HAL
open science

Dissolution viewed as a process

A. Magnaldo

To cite this version:

A. Magnaldo. Dissolution viewed as a process. Hydrometallurgy course, Mar 2016, Trondheim, Norway. cea-02442327

HAL Id: cea-02442327

https://cea.hal.science/cea-02442327v1

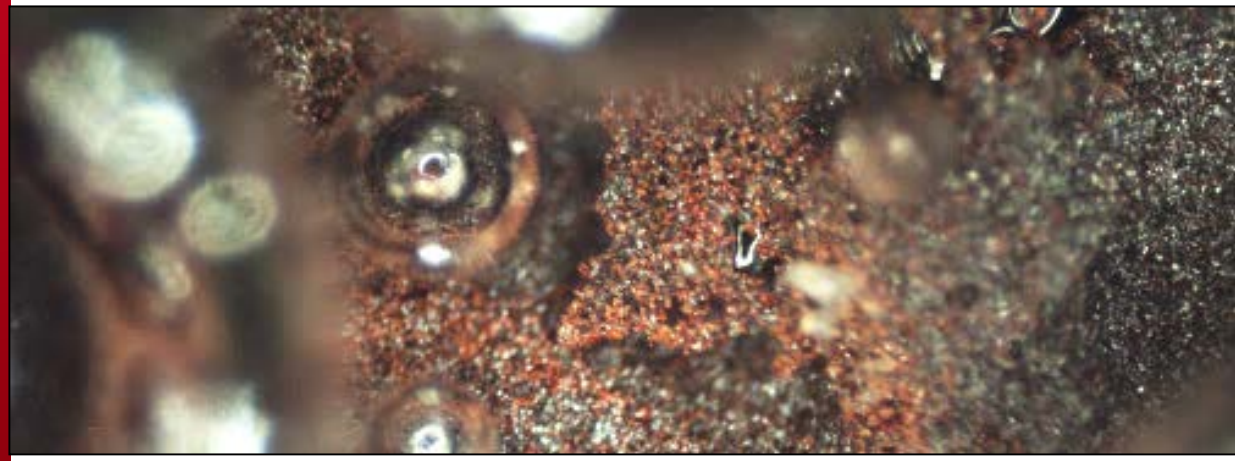
Submitted on 18 Mar 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

DE LA RECHERCHE À L'INDUSTRIE

DISSOLUTION VIEWED AS A PROCESS



Speaker: Alastair MAGNALDO

ENVIREE MEETING – 22ND OCTOBER 2015

www.cea.fr

DISCLAIMER !

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

GLOBAL DISSOLUTION PHENOMENA

The global chemistry

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

Accumulation

- Reaction products accumulate
- Reaction consumes reagents

Induce Secondary Reactions;

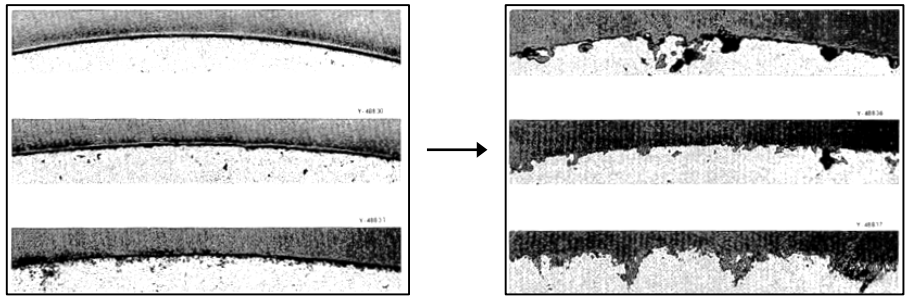
- Catalysis
- (Re)-Precipitation…
- Gas nucleation

= a variable set of reactions

1

The solid

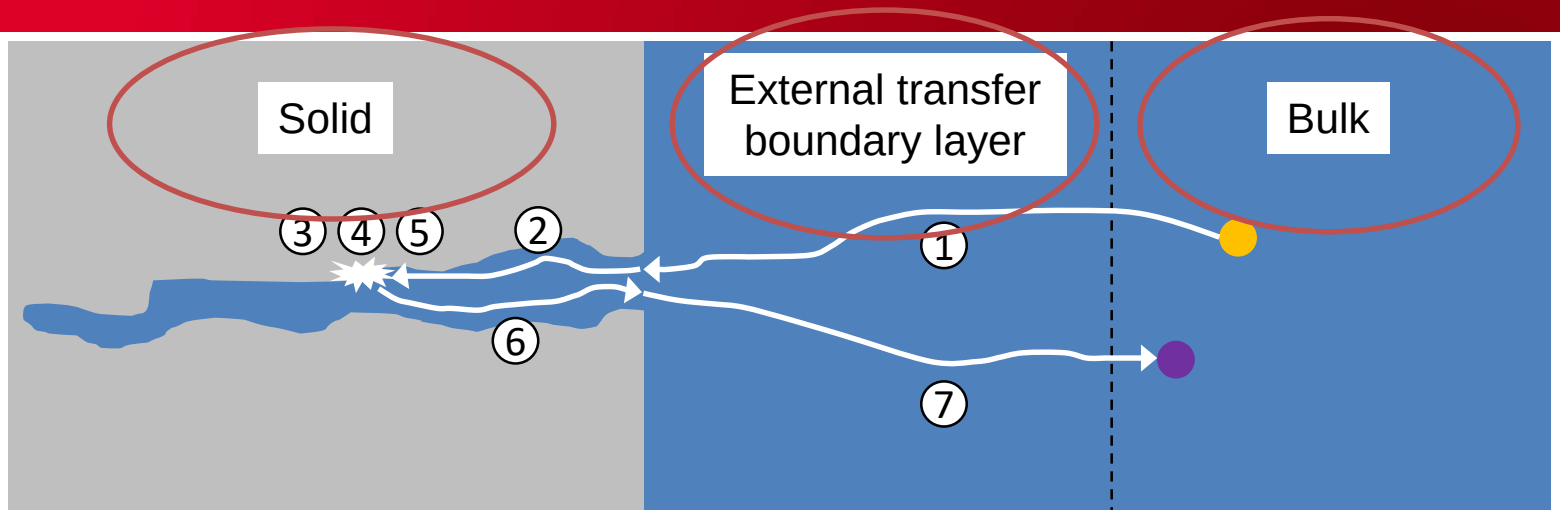
- The reactive solid is hard to d
- In permanent fast evolution



Transport

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

SOLID-LIQUID REACTION MECHANISMS



- Introduced the effects of accumulation complicates this picture:

  ① : external transport of reagents through the boundary layer
  ② : diffusion of reagents in the pores
  ③ : eventual adsorption of reagents on the solid
  ④ : chemical reaction
  ⑤ : eventual desorption of products
  ⑥ : diffusion of products in the pores
  ⑦ : external transport of reagents through the boundary layer

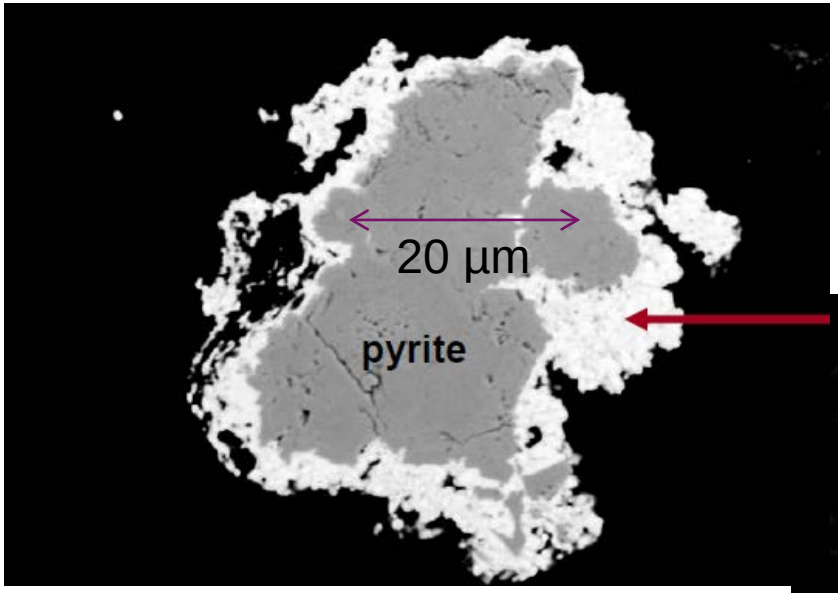
- Accumulation is present

  ❶ : at the scale of the pores and cracks,
  ❷ : at the scale of the external boundary layer,
  ❸ : at the scale of the bulk liquid

