EXPERIMENTAL AND MODELLING STUDY ON THE LONG-TERM PERFORMANCE OF THE ENGINEERING BARRIER SYSTEM OF TRU WASTE REPOSITORY

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ABSTRACT

The long-term properties of the barrier system of the TRU waste repository will be assessed using the model that analyzes the geochemical reaction and the mass transport in that system. But there are data and models whose validity isn't adequately clear yet. RWMC had started the project of laboratory scale tests, natural analogous studies and numerical model analysis to improve the reliability of that model. The result of the four years of the study made it possible to change some conservative assumption to more realistic ones, and to show longer time stabilities of the repository system.

1. Introduction

In Japan, TRU wastes are planned to be disposed in the tunnel in hundreds meters depth with the engineered barrier system (EBS) of low hydraulic conductive bentonite/sand mixture and low diffusive cementitious materials. The cementitious materials would slowly dissolve in the groundwater to form high pH and high Ca concentration zone around it, and both cementitious and bentonite materials would alter in that environment, and change the performance of EBS.

Conventional performance assessments conservatively treated the effect of these phenomena by assuming degraded properties of EBS for whole period of concern. RWMC of Japan had been trying to model the long-term alteration phenomena of EBS to understand the time dependent performance of it. With this model, initial high performance properties of EBS could reasonably and reliably considered in the assessment. The effects of the dissolution and mineralogical changes of minerals could also be considered in, which weren't sufficiently considered in the conventional assessment.

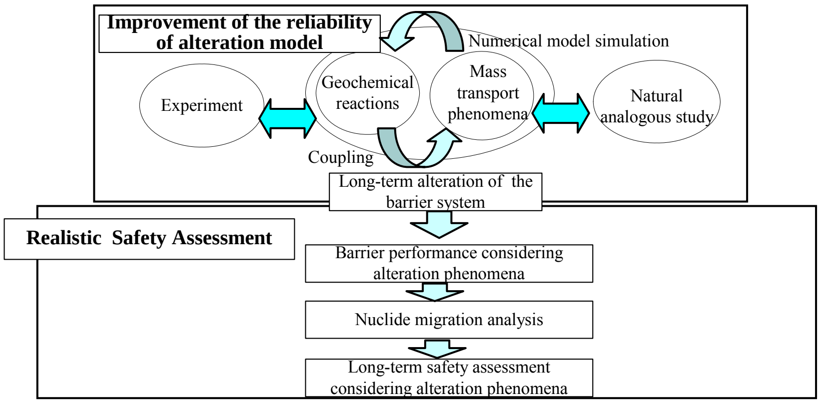

Fig.1 Experiment, natural analogous study and numerical model simulation are combined to improve long-term safety assessment

RWMC had constructed the first model in 2002 with the knowledge at that time, and started the project of laboratory scale alteration experiment, natural analogous studies and numerical model analysis to reduce the uncertainties in the model, parameters and assumptions in it. The purpose of the experiments is to precisely examine the alteration phenomena of months to several years.

Natural analogous data were used to observe the result of very long-term alteration. And these experimental and natural analogous data were compared with the numerical model.

2. Key issues and experiments

RWMC had discussed about the phenomena that can affect the performance of EBS, and selected important ones to make study plans to solve those problem. Most essential and important issue to consider the alteration of EBS is the geochemical model (i.e. thermodynamic data, dissolution rate, selection of minerals identified in EBS, and the position where secondary minerals are formed). In this project, experiments are mainly concentrated to identify the reactions in the system.

Crack is a specific property of cementitious materials, and mass transport related with chemical reaction might be greatly affected by this feature. Here, experiments were made to see the reactions would clog or broaden the crack in various water conditions. If crack is clogged by secondary minerals, cementitious material can be treated as highly resistible region for mass transport.

Though OPC has been treated as typical cement, fly ash cement (FAC), which has finer pore structure, might be preferable cementitious material. To use FAC, its chemical and physical properties should be studied sufficiently. Reaction with saline water is another important issue, because high concentration NaCl and relatively high Sulfate content can quite differently react with materials of EBS. Experiments and main results of them are summarized in Table 1.

