THE USE OF SORPTION DATA IN THE SAFETY CASE
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ILLUSTRATION OF THE ANDRA CIGÉO PROJECT

EURAD II annual meeting – September 2027 • P Henocq (Andra) – JC Robinet (Andra)

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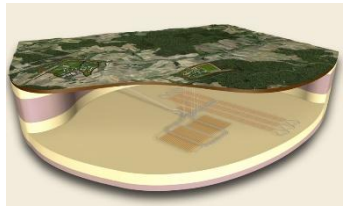
Long-term safety assessments aim to calculate the doses resulting from the release of radionuclides from the waste



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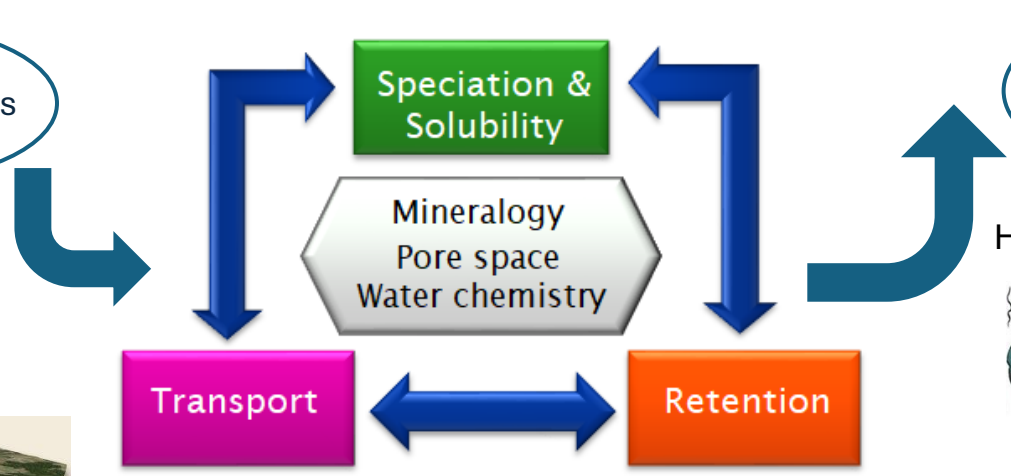
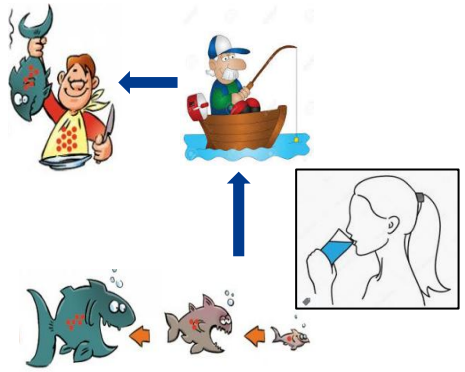


- Cells/vaults/repository **(+ pertubations)**
- Geological formations
- Surface environnements

Human/Non human biota



Accounting for sorption processes must incorporate the requirements of a safety case :

- Robust with respect to process representation
- Manageable for handling various safety scenarios (best-estimate, bounding/envelope, altered, etc.)
- Applicable to all the radionuclides and toxic chemicals concerned

To date the Kd approach remains the most appropriate for carrying out safety calculations

- Simple calculation methods that allow large scales of time and space to be represented
- The independence between radionuclides (as trace elements), which makes it possible to carry out calculations for almost all chemical elements
- Well suited to sensitivity analyses (single- or multi-parameter) allowing to manage the various scenarios

Limitations/implications of using the Kd approach

- Not particularly suitable for disturbed systems with strong geochemical gradients and changes in rock/materials properties over time → needs to adapt (cf. Task 5 of Rampec)
- Collection of data specific to a rock or material
- Selection of **best-estimated values** and a **range of values**
  - There is **no universal method**, and it requires expert judgement and justifications (analogy, statistics, etc.).

How to proceed with sorption data ?

