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Experimental and Modeling Study on the Long-Term Performance of the Engineered Barrier System of TRU Waste Repository

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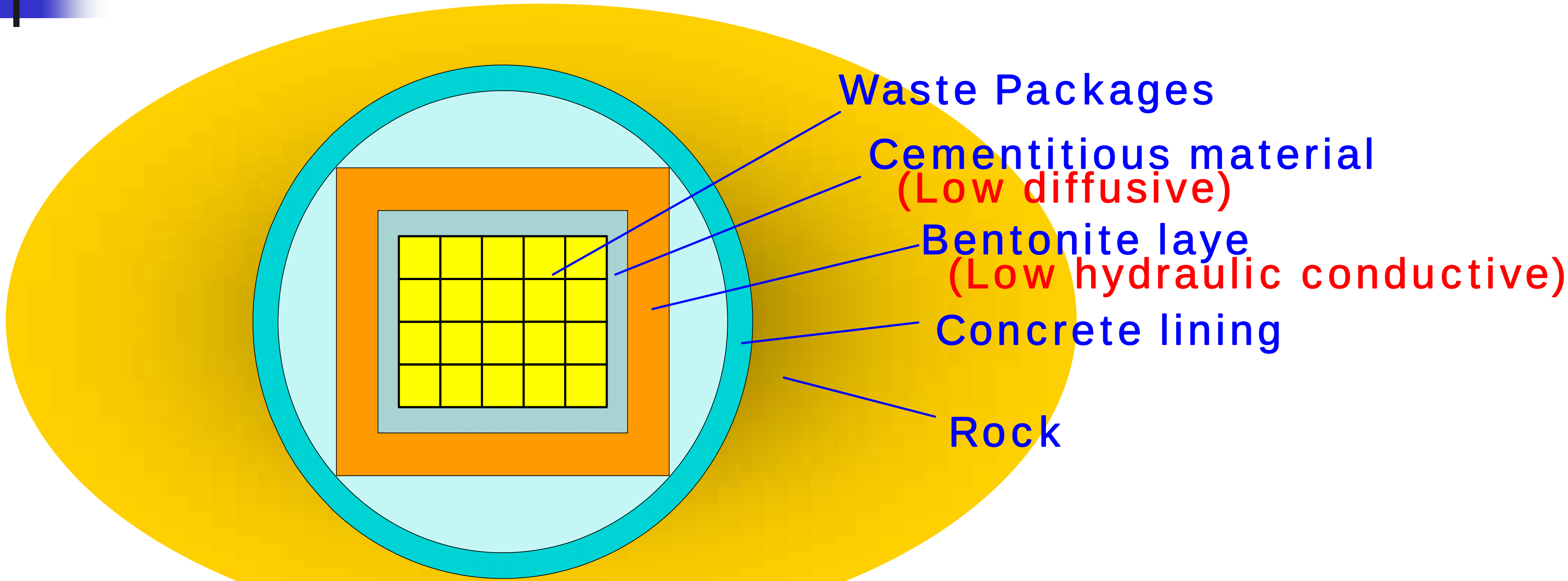
TRU waste repository planed in Japan



-Located a few hundreds meter depth

-Multi-barrier system of concrete/mortar and bentonite layer.

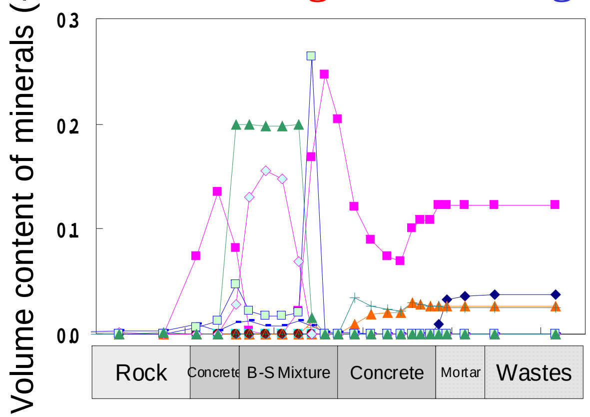
-bentonite layer (low Kw) -> Diffusive dominant in EBS

-concrete/mortar (low De) -> Restrict diffusion flux from EBS

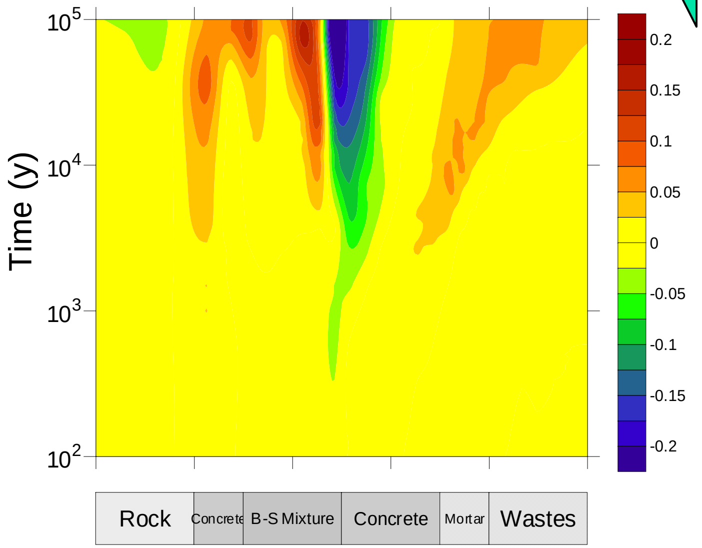
- Long-term alteration of EBS by the interaction of cementitious materials and bentonite should carefully be examined.

Preliminary analysis of the alteration of EBS analyzed by coupled method of geochemical reaction and mass transport

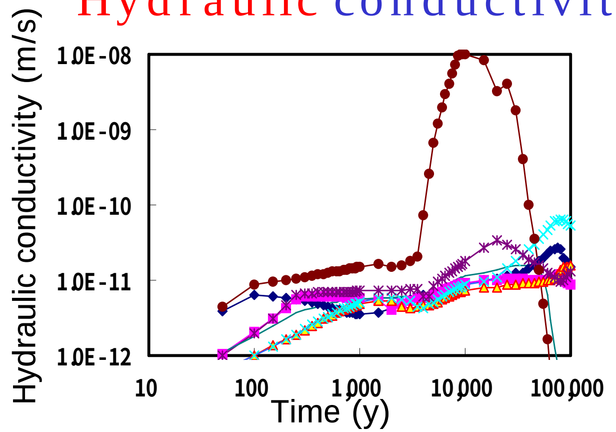
Mineralogical change



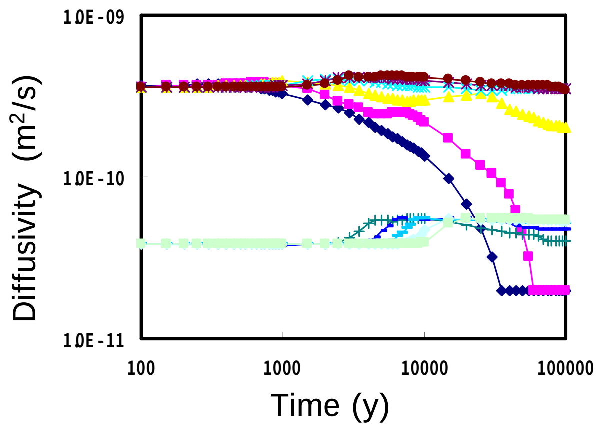
Change of the porosity



Hydraulic conductivity



Diffusivity



Data and assumptions in the preliminary analysis

- Data
  - Geochemical properties of initial and secondary minerals
    - Selection of minerals
    - Equilibrium constants
    - Dissolution rate / precipitation rate
    - Density of minerals
  - Mass transport properties of barrier materials
    - Relationship between De vs. porosities.
    - Relationship between Kw vs. bentonite density and mineral contents.
  - Influence of interactions
    - Mechanistic properties
    - Location of the precipitation of secondary minerals
- Assumptions
  - Minerals were selected from experiments and natural analogous studies.
  - Local equilibrium assumption was used in reference case.
  - De and Kw were estimated from empirical equations.
  - Mechanistic influence was neglected.

