Results and future plan of RWMC's R&D Regarding cement-bentonite interaction

Radioactive Waste Management Funding and Research Center
EBS Material Research and Assessment Project
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Motivation (1)

Japanese geological disposal largely depends on the performance of the buffer and backfill (bentonitic) material.

- Low water permeability to maintain the “diffusion dominant mass transport”
- Chemical and mechanical buffering
- Retardation of migration of radioactive nuclide by chemical and physical sorption, low diffusivity, low permeability and so ・・・・・・

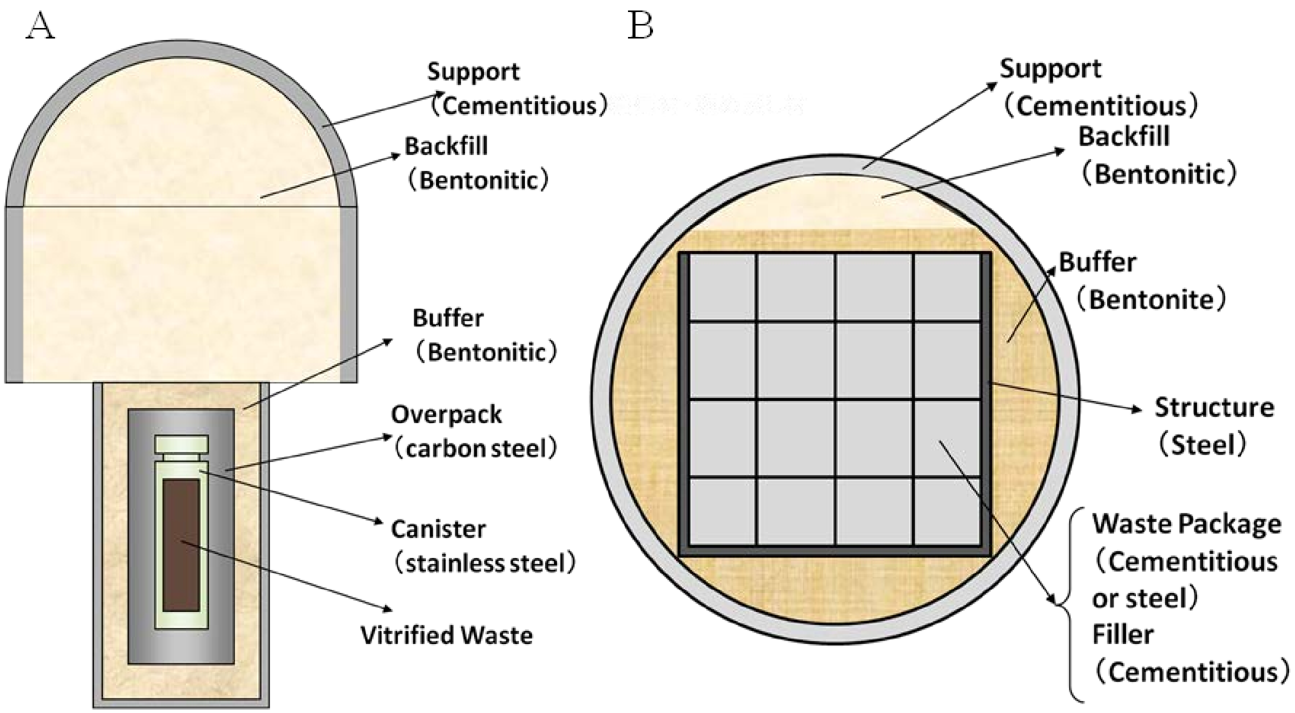


Fig.1 Japanese geological disposal concept of high level vitrified waste (A) and TRU (low heat long half life) waste (B)

Motivation (2)

There are many uncertainties in long term performance assessment of Japanese geological disposal because no candidate site for geological disposal has not been selected in Japan.

- Wide variety of design of disposal vault including the selection of EBS materials.
- Chemical environment such as composition of groundwater (salinity).

These uncertainties are thought to be effective to the performance of buffer material.

- Because the dissolution of cementitious materials are the source term of the alteration of the other EBS materials, accurate alteration model of actual, e.g. mixed, cement is necessary to predict the duration and long term performance of EBS.
- Is dissolution ratio of montmorilonite accurate under the compacted condition?
- Accurate “inputs” of primary and secondary minerals are necessary to assess the long-term performance of EBS.
  -secondary mineral near the C-B contact had not been identified.
- Long term alteration of mechanical properties of EBS material caused by chemical evolution.
- Does the change of the mechanical properties of buffer material accelerate the chemical evolution of EBS materials? (H-M-C coupling)