Sorption data are collected (referenced), organized and analyzed to select Kd values to use in the Safety Case

- For **clay-rocks**, each organization has their own "database" (and Kd values selection)
  - Data coming from mainly national programs + additional data coming from international collaborations
    - Natural variability with several locations
    - Effects of perturbations
  - Data on other clays-rocks and pure clays minerals are also collected
- For **cementitious materials** – which are materials used by everyone
  - Data from various national and international projects.
    - For several cement formula
    - For several degradation states
    - Effect of perturbations

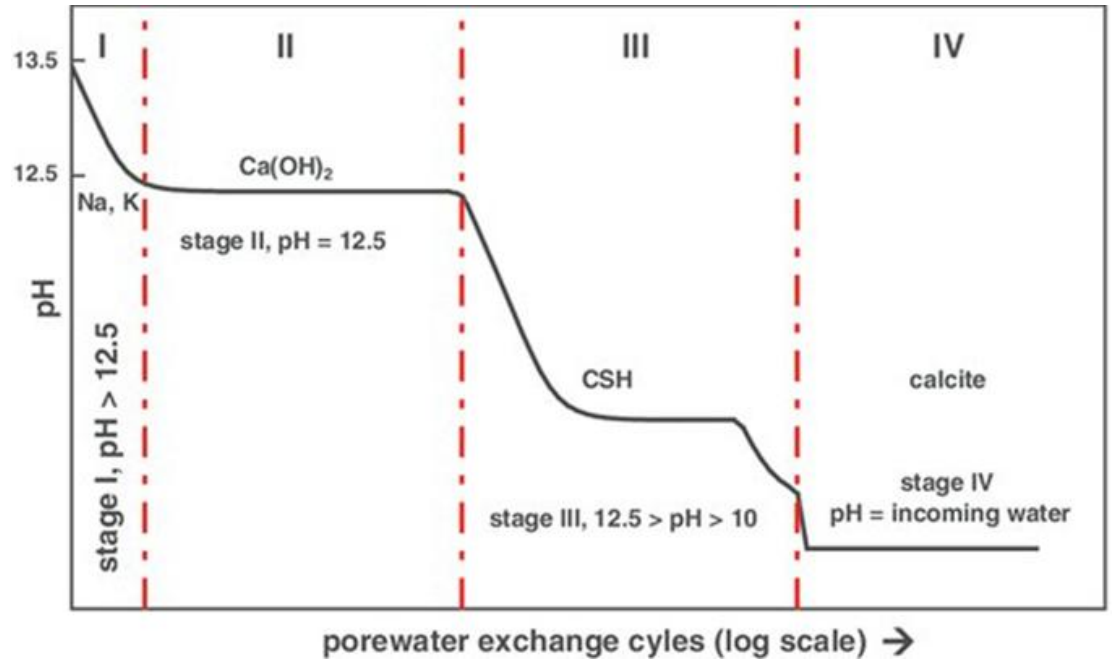
To date, these databases are **not digital databases** containing all the data acquired during sorption tests.

For each chemical element, the robustness of sorption data is analyzed to derive :

- Best-estimate values representative of the repository conditions
- Boundary values including the uncertainties which are related to:
  - Lack of knowledge and data
  - Natural variability for clay-rocks
  - Representativeness of the data toward the repository conditions
  - Concentration effect, competition… but also reversibility, slow kinetic processes