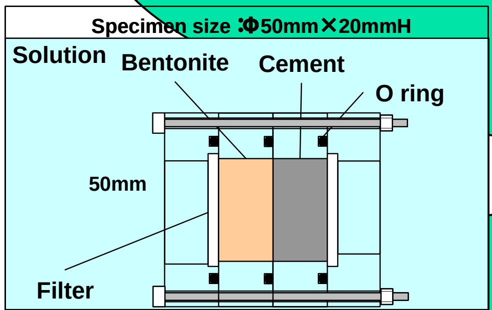
Study program of "Evaluation Experiments of Long Term Performances of Engineered Barriers" by RWMC

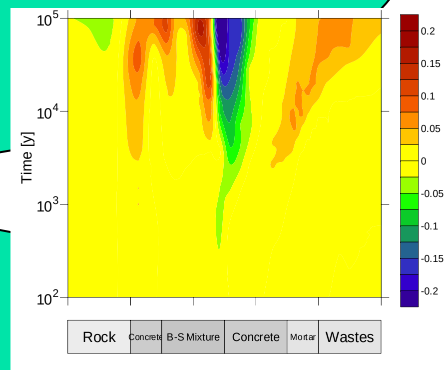
Improvement of the reliability of alteration model

Numerical model simulation

Experiment ⇔ *Geochemical reactions* ⇄ *Mass transport phenomena* ⇔ **Natural analogous study**

Coupling





Long-term alteration of the barrier system

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Barrier performance considering alteration phenomena

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Nuclide migration analysis

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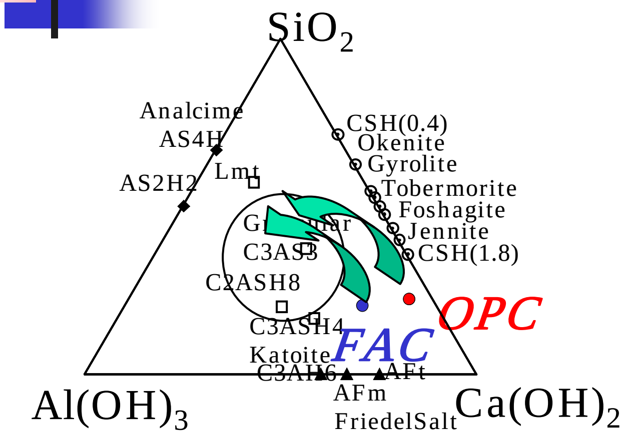
Long-term safety assessment considering alteration phenomena

Realistic Safety Assessment

Experiments and numerical model analysis

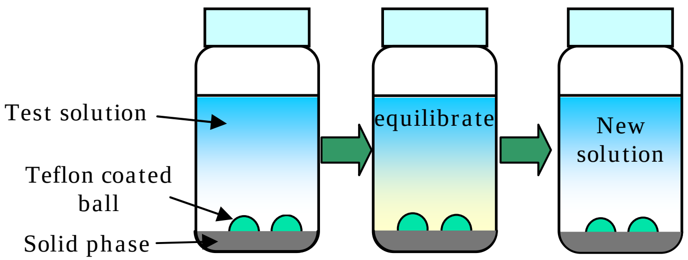
- Experiments
  - Cement alteration tests
  - Bentonite alteration tests
  - Interaction of bentonite/cementitious material
- Numerical model analysis
  - Analysis of experiments and modification of the model
  - Analysis of natural analogous studies and modification of the model
  - Long-term performance assessment of EBS using modified model

Can dissolution of Fray Ash Cement be predicted using geochemical model of OPC ?

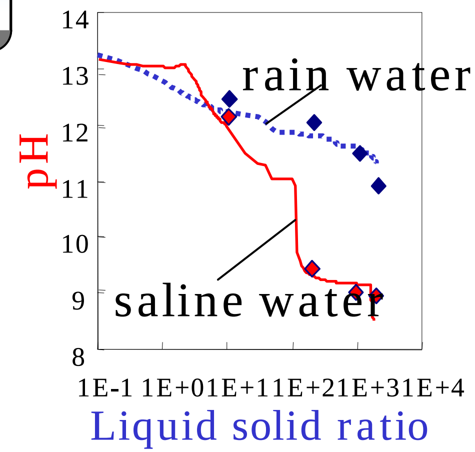


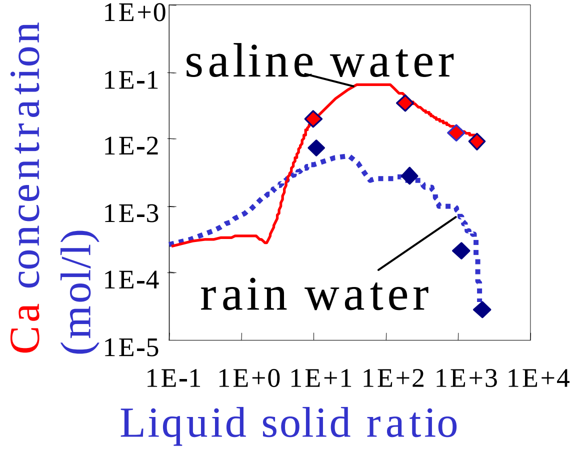
- OPC has been studied as the representative material of cements.
- Fry Ash Cement has fine structure and low De.
- Dissolution test of FAC has performed
- Concentrations of major elements were predicted using the model.

Experiment



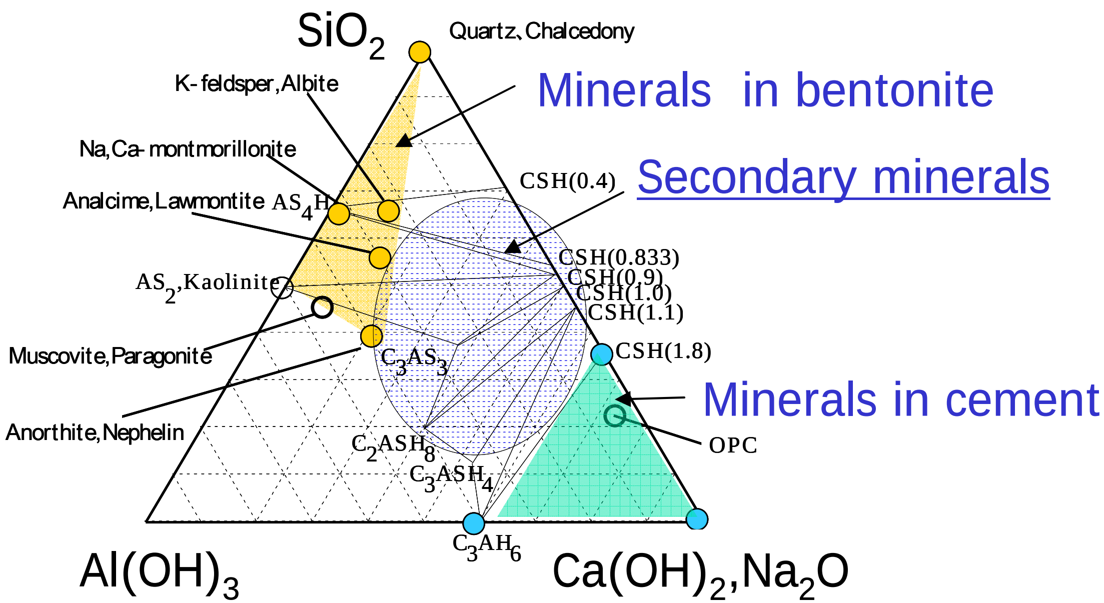
Comparison of the tests results and calculation