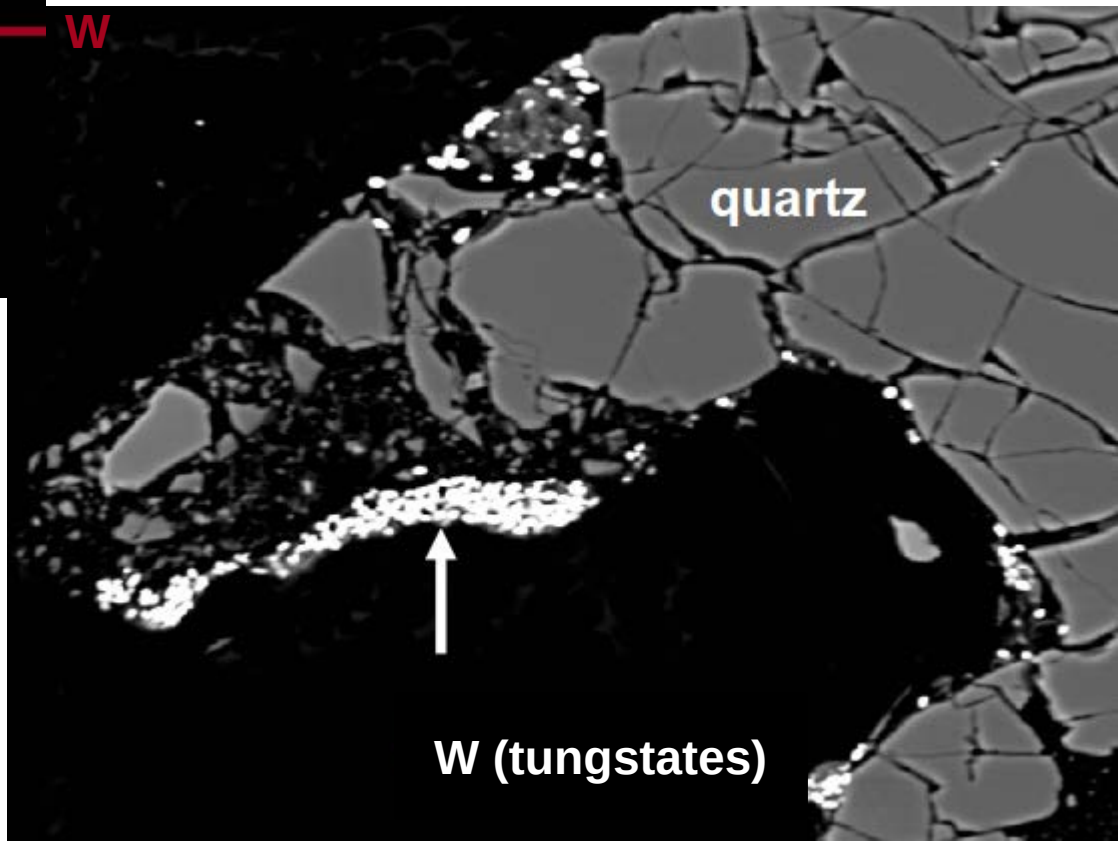
- Mainly Two kinds of controlling phenomena:

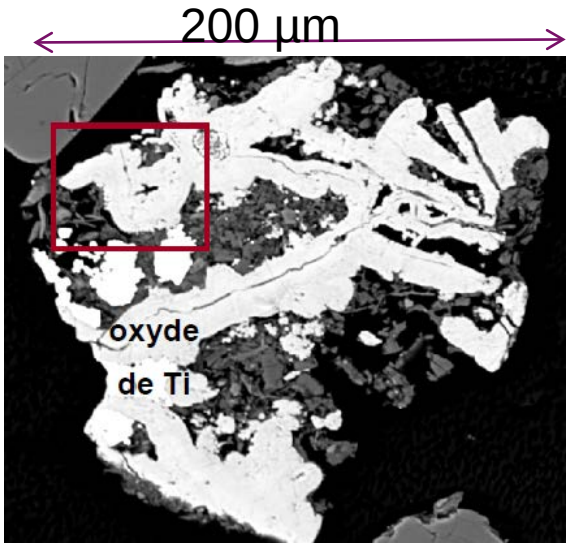
  - Chemical reaction controlled dissolution
  - Diffusion controlled dissolution

REAL SAMPLES



W





EXAMPLE

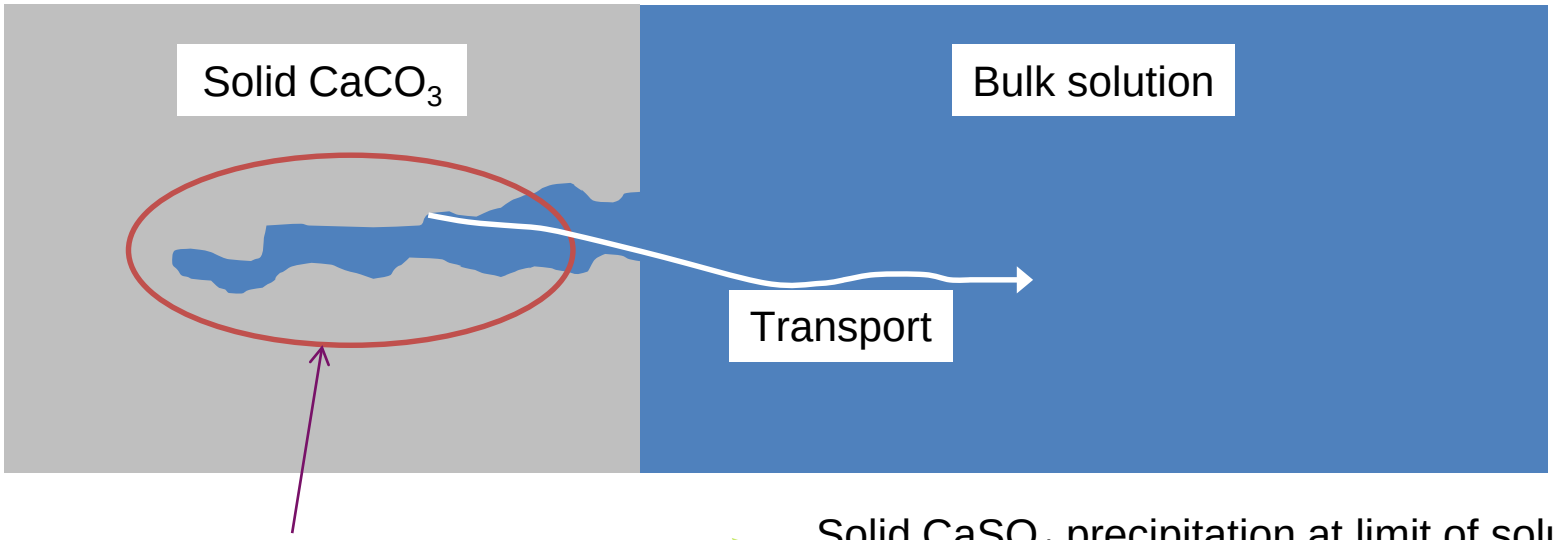
Global reaction

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$

Solid

Soluble complex

Dissolved gas



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

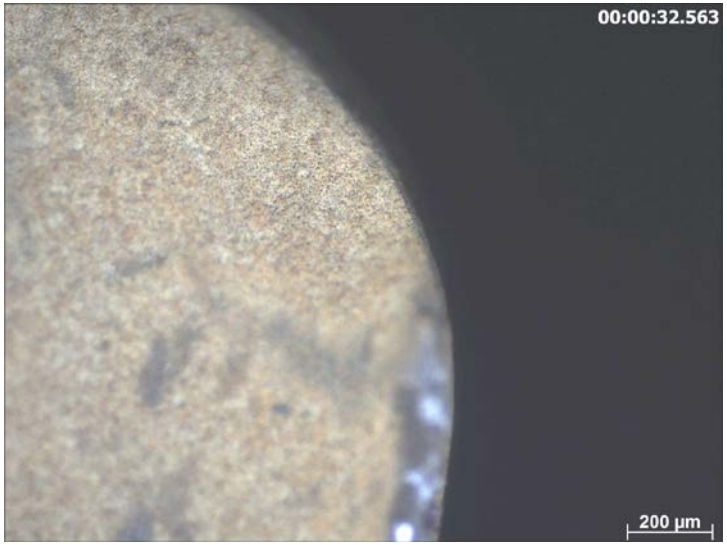
Solid $CaSO_4$ precipitation at limit of solubility

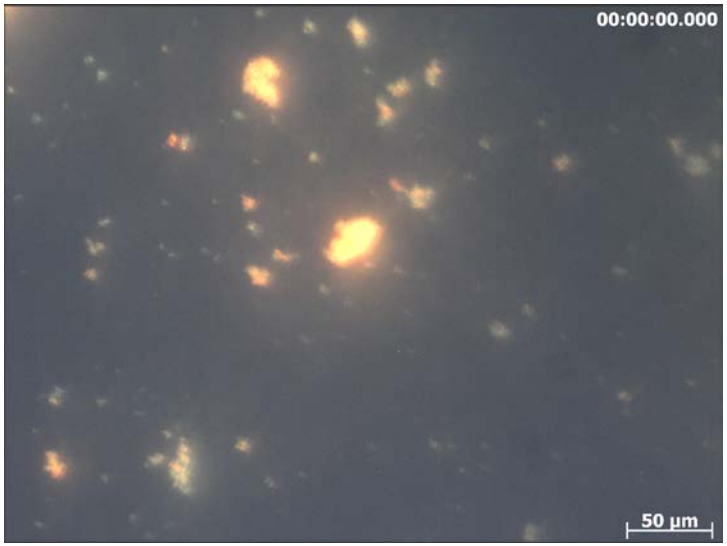
CO_2 gas nucleation

$CaSO_4$ -> very insoluble $Ca(OH)_2$

EXAMPLE OF THE EFFECT OF TRANSPORT ON ACCUMULATION

- 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





LETS FINISH FOR A MOMENT WITH 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)

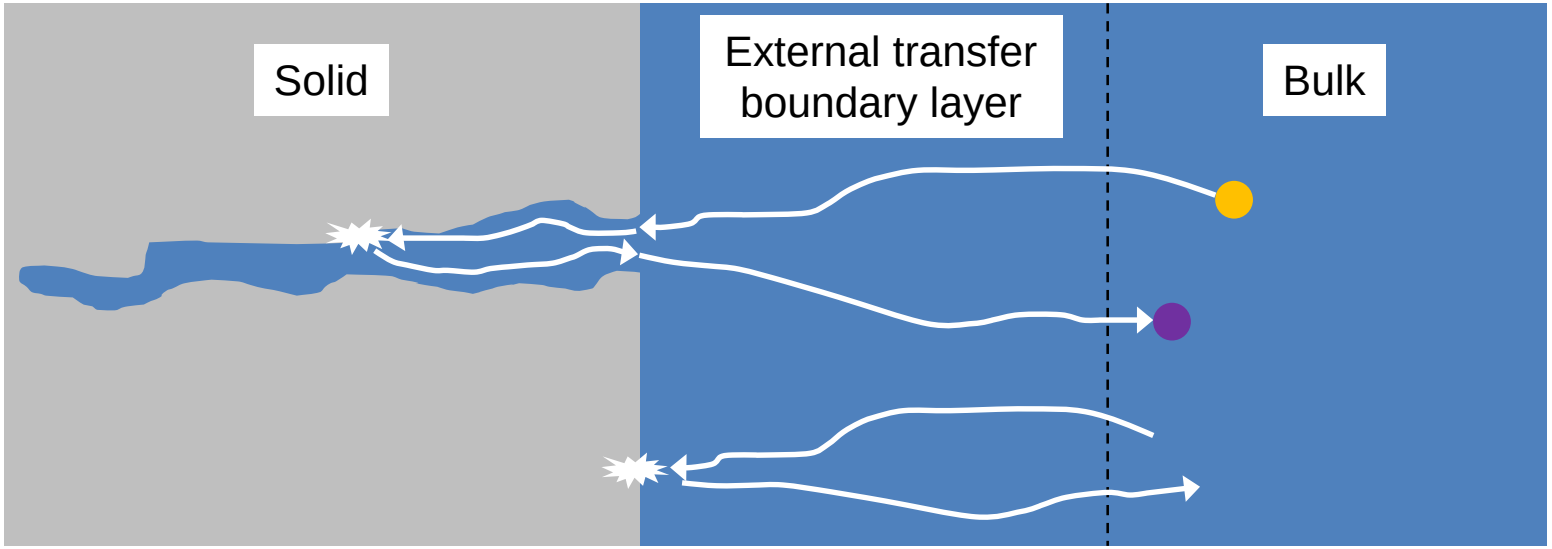
↓

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 feasability and economical viability of a dissolution process

