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Some Aspects of Natural Analogue Studies for Assessment of Long-term Durability of Engineered Barrier Materials

— Recent Activities at PNC Tokai, Japan —

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Some Aspects of Natural Analogue Studies for Assessment of Long-term Durability of Engineered Barrier Materials
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要　　旨

本研究は天然の類似試料の長期変質挙動を調べる事により，人工バリア材の長期耐久性を評価することを目的とする。

Ⅰ．対象試料の選定：天然の歴史試料は古いほどさまざまな要因が重複し，その環境条件も複雑でかつ変化し，把握できにくくなる。また，変質期間に関する情報も得られにくくなる。従って，比較的若い，単純な履歴の試料を研究することとした。

Ⅱ．研究の構成：①変質現象の調査，②環境条件の把握，③（組成差や環境条件の差を比較するための）サポート実験，を本研究の構成とする。

Ⅲ．調査例：人工バリア材，すなわち，①廃棄物ガラス，②オーバーパック，③緩衝材，④埋め戻し材，の耐久性評価のために，それぞれ，①玄武岩質ガラスの風化変質，②炭素鋼の土壌腐食，③熱（接触）変成作用によるスメクタイトのイライト化作用，④コンクリート構造材の化学的劣化，の研究を実施している。

なお，本論文はＣＥＣ主催第４回ナチュラルアナログ　ワーキンググループミーテング（1990年６月　Scotland Pitlochry）での発表をまとめたものであり，ＣＥＣ report n^0 ＥＵＲ 13014 ＥＮとして製本・公表される予定である。

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SOME ASPECTS OF NATURAL ANALOGUE STUDIES FOR ASSESSMENT OF LONG-TERM DURABILITY OF ENGINEERED BARRIER MATERIALS — RECENT ACTIVITIES AT PNC TOKAI, JAPAN —

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ABSTRACT

This paper contains an overview of analogue studies for the assessment of long-term durability of engineered barrier materials at PNC Tokai.

Materials of young age and with simple history are the most suitable for study as: 1) properties of the materials tend to deteriorate over longer historical time intervals; and 2) detailed quantitative data on time intervals and environmental conditions are more likely to be available. The following materials and their alteration phenomena were selected: 1) weathering alteration of basaltic glass (as vitrified waste form), 2) corrosion of iron in soil (as overpack), 3) illitization of smectite associated with contact metamorphism (as buffer material), 4) alteration of cement (as buffer or backfill material).

1. Weathering alteration of basaltic glass: Basaltic glasses, from the Fuji and the Izu-Ohshima pyroclastic fall deposits were studied. The observations were made: 1) Climatological conditions have not varied significantly during the last three thousand years. Therefore, values for temperature, amount, and chemistry of ground water are quantified. 2) The cases studied could be regarded as leaching experiments in groundwater, using mass balances in water-glass interaction. 3) Although the groundwater is of Ca(Mg)-HCO_3 type in the Fuji area and of Na-Cl type in the Izu-Ohshima, similar alteration ratios (2 ~ 3μm/1000yr) were obtained.

2. Corrosion of iron in soil: Industrial materials, such as gas/water service pipes of carbon steel or cast iron embedded in soil for 20 ~ 110 years, were selected for an analogue study of corrosion of iron in bentonite. The maximum corrosion rates obtained so far fall in the range of 0.04 ~ 0.09 mm/yr.

3. Illitization of smectite associated with contact metamorphism: In the Murakami bentonite deposit in central Japan, lateral variation of smectite to smectite/illite mixed-layer minerals are found in the aureole of the rhyolite intrusion body. Conversion of smectite to the mixed-layer mineral composed of 40% illite was found to have occurred in a period of 2.4 Ma over a temperature range of above 240 ($\pm$50) ℃ to 105 ℃.

4. Alteration of cement: Concrete components of fabrications, such as estuary walls, with a known age were studied. Chemical alteration of the cement were detected to a depth of few centimeters by EPMA, SEM, TEM and XRD.

5. Framework of our analogue studies: Our natural analogue programme has three

components: 1) investgation of alteration phenomena, 2) examination of environmental conditions, 3) support experiments. The support experiments are an essential part of our study in order to enhance the wider applicability of the natural analogue.

1. INTRODUCTION

1.1 COMPONENTS OF ENGINEERED BARRIERS

The Components, candidate materials, and functions of various types of engineered barriers are as follows:

Components	Candidate materials	Function expected
• Vitrified waste	• Borosilicate glass	• Restricts release*
• Overpack	• Carbon steel or Cast iron	• Retards water penetration * • Provides favourable chemistry *
• Buffer materials	• Bentonite	• Restricts water penetration * • Delays commencement of release* • Restricts radionuclides release *
• Backfill materials	• Concrete (Cement)	• Minimizes water access to package† • Alters groundwater chemistry † • Retards solute transport †

(* :NAGRA [1985], † :Chapman et al [1987])

As a part of the study on engineered barrier materials and systems for geological disposal of radioactive waste in Japan, analogue studies for the assessment of long-term durability of engineered barrier materials are conducted at PNC Tokai Works. This paper describes the state-of-the-art on the studies, specifying their main purposes and framework, and demonstrating our emphasis on natural materials. The results obtained to date will be summarized. Some parts of studies on natural glass and bentonite were already presented at the MRS Symposium (Arai et al., 1988; and Kamei et al., 1989), although revised and expanded data are shown here.

1.2 DEFINITION OF "NATURAL ANALOGUE"

One of the most critical aspects in the evaluation of the durability of candidate materials for engineered barriers is the extrapolation of the results of short-term experiments over a long time scale. Natural analogues currently provide the only means by which such extrapolated long-term behaviour can be confirmed.