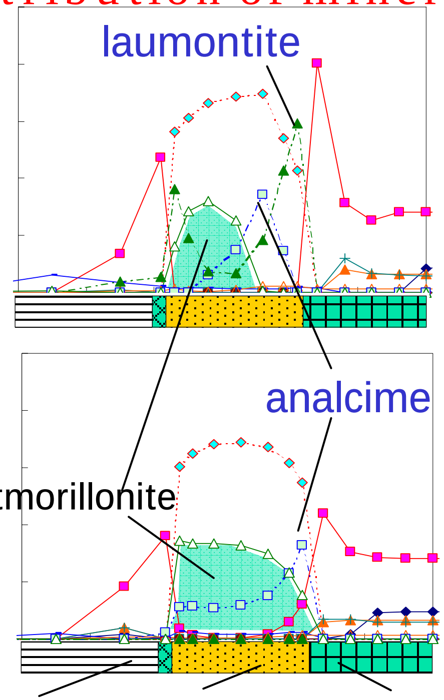


Selection of secondary minerals can change the result of the prediction of long-term performance of EBS

- Minerals identified in experiments or natural analogous studies are selected in the model.
- Alteration of montmorillonite to analcime is identified.
- Alteration of montmorillonite to CSH and laumontite isn't identified.
- Reverse reaction of analcime to montmorillonite isn't identified.



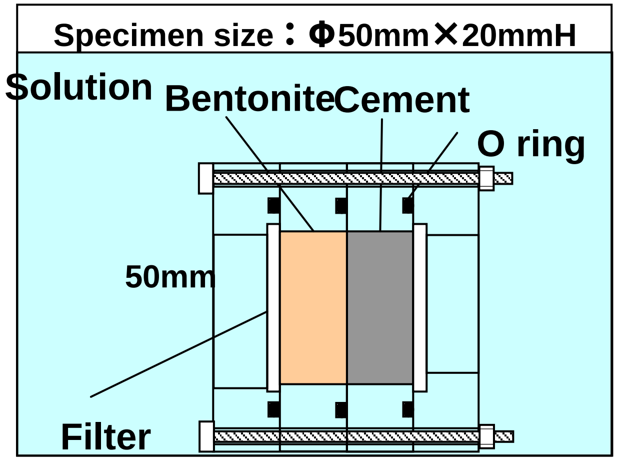
Distribution of minerals



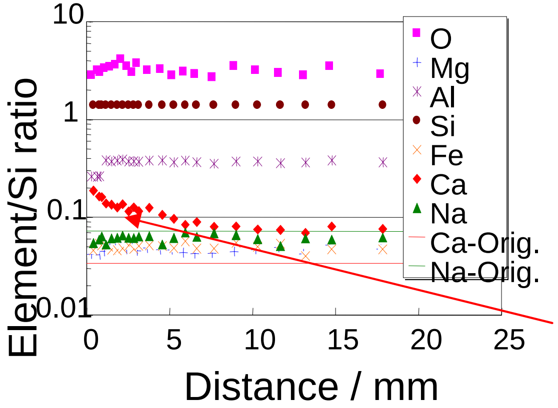
Reactions at the boundary of bentonite/cementitious materials

- In this experiments, geochemical reactions affected by mass transport phenomena will be observed.

Experiment of bentonite/cement

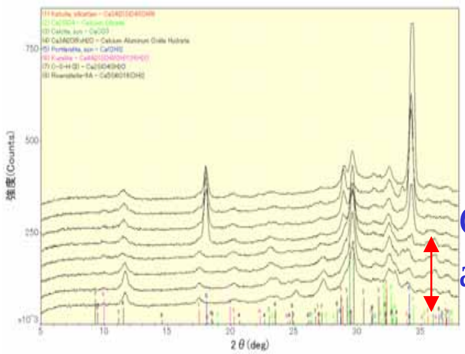


Element ratio in bentonite



Ca penetrate to this depth

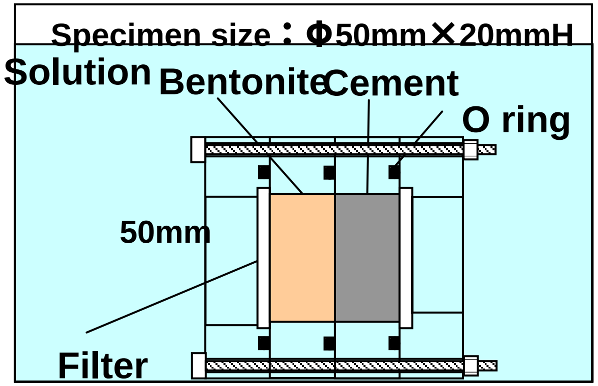
Minerals in cement



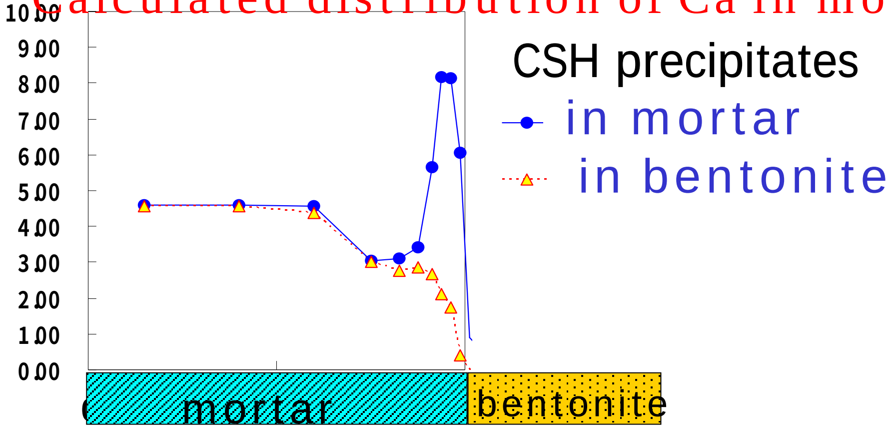
Ca(OH)2 dissolves at this depth

The location of CSH precipitation isn't made clear

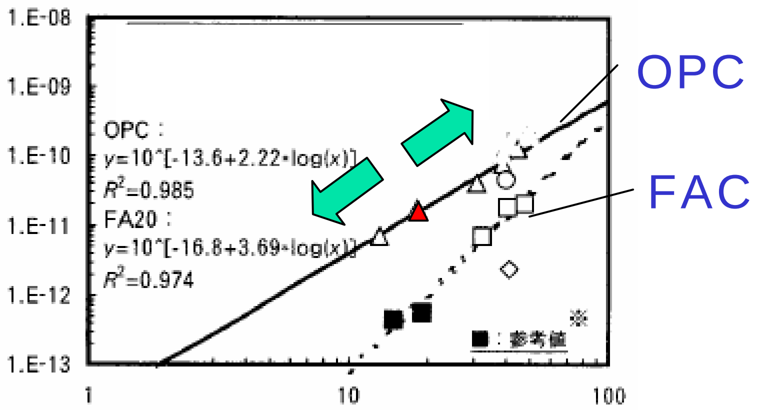
- It isn't clear that CSH precipitates in bentonite or mortar.
- The location of CSH precipitation can affect the change of diffusivity and mass transport conditions.