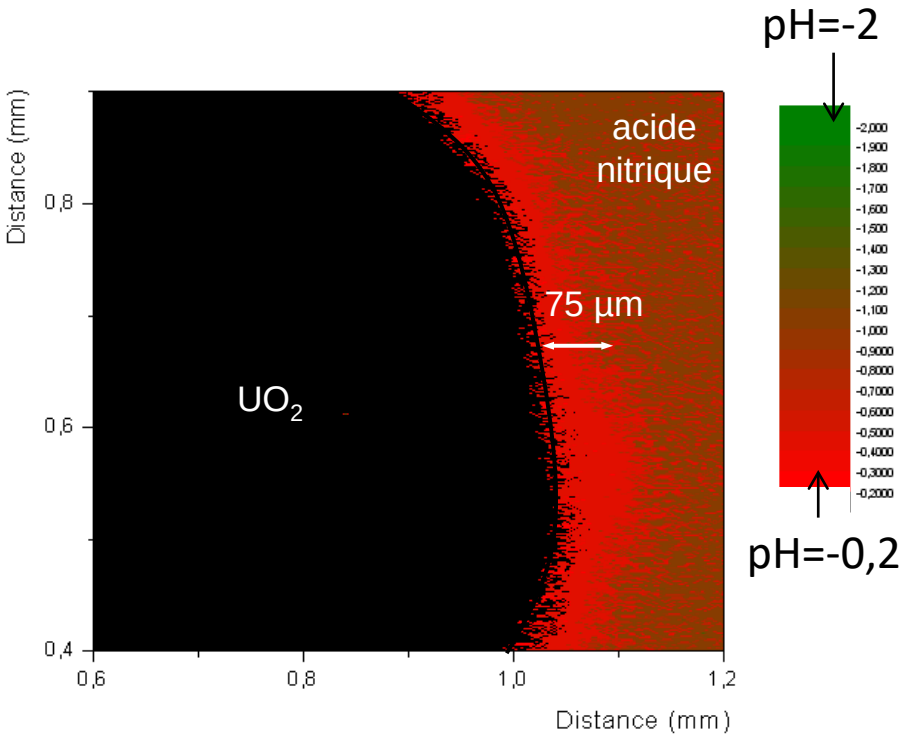
SO WHO CONTROLS THE GLOBAL REACTION ?



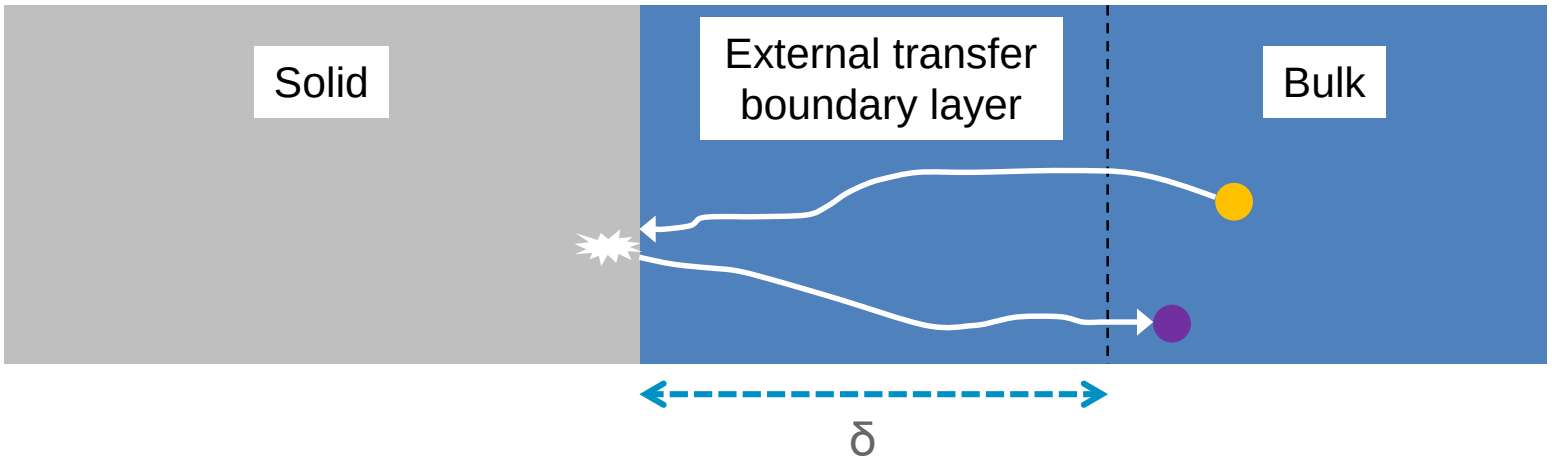
With chaining mechanisms, the slowest controls the global rate

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 mol.s^{-1}.m^{-2}
k_D is the matter transfer conductance in m.s^{-1}

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

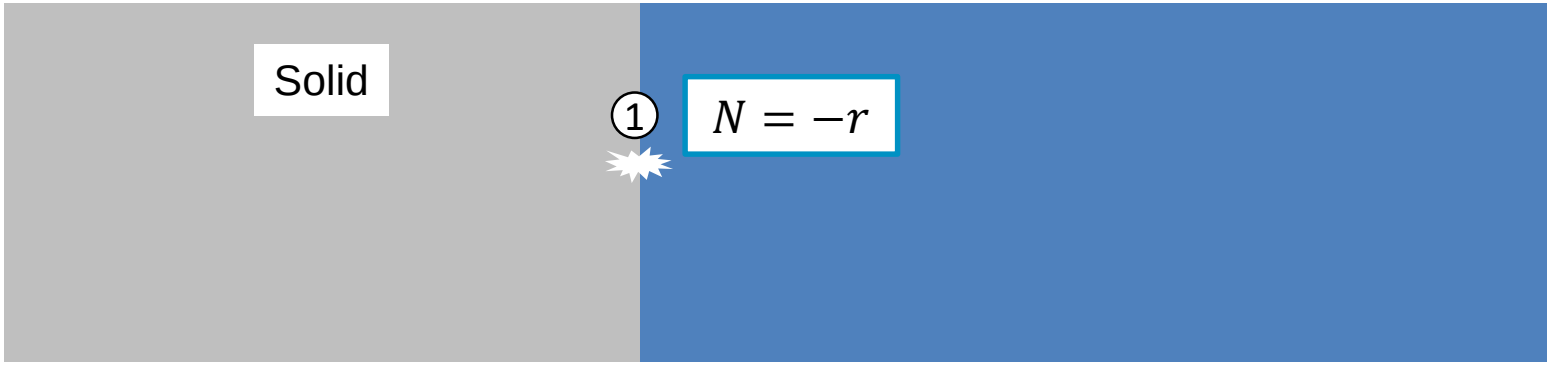
③ Obviously, hydrodynamics determine the boundary layer thickness. Many correlations (unproven - experimentally determined) give the Sherwood number, for example :
$Sh = \frac{k_D \emptyset_{particule}}{D} = 2 + 1.8 \times Re^{1/2} Sc^{1/3}$(Ranz-Levenspiel for small particules)
δ ranges from 10 to 100's 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 particules is not diffusion controlled, meaning that
- the end part of complete dissolution is always chemically controlled

PART II – A FOCUS ON « REACTION »

THE SURFACE REACTION IN BRIEF



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

$$N_{reaction} = -r(\mathrm{T}°, c_{surface}, \ldots)$$

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

See the following example with accumulation and catalysis:

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

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

A COMPLICATED CASE MADE SIMPLE

- Autocatalysis consists of 2 parallel reactions – initiation – catalysis

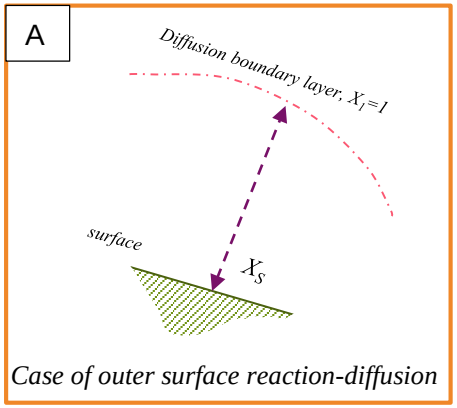
$$\nu_R\, R \rightarrow \nu_P\, P + \nu_Z\, \boldsymbol{Z}$$

