

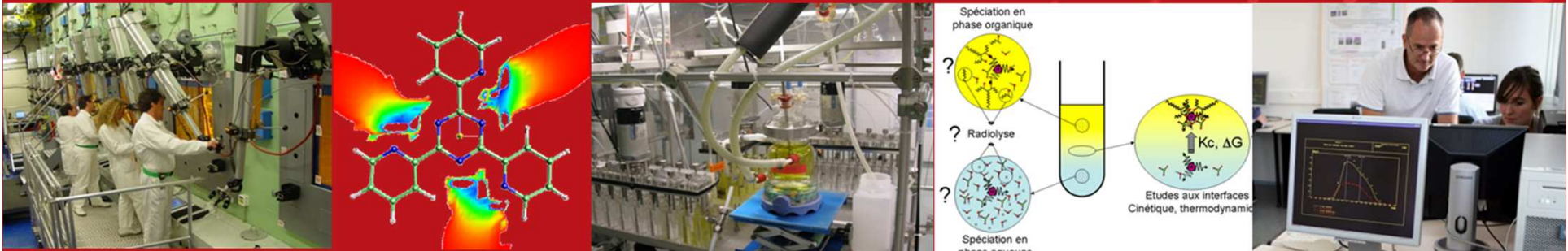
First INSPYRE School, May 13-17, 2019
" Generation IV reactors fuel cycle "



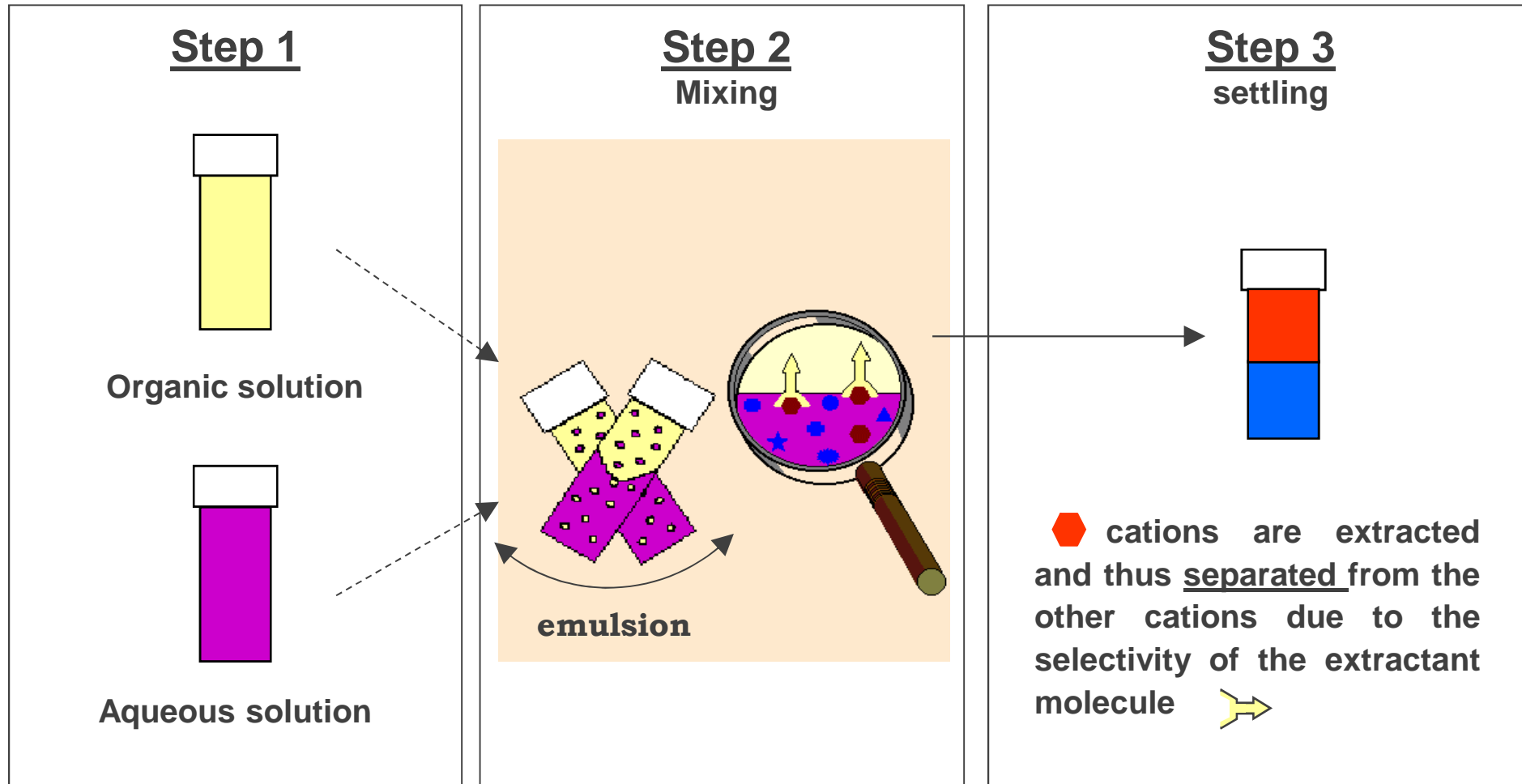
SOLVENT EXTRACTION PROCESS MODELLING

Binh DINH

May, 15th, 2019 - Delft



Commissariat à l'énergie atomique et aux énergies alternatives - www.cea.fr



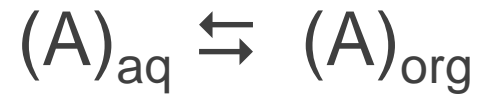
	<p>Extracting molecule</p> <p>Metallic cations</p>
--	--

$$D(\text{or } K_D) = \frac{[\bar{M}]_{\text{org}}}{[M]_{\text{aq}}}$$

(all organic species)

$$D_M = \frac{[\bar{M}] + [\overline{\text{complex1}}] + [\overline{\text{complex2}}] + \dots}{[M] + [\text{complex1}] + [\text{complex2}] + \dots}$$

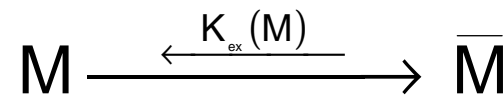
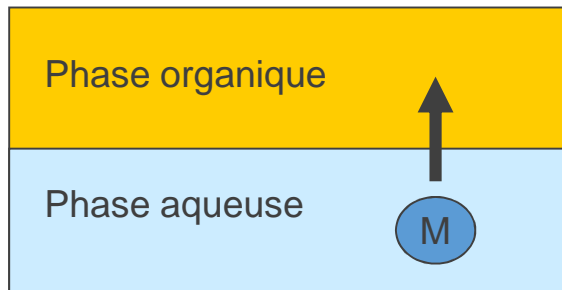
(all aqueous species)



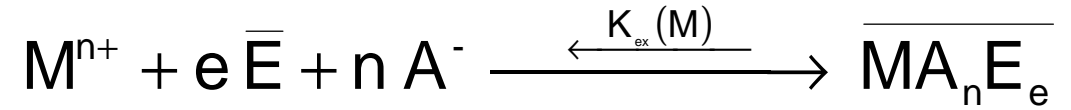
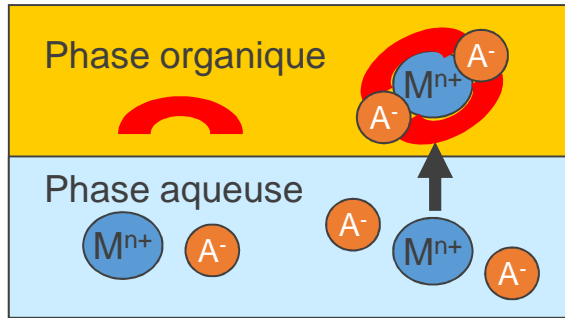
Very diverse mechanisms:

- Passive extraction
- Solvation (complexes)
- Ion exchange (anions, cations)
- Chelation

- ◆ « **Passive extraction** », solvation of a lipophilic compound in the organic phase

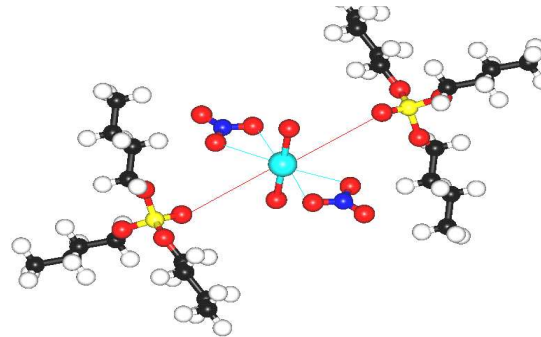


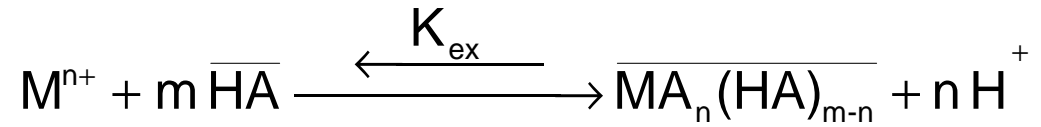
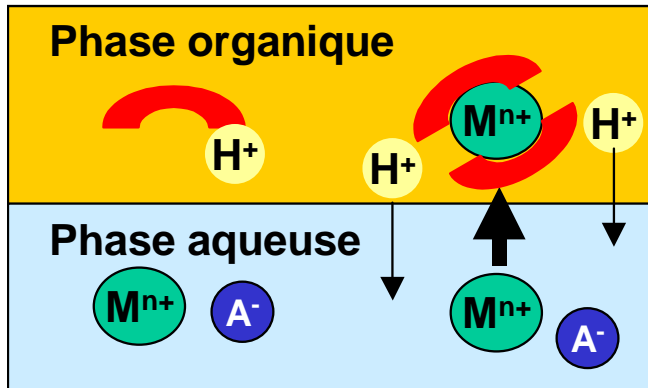
– *Iodine in the system: water/CCl₄*



$$K_{ex}(M) = \frac{[\overline{MA_n E_e}]}{[M^{n+}] \cdot [\bar{E}]^e \cdot [A^-]^n} = \frac{D_M}{[\bar{E}]^e \cdot [A^-]^n}$$

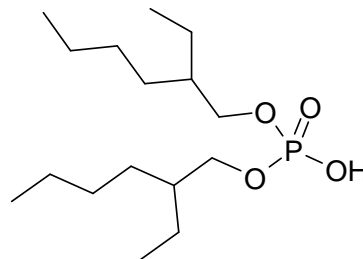
Extraction of uranyl nitrate
by TBP



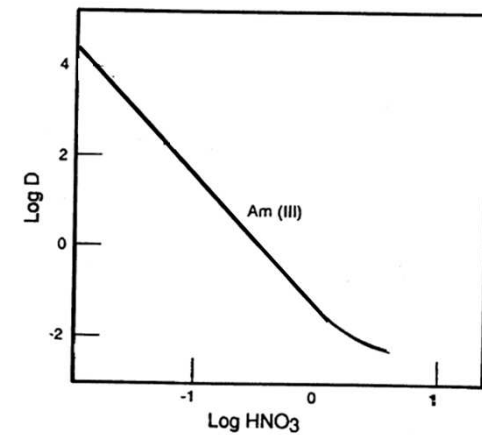


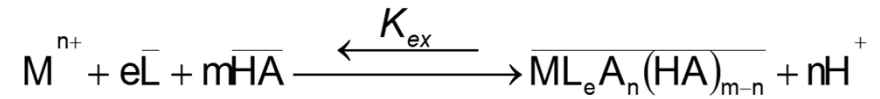
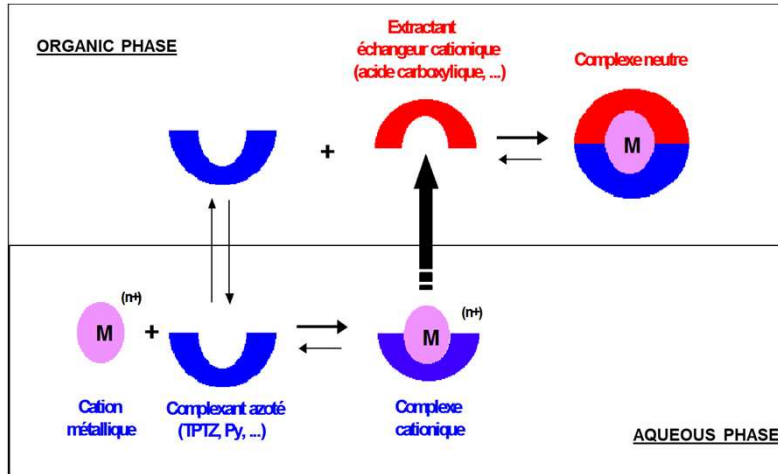
$$K_{ex} = \frac{[\overline{MA_n(HA)_{m-n}}][H^+]^n}{[M^{n+}][\overline{HA}]^m} = \frac{D_M \cdot [H^+]^n}{[\overline{HA}]^m}$$

— Example : Am^{3+} extraction by HDEHP



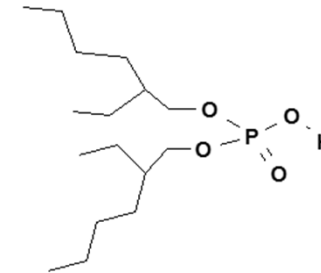
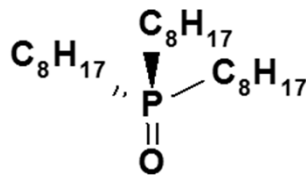
HDEHP

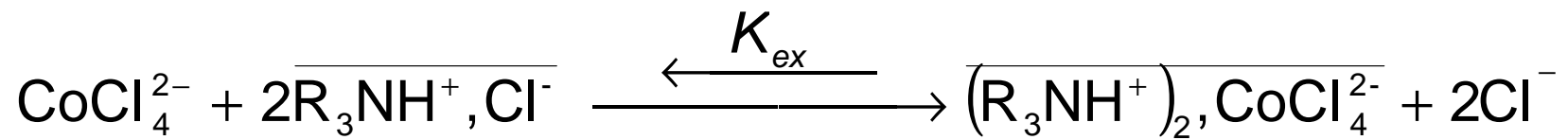
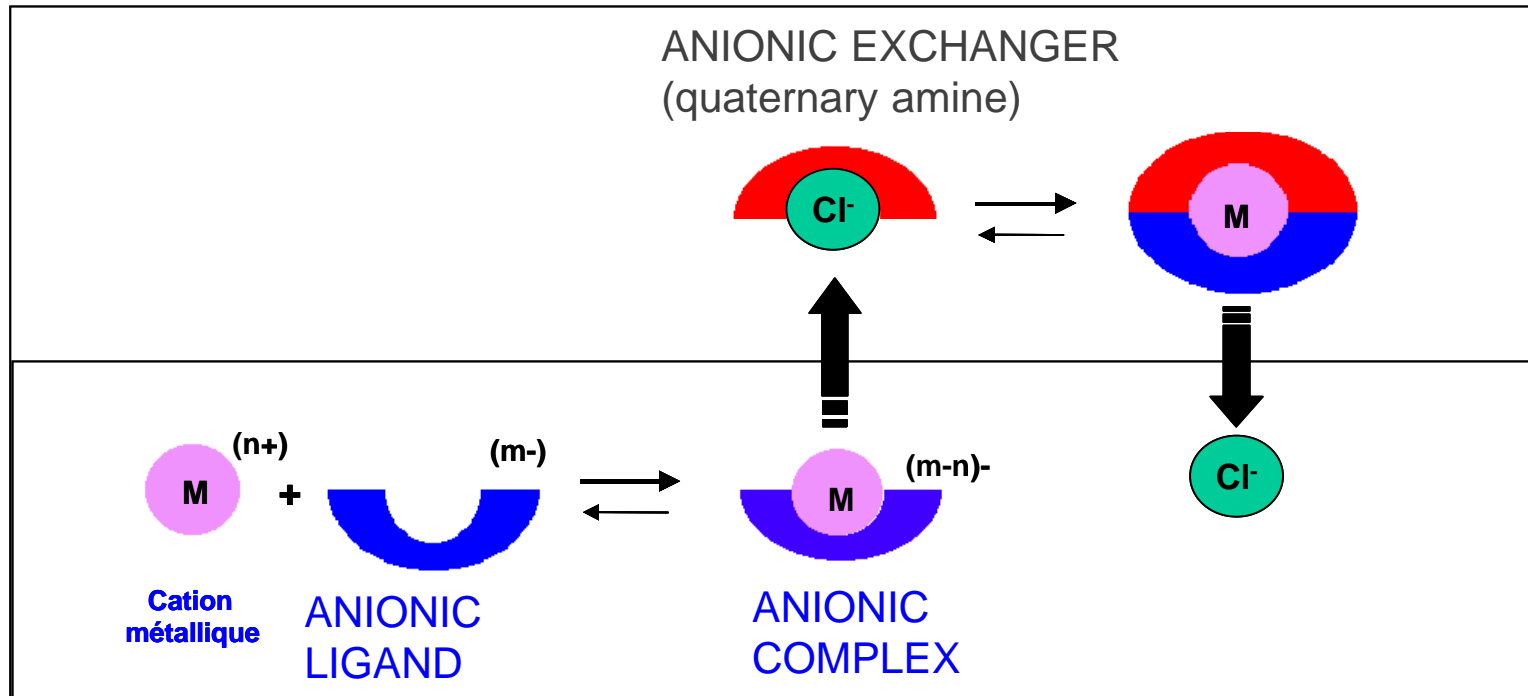