The term "natural analogue" can be defined as "natural phenomena which resemble those assumed in geological disposal scenarios". The selection of an appropriate natural analogue is the key issue which will determine whether the natural analogue study will be successful.

1.3 PROPERTIES OF NATURAL ANALOGUE

First, consideration is given to the properties of the natural analogues. In order to extrapolate the results of short-term experiments to the long-term, it is desirable that the natural phenomena can be individually and quantitatively described in terms of three constituents: 1) starting materials, 2) environmental conditions (including time scale), and 3) results. These are the three normal constituents of all "experiments".

However, there are some intrinsic difficulties in regarding such phenomena as experiments. Most naturally occurring materials, from which an relevant analogue must be selected, have complicated histories resulting the overprint of different processes, as shown in Table 1.

Table 1 Comparison between laboratory experiments and natural phenomena

	Laboratory Experiments	Natural Phenomena
(1) Materials	Candidates	Analogue
① Number	Many	Solitary, few
(2) Environmental (Experimental) Condition	Simple, Uniform Constant, Controlled Common Small Scale	Complicated Variable Individual Large Scale
(3) Period	Short-term	Long-term
(4) Results	Independent variables Discrimination among conditions is possible	Overprinting of factors Restoration is difficult

Secondly, geological and historical records are often incomplete, and errors in the determination of time scale and environmental conditions are not small. Although such disadvantages differ case to case and sample to sample, as materials age, their histories generally become more complicated; the factors with which alteration phenomena were related become overlapped, and quality and quantity of available data decreases. Thus, estimation from present observations becomes virtually impossible with very old samples (Figure 1).

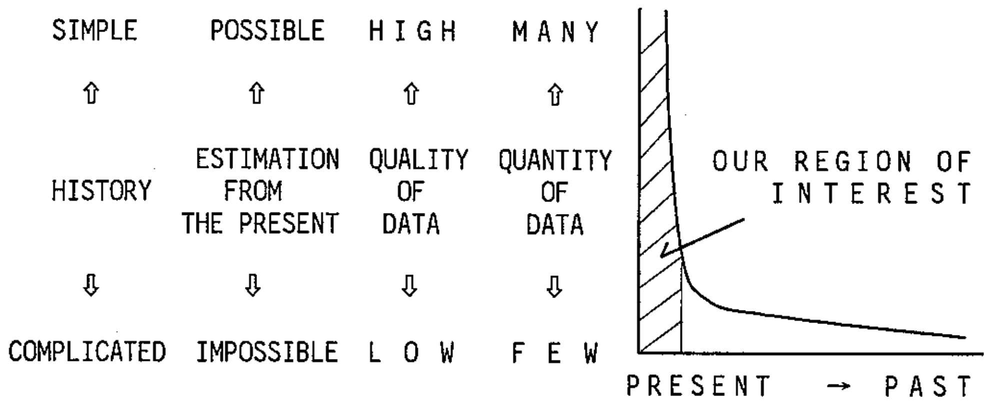

Fig. 1 Properties of historical materials

1.4 SELECTION OF SUBJECTS FOR THE STUDIES

Cases of younger age and simple process, therefore, are regarded as more suitable subjects for the studies, as quantitative data on time and environmental conditions are probably available. Many previous analogue studies consisted of descriptions of the results of natural experiments without incorporating data on well-defined environmental conditions.

We selected subjects for the analogue studies according to the following criteria: 1) analogy of materials with candidates, 2) analogy of environmental conditions with simulated repository conditions, 3) simplicity and availability on environmental conditions, and 4) availability of chronological data. Table 2 shows the subjects of our analogue studies on engineered barriered materials.

Table 2 The subjects of our analogue studies on engineered barrier materials

Engineered Barriers	Candidate Material	Assummed phenomena in Repository Conditions	Analogue Phenomena in Analogous Conditions
1.Waste Form	Boro-silicate Glass	Leaching of Waste Borosilicate Glass with Groundwater	Weathering Alteration of Basaltic Glass with Goundwater
2.Overpack	Carbon Steel	Corrosion of carbon steel in Bentonite	Corrosion of Iron in Soil
3.Buffer Materials	Compacted Bentonite	Illitization of Smectite in Bentonite	Illitization with Contact Metamorphism
4.Backfill Materials	Concrete (Cement)	Alteration of cement with Groundwater	Alteration of Cement with Groundwater

2. Weathering alteration of basaltic glass

2.1 SCOPE OF STUDIES

Many analogue studies of the alteration of natural glasses indicate that the alteration rates at low temperatures of natural glasses vary from 0.001 μm/1000 yr to 30 μm/1000 yr (Hekinian et al. 1975; Bryan et al. 1977; Allen 1982; Lutze et al. 1985 & 1987; Grambow et al. 1986; Ewing et al. 1987; Jercinovic et al. 1988). This variation is interpreted as the result of variations in environmental conditions. However, few detailed studies on environmental conditions have been reported.

Described below are the effects of alteration by weathering of basaltic glasses with well established environmental conditions and ages. The alteration is a long-term leach test carried out by nature with rainwater as the leachant and groundwater as the leachate. The young-aged (280 ~ 2800 years) samples were selected to investigate environmental conditions during alteration based on present meteorological data.

Samples

Volcanic glasses constituting scoria of pyroclastic fall deposits were studied. Scoria samples were collected at the foot of the Fuji and Izu-Ohshima volcanoes, on both of which the stratigraphy and chronology of pyroclastic fall deposits have been studied in detail.

