NA of far-field retardation: current status, what remains to be done?

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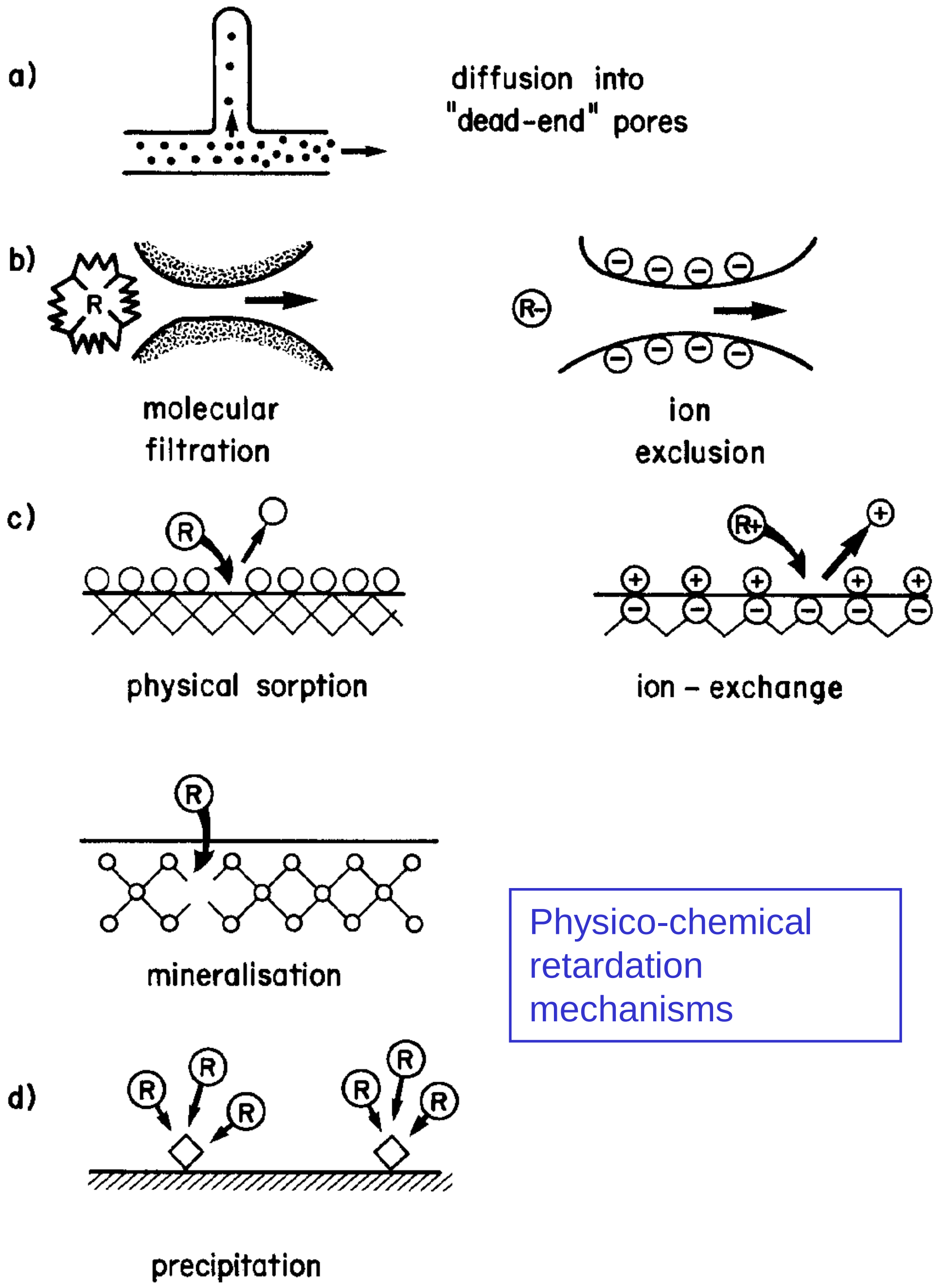
Radionuclide retardation processes

- A number of processes can limit the rate at which radionuclides released from waste can move back to the geosphere
- Although all retard movement of solute compared to bulk water, they involve different mechanisms that require separate model representations

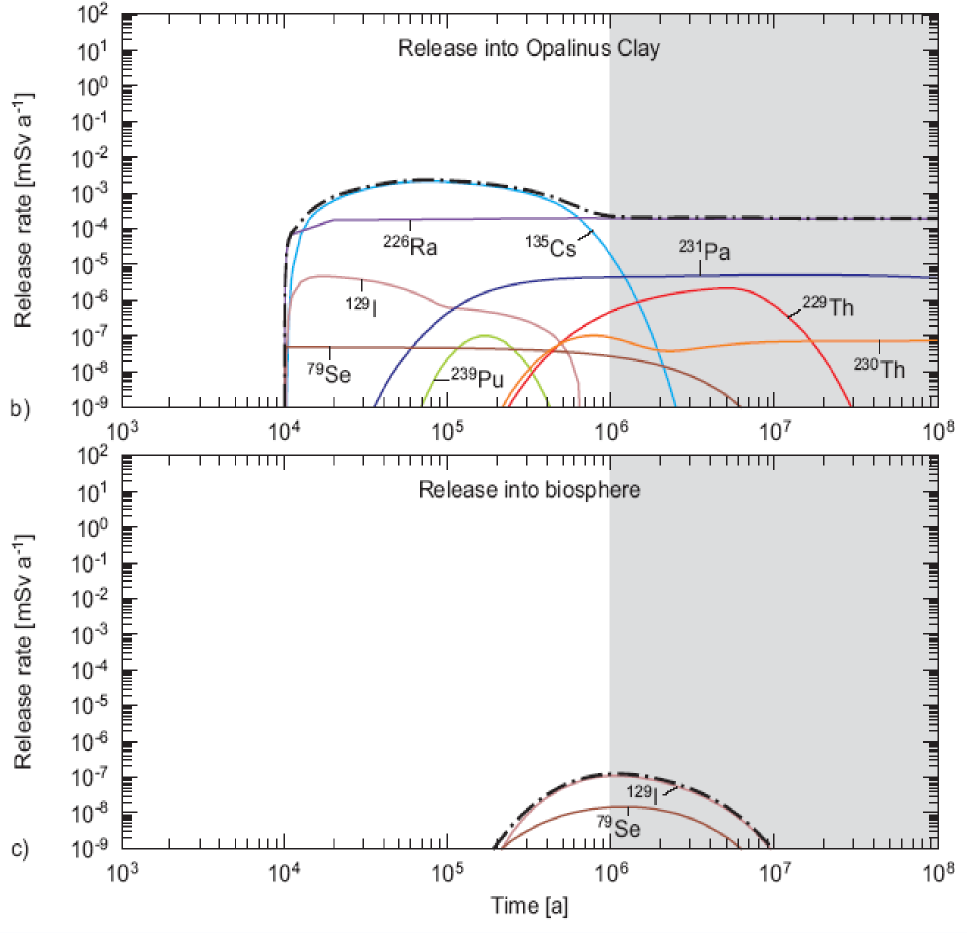
➔ Different processes must be carefully distinguished – as highlighted here in 1984