Table 1. Experiments and results to solve key technical issues

Key technical issues	Experiment	Results of the experiment
Geochemical model of FAC	Batch dissolution test of FAC	Dissolved chemical species cold be predicted using geochemical model for OPC with modification of initial mineral contents.
Dissolution of OPC in saline water	Batch dissolution test of OPC in saline water.	Dissolved major species and pH could be predicted using geochemical model for OPC. Concentration of S, Mg and formation of friedel-salt, ettringite had differences.
Reversible reaction of analcime to montmorillonite	Montmorillonite reprecipitation test in simulated pore water (120～150℃)	Trace of the reprecipitation of montmorillonite couldn't be detected.
Alteration of montmorillonite to analcime under saline water condition	Batch alteration test of montmorillonite in high Na concentration solution. (80-120℃)	Alteration to analcime was identified in Na concentration > 0.1mol/L, pH range of 11-13.
Clogging or dissolution at the crack in cementitious material	Diffusion and flow column test with cracked mortar specimen.	Most of cracks were clogged in the experiments.
Secondary minerals and its location at the interface of bentonite/cement.	Long-term alteration test of bentonite contacting with mortar (3 years)	Experiments are now going on.
Identification of precipitated CSH	Development of separation method of CSH from bentonite.	Using heavy solution method, added CSH could be separated from bentonite.

3. Numerical analysis

Reflecting the results of those experiments, numerical model analysis was performed to predict the long-term evolution of the EBS. In this analysis, geochemical reactions in each materials and diffusive/ advective solute transport were calculated simultaneously. Furthermore, the change of the physical properties (i.e. hydraulic conductivity (Kw), diffusivity (De) and porosity (ε)) was estimated in accordance with the mineralogical alteration of the EBS.

Analysis code is PhreeqC-Trans, which is the improved code of USGS's PhreeqC[1)] to treat the change of mass transport conditions according to the geochemical reactions. Thermodynamic database for minerals is Spron.JNC[2)] and A.Atkinson's data[3)]. Relationship of Kw and effective gel density of bentonite is from Mihara's data[4)]. Relationship of De and ε of cementitious material is from Yasda's data[5)].

Analyzed cases are listed in Table 2. In conservative case, De of cementitious material is estimated as the average of crack and intact matrix region. Contrary, in the reference case, De of matrix is selected. To consider the effect of mass transport properties in cementitious material, two cases are considered. The first one is crack model, in which crack and matrix is modelled in 2-dimentional geometry. The other case is monotonous increase of De of concrete. Numerical simulation indicates that, according to the precipitation of CSH, De of cementitious materials will decrease, but the location where CSH precipitates isn't clear yet.

For the selection of reacting minerals, three cases were considered. The first one treats reprecipitation of montmorillonite, which is predicted by simulation when pH decreases, but that isn't identified in the experiment. Alteration of montmorillonite to laumontite is also predicted but isn't identified. Dissolution rate of montmorillonite is known to be small, moreover when pore water approaches to equilibrium, it approaches to zero. This effect is more evident if there is non-liner relationship between dissolution rate and saturation index. This type of relationship is selected in "Second TRU progress report" [6].

FAC and saline water case were also analyzed, because the result of the experiment showed that geochemical model of cement minerals can be adopted for FAC or saline water condition.

