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MINES ParisTech

Modeling of actinide migration and wasteform reactivity in the geosphere

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Academics

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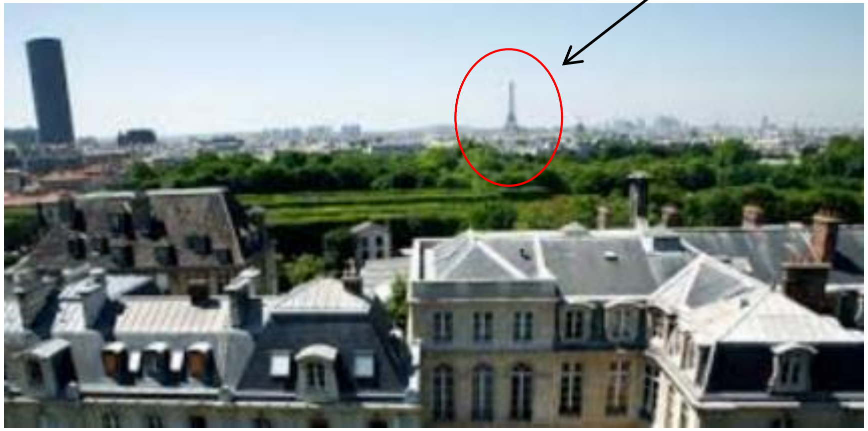
Eiffel Tower



Lab = geochemical
and reactive transport modeling

Dewindtite crystal

$Pb_3(H(UO_2)_3O_2(PO_4)_2)_2 \cdot 12H_2O$

Phosphate family,
named by Professor M.A. Schoep of the University
of Ghent (Belgium) in memory of his student Jean DeWindt-
a distant cousin?, drowned in Lake Tanganyika in Congo.

Cr Acad Sci Paris 174 (1922)

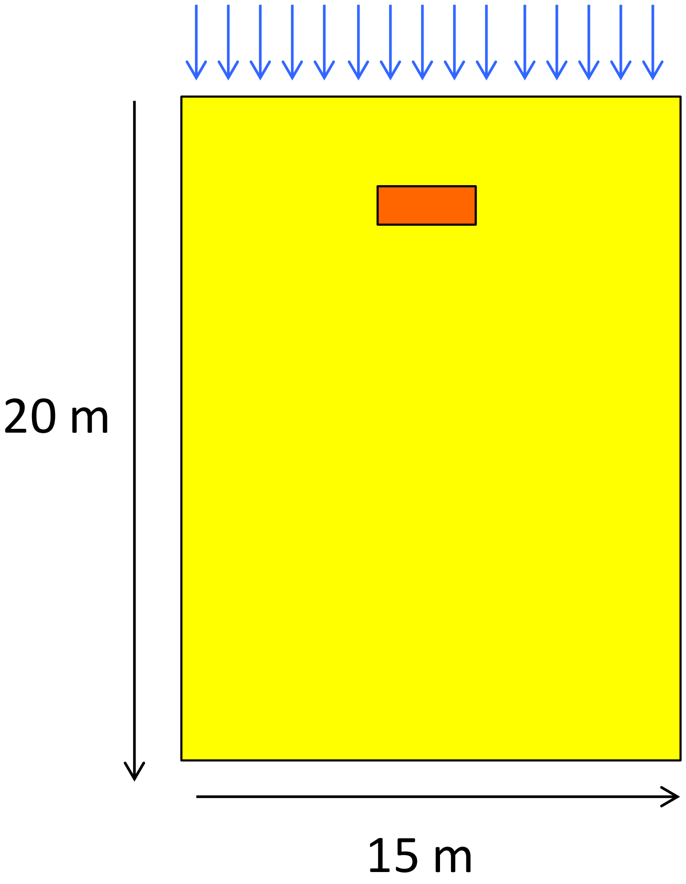
Outline

- Main processes of actinide migration in the geosphere
- Basis of reactive transport modeling
- Why using reactive modeling in underground radioactive waste disposal
- Modeling of spent-fuel (and vitrified waste) leaching experiments

- Approach = application of our code HYTEC with some references to the literature; references are given in the appendix
- Materials = a subsurface sandy aquifer & a deep argillaceous formation

Actinide migration

Schematic configuration



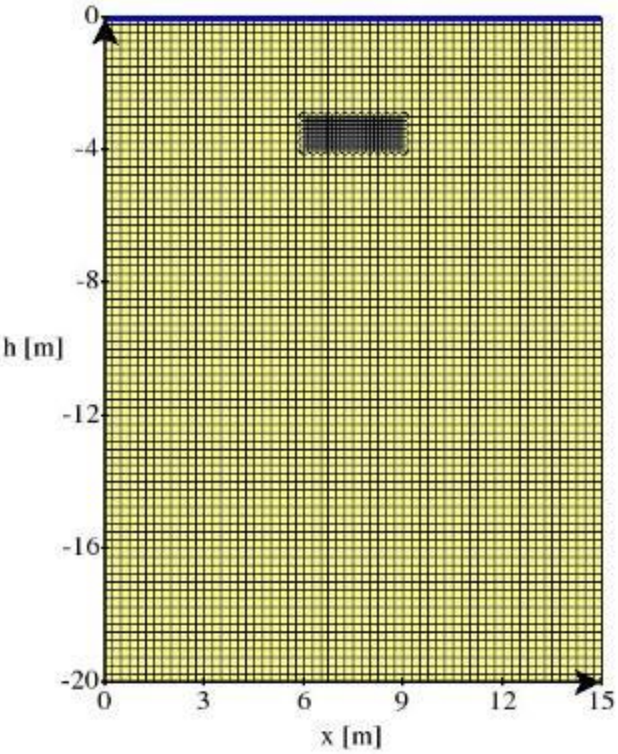
Rain water (i.e. active O_2 & CO_2 dissolved gas)

Contaminated zone with UO_2 debris

Sandy aquifer = quartz, calcite, & argillaceous and ferric phases fractions – organic matter not considered

Actinide migration

Hydrodynamics



$$\frac{\partial \omega c_i}{\partial t} = \operatorname{div}\left(D(\omega)\,\overrightarrow{\operatorname{grad}} c_i - c_i \vec{U}\right)$$

(Local) differential equation

c_i = water concentration of a chemical element *i*

D = diffusion/dispersion

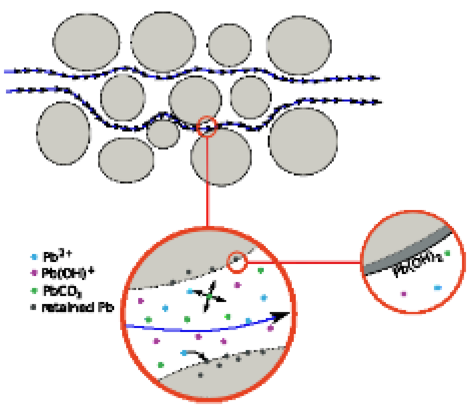
U = Darcy velocity

$$\vec{U} = -\underline{\underline{\mathbf{K}}} \cdot \overrightarrow{\operatorname{grad}}(h)$$

K = hydraulic conductivity

h = hydraulic head

Representative elementary volume REV

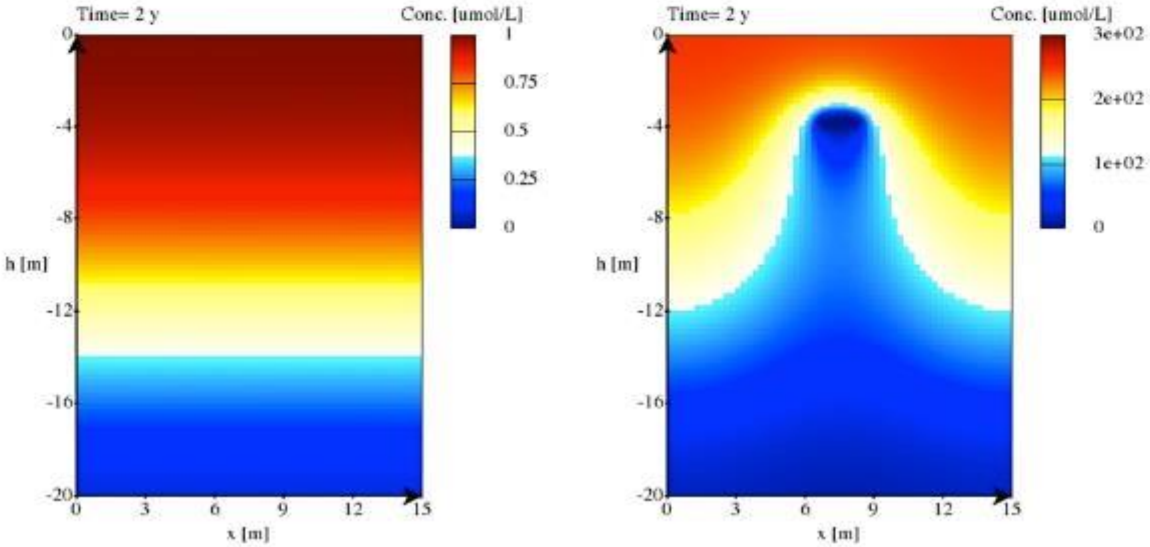


Submitted to boundary conditions, e.g. C_0.U

Actinide migration

Source term

Tracer (HTO) Dissolved O_2



$$\frac{\partial \omega c_i}{\partial t} = \mathrm{div}(D(\omega)\,\overrightarrow{\mathrm{grad}}\,c_i - c_i\,\vec{U}) - \frac{\partial \omega \overline{c_i}}{\partial t}$$

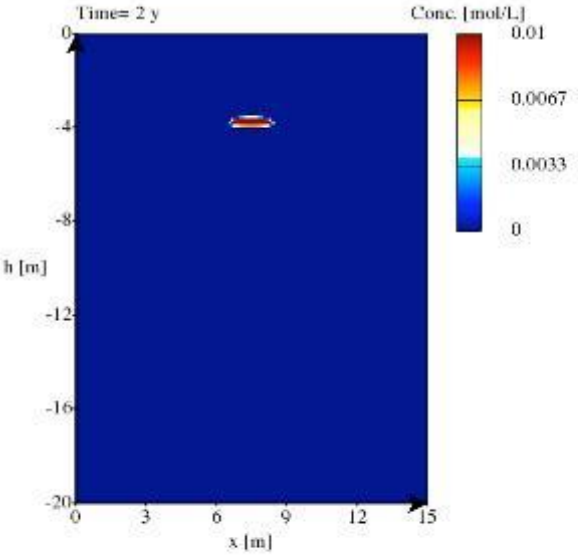
$\overline{c_i}$ = concentration in/on the solid phase

$$\frac{\partial \omega \overline{c_i}}{\partial t} \leftrightarrow \text{uraninite}\,(UO_2) + 2\,H^+ + \frac{1}{2}\,O_2(aq) \rightarrow {UO_2}^{2+} + H_2O$$

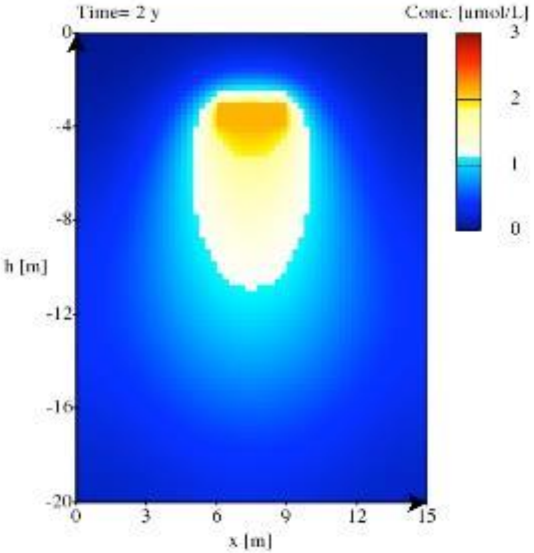
Actinide migration

Source term and complexation in solution

$UO_2(s)$



UO_2^{2+}



$$\frac{\partial \omega \overline{c_i}}{\partial t} \leftrightarrow \quad \text{uraninite}\,(UO_2) + 2\,H^+ + \frac{1}{2}\,O_2(aq) \rightarrow {UO_2}^{2+} + H_2O$$

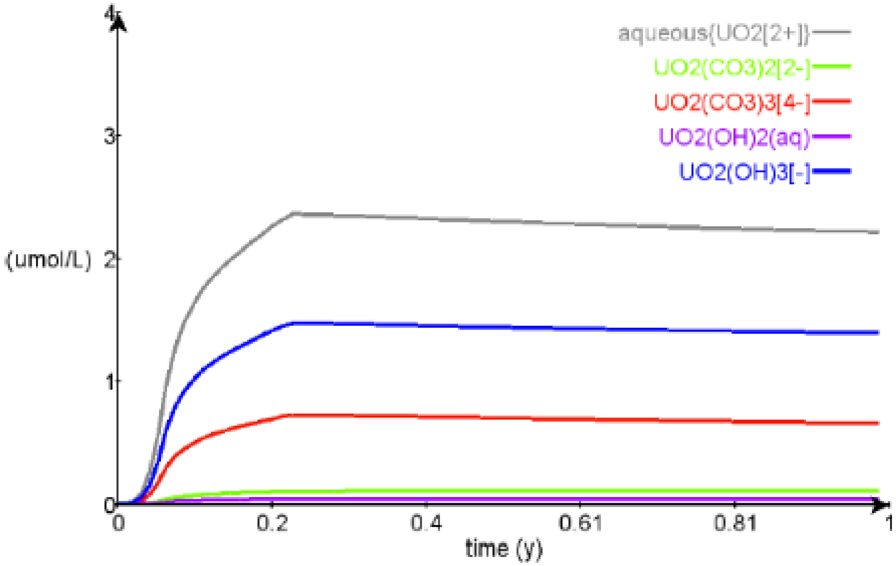
UO_2^{2+} (uranyl) aqueous speciation = competition between several ligands presents in the natural water, e.g. carbonates, hydroxyls, phosphates, small organic molecules

Note on thermodynamic data

Chemical reaction and speciation

$$\frac{\partial \omega \overline{c_i}}{\partial t} \leftrightarrow K = \frac{(C)^{n_c}(D)^{n_d}}{(A)^{n_a}(B)^{n_b}} = e^{\left(\frac{-\Delta_r G^0}{RT}\right)}$$

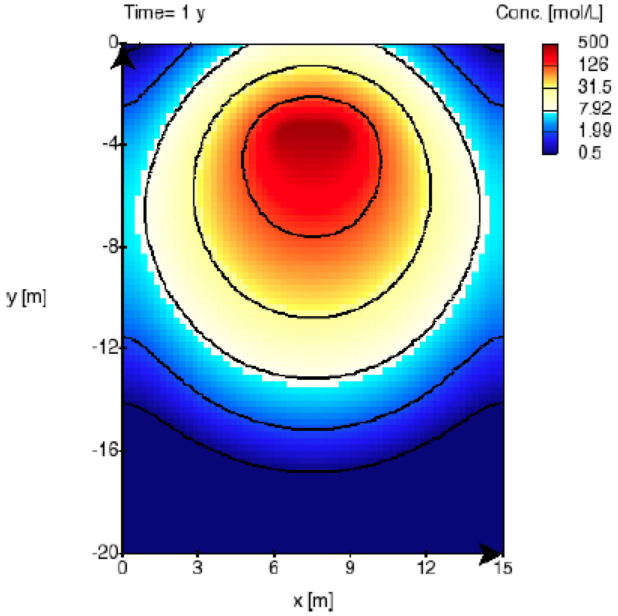
- Thermodynamic chemical equilibrium
- International databases, e.g. ThermoChimie,
  More than 1300 aqueous reactions, 900 minerals,
  of which the compilation of the NEA data (actinides,
  fission products, activation products, etc.