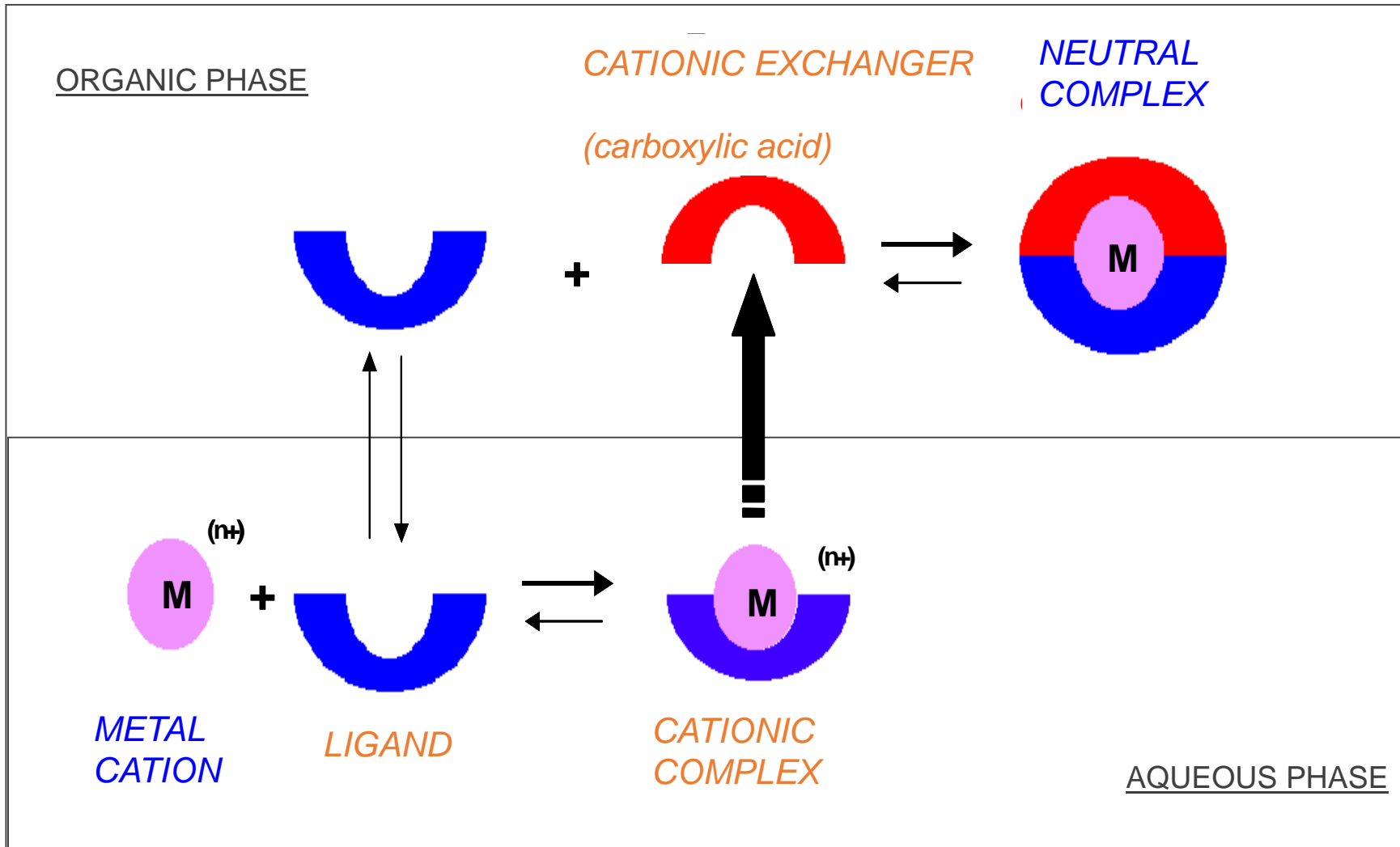


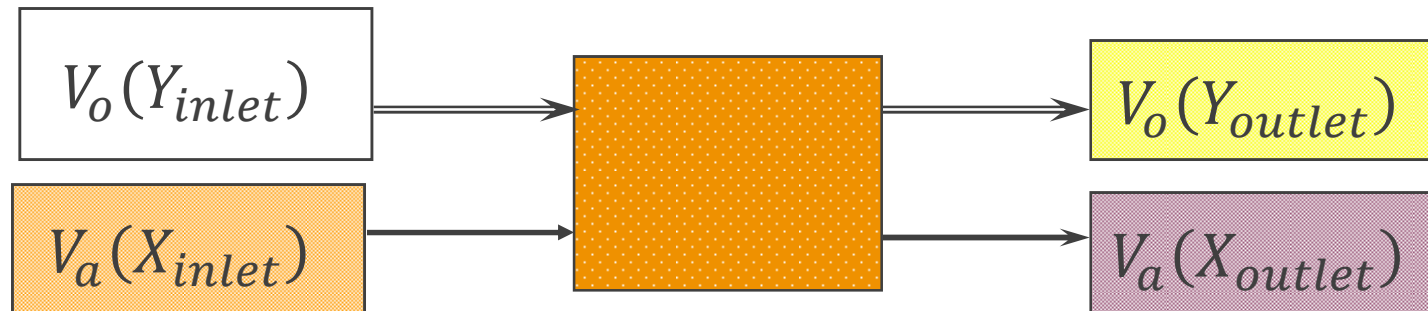
$$K_{ex} = \frac{[\overline{ML_e A_n (HA)_{m-n}}][H^+]^n}{[M^{n+}][HA]^m \cdot [L^-]^e} = \frac{D_M \cdot [H^+]^n}{[HA]^m \cdot [L^-]^e}$$

- **ex: UO₂²⁺ extraction by TOPO/HDEHP**









- Definition :
 - Outlet phases at thermodynamical equilibrium
 - Outlet phases perfectly separated
- Basic equations :
 - Thermodynamic equilibrium : $Y_{outlet} = D \cdot X_{outlet}$
 - Mass balance : $V_a(X_{inlet} - X_{outlet}) = V_o(Y_{outlet} - Y_{inlet})$

$$\frac{X_{inlet}}{X_{outlet}} = 1 + E \quad \text{with} \quad E = \frac{V_o}{V_a} D \quad (\text{extraction factor})$$

(1) HIGH THROUGHPUTS



CONTINUOUS OPERATIONS

(2) HIGH RECOVERY(PURIFICATION) YIELDS

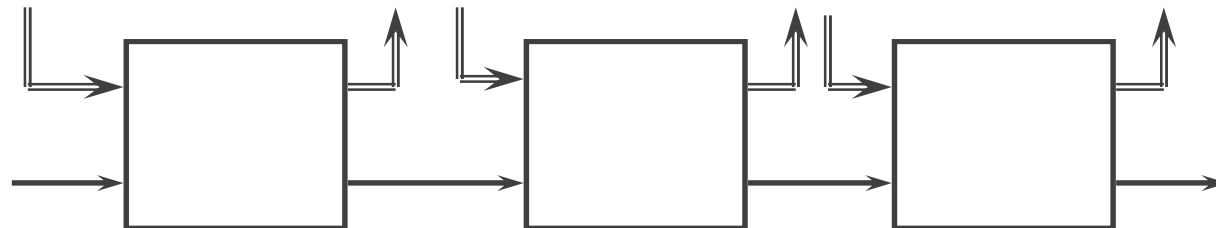


REPEATED OPERATIONS

Co-current flow : inefficient

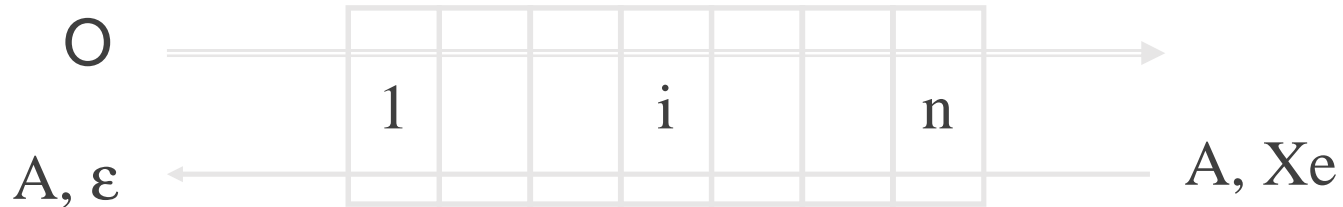


Cross-flow: inefficient use of solvent



Counter-current : efficient





$$\frac{X_{\text{inlet}}}{\mathcal{E}_{\text{residue}}} = \frac{E^{n+1} - 1}{E - 1}$$

with

$$E = \frac{O}{A} \cdot D$$

Ex: $D=10$, $O=A$, $n= 1$, residue fraction = $1/10$

2

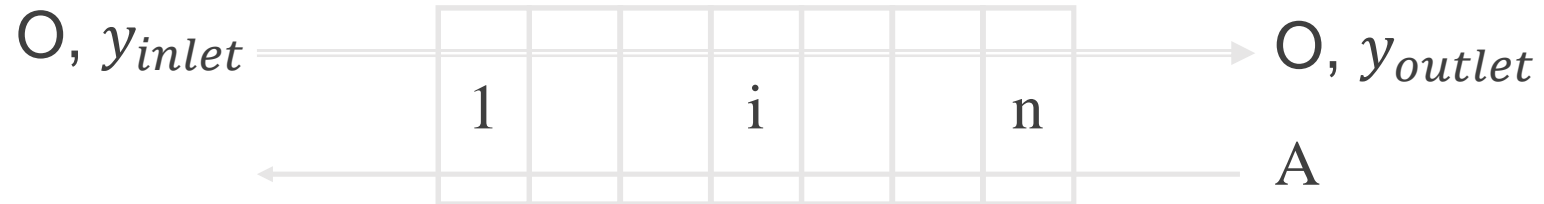
$1/100$

3

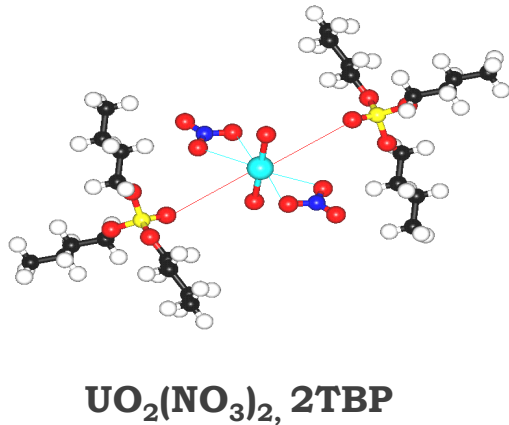
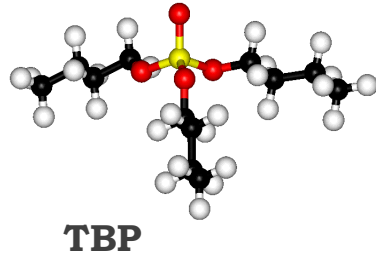
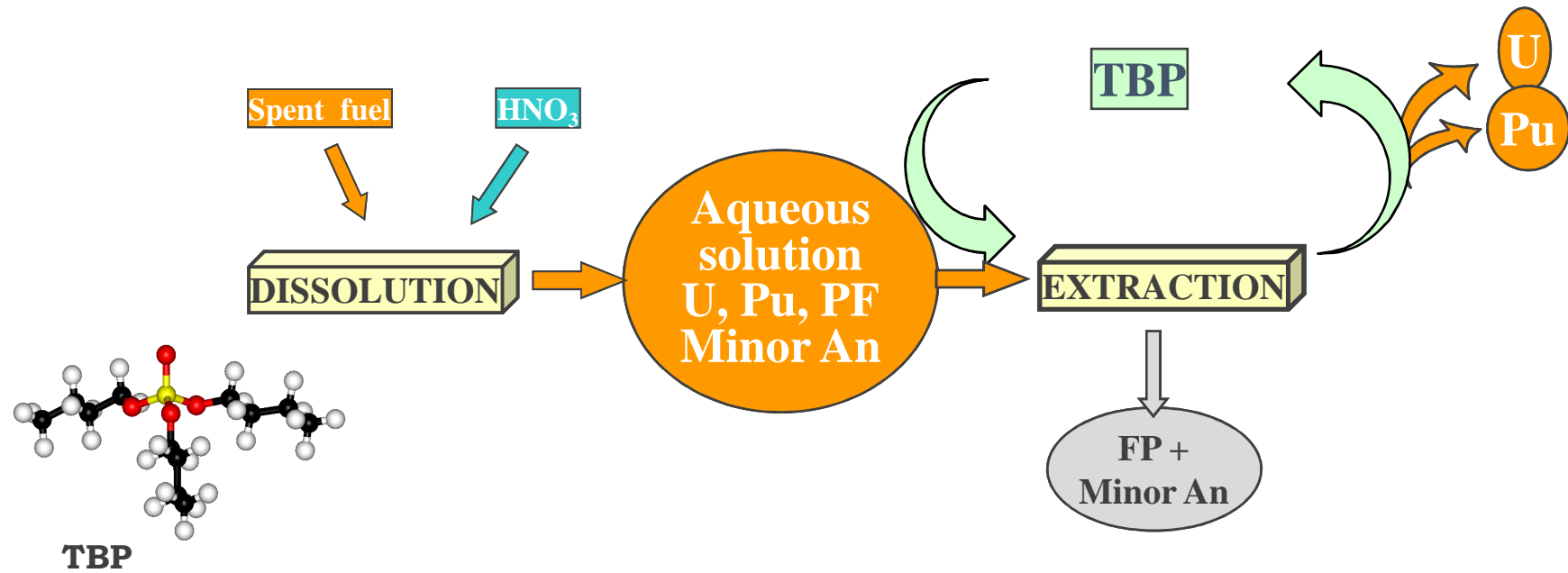
$1/1000$

...

....



