Thomas Zemb

lecture n°9:
Handling liquid contact in practice: column, centrifuge and pertraction

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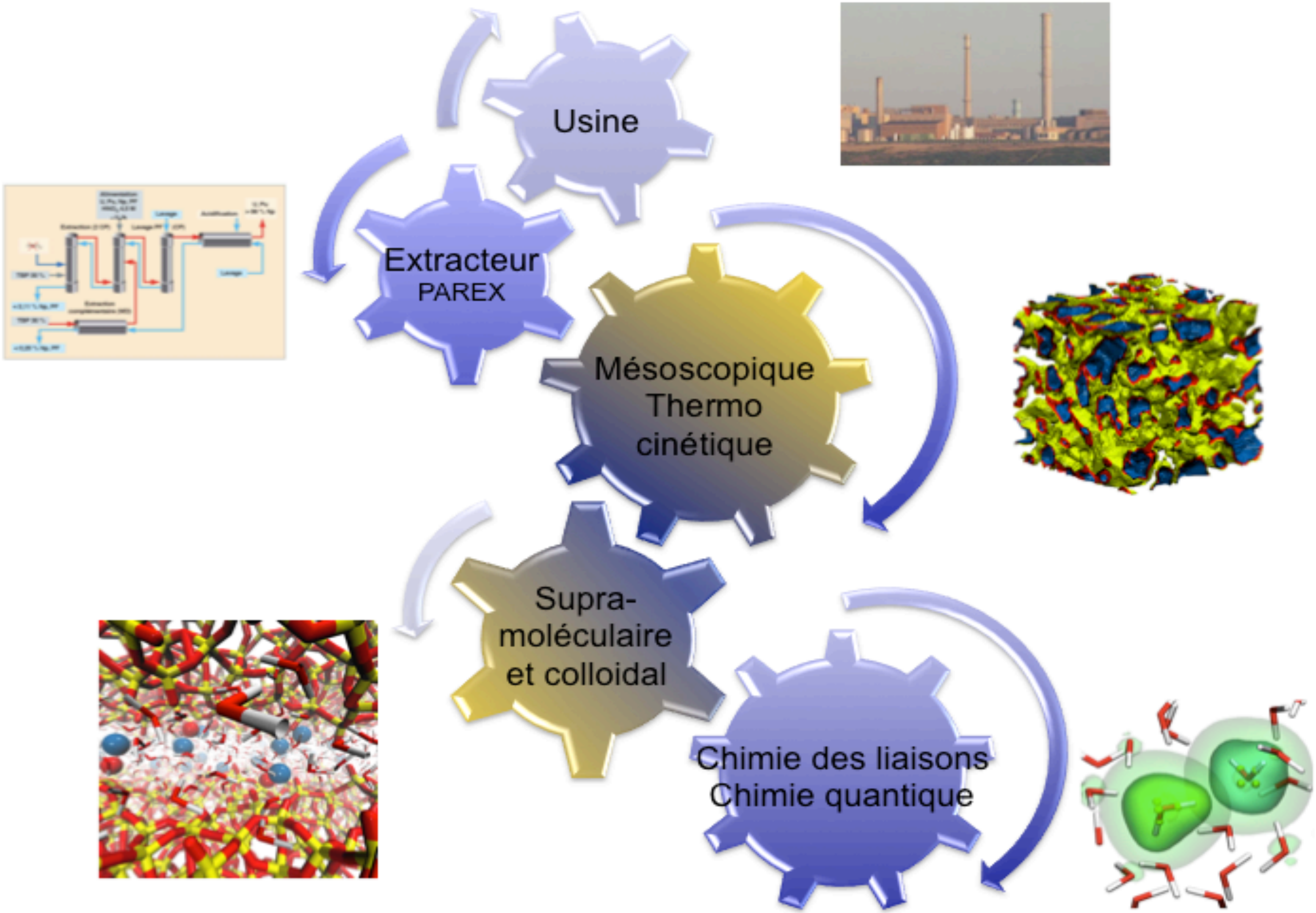
2014-2015

An intrinsic multi-scale approach :