Calculated distribution of Ca in mortar

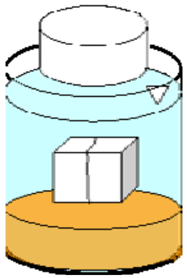


Diffusivity vs. porosity of mortar

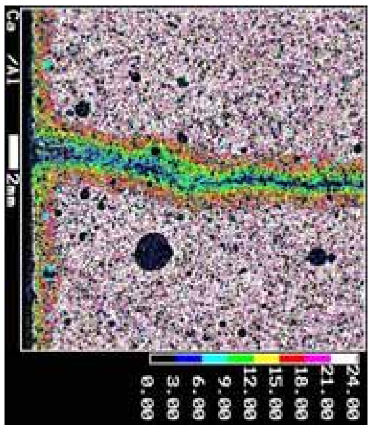


Will cracks of the mortar be clogged or grow ?

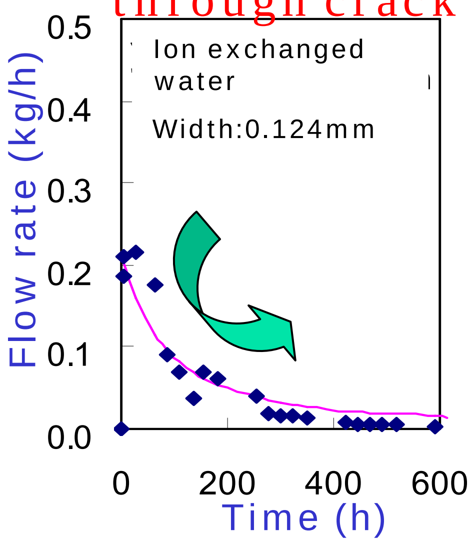
- Cementitious materials are made of cracks and intact matrix.
- Diffusion and advection column tests of cracked mortar were performed.



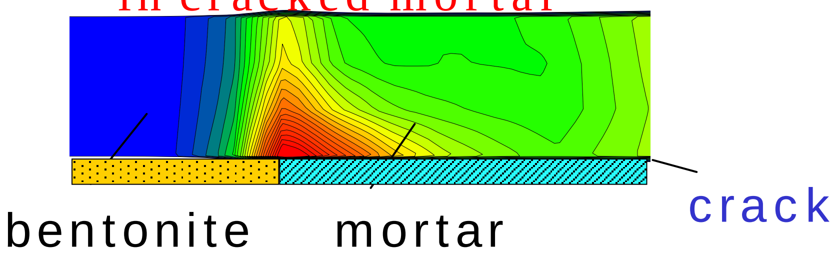
Ca content



Flow rate through crack



Calculated Ca content in cracked mortar



- Cracks were clogged by secondary minerals.
- Model calculation showed that, dissolution of mortar is controlled not by the flux in the crack but by the low diffusivity of matrix.
- These results indicates that, mortar can be treated as low De material.

Low dissolution rate of montmorillonite affects long-term alteration of EBS

Montmorillonite dissolution rate function

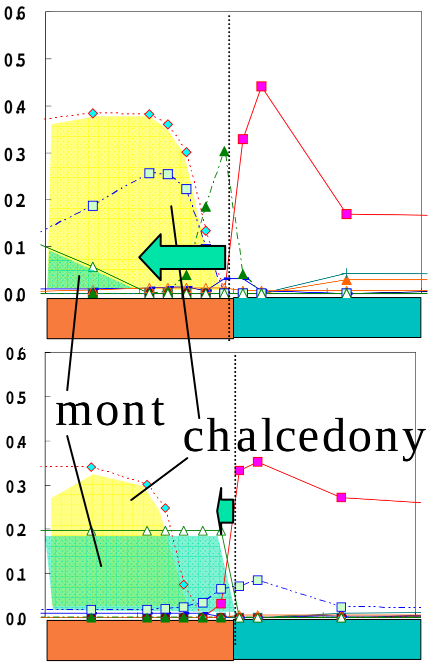
$$Rate = S_r \times k \times \exp\left(-\frac{E_{app}}{RT}\right) \times a_{H+}^{\;nH+} \times \Pi a_i^{\;ni} \times g(I) \times \left(1 - \exp\left(m\left(\frac{\Delta G}{RT}\right)^n\right)\right)$$

Surface area | Reaction rate | Temperature | pH | Catalyst/Inhibitor | Ionic strength | Saturation Indexes

Minerals distribution at the interface

Local equilibrium

Kinetic dissolution

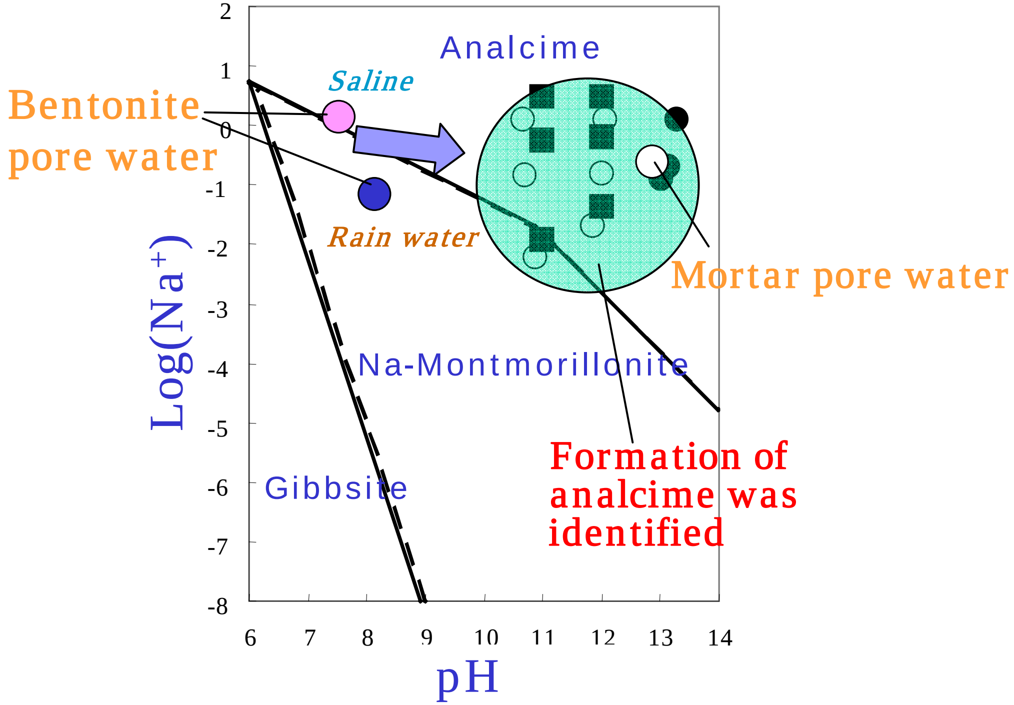


- Kinetic dissolution model of montmorillonite was selected in TRU-2 report. (Non-liner equation of Sato-Cama)
- Dissolution of montmorillonite is greatly affected by the kinetic models.