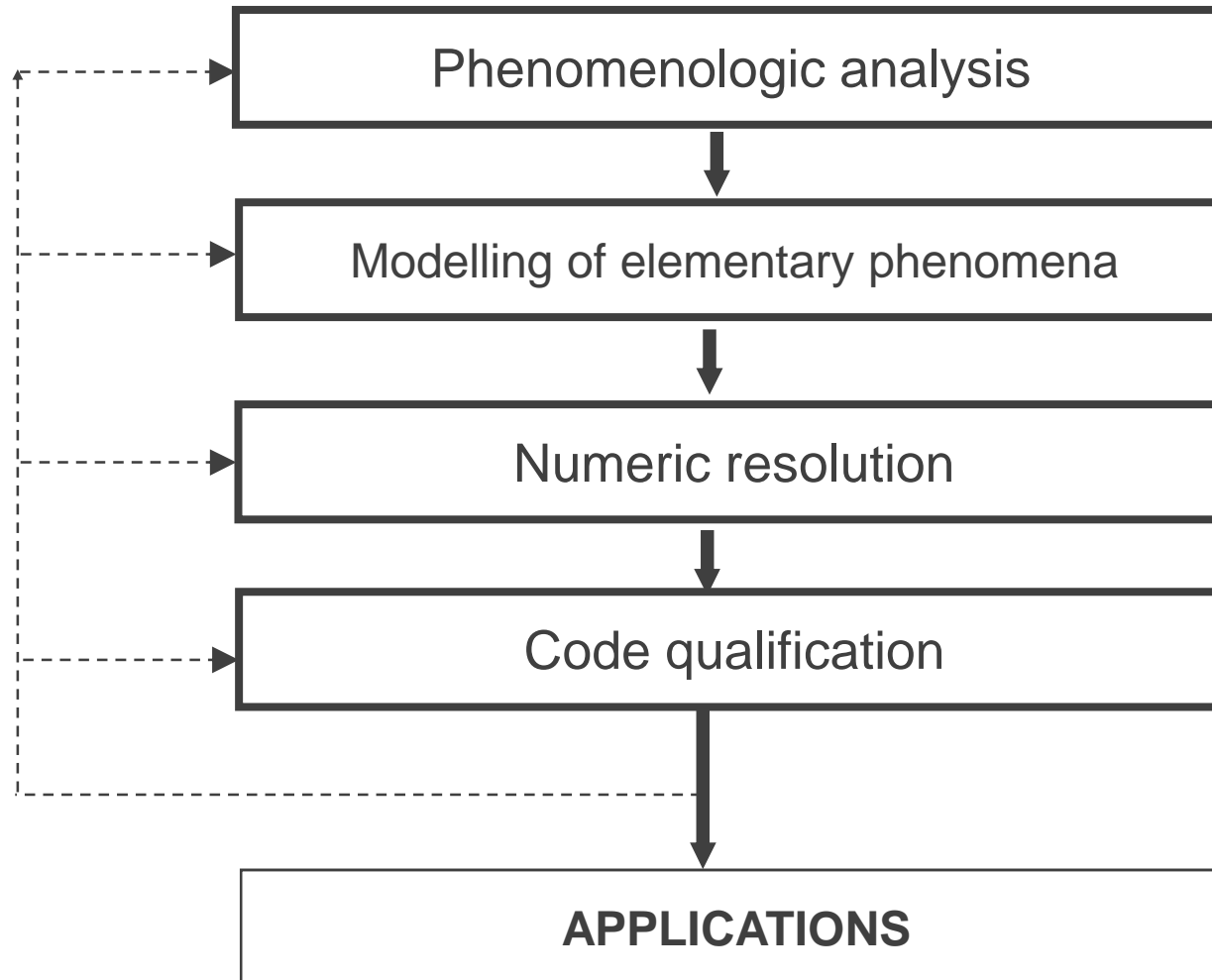
$$\frac{y_{inlet}}{y_{outlet}} = \frac{RE^{n+1} - 1}{RE - 1} \quad \text{with} \quad RE = \frac{A}{OD}$$



The PAREX code is a simulator of PUREX extraction operation.

It was used for

- the design / optimization of purification cycles flowsheet of the La Hague plant,
- the industrial implementation of PUREX process



An iterative approach, Based on modelling and appropriate data acquisition

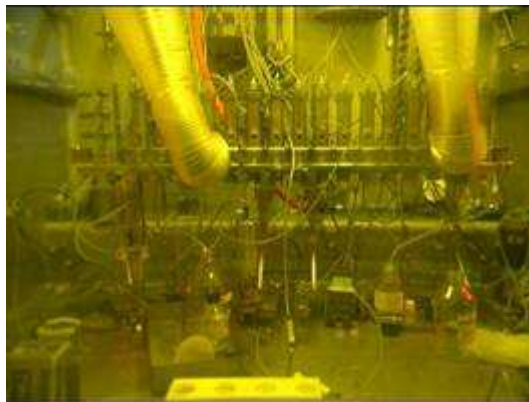
Applied laboratory experiment



Apparatus studies



Flow sheet experiment

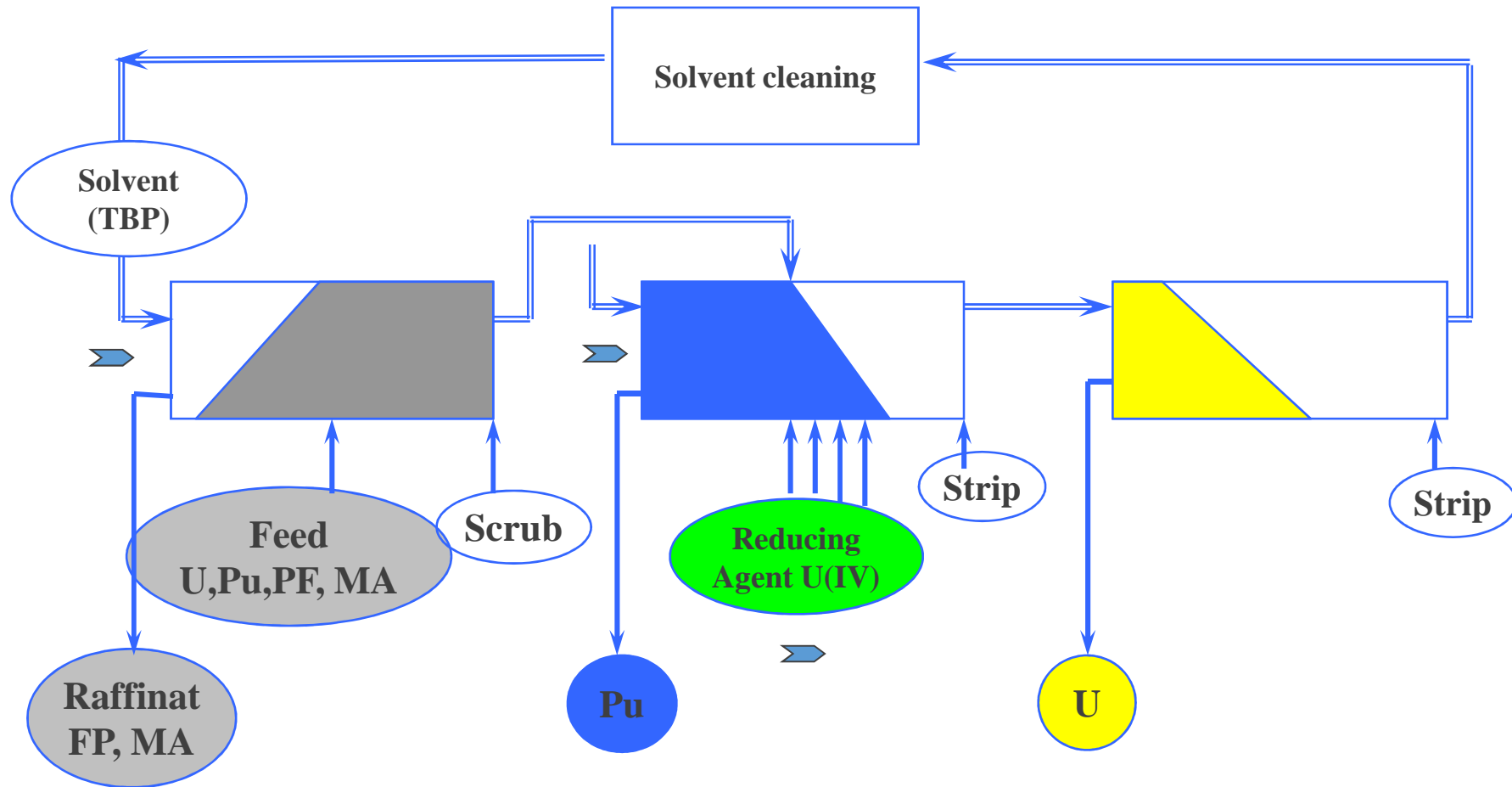


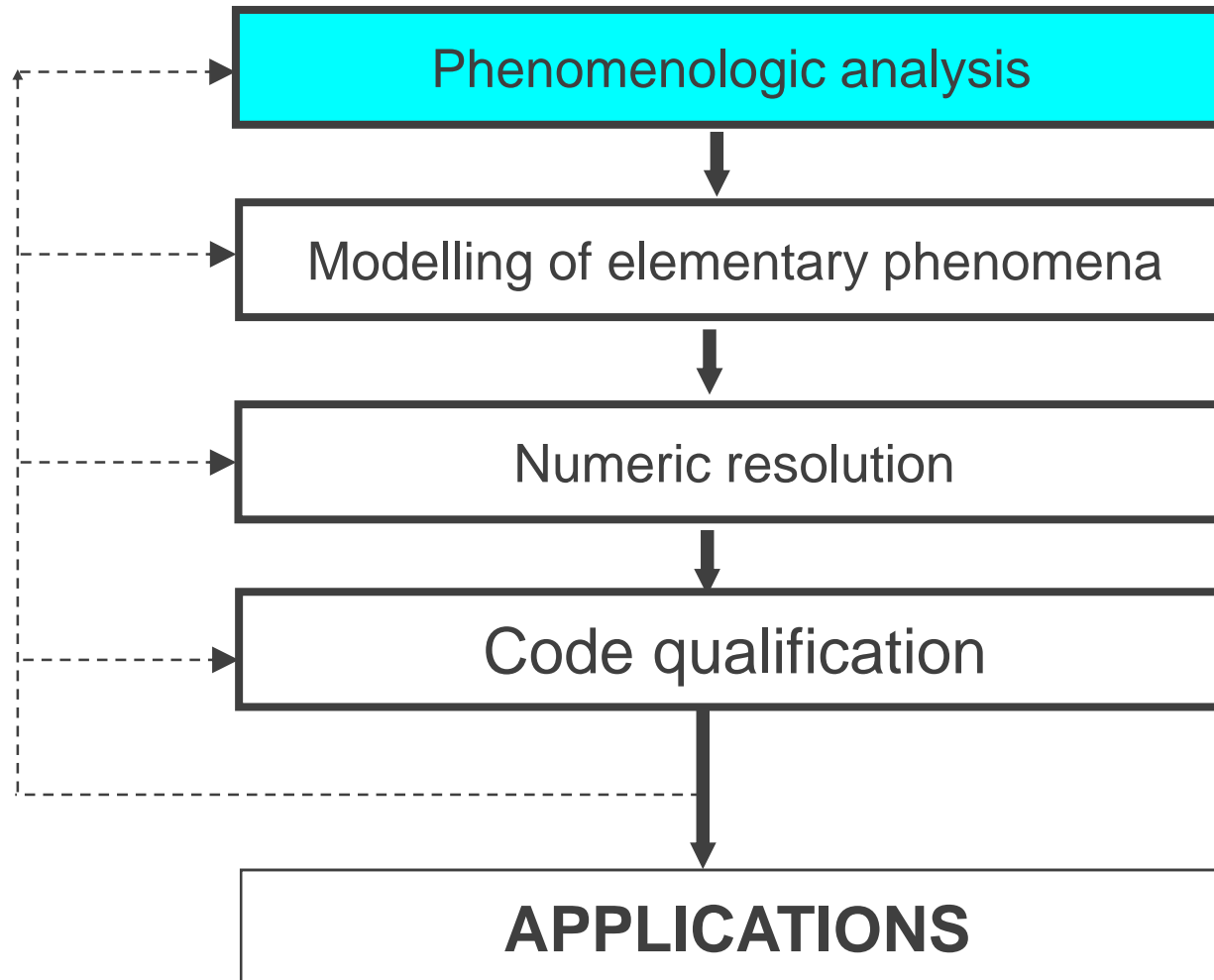
Process design

Facility operation analysis



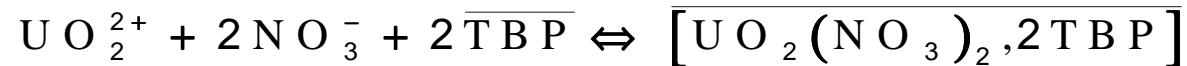
Tools for
plant operation aid





- Species distribution
(thermodynamic of extraction equilibrium)
$$M^{n+} + n.NO_3^- + x.TBP \Leftrightarrow M(NO_3)_n \cdot xTBP$$
- Mass transfer kinetics
 - Diffusion of species in phases, solvation kinetics at the interface
- Redox reaction kinetics
 - For U/Pu splitting operation (Pu(IV) reduction, ...)
- Contactor characteristic
 - Hydrodynamic characteristics affecting mass transfer efficiency
- Thermal release
 - Enthalpy of chemical reactions,
 - Thermal exchange with the surroundings

◆ Extraction mechanism



◆ Mass action law

$$K = \frac{\overline{\text{UO}_2(\text{NO}_3)_2, 2\text{TBP}} \cdot \gamma_{\overline{\text{UO}_2(\text{NO}_3)_2, 2\text{TBP}}}}{(\text{UO}_2^{2+})(\text{NO}_3^-)^2 (\overline{\text{TBP}})^2 \cdot \gamma_{(\text{UO}_2^{2+})}^2 \gamma_{(\text{NO}_3^-)}^2 \gamma_{(\overline{\text{TBP}})}^2}$$

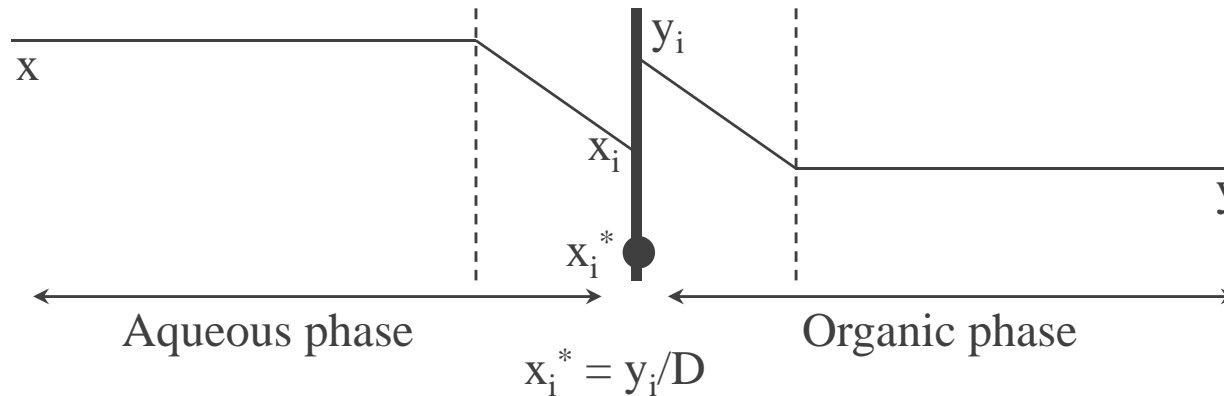
◆ Model

$$K_{\text{app}}(\text{NO}_3^-) = \frac{[\overline{\text{UO}_2(\text{NO}_3)_2, 2\text{TBP}}]}{[\text{UO}_2^{2+}][\overline{\text{TBP}}]^2}$$

avec $K_{\text{app}}(\text{NO}_3^-) = 6,8 \cdot [\text{NO}_3^-]^{1,5} + 3,7 \cdot [\text{NO}_3^-]^{3,4}$

Remarque: [] signifie concentrations en mole/litre de solvant libre





◆ Etapes du transfert

- Aqueous phase transport (diffusion in boundary layer)
- interfaciale reaction (réaction chimique de transfert)
- Organic phase transport (diffusion in boundary layer)