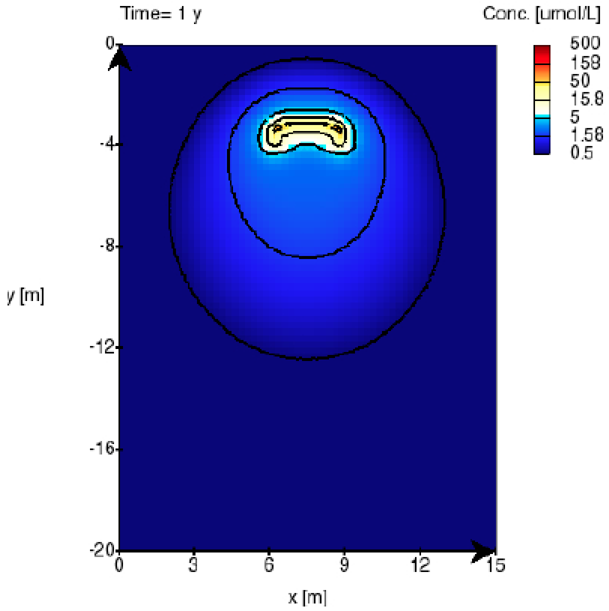
Actinide migration

Sink/attenuation terms = precipitation

UO_2^{2+} with no sink term



UO_2^{2+} with schoepite precipitation



$$UO_2^{2+} + 2\,OH^- + H_2O \rightleftharpoons \text{schoepite}$$

UO_2^{2+} is controlled by the precipitation of secondary minerals of U(VI), e.g.

1. hydrated oxides: becquerelite, schoepite…
2. silicates: soddyite, boltwoodite, uranophane…

Actinide migration

Sink/attenuation terms = precipitation

- Dissolution/precipitation rate of a mineral M :

$$\frac{d[M]}{dt} = kA_v \prod_i (A_i)^{a_i} \left(\left(\frac{Q}{Ks} \right)^p - 1 \right).$$

where $A_v = A_s[M]$ and A_s is the specific surface (m^2/kg).

- The term $\prod_i (A_i)^{a_i}$, (A_i) is either catalytic or inhibiting according to its signs.
- Temperature dependency is given by the Arrhenius's law:

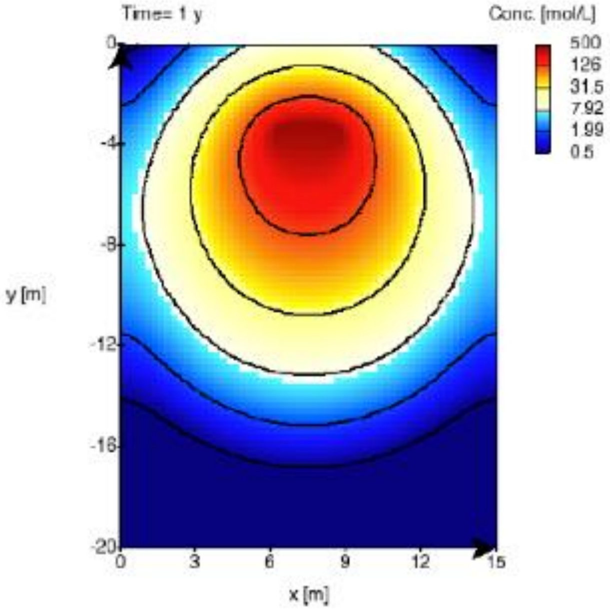
$$k = A \exp\left(\frac{-E_A}{RT} \right),$$

where E_A stands for the apparent activation energy (J/mol).

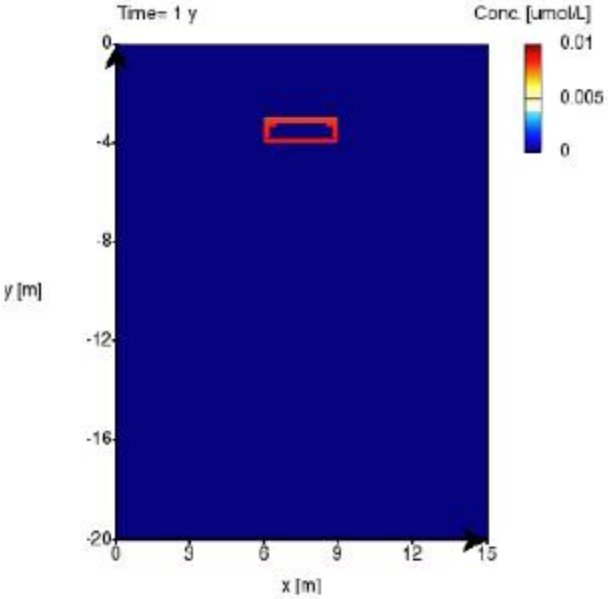
Actinide migration

Sink/attenuation terms = sorption

UO_2^{2+} with no sink term



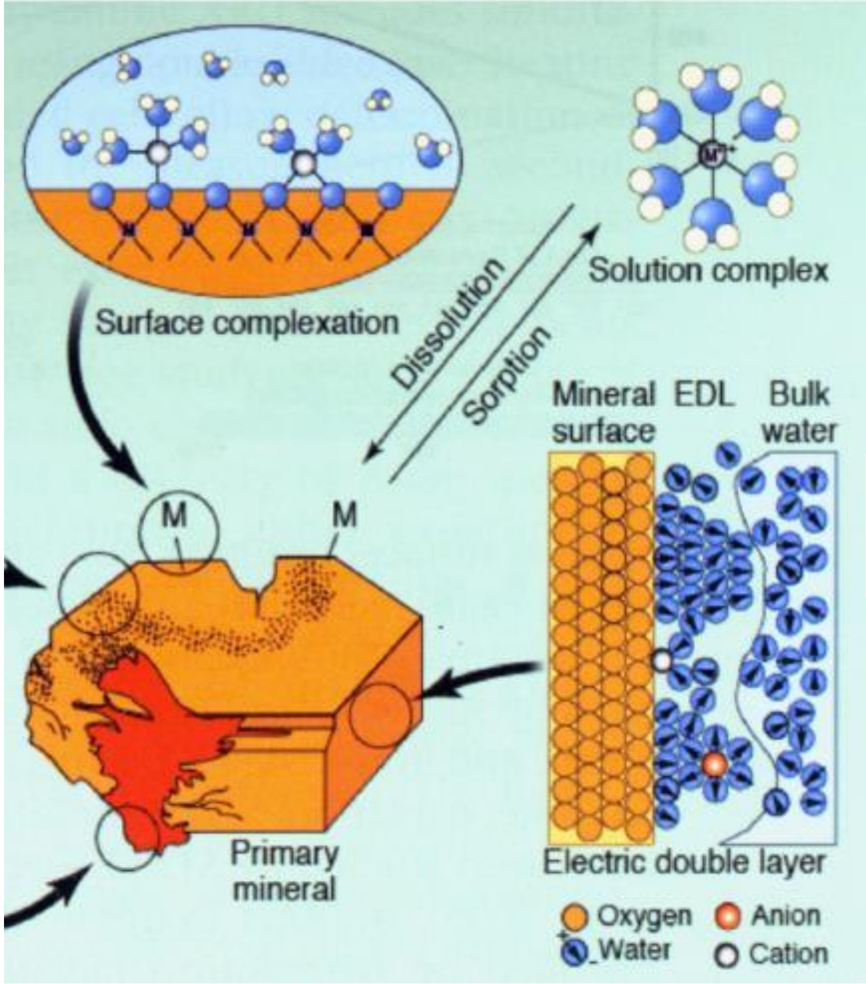
UO_2^{2+} with precipitation and sorption



Sorption plays a key role for actinide plume attenuation, especially in trace concentration levels

Actinide migration

Sink/attenuation terms = sorption



For ex.,
complexation on goethite surfaces:

$$\equiv\text{Fe-OH} + \text{UO}_2^{2+} \rightarrow \equiv\text{Fe-OUO}_2^{+} + \text{H}^{+}$$

$$\equiv\text{Fe-OH} + \text{UO}_2\text{OH}^{+} \rightarrow \equiv\text{Fe-OUO}_2\text{OH} + \text{H}^{+}$$

- Amphoteric functional groups at the solution/solid interface, i.e. acid or base according to pH:

$$\equiv\text{S-OH}_2^{+} \rightleftharpoons \equiv\text{S-OH} + \text{H}^{+},$$

$$\equiv\text{S-OH} \rightleftharpoons \equiv\text{S-O}^{-} + \text{H}^{+}.$$

Actinide migration

Sink/attenuation terms = sorption

- Density of surface charge σ :

$$\sigma = \frac{F}{A_s[M]} \sum_i Z_i[\equiv S_i].$$

- Usually positive at acidic pH and negative at basic pH.
- The sorption constant writes as:

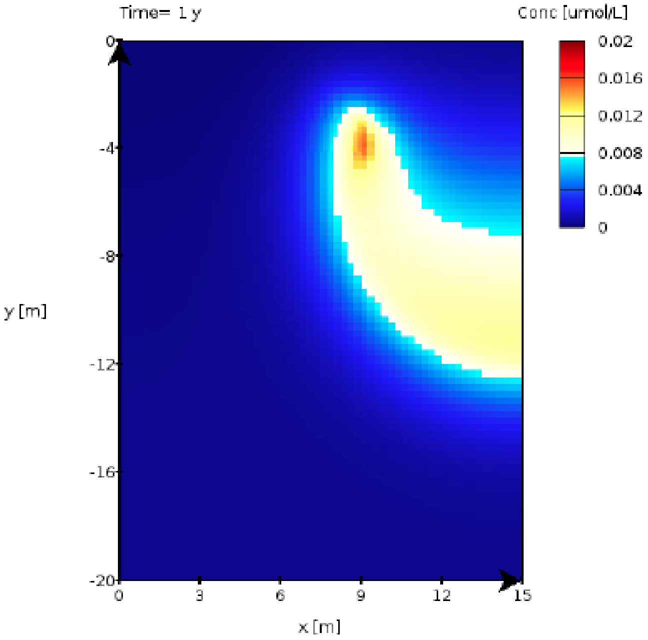
$$K_{ads} = K_{int} \exp\left(\frac{-\Delta Z F \Psi(x=0)}{RT}\right).$$

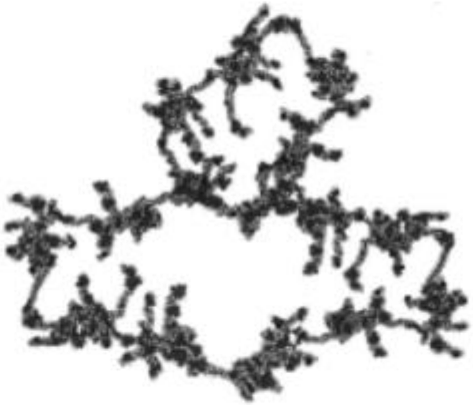
where the potential Ψ is a function of σ as well as the counter-ion distribution in the solution close to the solid surface.

Actinide migration

Colloidal migration

UO_2^{2+} sorbed onto mobile colloids





Colloids = submicrometric organic humics, hydrous ferric oxides, silica, etc.
Which are mobile in water

Negatively, sorption onto colloids will enhance the migration, especially in trace concentration levels

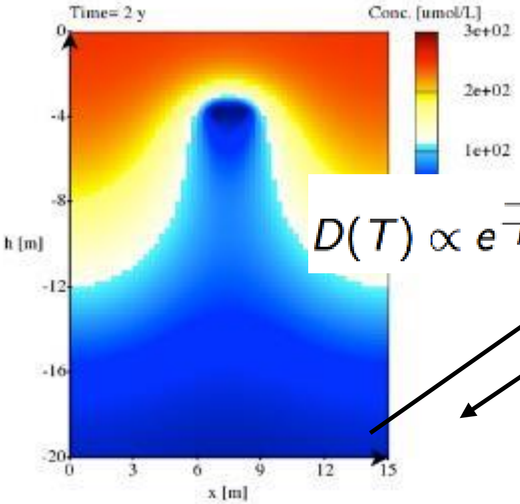
Actinide migration

Summary

1. Source term in water are often linked to a chemical reaction
2. Migration is driven by advection and/or diffusion
3. Complexation in solution may enhance stability in water
4. Sink terms = precipitation and sorption
5. Colloidal migration can enhance the contaminant plume

Reactive transport modeling

Coupling of H – C – T processes



$D(T) \propto e^{\frac{-E_A^D}{RT}}$

Thermic (T)

Conduction, convection

$K(\Delta H, C_p, T) \qquad k(T) \propto e^{\frac{-E_A^k}{RT}}$

$\overrightarrow{\mathrm{grad}}\, T,\ \Delta T$

Driving force

Transport (H)

(Un)-saturated diffusion/advection

Driving force

Coupling

Chemistry (C)