Structure of RWMC's project

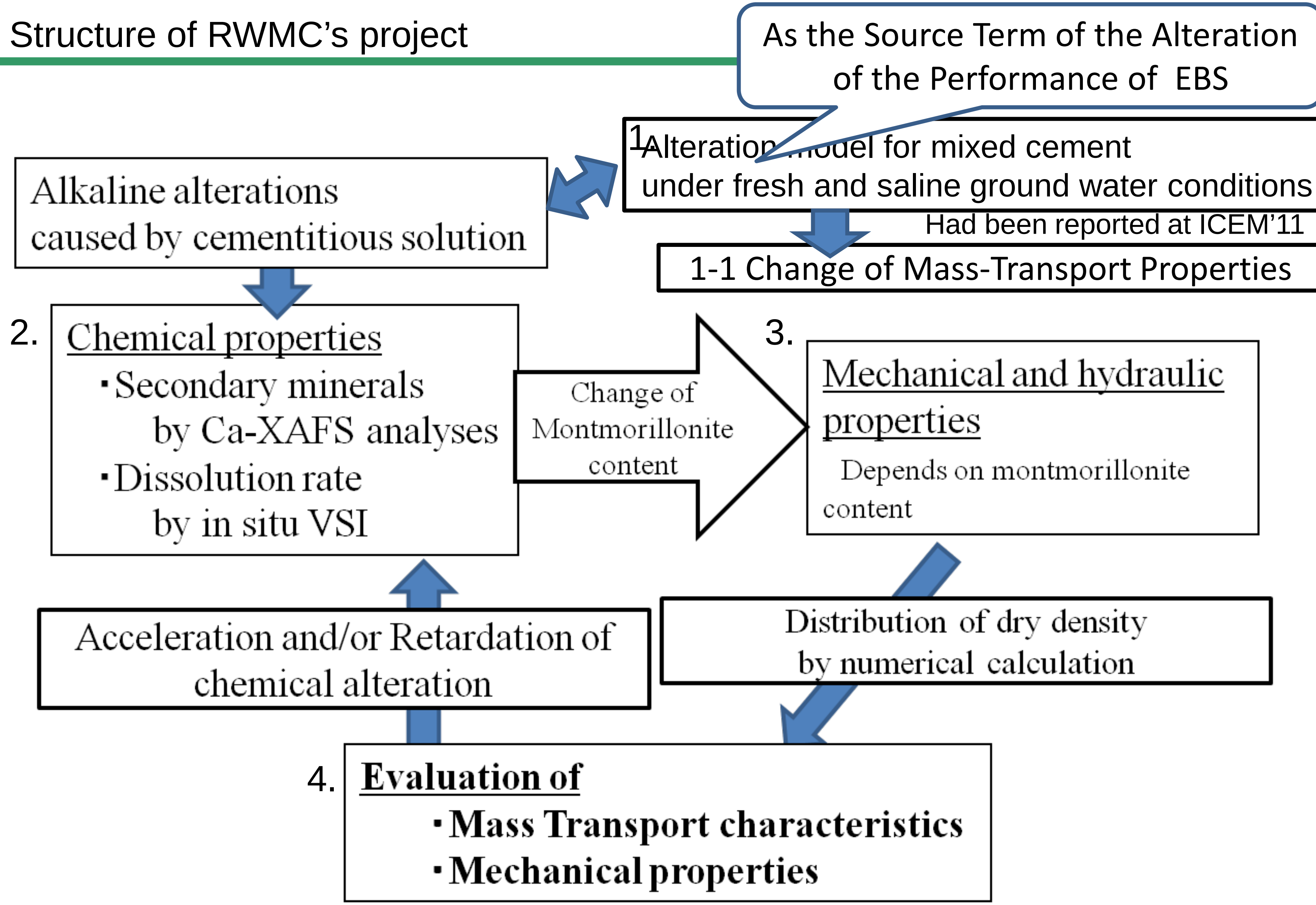


Fig. 2 Structure of this project

● As the source term of long-term chemical and mechanical alteration

RWMC had already developed

- Model of primary mineral composition for Mixed cement
- Improvement of alteration model for Fresh and Saline condition

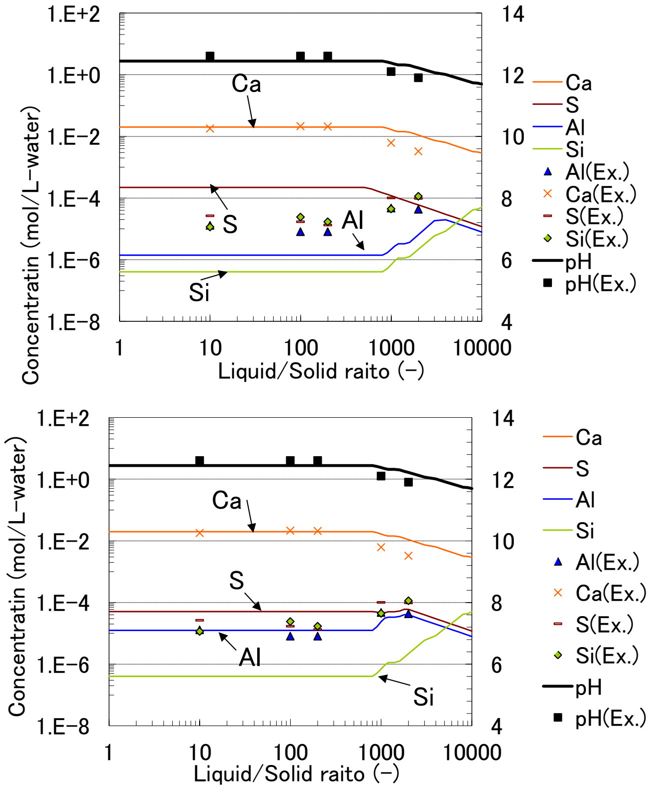
· pH value and Ca concentration are accurately calculated

- Limited by the C-S-H and $Ca(OH)_2$ dissolution

· Si, S and Al concentration are not accurate

- Limited by dissolution of C_3AH_6 ?

Those values had been calculated accurately by using the primary and secondary minerals without C_3AH_6.