Content

- **Basic concepts at macroscopic scale:**

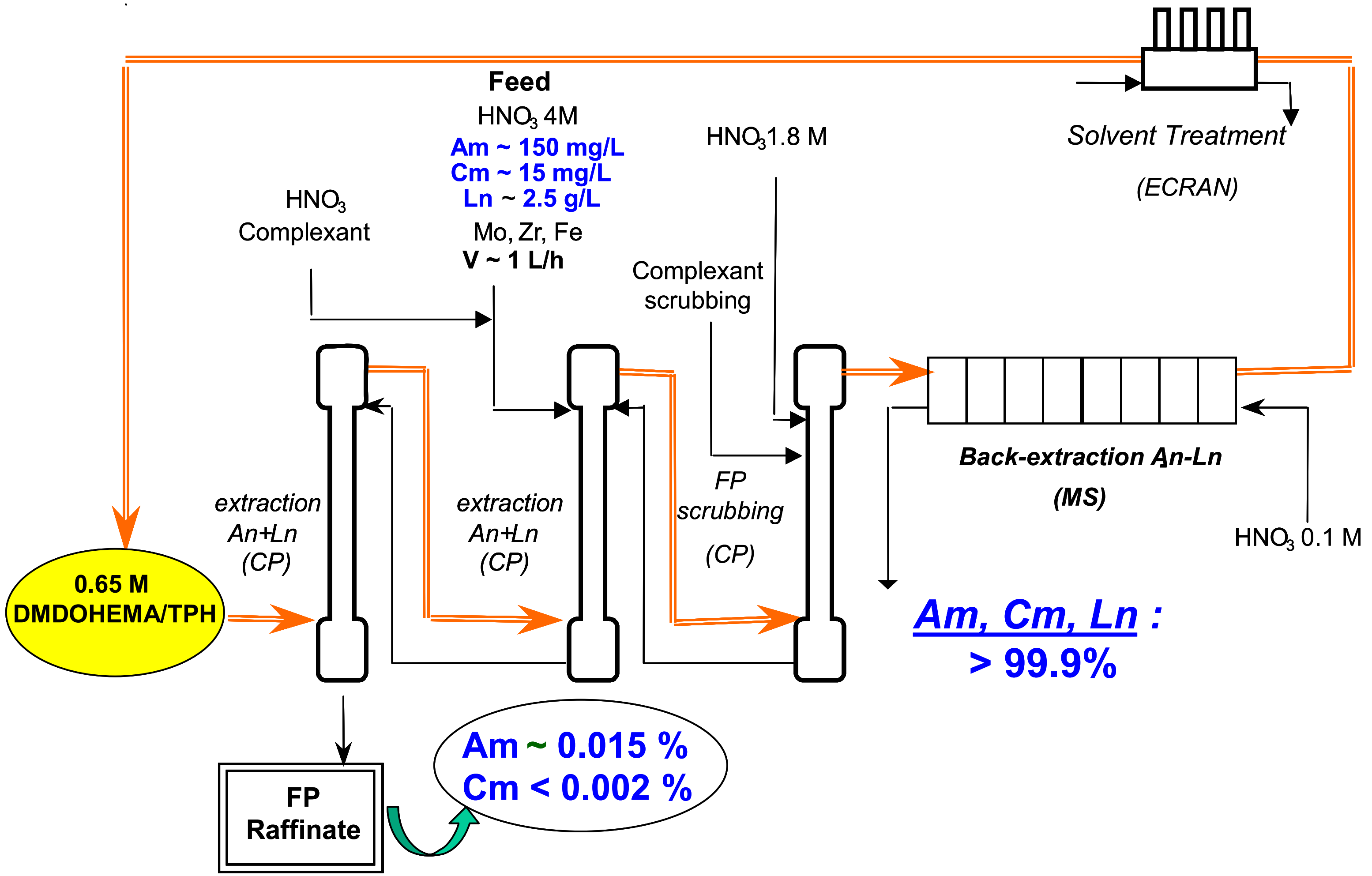
0/ Settling tanks

1/ Pulsed columns

2/ Centrifuges

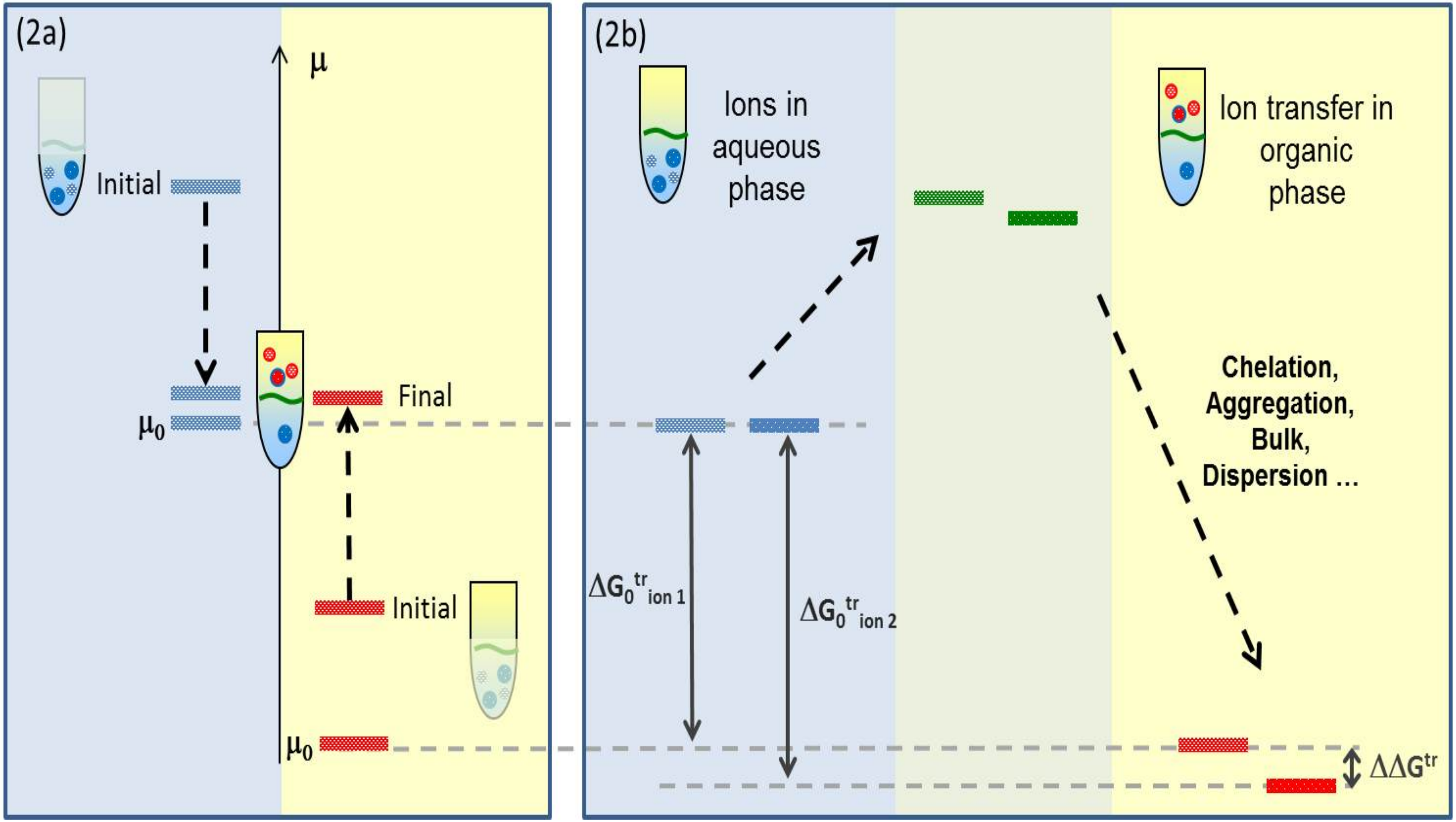
3/ Pertraction

The coupled cascades and solvent treatment



P. Baron et al., , Global 2007

The transfer between phases at meso-scale (next lecture)



Technologies of liquid-liquid extraction

All devices combine:

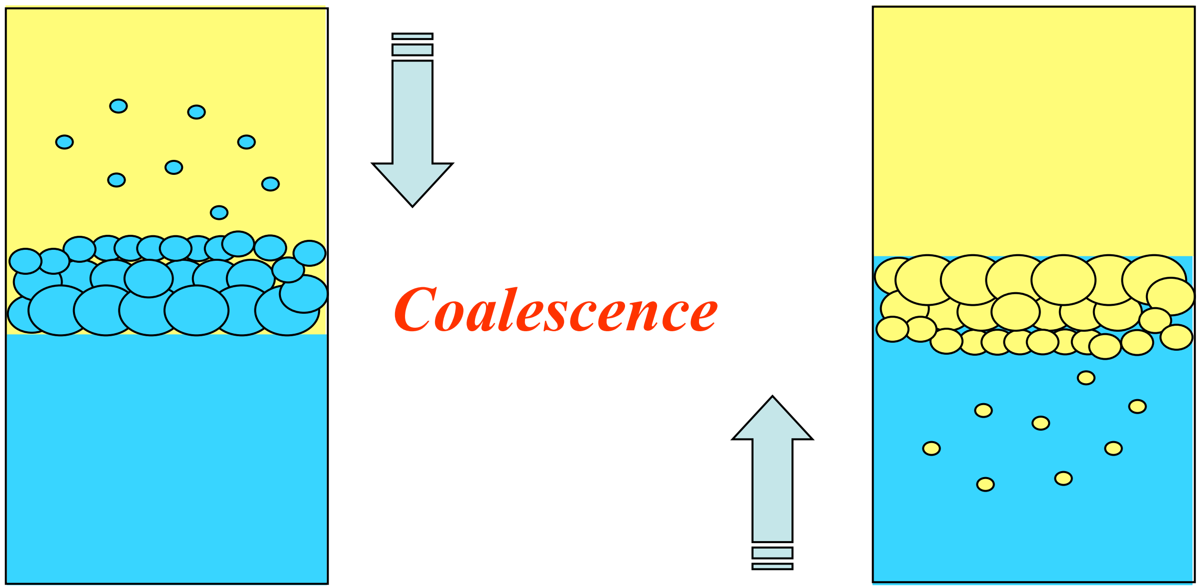
- Some part devoted to mixing/contact
- Some part devoted to phase separation: desemulsification, driven by surface tension effects

Continuous operation at optimized size:

- Large area of contact : expressed as Σ in (m2/g)
- Separation of the emulsion (most frequent case microemulsion/brine):

Depends on dynamic and static surface tension, viscosity and density difference that can be tuned by use of formulated solvents (see lecture by Werner Kunz)
When miroemulsions are formed, and concentration of aggregates becomes too high, the thermodynamcis goes from two phase to three phase « mayonnaise », (see next lecture)

W/O and O/W emulsions : the role of solutes



Émulsion FOC
***F**onctionnement*
***O**rganique **C**ontinu*

Émulsion FAC
***F**onctionnement*
***A**queux **C**ontinu*

Transport via sedimentation or creaming

(Average) « Sauter » Diameter

$$d_s = d_{32} = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2}$$

Volume fraction :

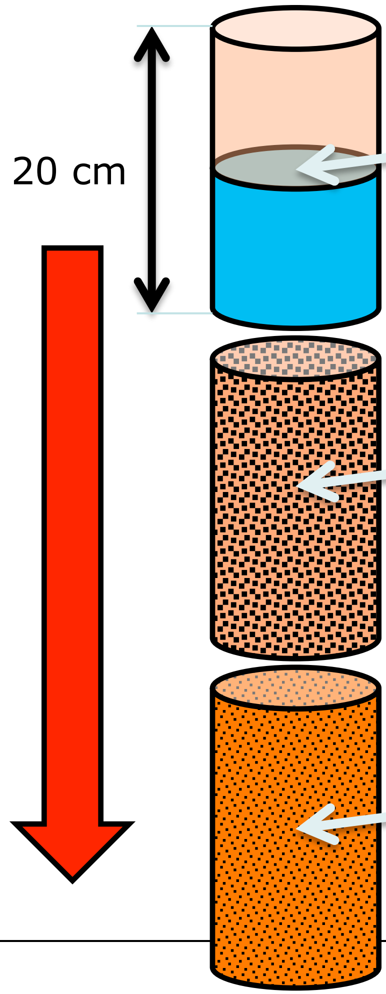
$$\phi = \frac{V_{dispersed}}{V_{Total}}$$