Physico-chemical retardation mechanisms

Significance of radionuclide retardation

- The significance of RN retardation is very site- and waste-specific
- In some cases, can ensure that releases are completely insignificant
  - Strongly retarded, short-lived RN decay in the geosphere or are released only in the far-distant future
  - Less retarded, long-lived RN released at trivial concentrations due to spatial and temporal dilution



Quantification of retardation

- Laboratory studies provide data on scales of months / cm, which occasionally can be extended up to a few years / m
- However, models often make extrapolations in excess of 10^6 years over flow paths of several km
- Such models can be readily **verified** but **validation** is much trickier
- Is process understanding correct? Values justified?
- **Validation must incorporate analogue support**

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Current status of RN transport models

- Little advance in modelling RN transport over the last 3 decades
- Simplistic representation of sorption in terms of a Kd and retardation by a constant Rf

Quantification of retardation processes

- Background information for **fractured rocks**
  - Hydrogeology & solute transport
  - Sorption & precipitation
  - Matrix diffusion
  - Colloids
  - Microbes
  - Reaction fronts
- Key uncertainties and data requirements
- **In order to identify required analogue support, it is important to understand the processes involved and how they are quantified in performance assessment**

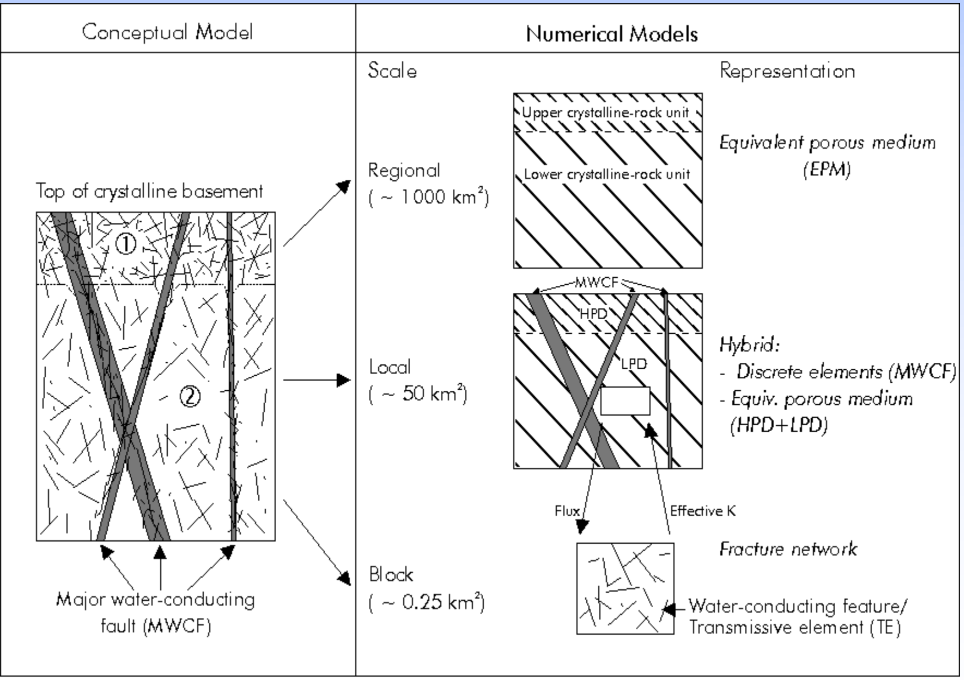
Hydrogeology & solute transport

Hydro models are developed on a range of physical scales:

- fracture-flow may be complex but treatment can involve considerable simplifications of the real system