The samples collected were Houei Scoria (HS, 280 years ago) and Zunazawa Scoria (ZS, 2800 years) from the Fuji, and N1 (880 years) and N4 Scoria (1240 years) from the Izu-Ohshima volcano.

All of the scoria samples contained pore water, and spring water was found about 2.5 m below the Zunazawa Scoria bed.

Methods

Glass compositions were determined by Electron Probe Microanalyser (EPMA). Alteration layers were studied by optical microscope, EPMA and Scanning Electron Microprobe (SEM). The thickness of alteration layers was measured from SEM photos of the sections oriented nearly perpendicular to the layers.

In the field, the pH and Eh of the spring water were measured by portable meters. The spring water was filtrated through a 0.45 μm filter and the filtrate was analyzed by absorption spectrophotometry, flame spectrometry and atomic absorption spectrometry.

2.2 RESULTS

The chemical compositions of the glasses are shown in Table 3. These are within the range of basalts.

Table 3 Chemical compositions of glasses.

Sample	Oxide (wt%)								
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3*	MgO	CaO	Na_2O	K_2O	Total
Fuji									
HS	52.9	2.3	12.1	16.5	3.9	8.5	1.8	1.2	99.2
ZS	50.7	1.6	15.0	13.8	4.9	8.8	2.9	0.9	98.6
Izu-Ohshima									
N1	53.7	1.4	13.0	15.6	3.4	8.8	2.3	0.5	96.9
N4	53.0	1.4	13.1	15.3	4.4	8.4	3.9	0.5	98.6

*: Total Fe as Fe_2O_3

Alteration layer

The alteration layer is optically isotropic and X-ray amorphous. The surface form of the alteration layer of the HS is grainy and that of ZS, N1, and N4 is flaky.
Despite the difference in morphology, the chemical composition of the alteration layer of the Houei Scoria is similar to that of the Zunazawa Scoria. The morphology of the alteration layers of both scoria is strikingly similar to that observed on the surface of experimentally altered borosilicate glasses (Hirose, unpublished data). Alteration layer thicknesses are summarized in Table 5. The elemental concentrations in the alteration layer are characterized by greater depletion of Mg, Ca, Na, and K, as compared to Si, Al, Fe, and Ti.

Table 4. Chemistry of pore water, spring water and rainwater.

Sample	Chemical composition (mg/l)									pH	Eh (mV)
	Na	K	Ca	Mg	Fe	HCO_3	SO_4	Cl	SiO_2		
Fuji											
HS P.W.	4.4	1.7	5.3	1.3	—	24	6.5	4.1	34	—	—
ZS P.W.	8.4	3.3	4.6	1.3	5.0	35	6.4	4.3	218	—	—
S.W.	5.0	1.4	8.9	6.9	2.9	67	4.4	2.6	41	7.0	178
Izu-Ohshima											
N1 P.W.	78	2.9	27	12	3.2	7.6	27	176	52	(6.0)	—
N4 P.W.	86	3.7	40	15	4.0	6.1	26	222	48	(6.0)	—
Rain water*	1.1	0.3	0.4	1.0	0.2	—	1.5	1.1	0.8	—	—

P.W. = Pore Water; S.W. = Spring water, * after Sugawara (1968)

Water chemistry

The chemistry of the pore and spring water is listed in Table 4, together with the average of rainwater in Japan (Sugawara, 1968). The elemental concentrations in ZS pore water are higher than those in HS pore water. This implies that elemental concentration in groundwater increases with depth.

2.3 DISCUSSION

Environmental Conditions

Analyses of paleo-sea level variations (Sugimura, 1977) and paleo-climatological data (Yamamoto, 1980; and Maejima, 1984), indicate that the climatic conditions in Japan have not varied significantly for the last 2800 years. Therefore, the temperature and the water supply rate are estimated from meteorological data such as mean annual temperature, annual rainfall, and evapotranspiration. The samples were situated in the unsaturated zone; accordingly, percolating meteoric water is the only source of pore water. The pore water flows downward in the deposits and dissolves the components of scoria. This natural phenomenon can be regarded as a leach test being constantly renewed fresh rainwater.

Alteration Rate

In natural alteration systems, it is generally difficult to know the exposure age of a sample, that is, the time that the glass has actually been in contact with water (Jercinovic et al., 1988). The exposure ages of the samples in this study are equivalent to the samples ages as their surfaces were always in wet conditions and were always in contact with renewed pore water.

