Apport du génie des procédés à l'hydrométallurgie

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Hydrometallurgy is great but has to be/remain a science

It relies upon grounds of a number of disciplines
needs sometimes sort of humility

Two examples treated

1- Electroleaching for metal recovery from used Ni/Cd batteries (Ph.D C. Hazotte, 2014 – IJL)

Institut Jean Lamour

Metal salt or oxide + X → M^{2+} + Y (Leaching reaction)

Y ± e → X (Electrochemical step)

$M(OH)_2 + 2\ H^+ \rightarrow M^{2+} + 2H_2O$

or $ZnO + 2\ H^+ \rightarrow Zn^{2+} + H_2O$

$H_2O \rightarrow 2H^+ + 2^e + ½\ O_2$

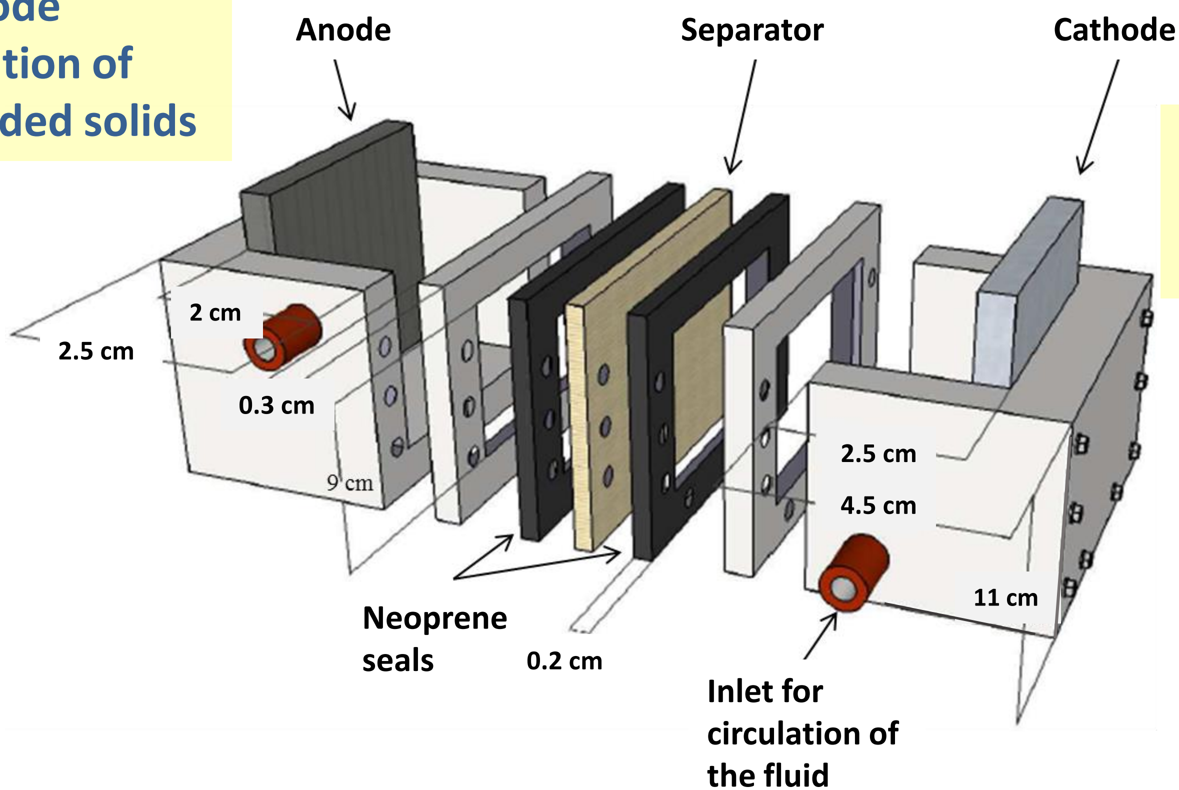
What to do with M^{2+}?

- Salt solution
- E-reduction to metal etc..

The cell used for electrochemical leaching (C. Hazotte, IJL)

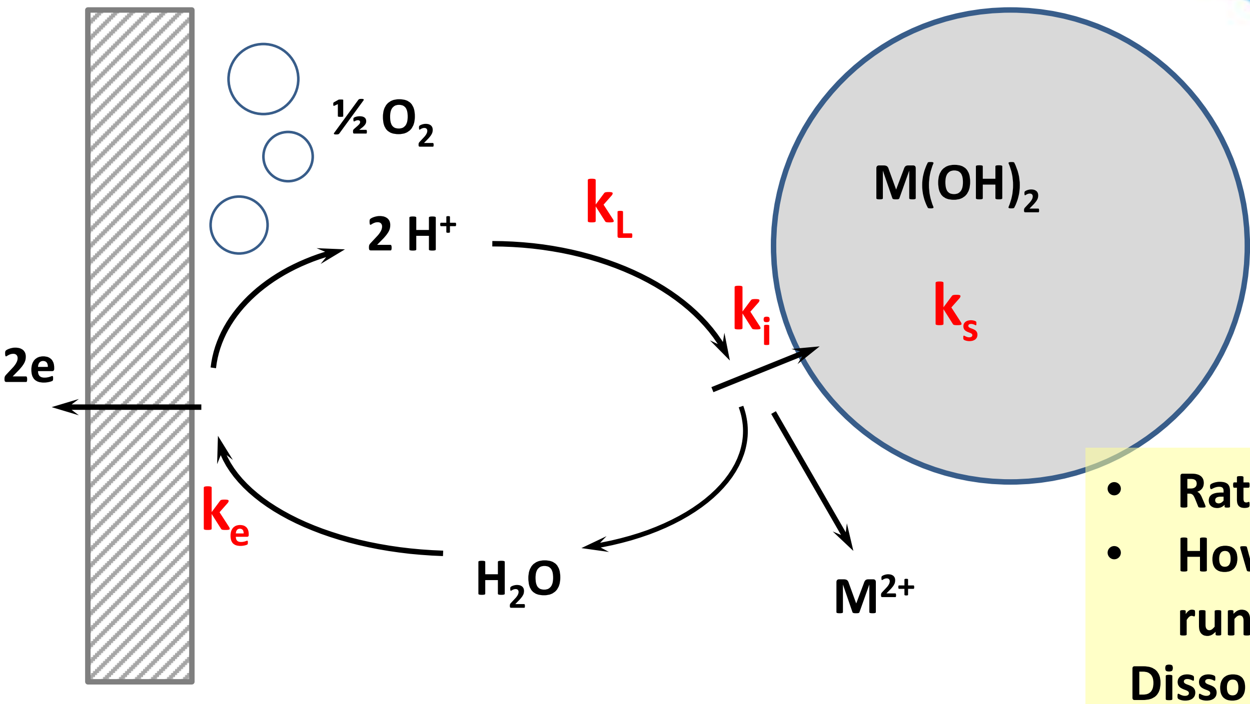
- H^+ formation at the anode
- Dissolution of suspended solids

