Does a stability constant decide on a repository permit?

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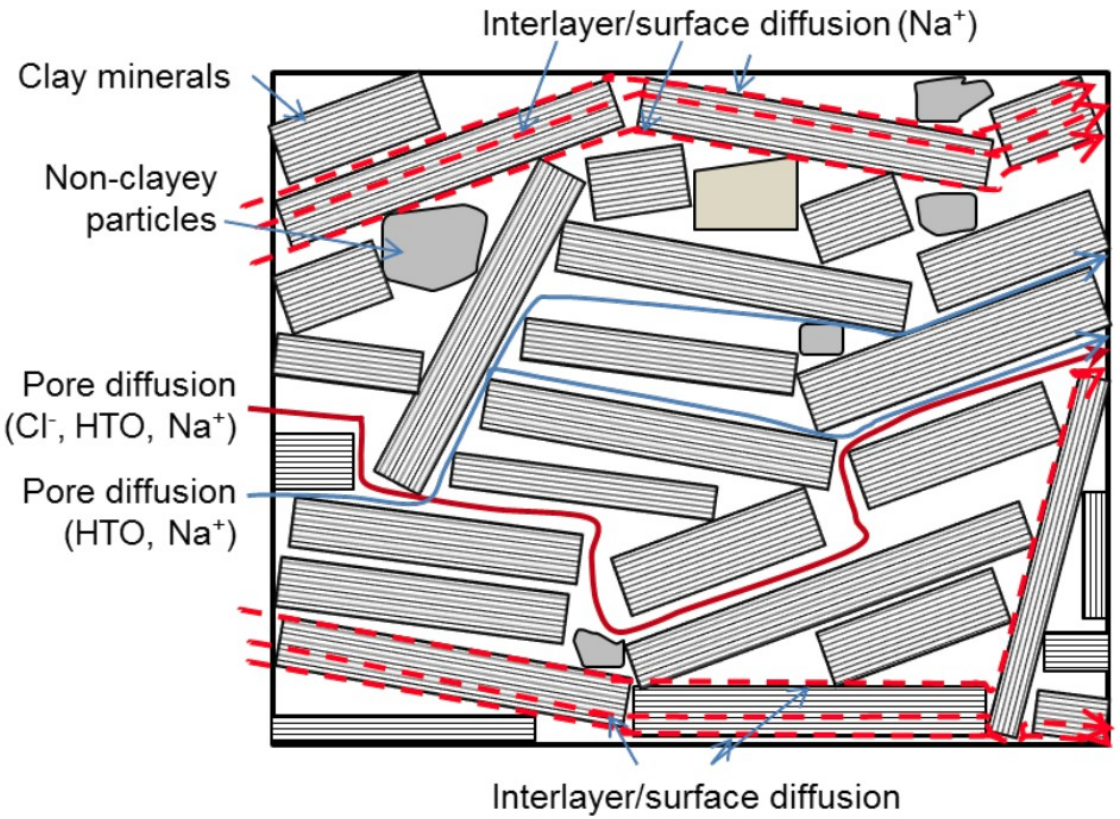
RESEARCH FOR GRAND CHALLENGES

Speciation depends on the porewater chemistry and determines diffusive transport pathways

For the multi-component diffusion option in PHREEQC:

- each species is assigned its own diffusion coefficient
- transport is considered both in the 'free' porewater and in the diffuse double layers