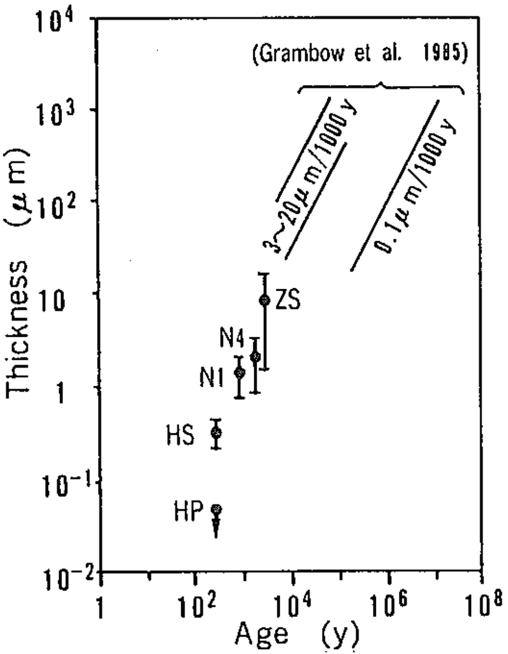

Fig. 2 The relation between age of samples and thickness of alteration layer

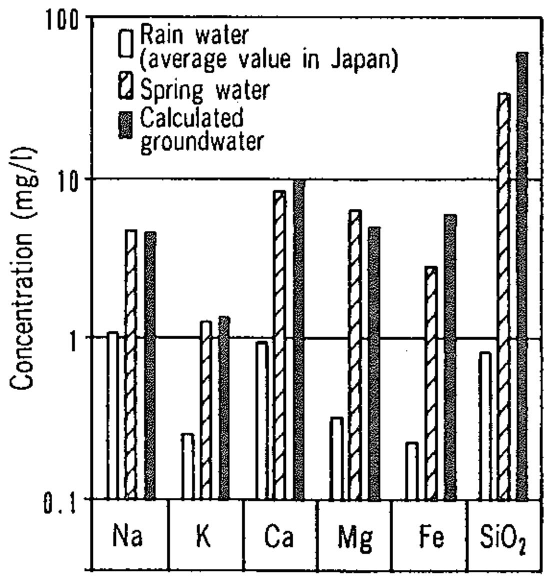

Fig. 3 The comparison between elemental concentrations of spring water and calculated groundwater

The relation between alteration layer thickness and age is shown in Figure 2. The two kinds of alteration rates, the forward rate of alteration (3 ~ 20 μm/1000 yr, under silica-unsaturated conditions) and the final rate of alteration (0.1 μm/1000yr, under silica-saturated conditions) by Grambow et al.(1985), are also shown in Figure 2. The alteration rates estimated in this study are near or below the forward rate of alteration.

Mass Balance Between Alteration Layer and Spring Water

Spring water can be regarded as the leachate. In order to discuss the leaching behaviour of glass, it is necessary to clarify the relation between the elemental concentration in the leachate and the elemental loss from the alteration layer. Elemental concentrations in groundwater have previously examined (Arai et al., 1989) and the results indicate that the calculated composition of groundwater is in fair agreement with the composition of spring water (Figure 3). The discrepancies in the concentrations of Fe and SiO_2 can be explained by the precipitation of iron hydroxides and silica gel respectively among scoria grains.

Table 5 Summary on alteration behaviour of volcanic glasses and their environmental conditions

(1) MATERIALS STUDIED	FUJI			IZU-OHSHIMA	
	HP	HS	ZS	N1	N4
(2) GLASS COMPOSITION[SiO_2wt%]	64	53	51	54	53
(3) ENVIRONMENTAL CONDITIONS					
①TEMPERATURE(℃)	14			15	
②WATER CHEMISTRY	Ca(Mg) - HCO_3 type			Na - Cl type	
③WATER SUPPLY RATE(ℓ /cm² /yr)	0.20			0.21	
(4) PERIOD (yr)	280	280	2800	880	1240
(5) RESULTS					
①ALTERATION RATE(μm/1000yr)	<0.2	1.6	3.1	1.7	1.8
[Alteration Layer Thickness:μm]	<0.05	0.44	8.8	1.5	2.2
②ALTERATION PRODUCTS					
· Amorphous Materials	N.D.	○	○	○	○
· Goethite	N.D.	○	○	○	○
· Smectite	N.D.	×	○	○	○

N.D. : Not Determined, ○ : Present, × : Absent

2.4 CONCLUSION

1) It was possible to determine the alteration behaviour of volcanic glasses from three experimental constituents: 1) starting materials, 2) environmental conditions and time scale, and 3) results (Table 5).

2) Calculation of the mass balance between the elements depleted from the glasses and the chemical composition of groundwater permitted us to regard the cases studied as experiments in the leaching of glasses by groundwater.

3) The natural alteration products of the volcanic glasses were very similar to those of laboratory experiments with simulated waste glasses.

4) Although the groundwater is Ca(Mg)-HCO_3 type in the Fuji area, and of Na-Cl type in the Izu-Ohshima area, similar alteration rates (2~ 3 μm/1000 yr) were obtained.

3. CORROSION OF IRON IN SOIL

Industrial materials such as water service pipes, were studied for the following reasons: 1) iron or steel is one of the candidate materials for waste package, 2) soil environment is probably similar to the bentonite fill environment, 3) samplavailability, and 4) chronology and environmental data are fairly assessable in ccomparison to those of archeological artifacts. One of the purposes of this analogue study is to validate whether the results of corrosion rates and models derived from the results of laboratory experiments can be extrapolated to a few tens of years (Figure 4).

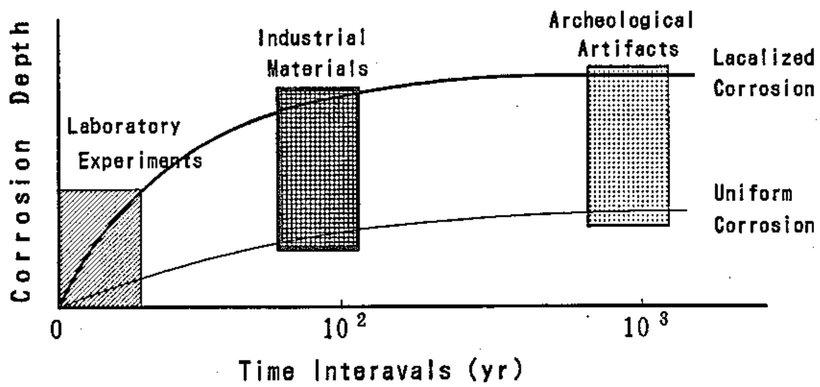

Fig. 4 The relation between the subjects for studies on corrosion of iron and their time interval

The samples studied were gas or water service pipes, composed of cast iron or carbon steel. The soil or clay adjacent to the pipe was examined in order to avoid the influence of the macro-cell effect. The corrosivities of the soil environment at each site were estimated as not being very severe from the viewpoint of both electrochemical and chemical characteristics of the soil. Corrosion rates were derived from the measurements of the thickness of the pipe, and chemical composition of the material were determined. The corrosion products were identified with X-ray diffraction (XRD). The results obtained to date are shown in Figure 5 and Table 6.