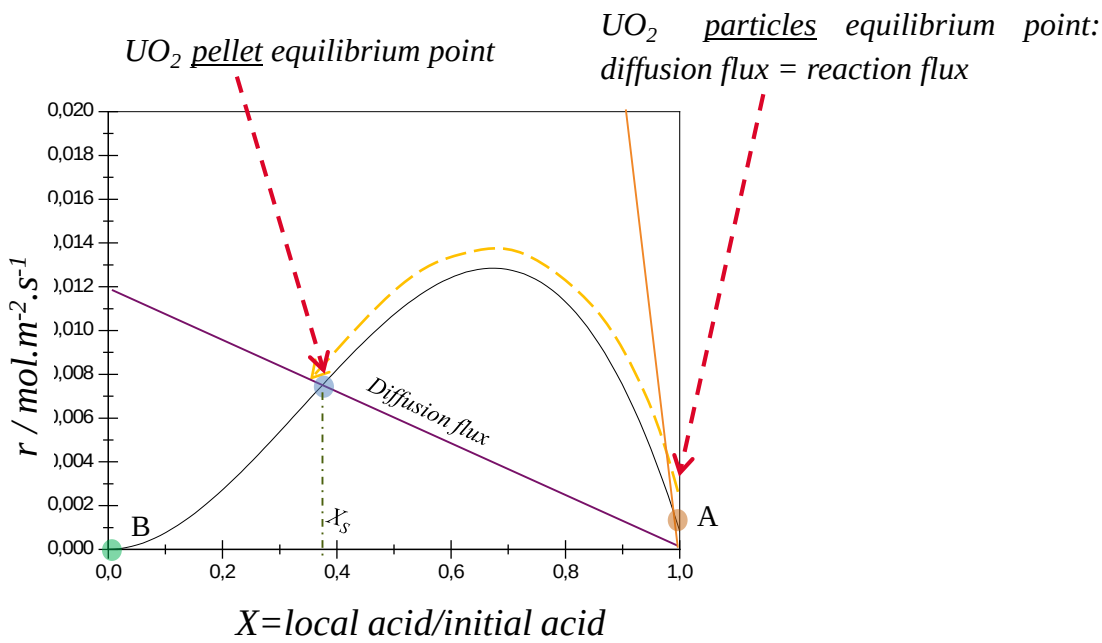
$$\nu_R\, R + \nu'_Z\, \boldsymbol{Z} \rightarrow \nu_P\, P + (\nu_Z + \nu'_Z)\, \boldsymbol{Z}$$

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

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

Case A:





YOU DIDN'T GET AWAY WITH IT !!!

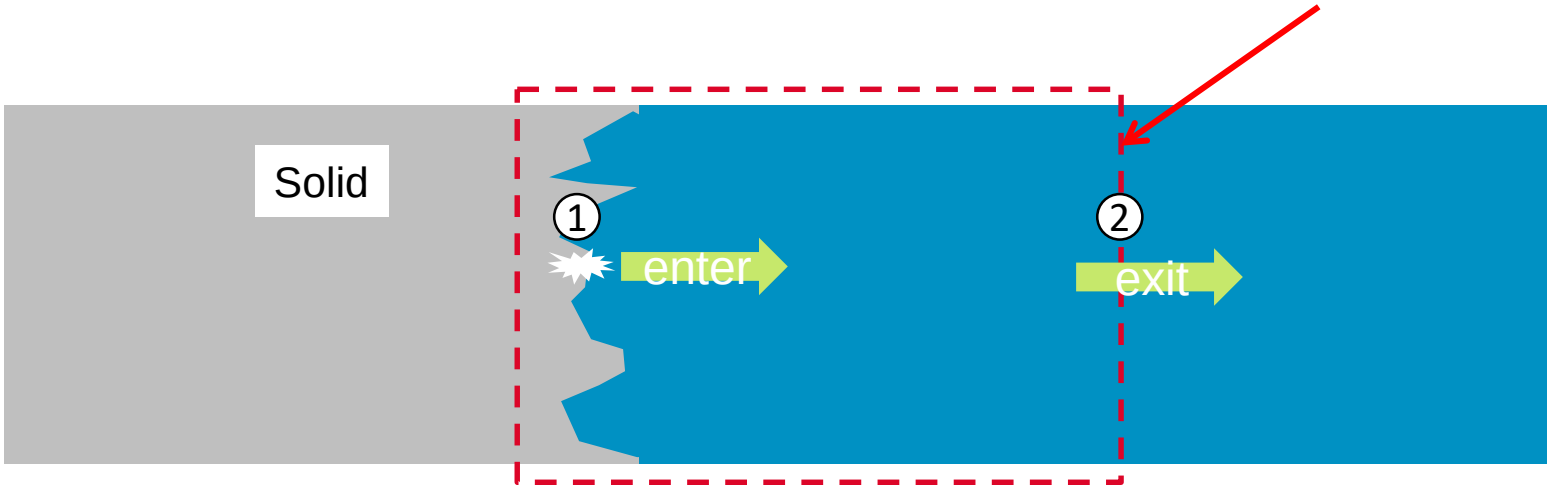
① $N_{reaction} = -r$ is the reaction flux **density** of matter in mol.s^{-1}.m^{-2}

$n_{reaction} = N_{reaction} \times S_{reaction}$ is the reaction flux

$S_{reaction}$ is the reactive surface

② $n_{diff} = N_{diff} \times S_{any\ surface\ as\ long\ as\ a\ vectoriel\ product\ is\ considered}$

$and\ can\ be\ for\ ex.a\ "geometrical\ enveloppe"\ of\ the\ surface$

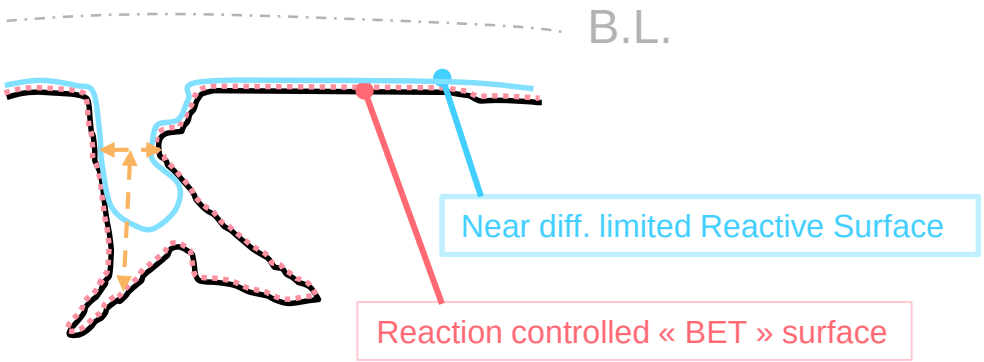


$-r \times S_{reaction} = k_D\left(c_{bulk} - c_{surface}\right) \times S_{geo}$ is the real relation

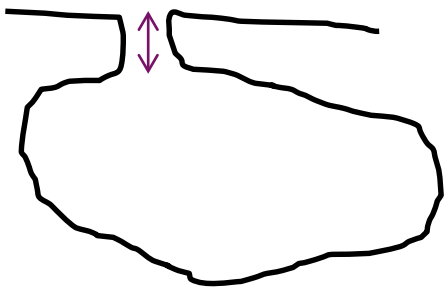
WHAT IS THE REACTIVE DISSOLUTION SURFACE $S_{reaction}$?

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

slow reaction kinetics = more surface involved

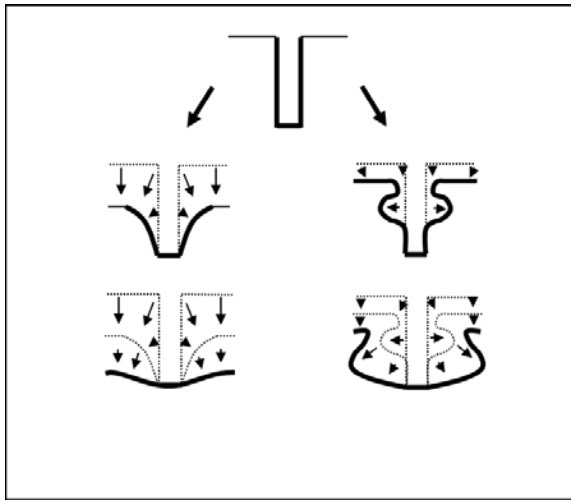


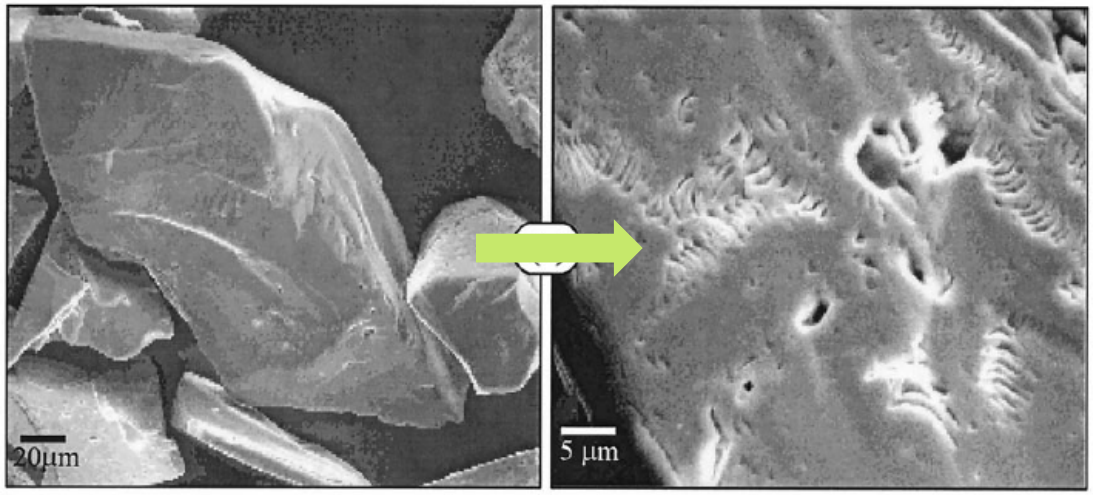
- Bottleneck effects



- Strong time variability

Gauthier et al.

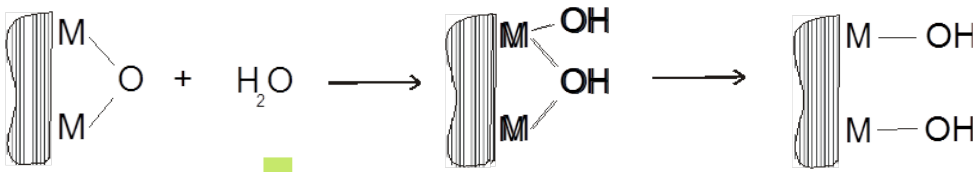




WHAT IS THE REACTIVE DISSOLUTION SURFACE $S_{reaction}$?