Figs.1 Analyzed (dots) and calculated (lines) liquid composition for OPC with Case 1 (A) and Case 2 (B).

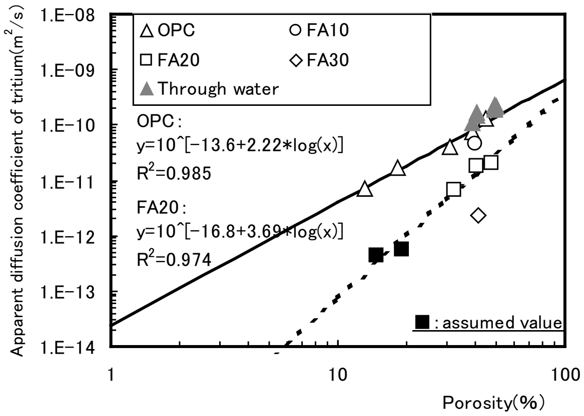
●RWMC can provide the results of many immersion tests.

1-1 Change of Mass-Transport Properties

●Diffusion Coefficient and water permeability of cementitious materials increased with dissolution

RWMC has been developing the mass-transport model for mixed and altered cement.

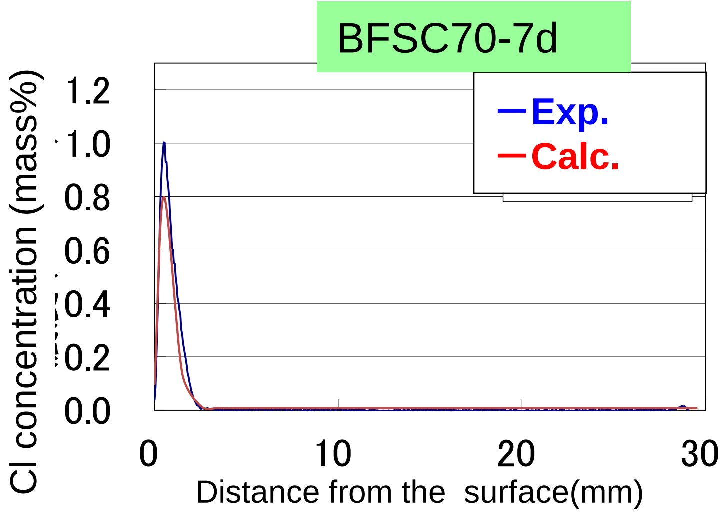
- Diffusion coefficient depends on the porosity
- The slope of the diffusion change are depends on the kind of cement.



→ Is diffusivity depends on the pore structure?

RWMC is trying to develop the diffusion model for mixed and altered cement.

●RWMC can share the results of diffusion experiment and can exchange the Information regarding the modeling.



2 Secondary minerals near C-B contact

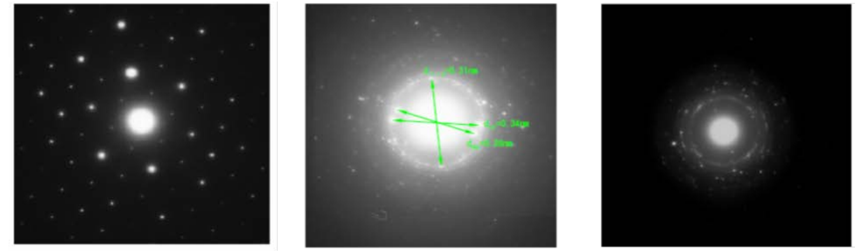
Although many numerical simulations had been suggested that C-S-H gel will precipitate around the C-B interface, that has not been detected by experiment.

Secondary minerals precipitated around the C-B interface are hardly to identify, because・・・・・・

・The amount of secondary minerals are much smaller than the detection limit of XRD and usual chemical analyses.

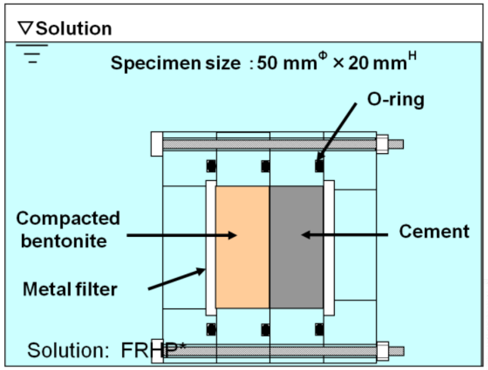
・Spectroscopic analyses is difficult to identify the C-S-H gel because it is an amorphous phase.

●RWMC had already identified and quantitated the secondary C-S-H by Ca-XAFS analysis as the collaboration with KEK Tsukuba Japan.