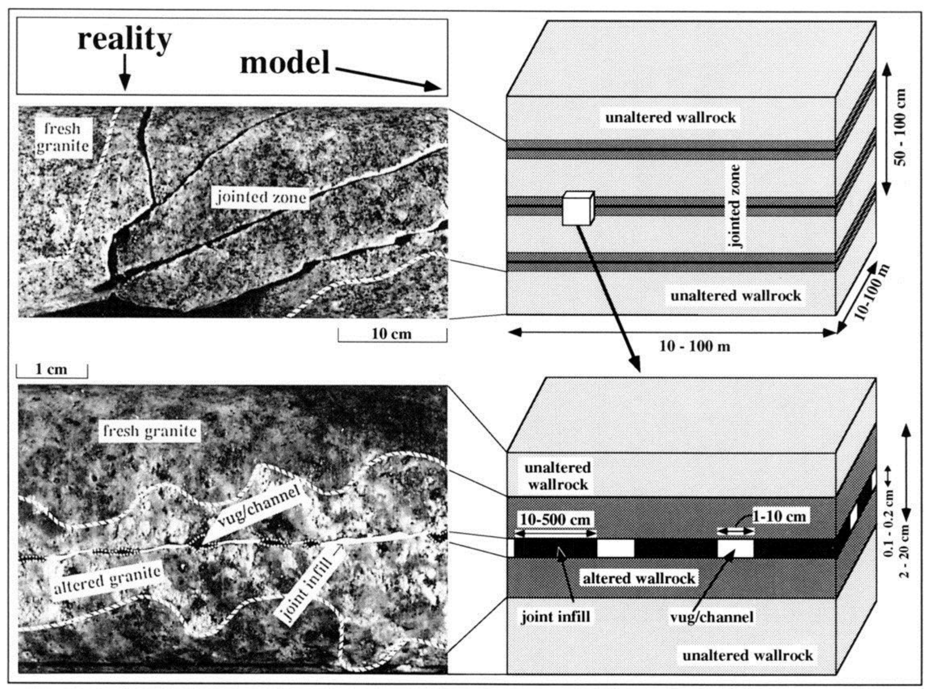
Solute transport models require flow paths to be specified in much more detail:

- both physical and chemical processes can contribute to RN retardation



① Upper crystalline-rock domain; designated as higher-permeability domain (HPD) in area West

② Lower crystalline-rock domain; designated as low- permeability domain (LPD) in area West



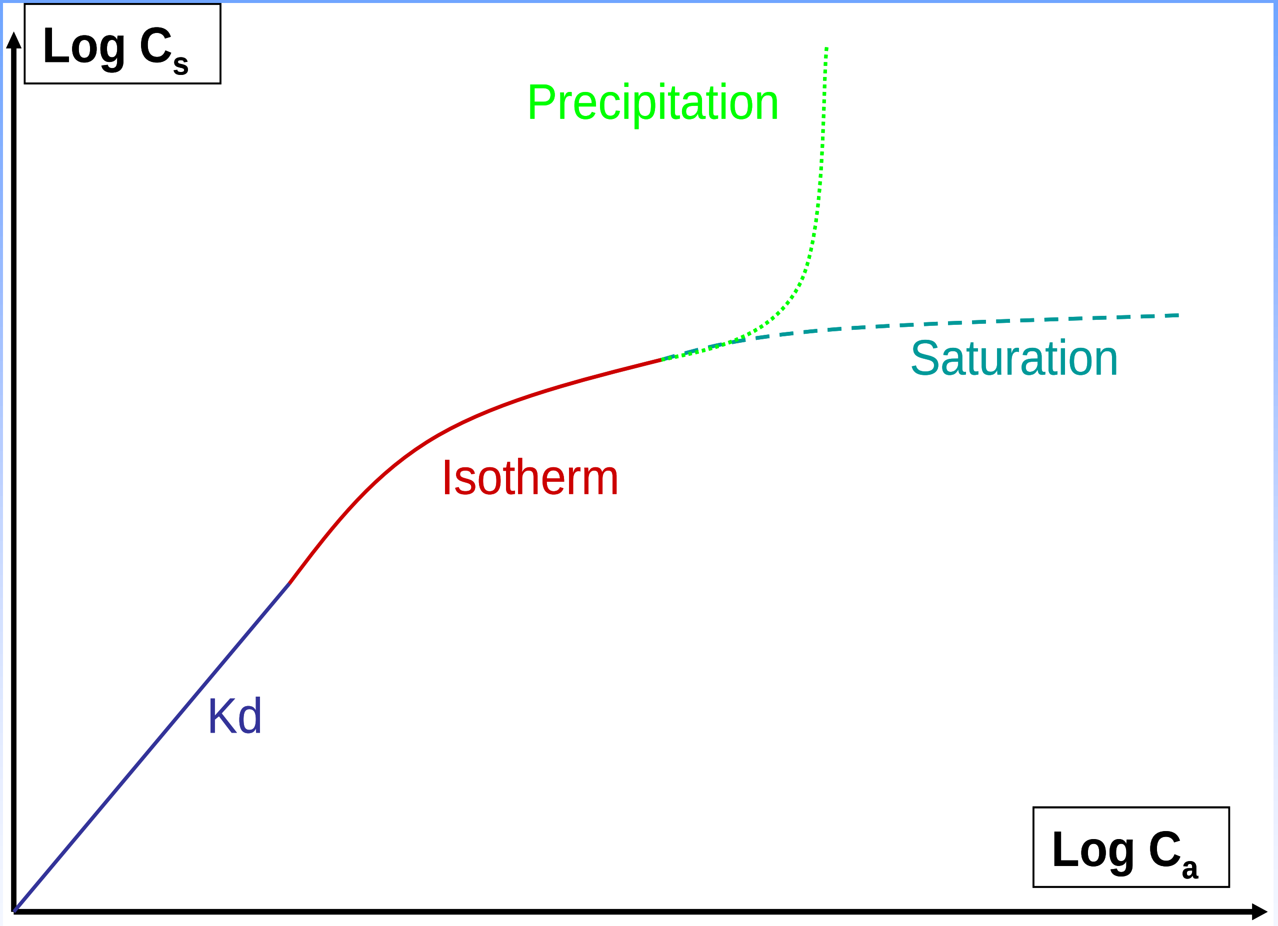
Sorption & precipitation

It is essential to rigorously distinguish between sorption and precipitation:

Sorption - dependent on properties of solution and solid phase, causes retardation until saturation is reached

Precipitation - dependent on solution only and causes retardation only when solubility limit is exceeded