◆ Phenomenologic law

$$\Phi = K_x (x - x^*) = k_x (x - x_i) = k_e (x_i - x_i^*) = k_y (y_i - y)$$

$$1/K_x = 1/k_x + 1/k_e + 1/(D \cdot k_y)$$

MAIN REDOX REACTIONS

- ◆ **Functional reaction : Pu(IV) reduction**



- ◆ **Interferent reaction : Pu(III) oxydation**



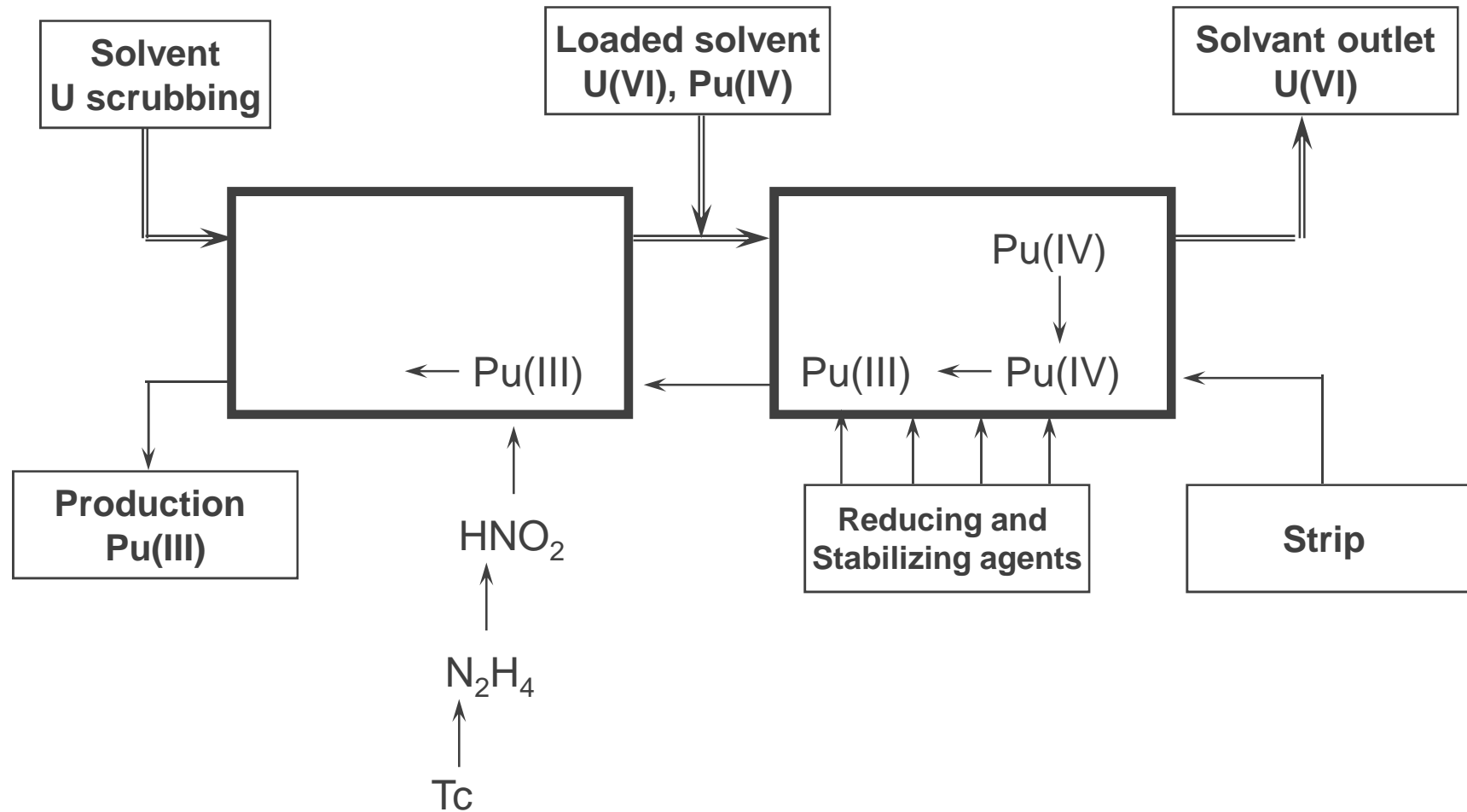
- ◆ **Stabilizing reaction : HNO₂ scavenging**

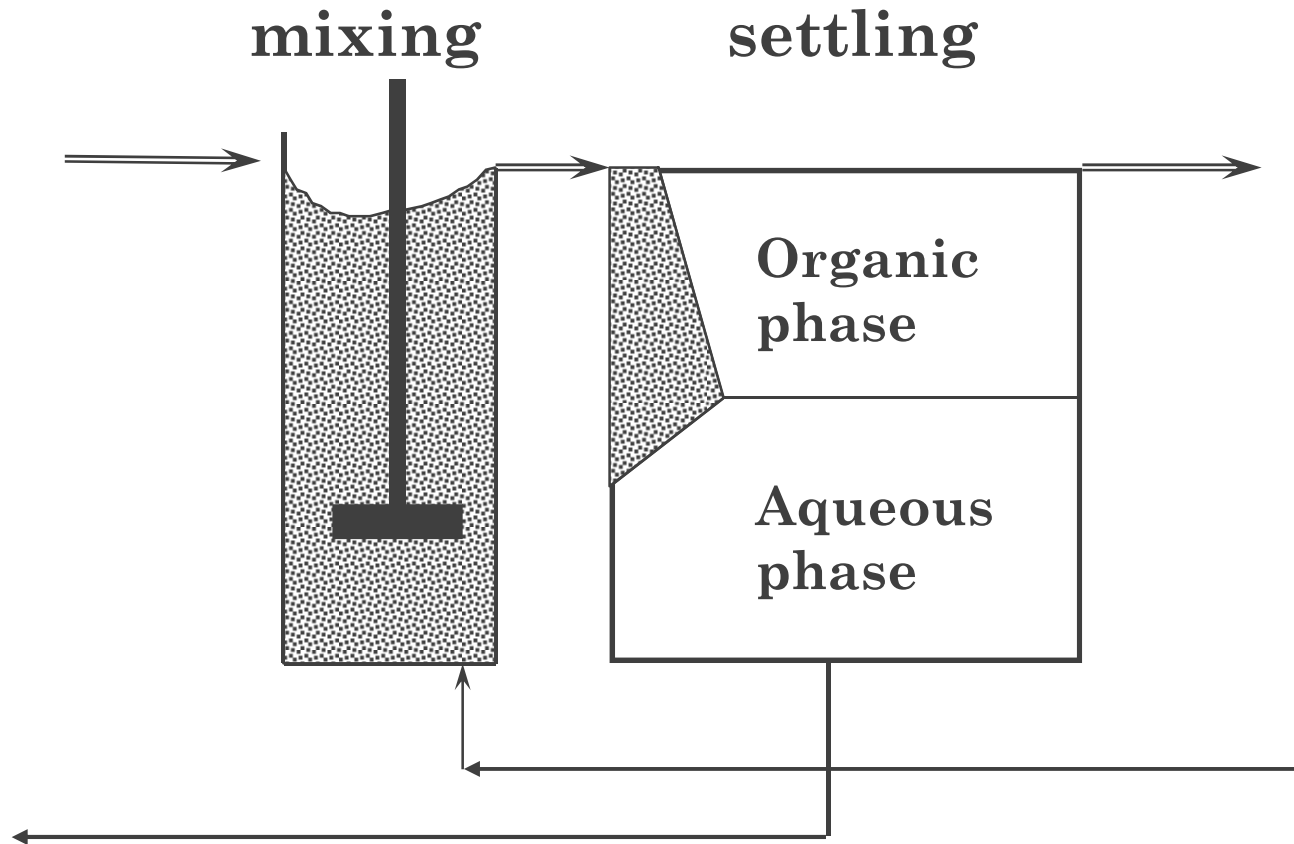


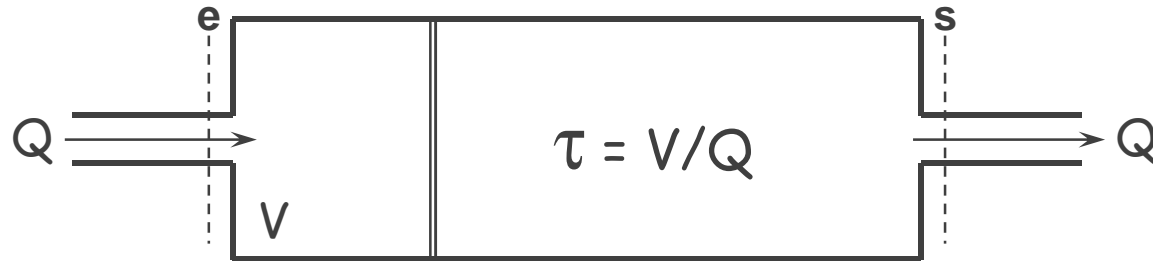
- ◆ **Interference sides reactions : Hydrazine consumption**



U/Pu splitting



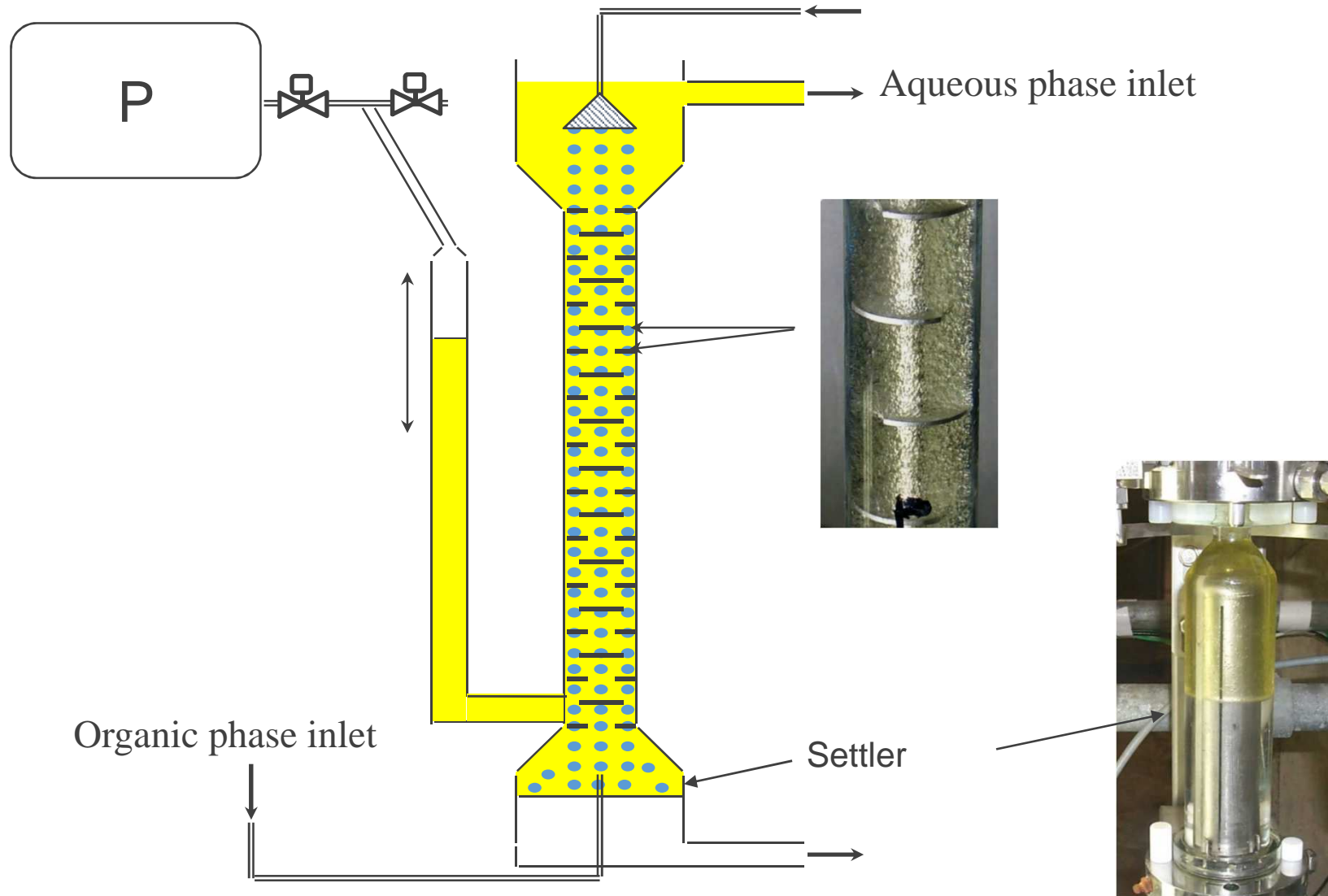




characterised by

- τ Mean residence time (dead volumes, short morts , short circuit ...)
- residence time distribution (DTS)

Plug flow model	Perfectly mixed
$C_s(t) = C_e(t-\tau)$ pur lag τ	$C_s(t) = c_0 \cdot \exp(-t/\tau)$
Complex digital treatment	Easily digital solved



Origin

Flow non idealities (deviation from plug flow)

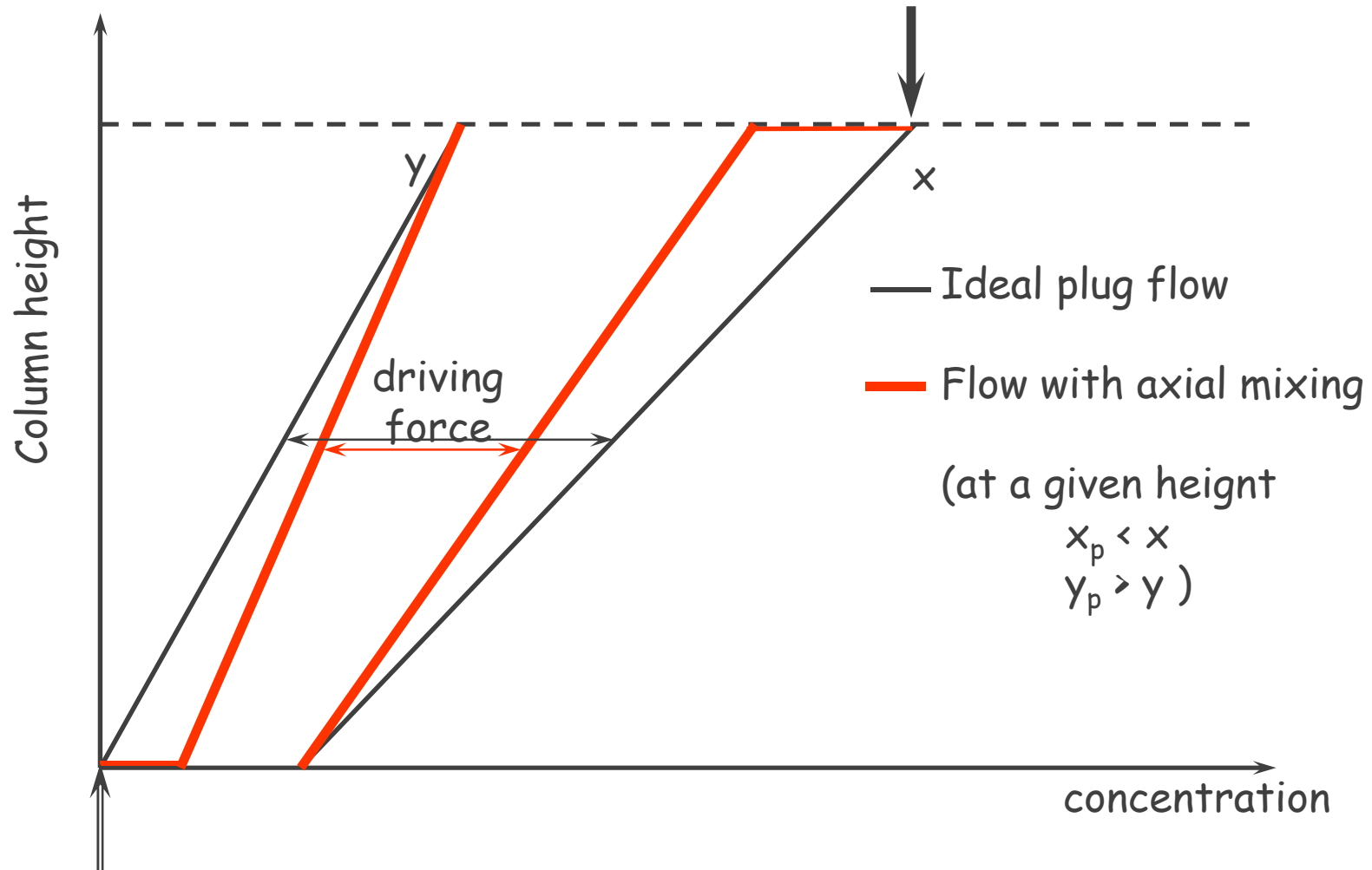
- Convective currents
- Droplet velocity distribution