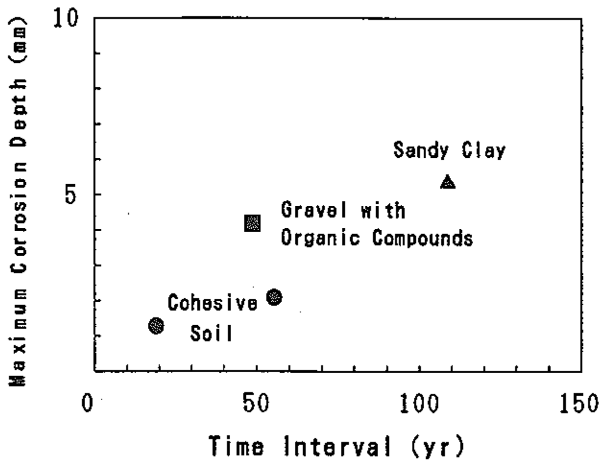

Fig. 5 Maximum corrosion depth as a function of time intervals

In conclusion, the maximum corrosion rates of cast iron and carbon steel embedded in soils were estimated in the range of 0.04～0.09 mm/yr. Corrosion of industrials materials in soil is a useful analogue and further studies are planned.

Table 6 Corrosion behaviour of iron in soil

(1)MATERIALS STUDIED				
① Site	Yokohama	Nagasaki	Tokyo	Tokyo
② Sample	Gas S.P.	Water S.P.	Water S.P.	Water S.P.
③ Material	Cast Iron	Carbon Steel	Cast Iron	Cast Iron
(2)ENVIRONMENTAL CONDITIONS	Sandy Clay	Gravel with Org. Comp.	Cohesive Soil	Cohesive Soil
(3)PERIOD (yr)	110	50	56	20
(4)RESULTS				
① CORROSION RATE(mm/yr)				
Uniform Corrosion	0.03	0.01	N.D.	N.D.
Pitting Corrosion	0.05	0.08	0.04	0.06
② CORROSION PRODUCTS	$FeCO_3$	Not identified	$FeCO_3$, α-FeO(OH)	$FeCO_3$, α-FeO(OH)

S.P. = Service Pipe; Org. Comp. = Organic Compounds

4 . ILLITIZATION WITH CONTACT METAMORPHISM

4.1 SCOPE OF STUDIES

The research on illitization of smectite in the natural environment affords indispensable information on the long-term durability of bentonite.

Geological processes associated with smectite-illite conversion can be classified as follows:
1) Diagenesis, 2) Regional metamorphism, 3) Contact(or thermal) metamorphism,

4) Hydrothermal alteration

Among theses, contact metamorphism has been selected as being a suitable analogue because of the prevailing temperature and the water/rock ratio. Furthermore, a study of contact metamorphism has potentiality to give clear-cut data on the reaction term and the thermal conditions of illitization of smectite, provided that: 1) the bentonite bed is distributed, and 2) simple history and simple geology can be recognized.

One such case of contact metamorphism is the Murakami bentonite deposit in central Japan, where a homogeneous bentonite bed and rhyolitic intrusive rock are present. Geological, petrological and geochronological studies have already been presented at the MRS symposium in Boston, 1989 (Kamei et al. 1990), so only a brief description of this deposit is given below:

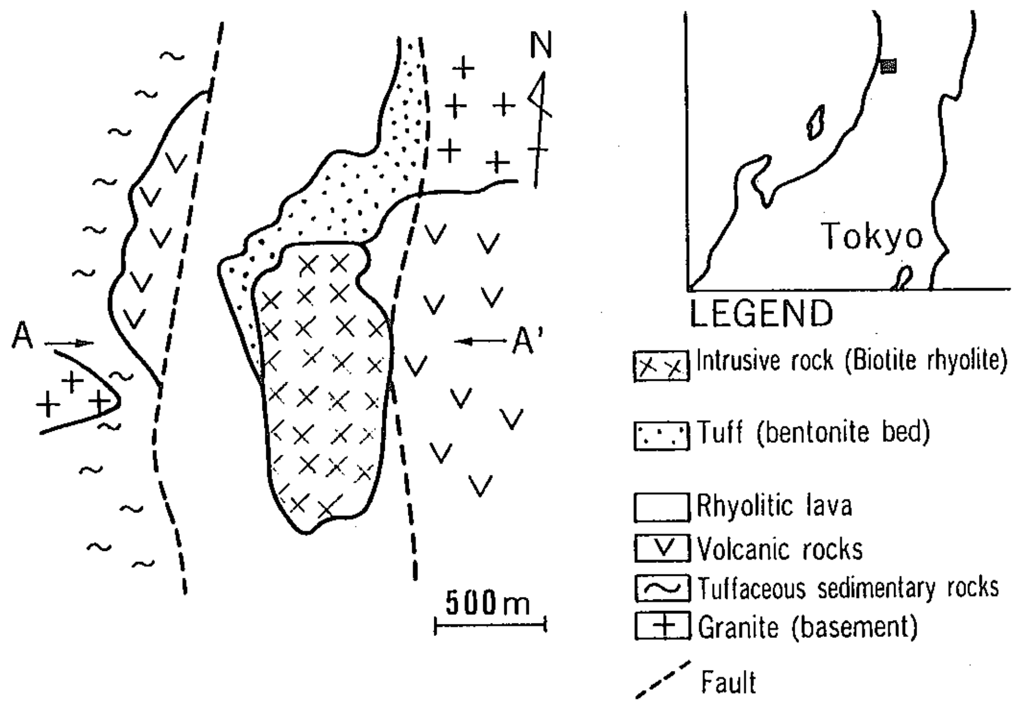

Fig. 6 Geological map of the Murakami deposit

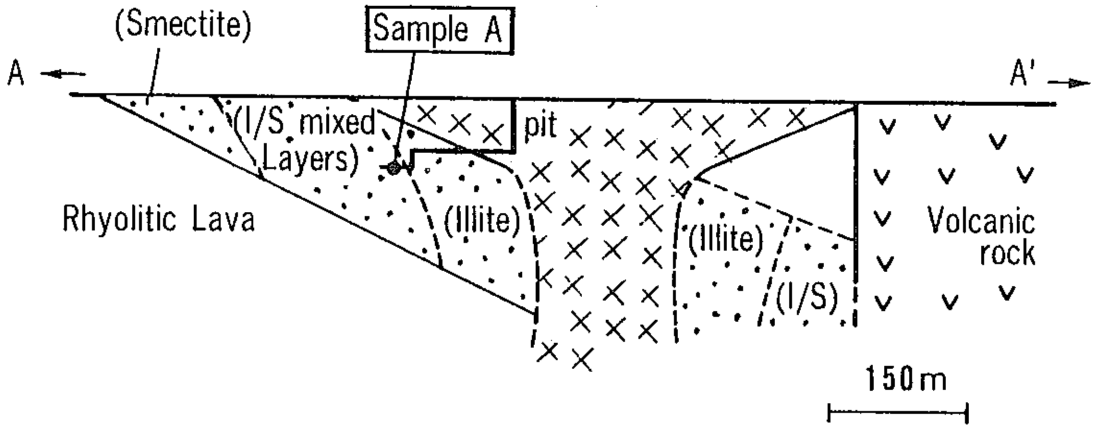

Fig. 7 An idealized geological section of the Murakami deposit

Geology

A geological map and an idealized section of the Murakami deposit area are shown in Figure 6 and 7, respectively. Rhyolitic lava and tuff are distributed in a graven with a width of approximately one kilometer. The reported age of deposition of this unit ranges from 18 to 14 Ma (Muramatsu, 1988). The tuff is regarded as being deposited in a marine environment, and was converted into bentonite possibly due to diagenetic reaction. Subsequent intrusions of biotite rhyolite are found in the bentonite bed. The contact between the intrusive rock and the tuff dips about 30° near the surface of the ground, and the intrusive rock body is assumed to form a funnel with a diameter of less than 200 meters (Figure 7).

Samples

Sample A was collected from a point 30 meters distant from the contact between the intrusive body and the bentonite bed. X-ray diffraction showed that sample A contained illite-smectite mixed layers with an illite ratio of about 40 %.

4.2 RESULTS

Thermal History

The cooling rate of the intrusive rock was determined from combining radiometric mineral ages and each closure temperature. The cooling rate of sample A was estimated by the "TRUMP" thermal analysis code. The results are shown in Figure 8. The cooling rates of the intrusive rock and of sample A were 70 ℃/Ma, and 60 ℃/Ma, respectively. (Figure 8 and the values for cooling rates are newly revised, therefore those reported in the MRS Proceedings (Kamei et al. 1990), should be ignored.)

The Illitization Period

In the Murakami deposit area, a minimum temperature of illitization is regarded as 105℃, because this was the temperature estimate made by Oda et al. (1985) for the appearance of illite-smectite mixed layers in Japanese oil fields, of which the Murakami deposit form a part. In the vicinity where sample A was collected, the temperature at 6.4 Ma was presumed to be 240 ±50℃. Therefore, a period of about 2.4 Ma was required to cool these rocks from 240 to 105℃.

In short, smectite was converted into illite-smectite mixed layers, in which the illite ratio is approximately 40 %, in the period of more than 2.4 Ma.

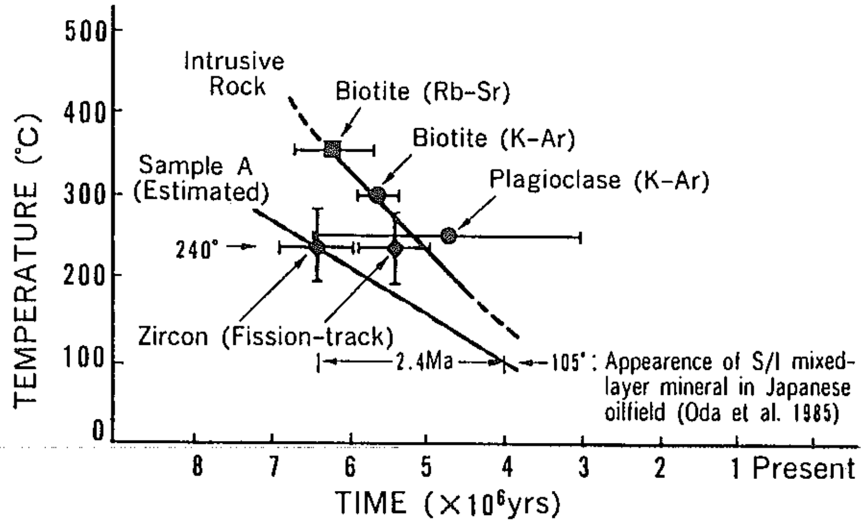

Fig. 8 Thermal history of intrusive body and sample A

Water Chemistry

The chemical composition of the rocks distributed in the Murakami area is mostly rhyolitic, and the tuff, now converted into bentonite bed, is of marine origin. The geological evidence leads to the idea that the chemistry of the water related to illitization was very similar to that of seawater after it was modified by interaction with rocks of rhyolitic composition.