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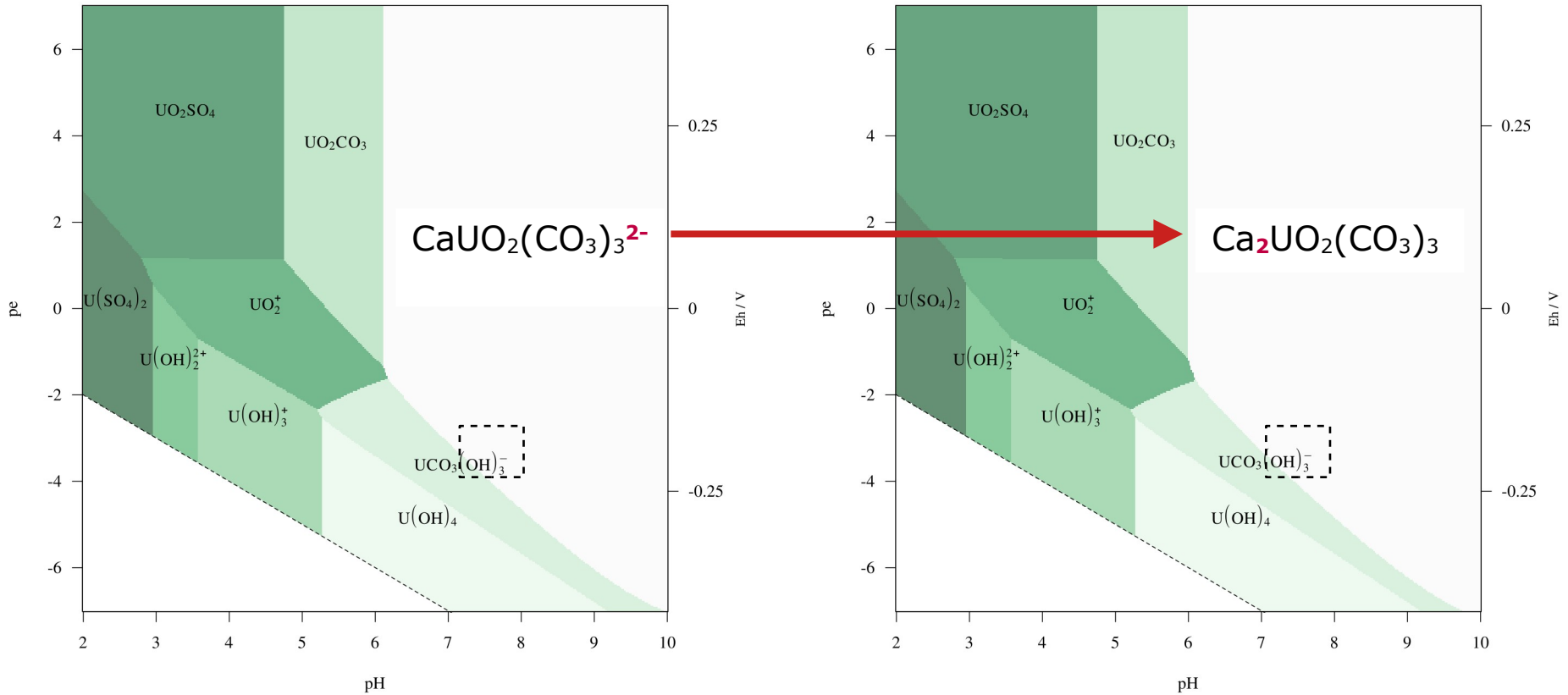
Stability constant of the neutral, ternary uranyl complex governs predominant species

Log k = 29.22
PSI/Nagra Database 12/07

Log k = 30.55
Bernhard et al. (2001)



Speciation:

$CaUO_2(CO_3)_3^{2-}$	**70 %**	**–>**	**32 %**
$Ca_2UO_2(CO_3)_3$	**6 %**	**–>**	**57 %**

= pH/Eh range of Opalinus Clay porewater

De Lucia & Kühn, 2013
DOI: 10.1016/j.egypro.2013.08.053
Hennig et al., 2020
DOI:10.1016/j.apgeochem.2020.104777

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Multi-component diffusion calculates diffusive flux via electrochemical potential

- Single-component diffusion: Diffusive flux J (mol/m²s) of a solution in porous media calculated via concentration gradient with Fick's 1st law:

$$J = -D_e \cdot \frac{\partial c}{\partial x}$$

Same D_e for all species

$$D_e = \frac{\epsilon_a \cdot D_w \cdot \delta}{\tau}$$

- Implementation of multi-component diffusion in PHREEQC to calculate diffusive flux J_i for every species:

$$J_i = -\frac{u_i c_i}{|z_i| F} \cdot \frac{\partial \mu_i}{\partial x}$$

$$D_{w,i} = \frac{u_i RT}{|z_i| F}$$

$$J_i = -(D_w \cdot \epsilon_a^n) \frac{\partial \mu_i}{\partial x_i}$$

$D_{e,i}$ of every species is defined by Archie's law with n as medium specific parameter