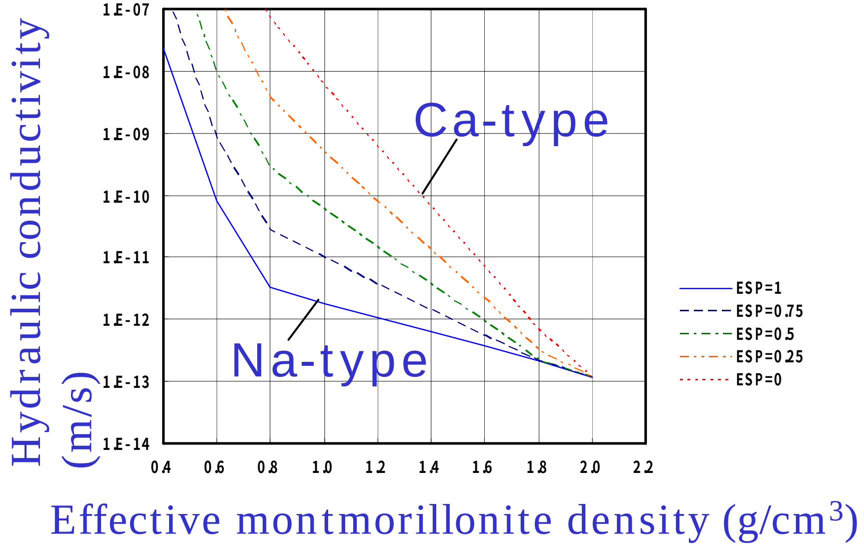
Bentonite can greatly alter in saline ground water condition

- Repository can be constructed near the ocean.
- Cement model was examined under saline water condition.
- Alteration of montmorillonite to analcime was identified under high Na concentration and relatively low pH condition.
- Kw model of bentonite was expanded to saline water condition.

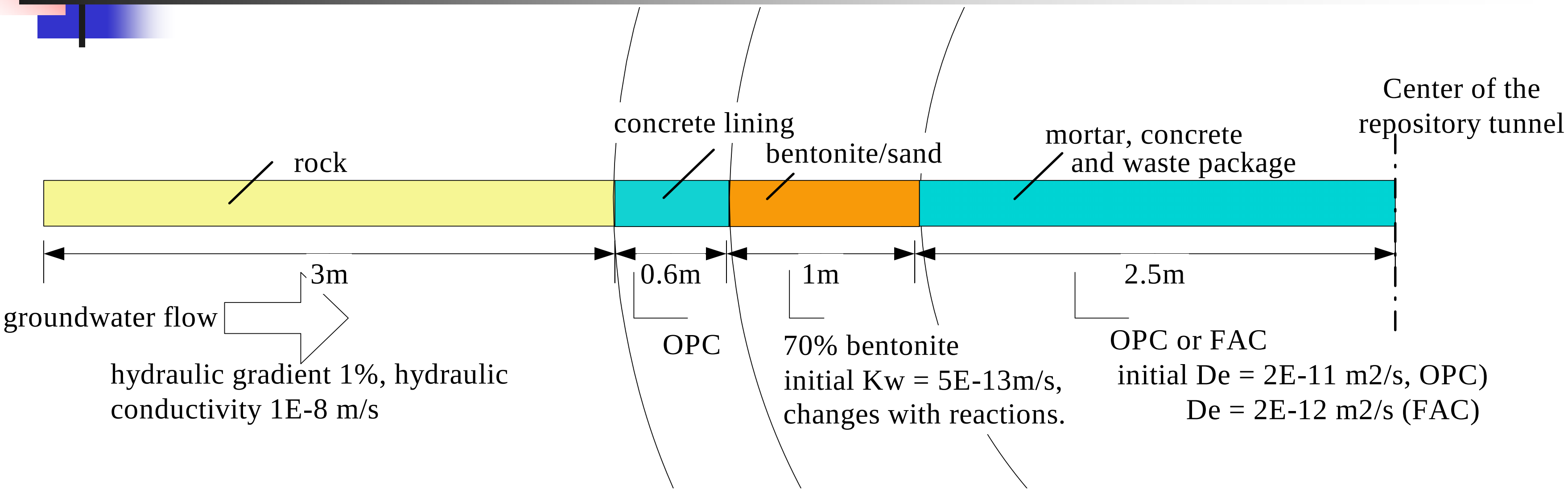
Phase diagram of montmorillonite and analcime



Hydraulic conductivity vs. Effective montmorillonite density



Geometry and conditions of the numerical model analysis



Conditions of reference case

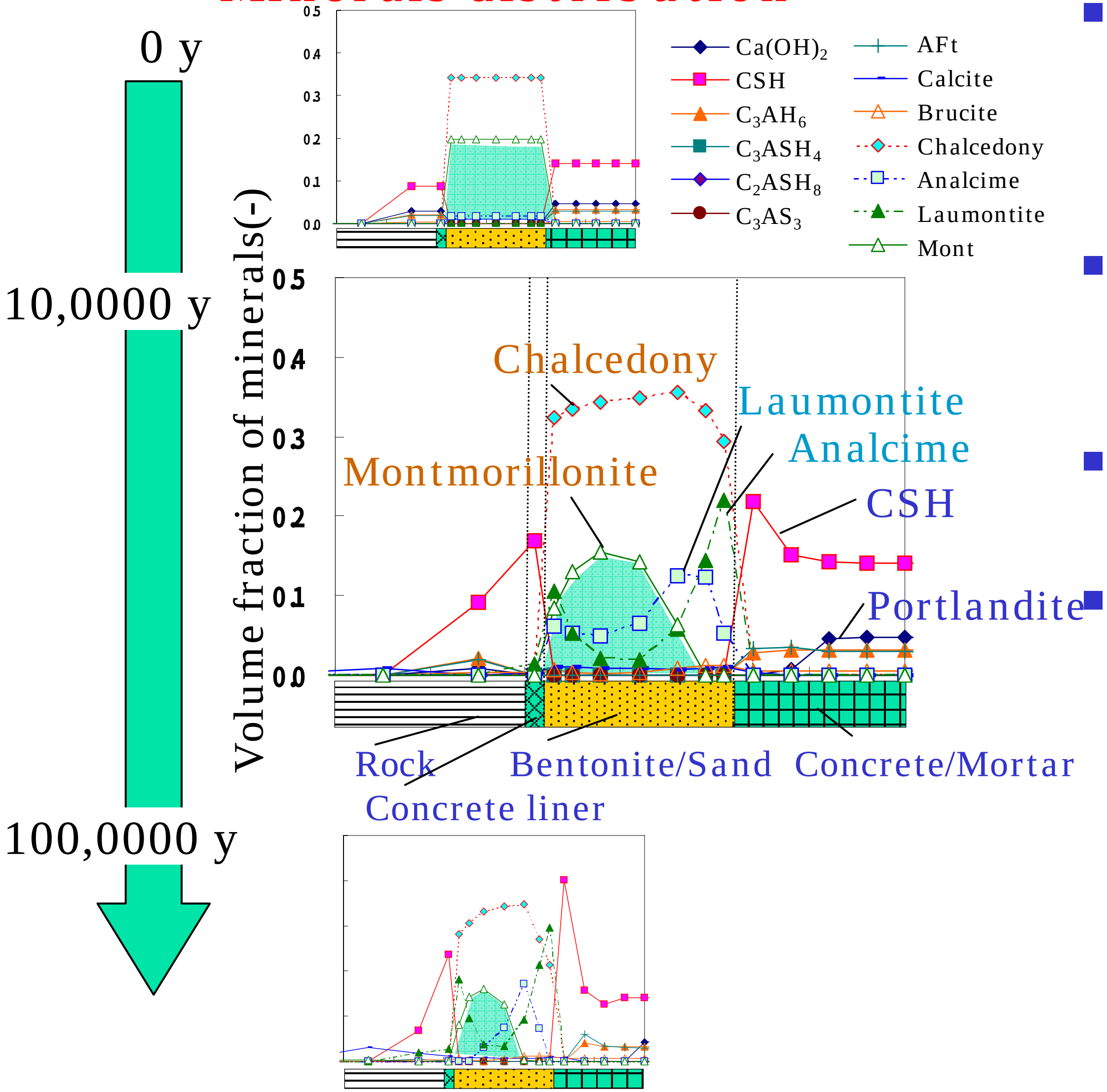
- OPC is selected. (FAC is selected in another case.)
- De of mortar/concrete is assume to be that of low diffusive matrix region.
  (Averaged De of matrix and crack is assumed in conservative high De case.)
- Local equilibrium is assumed. (Kinetic dissolution is assumed in another case)
- Rain water case is selected. (Saline water is selected in another case)