- 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 oxyde and multisite surface complexation and charge distribution model, maybe wrong but who cares… the principle is OK



Hydroxylation

$$\equiv M\text{-}OH_2^+ \leftrightarrow \equiv M\text{-}OH + H^+$$

$$\equiv M\text{-}OH \leftrightarrow \equiv M\text{-}O^- + H^+$$

Protonation – deprotonation of surface sites

$Ce_1\text{-}O^{-3/2} + H^+$	<=>	$Ce_1\text{-}OH^{-1/2}$	pK=23
$Ce_1\text{-}OH^{-1/2} + H^+$	<=>	**$Ce_1\text{-}OH_2^{+1/2}$**	pK=9.2
$Ce_2\text{-}O^- + H^+$	<=>	$Ce_2\text{-}OH^0$	pK=14
$Ce_2\text{-}OH^0$ $+ H^+$	<=>	**$Ce_2\text{-}OH_2^+$**	pK=0
$Ce_3\text{-}O^{-1/2} + H^+$	<=>	**$Ce_3\text{-}OH^{+1/2}$**	pK=4.2
$Ce_3\text{-}OH^{+1/2} + H^+$	<=>	$Ce_3\text{-}OH_2^{+3/2}$	pK=-9.8

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

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

Disclaimer: spherical particules, 1 reagent etc..

$$\begin{cases} \dfrac{dR}{dt} = -k_0 \cdot r \\ \dfrac{dC_{sol}}{dt} = \dfrac{4\pi}{V} \cdot k_D \cdot R^2 \cdot (C_{surf} - C_{sol}) \\ k_D \cdot \left(C_{Sol} - C_{Surf}\right) = \gamma \cdot r \end{cases}$$

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…

$$\frac{dm}{dt} = -r \times S_{reaction} \xrightarrow{\text{yields}} \frac{dR}{dt} = -r \times \frac{S_{reaction}}{S_{geo}} = \mathrm{v}$$

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 !

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

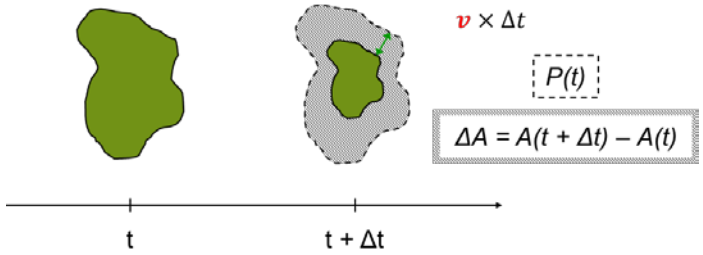
Needs a fractal description !

Allows fractal description

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

FRACTAL DESCRIPTION

- *A and P the projected surface and perimeter*



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

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

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

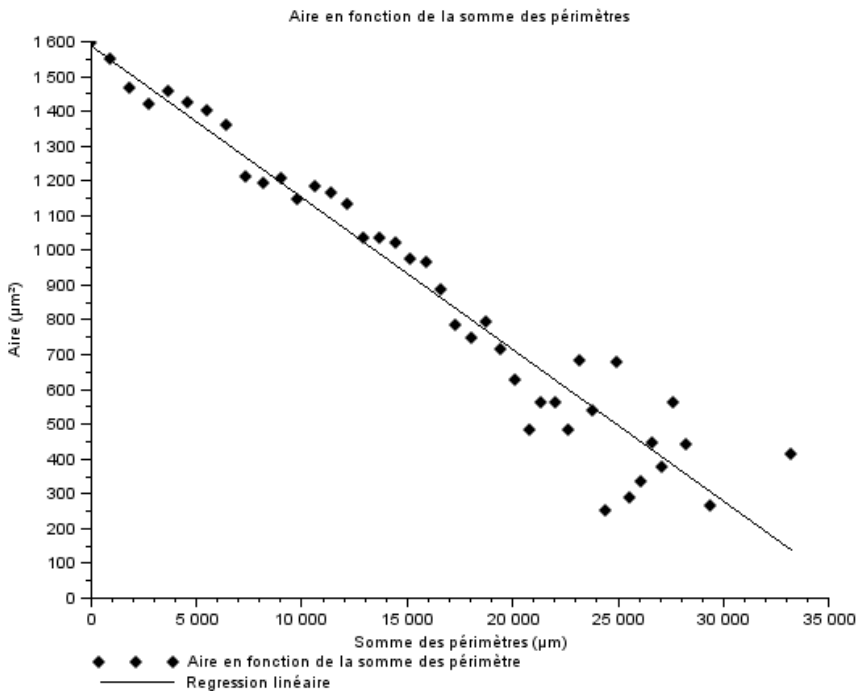
$$\frac{dR}{dt} = -k' \times R^{D_r - 2}$$

D_r fractal dimension of reactive surface

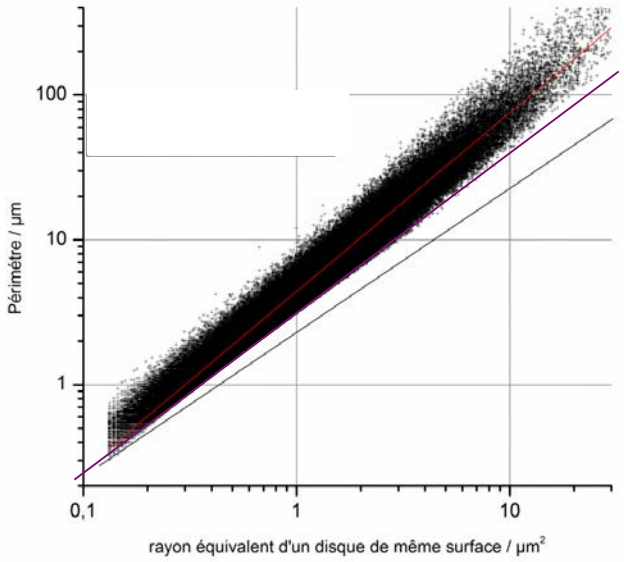
$$v = -\beta r^{D_r - D_{surface}}$$

FRACTAL DESCRIPTION

- *We have v…*



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



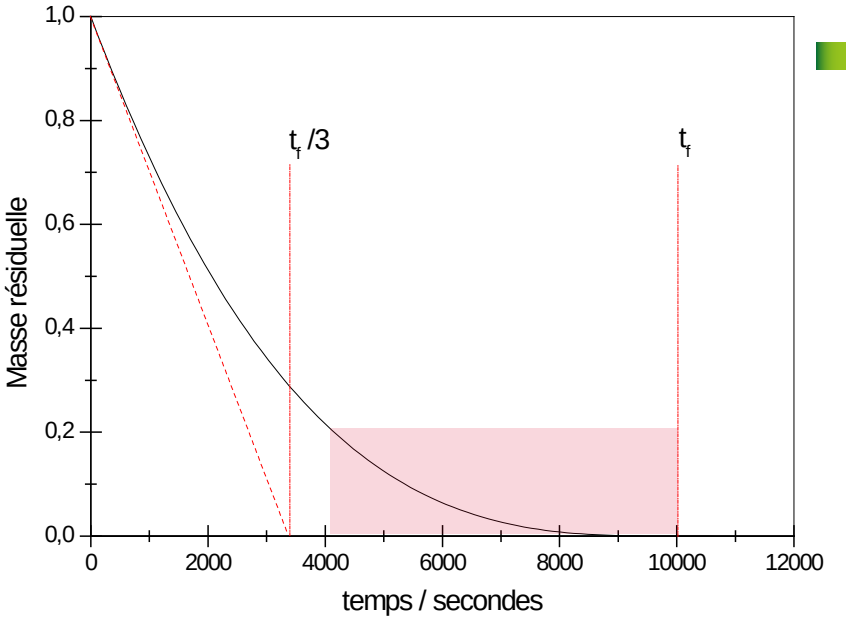
$we\ extract\ D_R \ldots$ hopefully

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

QUICK BREAK SUMMARY

- Diffusion or reaction limited kinetics
- Small particules are always chemicaly 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