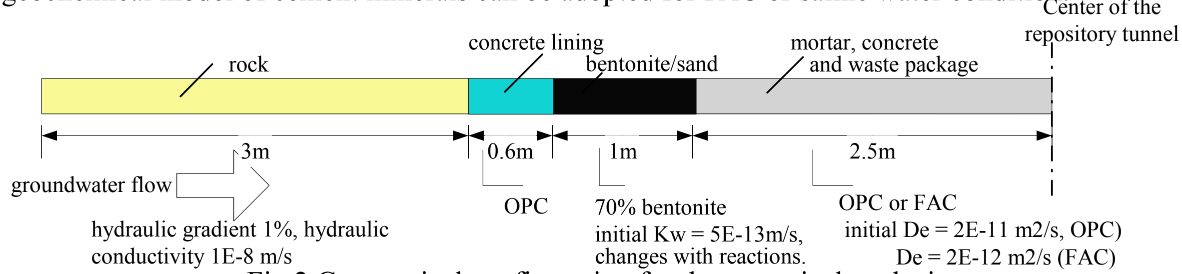

Fig.2 Geometrical configuration for the numerical analys

Table2 Numerical model analysis cases

Conservative case	Conservative high De in mortar/concrete	De in mortar/concrete is estimated as the average of crack and matrix region.
Reference	Reference case (OPC)	De of concrete is De of matrix. Instantaneous equilibrium is assumed.
Mass transport property of cementitious material	Crack model case	Crack and matrix of concrete is model in 2-dimensional geometry.
	Monotonous increase of De of concrete	Decrease of De with the decrease of ε by the formation of CSH is conservatively neglected.
Selection of the minerals	No reprecipitation of montmorillonite	Reprecipitation reaction of montmorillonite from analcime is inhibited.
	No formation of laumontite	Laumontite is excluded from secondary minerals list.
	Kinetic dissolution of montmorillonite.	Dissolution rate of montmorillonite is calculated by Sato-Cama's equation[6].
Cement type	FAC case	Fly ash cement is used instead of OPC
Groundwater type	Saline water case	Ground water around the repository has high salinity.

4. Results and discussion

Distribution of the minerals after 10,000 years is described in Fig.3. Remarkable change of minerals could be seen at the interface of bentonite and cementitious material. In the bentonite layer, montmorillonite and chalcedony dissolve to form zeolite such as analcime or laumontite. In the cementitious material, portlandite and CASH dissolve to form CSH of low Ca/Si ratio. At conservative high De case, most of montmorillonite are predicted to dissolve, whereas the crack model case shows similar result to that of the reference case. These results indicate that, supply of Ca and other ions aren't dominated by the diffusion through the crack but by the dissolution of the intact cement matrix. Moreover, the clog of the crack in mortar is shown by the test. These results justify expecting low De in the cementitious materials. In low diffusive FAC case, altered zone is small and most of montmorillonite remains even after 10,000 years.

These alteration phenomena strongly affected by selection of the secondary minerals. If laumontite is excluded, most of montmorillonite remains even OPC is used.

When kinetic dissolution of montmorillonite is considered by Sato-Cama's equation, dissolution of montmorillonite in the repository is very small.

Most remarkable alteration of montmorillonite is seen in saline water case. In this case, all of montmorillonite is dissolved to form analcime within 1,000 years.