Numerical model analyzed cases

Conservative case	Conservative **high De** in mortar/concrete
Reference	Reference case (OPC)
Mass transport property of cementitious material	**Crack** model case
	Monotonous increase of De of concrete
Selection of the minerals	**No reprecipitation** of **montmorillonite**
	No formation of **laumontite**
	Kinetic dissolution of montmorillonite.
Cement type	**FAC** case
Groundwater type	**Saline water** case

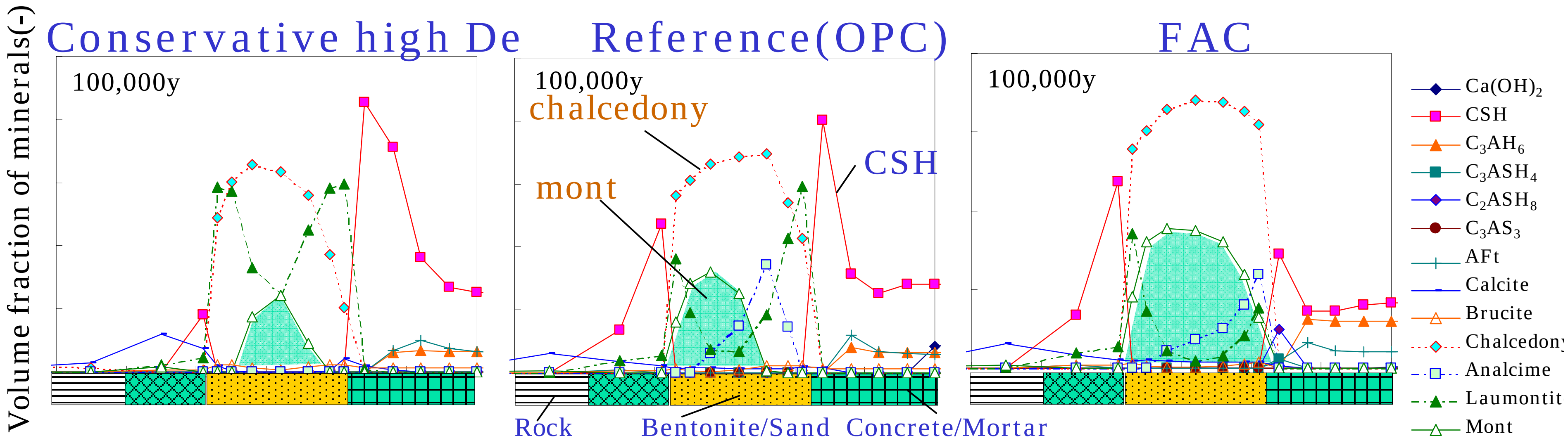
Time dependent alteration of EBS

Minerals distribution



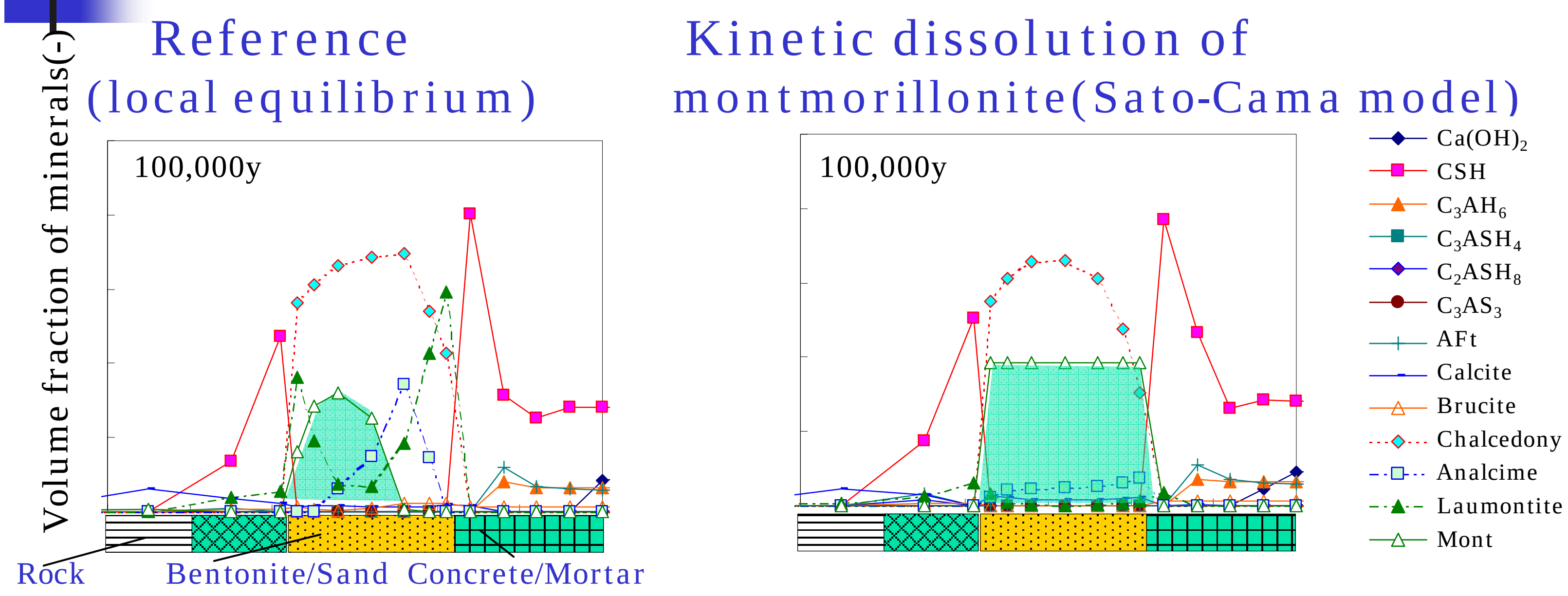
- Alterations occur from the interface of bentonite and mortar/ concrete.
- Montmorillonite alters to zeorite (laumontite and analcime).
- CSH precipitates at the interface.
- Alteration speed is high at the early stage, but it slows down as time extends.