Specific area :

$$\Sigma = \frac{6\phi}{d_{32}}$$

Order of magnitude of area of contact

Numerical Example : 1 liter, with $\phi_O = 50\%$



Area of contact : 50 cm²

Increasing
Shearing
Stress
(Pa)

Droplet diameter : 1 mm
Exchange area : 30 000 cm²
(x 600)

Droplet diameter 0,1 mm
Exchange area : 300 000 cm²
(x 6 000)

Industrial implementation

(1) High yield

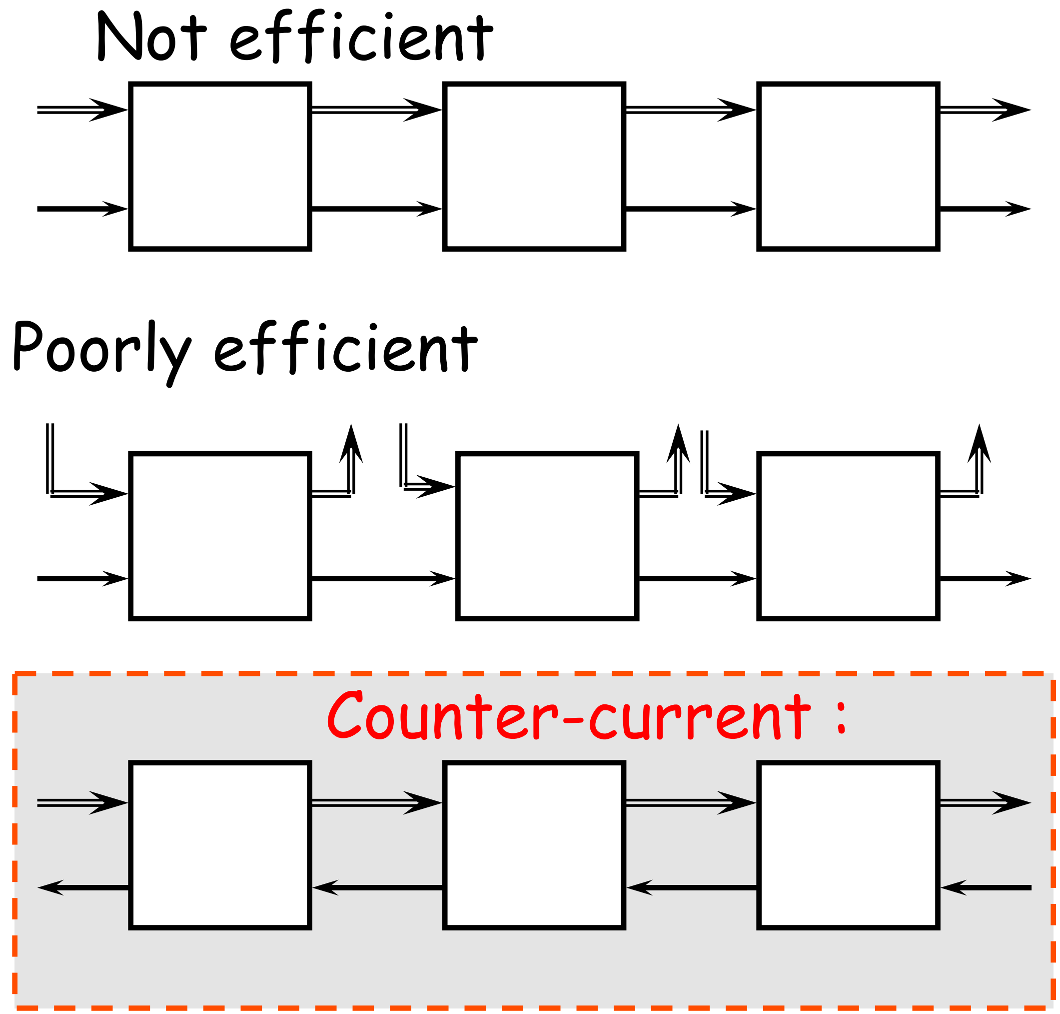
➔ Continuous operation

(2) High performance

➔ Coupling devices

➔ In cascades

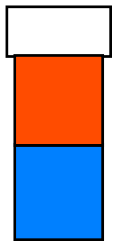
(3) Counter-current implmentation



The distribution coeffcient and the extraction yield

<u>Étape 3</u>
Décantation des phases

V_o Y_f



V_a X_f

V_A : Vol. aq phase
V_o : Vol. org phase
X_f : final C aq phase
Y_f : final C org phase
X_i : Ini Conc aq phase

Mass balance

$$V_a.X_i = V_a.X_f + V_o.Y_f$$

Distribution coeff.

$$Y_f = D.X_f$$

Extraction eff:

$$E = \frac{V_o}{V_a} \cdot D$$

Performance d'extraction

One « stage » of extraction

$$\frac{X_i}{X_f} = 1 + E$$

N stage in counter-current configuration (Kremser)

$$\frac{X_i}{X_f} = \frac{E^{N+1} - 1}{E - 1}$$

… interest of high values of E per stage (typically ten)
… if E too high: desextration impossible

Transfer versus separation optimisation

High stirring stress

Fine emulsion : high Σ

Temperature élevation ?

Micelle existence ?

Visco-elastic effect ?