Ion transport through the separator



Metal deposition
H_2 generation
Ion accumulation

Dissolution of solids in the anode chamber



- Rate-controlling transfer?
- How to interpret data in batch runs?

Dissolution extent α, $[M^{2+}]$, $[H^+]$

Reduced diameter $X=d_p(t)/d_{p0}$

Dissolution of solids in the anode chamber (C'td)

In numerous papers …
Direct use of formula formerly established
without justification of the model used
(shrinking core model, instantaneous nucleation etc.)

e.g. Diffusion-controlled process at spheres

$$\left[\frac{1}{(1-\alpha)^{1/3}-1}\right]^2 = kt$$

*** Dickinson and Heal (1999): a great catalogue for all model formula to be used**
*** Most equations are valid only when « the particle is surrounded by a sea of liquid »**

Practical application with concentrated suspensions?
A couple of thorough papers published these recent years (!)

Development of the dissolution model (Hazotte et al., 2015)

Single metal system, no current

$$\frac{d\alpha}{dt} = -\frac{M}{\rho d_{p0}} k_L \left(\frac{Da}{1+Da} \right) \left[H^+ \right]$$

Damköhler = k_s/k_L

$$\frac{d\left[H^+\right]}{dt} = -\frac{6 m_{p0} k_L}{d_{p0} V_L} \alpha^2 \left(\frac{Da}{1+Da} \right) \left[H^+ \right]$$

Spherical monodisperse particles

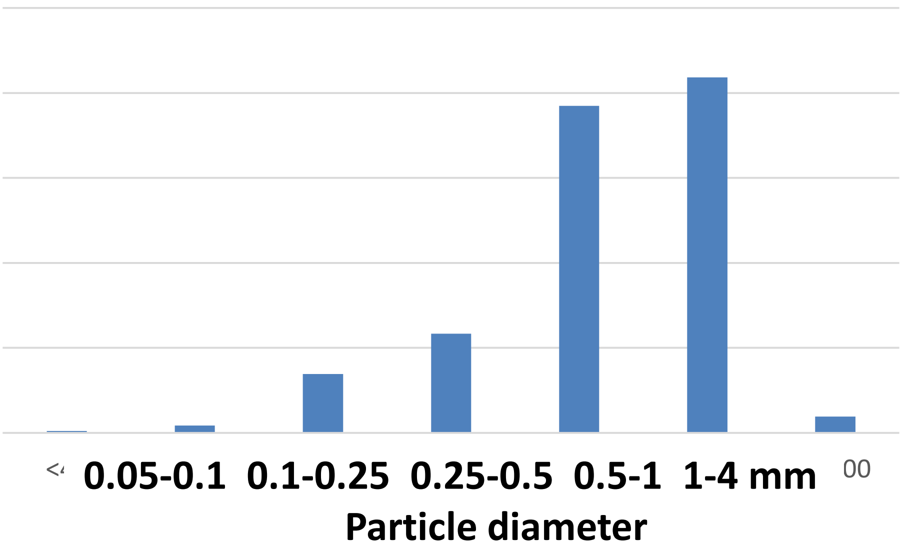
Multicomponent system, Current I

$$\frac{d\left[H^+\right]}{dt} = -\frac{k_L \pi N \rho d_{p0}^2}{V_L} \sum_i x_{i0} \alpha_i^2 \left(\frac{Da_i}{1+Da_i} \right) \left[H^+ \right] + \frac{I}{VF}$$

The substrate to be treated (Down to reality)