EXAMPLE : SORPTION IN THE CEMENT-BASED MATERIALS

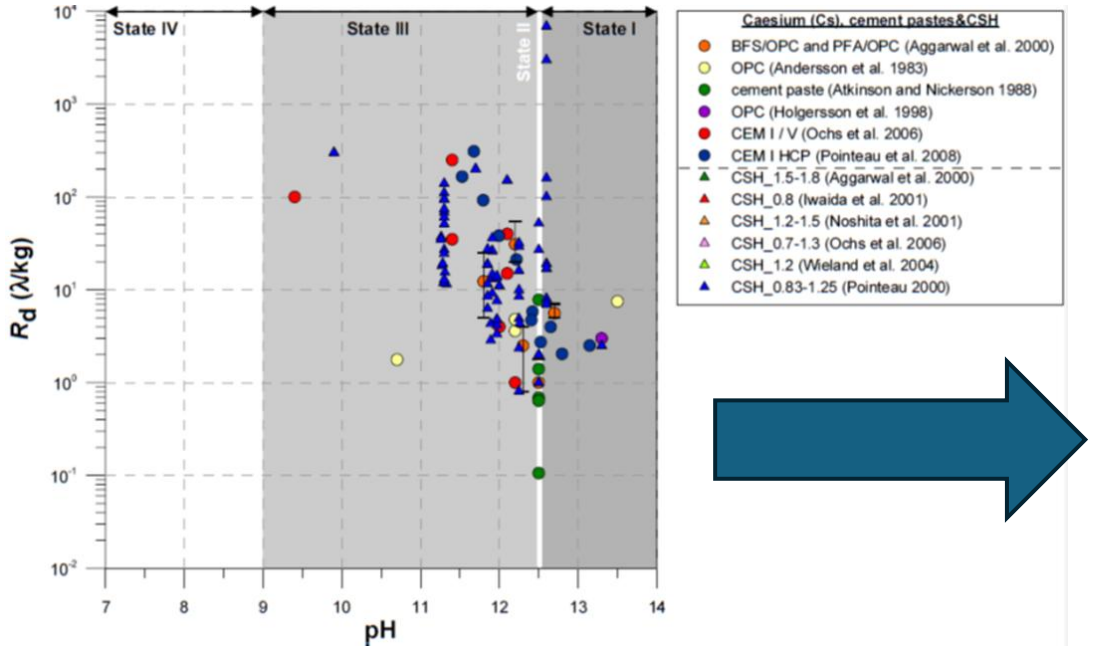
- **4 degradation stages to take into account the chemical evolution with time of the cement-based materials**
- **144 radionuclides**
- **One Kd dataset for each stage**
- **Kd values applied to all the cement-based Materials :**
  - Independently on the formulation (Cement type, W/C)
- **Kd detetermination : Batch experiments**
  - Pastes, mortars
  - Individual phases: C-S-H, Ettringite, Afms, Portlandite
- **Kd evaluation:**
  - Isotherms
  - Empirical models
  - Isotopic models
  - Chemical analogy



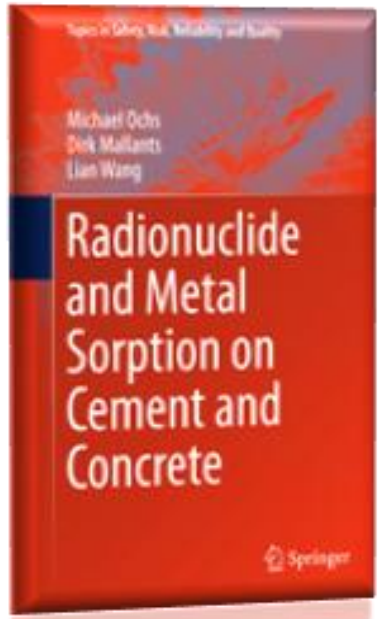
Ochs et al., 2016

A REFERENCE FOR KD VALUES IN CEMENT-BASED MATERIALS

- In the case of cement-based materials, many sorption studies of radionuclides have been carried out in Europe and in many countries
- In 2009 and 2011, an european review of Kd values for the main radionuclides (25) in cement-based materials has been released by Ondraf/NIRAS (Wang et al., 2009 & 2011) and published by Ochs et al. (2016)
- **Approach:**



pH state	Best estimate (ℓ/kg)	Upper limit (ℓ/kg)	Lower limit (ℓ/kg)
State I	i.d.	10^{1}	1×10^{-1}
State II	2×10^{0}	5×10^{1}	1×10^{-1}
State III	2×10^{1}	3×10^{2}	1×10^{0}
State IV	i.d.	i.d.	i.d.



Ochs et al., 2016

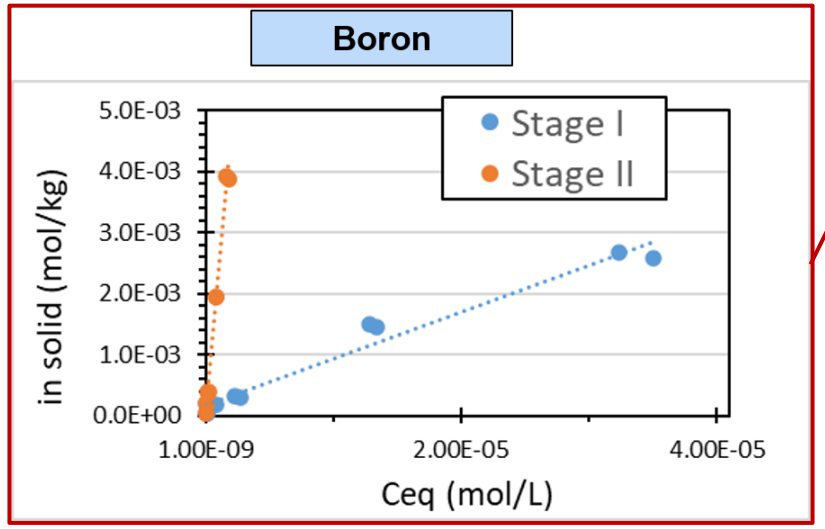
EXAMPLE : SORPTION IN THE CEMENT-BASED MATERIALS