Solvent Flash point

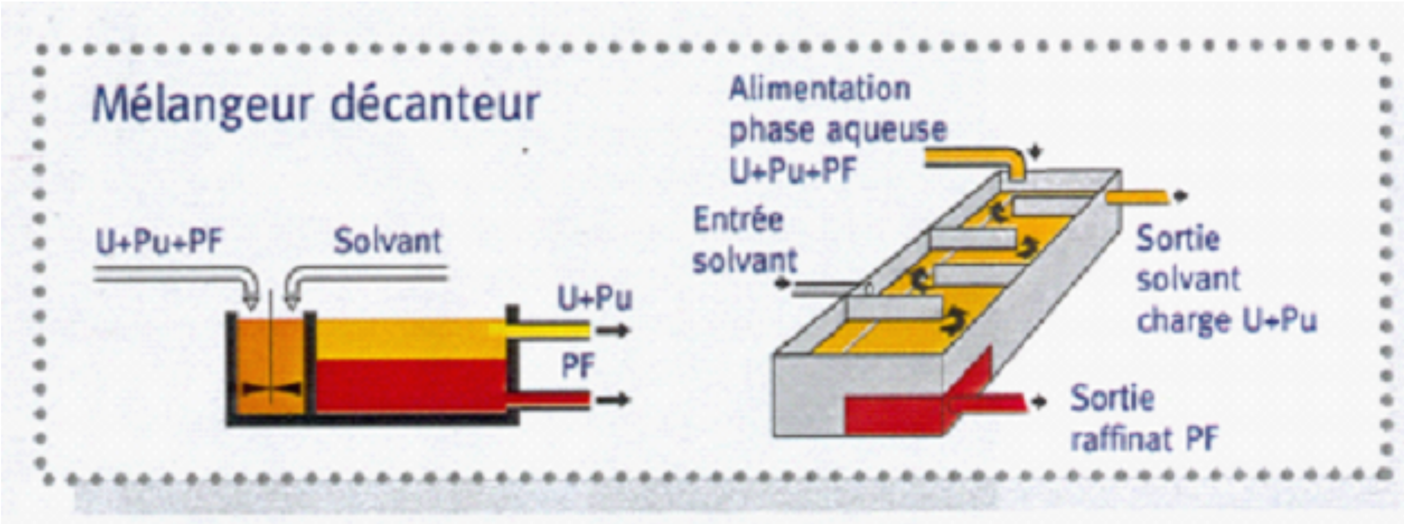
Low stirring stress

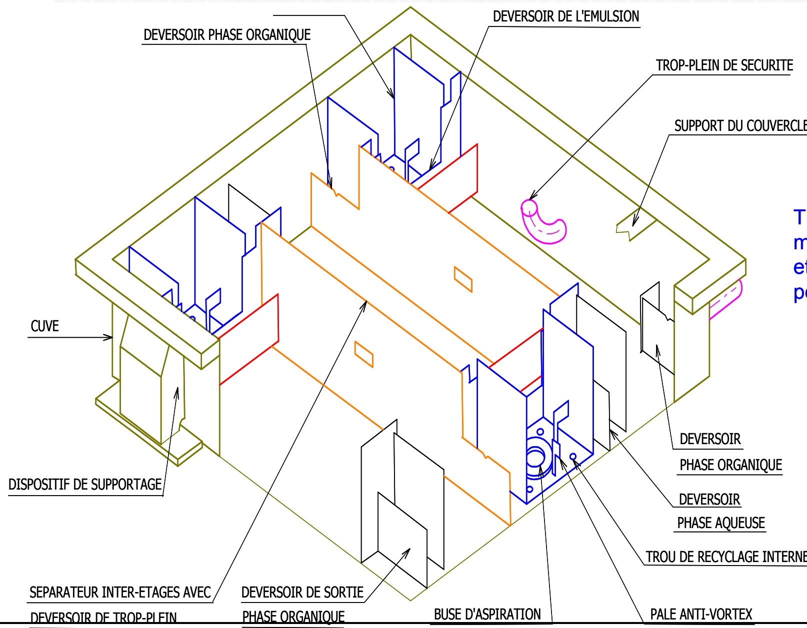
Easy separation between coarse emulsion droplets

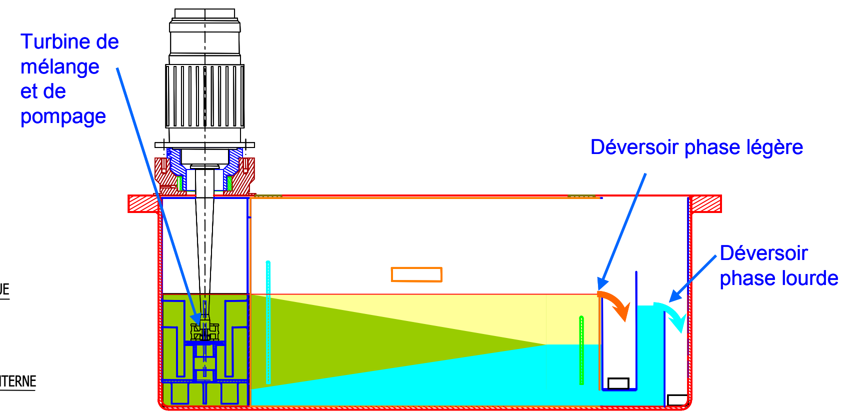
Low yield in feeding/ extracting fluids

Efficiency of hydrodynamic power

Mixers -settlers in reality



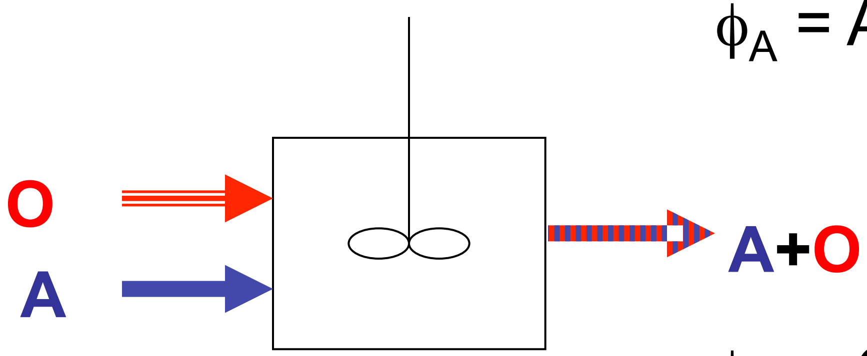




An example at « La Hague »

Improving yield of a single stage: partialreinjection

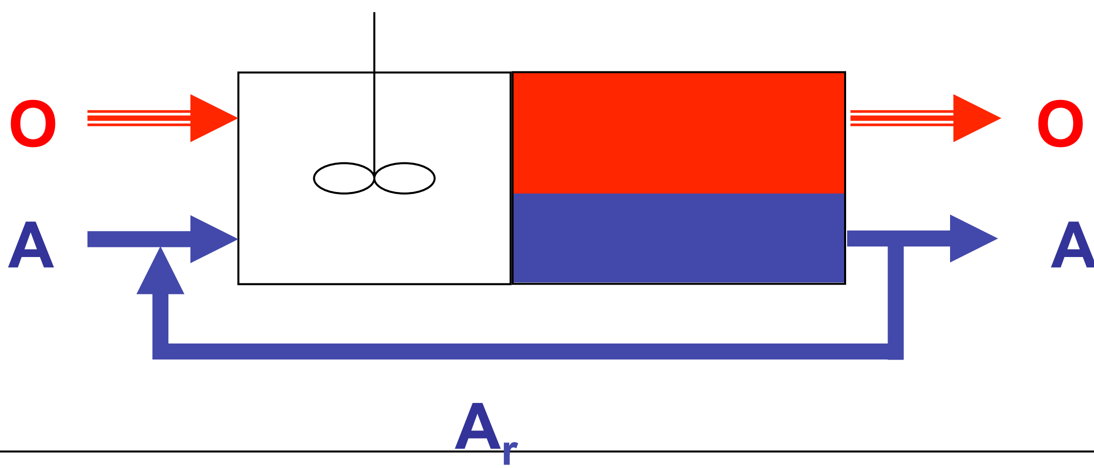
$\phi_A = A/(A+O)$



$\phi_O = O/(A+O)$

$A << O \rightarrow \phi_A << 1 \rightarrow$ small Σ

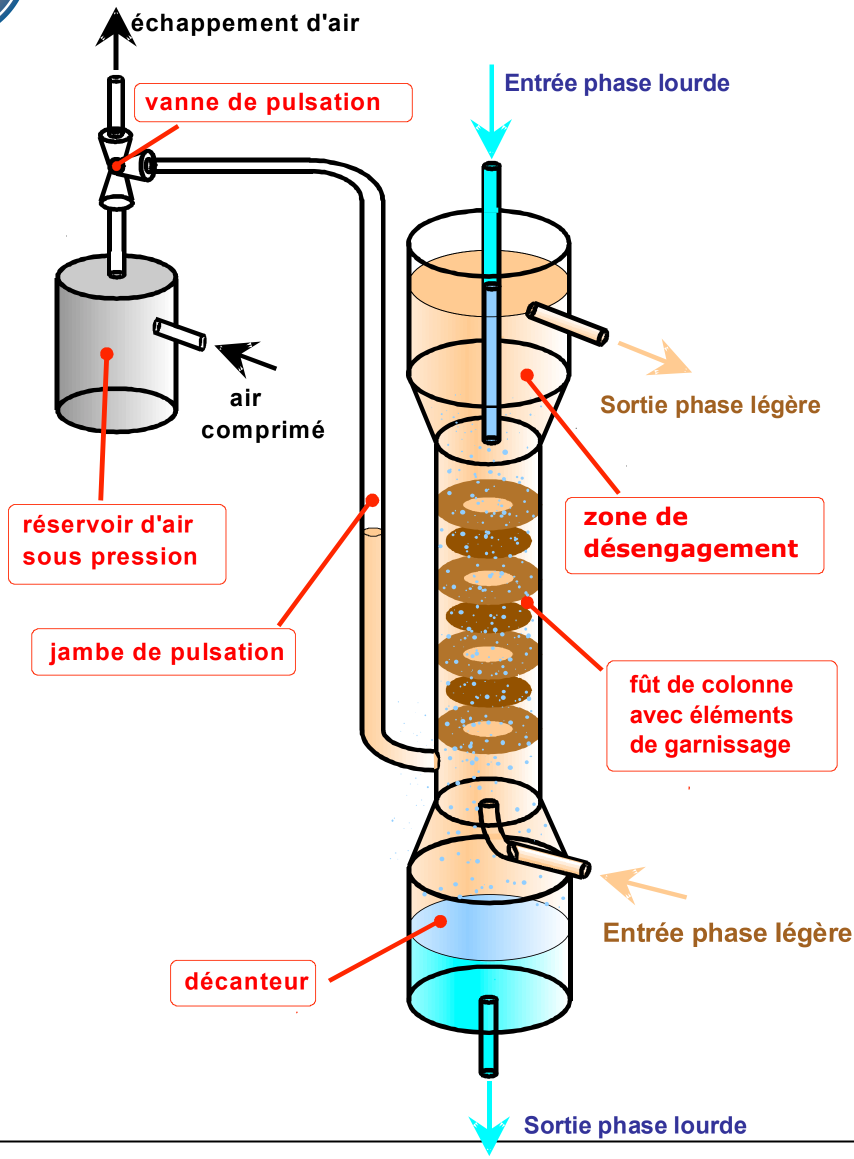
Trick > increase ϕ_A by partial reinjection of aqueous phase