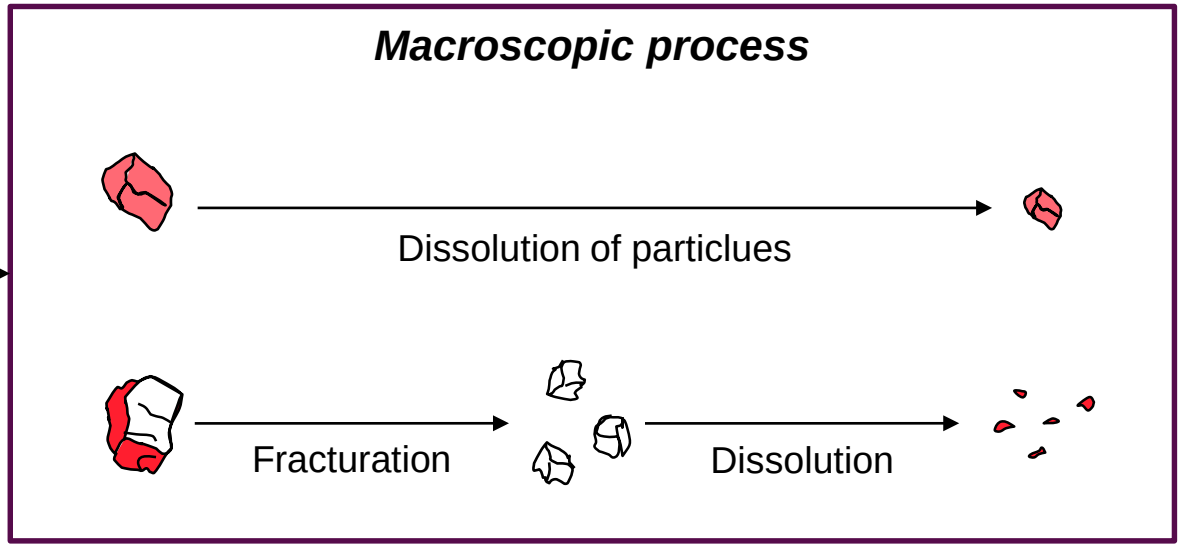


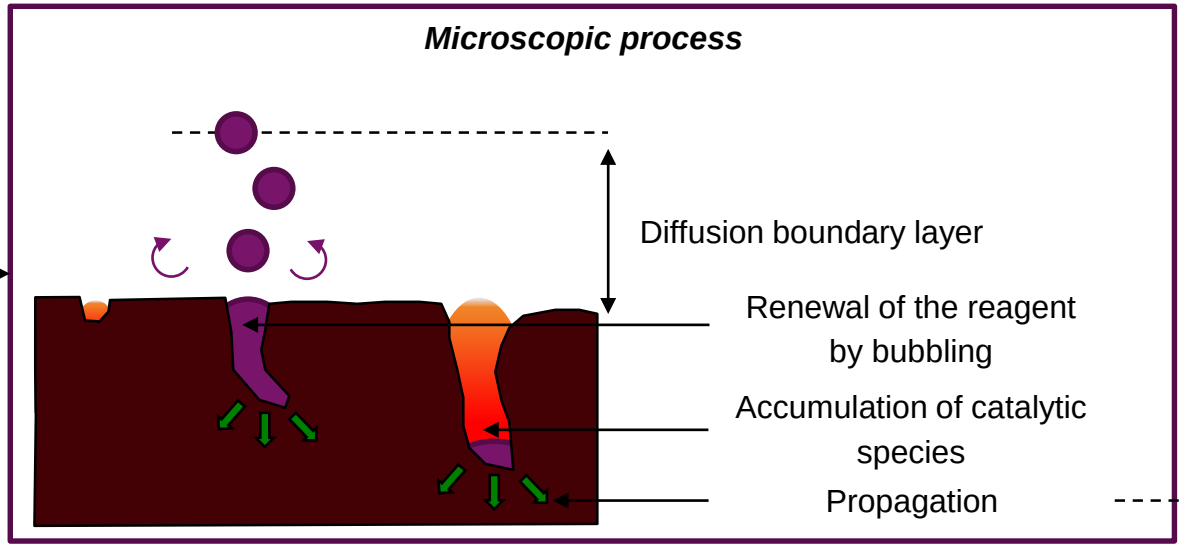
- *More than half the processe time spent to recuperate less than 20 % of the residual mass… pffff…*

PART III – A MORE COMPLICATED EXAMLPE

BUT SOME PROCESSES ARE MUCH MORE COMPLEX !

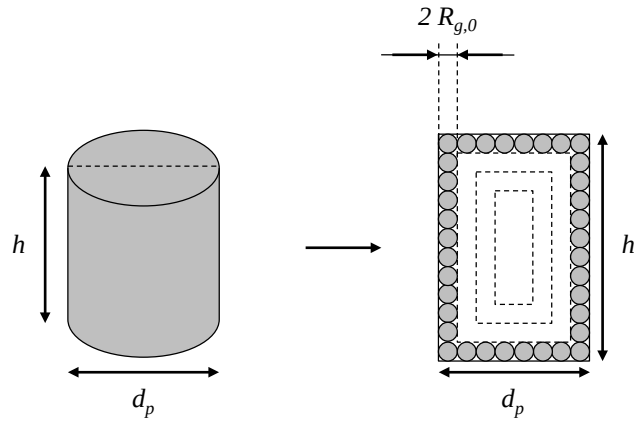
Crumbling of a chunk of material





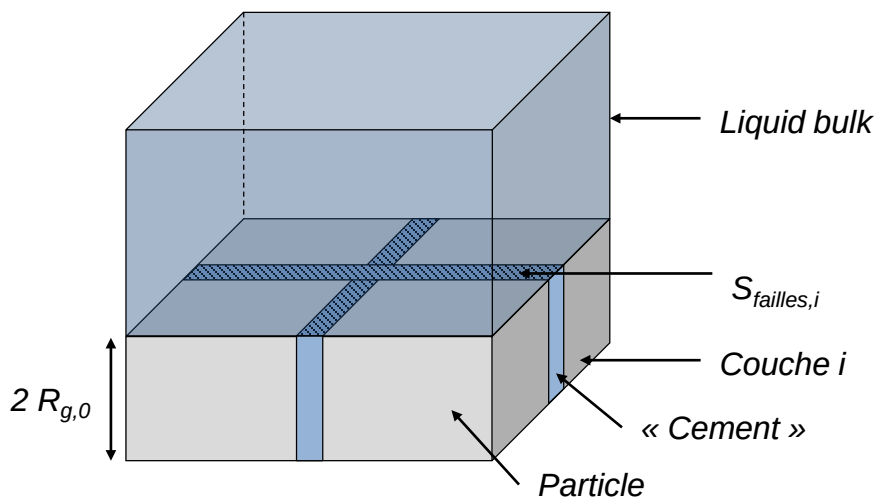
AND NEED SOME EFFORT FOR MODELING

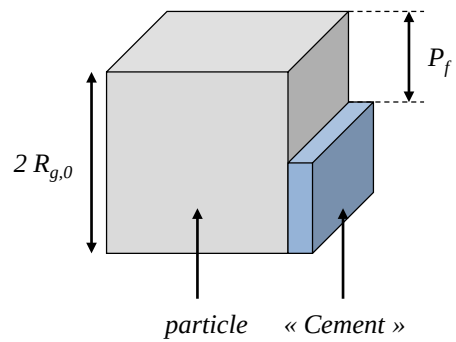
Bulk solid is a aggregate of individuel particules:



Modeling the crumbling:

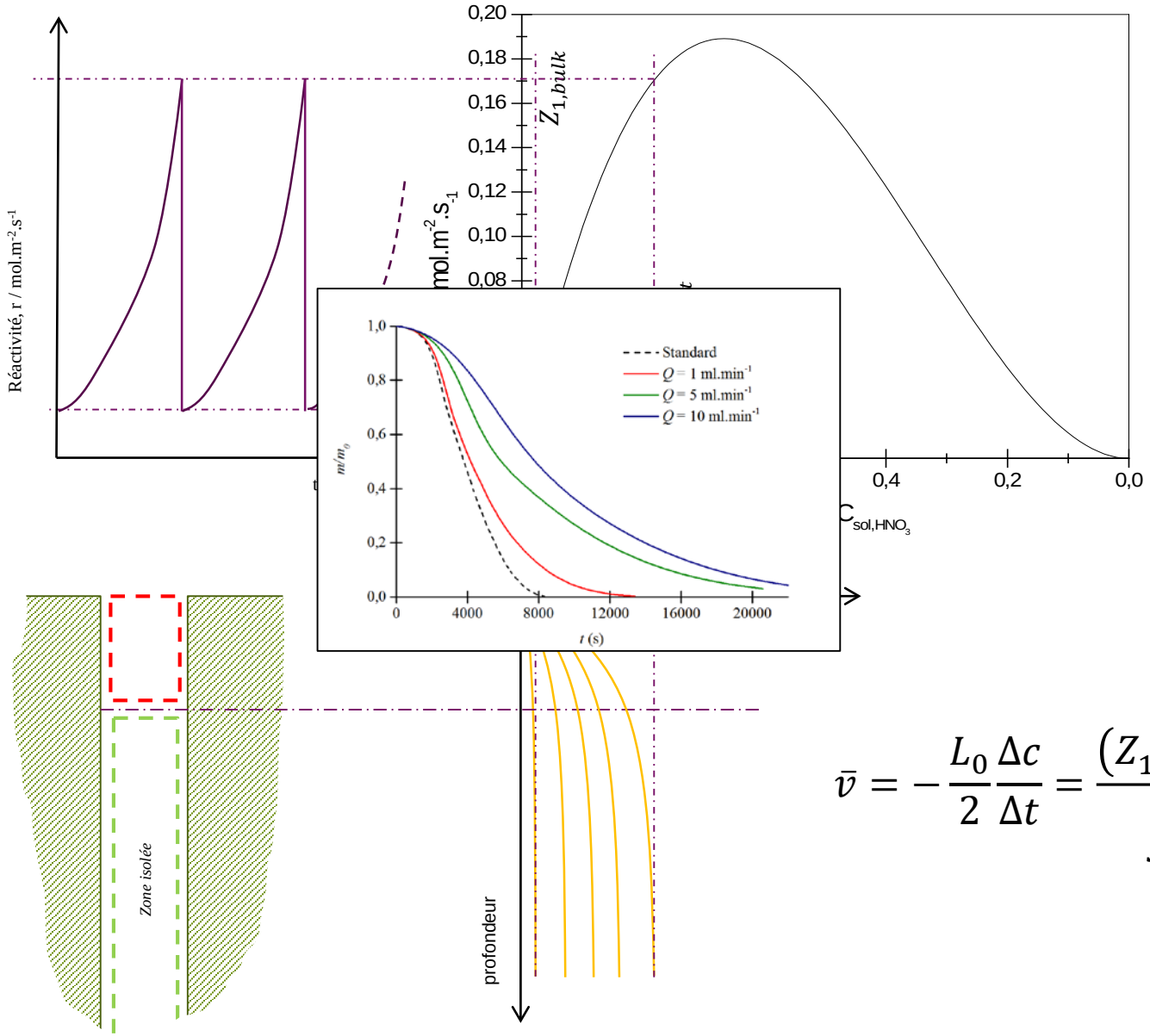
- Particules held together by a dissolving « cement »
- Liberation of the particules as the cement dissolves