9ヶ月 17ヶ月 28ヶ月

TEM (electron diffraction) of bentonite near C-B interface



Bentonite: Kunigel-V1

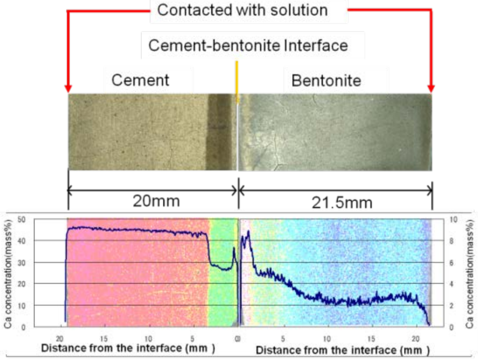
Bentonite dry densities: 1.6 Mg/m^3

Cement: OPC

Water/Cement ratios: 0.6

Immersion period:76 Months

*FRHP: Fresh, reduced and high pH water



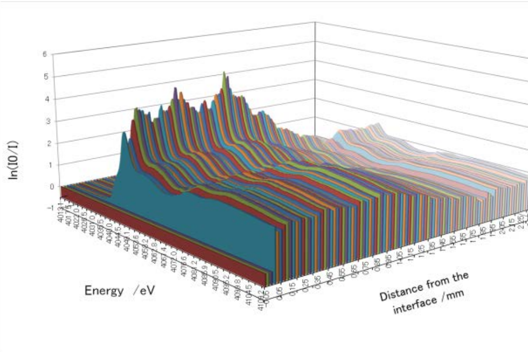
Cross section of the cement block-compacted bentonite interface and Ca concentration profile in the specimen

●RWMC can provide the results of long-term immersion test of “coupled” specimen.

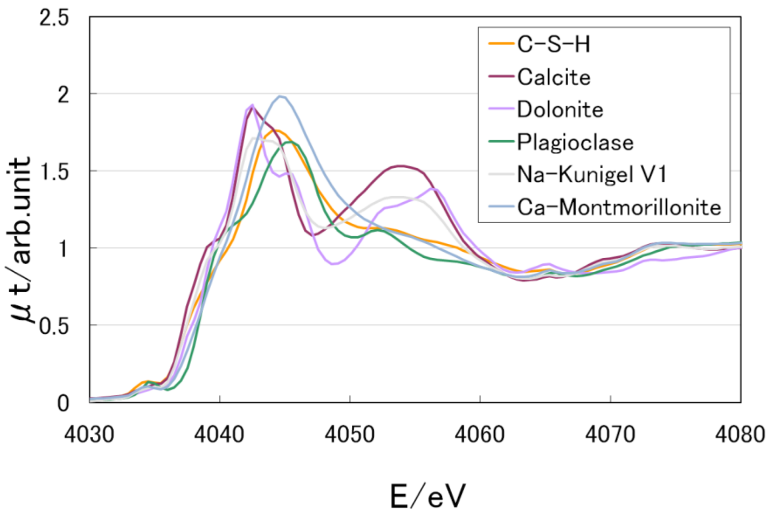
2 Secondary minerals near C-B contact

● RWMC can share the standard Ca-XANES spectra and the results of XAFS analyses.

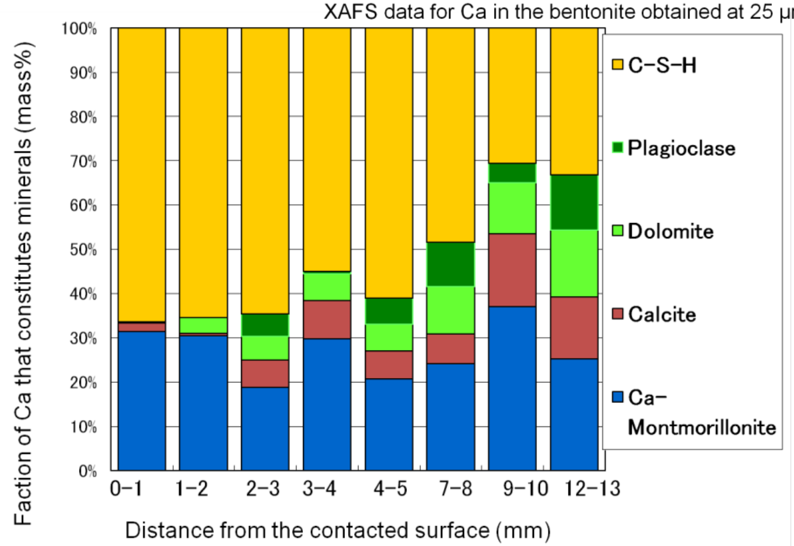
- ･Standard XANES spectra of possible Ca-containing minerals Obtained.
- ・Specimens had been obtained from bentonites Immersed for 3 to five years with contacted cement under ion exchanged water or artificial sea water.
- ・XANES spectra of specimens have been compaired with those of standard minerals.



XAFS data for Ca in the bentonite obtained at 25 μm intervals



Comparison of XAFS data among Kunigel V1, minerals that constitute the bentonite and C-S-H



Fraction of Ca that constitutes minerals based on pattern fitting of XAFS data of the homogeneous specimens

2-2 Dissolution rate of montmorillonite under compacted condition

Dissolution ratio of montmorilonite was obtained by "in-situ" Vertical Shift Interferometry.

There are still argument around the dissolution ratio of montmorilonite under compacted condition.

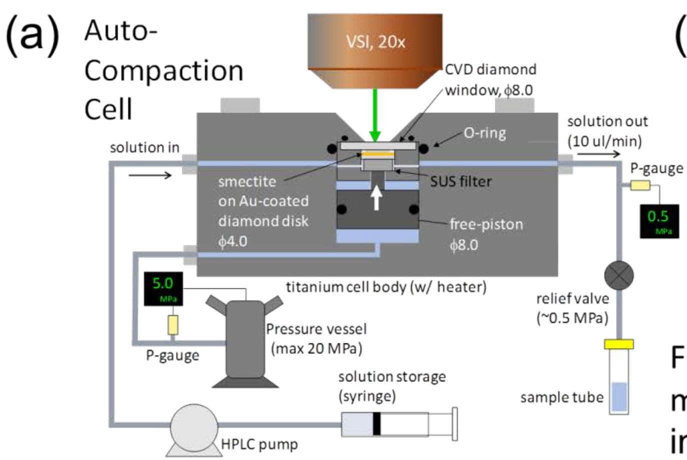
From the point of view of mineralogy, dissolution of minerals will be accelerated by compaction because of increase of defect.