Aqueous chemistry, dissolution/precipitation, sorption

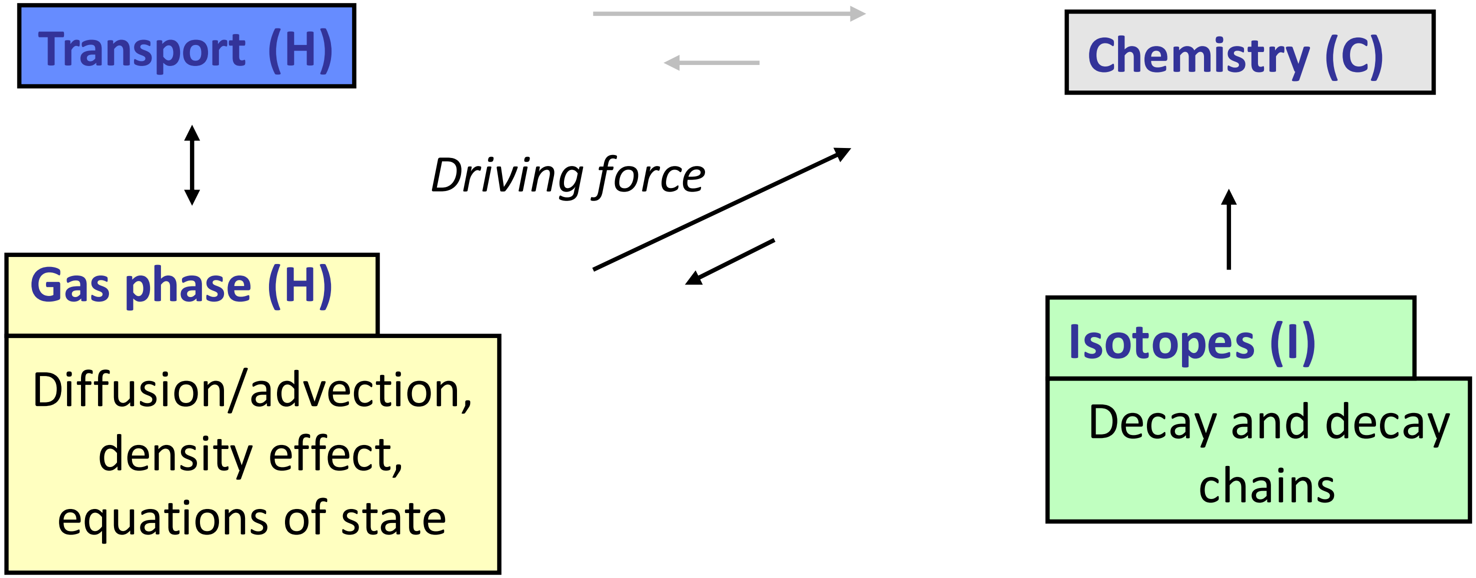
$$\frac{\partial \omega c_i}{\partial t} = \mathrm{div}(D(\omega)\, \overrightarrow{\mathrm{grad}} c_i - c_i \vec{U}) - \frac{\partial \omega \overline{c_i}}{\partial t}$$

$$\frac{\partial \omega \overline{c_i}}{\partial t} \leftrightarrow K = \frac{(C)^{n_c}(D)^{n_d}}{(A)^{n_a}(B)^{n_b}} = e^{\left(\frac{-\Delta_r G^0}{RT}\right)}$$

$$D_e(\omega) = D_e(\omega_0)\left(\frac{\omega - \omega_c}{\omega_0 - \omega_c}\right)^m \qquad \Delta V_{m,tot} = \sum V_{m,i}\, \Delta C_{m,i}$$

Reactive transport modeling

Implementation of new processes



Transport (H)

Chemistry (C)

Driving force

Gas phase (H)

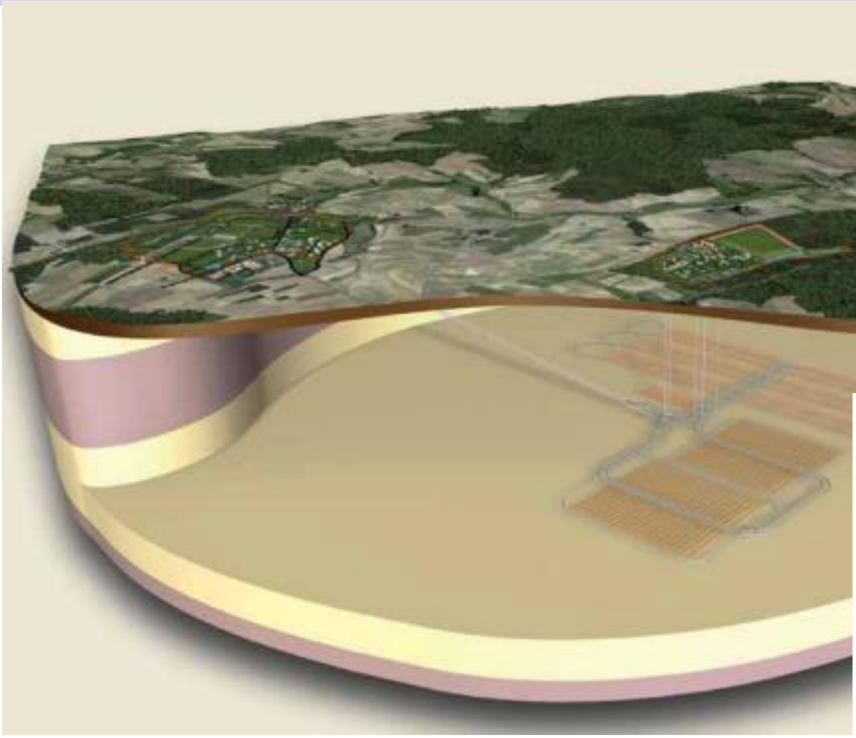
Diffusion/advection, density effect, equations of state

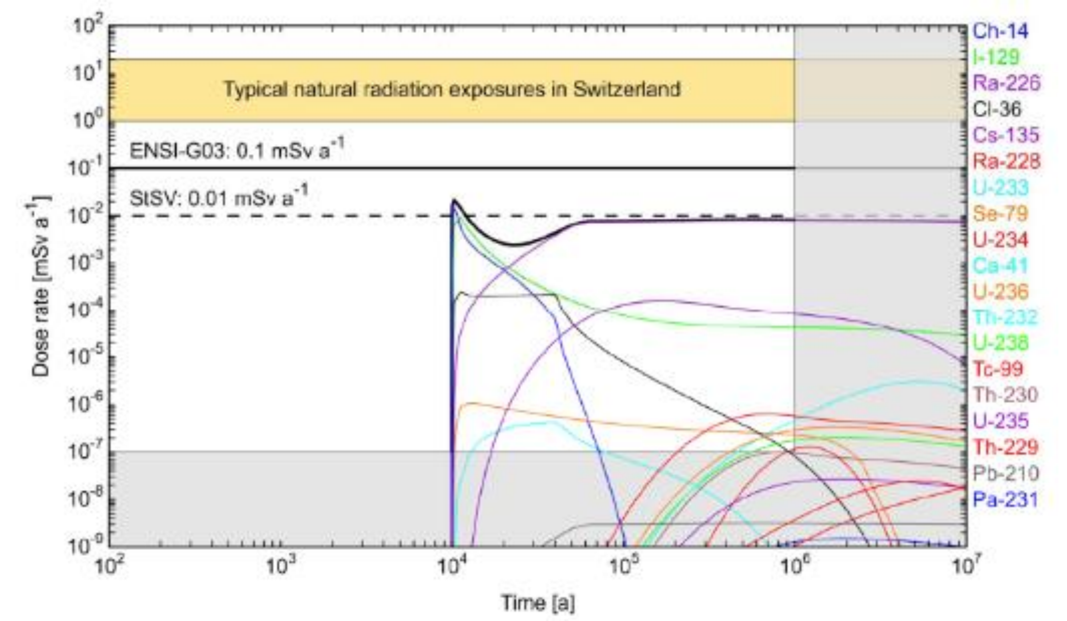
Isotopes (I)

Decay and decay chains

Actinide migration

Kd et solubility limit simplification





Safety assessment of underground radioactive waste disposal generally uses a simplified chemical approach, i.e. Kd and solubility limit

Actinide migration

Kd simplification

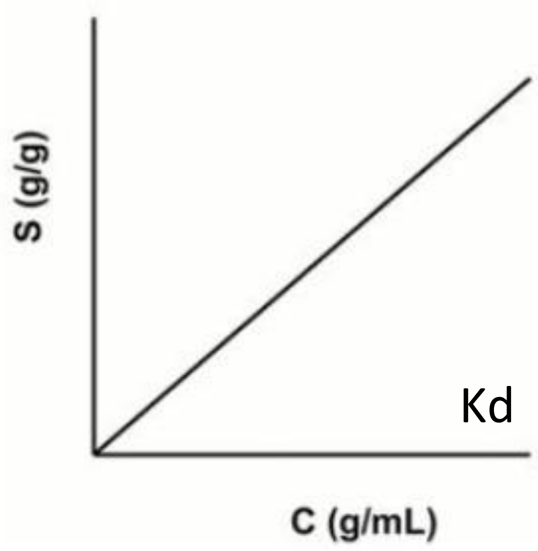
$$R\frac{\partial \omega c}{\partial t} = div(D_e(\omega)\overrightarrow{grad}(c) - c\vec{U}) - \lambda\omega c$$

$$R = 1 + K_d$$

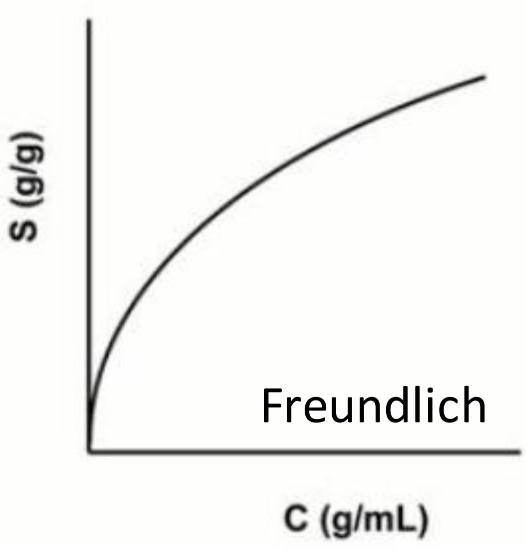
λ = radioactive decay constant

R = retardation factor

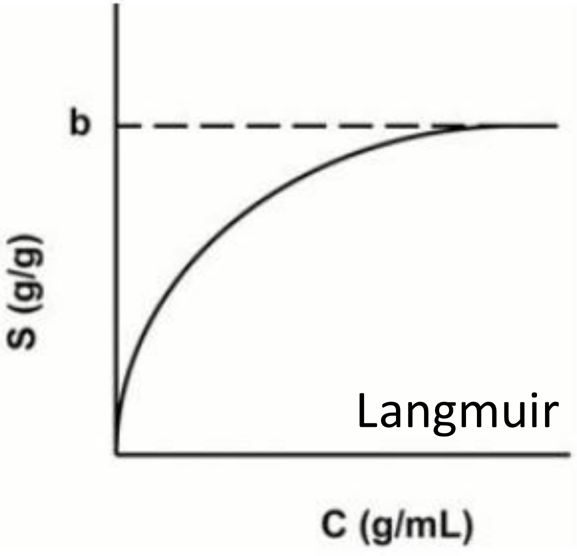
$$S = K_d C$$



$$S = K_f C^n$$

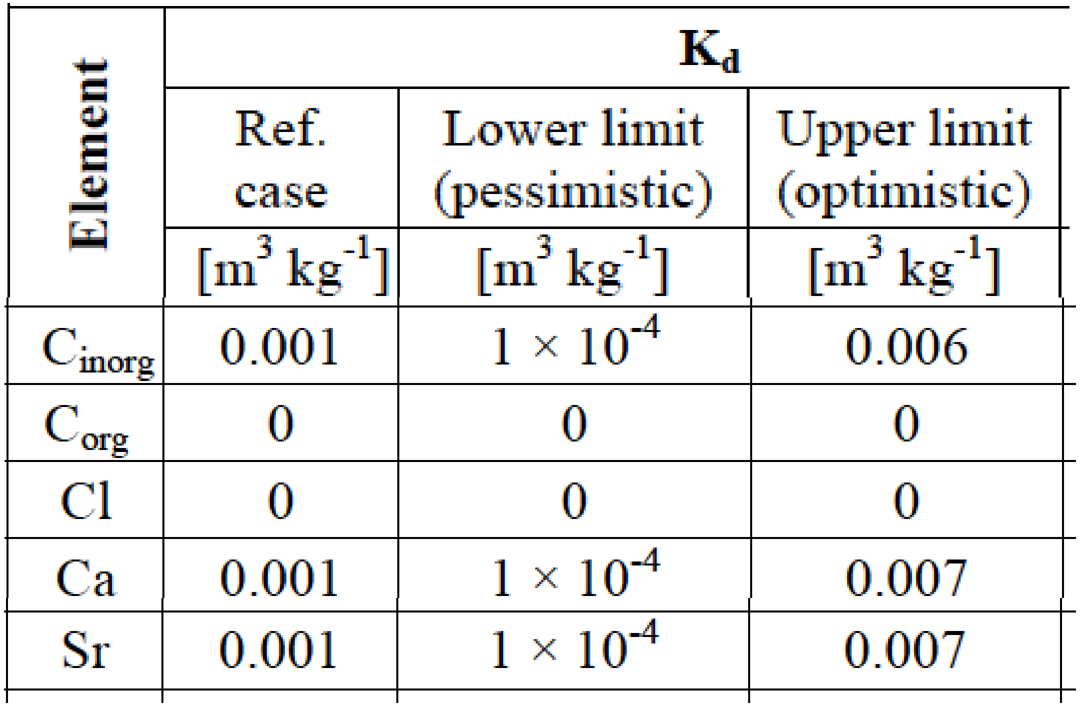


$$S = S_m \frac{K_l C}{1 + K_l C}$$

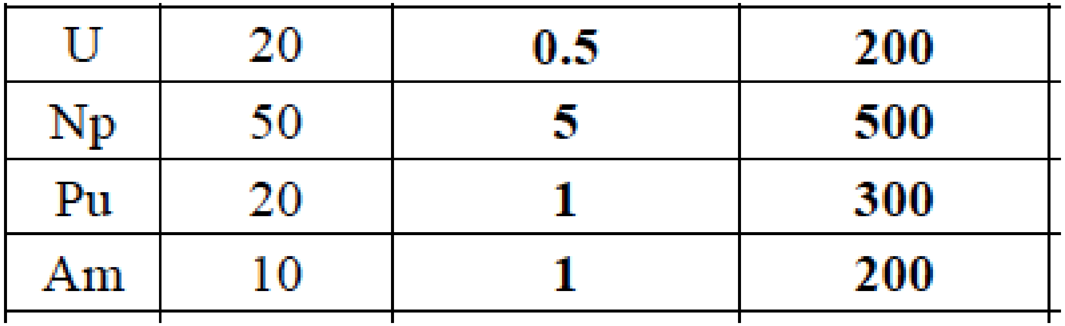


Actinide migration

Kd simplification



Element	K_d		
	Ref. case $[m^3\,kg^{-1}]$	Lower limit (pessimistic) $[m^3\,kg^{-1}]$	Upper limit (optimistic) $[m^3\,kg^{-1}]$
C_{inorg}	0.001	1×10^{-4}	0.006
C_{org}	0	0	0
Cl	0	0	0
Ca	0.001	1×10^{-4}	0.007
Sr	0.001	1×10^{-4}	0.007