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

DISSOLUTION IS AN OSCILATING REACTION



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

BACK TO ACCUMULATION

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

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

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

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

- 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

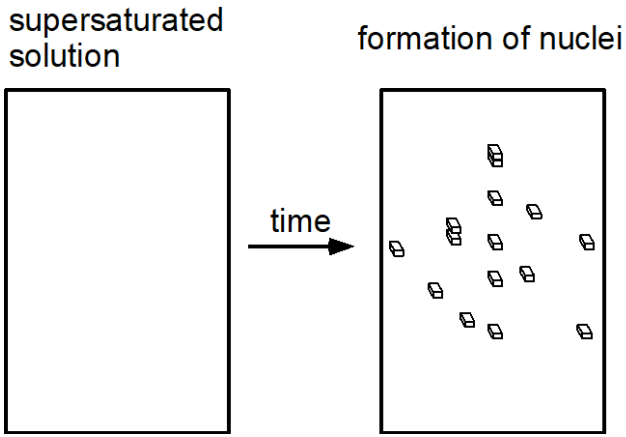
Again : the problems induced by accumulation at every scale will generally be a good indicator of the feasability and economical viability of a dissolution process

PART IV – BACK TO ACCUMULATION

BASICS ON PRECIPITATION

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

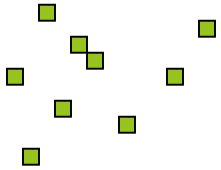
Nucleation

primary

Not influenced by presence of same solid phase

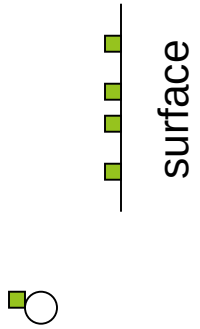
homogeneous

No influence of foreign phase



heterogeneous

Catalysed by presence of foreign phase



secondary

Influenced by presence of same solid phase

THE DRIVING FORCE FOR NUCLEATION

supersaturation

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

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

S_c is molar concentration supersaturation ratio

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

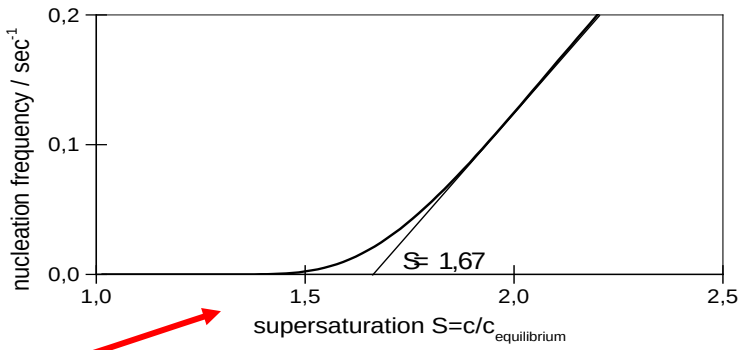
NUCLEATION FREQUENCY AND CRITICAL SUPERSATURATION

Nucleation frequency = 1/induction period

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

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

is characteristic of the solid, mainly, interfacial energy



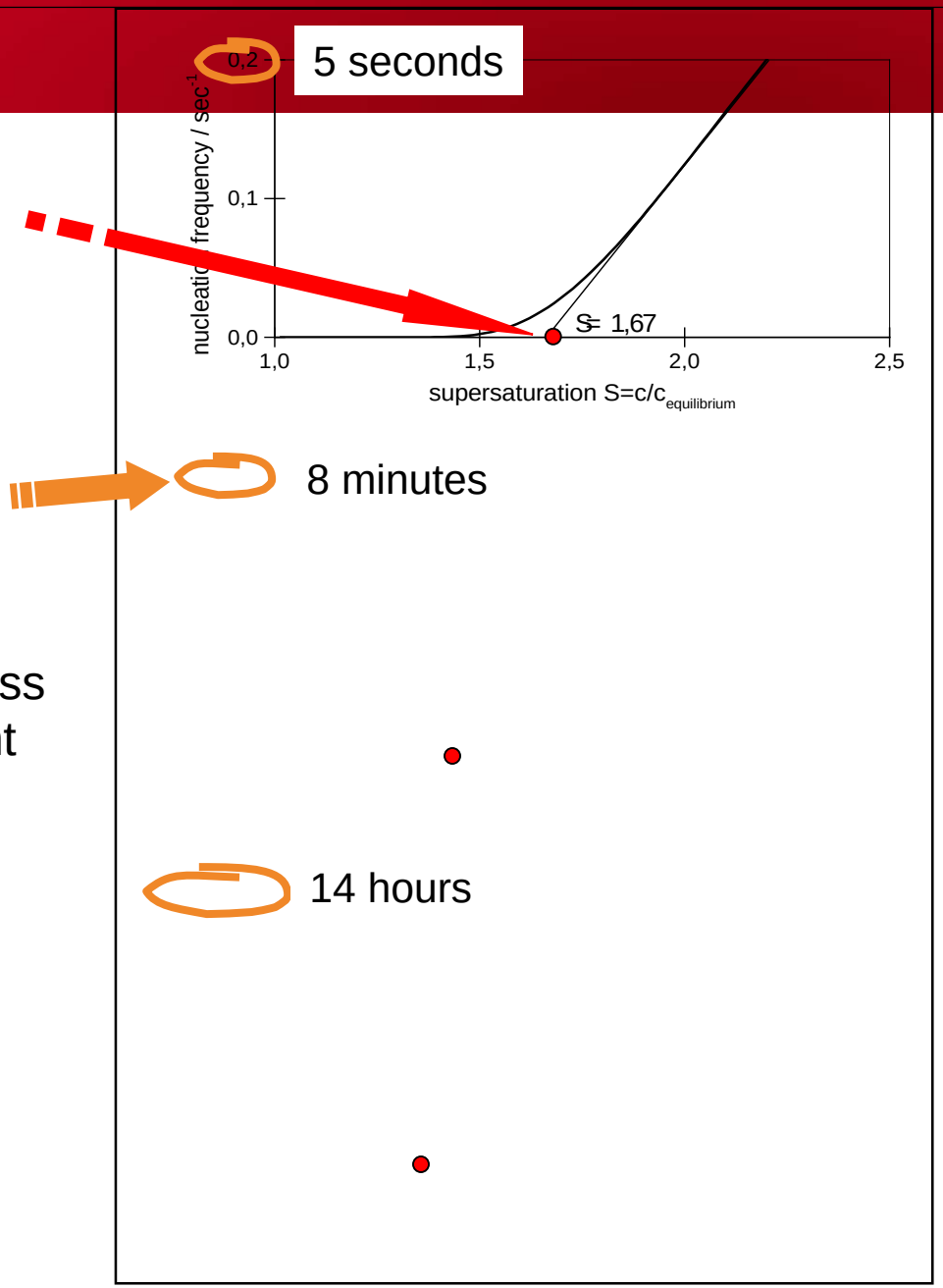
NUCLEATION FREQUENCY AND CRITICAL SUPERSATURATION

