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NATURAL ANALOGUE STUDIES OF ENGINEERED BARRIER MATERIALS AT PNC TOKAI, JAPAN －THEIR FRAMEWORK AND RECENT ACTIVITIES－

亀井　玄人*　湯佐　泰久*
山形　順二*　井上　邦博*

要　旨

本資料は，第3回原子力先端研究国際シンポジウム（平成3年3月，於水戸）の報文集に掲載されたものである。人工バリアの長期耐久性評価のために行ったナチュラルアナログ研究について、①ナチュラルアナログとは何か，②その必要性，③調査対象選定のための考え方，④研究の構成，について述べた。具体的成果として，①玄武岩質ガラスの風化変質（廃棄物ガラスの変質のアナログ），②土中埋設鋼管（緩衝材に包まれた鉄製オーバーパックのアナログ），②火成岩体の貫入によるベントナイトのイライト化（緩衝材の変質のアナログ），④コンクリート構造物の地下水又は海水による変質（バックフィル材等としてのセメントの化学的変質のアナログ）の4項目について記述した。

本資料は，共同発表者の湯佐による外部発表許可済資料（2ＫＡ 29,80-02-131)に，その後の知見を加えてまとめなおしたものである。

* 環境技術開発部　地層処分開発室

NATURAL ANALOGUE STUDIES OF ENGINEERED BARRIER MATERIALS AT PNC TOKAI, JAPAN
— THEIR FRAMEWORK AND RECENT ACTIVITIES —

Kamei G., Yusa Y., Yamagata J., Inoue K.

Geological Isolation Technology Section,
Tokai Works, Power Reactor and Nuclear Fuel
Development Corporation
Tokai Ibaraki,319-11 JAPAN

ABSTRACT

Long-term extrapolations concerning the safety of a nuclear waste repository cannot be satisfactorily made on the sole basis of short-term laboratory tests. Natural analogues, which are the only means by which very slow mechanisms can be identified and by which long-term predictions of models can be tested for pertinence. Our studies for the assessment of long-term durability of engineered barrier materials are outlined.

Materials of young age and with simple history are the most suitable for these studies as: 1) properties of the materials tend to deteriorate over the longer term; and 2) detailed quantitative data on the term and on the environmental conditions can be obtained. The framework of our studies includes: 1) clarification of alteration phenomena, 2) examination of the environmental conditions, and 3) support experiments.

The following four materials and their alteration phenomena were selected:

1. Weathering alteration of basaltic glass (as vitrified waste form) : Basaltic glasses within 2800 years, from the Fuji and the Izu-Ohshima , were studied.
2. Corrosion of iron in soil (as overpack): Corrosion of Industrial materials, gas/water service pipes of carbon steel or cast iron embedded in soil for the range from 20 to 110 years, were studied as analogy of alteration of iron in bentonite.
3. Illitization of smectite associated with contact metamorphism (as buffer material): A lateral variation of smectite to smectite/illite mixed-layer minerals, found in the aureole of the rhyolite intrusion, were studied.
4. Alteration of cement (as buffer or backfill material): Concrete components of fabrications with a known age were studied.

1. INTRODUCTION

1.1 Components of Engineered Barriers

The Components, candidate materials, and functions of various types of engineered barriers are shown in Table 1.

As a part of the study on engineered barrier materials and systems for geological disposal of radioactive waste in Japan, natural analogue studies are conducted for the assessment of long-term durability of engineered barrier materials at PNC Tokai Works. Yusa et al.(1990) revealed the state-of-the-art on the studies, the purposes and framework, and the demonstrating emphasis on natural materials. This paper summarises the details.

1.2 Reasoning by Natural Analogue

One of the most critical aspects in the estimation of the materials durabilities is the extrapolation of the results from short term experiments over a very long term. The term "natural analogue" can be defined as natural process which resemble that assumed in a nuclear waste repository condition. Natural analogue provides the only means by which such extrapolated long-term behaviour can be confirmed.