The hydrogen isotopic composition (D/H) of water, in the form of hydroxyl groups, in the illite and the smectite-illite mixed layers, were measured, and from this an assessment of the water involved in illitization was made. The results supported the idea noted above.

Provisional Calculation of Activation Energy

The activation energy for illitization at the Murakami deposit was provisionally calculated on the basis of the estimated thermal history. The calculation procedure was already described in Kamei et al. (1990). Using the revised cooling rate of 60 ℃/Ma and a period of 2.4 Ma. the activation energy is approximately 27 kcal/mol. This value is close to that obtained by Roberson & Lahann(1981) of approximately 30 kcal/mol. The water used for their experiments contained 400 ppm K^+ and 9400 ppm Na^+, the chemistry of seawater. A similar water chemistry can be inferred at Murakami.

Table 7 Summary of a study on illitization of smectite associated contact metamorphism— A case study at the Murakami deposit

(1) Material	Smectite in marine sediment
(2) Environment ① Water chemistry ② Temperature	 Modified seawater > 240 ℃ ~ 105 ℃
(3) Period	2.4 Ma
(4) Result	I/S mixed layers mineral (Illite;approximate 40%)
(5) Activation energy	Approximate 27 kcal/mol

4.3 CONCLUSION

Once again returning to the three-part concept of starting materials, environmental and chronological conditions, and results, it was possible to describe the illitization of smectite associated with contact metamorphism in terms of 1) material studied, 2) environment, 3) period, and 4) results (Table 7). A more precise estimation of activation energy is possible through an estimation of the overall thermal history during contact metamorphism, using a thermal analysis code. This work is in progress.

5. ALTERATION OF CEMENT

Concrete components such as tunnels or estuary walls with known ages were studied. Environmental conditions such as temperature, surrounding materials, water content, and water chemistry ware either measured or estimated. The alteration of cement materials has been analyzed by EPMA, SEM, TEM(Transmission Electron Microscopy), and XRD. Results obtained to date are shown in Table 8.

The following alteration features of cement materials was able to be traced:

(1) Decrease in pH of pore water,
(2) Decrease of CaO/SiO_2 ratio of C-S-H gel,
(3) Partial dissolution of C-S-H gel,
(4) Formation of $CaCO_3$,
(5) Permeation of Cl, resulting in formation of Friedel'Salt.
(6) Dissolution of Calcium hydroxide,
(7) Dissolution of Calcium which cause dissolution of $CaCO_3$,

Such alteration phenomena were detected within a range of a few centimeters. Further studies are necessary to permit any definite conclusions.

Table 8. Alteration behaviour of cement fabrics

(1) MATERIALS STUDIED ① SITE ② SAMPLE MATERIALS	Kanagawa Concrete of Tunnel Wall	Yokohama Concrete of Estuary Wall
(2) ENVIRONMENT ① Temperature ② Surrounding Materials ③ Water Content ④ Water Chemistry	13 ℃ Lapilli tuff 40 % Ca - $NO_3(HCO_3)$	15 ℃ Soil 33 % Na - Cl
(3) PERIOD (yr)	67	61
(4) RESULTS OF ALTERATION	Ca depletion <few mm	Cl permeation >10 cm $CaCO_3$ formation >8 cm $CaCO_3$ dissolution >5 cm

Table 9 The present state of PNC analogue studies on engineered barrier Materials

Barrier Components (Candidate Materials)	Materials and Mode of Occurrence	Period (yr)	Estimation of Period	Estimation of Environmental Conditions
Waste Form (Borosilicate glass)	Scoria (Pyroclastic Fall Deposit)	$10^2 \sim 10^4$	Tephro-chronology	From Recent Climatological Conditions
Buffer (Compacted Bentonite)	Contact Metamorphosed (Natural) Bentonite	$10^6 \sim 10^7$	Radiometric Age Determination	Closure Temperature of Radiometric Ages Geological and Geochemical Data
Overpack (Carbon Steel)	Industrial Materials (Pipe)	$10^1 \sim 10^2$	Documents	From Present Embedded Conditions
Backfill (Concrete)	Industrial Materials (Components of Fabrics)	$10^1 \sim 10^2$	Documents	From Present Embedded Conditions

6. SUMMARY AND FUTURE PROSPECTS

Table 9 summarizes the present state of PNC analogue studies on engineered barrier materials, and Figure 9 shows the framework of our analogue studies.