On the other hand, the dissolution rate should be slower than that of "free" condition because the concentration of pore solution will be much higher, that likes over saturated solution.

We tried to obtain the dissolution ratio under compacted condition in situ by "VSI" technique.

・VSI can observe the change of hight precisely and continuously, the dissolution amount can be obtained.

Optical metrology and in-situ technique



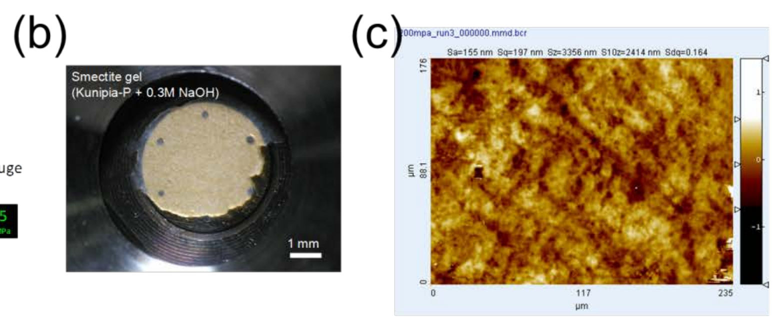


Fig. 3 Auto-compaction cell system for in-situ VSI measurement (a), sample in the cell (b) and VSI image (P = 8.0 MPa).

2. Dissolution rate and density

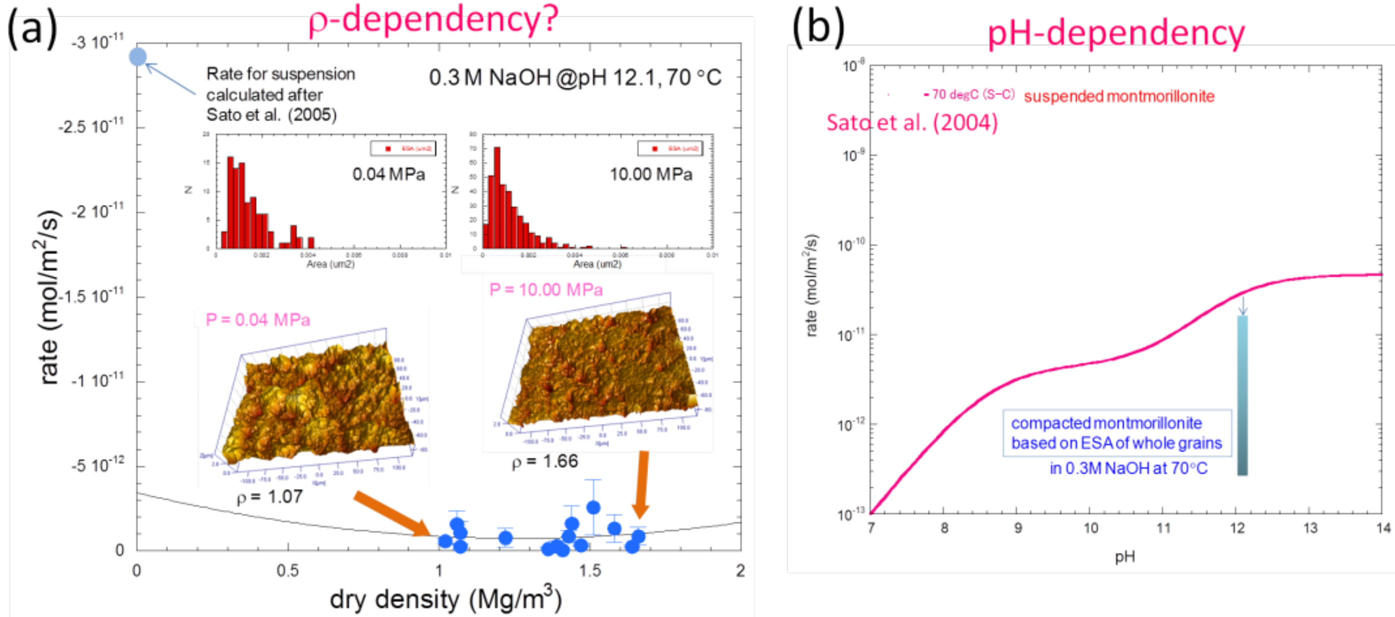


Fig. 11 Plots of dry density vs. rate at 0.04 to 10.00 MPa compaction (a) and pH vs. rate (b).

