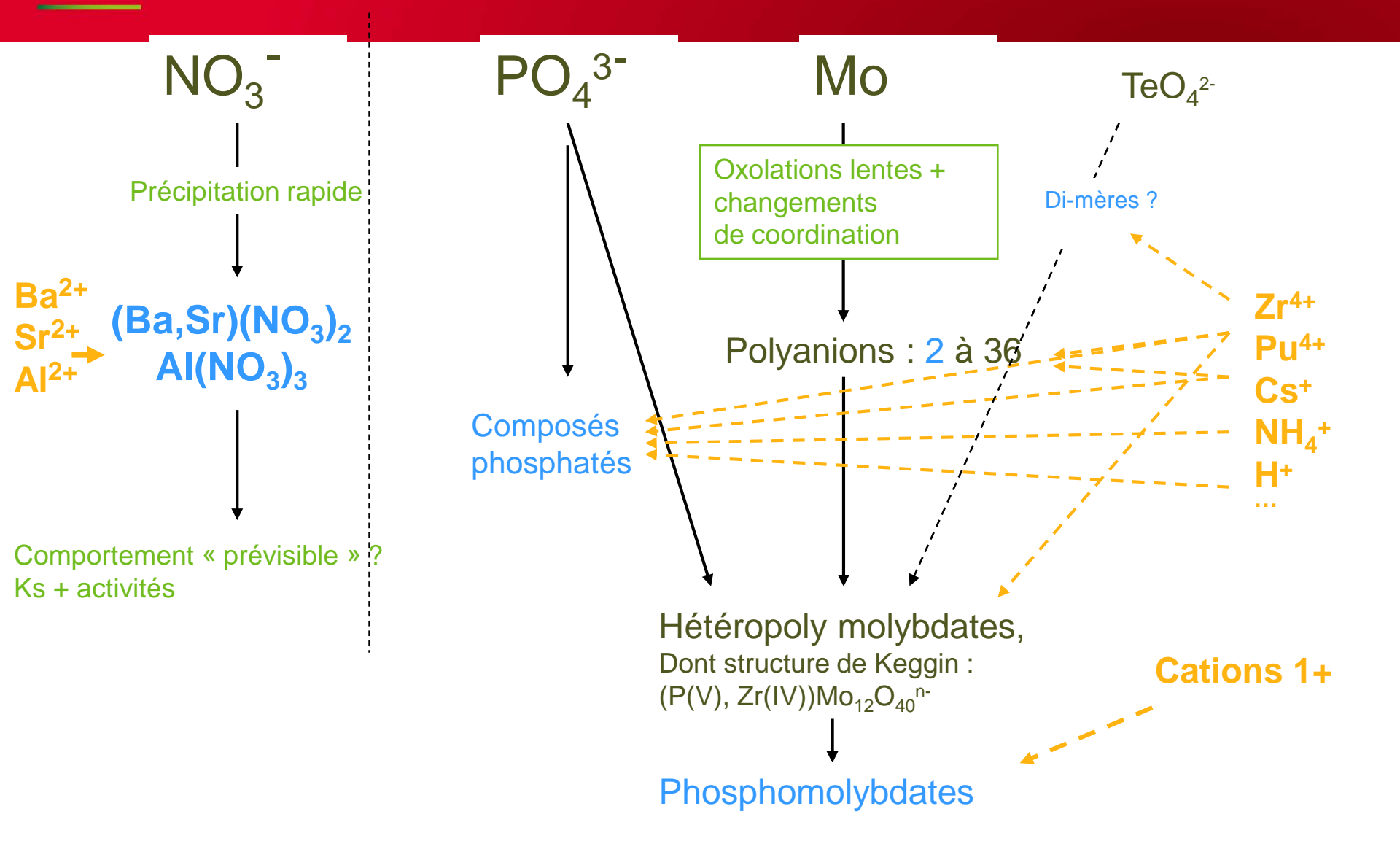
Phosphomolybdates



Di-mères ?



Cations 1+



Thank you !