Black mass recovered from Ni/Cd batteries

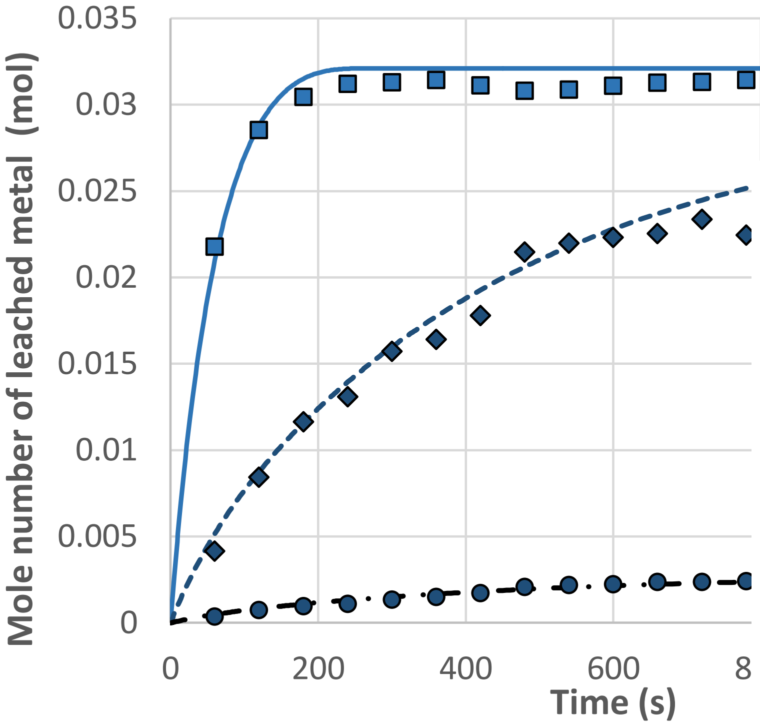
Ni, Cd and Co hydroxides + Ni



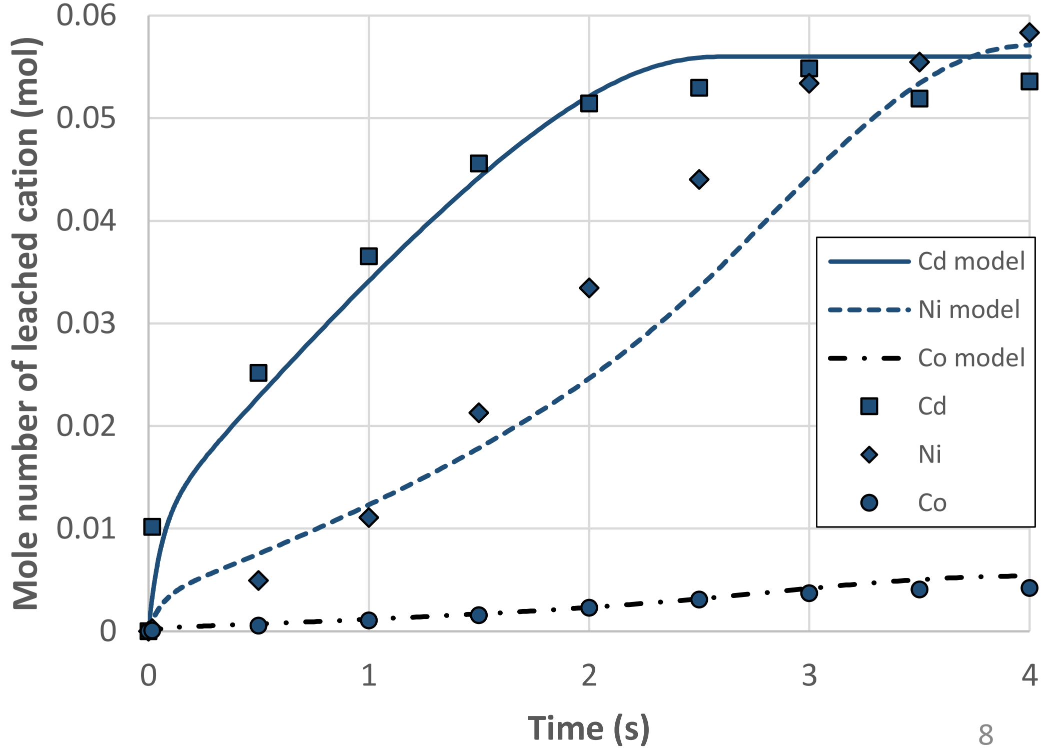
Spherical monodisperse particles (d_p=1 mm)?

Without current

$Cd(OH)_2$ dissolves faster than $Ni(OH)_2$ and $Co(OH)_2$

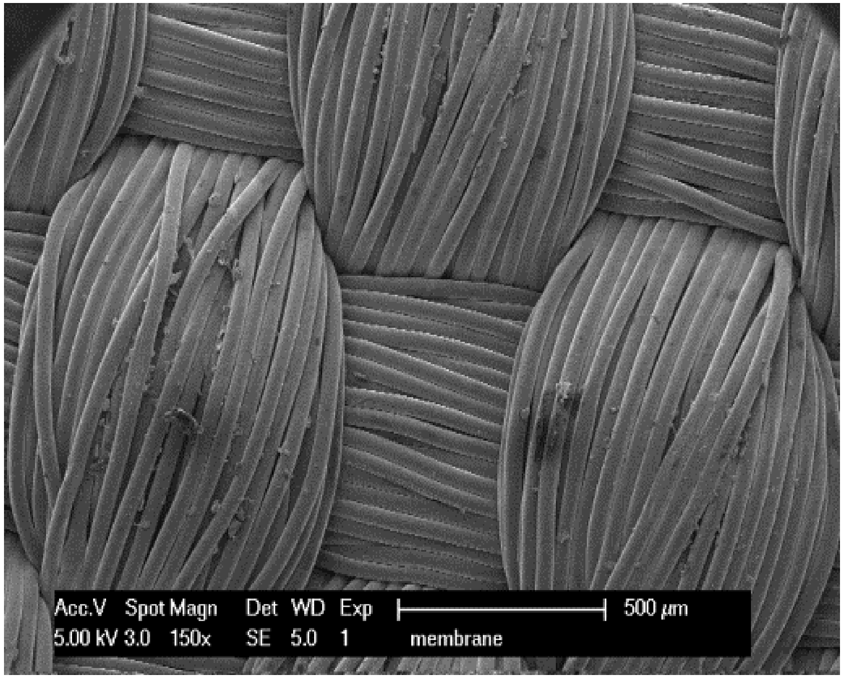


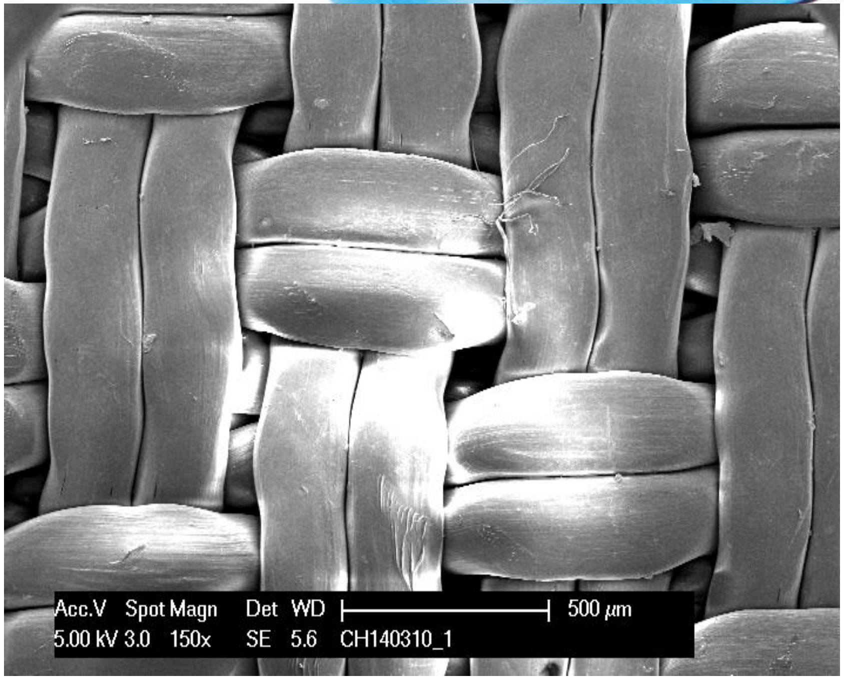
With current (1.85 A)