Results

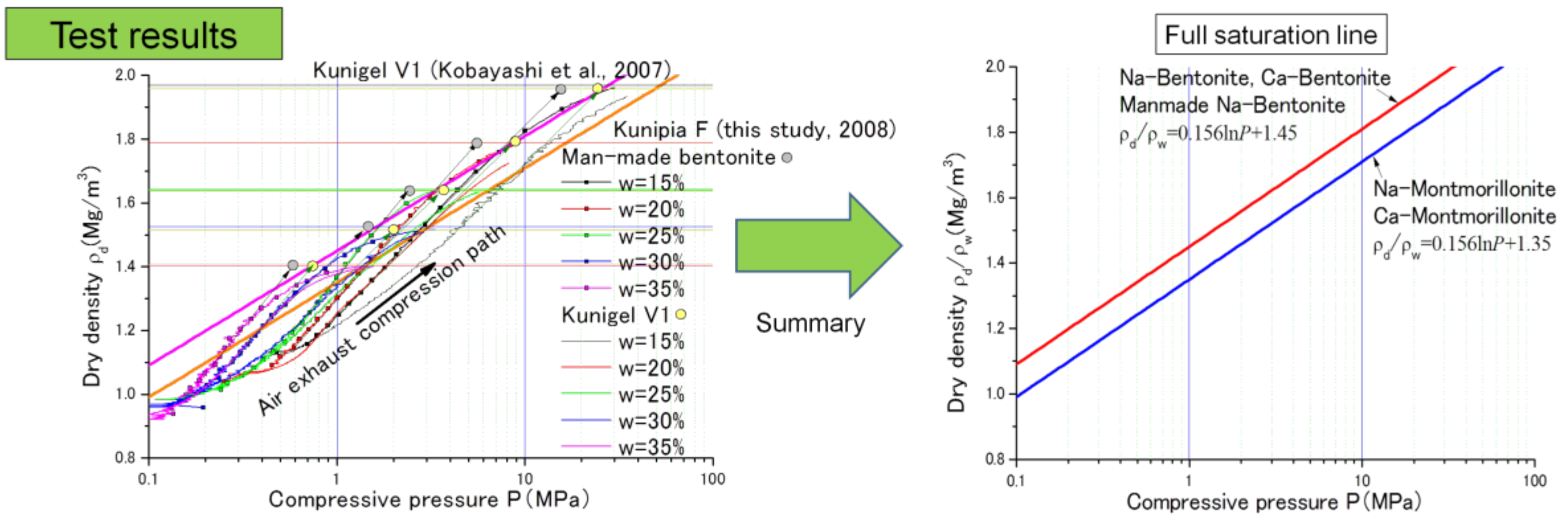
Dissolution of montmorilonite under compacted condition was lower than that obtained by using the column experiment (slurry or gelly shape specimen).

・Compaction accelerates dissolution of montmorilonite, but the dissolution rate will slowned with time.

● RWMC can provide the data of dissolution rate of montmorillonite.

In the performance assessment of geological disposal in Japan, mechanical and hydraulic properties of bentonitic material are empirically described as functions with smectite content.

●RWMC are trying to describe those, e.g. swelling pressure, water permeability, diffusivity and so…, theoretically.



COCLUSION-1

・The gradient of the full saturation lines for montmorillonite was same as bentonite .
・The position of full saturation lines of the bentonite moved to the left with increasing of montmorillonite content.
・The full saturation lines did not depend on type of interlayer exchangeable cations, but the montmorillonite content.

Mechanical and Hydrauluc properties

Pressented at Montpellier 2012

Test for measurement of 2 water molecular layer hydration content

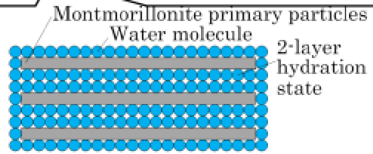
Coefficient of permeability

Kozeny-Carman law

$$k = k(\mu, \rho, e, S_v) = \frac{1}{5}\frac{\rho g}{\mu}\frac{1}{S_v^2}\frac{e^3}{1+e}$$

Sv: Specific Surface Area (m²/m³)

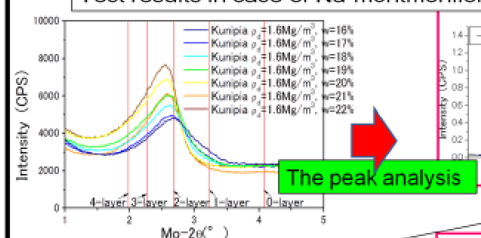
$$Sv = 36 w^* \rho_d \,(m^2/m^3)$$

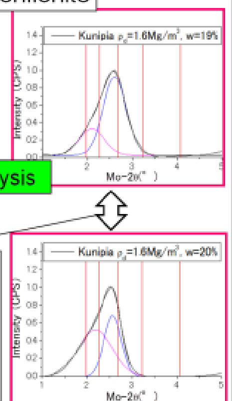


w^*:2 water molecular layer hydration content

measured as basal spacing by XRD

Test results in case of Na-montmorillonite





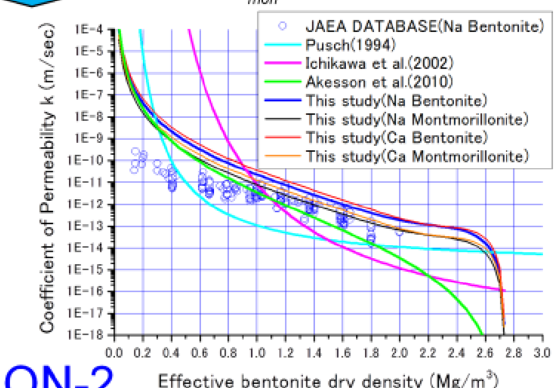
The peak intensity at the 2-hydration became small remarkably between 19% to 20% of water content. Therefore, 2-hydration water content can be estimated as 19%.