Effects

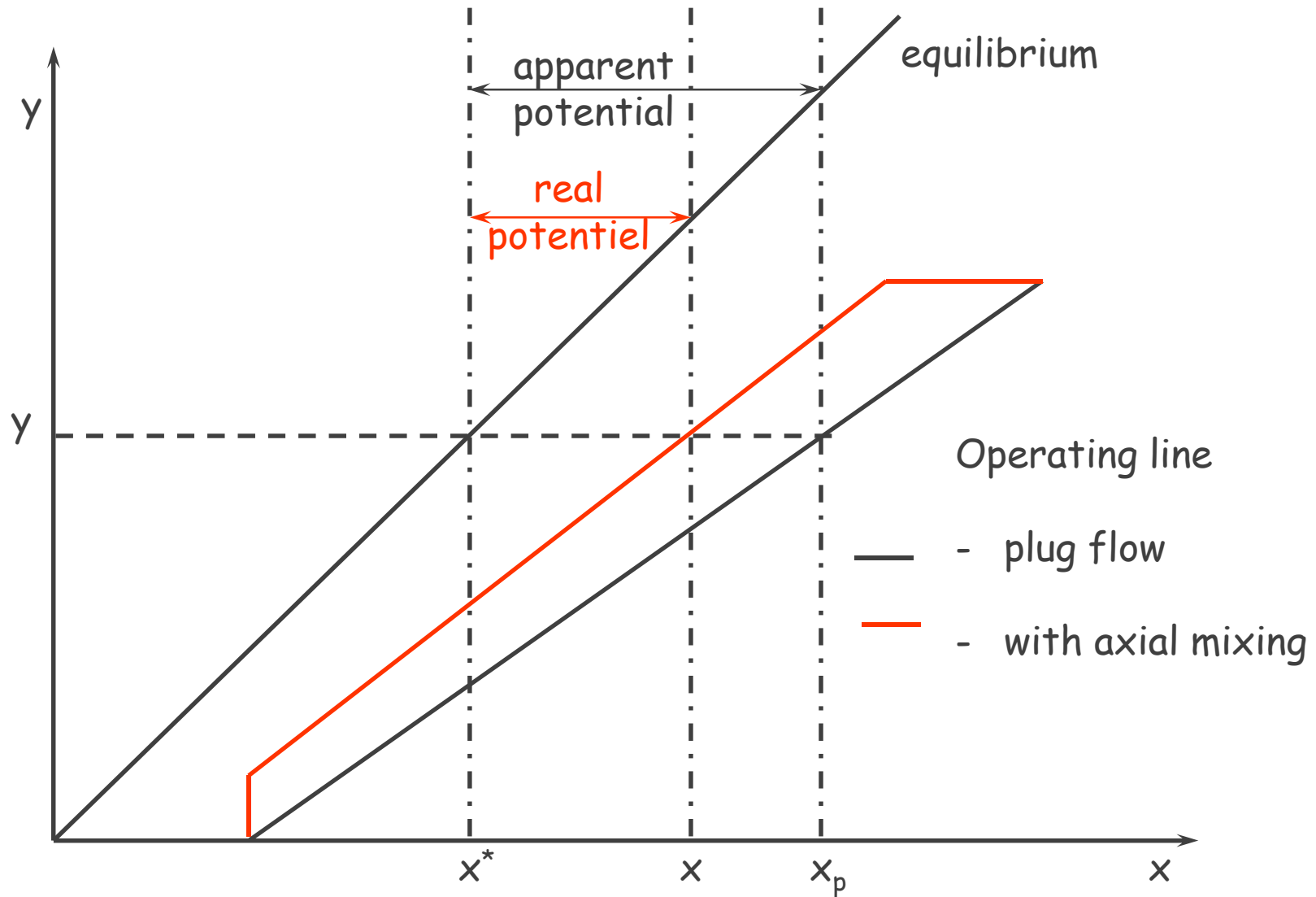
- Phase inlet concentration jump
- Reduction of concentration gradient
- Mass transfer potential lessened
- Lower specific mass flow transferred

Acuteness

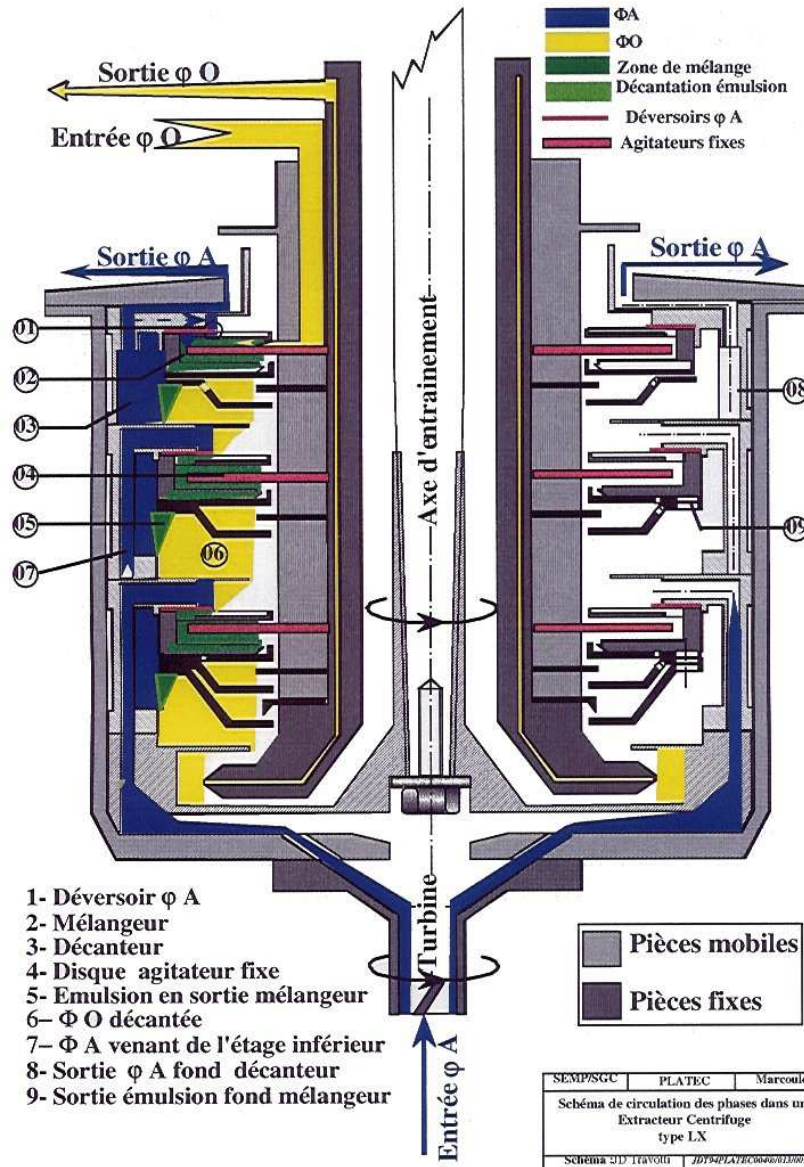
- Operations conditions dependant
(agitation intensity / specific flowrate)



AXIAL MIXING EFFECT ON MAC CABE & THIELE CHART

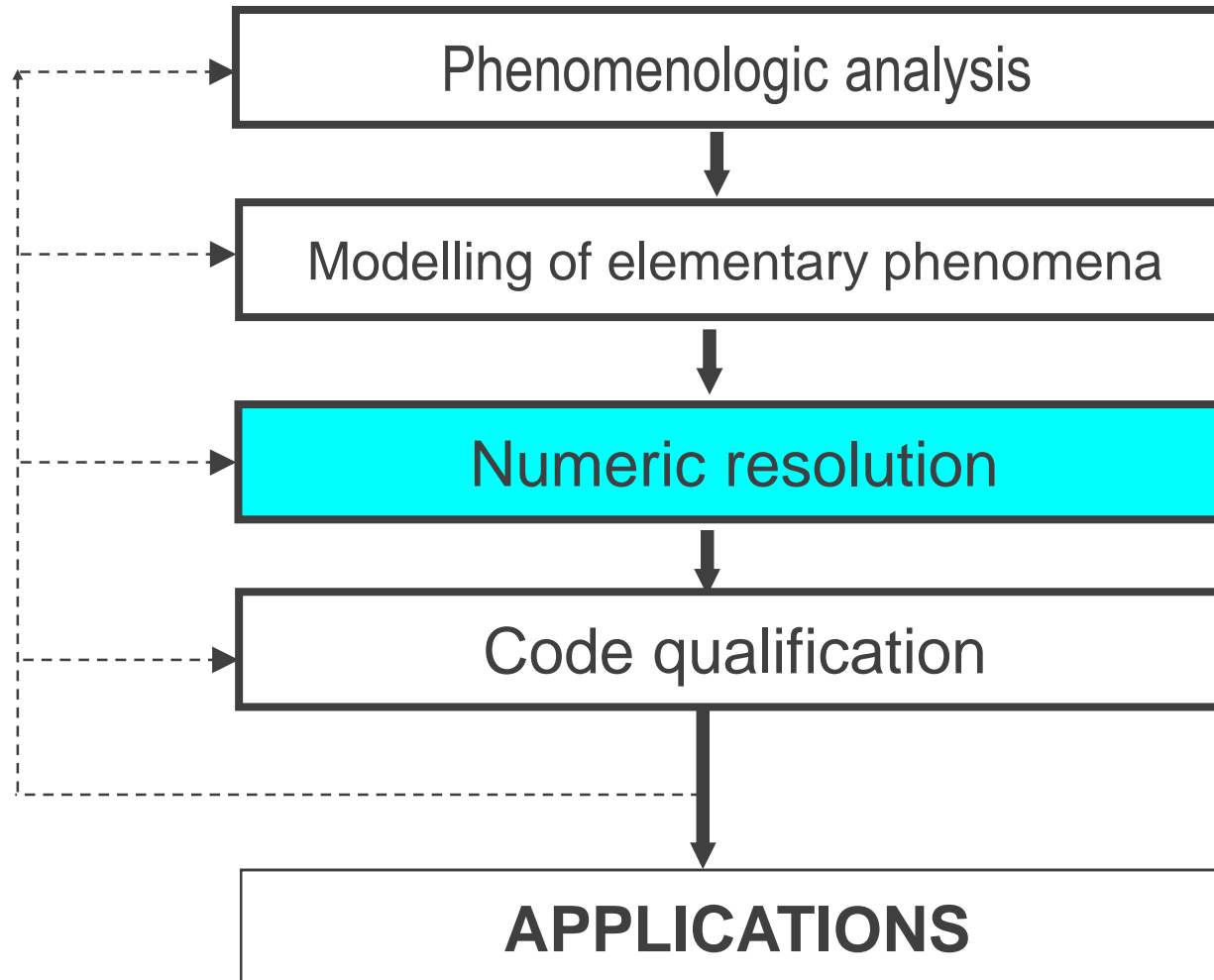


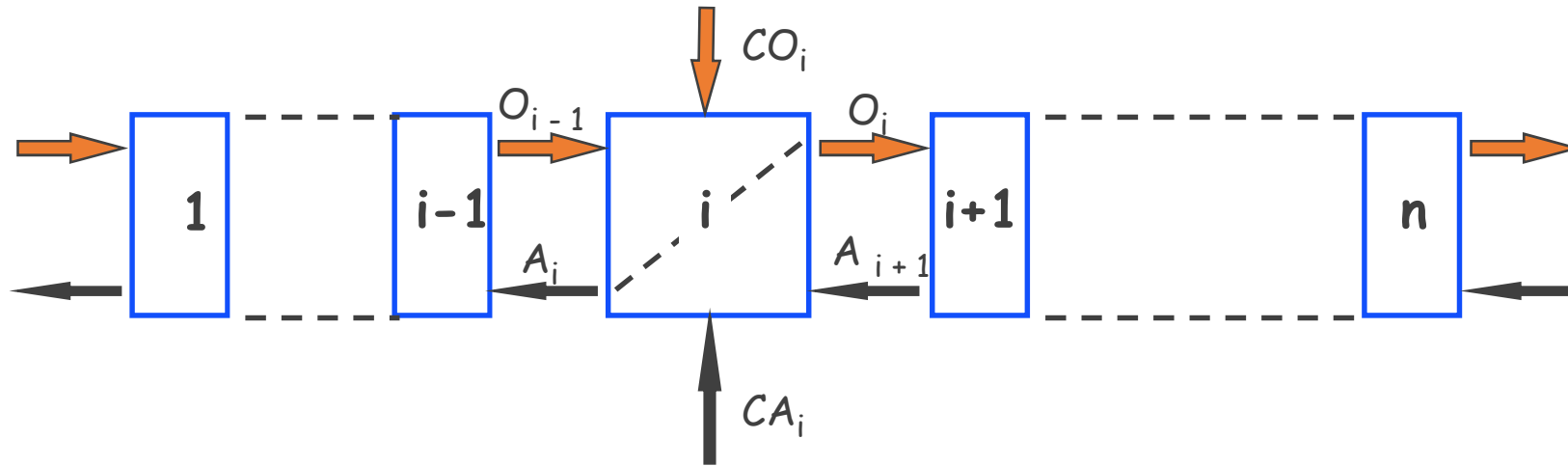
Centrifugal contactor



Phenomena to be considered

- Phases heating due to mechanical effects
- Phases carry-over





A aqueous phase flow rate
O organic phase flow rate
CA aqueous load
CO organic load

x aqueous concentration
y organic concentration
i characterise stage *i* outlet
 (numbering in the direction of progression of solvent phase)

stage *i* → thermodynamic equilibrium : $y_i = f(x_i)$
 stage *i* → mass balance : $A_{i+1}x_{i+1} + O_{i-1}y_{i-1} + CA_i + CO_i = A_i x_i + O_i y_i$

MATRIX RELATIONS

Concentration vectors (for each solute)

$$X = \begin{bmatrix} x_1 \\ M \\ x_n \end{bmatrix} \quad Y = \begin{bmatrix} y_1 \\ M \\ y_n \end{bmatrix} \quad C = \begin{bmatrix} ca_1 + co_1 \\ M \\ ca_n + co_n \end{bmatrix}$$

Flowrate Matrix

$$A = \begin{bmatrix} A_1 & -A_2 & & & & \\ & A_i & -A_{i+1} & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & A_n \end{bmatrix} \quad O = \begin{bmatrix} O_1 & & & & & \\ -O_{i-1} & O_i & & & & \\ & & & & & \\ & & & & & \\ & & & & -O_{n-1} & O_n \end{bmatrix}$$

Equations

$$\begin{array}{ll} A.X + O.Y - C = 0 & \text{(mass balance)} \\ Y = F(X) & \text{(equilibrium)} \end{array}$$

nc species considered = nc matrix systems

Mass balance function: $R(X) = AX + OY - C$

If X_0 is the solution then $R(X_0) = 0$

Taylor development around X_0 :

$$R(X) = R(X_0) + J(X-X_0) + \dots$$

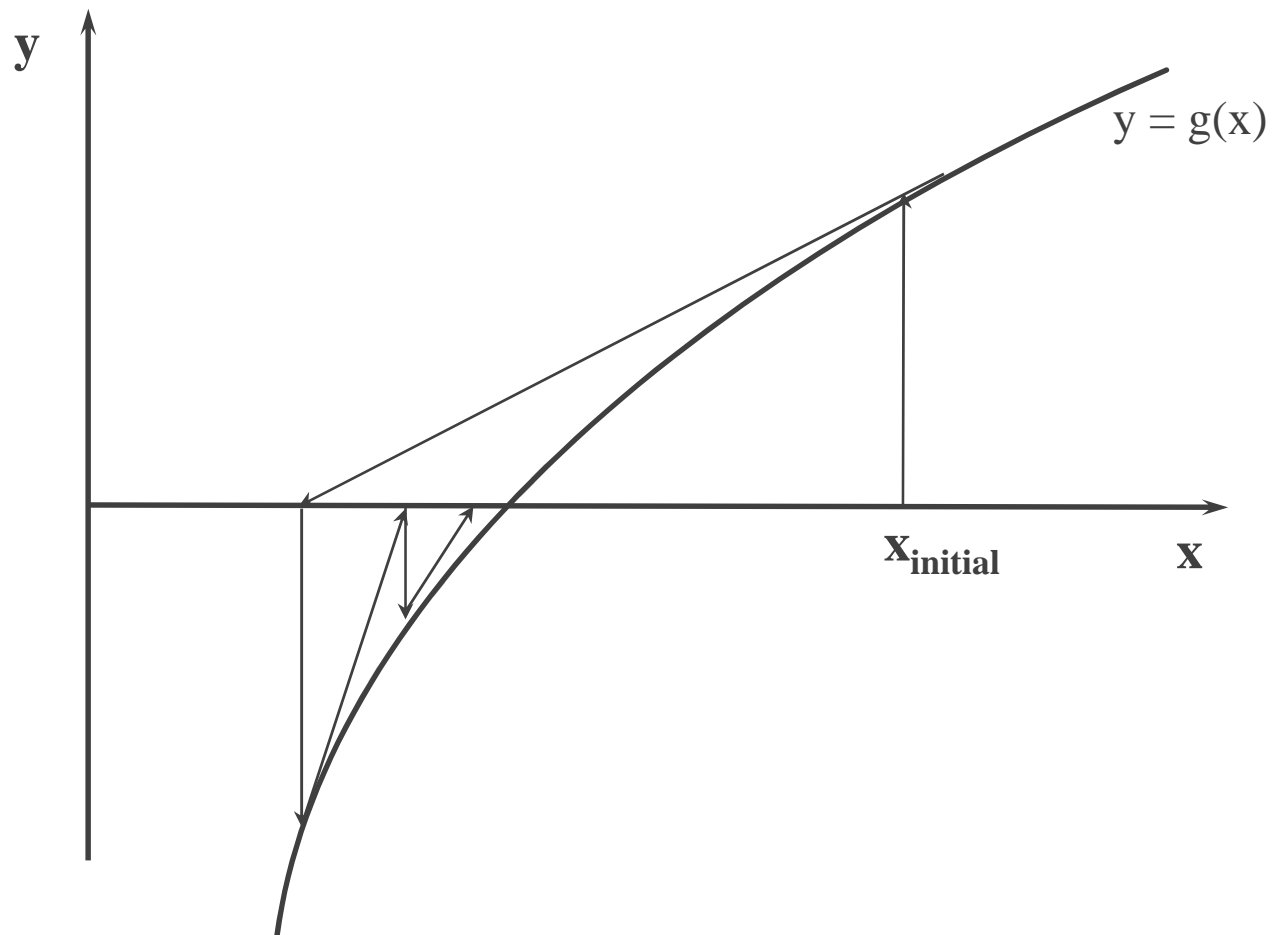
J being the jacobian of R : $J_{ij} = \left[\frac{\delta r_i}{\delta x_j} \right]$

$$X_0 = X - J^{-1} R(X)$$

Iterative scheme:

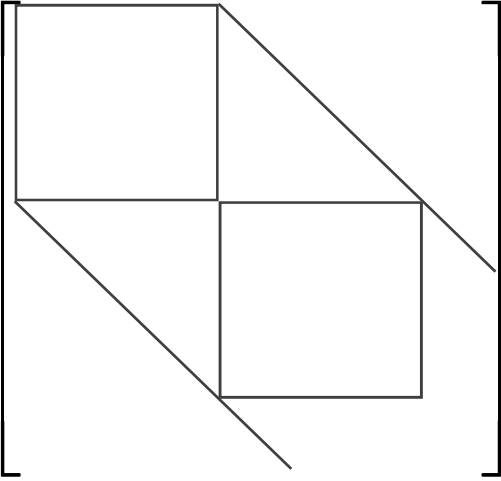
$$X^{n+1} = X^n - J^{-1} R(X^n)$$

$$\text{avec } R(X^n) = AX^n + OF(X^n) - C$$



- nc systems of equations grouped in one

$$A.X + O.F(X) - C = 0$$

$$\left\{ \begin{array}{l} \text{corps} \\ \text{étage1} \\ \\ \text{corps} \\ \text{étage2} \\ \\ M \end{array} \right. \begin{bmatrix} x_1^1 \\ M \\ x_1^{nc} \\ x_2^1 \\ M \\ x_2^{nc} \\ M \end{bmatrix} = X$$


$$= A \quad \Lambda \quad \Lambda$$

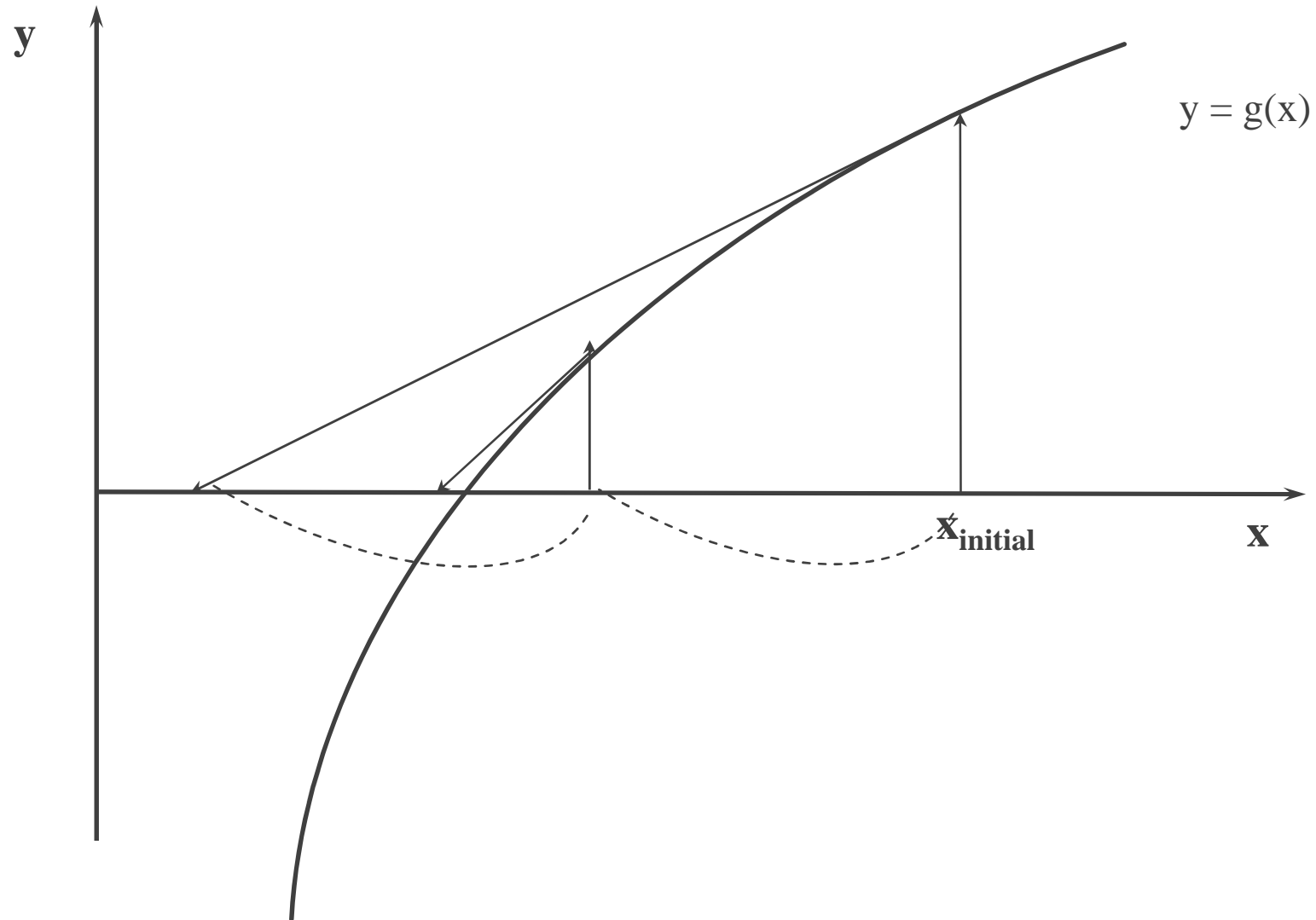
- resolution method:

NEWTON

$$X^{n+1} = X^n - J^{-1} R(X^n)$$

NEWTON "relaxed"

$$X^{n+1} = X^n - \alpha.J^{-1} R(X^n)$$



◆ Principles

- Modified mass balance equation
- Mass transfer formulation unchanged

N.B. : flow model need to be define

◆ Example of formulation

case of a mixer with organic continuous phase, perfectly mixed reactor

$$V_{AM}^i dx_M^i/dt = A_D^{i+1} \cdot X_D^{i+1} - A_M^i \cdot X_M^i \quad \text{plug flow}$$

$$- k_x \cdot 6/d_{32} \cdot V_{OM}^i \cdot (X_M^i - X_{Mi}^i) \quad \text{mass transfer}$$

$$+ \sum V_{AM}^i \cdot Sto_{ar} \cdot C_{i_{ar}} \quad \text{chemical reactions}$$

$$+ \sum \text{charges aqueuses étage } i$$

1. Runge-Kutta method

$\frac{dx}{dt}$ fonction explicite de X

$$X_{n+1} = X_n + \Delta t \cdot X_{n+0.5}$$

$X_{n+0.5}$ approximate ponderation

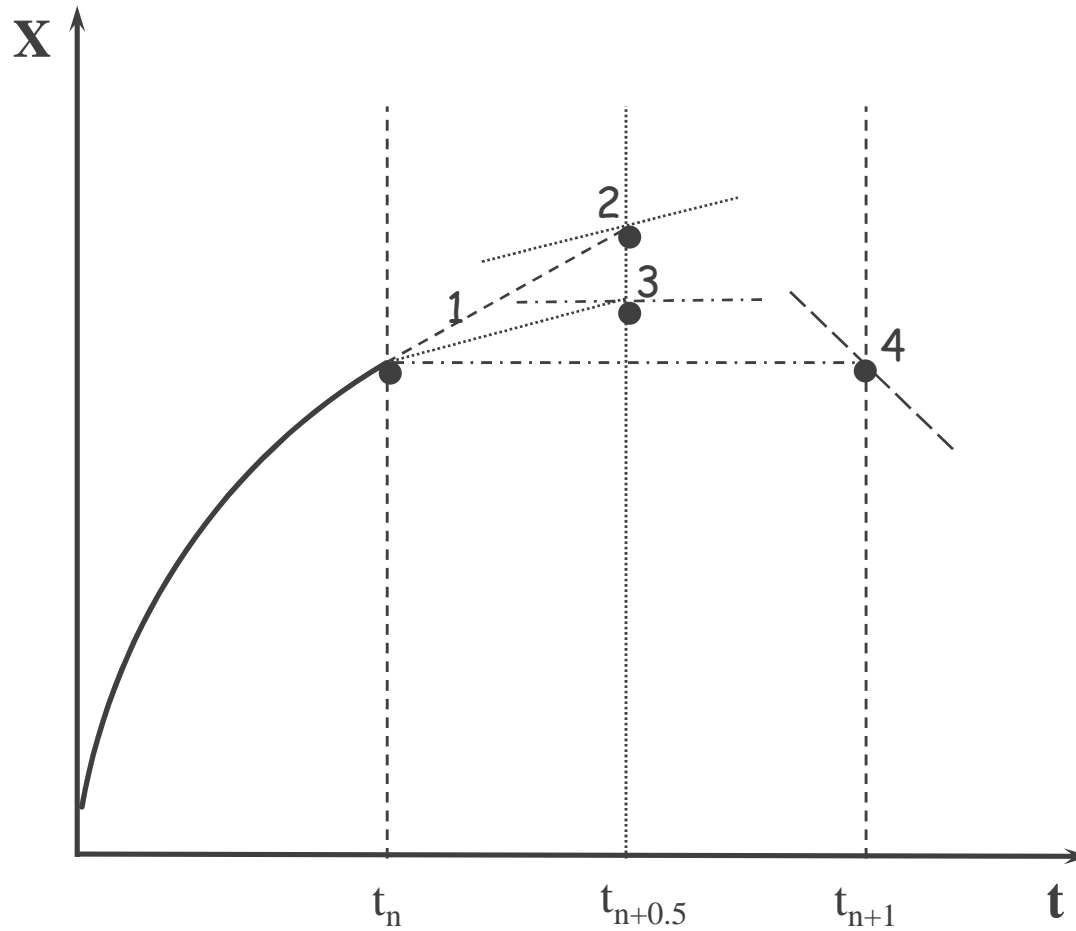
2. Gear method

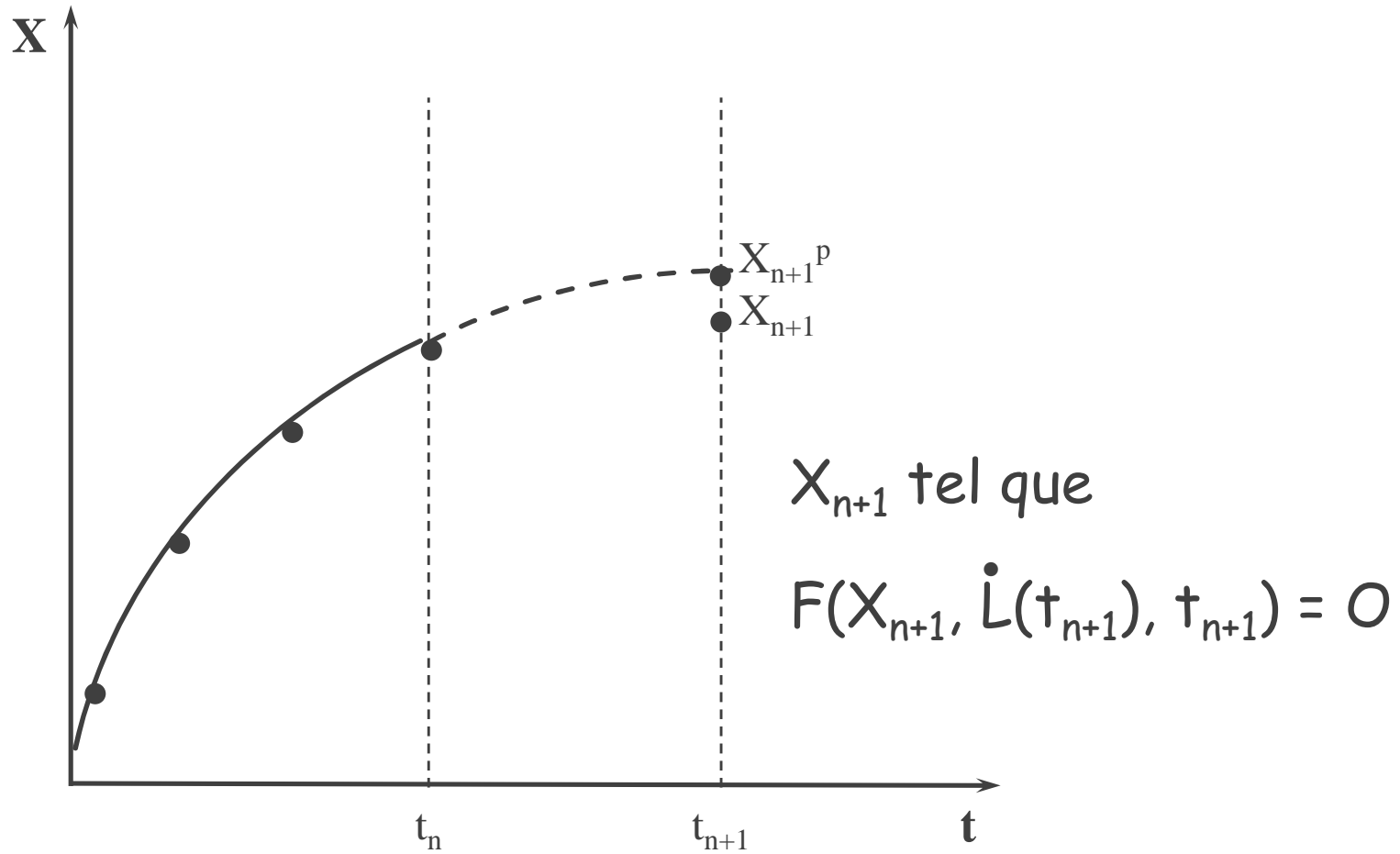
$$F(X_{n+1}, \dot{X}_{n+1}, t_{n+1}) = 0$$