1.3 Properties of Natural Analogue

The natural process must be described in terms of three constituents: (1) Starting materials and their alteration, (2) The time scale, and (3) The environmental conditions(i.e. temperature, water/material ratio, water chemistry). These constituents are regarded as the results and valuables of the " natural experiment".

However, most naturally occurring materials have complicated histories resulting the overprint of different process. Errors with the determination of environmental conditions (including time scale) may increase with the lapse of materials age. Thus, estimation from present observations is difficult to very old sample (Figure 1).

Table 1. Components of engineered barriers and their functuons

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])

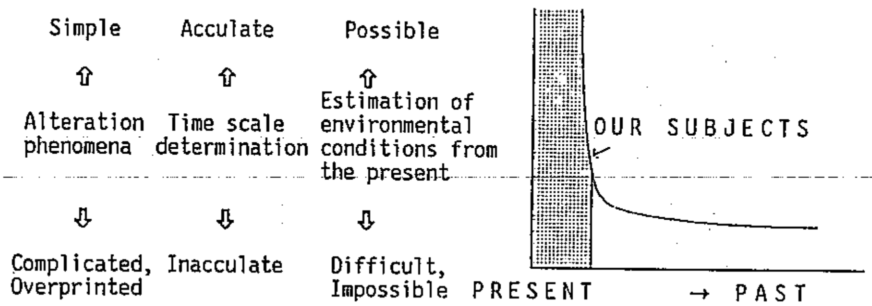

Fig. 1 Properties of historical materials

1.4 Selection of Subjects for The Studies

We selected cases of younger age and of simple process. Because data on term and environment can be inferred exactly as shown figure 1. Subjects for our studies have the following criteria: 1) analogy of subjects with the barrier materials, 2) analogy of the environmental conditions with simulated repository conditions, 3) simplicity on the environmental conditions, and 4) Reliability of the chronological data. Table 2 shows the subjects of our studies.

2. WEATHERING ALTERATION OF BASALTIC GLASS

2.1 Scope

We investigated alteration by weathering of basaltic glasses well established environmental conditions and ages. The alteration is a long-term leach test carried out with rainwater as the leachant and groundwater as the leachate. Many analogue studies on the alteration of natural glasses indicate that the alteration rates at low temperatures vary from 0.001 to 30 μm/1000 y (Hekinian et al. 1975; Bryan et al.

Table 2 The subjects for our studies on engineered barrier materials

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

1977; Allen 1982; Lutze et al. 1985 & 1987; Grambow et al. 1986; Ewing et al. 1987; Jercinovic et al. 1988). However, few detailed studies on environmental conditions have been reported.

2.2 Starting Materials

Volcanic glasses, constituting scoria on the foot of Fuji and Izu-Ohsima volcanoes, were studied. Their ages range from 280 to 2800 years according to the reported stratigraphical and chronological data (see Table 3). These scoria are porous, and porewater present invariably in all samples.

2.3 Environmental Conditions

All of the scoria were situated in the unsaturated zone, accordingly, percolating meteoric water was the only source of the porewater.

Analyses of paleo-sea level variating (Sugimura,1977) and paleo-climatological data (Yamamoto,1980, Maejima,1984) indicata that the climatological condition have not varied significantly for the last 2800 years. Hence, the environmental conditions(i.e. temperature, water supply rate) during the alteration can be estimated based on present meteorological data, such as mean annual temperature, annual rainfall, and evapotranspiration.

Calculation on the mass balance between the elements depleted from the glass (Fuji scoria, 2800y) and the chemical composition of the groundwater allowed us to regard as an experiment of glass leaching by groundwater(Arai et al.,1989). The water with the glass alteration was Ca(Mg)-HCO_3 type in the Fuji area and of Na-Cl type in the Izu-Ohshima.