Grey area - surface precipitation



Kd (linear isotherm): C_s = Kd C_a

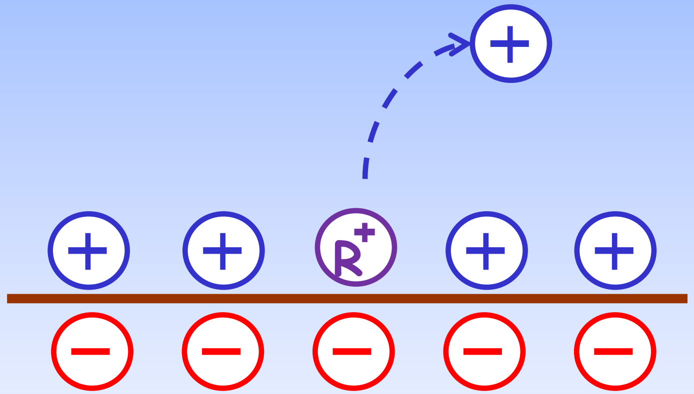
Non-linear isotherm: e.g. $C_s = \alpha C_a{}^{\beta}$

Saturation: C_s = const.

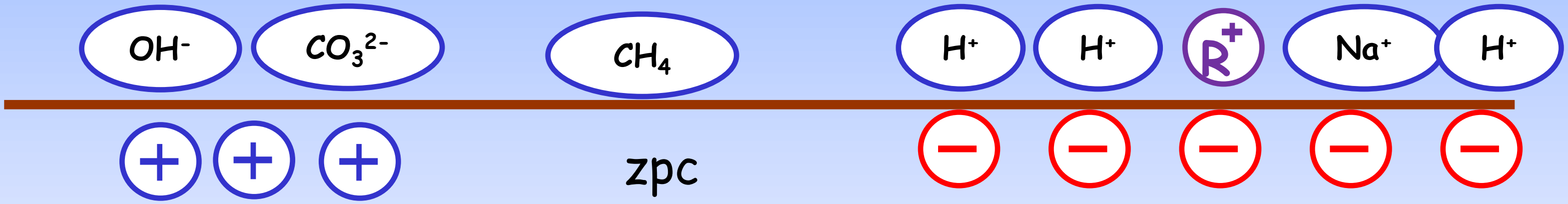
Precipitation: C_a = const.