- Database of Kd values (extract)
- Best-estimate & Range of values
- Stage I

Element	Kd ($m^3.kg^{-1}$)	Range of values	Element	Kd ($m^3.kg^{-1}$)	Range of values
HTO	0	-	Sm	10	0,1 – 5 000
Be	5	1 - 50	Gd		
B	1×10^{-1}	5×10^{-3} – $2,5 \times 10^{-1}$	Dy		
C(IV)	2	0,5 - 3	Ho		
C(-IV)	-	-	Lu		
Al	-	-	Hf	-	-
Cl	2×10^{-2}	5×10^{-3} – 5×10^{-2}	Re	1×10^{-3}	-
K	-	-	Hg	-	-
Ca	7×10^{-3}	2×10^{-3} – $2,3 \times 10^{-2}$	Pb	0,3	0,1 – 1
Cr	10	0,1 - 5000	Sr	0,1	0,03 – 0,3
Mn	-	-	Ra	0,3	0,1 – 1
Ni	$6,5 \times 10^{-2}$	3×10^{-2} – $7,3 \times 10^{-1}$	Th	30	1 - 1 000

EXAMPLE : SORPTION IN THE CEMENT-BASED MATERIALS

- **Database of Kd values (extract)**
- **Stage I**
- Boron (B) - Isotherm



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EXAMPLE : SORPTION IN THE CEMENT-BASED MATERIALS

- **Database of Kd values (extract)**
- **Stage I**
- Nickel (Ni) – Isotopic model

Conditions	R_{d,M^*} [m³ kg⁻¹]	$R_{d,M}$ [m³ kg⁻¹]	α
No Ni addition	0.15 ± 0.02	4.6 ± 2.3	(3.3 ± 1.7) × 10^{-2}
$[Ni]_{add} = 10^{-6}$ M			
7 days equilibration	0.22 ± 0.02	4.9 ± 1.0	(4.5 ± 1.0) × 10^{-2}
30 days equilibration	0.20 ± 0.02	6.9 ± 1.4	(2.9 ± 0.6) × 10^{-2}
$[Ni]_{add} = 10^{-4}$ M			
7 days equilibration	1.1 ± 0.1	38.6 ± 7.5	(2.8 ± 0.6) × 10^{-2}
30 days equilibration	1.2 ± 0.1	26.8 ± 5.4	(4.5 ± 1.0) × 10^{-2}

Partition coefficient:

$$\alpha = \frac{(n_{s,M^*}/n_{s,M})}{(n_{l,M^*}/n_{l,M})} = \frac{R_{d,M^*}}{R_{d,M}}$$

Wieland et al. (2006)

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EXAMPLE : SORPTION IN THE CEMENT-BASED MATERIALS

- **Database of Kd values (extract)**
- **Stage I**
- Lanthanides – Am as analogue

Chemical analogy with Am

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HTO	0	-	Sm		
Be	5	1 - 50	Gd		
B	1×10^{-1}	5×10^{-3} – $2,5 \times 10^{-1}$	Dy	10	0,1 – 5 000
C(IV)	2	0,5 - 3	Ho		
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CONCLUSION

- **A Kd model is widely used to support the safety assessments**
  - Suitable for many cases
  - Easily manageable in terms of modelling
  - Simplifications inducing uncertainties → several sorption mecanisms do not verified the Kd conditions (incorporation, isotopic exchange,..)

- **A Kd value is associated to**
  - One system : a given solution in equilibrium with the solid (clay- or cement-based materials)
  - → if the system evolves, Kd should modify (need to have the corresponding experimental data)

- **The safety case need to collect Kd data**
  - Numercial database with all experimental conditions is not required
  - But justifications of how the Kd is selected are needed
  - For cement based materials, international initiatives could be generalized to create (numerical) databases

- **Further comparisons between Kd and geochemical models are required for disturbed systems**
  - Aim of WP RAMPEC : TASKs 4&5