Low De in the mortar reduces the alteration of EBS



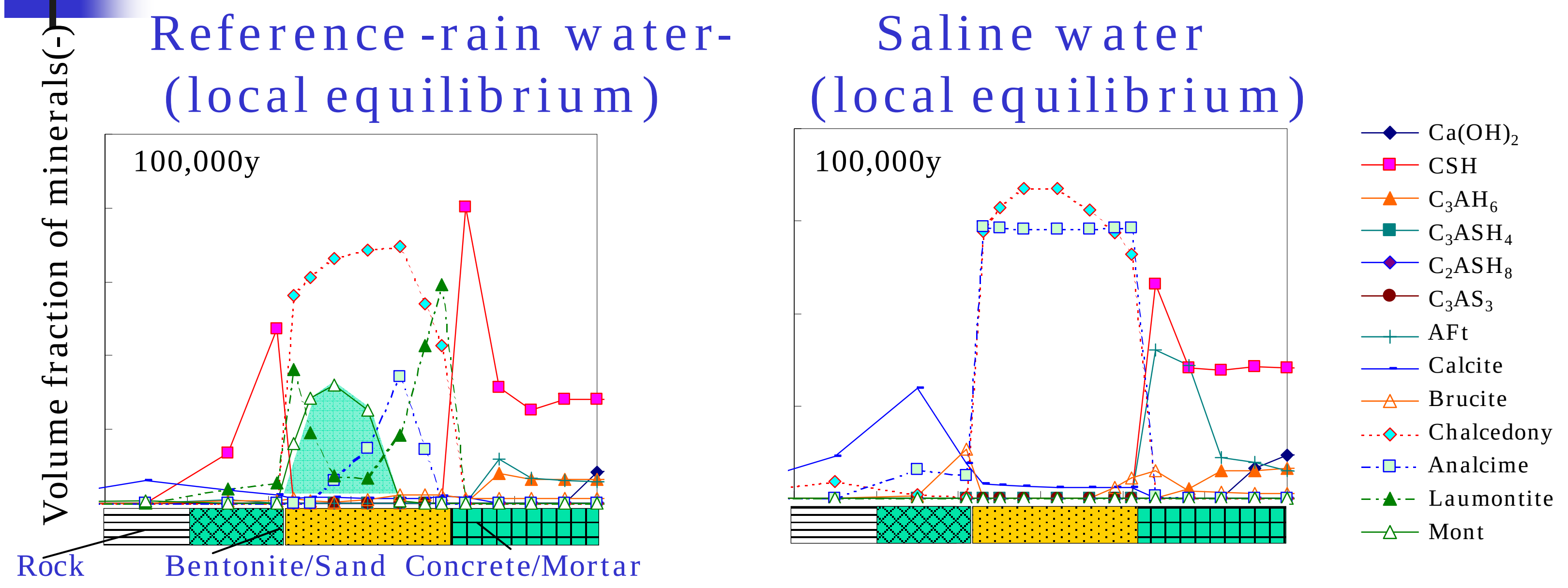
- In conservative high De case, small portion of montmorillonite remains at the center of bentonite.
- In reference case, montmorillonite remains at the outer part of bentonite layer.
- If low diffusive FAC is used, most of montmorillonite remains even after 100,000 years.

Non-liner kinetic dissolution of montmorillonite greatly restricts the alteration of EBS



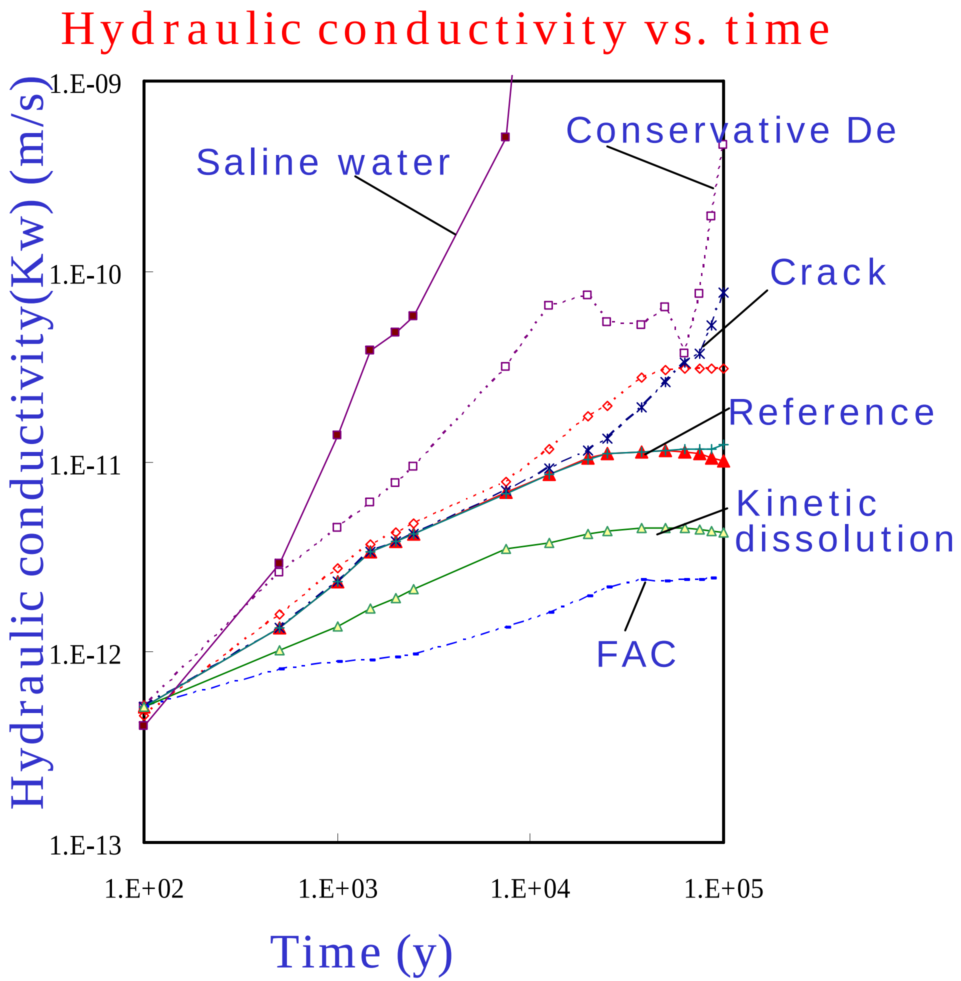
- Dissolution rate function significantly affect the alteration of EBS.
- If Sato-Cama's non-liner equation model is selected, in which dissolution rate is extremely low near equilibrium condition, most of montmorillonite remains after 100,000 years.