Sorption

The simple ion exchange model

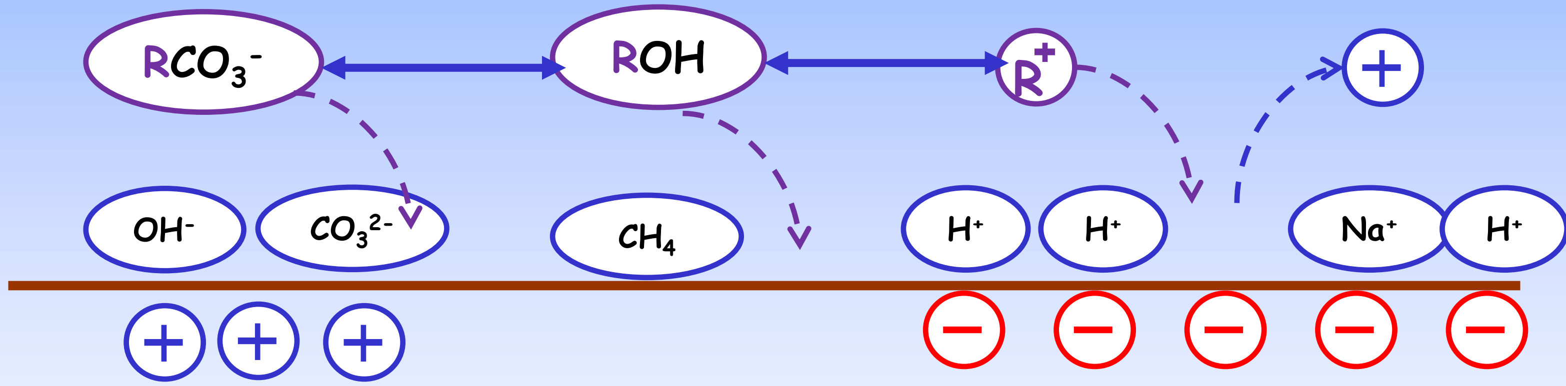


…but rock is not a simple ion exchanger



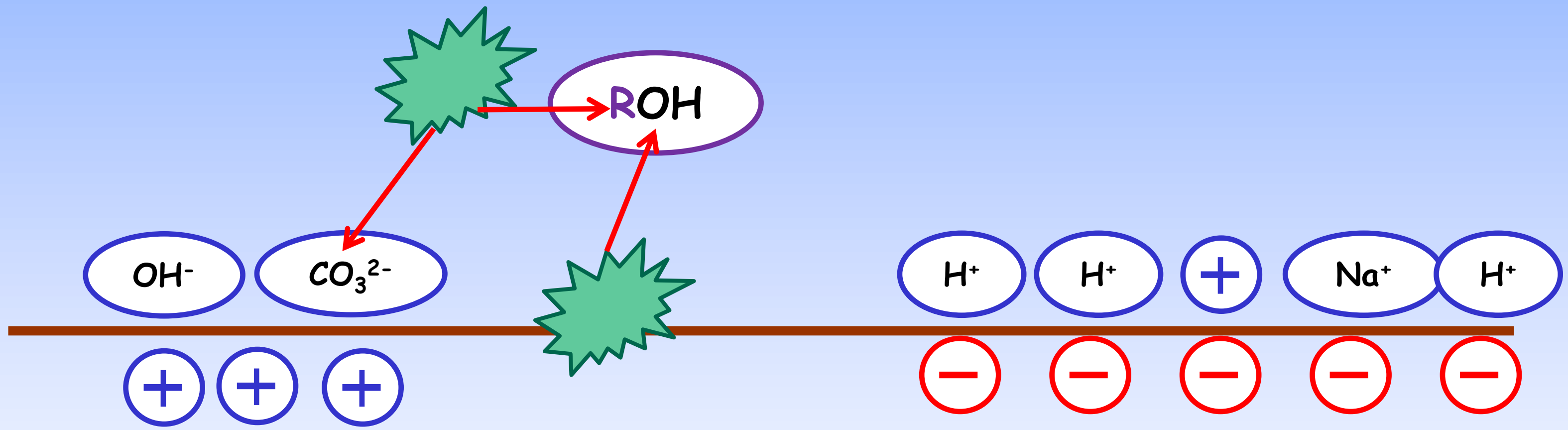
And charge is pH dependent

…and solution speciation is complex

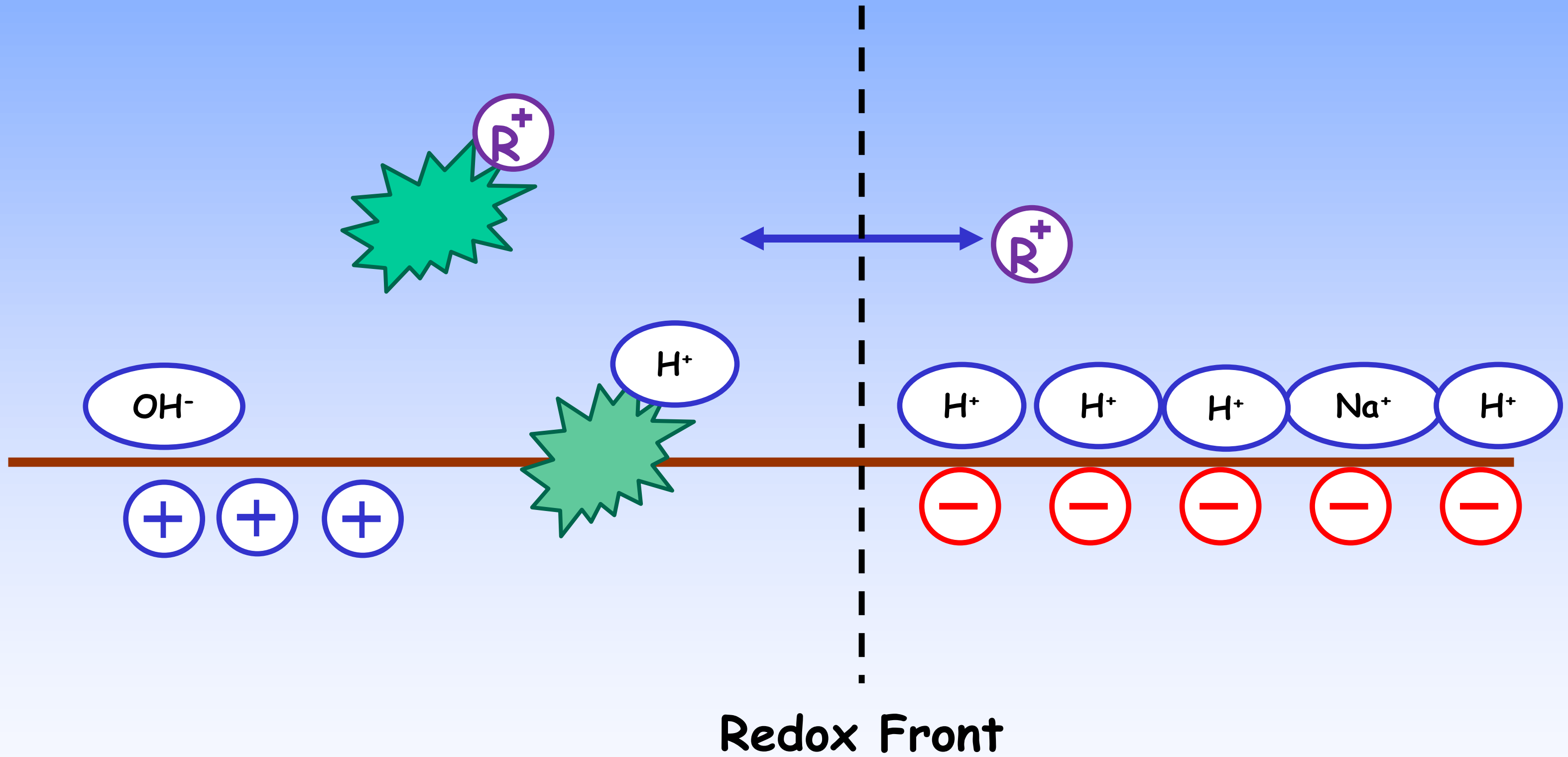


Speciation is pH dependent

…then we have, microbes, colloids, gas…



…then there are extra complications…



…and interactions with surfaces are not limited to simple reversible sorption

?

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Matrix diffusion

- A mechanism which allows solutes access to the bulk rock, in addition to fracture surfaces
- Greatly increases surface area for sorption
- Non-sorbing RNs may be diluted in the rock matrix
  - Could significantly increase retardation in the FF
  - When migration time is greater than $t_{1/2}$ eventual releases could decreased by several orders of magnitude
- Conc^n maximum of pulse released RNs will also be reduced by temporal dilution
- For quantification, 2 key parameters are required
  - Depth to which interconnected porosity extends into bulk rock
  - Diffusion rate of a particular RN in rock

…OK, where do we go now?