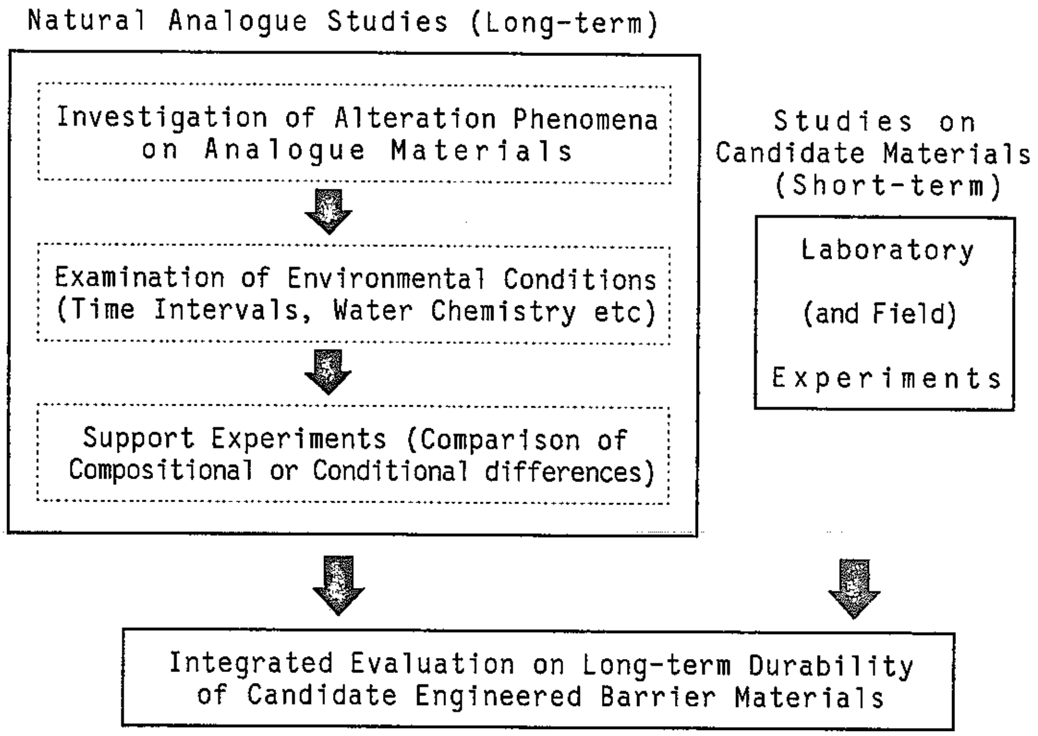

Fig. 9 Framework of analogue studies on engineered barrier materials

Our natural analogue studies have three components:

1) investigation of alteration phenomena of analogue materials,
2) examination of environmental conditions (time intervals, water chemistry etc) ,
3) support experiments

The validity of the analogue study is determined by the selection of alteration phenomena of analogue materials out of various natural phenomena acting on historical materials from the point of view of best analogical fit.

An examination of environmental conditions occupies an inevitable part of the study. Time intervals, prevailing temperature, and water chemistry related to the alteration are key items.

Support experiments are indispensable to the study in order to enhance the wider applicability of the natural analogue. Comparison of differences in composition or condition is the key issue for laboratory support experiments. Such experiments for the comparison of compositional differences between basaltic glasses and candidate waste glass have already started, and the results to date indicate that there is no significant recognizable difference in the leaching rates.

From a combination of the natural analogue studies outlined above and laboratory experiments on the candidate materials, an integrated evaluation of the long-tem durability of candidate engineered barrier materials can be conducted.

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REFERENCES

1. Allen, C.C. (1982) Mat. Res. Soc. Proc., 5, 37-44.
2. Arai, T., Yusa, Y., Sasaki, N., Tsunoda, N., and Takano, H., (1989) Mat. Res. Soc. Symp. Proc., 127, 73-80.

3. Chapman,N.A., and McKinley, I.G. (1987) The Geological Disposal of Nuclear Waste, John Wiley & Sons,
4. Ewing, R.C., and Jercinovic, M.J., (1987) Mat. Res. Soc. Proc., 84, 67-83.
5. Bryan, W., and Moore, J.G. (1977) Geol. Soc. Amer. Bull., 88, 556-570.
6. Grambow, B., Jercinovic, M.J., Ewing, R.C. and Byers, C.D. (1986) Mat. Res. Soc. Proc., 9, 263-272.
7. Hekinian,H., and Hoffert, M., (1975) Marine Geology, 19, 91-109.
8. Jercinovic M.J. and Ewing, R.C.(1988) JSS Project Technical Report, 88-01, 21.
9. Kamei, G., Arai, T., Yusa, Y., Sasaki, N., and Sakuramoto Y., (1990) Mat. Res. Soc. Symp. Proc., 176, 657-663.
10. Lutze, W. Malow, G., Ewing, R.C., Jercinovic, M.J. and Keil,K., (1985) Nature, 314, 252-255.
11. Lutze, W., Grambow, B., Ewing, R.C. and Jercinovic, M.J. (1987) Natural Analogues in Radioactive Waste Disposal, 142-152.
12. Maejima, I., (1984) Jour. of Geol., 93, 413-419 (in Japanene).
13. Muramatsu, T., (1988) Regional Geology of Japan Ⅳ. CHUBU-Ⅰ, p.62.
14. NAGRA (1985) Project Report NGB 85-09.
15. Oda, y., Suzuki, S., and Ohyama, Y., (1985) Jour. Petrol. Mineral. Econ. Geol. 80, 526-536 (in Japanene).
16. Roberson, H.E. and Lahann, R.W., (1981) Clays and Clay Minerals, 29, 1-29.
17. Sugawara, K., (1967) Tikyu Kagaku (Geochemistry) 2, 501 (in Japanene).
18. Sugimura, S., (1977) Kagaku (Science) 47, 749-755 (in Japanene).
19. Yamamoto, T., (1980) Tenki (Weather), 27, 76-855 (in Japanene).