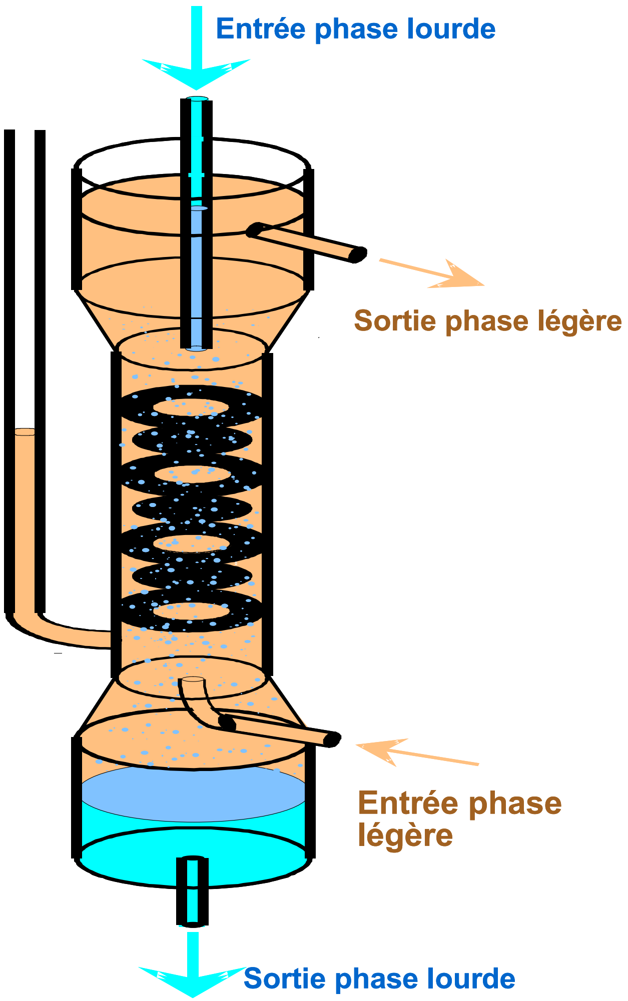
$\phi_A = (A+A_r)/(A+A_r+O)$

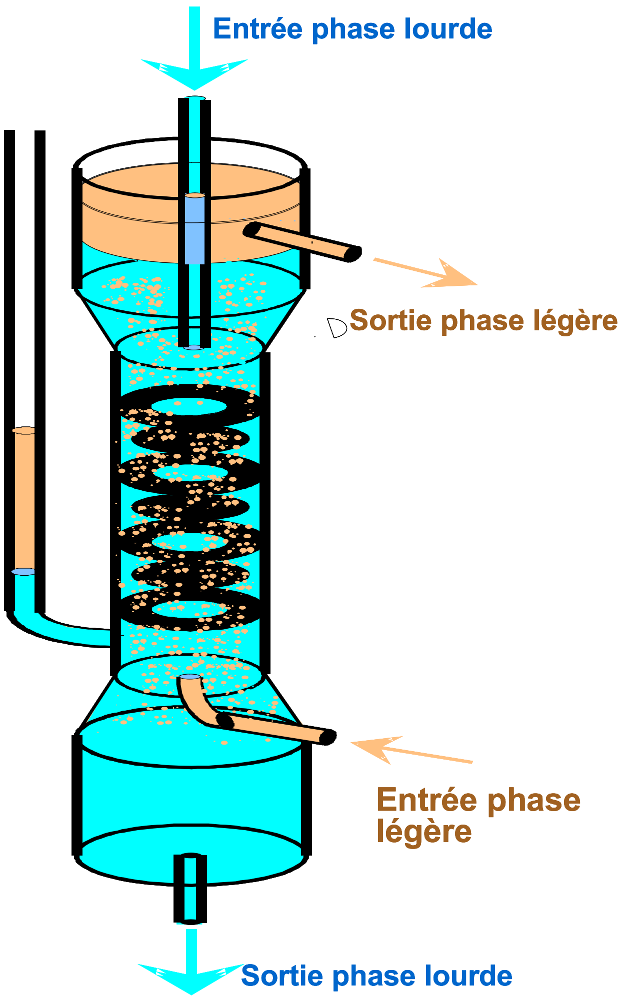
Same trick with organic phase if O<<A

1- pulsed columns



Pulsed columns : o/W or w/o exchange zone



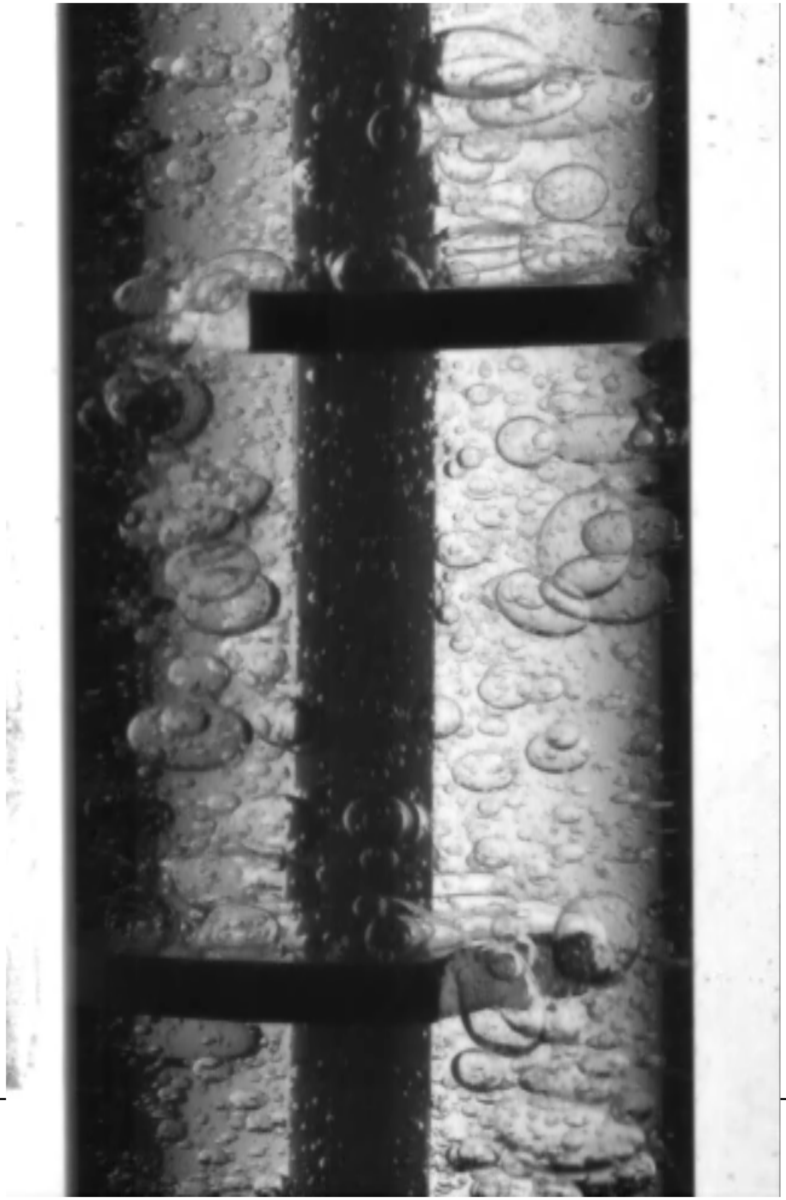


Emulsions filmed in a real column

Registering :1000 frames/s

View à 25 frames/s

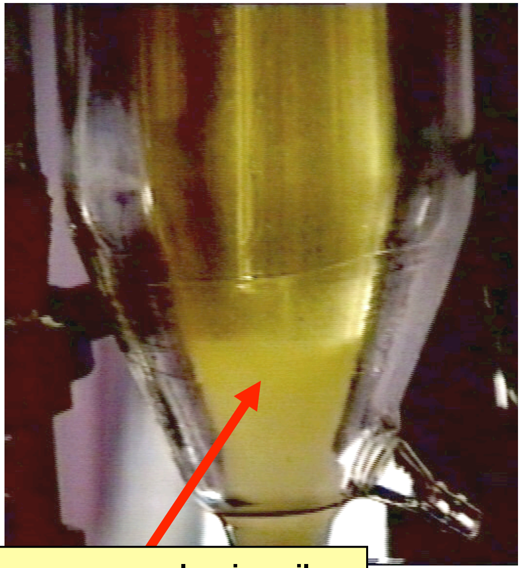
Pulsed columns 15 mm diameter



Useful quantities: order of magnitude

- **Density of the two coexisting phases**