U	20	**0.5**	**200**
Np	50	**5**	**500**
Pu	20	**1**	**300**
Am	10	**1**	**200**

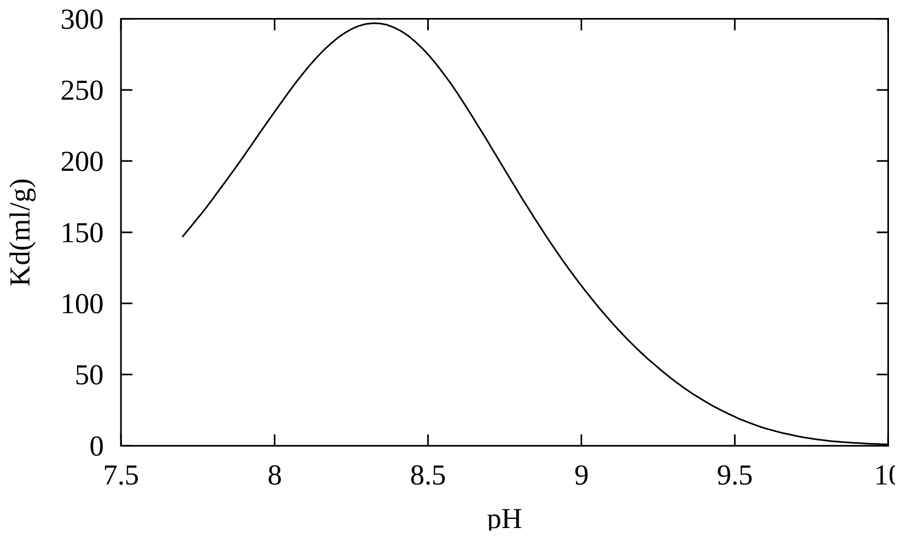
$$K_d\,[m^3/kg] = \frac{w}{(1-w)\,r_s}\,\frac{F(Np)}{(Np)} = \frac{w}{(1-w)\,r_s}\,K_d\,[-]$$

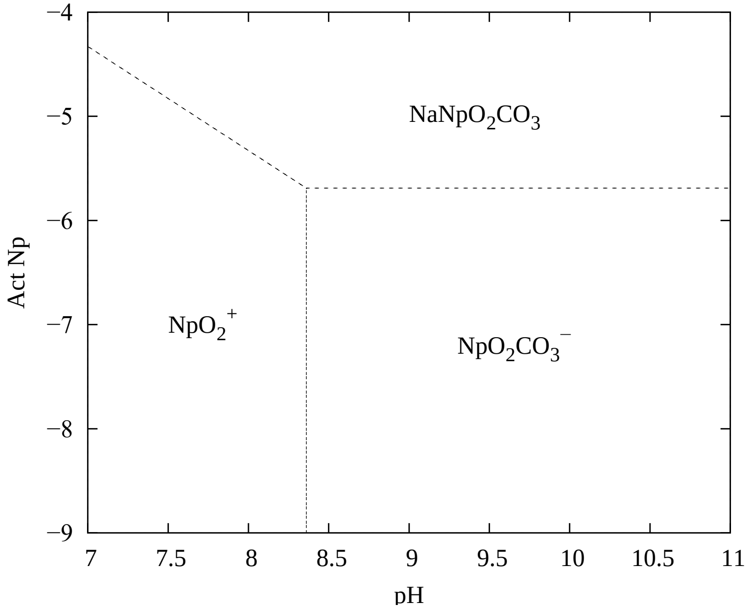
Spent fuel disposal in Opalinus clay

Values for the Opalinus Clay

Actinides are strongly sorbed onto the clayey rock

Note on Kd sensitivity to pH…





Kd values can significantly change according to the chemistry (pH, etc.) and this can be estimated by reactive transport modeling.

Actinide migration

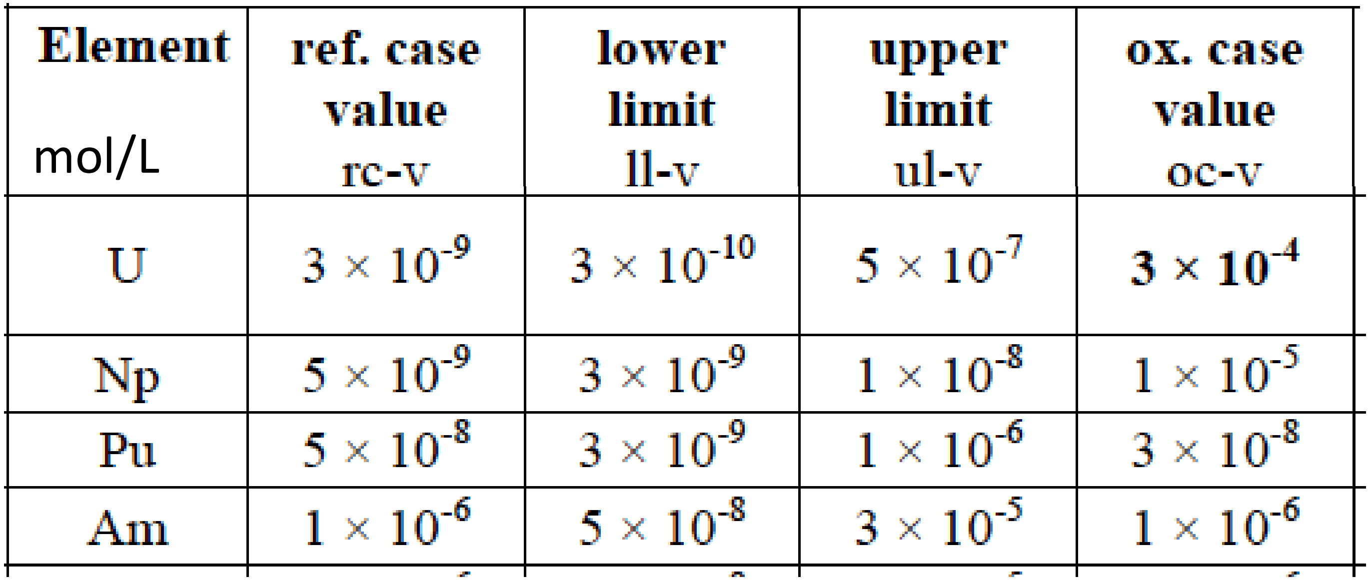
Solubility limit simplification

$$R\frac{\partial \omega c}{\partial t} = div(D_e(\omega)\overrightarrow{grad}(c) - c\vec{U}) - \lambda \omega c$$

with the constraint that *c* ≤ *solubility limit*

Actinide migration

Solubility limit simplification



Element mol/L	ref. case value rc-v	lower limit ll-v	upper limit ul-v	ox. case value oc-v
U	3×10^{-9}	3×10^{-10}	5×10^{-7}	$\mathbf{3 \times 10^{-4}}$
Np	5×10^{-9}	3×10^{-9}	1×10^{-8}	1×10^{-5}
Pu	5×10^{-8}	3×10^{-9}	1×10^{-6}	3×10^{-8}
Am	1×10^{-6}	5×10^{-8}	3×10^{-5}	1×10^{-6}

Spent fuel disposal in Opalinus clay

Values for the Opalinus Clay

U – Np – Pu solubility is slow under reducing condition but can strongly increase under oxic conditions

Am solubility is relatively high but non sensitive to redox conditions

Actinide migration

Solubility limit simplification

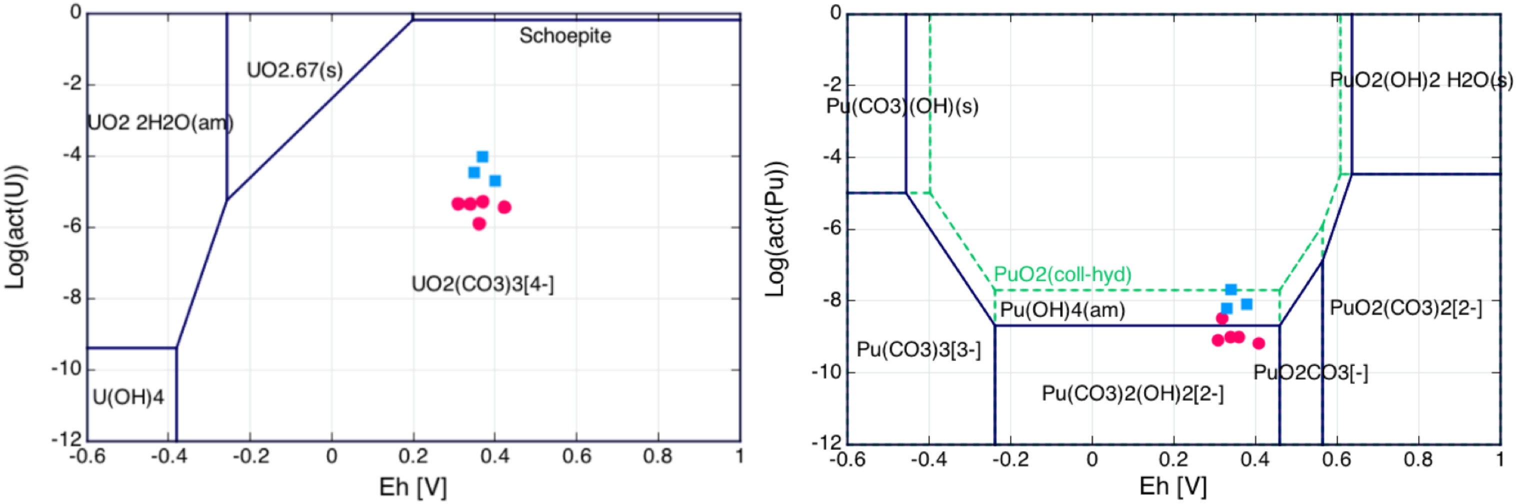
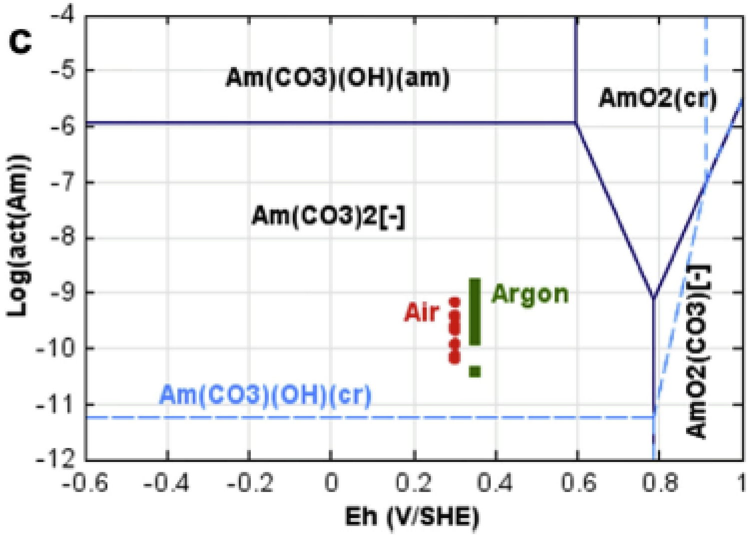


Figure 1: U and Pu activity vs Eh diagram in carbonated water (10^{-2}M) at pH 9. Red dot: homogeneous MOx. Blue square : heterogeneous MOx [19]

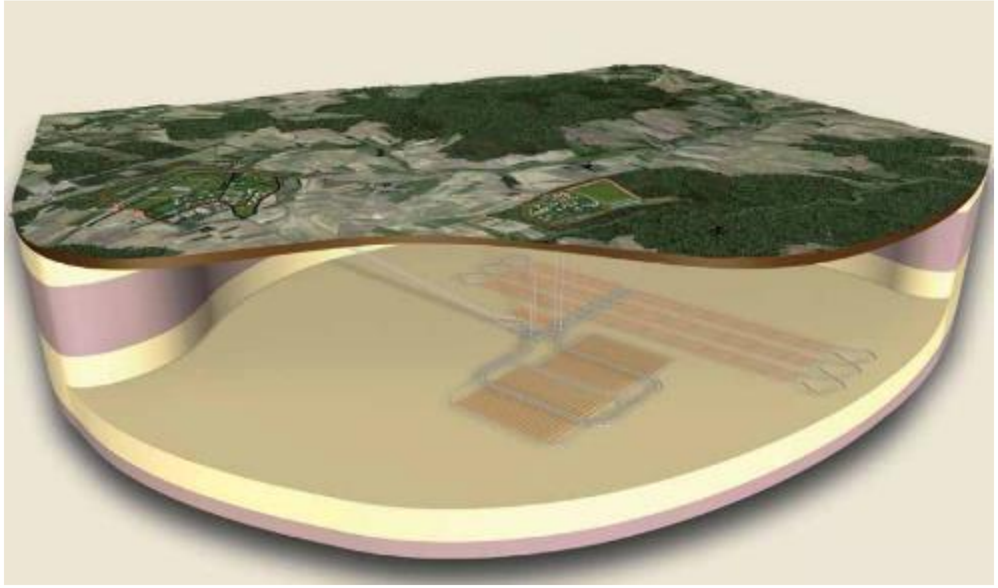


Outline

- Main processes of actinide migration in the geosphere
- Basis of reactive transport modeling
- Why using reactive modeling in underground radioactive waste disposal
- Modeling of spent-fuel (and vitrified waste) leaching experiments