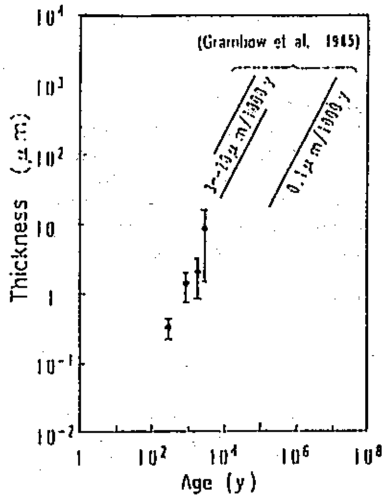

Fig. 2 The relation between age of samples and thickness of alteration layer

2.4 Results

(1) Alteration rate

The thickness of alteration layers was measured on SEM photographs. Figure 2 shows the relation between the thickness and the age. The forward rates of alteration (3-20 μm/1000 y, under silica unsaturated condition) and final rate (0.1 μm/1000 y, silica saturated) by Grambow et al.(1985) were also shown in the figure. The rates in this study were near or below the forward rate. Although the groundwater is Ca(Mg)-HCO_3 type in Fuji area and of Na-Cl in the Izu-Ohshima, the similar

Table 3 Summary on alteration processes of volcanic glasses and their environmental conditions

MATERIALS	FUJI			IZU-OHSHIMA	
	pumice	scoria	scoria	scoria	scoria
GLASS SiO_2 wt %	64	53	51	54	53
TERM (y)	280	280	2800	880	1240
ENVIRONMENTAL CONDITIONS TEMPERATURE(℃) WATER CHEMISTRY WATER SUPPLY (l/cm²/y)	 14 Ca(Mg) - HCO_3 type 0.20			 15 Na - Cl type 0.21	
ALTERATION RATE(μm/1000y) [Alteration Layer Thickness: μm]	<0.2 <0.05	1.6 0.44	3.1 8.8	1.7 1.5	1.8 2.2
ALTERATION PRODUCTS · Amorphous Materials · Goethite · Smectite	 N.D. N.D. N.D.	 ○ ○ ×	 ○ ○ ○	 ○ ○ ○	 ○ ○ ○

N.D. : Not Determined, ○ : Present , × : Absent alteration rates (2-3 μm/1000 y) were measured for all basaltic glasses.

(2) Alteration products

Alteration proucts observed in the scoria consist of amorphous phase and goethite for the youngest sample (280y), amprphous phase, goethite, and smectite for others (Table 3). These morphorogy and minerals of alteration layers were quite similar to those of experimentaly altered bolosillicate glass (unpublished data).

3. CORROSION OF IRON IN SOIL

Industrial materials embedded in soil, water and gas 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 environment filled with bentonite, 3) sample availability, and 4) chronological and environmental data are fairly assessable in ccomparison to those of archeological artifacts. One of the objects of this study is to verify whether the corrosion rates values and models derived from the results of laboratory experiments can be extrapolated to a few decades(Figure 3).

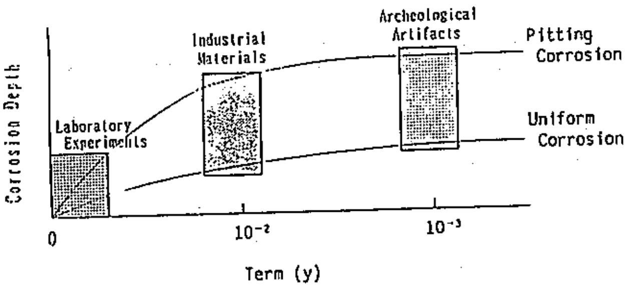

Fig. 3 The relation between the subjects for studies on corrosion of iron and their time interval.