- We know that the current level of system understanding far exceeds representation in PA models
- We know that some past analogue approaches were fundamentally flawed…

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Abuses of analogues – the "in-situ Kd" story

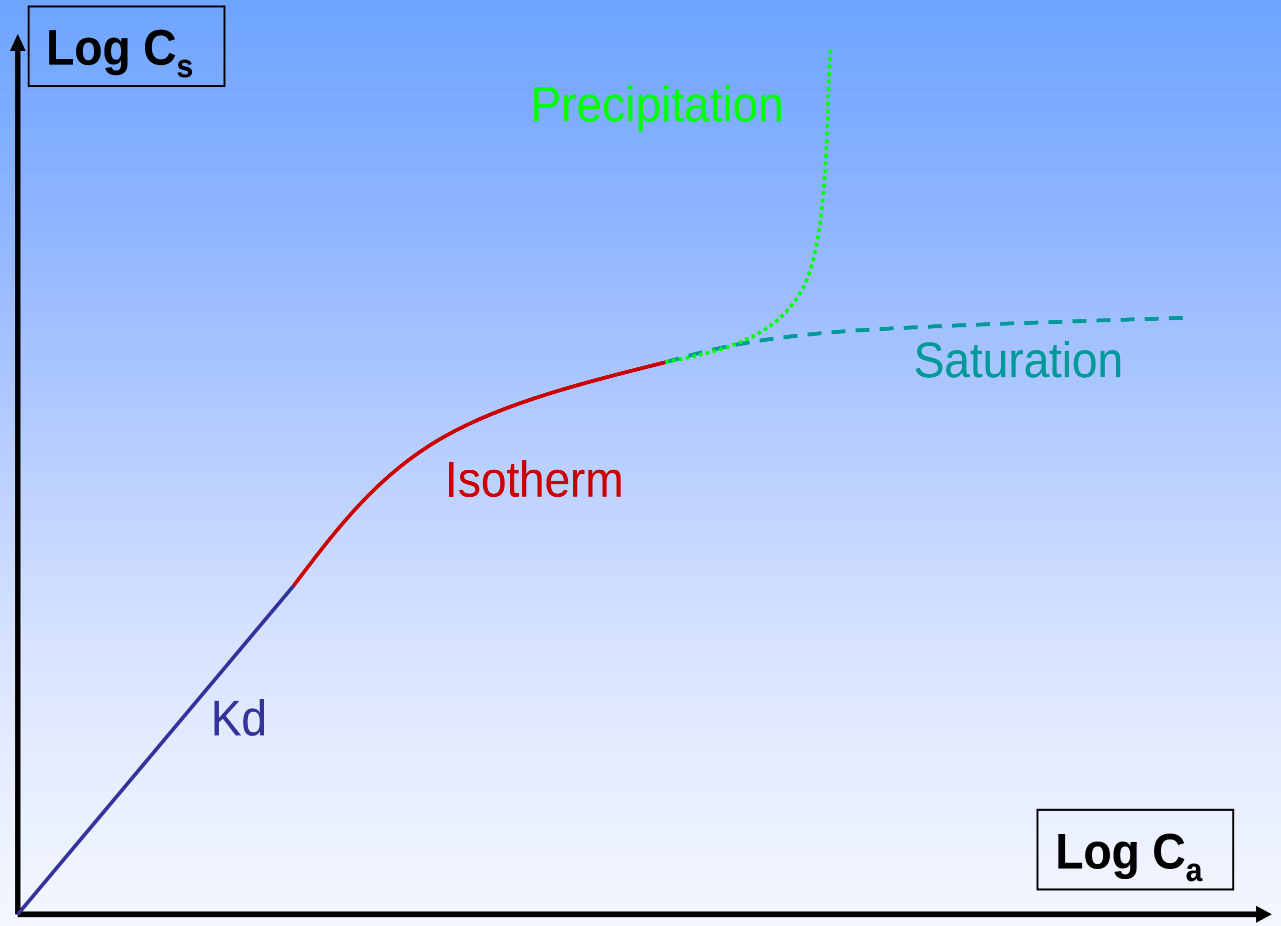
Finding systems to quantitatively define RN sorption in-situ has been considered the "Holy Grail" of NA studies;

- A wide number of approaches have been published
  - geochemists measuring data supposed to be of relevance to the PA modellers
  - PA modellers trawling the geochemical literature to derive relevant data
- Unfortunately most (all?) of such work involves overinterpretation / flawed analysis hence great care is needed even with
  - publications in "quality" journals
  - work from well-established groups (outside the radwaste field)
  - In-situ Kd's still being used
- It can be instructive to examine the approaches that have been (and sometimes still are) used - what are they doing wrong?

Starting point - definition of Kd

Kd relates the concentration of any species sorbed on a solid phase to the concentration in solution

PA models further assume that sorption is fast and reversible (clearly implied by the Kd definition)



Kd (linear isotherm): $C_s = Kd\, C_a$
Non-linear isotherm: e.g. $C_s = \alpha\, C_a{}^{\beta}$
Saturation: C_s = const.
Precipitation: C_a = const.

Sorption

In-situ Kd quiz - what is wrong here?

Q1

Approach:

- measure introduced tracer concentration in a rock sample (C_{rock})
- measure tracer concentration in associated groundwater sample (C_{water})
- Kd = (C_{rock}) / (C_{water})

In-situ Kd quiz - what is wrong here?

A1

Approach:

- measure introduced tracer concentration in a rock sample (C_{rock})
- measure tracer concentration in associated groundwater sample (C_{water})
- Kd = (C_{rock}) / (C_{water})

==> need to demonstrate no background of tracer in the system

==> need to ensure linear sorption is the only uptake process (NB precipitation / co-precipitation)

==> must ensure no colloidal association of RN (Kd applies only to 2-phase system)

==> must ensure no role of microbes (almost certainly present in system)

==> Equilibrium has to be demonstrated between water & rock

==> C_{rock} has to be proven to include only sorbed phase???

==> C_{water} has to be proven to include only species in true solution (NB conventional water samples filtered only to 0.45 μm)

In-situ Kd - overview

- No rigorously proven methodology
- Many problems result from unjustified simplification of the natural systems
- Published Kd values incorrect - and could be highly non-conservative (over-predicting actual retardation)
- Nevertheless, possible in principle - but requires very extensive characterisation of the system and testing of methodology - there are no fast shortcuts!