Electroleaching – Transport of cations through the separator

Separator: woven (inert) clothes (PP236 and PP289, Mortelecque)

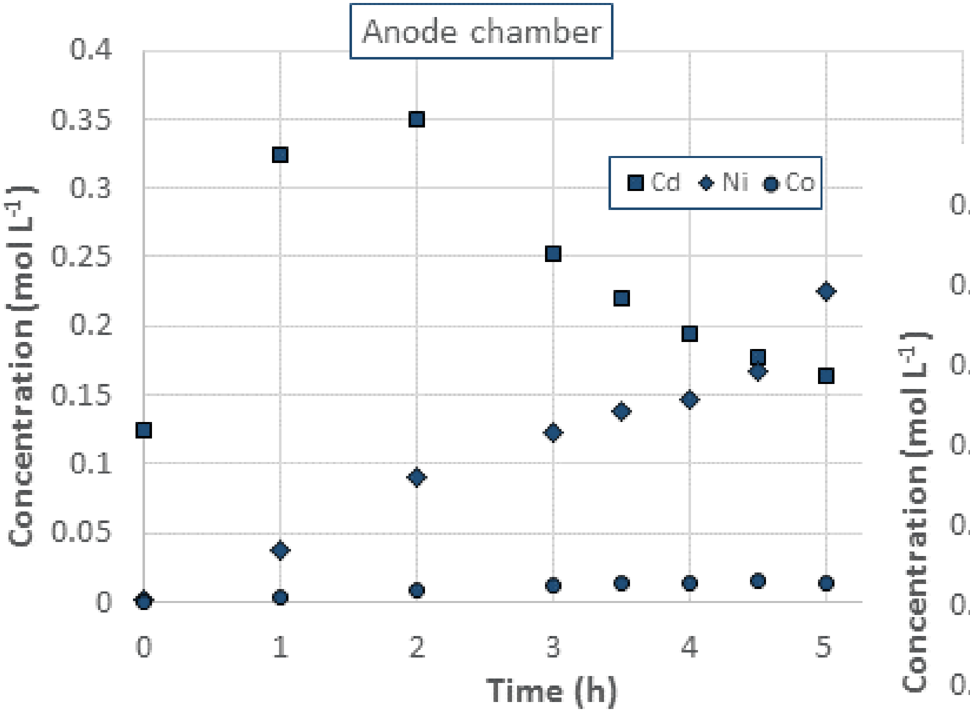


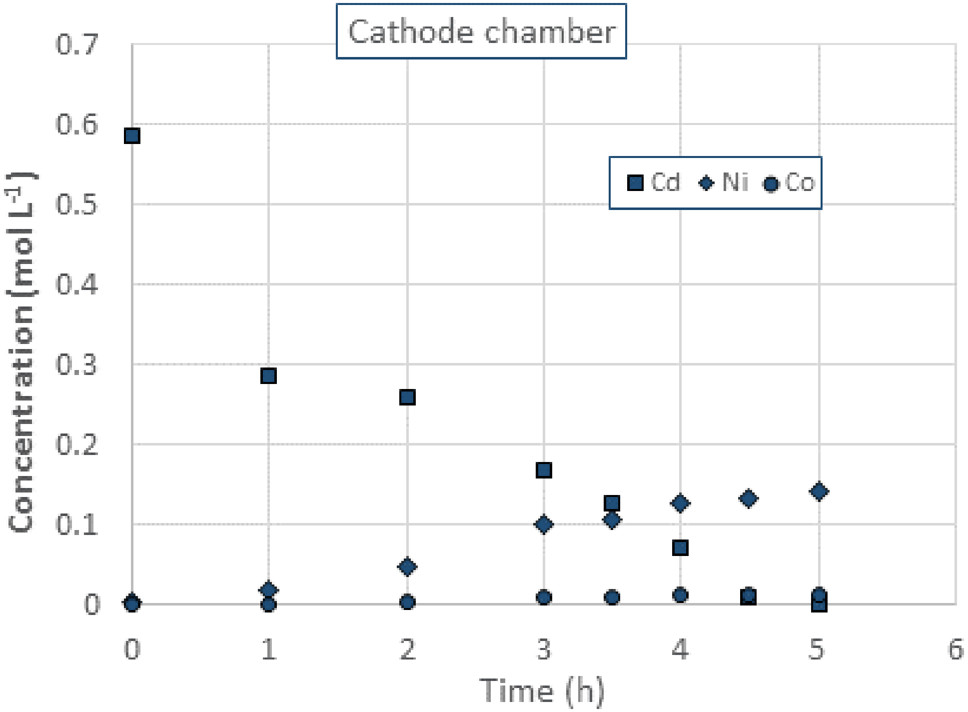


How occur transport phenomena through that?