- **Viscosity and viscosity ratio**
- **Interfacial tension (at rest)**

Engorgement d'une colonne pulsée

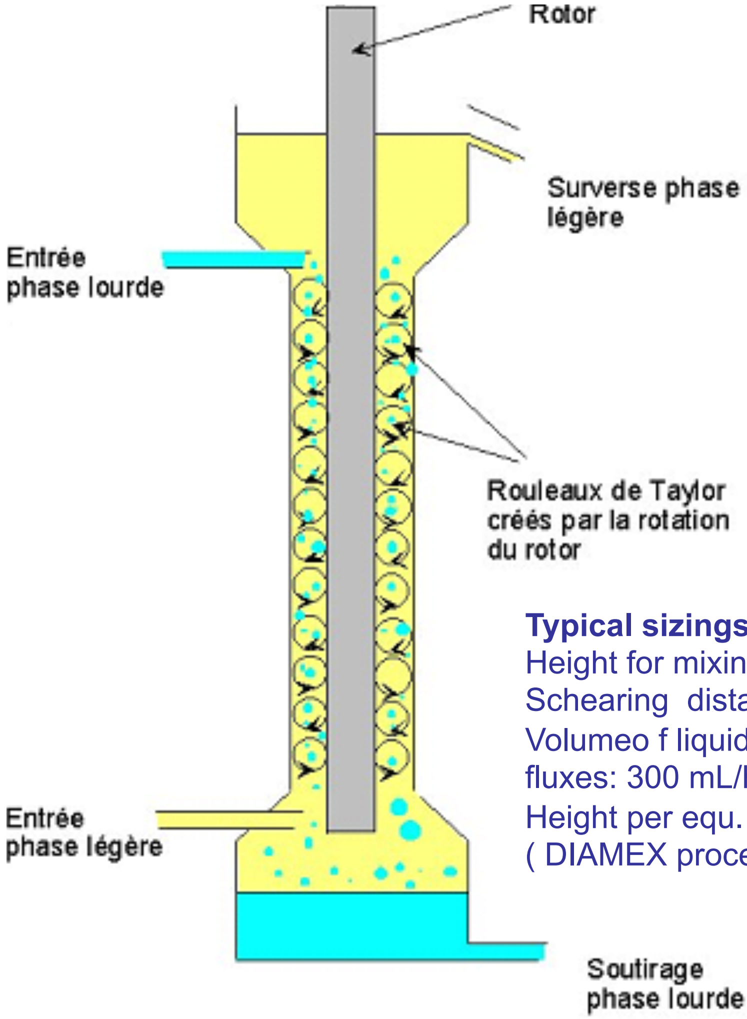


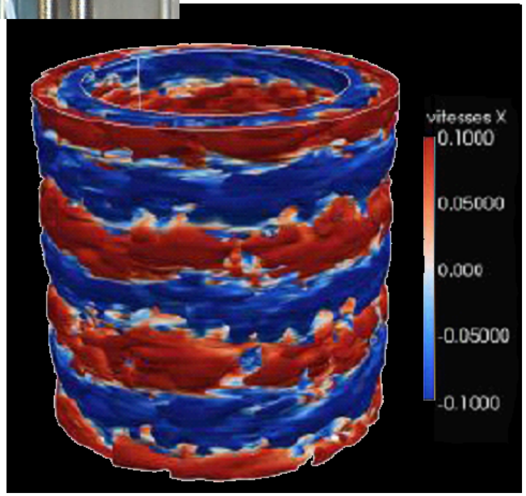
Excess non coalescing oil droplets….

Système de phases	Densité solvant		Viscosité solvant (mPa.s)		Tension interfaciale à 25 °C ($mN.m^{-1}$)
	20°C	25°C	20°C	25°C	
TBP 30%-TPH **HNO_3 2,4 M**		0,8459		1,85	10,4
DMDOHEMA 0,65M **HNO_3 3 M**	0,8354	0,8316	6,63	5,57	7,07
DMDOHEMA 0,5M-HDEHP 0,3 M **HNO_3 3 M**	0,8415	0,8378	6,20	5,25	8,21