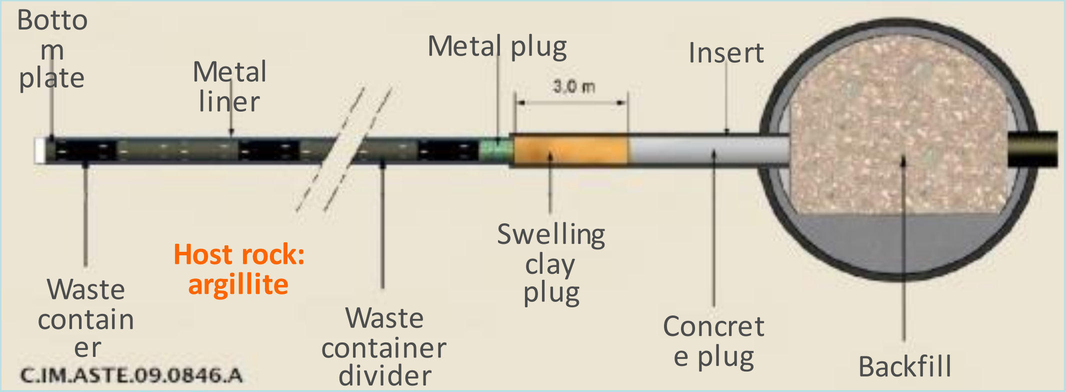
Wasteform reactivity in disposals

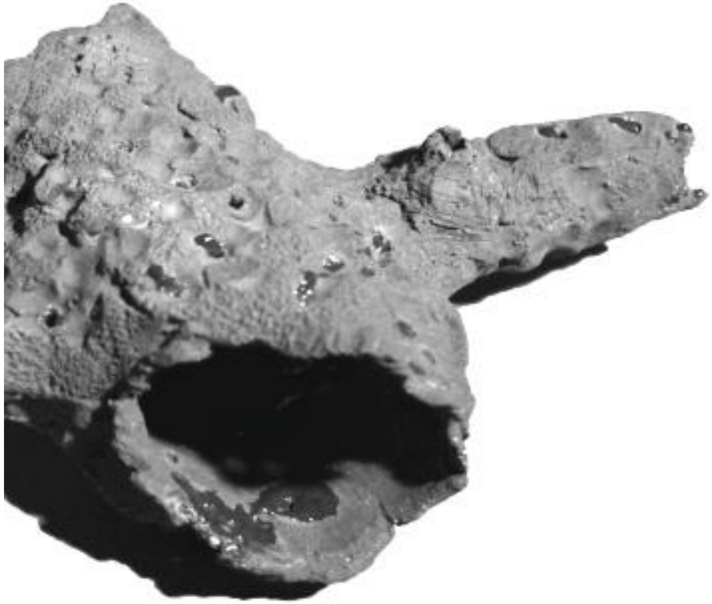
Long term evolution



Underground radioactive waste disposals = multi-barrier system

Assess of the durability of an industrial facility for several thousands of years





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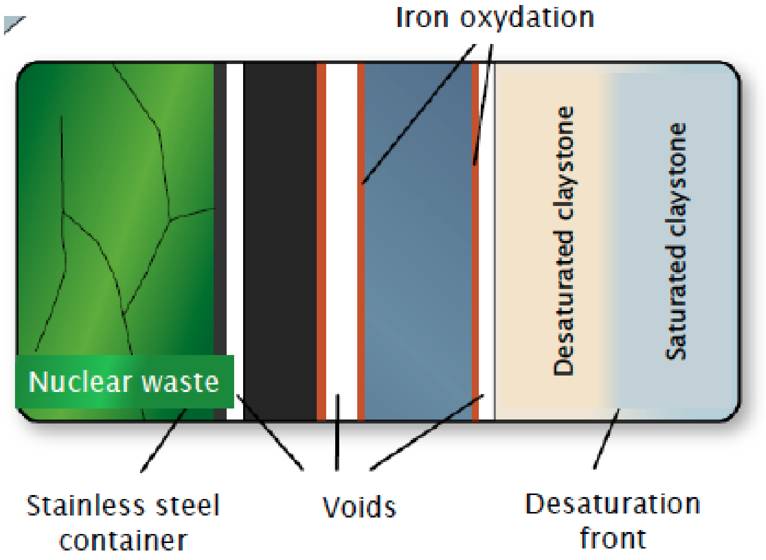
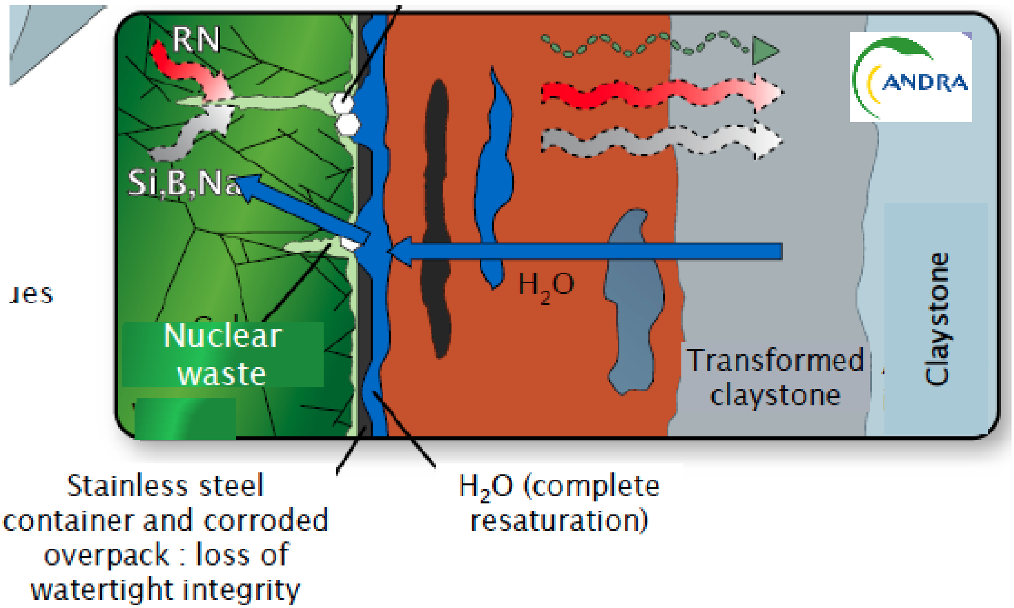
Wasteform reactivity in disposals

Long term evolution





Reactive transport modeling

Wasteform reactivity

- Reactive transport modeling is applied to
    - the other engineered materials (clay, glass, steel)
    - the geosphere (unsaturated zone, host rock)

- Share the same databases, e.g. ThermoChimie, Thermoddem, CEMDATA-PSI…

- Can be coupled to thermic and gas processes

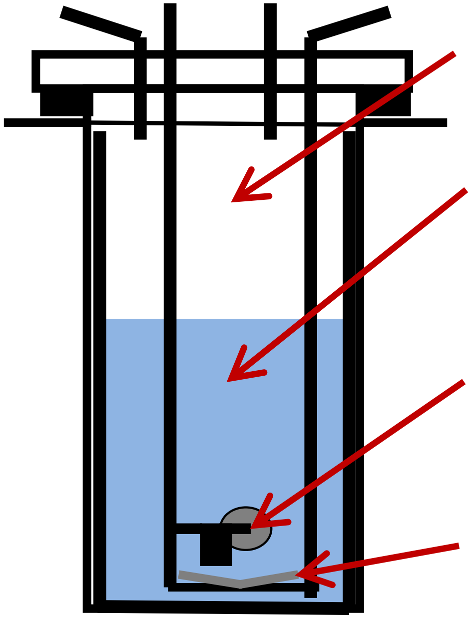
- Can simulate long-term duration, from century to 100 000 years

- Therefore, great generality and flexibility

- However, complexity and strong coupling ==> specialized (and more efficient) approaches, especially in terms of mechanics

Pu-doped UO_2 leaching

In a synthetic clayey pore water and iron foil



Gaseous phase Ar/CO_2 3000 ppm (P=3,5 bars)

↳ Anoxic atmosphere

Carbonated water/Synthetic COx water

↳ To simulate environmental water chemistry

Different kinds of nuclear fuel (Pu-doped UO_2 pellets, MOx 7% pellets, or spent fuel fragments)

↳ To test their reactivity

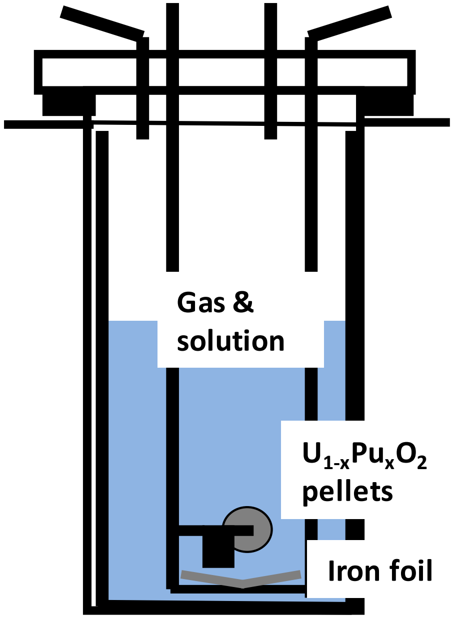
Iron foil

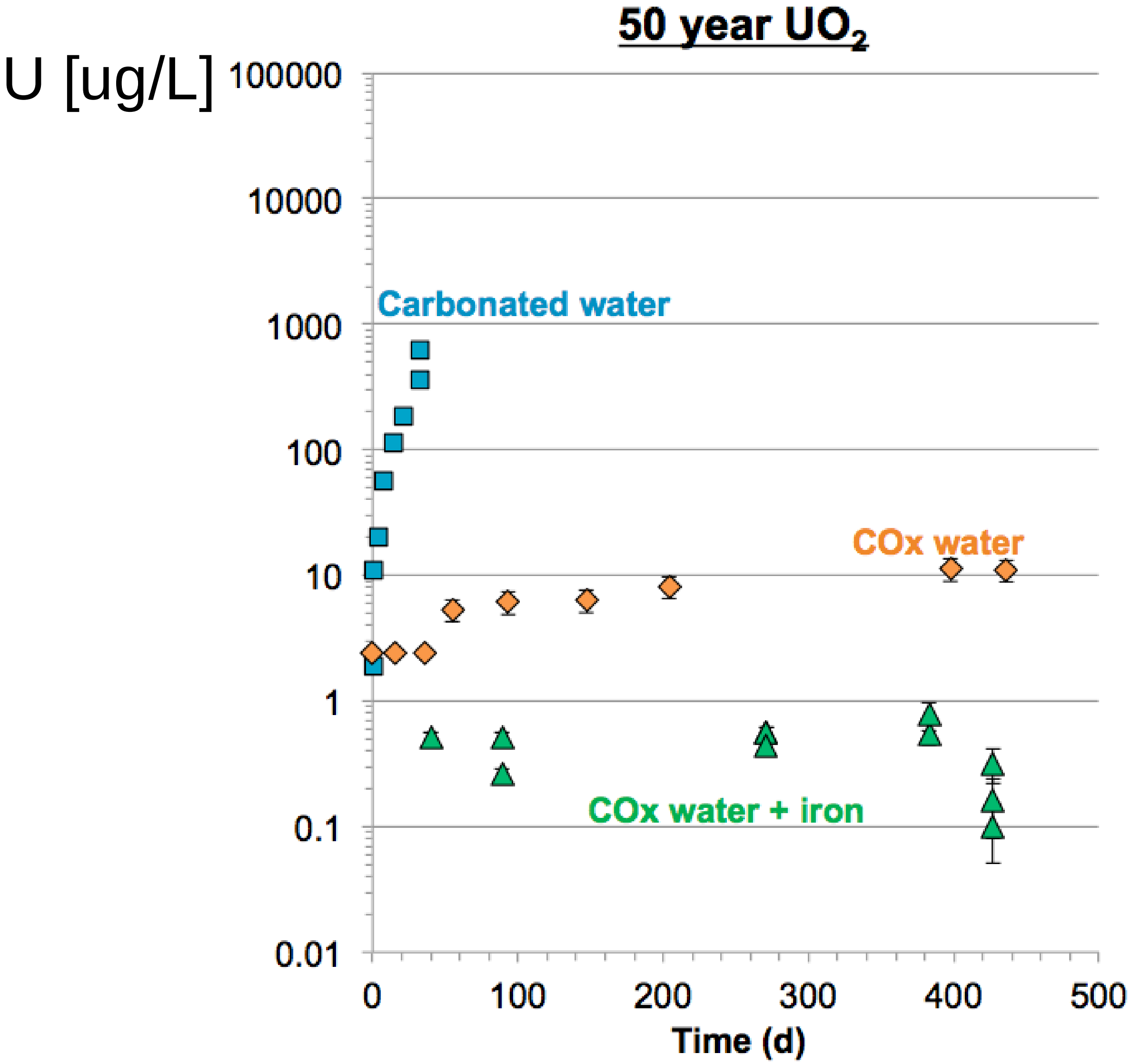
↳ To simulate the steel container

T = 25 °C

Pu-doped UO_2 leaching

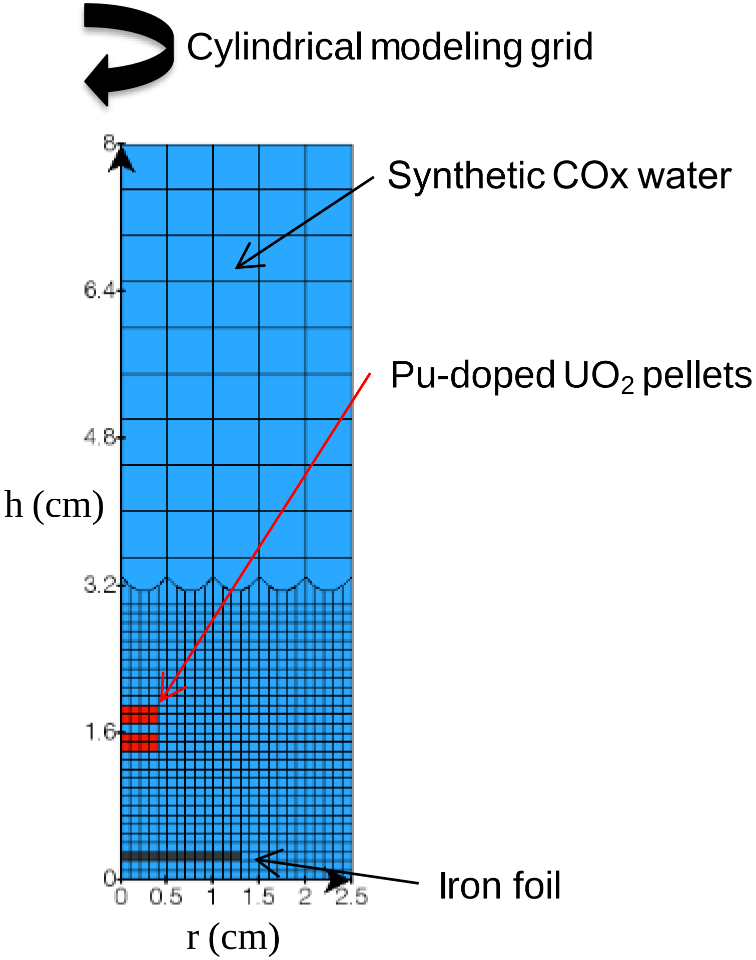
In a synthetic clayey pore water and iron foil





Pu-doped UO_2 leaching

Reactive transport


Cylindrical modeling grid

Synthetic COx water

Pu-doped UO_2 pellets

Iron foil

No stirring during lab test
=> diffusion and coupling

$$\frac{\partial \omega c_i}{\partial t} = \nabla(D_e.\nabla c_i) - \frac{\partial \omega \bar{c}_i}{\partial t}$$

Pu-doped UO_2 leaching

Geochemical thermodynamics and kinetics

- Code : **CHESS - HYTEC**
- Database: **ThermoChimie** (Andra)
  + added species (H_2O_2, Pu-doped UO_2,…)
- Added kinetic laws:

H_2O_2 production

$$\frac{d[H_2O_2(aq)]}{dt} = \frac{d[H_2(aq)]}{dt} = k_{rad}\, A_{UO_2}$$

$$k_{rad} = 10^{-9}\ mol.m^{-2}.sec^{-1}\ \left(385\ MBq.g_{UO_2}^{-1}\right)$$

H_2O_2 disproportionation

$$H_2O_2(aq) \rightarrow H_2O + 0.5O_2(aq)$$

$$\frac{d[H_2O_2(aq)]}{dt} = k_{disp}\,[H_2O_2(aq)]$$

Iron corrosion

$$Fe + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2(aq)$$

$$\frac{d[Fe]}{dt} = k_{anox}\, A_{Fe}\ ;\ k_{anox} = 10^{-9}\ mol.m^{-2}.sec^{-1}$$

Pu-doped UO_2 dissolution

$$\frac{d[UO_2]}{dt} = R_{total} = R_{red} + R_{O_2} + R_{H_2O_2}$$

In reducing media

$$UO_2 + H_2O \rightleftharpoons U(OH)_4(aq)$$

$$R_{red} = \frac{d[UO_2]}{dt} = k_{red}\, A_{UO_2}\left(\frac{IAP}{K_{UO_2}} - 1\right)$$

$$k_{red} = 10^{-12}\ mol.m^{-2}.sec^{-1}$$

In oxidizing media

H_2O_2

$$UO_2 + 2H^+ + H_2O_2(aq) \rightarrow {UO_2}^{2+} + 2H_2O$$

$$R_{H_2O_2} = \frac{d[UO_2]}{dt} = k_{ox}^{H_2O_2}\, A_{UO_2}\,(H_2O_2(aq))^{0.59}$$

$$k_{ox}^{H_2O_2} = 10^{-6}\ mol.m^{-2}.sec^{-1}$$

O_2

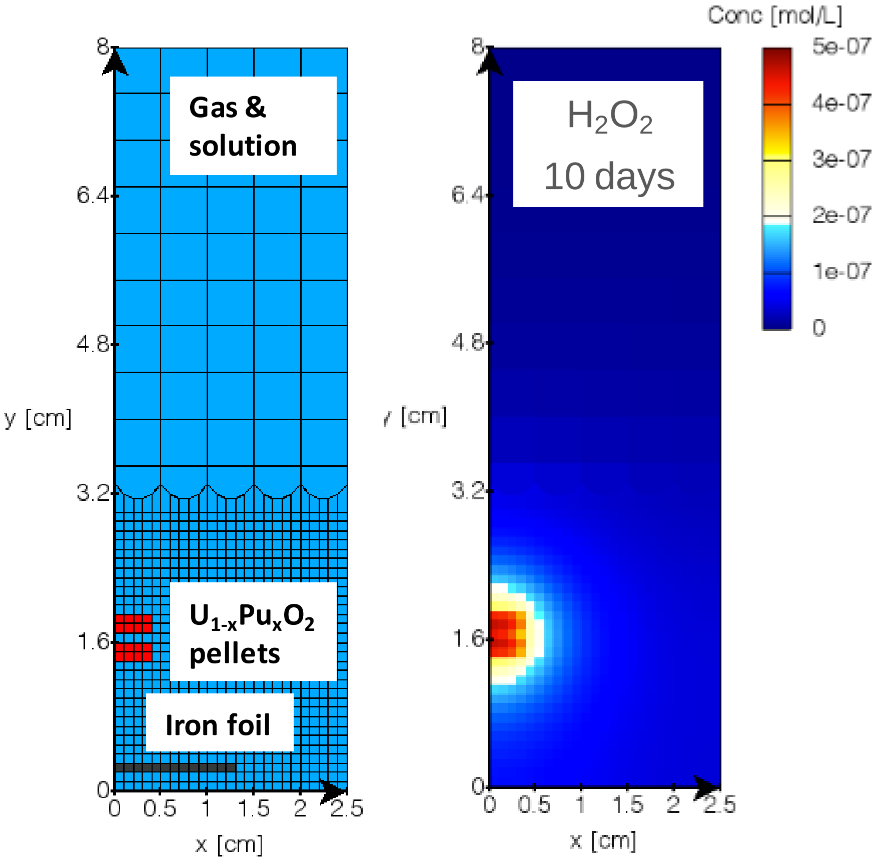
$$UO_2 + 2H^+ + 0.5O_2(aq) \rightarrow {UO_2}^{2+} + H_2O$$

$$R_{O_2} = \frac{d[UO_2]}{dt} = k_{ox}^{O_2}\, A_{UO_2}\,(O_2(aq))^{0.74}$$

$$k_{ox}^{O_2} = 10^{-7}\ mol.m^{-2}.sec^{-1}$$

Pu-doped UO_2 leaching

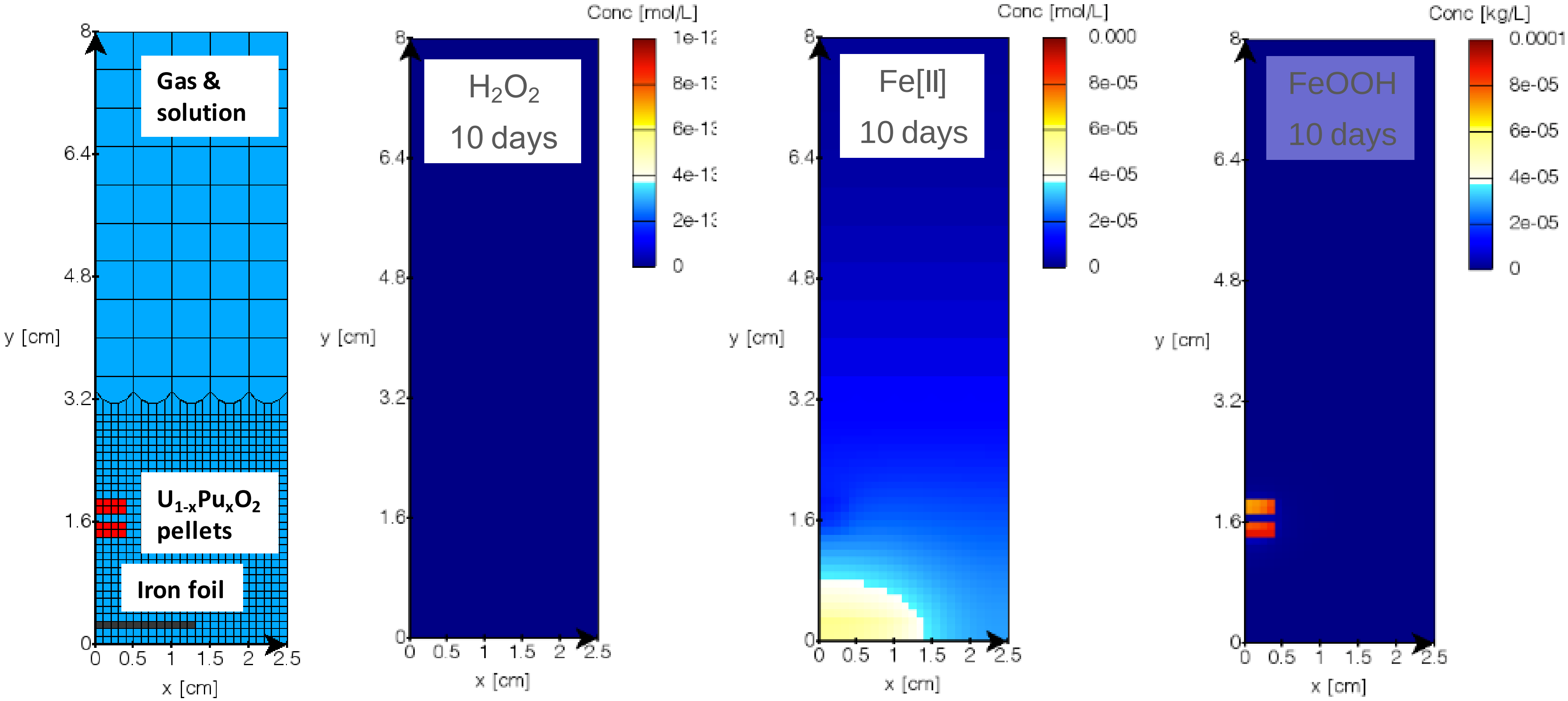
Reaction H_2O_2 / Fe^{2+} at the UO_2 surface



$$2H_2O \rightarrow H_2O_2(aq) + H_2(aq)$$

Pu-doped UO_2 leaching

Reaction H_2O_2 / Fe^{2+} at the UO_2 surface

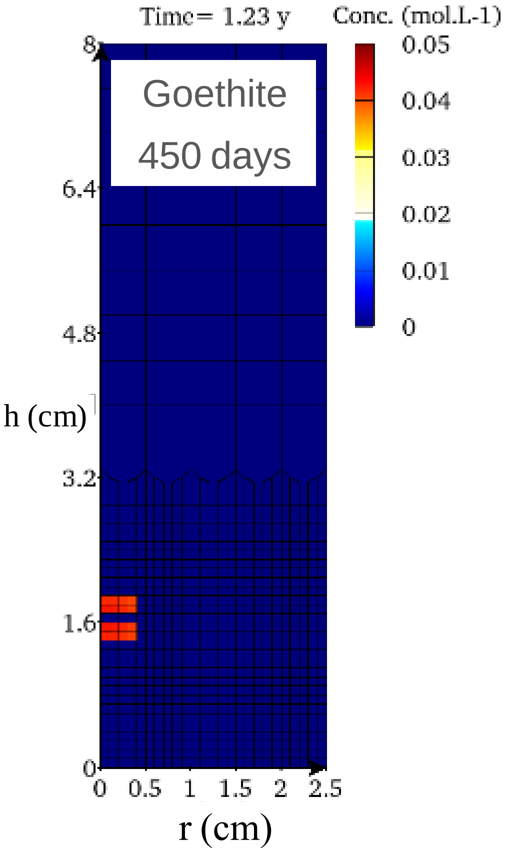


$$Fe + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2(aq)$$

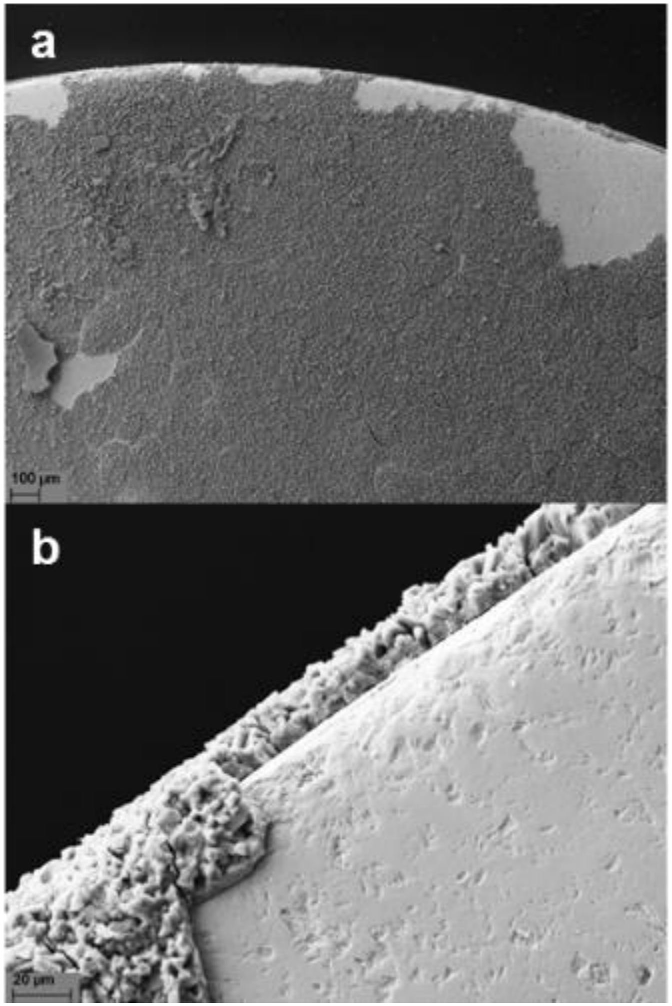
$$Fe^{2+} + 0.5H_2O_2(aq) + 2OH^- \rightarrow FeOOH(s) + H_2O$$