OK, where do we go now?

- We know that the current level of system understanding far exceeds representation in PA models
- We know that some past analogue approaches were fundamentally flawed…
- …but we can do better! We need to..
- Nail down mechanisms
- Nail down timescales
- Nail down uncertainties!
- Check assumptions on an analogue
- Three types of conditions we need to consider

…steady state conditions

- Well defined source term (e.g. U ore body)
- Well-defined hydrogeological conditions
  - Diffusion dominated
  - Advection defined by constant hydraulic gradient
  - Timescales set by radionuclide decay / ingrowth
- Careful sampling
  - Water, for major chemistry, RNs, colloids, microbes – should also include determination of RN speciation
  - Rock, for mineralogy, porosity, flow paths, microbes, RN – with comprehensive selective extraction analysis

…dynamic conditions

- Well dated source term (e.g. characteristic sediment)
- Well-defined hydrogeological conditions
  - Diffusion dominated
  - Advection defined by constant hydraulic gradient
- Careful sampling
  - Water, for major chemistry, trace elements / RNs, colloids, microbes – should also include determination of RN speciation
  - Rock, for mineralogy, porosity, flow paths, microbes, trace elements / RN – with comprehensive selective extraction analysis

…perturbed conditions

- High pH plume
- Redox front
- More complicated, but…

The Ideal Analogue

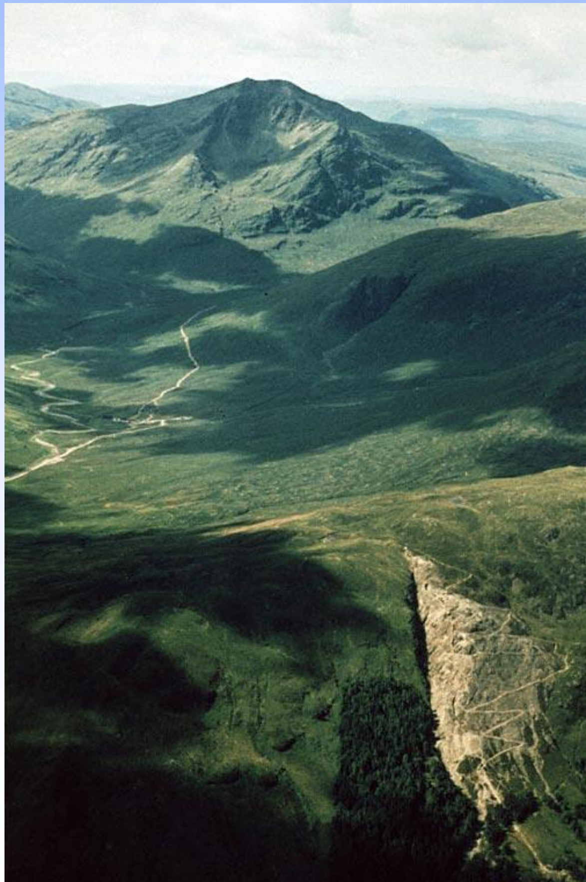
- Need to find an analogue with the same boundary conditions as your repository
  - Same or similar host rock
  - Need a source of relevant RNs, e.g. a U ore body or ore body with U association, e.g. Sn, Cu, Pb, Fe, or
  - Well defined geochemical anomaly such as a marine transgression
  - Need to determine the depth to which the interconnected porosity extends in the bulk rock
  - Steady state - well defined constant hydrogeology, e.g. site with a steep topographical gradient, or
  - Site where diffusion is dominant transport mechanism
  - Fracture flow system also important
  - Perturbations: high pH plume, redox front

The Ideal Analyses

- Simple Kd not adequate for transport models (no system understanding required for the SC). Desorption often slow or incomplete (hysteresis)
- Need to account for precipitation, co-precipitation, microbes & colloids
- Speciation necessary, sequential extraction of the solid phase and ion exchange or solvent extraction of aqueous phase – but inherently dynamic
- Use more than one technique for consistency check
- Stable isotope analysis ($\delta^{34}S$) for microbial activity check

Steady state site?

- Tyndrum, Scotland – Pb-Zn mine, SS since deglaciation
- U mineralisation within fractured crystalline rock
- Natural decay series RNs, timescale set by ^{226}Ra
- Measure the water velocity at the site
- Measure 2 isotopes of the same element to check Rf
- Measure isotopes of different elements to examine relative difference in Rf (allows test of the model output for Rfs)
- But: background U in rock?



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Dynamic sites?

- Geochemical anomaly – dateable ash fall with different chemistry from surrounding sediments. Tuffs??
  - Perhaps ash fall into a lake (freshwater)
  - Ideal timeframe: 10-100 thousand years
  - Longer better but harder to define constant conditions
  - If more than one ash fall, model can be checked
- Marine transgression similar to Loch Lomond – is there a site where there has been more than one??
- Both analogues will allow you to measure element profiles, sorption
- If well dated can calculate diffusion rates for marine and freshwater systems