Summary of the test results

Material	w^*	Effective bentonite dry density and 2-layer hydration state water content relation
Na-Montmorillonite	19%	$w^* = 1/\left(0.052 + 3.8E - 6\rho_d^{12.1}\right)$
Na-Bentonite (KuniGel V1)	11%	$w_{ben} = 1/\left(0.091 + 2.2E - 8\rho_d^{17.57}\right)$ $w^* = \alpha_{mon}/\left(0.052 + 3.8E - 6\rho_d^{12.1}\right)$
Man-made KuniGel V1	11%	$w_{ben} = 1/\left(0.091 + 2.2E - 8\rho_d^{17.57}\right)$ $w^* = \alpha_{mon}/\left(0.052 + 3.8E - 6\rho_d^{12.1}\right)$
Ca- Montmorillonite	15%	$w_{ca}{}^* = 1/(0.066 + 2.6E - 7\rho_d^{15.16})$ $w_{caben}{}^* = 1/(0.11 + 3.9E - 11\rho_d^{24.5})$
Ca-Bentonite (Ca-KuniGel V1)	9%	$w_{ca}{}^* = \alpha_{mon}/(0.066 + 2.6E - 7\rho_d^{15.16})$

Kozeny-Carman law

w^*:2-layer hydration state water content
α_{mon} : montmorillonite conten



COCLUSION-2

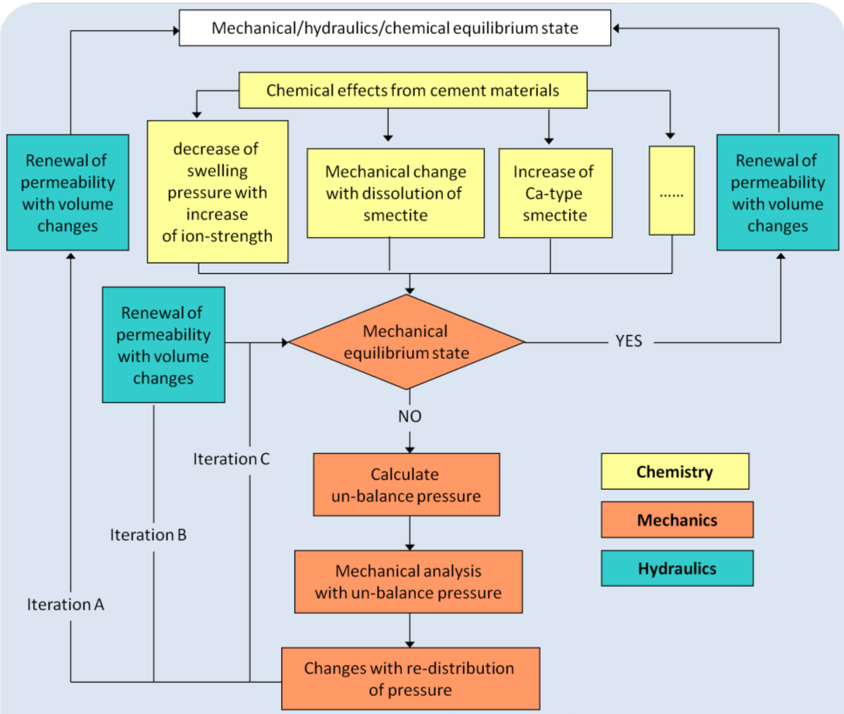
・These results calculated by the Kozeny-Carman equation are consistent with the existing results.
・The variation of the hydraulic conductivity due to the difference of the materials, which is about 10 times range, can be explained by the change in the specific surface area solely.

Coupled Analysis Method

We used a weakly coupled analysis in order to allow the following:

1) shortened analysis time, despite the lower accuracy of the solution.
2) development of separate chemical and hydraulic/mechanical analysis tools.

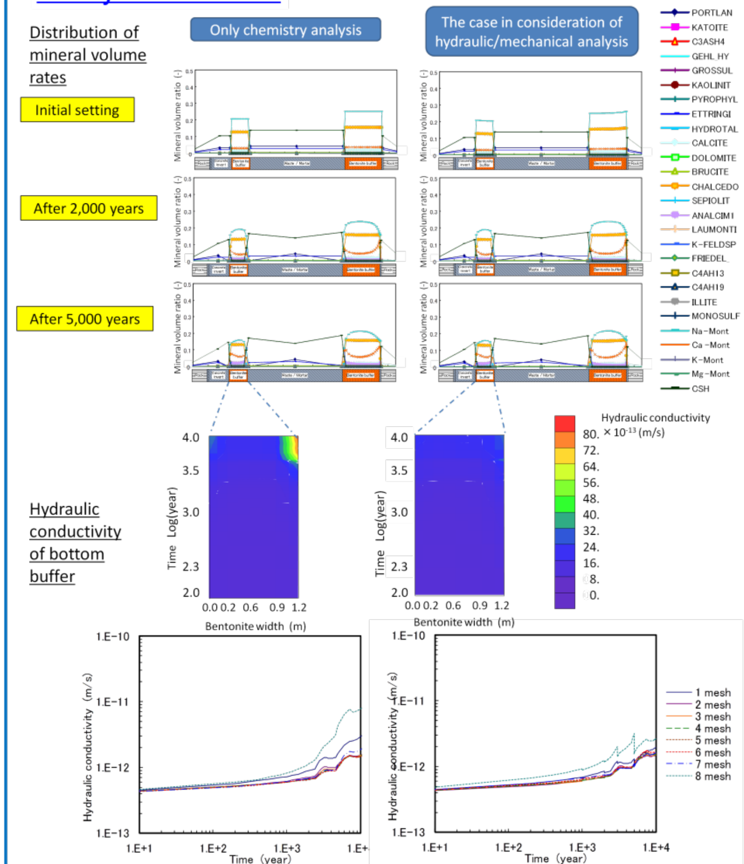
The geochemical code : **PHREEQC-TRANS**[1]
The hydraulic/mechanical code **: DACSAR-MP**[2]