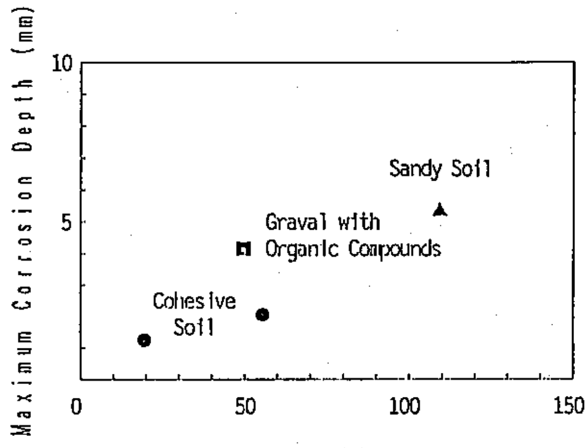

Fig. 4 Maximum corrosion depth as a function of time intervals

The soil adjacent to the pipe was examined. The maximum corrosion rates of cast iron and carbon steel embedded in soil range between 0.04 and 0.08 mm/y. The results obtained to date are shown in Figure 4 and Table 4.

4. ILLITIZATION WITH CONTACT METAMORPHISM

4.1 Scope

Research on illitization of smectite in the natural environment affords indispensable information on the long-term durability of bentonite. Geological process associated with smectite-illite conversion can be classified as follows: 1) Diagenesis, 2) Regional metamorphism, 3) Contact(or thermal) metamorphism, and 4) Hydrothermal alteration. We selected contact metamorphism as a suitable analogue because of the prevailing temperature and the water/rock ratio. A study of contact metamorphism has potentiality to give clear-cut

Table 4 Corrosion process of iron in soil

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

S.P. = Service Pipe, Org. Comp. = Organic Compounds,
N.D. = Not Determined

data on the reaction term and the thermal conditions of illitization of smectite.

4.2 Subject

A contact metamorphism is observed at the Murakami bentonite deposit in central Japan. A homogeneous tuff (bentonite bed) and a rhyolitic intrusive rock are distributed at the deposit. An idealized section of the Murakami deposit area are shown in Figure 5.

"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 the sample A contained illite-smectite mixed layers with an illite ratio of approxemate 40 %.

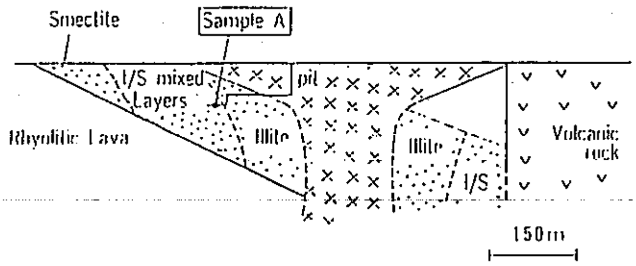

Fig.5 An idealized geological section of Murakami deposit.

4.3 Results

(1) Thermal history

By plotting on a graph the mineral age compared with the assumed closure temperature, the cooling rate of the intrusive body was established to be -70 ℃/10^6y .

Cooling rate at the sample A locality was calculated by the "TRUMP" thermal analysis code by use of the cooling rate of intrusive body. The results are shown in Figure 6. The cooling rates at the sample A locality was obtained to be -60 ℃/10^6y. Oda et al.(1985) proposed that the temperature for apperance of illite/smectite mixed layer minerals was 105℃ at the Japanese oil fields; the Murakami deposit belonged to the area, hence, a minimum temperature of illitization was regarded as 105 ℃ at the deposit.

In the sample A locality, the temperature was assumed to be 240 ±50℃ at the age before 6.4×10^6years (see figure 6). A term of approximate 2.4 ×10^6years was accordingly required for the cooling from 240 to 105 ℃.