Electroleaching – Transport of cations through the separator

Available data:
Time variations of ion concentrations in the two chambers





Electroleaching – Transport of cations through the separator

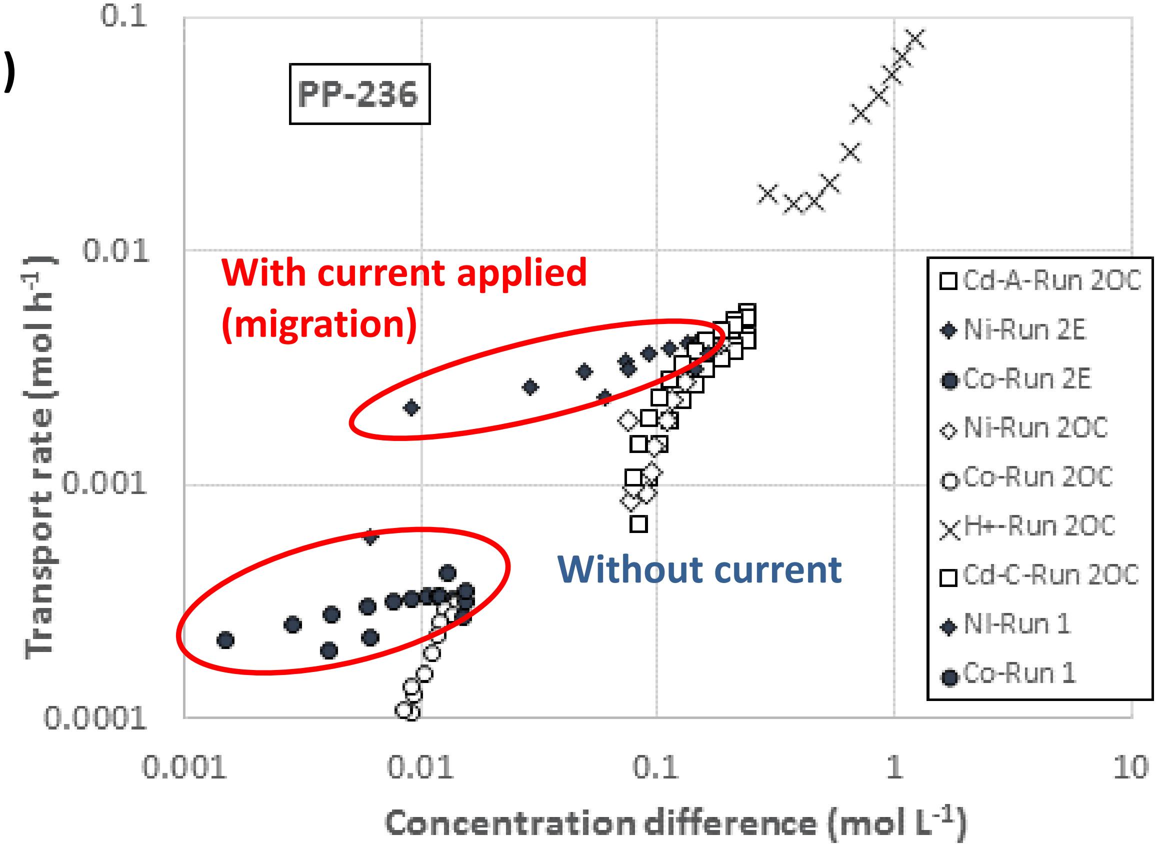
A very basic expression for the mass transport flux N_i (species i)

$$N_i = k_{t,i} S\left(C_{a,i} - C_{c,i}\right)$$

Overall coefficient ($k_{t,i}$); anode ($C_{a,i}$); cathode ($C_{c,i}$)

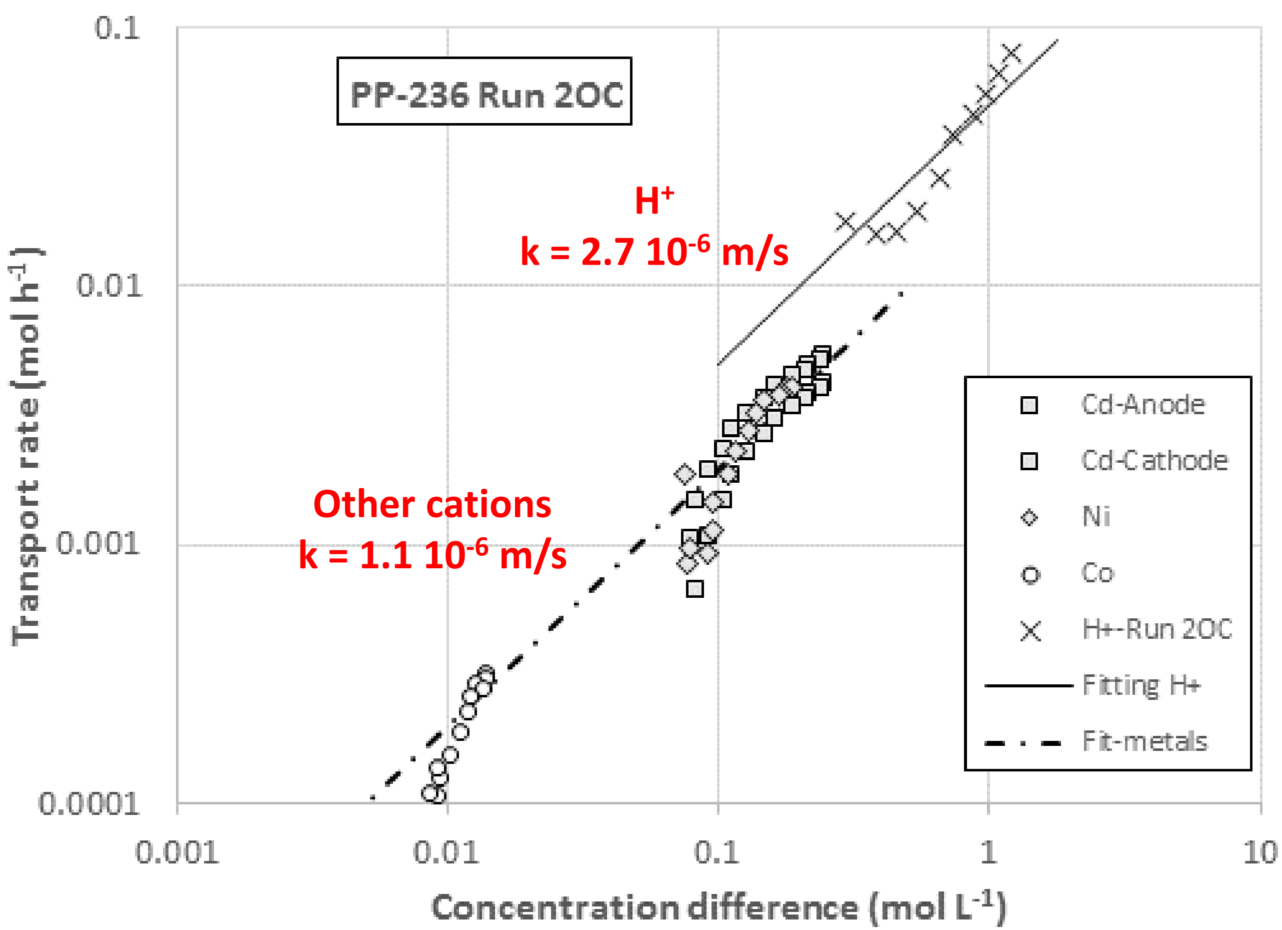
Not valid for migration:

$$N_{i,m} \approx C_i \nabla \Phi$$



Electroleaching – Transport of cations through the separator

Only data for tests at I=0



2- Separation of chromite from olivine by flotation

(Ph.D L. Turri avec H. Muhr (Valorco, avec ArcelorMittal …)

ADEME

Context:

CO_2 produced in steel manufacturing is to be sequestrated
by chemical reaction of olivine (silicate) at 20-100 bars CO_2, 150°C

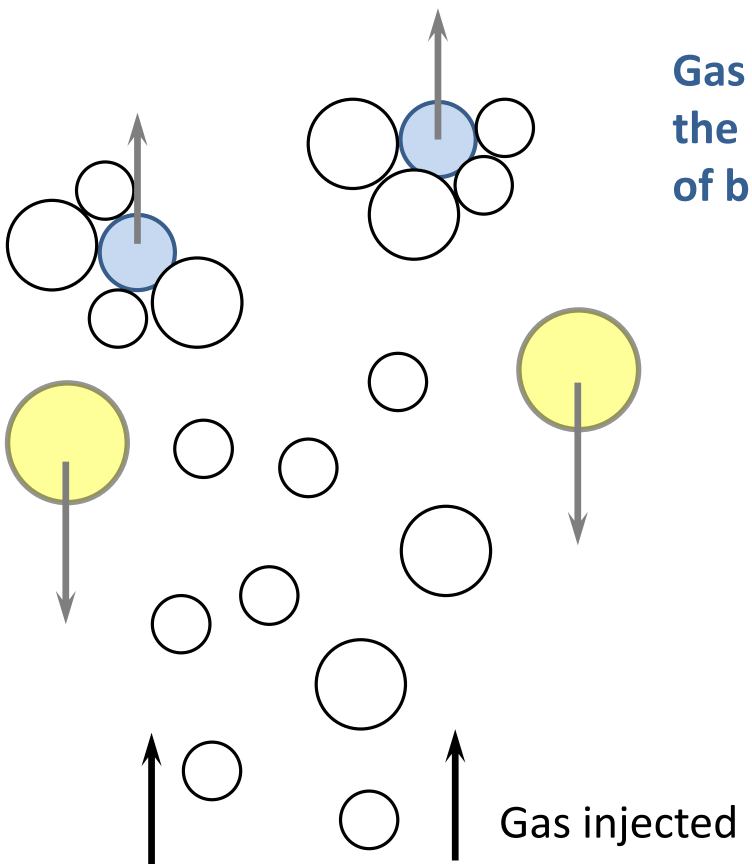
Mg-Fe silicates + CO_2 = SiO_2 + Mg-Fe carbonates

For possible viability of the process, all mineral fractions (SiO_2, carbonates and the traces of chromite (Cr_2O_3-FeO) have to be recovered with a high purity

Olivine (pure) is in the form of 120 µm particles, chromite at 70 µm

Possible technique: flotation of chromite

Principle of flotation (a 3-Phase process)



Gas bubbles adsorb on the hydrophobic surface of blue particles

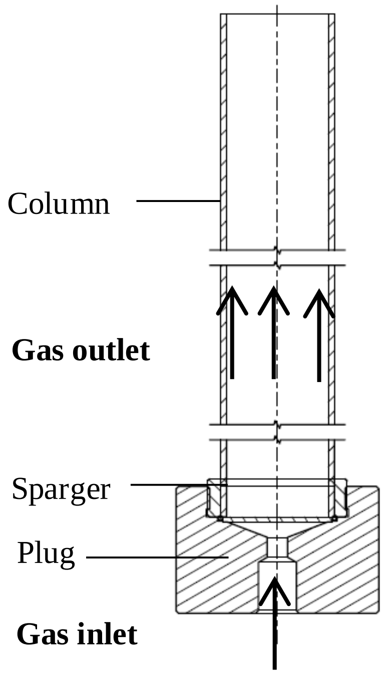
Yellow particles with hydrophilic surface fall down

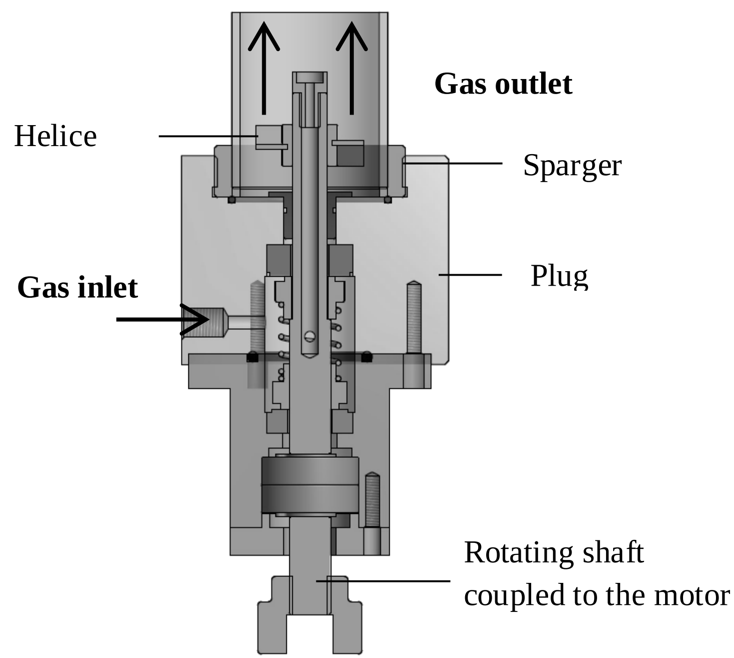
Find the right additive and pH conditions so that the surface of blue particles gets hydrophobic: pH 11, CTMAB =150 mg/L