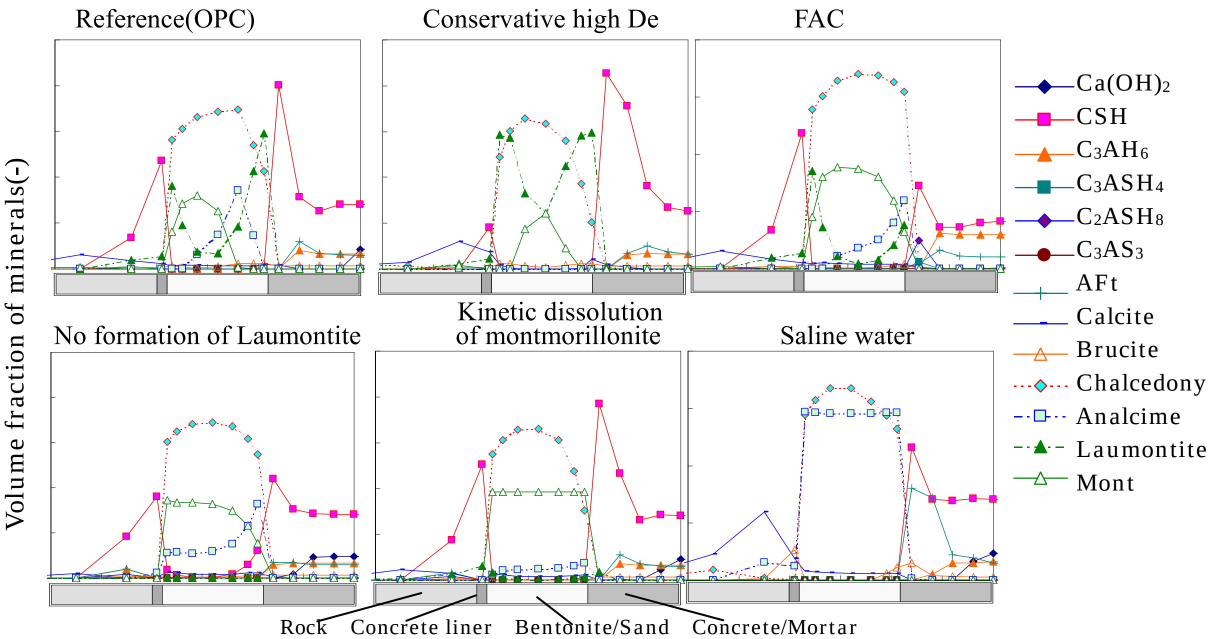

Fig.3 Distribution of minerals in EBS after 10,000 years. The extent of alteration depends on De, selection of minerals, dissolution rate and groundwater contents.

Time dependent Kw in the bentonite layer is shown in Fig.4. Kw increases with the dissolution of montmorillonite, and other associated minerals. Kw of the reference case is smaller than that of conservative high De case. It maintains about 1E-11 m/s until 100,000 years. If FAC is used, smaller Kw for long period is expected. In addition, if kinetic dissolution of montmorillonite is considered, Kw will remain about 2E-12 even after 100,000 years.

As the result of these calculations, if the reliability of realistic parameter and model is validated, stability of the EBS can be shown for longer-term.

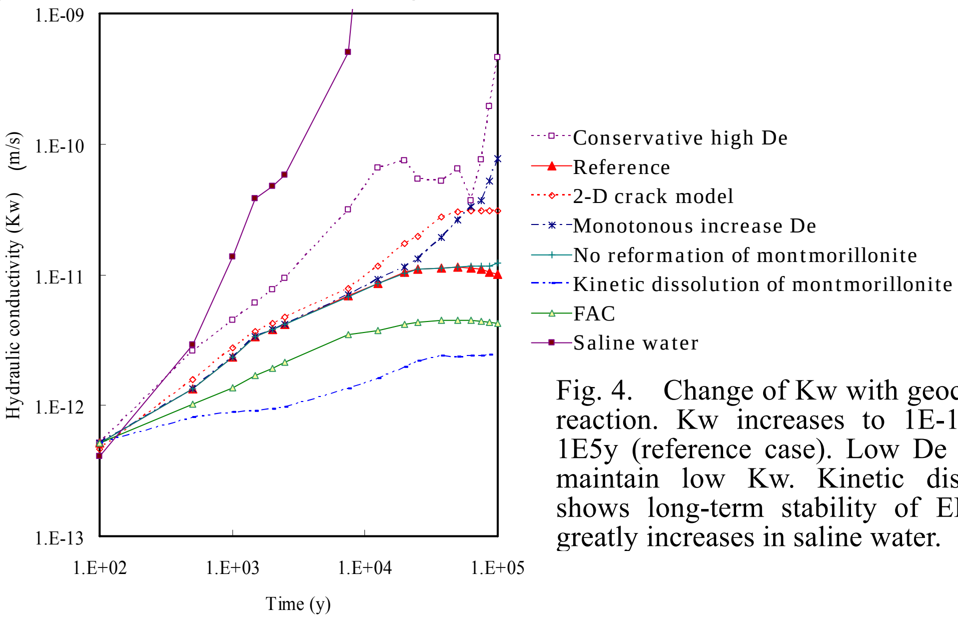

Fig. 4. Change of Kw with geochemical reaction. Kw increases to 1E-11m/s in 1E5y (reference case). Low De leads to maintain low Kw. Kinetic dissolution shows long-term stability of EBS. Kw greatly increases in saline water.