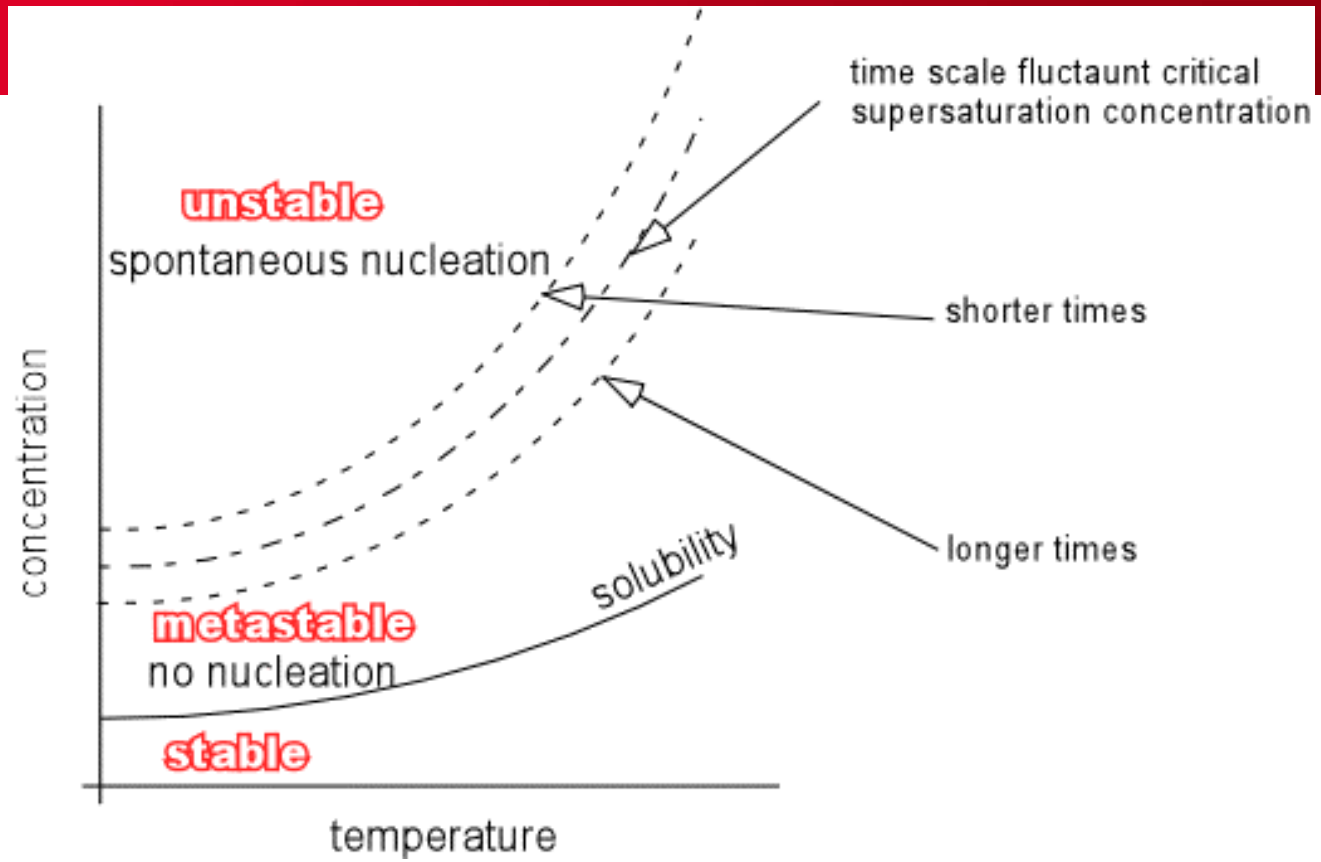
critical supersaturation

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…

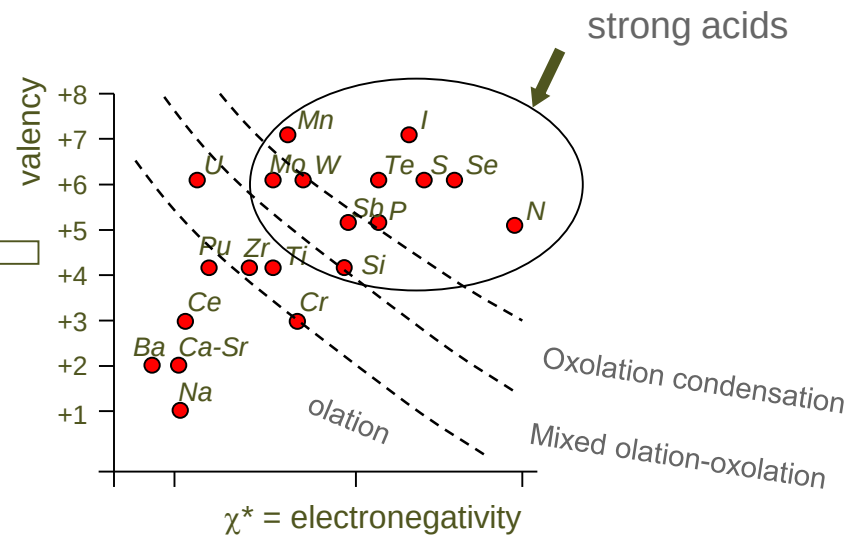
Few neutral or anionic candidates other than NO_3^-

Sufficiently acid species = species without hydroxo ligand

<u>Rule of the thumb</u>

Few candidates for making neutral species… so usually *always the same ones*

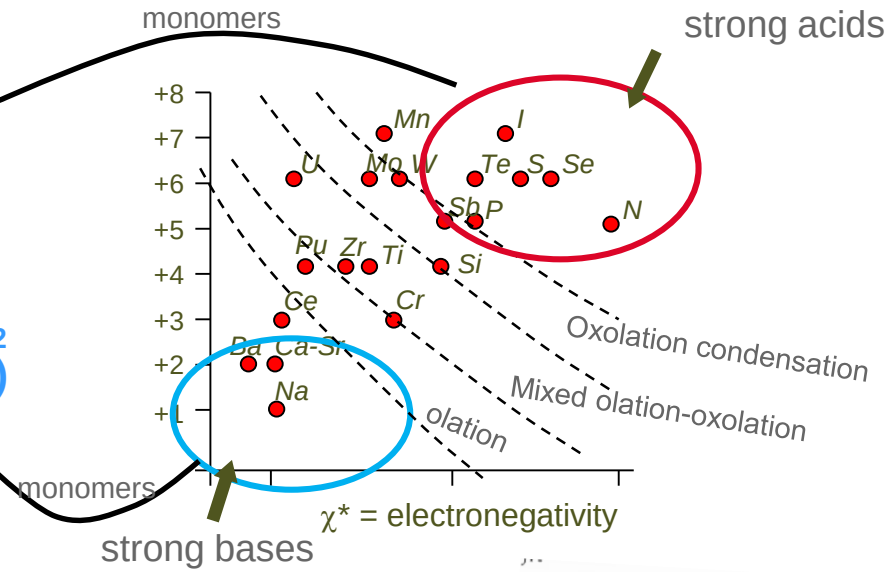
But very complex chemistries…



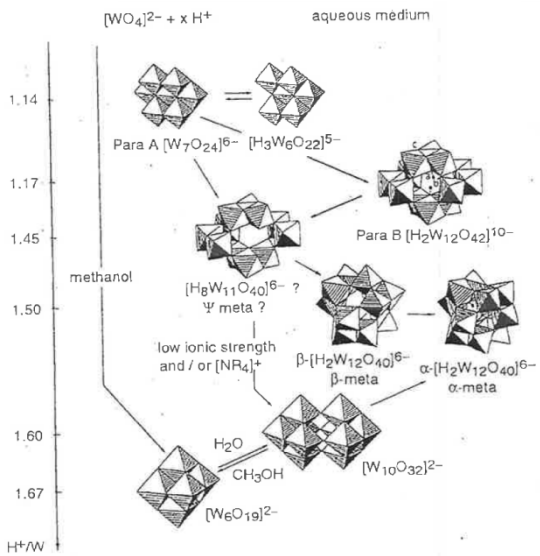
N, P, W, Si, Mo, V but also Te, Sb, Se, etc..

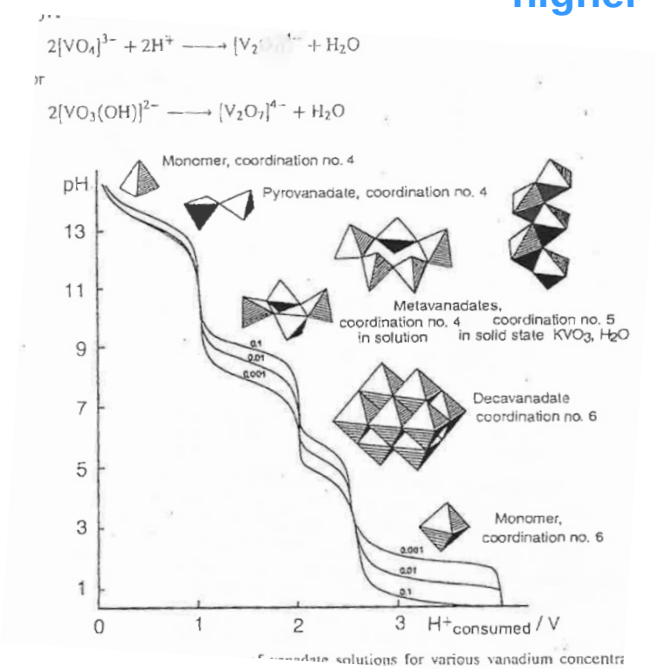
RULE OF THE THUMB CHEMISTRY

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

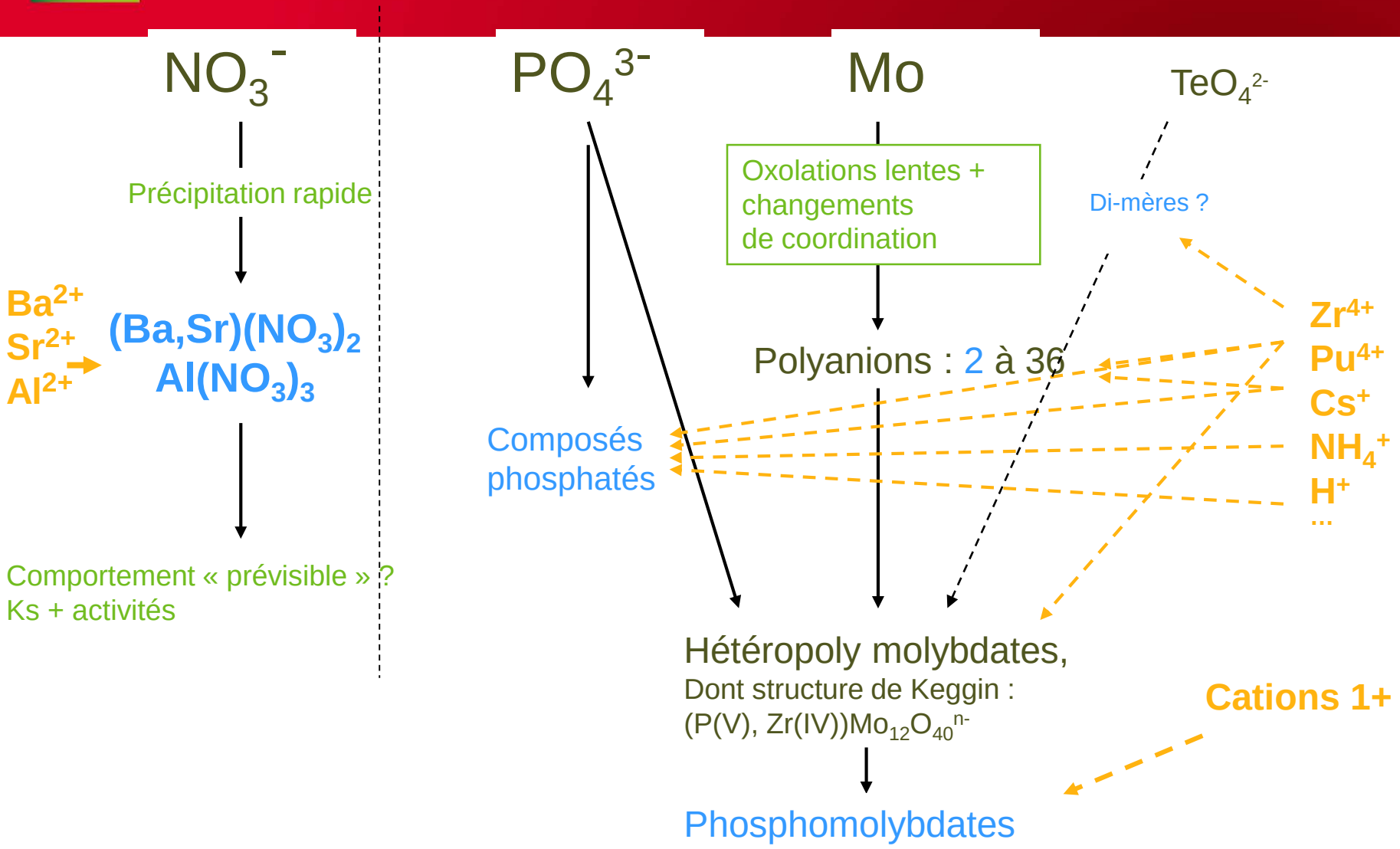


Slow condensation in mild acidities – decondensation in higher acidities





LES ESPÈCES D'INTÉRÊT



Thank you !