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

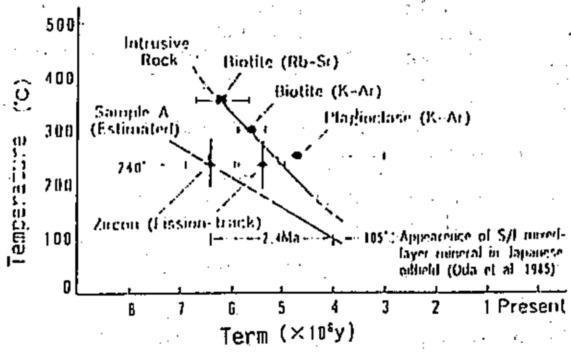

Fig.6 Thermal history of intrusive body and sample A.

(2) Water chemistry

The tuff in the Murakami area, now converted into bentonite bed, is rhyolitic and of marine origin. The geological evidence and a comparison between bulk compositions of illitized rock and of non-illitized rock lead to an idea ; The water related to the illitization might be water modified by a seawater/rhyolitic rock interaction. Hydrogen isotopic composition (D/H) in the form of hydroxyl groups of the illite (Kamei et al. 1990) and oxygen isotopic ratio ($^{18}O/^{16}O$) of the illite (unpublished) were measured. The results supported the idea noted above.

4.4 Conclusion

Table 5 showed a conclusion of the case study. A precise value of activation energy can be obtained through an estimation of the overall thermal history during contact metamorphism by use of a thermal analysis code. This work is in progress.

Table 5 Summary of a study on illitization of smectite associated contact metamorphism — A case study at the Murakami deposit

MATERIAL	Smectite in marine sediment
ENVIRONMENT Water chemistry Temperature	 Modified seawater > 240 ～ 105 ℃
TERM	2.4 ×10^6 y
RESULT	I/S mixed layers mineral (Illite;approximate 40%)

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. Results obtained to date are shown in Table 6.

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 Friédel'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.

6. FUTURE PROSPECTS

The framework of our natural analogue studies is shown in figure 7. The 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 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 the experiments. Such experiment, for the comparison of compositional differences between basaltic glasses and waste glass, has been conducting. The result to date indicates that there is no recognizable difference in the leaching rates.

An integrated evaluation of the long-tem durability of engineered barrier materials can be obtained on the basis of a combination of

Table 6 Alteration behaviour of cement fabrics

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

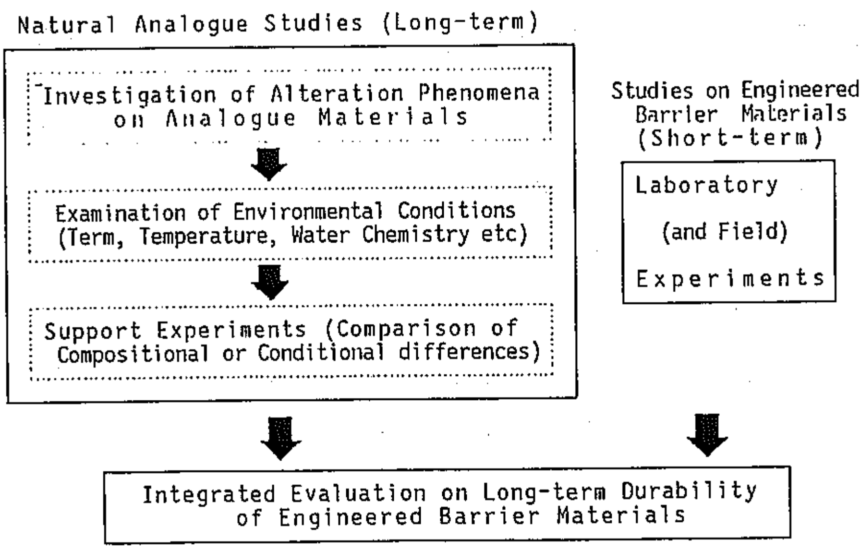

Fig. 7 Framework of analogue studies on engineered barrier materials

the natural analogue studies mentioned above and laboratory experiments on the engineered barrier materials.

7. ACKNOWLEDGMENTS

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