2- Couette cells as separator

Working scheme

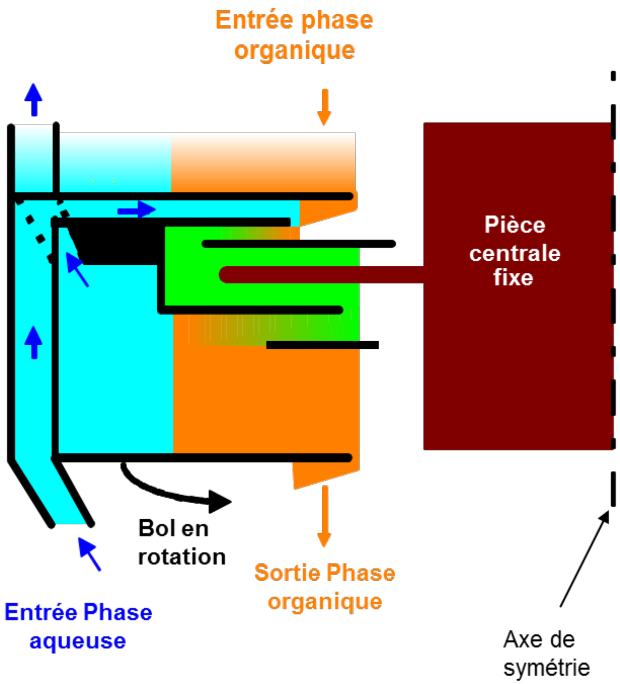


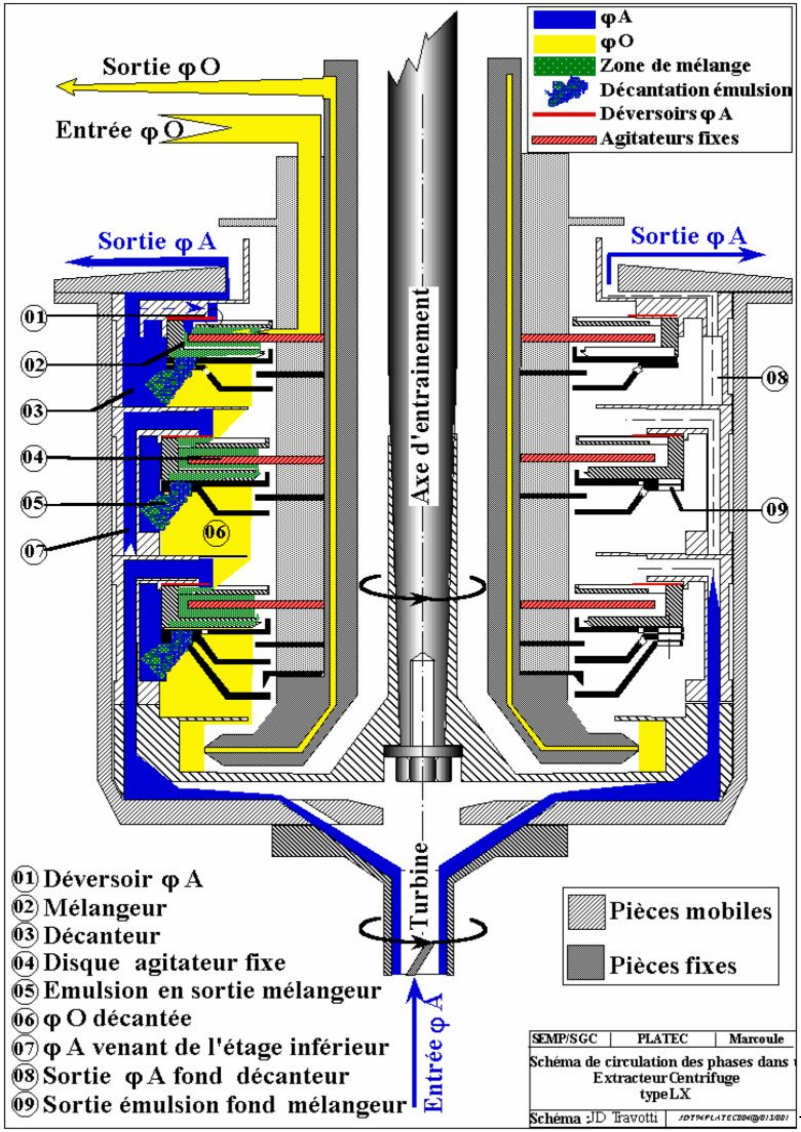


Typical sizings
Height for mixing: 50 à 75 cm
Schearing distance: 1,5 mm
Volumeo f liquid: 80 à 100 mL
fluxes: 300 mL/h (A+O)
Height per equ. stage : 5 cm
(DIAMEX process)

Equivalent to a pulsed column ten times higher

Multi-stage indutrial Couette extractor





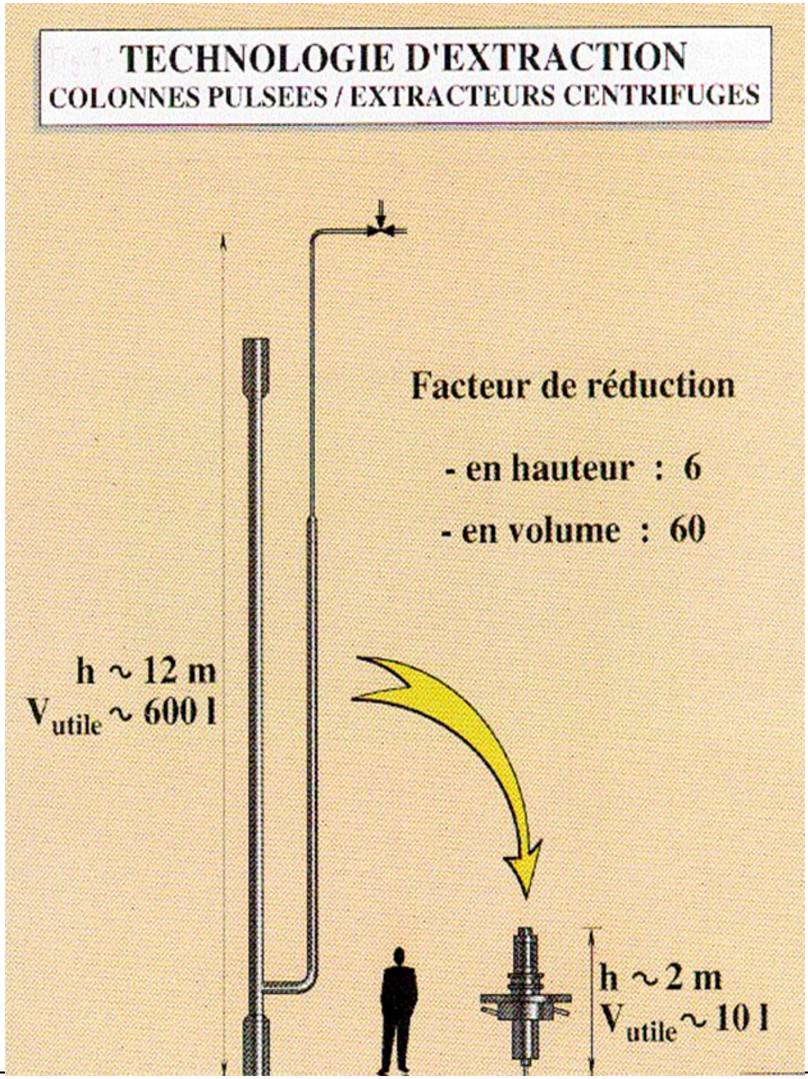
Comparison with pulsed columns

positive

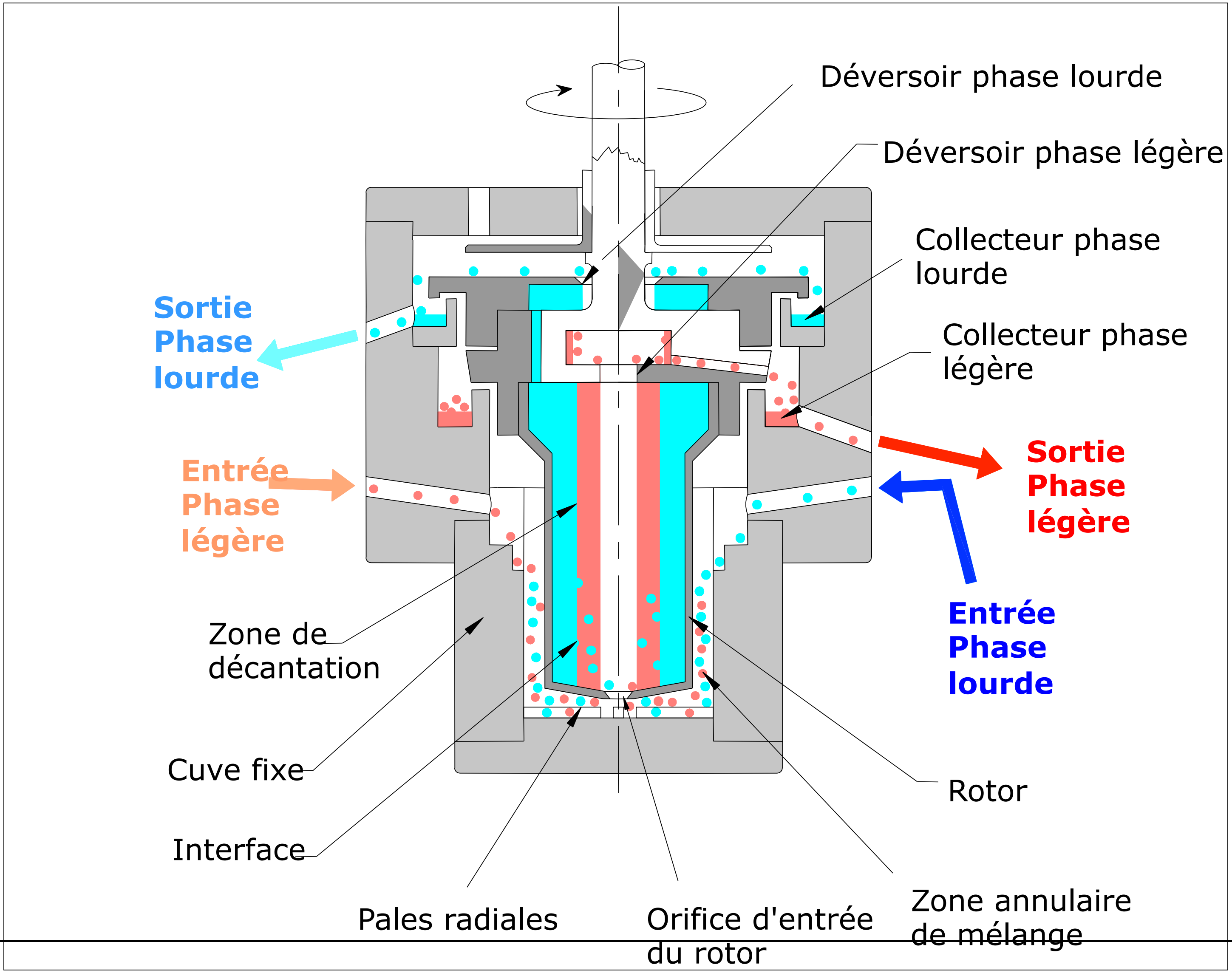
- Compacity
- Limitation of solvent radiolysis
- Low dosis: less fluid present
- Quick equilibration time