Flotation in a lab column

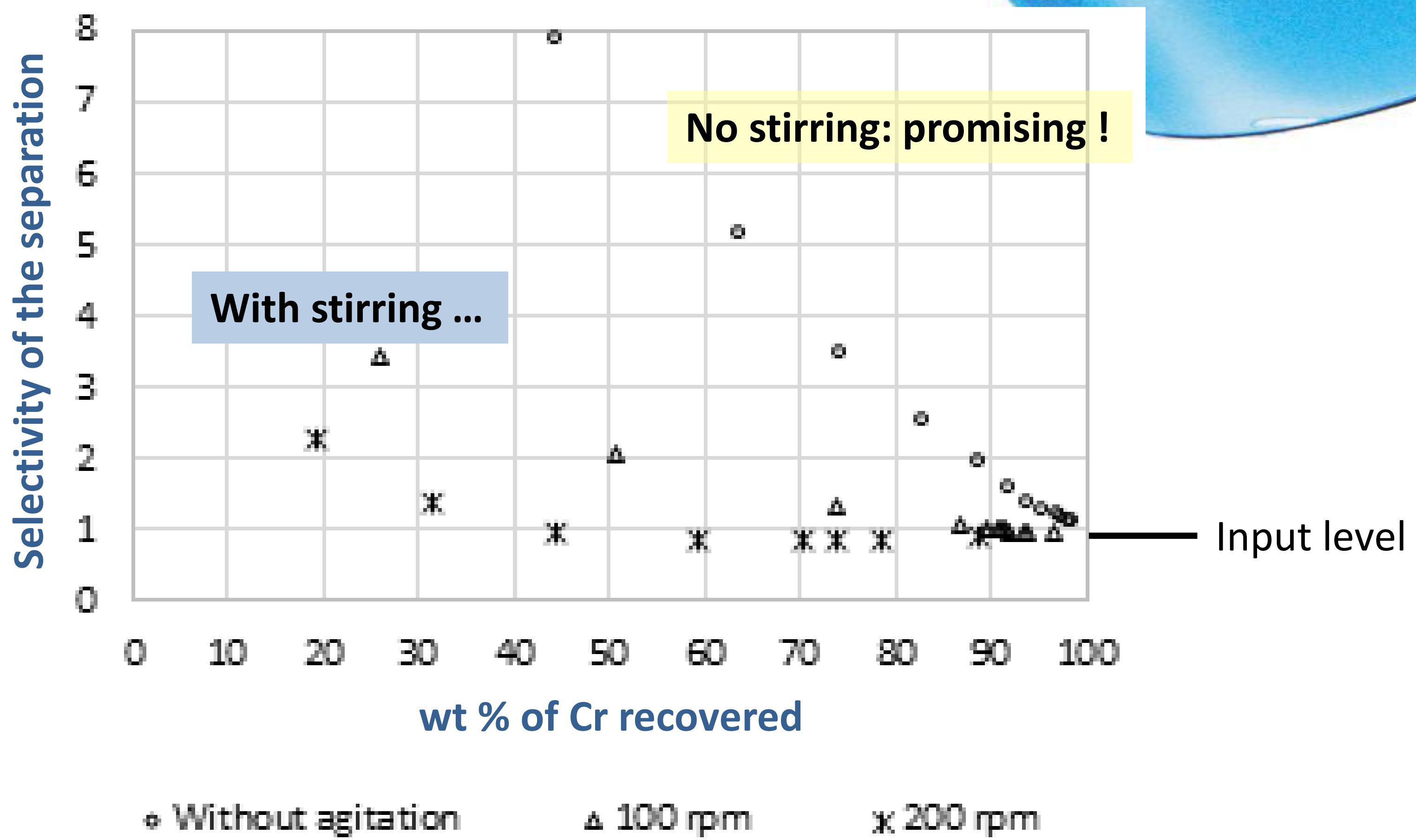
The column
(40 mm ID, 600 mm long)
Sintered plate
for gas injection

Avoid too rapid settling of particles and favour flow circulation?
Hint: insertion of a stirring system at the bottom (LRGP workshop)



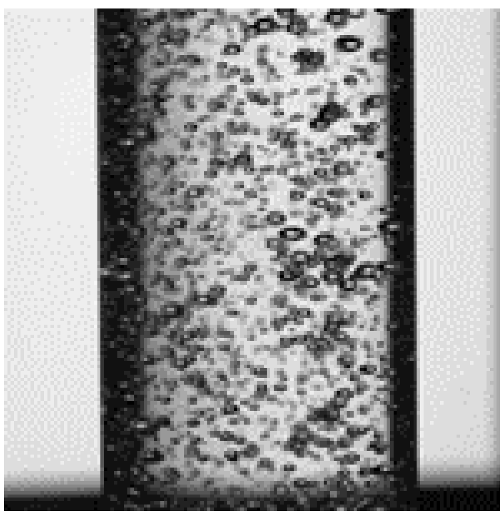


Flotation for chromite separation

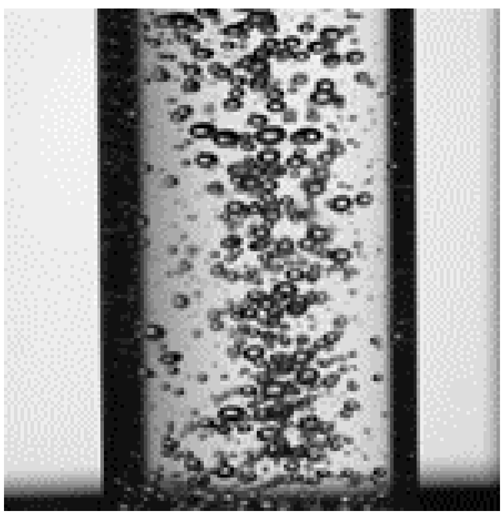


Flotation: cause of poor efficiency with stirring?