2Schematic of coupled hydraulic/mechanical/chemical analysis

Although iteration A of the coupling method has a stronger effect, the computation time is very long. Therefore, in this study we considered the effect on the evaluation of long term alteration caused by use of **Iteration C.**

Analysis Results



Hydraulic conductivity of bottom buffer

Conclusion

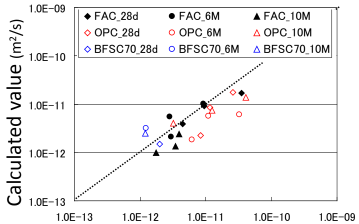
- The coupled analysis showed that the dissolution of the montmorillonite in the section that touches the cement material is suppressed.
- The equivalent hydraulic conductivity of bentonite showed virtually no change. However, inspection of the entire mesh for the bentonite section showed that the effect from the coupling varied by location.
- At the time of moisture saturation, there was almost no change in the state of chemical alteration for either the homogenous density distribution or the heterogeneous density distribution.

Long-term performance of EB

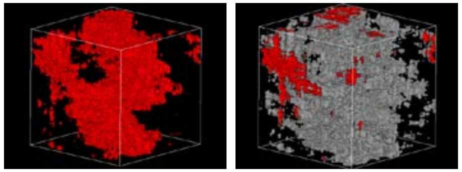
Alteration of cementitious material

➢**The modeling of the characteristic change corresponding to various materials**
- Diffusion Coefficient of ion in consideration of solid-phase adsorption
- Diffusion Coefficient and compressive strength in consideration of the alteration

Estimate of Diffusion Coefficient



3D image of pore structure



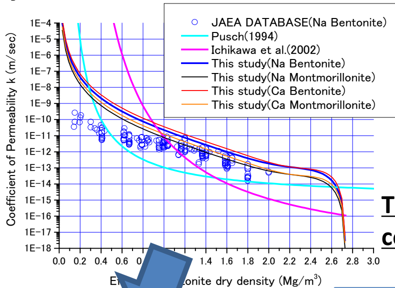
(a)Pore image (b)Pore and C-S-H (C-S-H contain fine pore)

➢**Grasp of the initial condition and second mineral setting of the long-term prediction**
- Experiment about alternation of various cementitious material
- Analysis of the concrete from structure that was build 80 years ago (natural analog study)

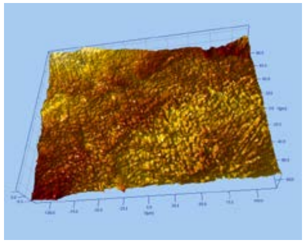
Cement-Bentonite interactions

➢**The measurement of dissolution rate of compacted smectite under hyperalkaline condition**
- In-situ interferometric measurements
- Column examination

➢**Hydraulic/Mechanical modeling of smectitic materials for HMC analytical evaluation**

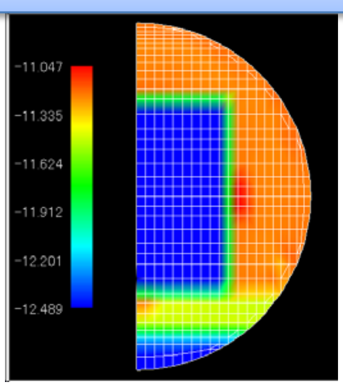


The effective bentonite dry density and coefficient of permeability



3D plot of compacted smectite

Development of calculation for long-term alteration



Distribution of hydraulic conductivity
At 1000y after closure, with HMC coupling.

Accurate modeling?

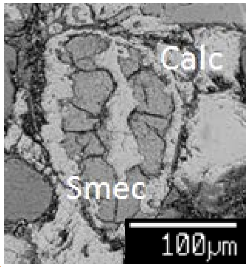
- Alteration model for mixed cement with other pozzolanic materials such as BFS, fly ash and silica .
- To reflect the "slow" dissolution rate of smectite under compacted condition to the Alteration calculation.

HMC coupling caluculation

- To reflect the model for the hydraulic and mechanical alteration of buffer material to the chemical alteration calculation of the repository.

Natural Analog Study

To upgrade the knowledge of interactions of smectite with alkaline fluids, smectite-rich rocks and Ca-rich fluids were obtained from a 250-meter-depth drill hole in the campus of Tokai University.



- Calcite deposited after Smectite.
- Smectite had a variety in Ca/Na composition.
- Ca-rich fluids had a ^{36}Cl age of ca 1.9 Ma.

RWMC can share ････

・Long term alteration model of Mixed cement

・Modeling of the diffusion property of mixed and altered cementitious material

・Alteration modeling of Bentonitic material

・H-M-C coupling calculation of Bentonitic material under the influence of High
Ca solution.

・Natural Analogue study of altered bentonite(Clay) formation caused alkaline
($9.5 \leqq pH \leqq 11.3$) .