Montmorillonite alters to analcime under saline water condition



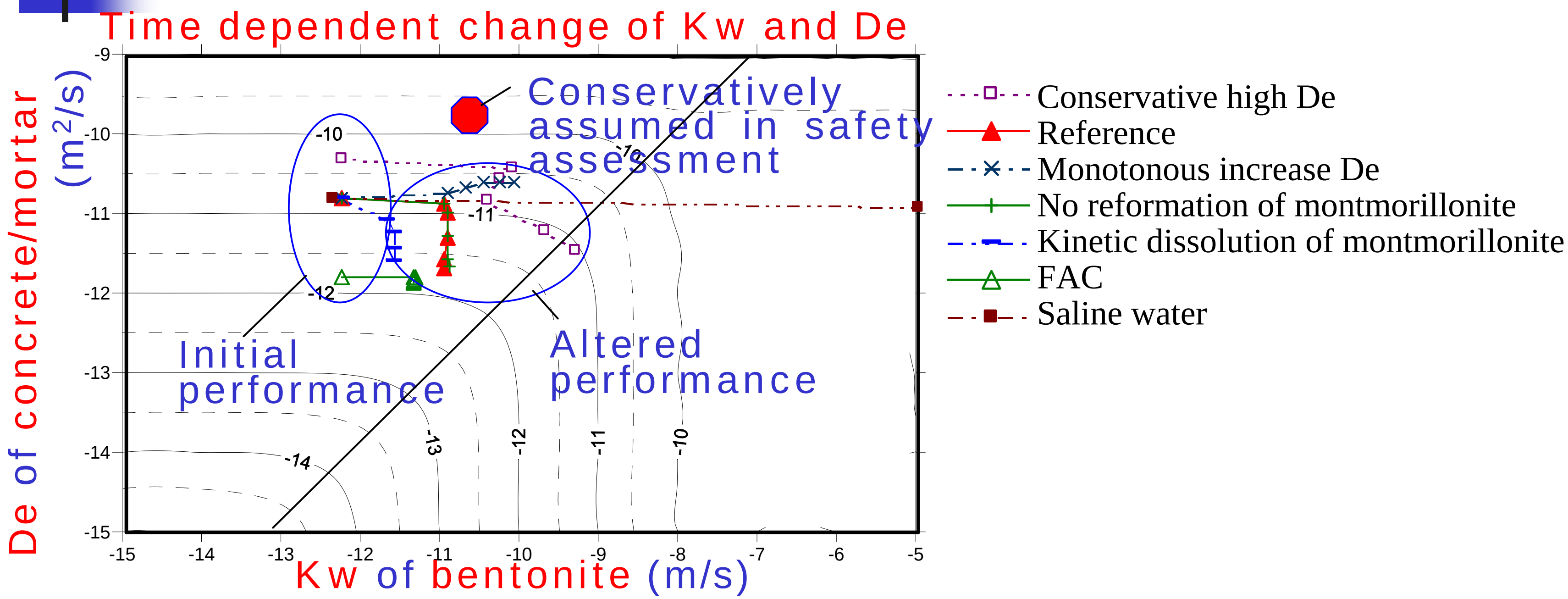
- With high Na concentration of saline water and high pH condition of mortar/concrete, most of montmorillonite alter to analcime in relatively short time.

Time dependent change of Kw of bentonite layer



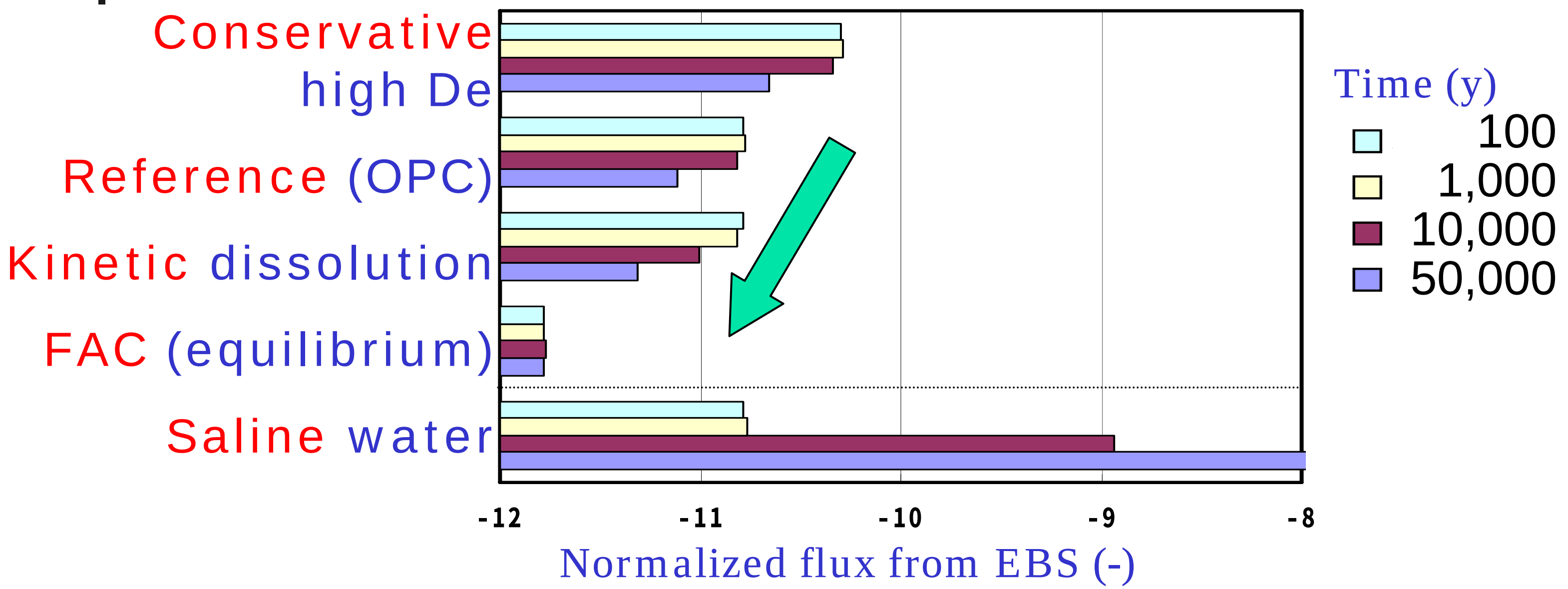
- Kw changes with alteration of bentonite.
- Kw increases to 1E-11m/s in 100,000 y (reference case)
- Low De leads to maintain low Kw. (Conservative De and FAC case)
- Kinetic dissolution shows long-term stability of EBS
- Kw greatly increases in saline water

Time dependent change of Kw and De



- Initial De and Kw of EBS is smaller than conservatively assumed values in TRU-1 report(2000).
- Kw increases with the alteration of montmorillonite. In some cases, Kw exceed the “conservative value” of TRU-1 report, in which only ion-exchange of Na to Ca was selected as the alteration mechanism.
- De maintains initial value. In some cased, it decreases with the precipitation of CSH.

Flux from EBS decreases by considering realistic conditions



- As derivation of De of mortar/cement from De of intact matrix is justified, nuclide flux from EBS decreased.
- As it was showed that, alteration of EBS with FAC can be predicted by model, smaller flux can be expected.
- If kinetic dissolution model is confirmed, much smaller flux in long-term will be able to expected.
- If EBS is constructed near the ocean, extreme growth of flux might occur. (If local equilibrium is assumed)

Conclusion

- Reflecting the results of the experiment, long-term model analysis was performed.
- The modification of conservative assumptions to the realistic ones made it possible to expect higher performance of the EBS for longer time.

Technical issues to be solved

- Properness of the selection of minerals isn't clear yet.
- Though chemical reactions in batch experiment could be understood by model calculation, there are differences in column experiment where mass transport also takes important role.
- In most experiments, cracks of mortar were clogged, but they aren't fully reproduced by model calculations.
- Much efforts are being paid now, to construct kinetic dissolution model of montmorillonite.

- More detailed information of the geochemical reactions and mass transport will be shown by the results of the long-term alteration test of bentonite/mortar.