Gratwohl, 1958
Appelo & Wersin, 2007
DOI: 10.1021/es0629256
Appelo et al., 2010
DOI: 10.1016/j.gca.2009.11.013

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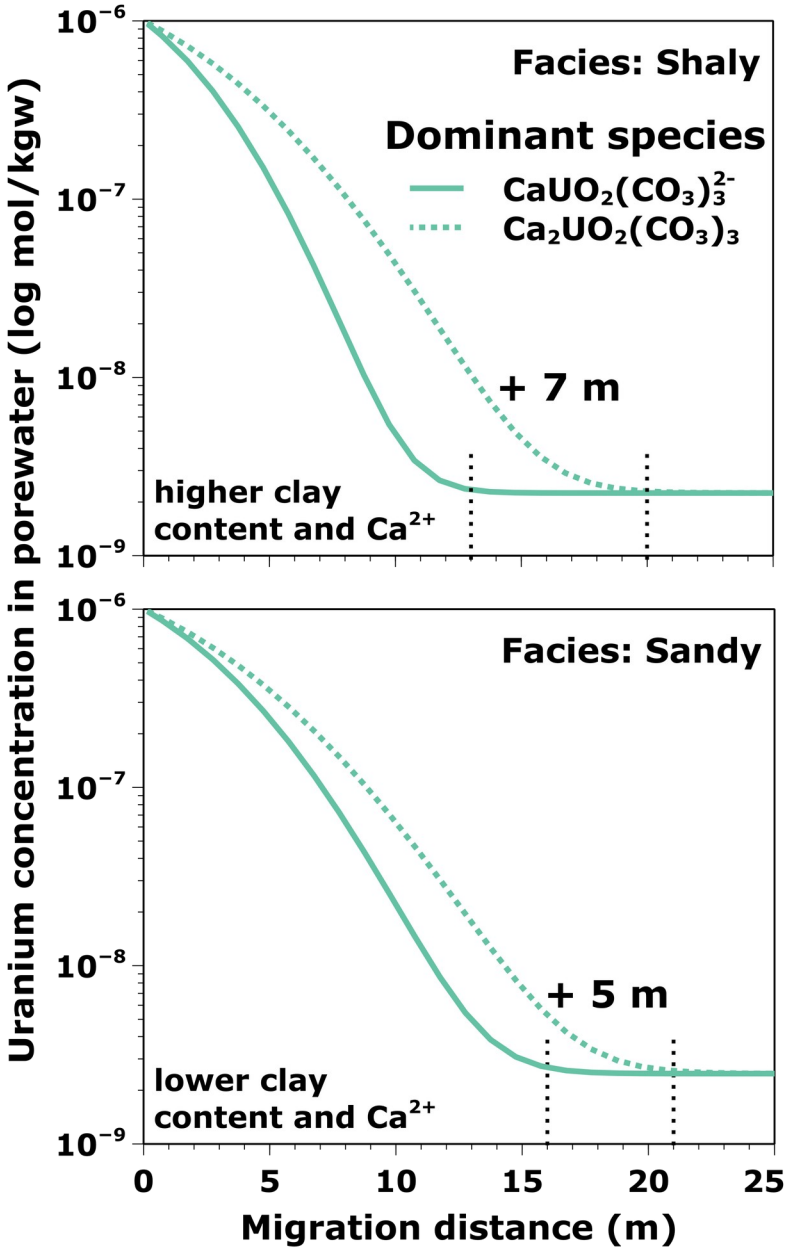
No: A stability constant does not decide on a repository permit as uranium is retained

- The stability constant of the neutral complex governs the predominant uranium species and consequently migration due to the different interaction with the clay mineral surfaces
- How strong uranium migration is affected by the selected constant is controlled by the porewater composition and thus by the facies
- After one million years, maximum diffusion lengths of uranium vary between 13 m or 21 m depending on the facies and the selected stability constant for the neutral uranyl complex
- § 23 Article 2 StandAG:

  → Host rock thickness of at least 100 m to fulfil minimum requirements for the effective containment zone



Hennig et al., 2020
DOI:10.1016/j.apgeochem.2020.104777
Hennig & Kühn, 2021
DOI:10.3390/app11020786

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