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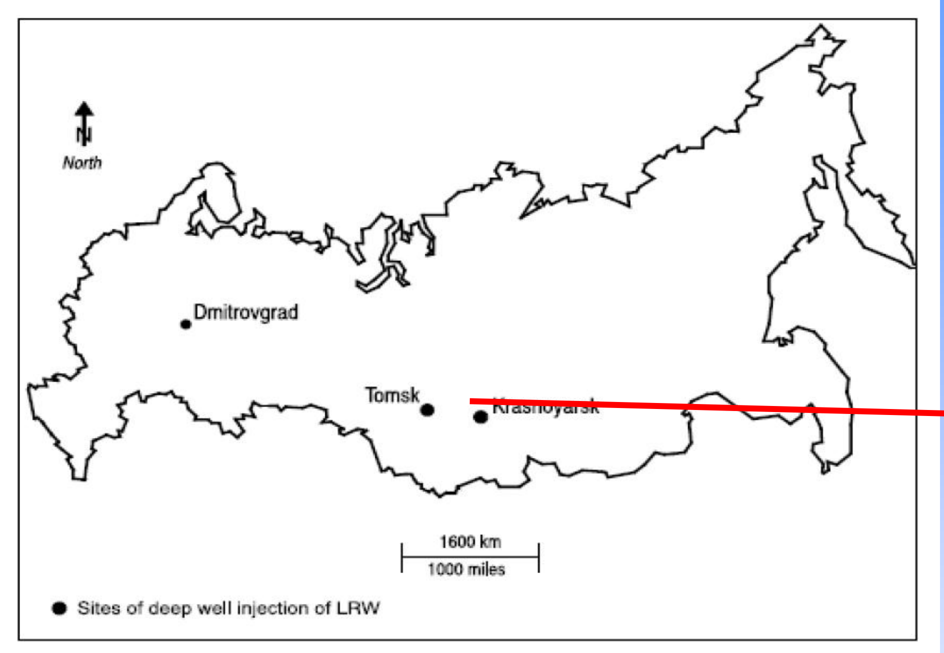
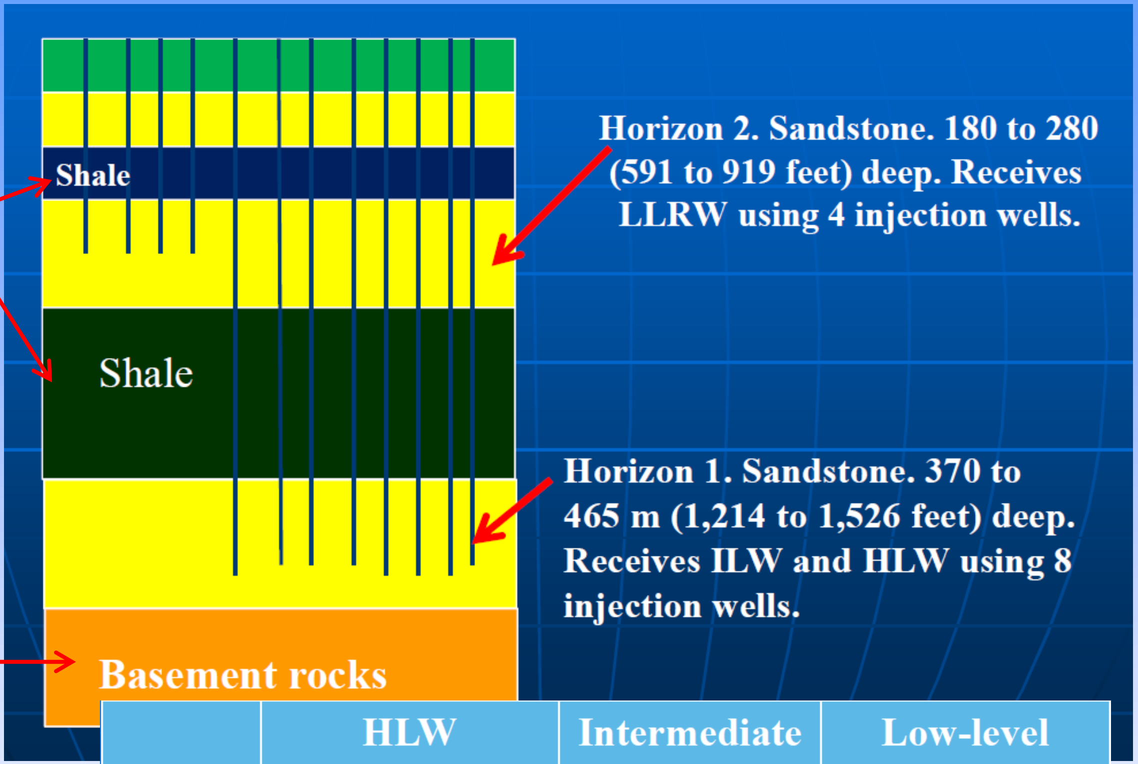
Perturbed sites - anthropogenic



Severniy site, Russia - Waste disposal started in 1967. The waste includes both radioactive fission products and nonradioactive chemicals used in reprocessing of spent fuel.

The total activity was approximately 250 million Curies (Ci).

Severny site, Russia



Horizon 2. Sandstone. 180 to 280 (591 to 919 feet) deep. Receives LLRW using 4 injection wells.

Horizon 1. Sandstone. 370 to 465 m (1,214 to 1,526 feet) deep. Receives ILW and HLW using 8 injection wells.

Shale host rock – CH, CAN, ?

Basement host rock – UK, J?

Low pH front analogue?

High pH front analogue?

	HLW Process waste	Intermediate waste	Low-level waste
pH	1 to 3	~ 13	~8
TBP	50 mg/L	30 mg/L	None
^{90}Sr	2.49 Ci/L	0.51 mCi/L	2.97 µCi/L
^{137}Cs	0.30 Ci/L	0.41 Ci/L	4.05 µCi/L
^{239}Pu	100 to 500 µg/L	10 to 30 µg/L	< 1 µg/L

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Perturbed sites - natural

- Philippines analogue project - bentonite on top of an ophiolite
- High pH waters contacting the bottom of bentonite & Mn nodules present (source term)
- Study elemental movement in a diffusion dominated system
- Study diffusion of high pH waters into clay
- Advantage: study site already characterised so can study the transport of relevant solute in this system

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Conclusions

- In a safety case you need to validate the models of radionuclide transport
- Can only done with natural analogue support
- Models currently simplistic and don't match our understanding of the complexity of the system
- If a good site found is found, we have the system understanding and technology to understand the processes effecting migration of key elements
- Not easy, large investment required: best done as part of an international project??

Thanks for listening!

Any questions?

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