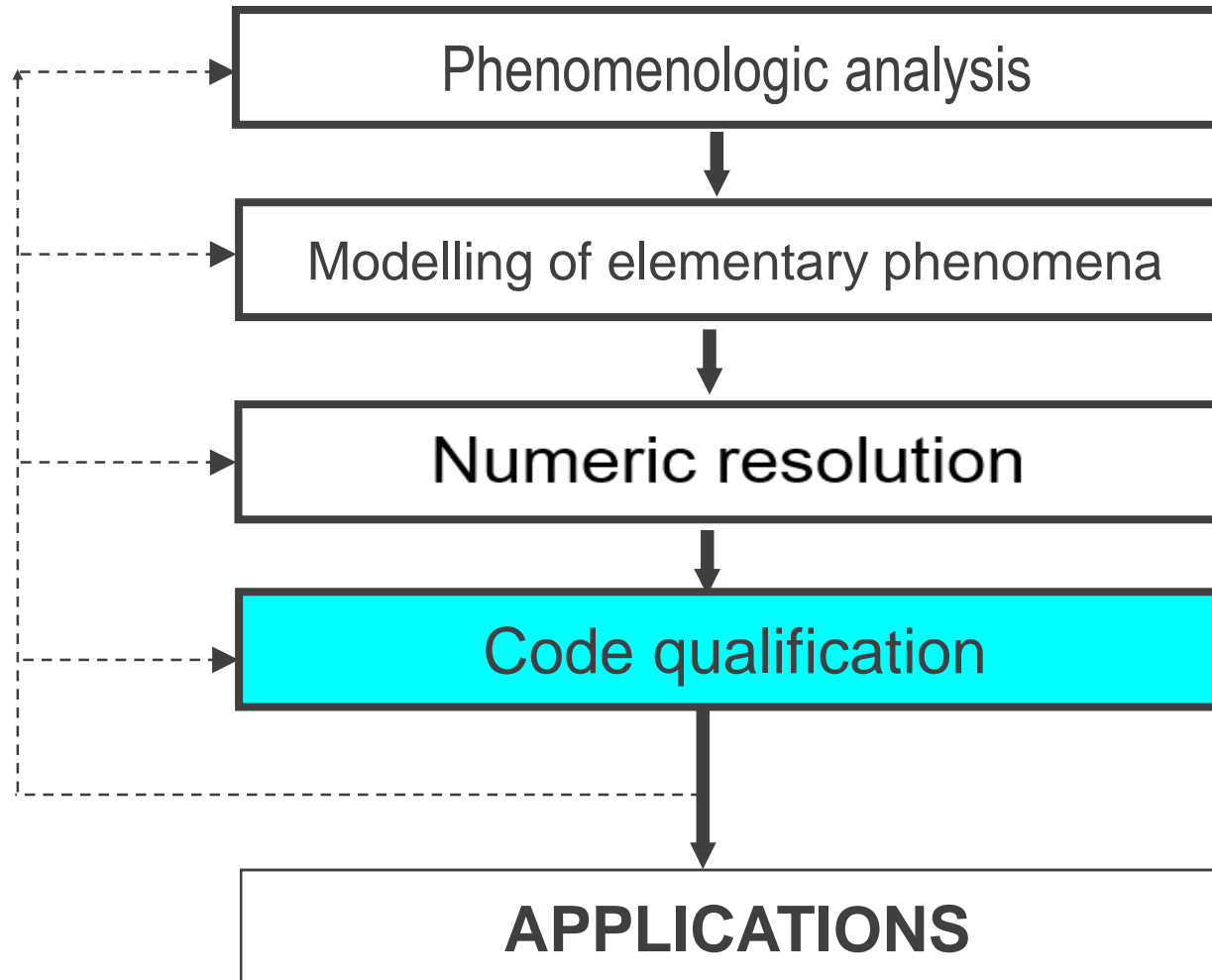
$$\dot{X}(t_{n+1}) = L(t_{n+1}, X_{n+1}, X_n, X_{n-1} \dots)$$

L polynome de Lagrange

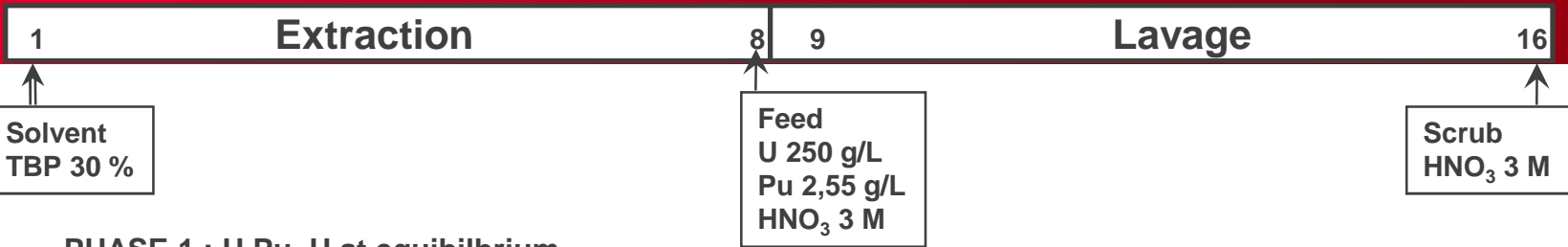
implicit method
with related time steps
with variable Δt
prediction - correction
with error estimation



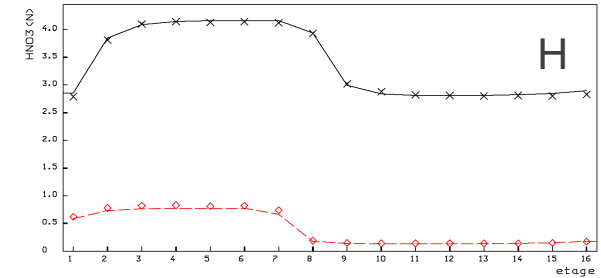
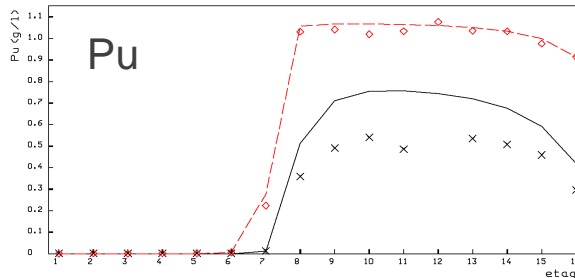
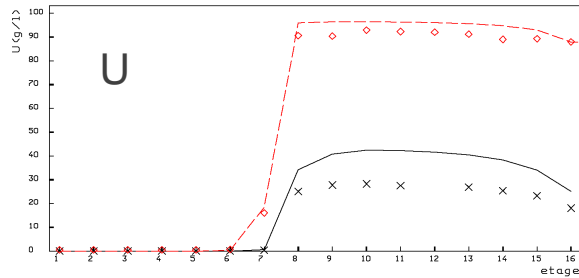




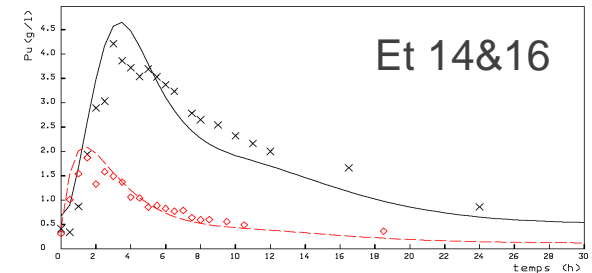
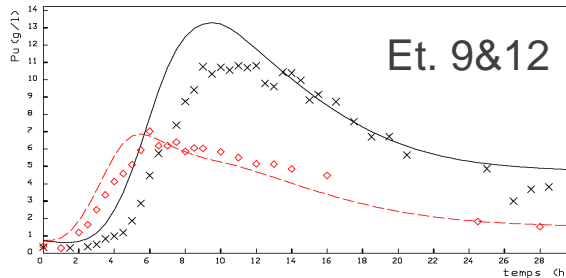
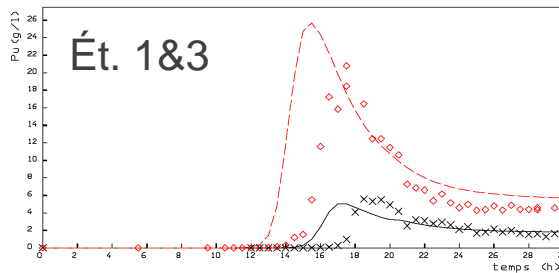
Qualification example



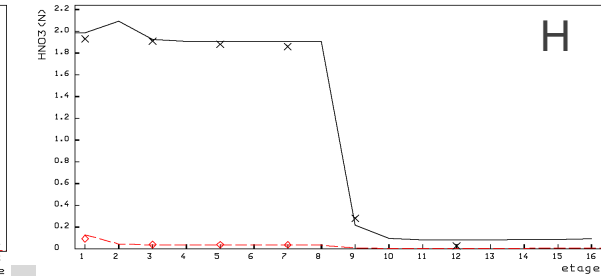
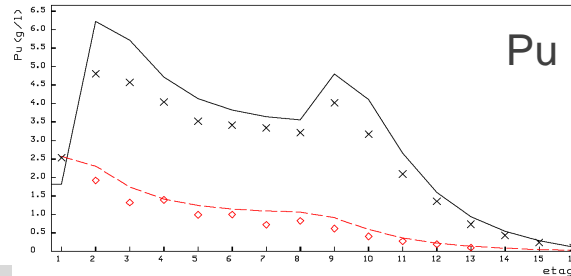
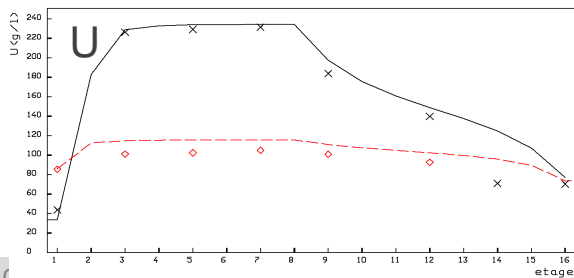
PHASE 1 : U,Pu, H at equilibrium

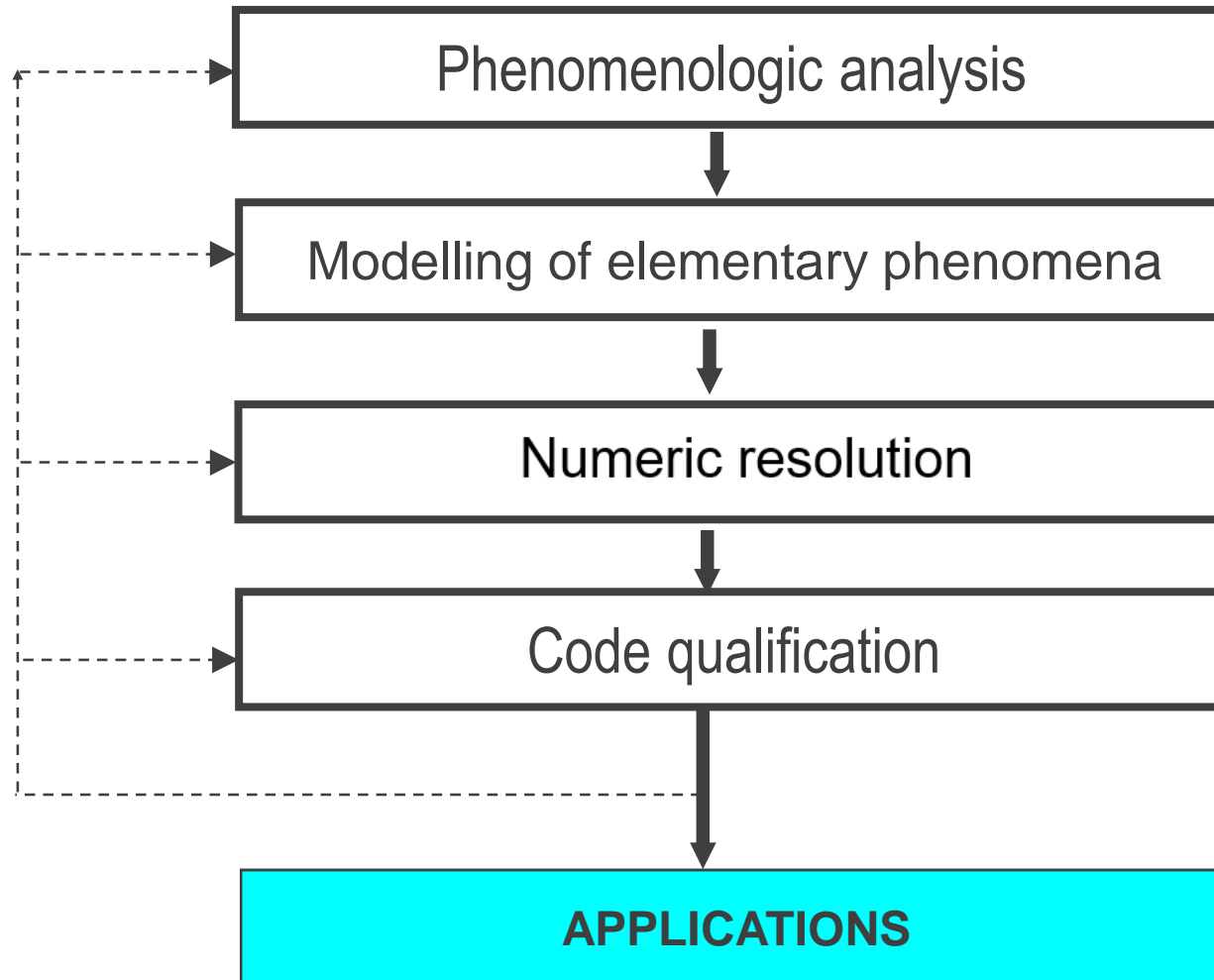


PHASE 2 : Plutonium build-up in case of « water scrubbing »



PHASE 3 : Concentration profiles in final equilibrium

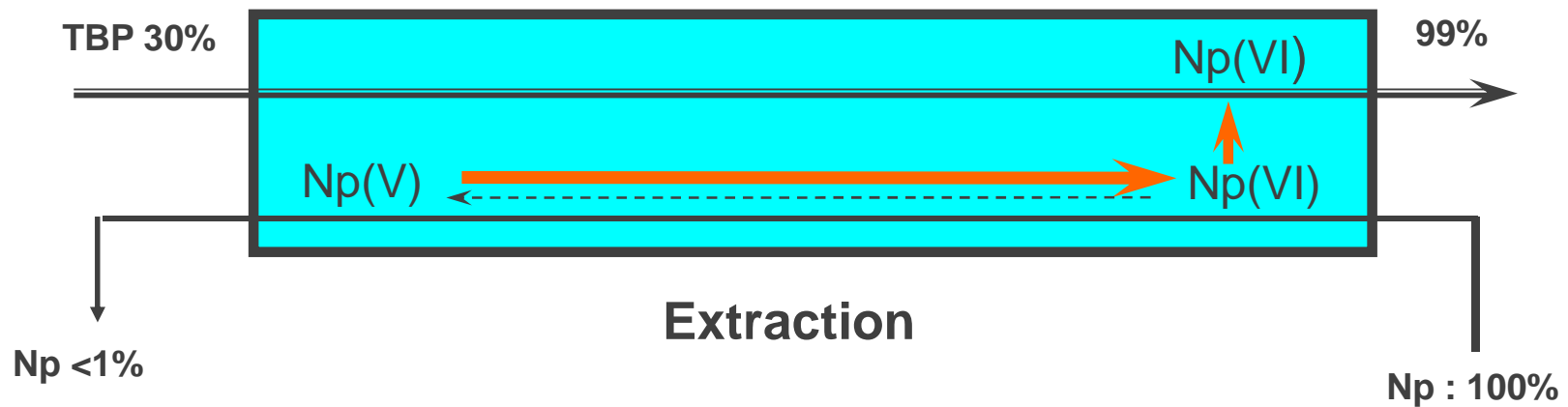




FLOW SHEET

DESIGN and OPTIMIZATION

ENHANCED SEPARATION: NEPTUNIUM QUANTITATIVE EXTRACTION



Redox kinetics Np(V)/Np(VI) implemented in the PAREX code
Nitric acid concentration of feed solution raised to enhance Np extraction yield

Increase determined using the PAREX code : from 3M to 4,5M

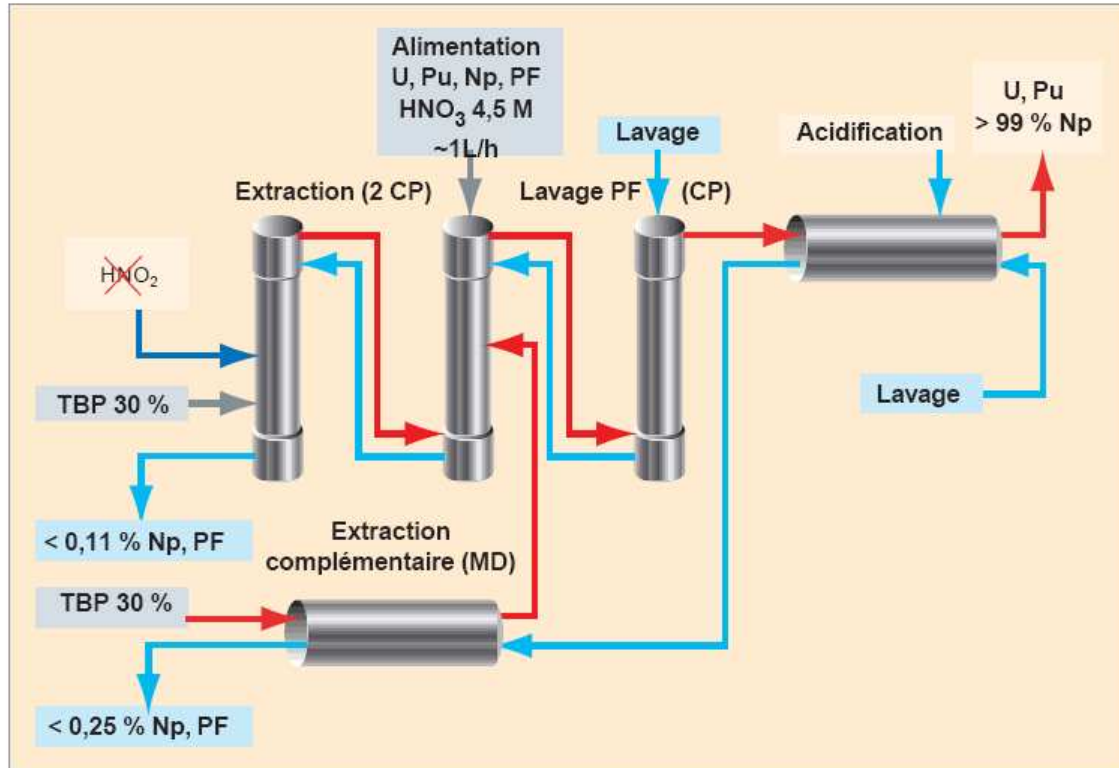


Fig. 103. Schéma de l'essai d'extraction du neptunium opéré dans la cellule blindée procédé d'ATALANTE.