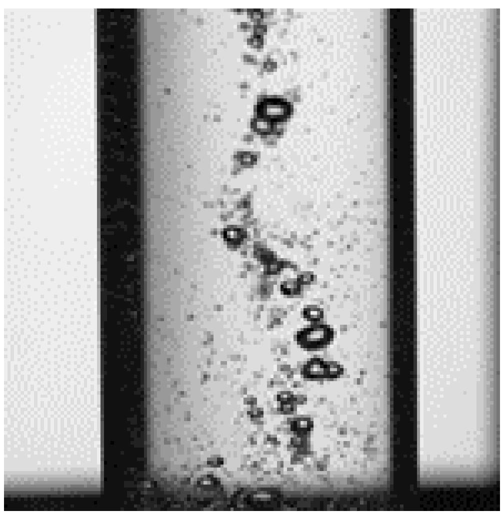
Visualisation tests : pure water and air injected
Photos after 15 s



No stirring



200 rpm

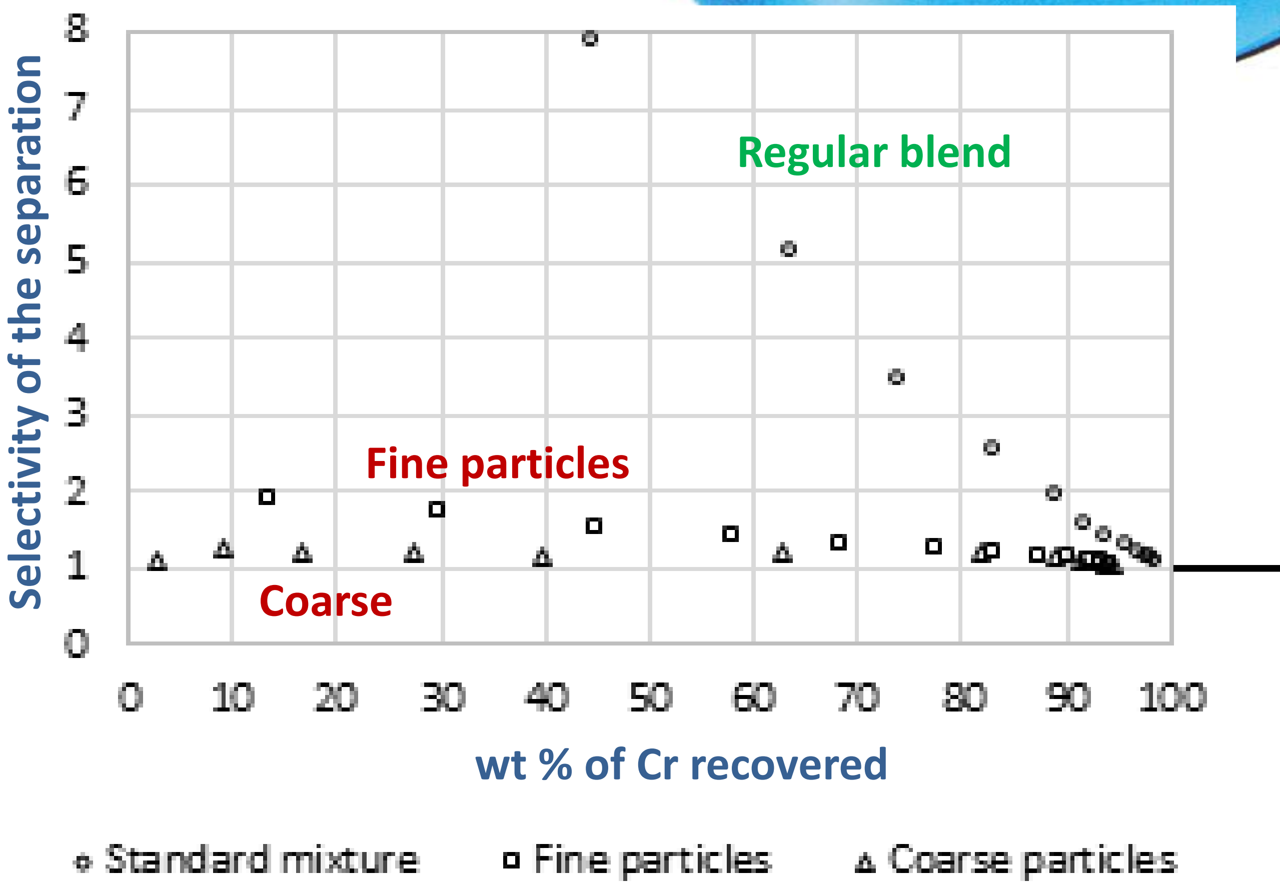


650 rpm

Effect of particle size on the flotation efficiency

Three Olivine/Chromite blends investigated with different sizes:

	Olivine/Chromite
Regular	120 / 70 µm
Fine	20 / 35 µm
Coarse	120 / 120 µm
Density	3.3 / 4.1 g/cm³



Effect of particle size on the flotation efficiency

Flotation: results actually from two phenomena:

- **Adhesion of/to gas bubbles for suitable surface conditions**
- **Gravity: heavier particles can fall more easily**

Use of the terminal falling velocity to quantify this effect

Particle blend	Terminal velocity (mm/s) Olivine	Chromite	Gravity	Surface phenomena	Overall
Regular	15	7.8	✓	✓	✓✓
Fine	0.5	1.6	✗	✓	⊜
Coarse	15	20	✗	✓	⊜

NB: the effect of gas bubbles on flow phenomena is not taken into account here

Conclusions

A few examples on the input of chemical engineering have been shown here

Hydrometallurgy, a wonderful combination of numerous disciplines:
Great, enthousiastic
but ground knowledge does not have to be disregarded

Thanks are due to

lorraine ADEME

Thanks a lot for your kind attention