Kw and De of the EBS are plotted on Fig.5 at every 20,000 years. In this figure, contour of normalized nuclide flux at near field is also plotted. Initial properties of each condition are located at the left side of the graph. According to the time evolves, hydraulic conductivities increase and De decreases in most cases. Painted circle is the value used in first TRU report. At that time, low De of cementitious materials was conservatively neglected. On the other hand, in some cases, Kw after long time exceeds the “conservative” value. That is because, many mineralogical reactions are considered, instead ion-exchange of Na type montmorillonite to Ca type only was considered at first TRU report. However, with the precise knowledge about those geochemical reactions, it can be possible to show the performance of the EBS with confidence.

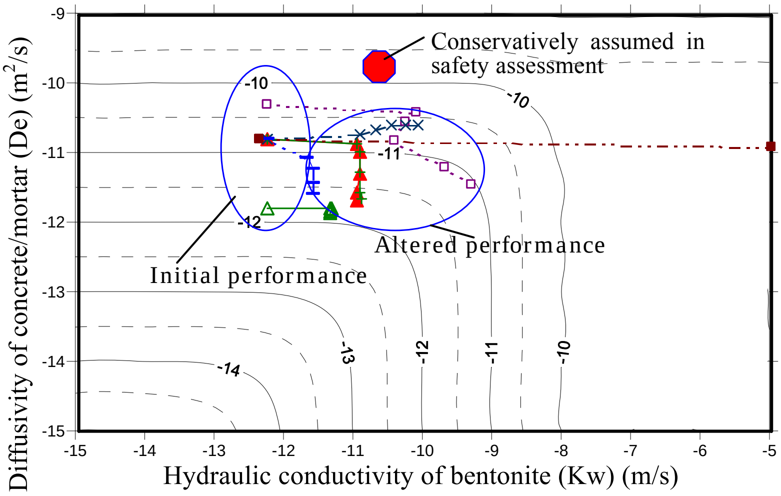

Fig. 5. Change of Kw and De of EBS are plotted at every 20,000y. Normalized flux is shown as contour line.
Kw increases with the alteration of montmorillonite, whereas De decreases with the precipitation of CSH.

5. Conclusion

Reflecting the results of the experiment, long-term model analysis was performed. With the modification of conservative assumptions to the realistic ones made it possible to expect higher performance of the EBS for longer time. Whereas, there remain technical issues to be solved, i.e.

- The location where CSH precipitates at isn’t clear from the experiment. That can affect the change of ε and mass transport properties at the interface region.
- In most cases, cracks of mortar were clogged, but they aren’t fully re-produced by model.
- Though chemical reaction in batch experiment could be understood by model calculation, there are differences in column experiment where mass transport also takes important role.

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

6. Acknowledgment

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7. References

1) D.L.Parkhurst, C.A.J.Appelo, “User’s Guide to PHREEQC(Version 2)”, Water-Resources Investigations Report 99-4259, (1999)
2) R.C.Arthur, et al., “Development of Thermodynamic Databases for Geochemical Calculations”, JNC Technical report, JNC TN8400 99-079, (1999).
3) A.Atkinson, et al., “Evolution of pH in a Radwaste Repository: Experimental Simulation of Cement Leaching”, DOE/RW/89/025, (1987)
4) M.Maeda, et al., “Mechanical properties of the Ca Exchanged and Ca bentonite-swelling pressure, hydraulic conductivity, compressive strength and elastic modulus”, JNC Technical report, PNC TN8410 98-021, p.142, (1998)
5) K.Yasuda, et al., “Physical and transportation properties of concrete due to calcium leaching”, collected papers of cement and concrete, JCA, No.56, p.492, (2002)
6) “Second TRU progress report”, JNC TY1400 2005-013, FEPC TRU-TR2-2005-02,(2005)