Pu-doped UO_2 leaching

Reaction H_2O_2 / Fe^{2+} at the UO_2 surface

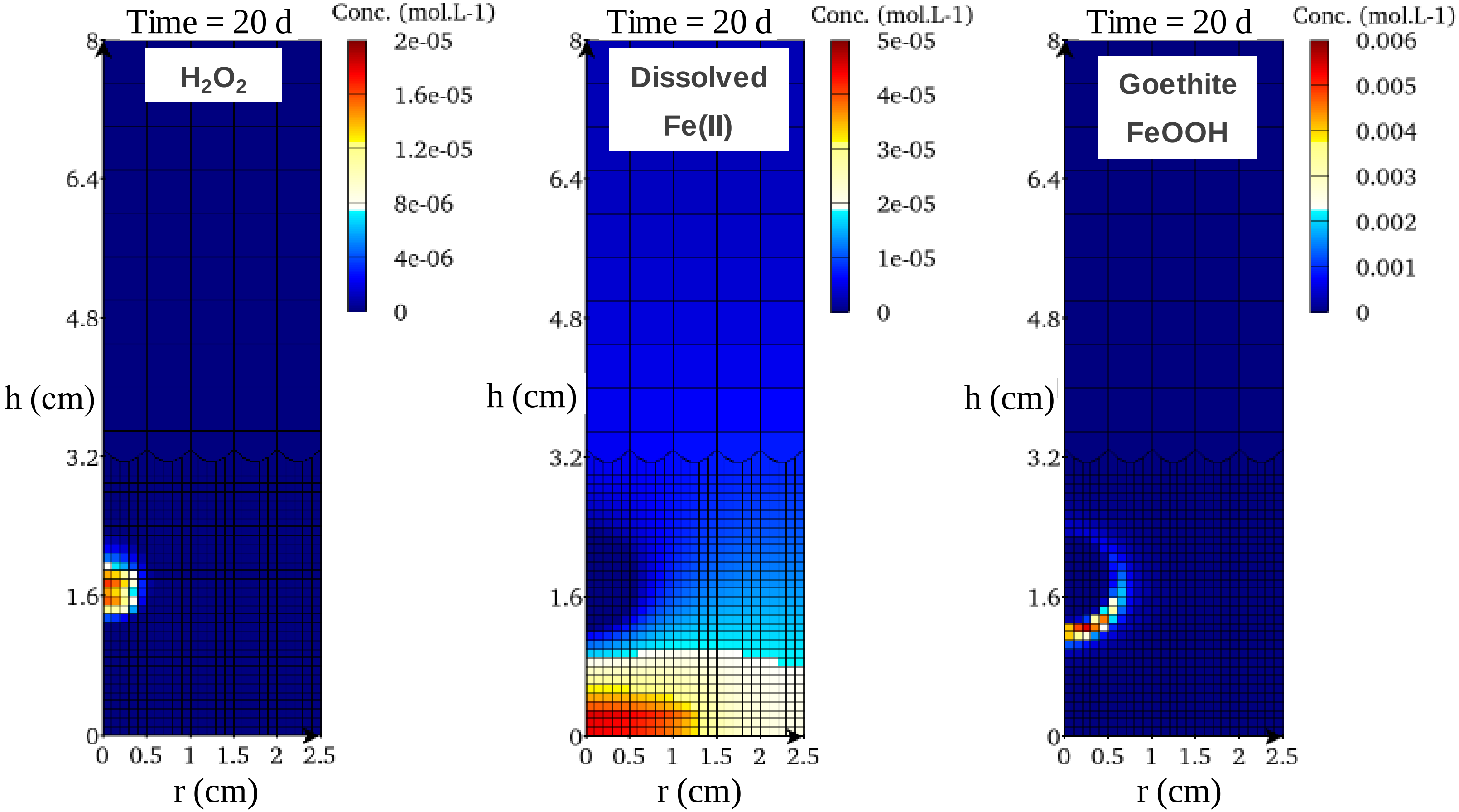


50-years UO_2



Pu-doped UO_2 leaching

Displacement of the redox front

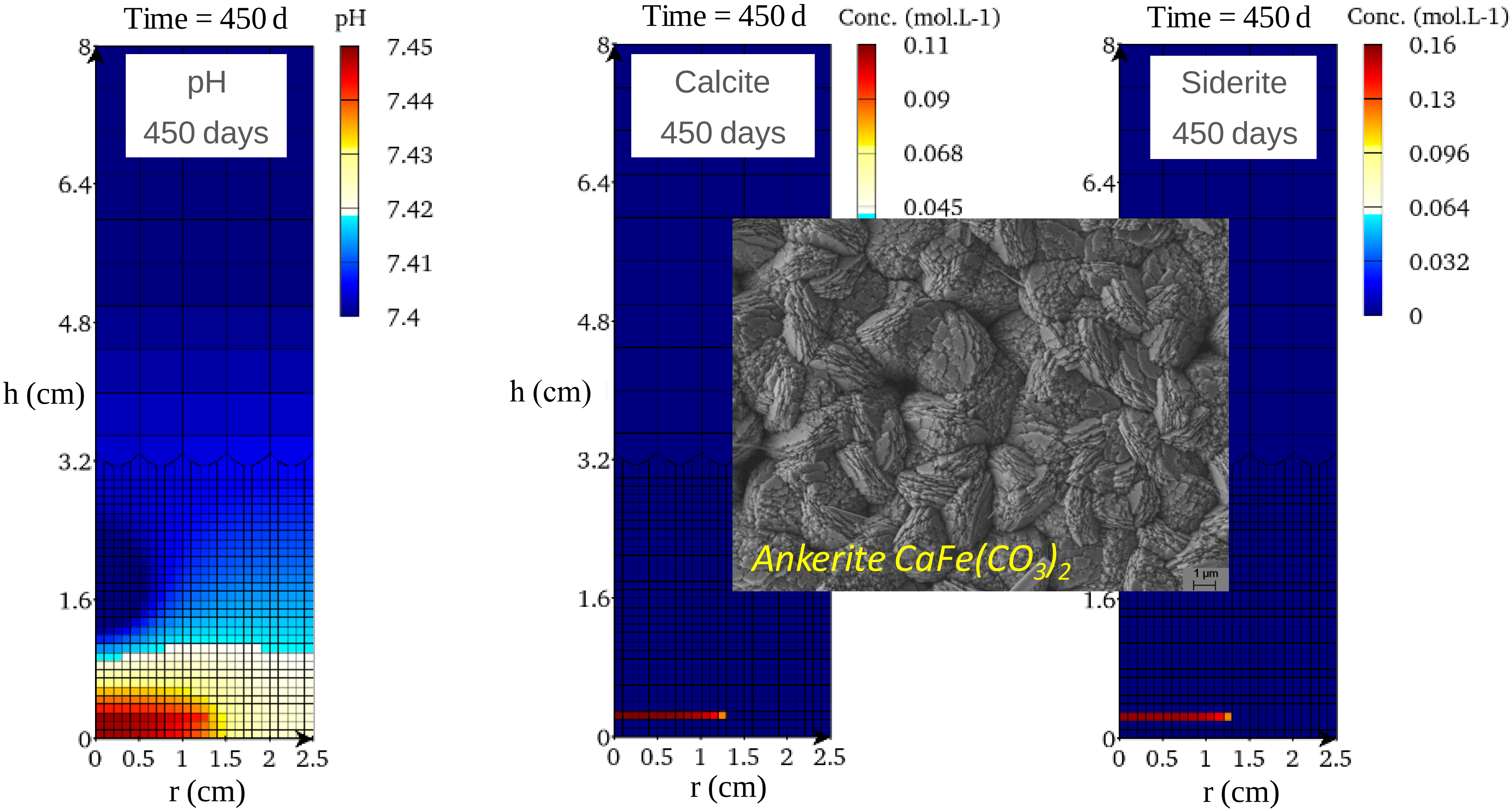


If H_2O_2 primary production is increased by 50

→ the precipitation front of FeOOH is shifted in solution

Pu-doped UO_2 leaching

Corrosion products on the iron foil surface



Ankerite $CaFe(CO_3)_2$

$Fe° + 2\ H_2O \rightarrow Fe^{2+} + 2\ OH^- + H_{2(g)}$

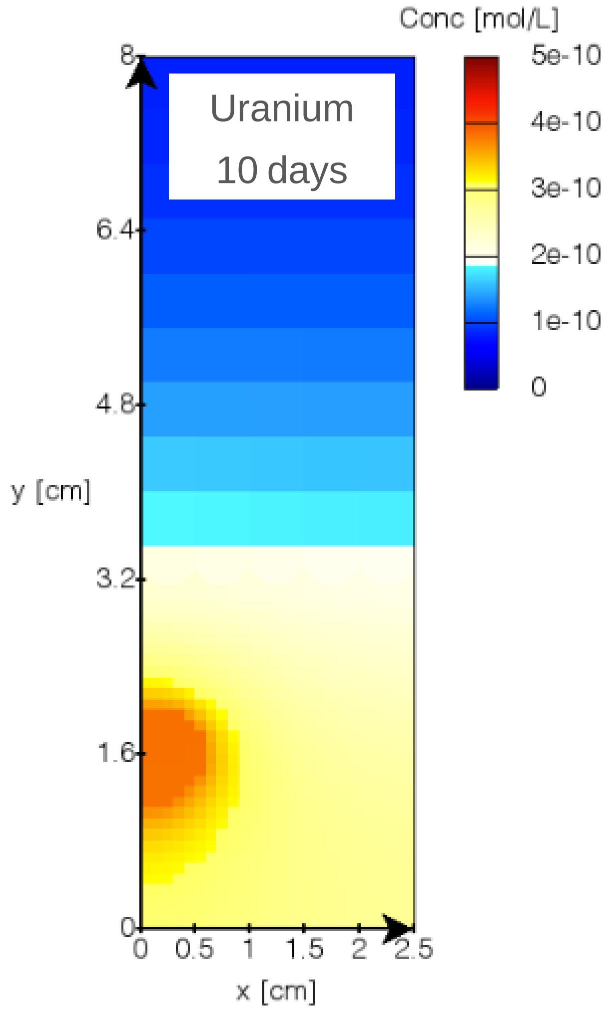
$HCO_3^+ + OH^- \rightleftharpoons CO_3^{2-} + H_2O$

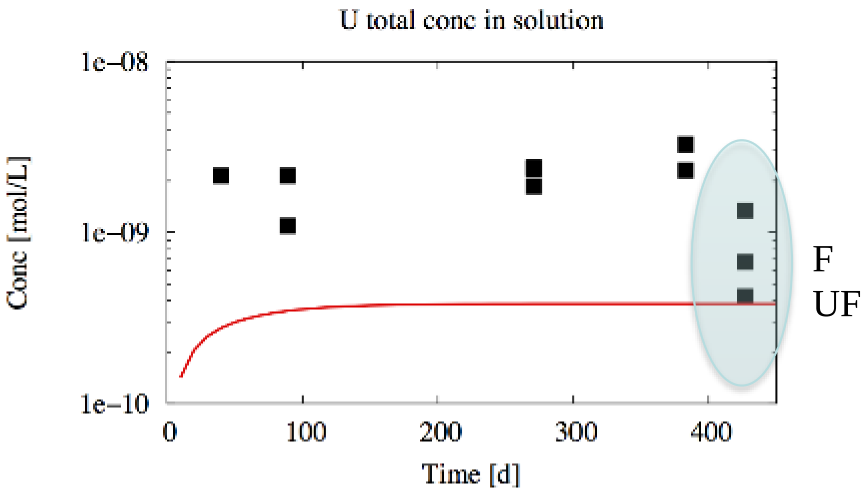
$Ca^{2+} + CO_3^{2-} \rightleftharpoons$ calcite

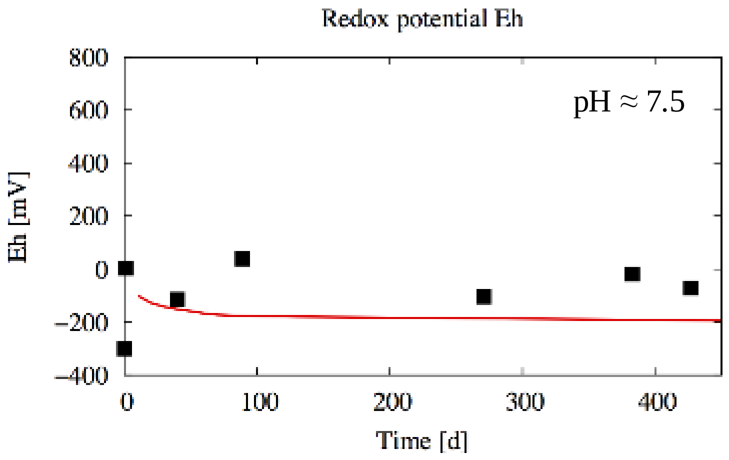
$Fe^{2+} + CO_3^{2-} \rightleftharpoons$ siderite