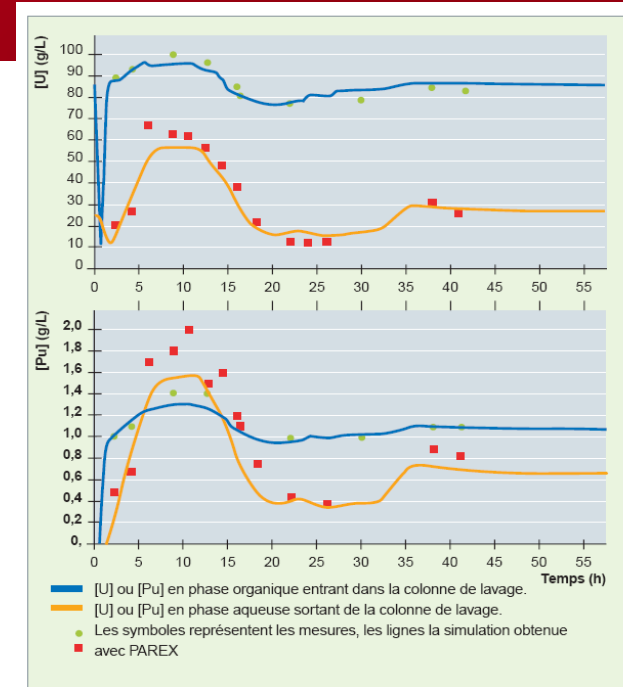


Fig. 105. Comparaison entre les données expérimentales d'extraction de l'uranium et du plutonium de l'essai CBP et les valeurs calculées par le code de simulation PAREX.

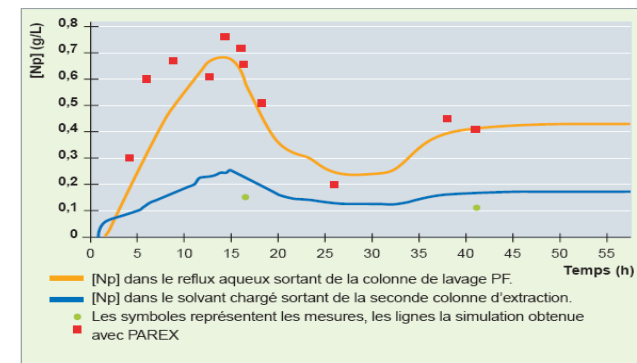


Fig. 104. Comparaison entre les données expérimentales d'extraction de neptunium de l'essai CBP et les valeurs calculées par le code de simulation PAREX.

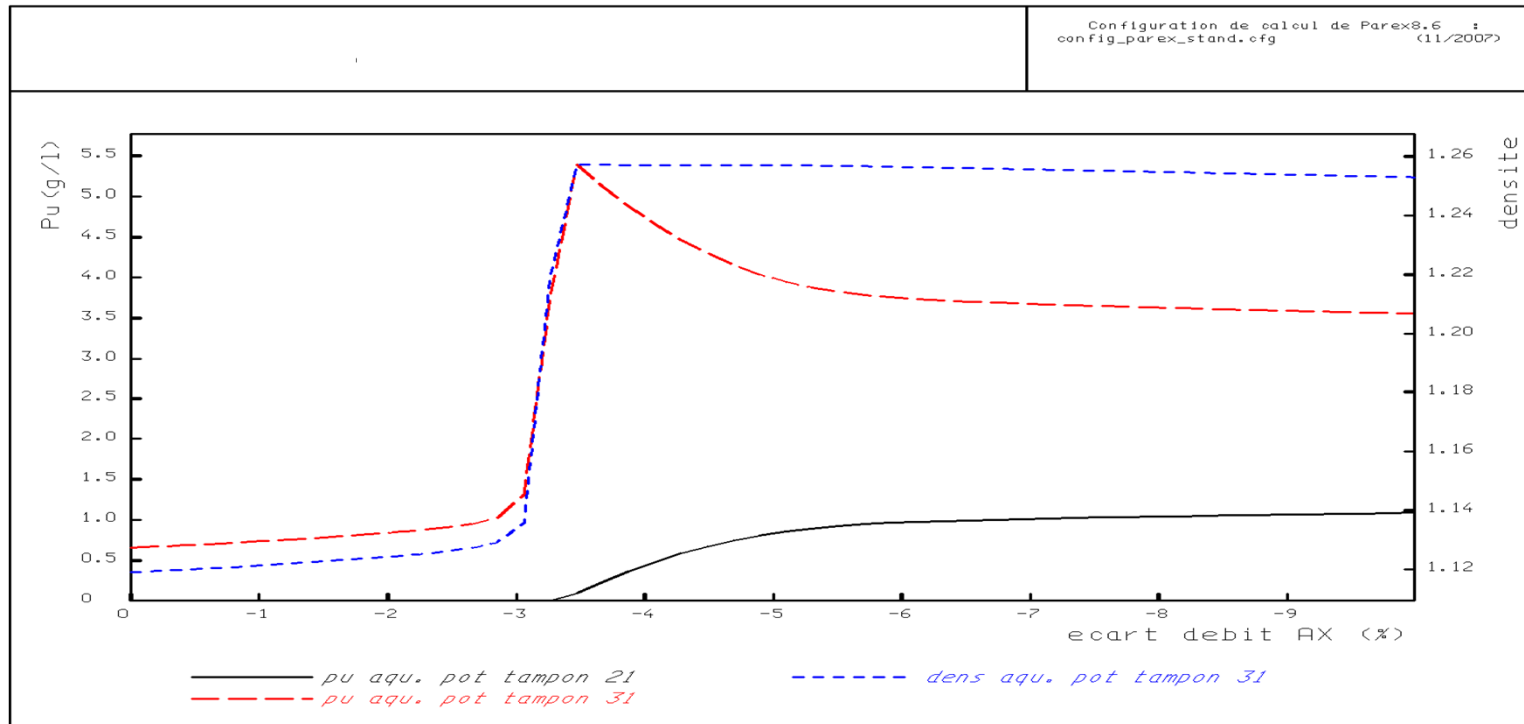
PLANT OPERATION ANALYSIS

- Flow sheet evaluation towards safety risks
 - Criticality, solvent inflammability

- Approach
 - Steady-state studies of mis-adjusted operation
 - Available margin determination for each operating parameter / plutonium build-up and leakage

 - Identification of process state indicator

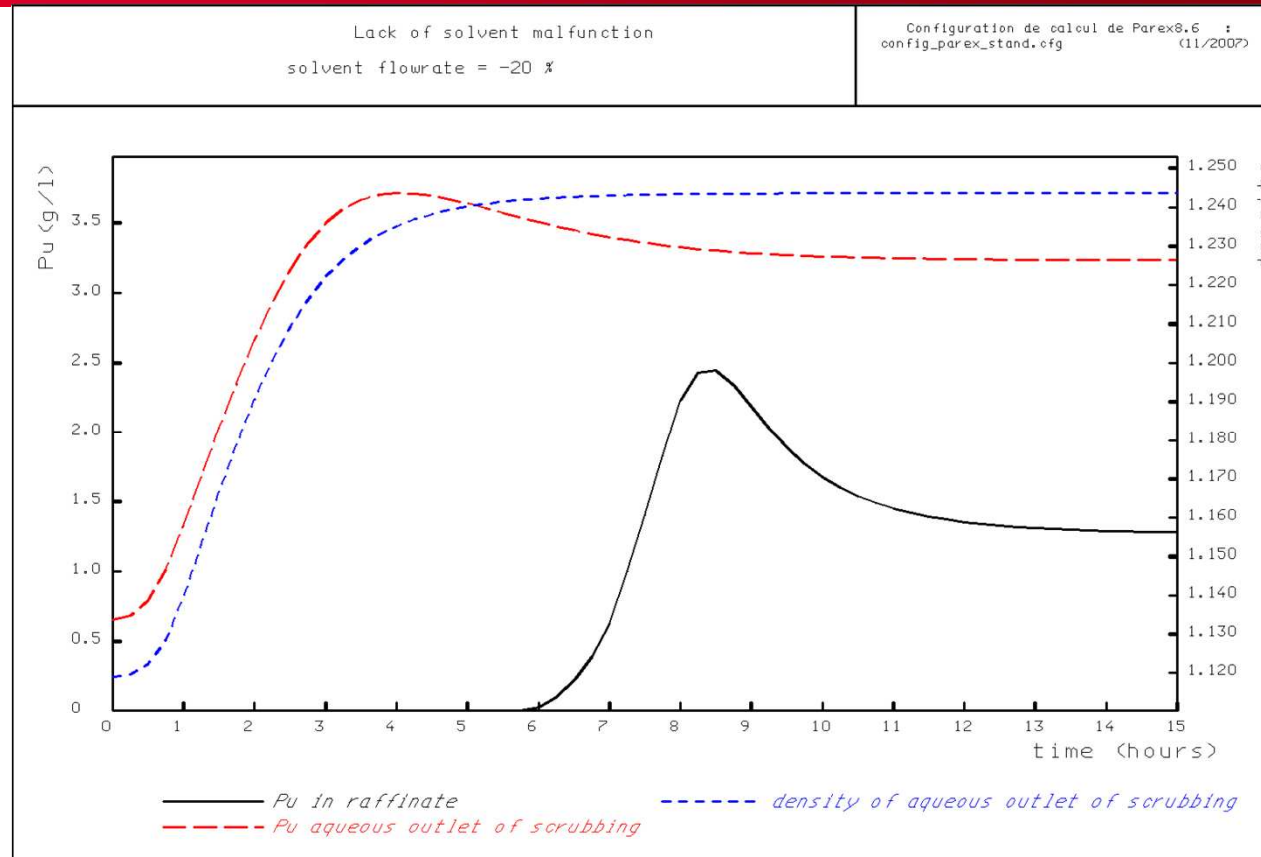
 - Transient behaviour of the process in case of severe malfunction
 - Dynamic response of the process
 - Verify the reliability of the chosen indicators for process monitoring, (early information to permit appropriate corrective action)
 - Procedure elaboration to drive the process back to a safe state



Available margin on solvent flow rate

Identification of process indicators

Density , [Pu] of the aqueous outlet of the scrubbing column



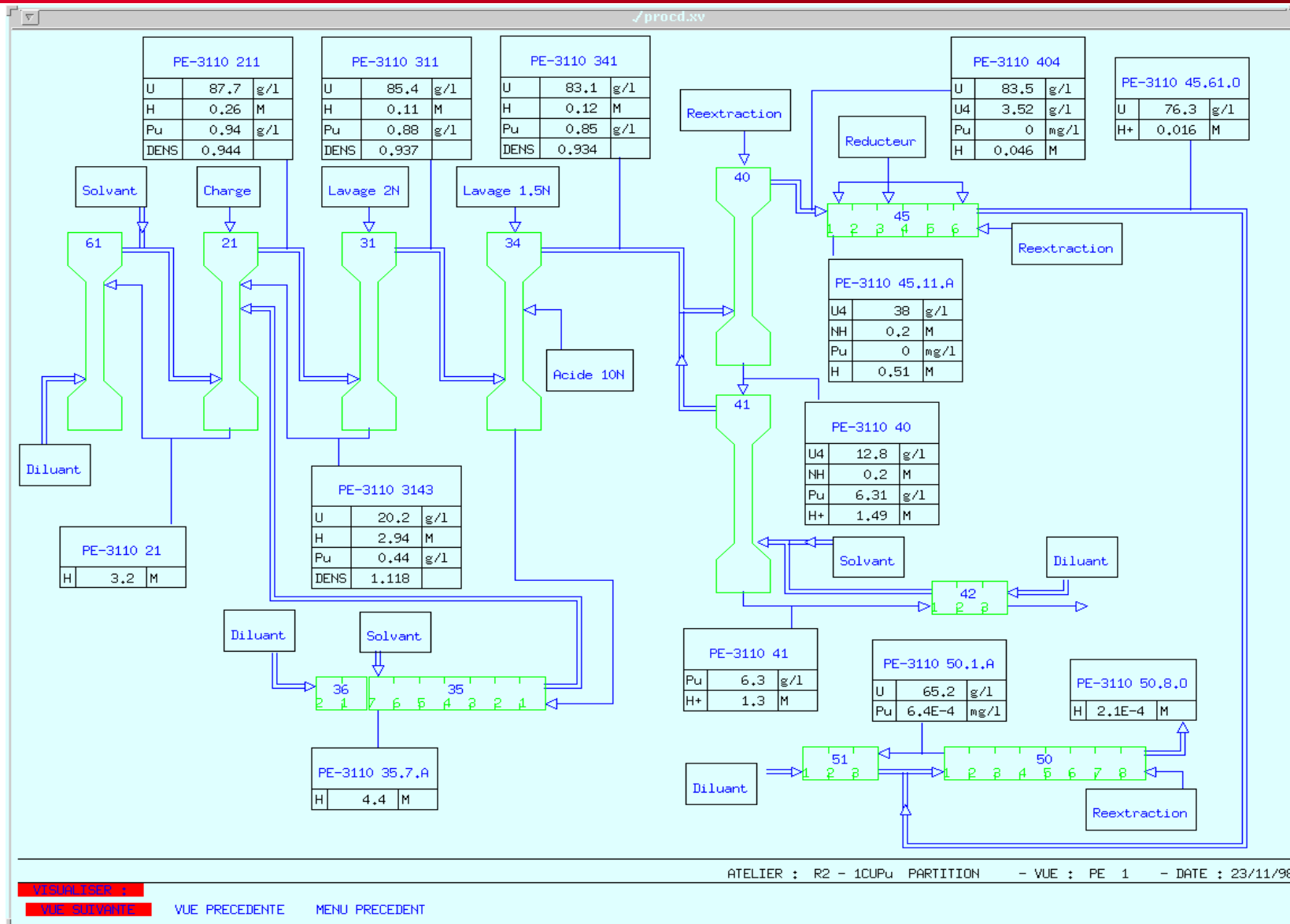
Transient behaviour of the process in case of severe decrease of solvent flow rate analysis

Verification of the reliability of the chosen process indicators : sufficient early information given to allow appropriate corrective action of plant operators

TOOLS FOR PLANT OPERATION AID

Flow sheet calculation
Training simulator
Diagnosis tool

FLOW SHEET CALCULATION PROCESS INDICATORS VIEW (PREDICTED VALUES)



TRAINING SIMULATOR