Negative

- O (and w) phase heating
- Fast evolution off spec. working
- Intolerance towards ppresence of particles
- Maintenance and emptying and refilling problems



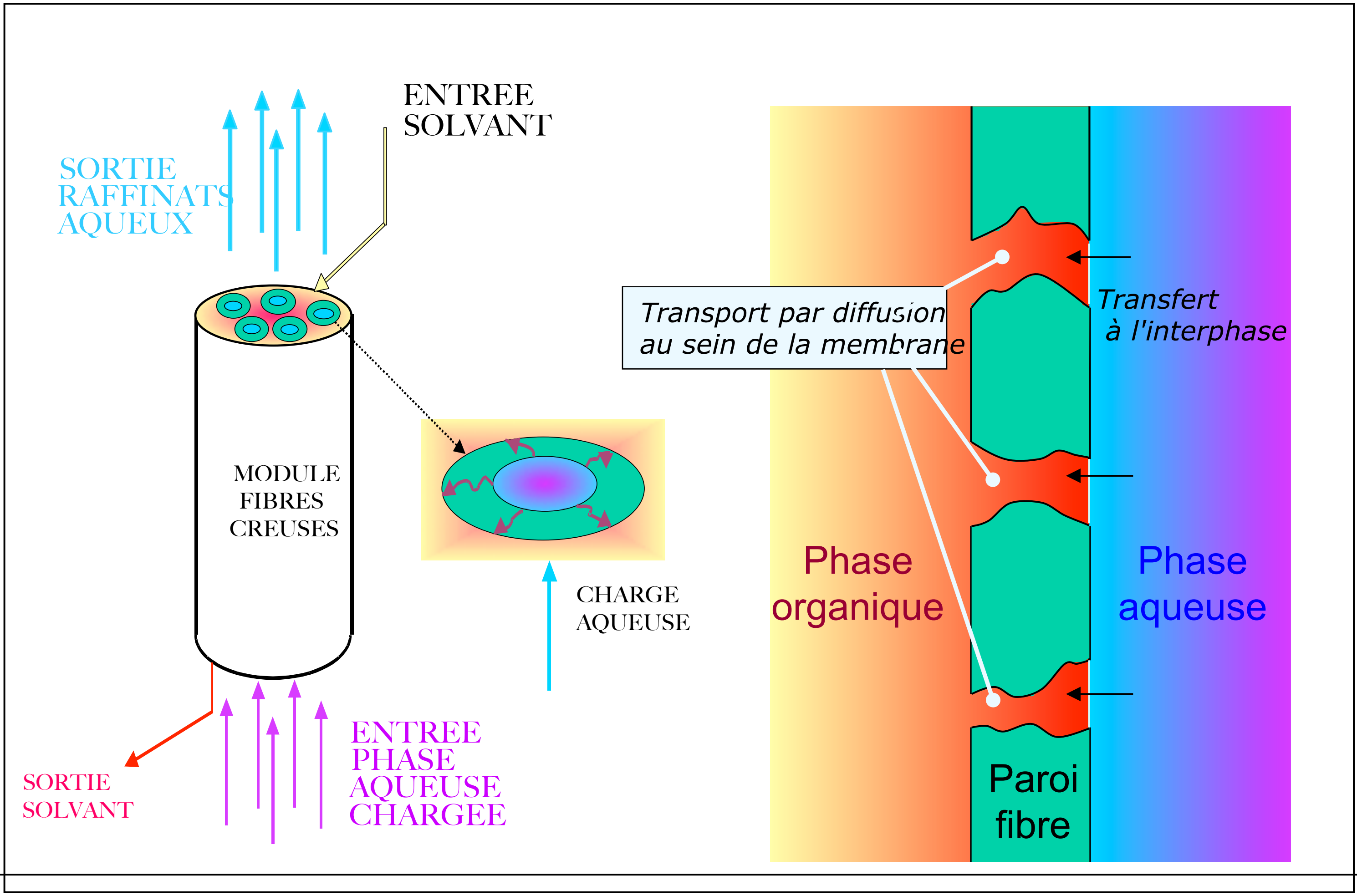
Centrifuge extractor designed for La Hague plant



Comparison Mixer/settler, Centrifuge, pulsed column

Device	Mixing time	Separation time	Droplet Diameter	Specific area
Mixer/settler	**~ 1 mn**	**~ 10 mn**	**~ 0,2 mm**	**15 000 m^2.m^{-3}**
Centrifuge Extracto rLX Robatel	**~ 1 s**	**~ 10 s**	**~ 0,05 mm**	**60 000 m^2.m^{-3}**
Colonne Pulsée	continuous Phase 40 mn	dispersed phase 10 mn	**~ 1 à 2 mm**	**400 à 900 m^2.m^{-3}**
Extracteur Centrifuge laboratoire	**1 s à 1 mn**	**3 s à 3 mn**	**~ 0,1 mm**	**30 000 m^2.m^{-3}**

A new combined method : pertraction…



Porous fibre extraction :

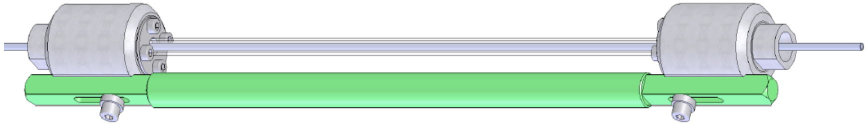
- Ideal for
  - spontneaousły emulsifying systems (low interfacial tension)
  - Solvents of high viscosity
  - No influence of density difference
- Possibilité to use solvent-free systems (or extrcatant-free systems)
- Simple to operate
- Up-scaling easy

Example using polypropylene fibre

CCharacteristics

Property		Unit
DiamInternal diameter	1,8	mm
Thisckness	400	nm
Length	23	cm
Porosity	75-80	%
Pore diameter	200	nm
Calender diameter	4,5	mm
Airea of contact	1,3 x 10^{-3}	m²

Typicla fluxes treated : 1 à 10 $mL.h^{-1}$



Industrial scale pertraction

Exchange area: 220 m^2

Liquid voume *inside* fibers : 21,7 L

Liquid voume *outside* fibers : 33,5 L

Typically 100 000 fibres with 300 µm diameter