Pu-doped UO_2 leaching

Uranium in solution and redox potential

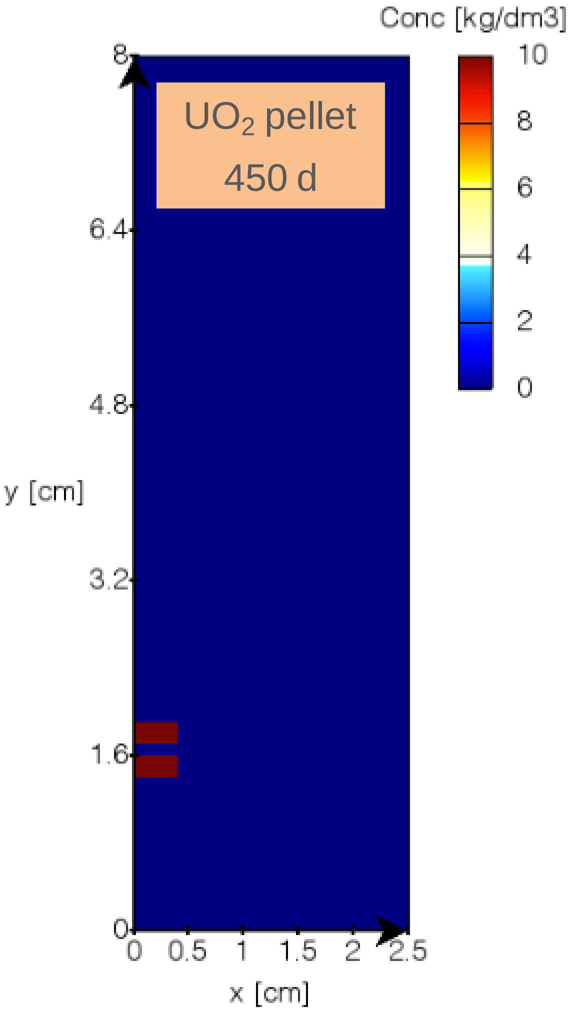


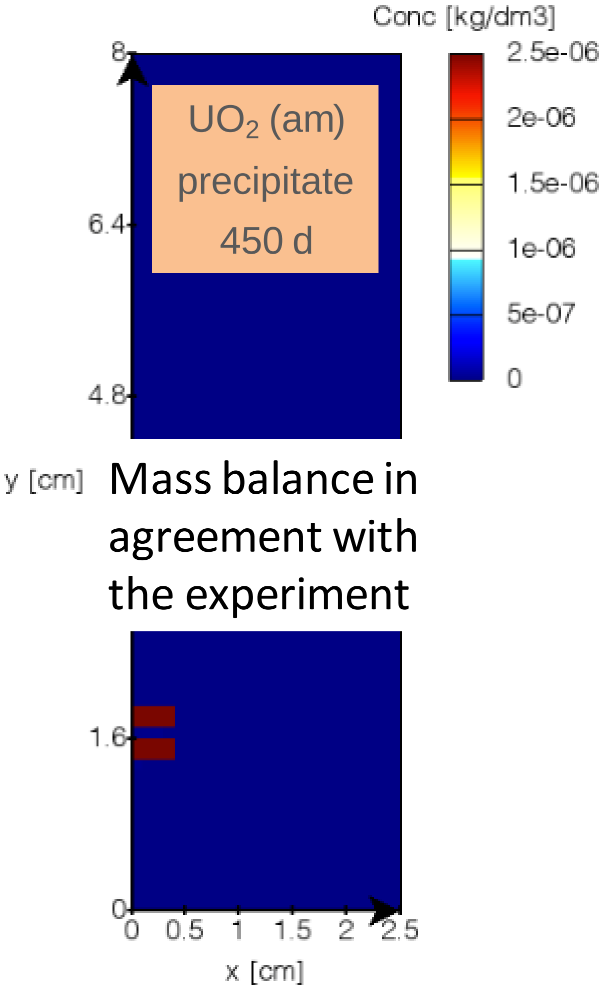




Pu-doped UO_2 leaching

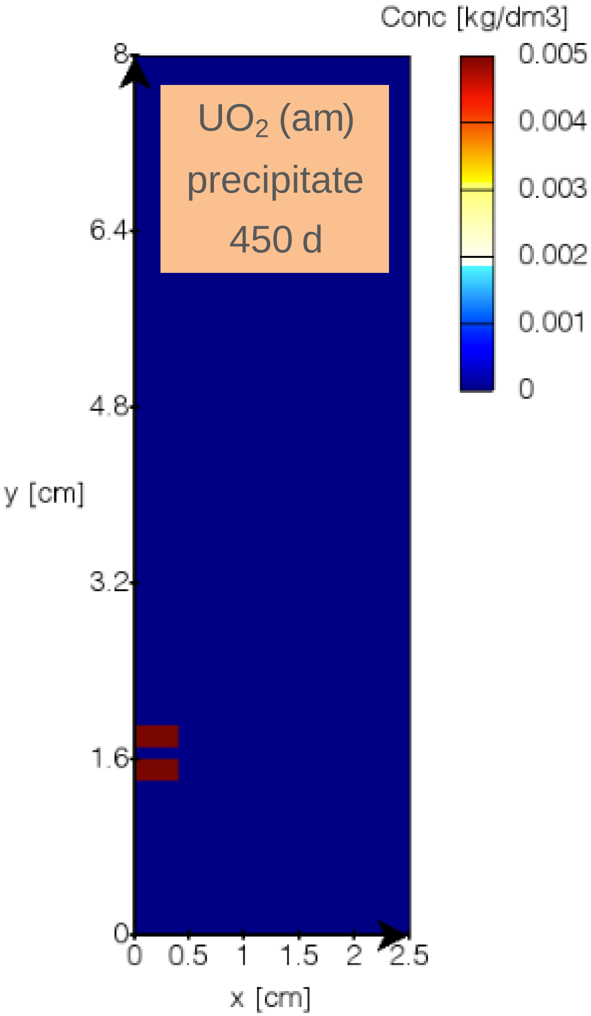
Uranium release





Mass balance in agreement with the experiment

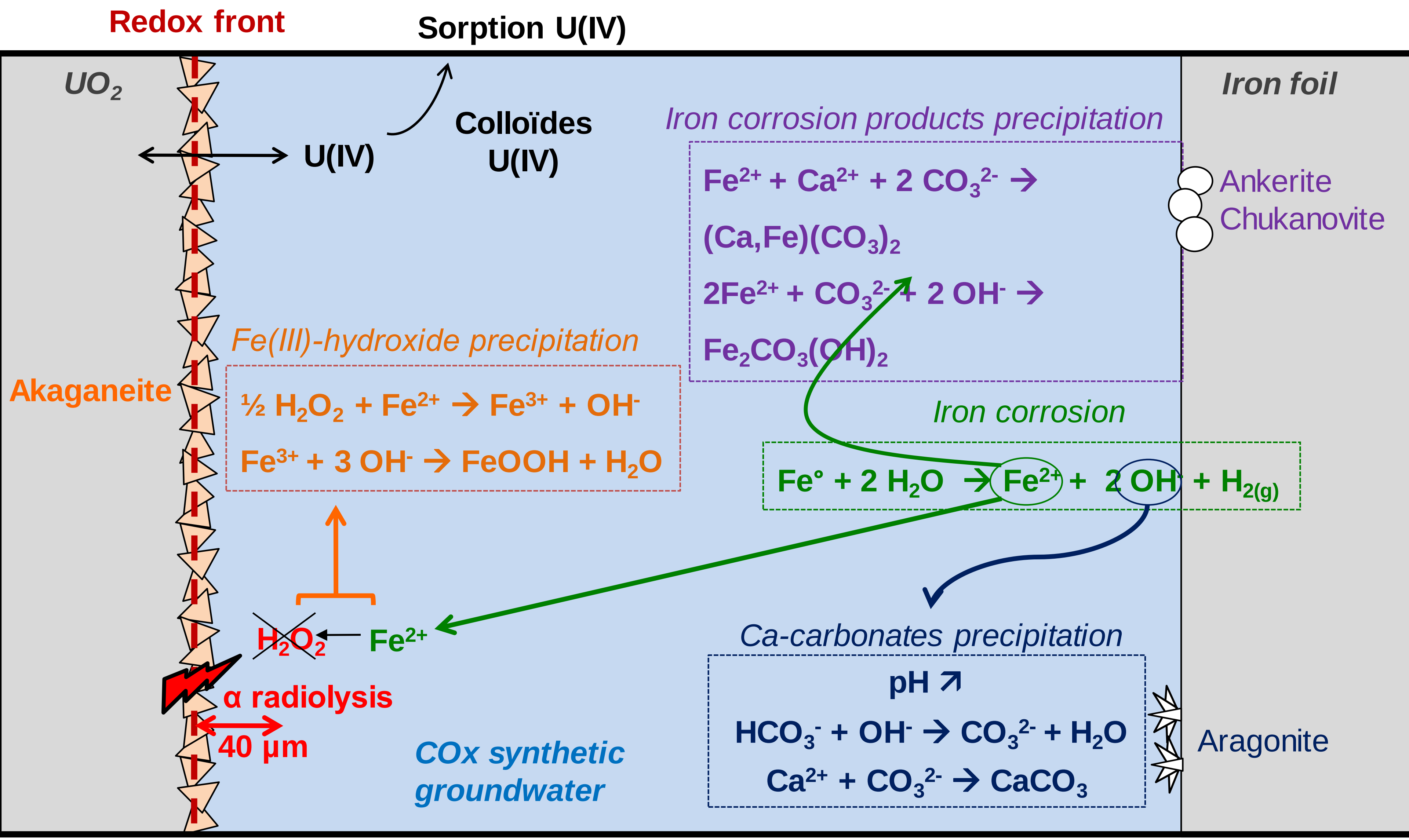
H_2O_2 scavenging by Fe(II)



U(VI) secondary reduction by Fe(II)

Pu-doped UO_2 leaching

Common experiment/modeling mechanisms



Redox front

Sorption U(IV)

UO_2

U(IV)

Colloïdes U(IV)

Iron foil

Iron corrosion products precipitation

$Fe^{2+} + Ca^{2+} + 2\,CO_3^{2-} \rightarrow (Ca,Fe)(CO_3)_2$

$2Fe^{2+} + CO_3^{2-} + 2\,OH^- \rightarrow Fe_2CO_3(OH)_2$

Ankerite

Chukanovite

Fe(III)-hydroxide precipitation

Akaganeite

$\frac{1}{2}\,H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^-$

$Fe^{3+} + 3\,OH^- \rightarrow FeOOH + H_2O$

Iron corrosion

$Fe° + 2\,H_2O \rightarrow Fe^{2+} + 2\,OH^- + H_{2(g)}$

$\cancel{H_2O_2} \leftarrow Fe^{2+}$

α radiolysis

40 µm

COx synthetic groundwater

Ca-carbonates precipitation

pH ↗

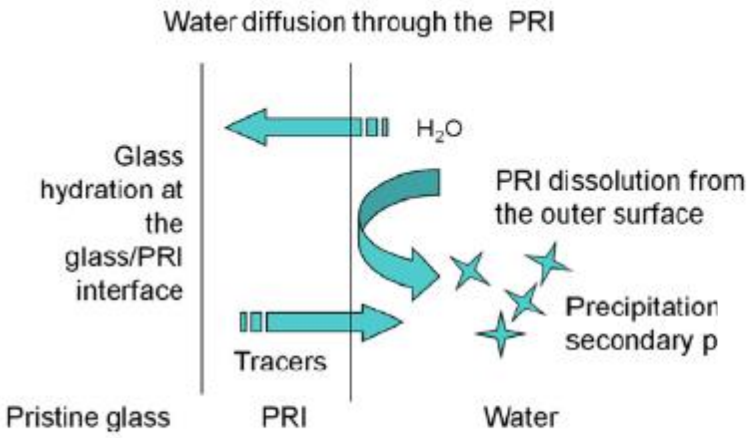
$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$

$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$

Aragonite

Borosilicate glass leaching

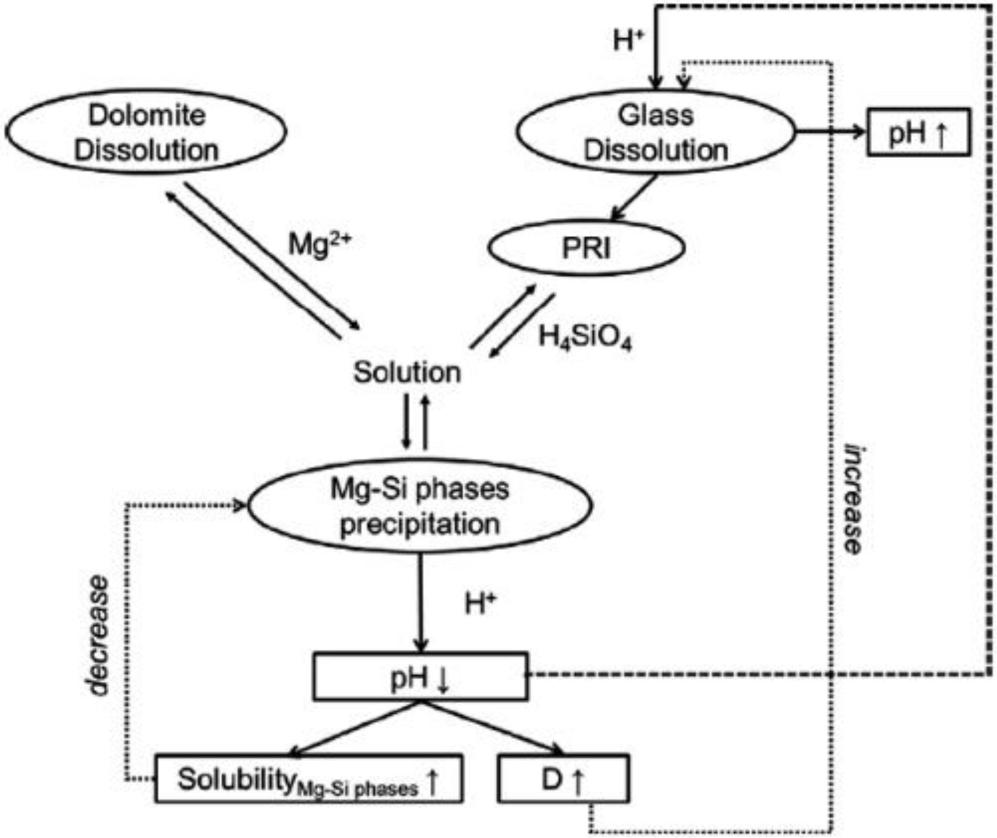
In Mg-rich environment



Stages I – II and III

have demonstrated than Mg sustains glass dissolution at a high rate due to Mg-Si phase precipitation and pH effect

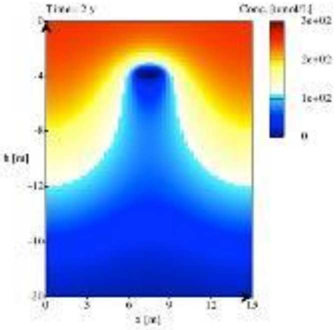
Implementation of the GRAAL model in HYTEC …



To conclude

Actinide migration

- Source term chemical reaction + advection and/or diffusion
- Complexation enhance stability
- Sink terms = precipitation and sorption
- Colloids can enhance migration

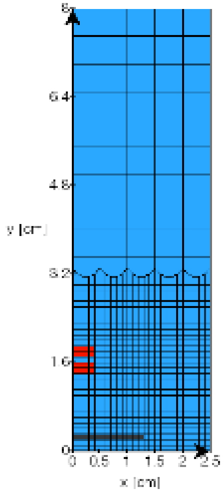


In deep clayey rocks,

- Actinides are strongly sorbed and have a low solubility (Am excepted) but their chemistry is highly sensitive to redox.

Reactive transport modeling

- Couple chemical – hydrodynamic – thermal processes
- Simulate both actinide migration and waste/rock interactions
- Support but not replace safety assessment (Kd, etc.)
- Useful to interpret actinide waste immobilization experiments,
    - but ask the modeler the parameters he needs before starting ;)



References for this talk

Reactive transport modeling (RTM)

- De Windt, L., van der Lee, J., Schmitt, J.-M. (2005). Modélisation en géochimie des eaux. Concepts et applications aux problèmes d'environnement, Techniques de l'Ingénieur AF6530.

- Steefel, C.I. et al. (2015). Reactive transport codes for subsurface environmental simulation, Computational Geosciences 19, 445–478.

- van der Lee, J., De Windt, L. (2001). Present state and future modeling of geochemistry in hydrogeological systems, Journal of Contaminant Hydrology 47, 265-282.

- van der Lee, J., De Windt, L., Lagneau, V., Goblet, P. (2003). Module-oriented modeling of reactive transport with HYTEC, Computers and Geosciences 29, 265-275.

Some applications of RTM to wasteform leaching experiments

- Debure, M., De Windt, L., Frugier, P., Gin, S. (2013). HLW glass dissolution in the presence of magnesium carbonate : Diffusion cell experiment and coupled modeling of diffusion and geochemical interactions, Journal of Nuclear Materials 443, 507–521.

- De Windt, L., Pellegrini, D., van der Lee, J. (2004). Coupled modeling of cement/ claystone interactions and radionuclides migration, Journal of Contaminant Hydrology 68, 165-182.

- Frugier, P., Gin, S., Minet, Y., Chave, T., Bonin, B., Godon, N., Lartigue, J.E., Jollivet, P., Ayral, A., De Windt, L., Santarini, G. (2008). SON68 nuclear glass dissolution kinetics : Current state of knowledge and basis of the new GRAAL model, Journal of Nuclear Materials 380, 8-21.

- Odorowski, M., Jegou, C., De Windt, L., Broudic, V., Jouan, G., Peuget, S., Martin, C. (2017). Effect of metallic iron on the oxidative dissolution of UO2 doped with a radioactive alpha emitter in synthetic Callovian-Oxfordian groundwater, Geochimica et Cosmochimica Acta 219, 1–21.

References for this talk

Kd, solubility limits and thermodynamic data

- Altmaier, M., Gaona, X., Fanghänel, F. (2013). Recent Advances in Aqueous Actinide Chemistry and Thermodynamics, Chem Rev 113, 901-943.
- Bradbury, M.H. , Baeyens, B., Thoenen, T. (2010). Sorption Data Bases for Generic Swiss Argillaceous Rock Systems, Technical Report 09-03, Nagra (CH).
- Giffaut E., et al. (2014). Andra thermodynamic database for performance assessment: ThermoChimie. Appl. Geochem. 49, 225–236.
- Wersin, P., Schwyn, B. (2004), Project Opalinus Clay, Integrated approach for the development of geochemical databases used for Safety Assessment, Technical report 03-06, Nagra (CH).
- Wilhelm, R.G. (2004). Understanding variation in partition coefficient Kd values, Volume III: Review of Geochemistry and Available Kd Values for Americium, Arsenic, Curium, Iodine, Neptunium, Radium, and Technetium, EPA 402-R-04-002C report (USA).