

# STATIC AND PERMEABILITY SORPTION TESTS OF BUFFER MATERIALS FOR GEOLOGIC DISPOSAL FOR HIGH-LEVEL WASTES

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## ABSTRACT

Sorption tests have been carried out using sodium bentonite powder and compacted bentonite/quartz sand blocks with simulated groundwater solutions containing Fe, Cr, Ni, Cu and Ti to evaluate transport behaviors of corrosion products of overpack materials. Sorption amounts of these metallic ions in the solutions contacting with bentonite clay were varied with the temperature. The hydraulic conductivities of compacted bentonite/quartz sand for the solution containing Fe, Cr and Ni ions were a little lower than that for desalted water.

## INTRODUCTION

Compacted blocks of the mixture of sodium bentonite and sand have been considered, as the most promising candidate, buffer materials for HLW geologic disposal in some countries, e.g. U.S.A., Sweden, Switzerland and also Japan (1, 2, 3, 4, 5). The effect of compacted bentonite buffer materials on the corrosion phenomena of metallic containers is important. The chemical buffering effect on the groundwater approaching the container will be the most notable one in terms of corrosion. For steel materials, the corrosion behavior in a repository is considered as follows (4):

1. By the chemical buffering effects of sodium bentonite, the groundwater pH-value shift into an alkaline range while the redox potential becomes more reducing.
2. Iron is oxidized mainly by the water and the dissolved oxygen introduced into the repository during the operational phase, while hydrogen gas and hydrated iron oxide/iron hydroxide are produced.
3. Solid corrosion products are insoluble in the chemical environment of a repository.

Moreover, swelling pressure of bentonite will act on the container. After the corrosion of the container occurs, the corrosion products will also be compressed by the swelled bentonite. It is not known at this time how this mechanical compression affects the separation behavior of the corrosion product layers from the metal surface.

Corrosion products such as hydrated iron oxide or iron hydroxide are insoluble. Therefore, those products separated from the metal surface may form colloids. The size of the colloids has not been determined at this time. If these colloids can not permeate swelled buffer materials, corrosion products stay near the container surface and prevent fresh metal from appearing.

In order to examine the corrosion products' behavior within the buffer materials, we have started sorption experiments of candidate container materials, using bentonite clays. In this study, as the first stage, we examined the permeability of acidified, simulated groundwater, in which metallic ions were added, within the compacted sodium bentonite/quartz sand blocks. Prior to these experiments,

static sorption tests of bentonite clay powder, using the same solutions, were carried out.

## EXPERIMENTAL FEATURES

The bentonite clay used in this study was provided by the Kunimine Industries Col., Ltd. (trade name-Kunigel V1), and is commercially available. Chemical constitution of the bentonite is given in Table I. It is similar to Greekish bentonite. Compared with the MX-80 (trade name, from the American Colloid Company), this bentonite is a little rich in silicon dioxide (3).

TABLE I

Chemical Analysis of Bentonite

COMPOSITION	%
SiO <sub>2</sub>	70.2
Al <sub>2</sub> O <sub>3</sub>	14.2
Fe <sub>2</sub> O <sub>3</sub>	2.5
CaO	2.0
MgO	2.2
MgO	2.2
Na <sub>2</sub> O	2.5
K <sub>2</sub> O	0.2
Ig-loss	4.6

TABLE II

Composition of Simulated Groundwater

Species	Concentration (mg/L)
HCO <sub>3</sub> <sup>-</sup>	123.26
SO <sub>4</sub> <sup>2-</sup>	9.61
Cl <sup>-</sup>	60.97
Ca <sup>2+</sup>	18.04
Mg <sup>2+</sup>	4.38
Na <sup>+</sup>	61.38
K <sup>+</sup>	3.91
SiO <sub>2</sub>	10.81
I <sup>-</sup>	12.69

The density of compacted bentonite/quartz sand (bentonite-60 wt.%, sand-40 wt.%) test pieces were about 2.0

g/cm, and the water content was 10.5 percent. These test pieces were circular disks (diameter 50.8 mm, thickness 5.0 mm).

The simulated groundwater composition used in this study is listed in Table II. In order to acidify this solution, hydrochloric acid was added. Metallic ions were added as the following substances:

- Fe - ferric chloride,
- Cr - potassium dichromate,
- Ni - nickel chloride,
- Cu - copper chloride, and
- Ti - titanium (IV) sulfate.

**Static Sorption Tests**

In static sorption tests, three simulated groundwater solutions were used. Iron, chromium and nickel ions were added to the first solution. Copper and titanium ions were added to the second and the third solutions, respectively. The bentonite powder (2 g) was stirred into each solution (200 ml) described above in the beaker. The beaker was put in a thermostat. Static sorption tests were carried out in the temperature range from 20 to 70 degrees Celsius. We took 48 hours for the contact time of the bentonite with the solution. Each cation concentration was analyzed by using an absorption spectrum photometer.

**Permeability Sorption Tests**

The compacted bentonite test piece set between filter papers and metallic filters was contained in a Type 304 stainless steel pressure vessel. Permeating solutions were pressurized at 15 MPa by a plunger pump and supplied into the vessel. At first, we used desalted water to measure the hydraulic conductivity and to evaluate the chemical buffering effects of this compacted bentonite/quartz sand test piece. Next, the same solution containing Fe, Cr and Ni ions as in the static sorption test was used to examine the permeability of those metallic elements. In this case, the temperature range was set between 20 to 60 degrees Celsius.

**RESULT AND DISCUSSION**

The variations of the concentration of cations in each solution which contacted with the bentonite clay powder for 48 hours are shown in Figs. 1, 2 and 3, with initial concentrations of each element. Experimental results about the solution containing Fe, Cr and Ni are shown in Fig. 1. As shown in this figure, the concentration of sodium, calcium and magnesium ions is increased, while those of iron and chromium are decreased. Potassium and nickel are changed little. As far as the differences of temperature conditions are concerned, the decrease of iron concentration becomes higher with the increase in temperature. Effects of temperature on the sorption amount of these metallic ions are described later. Figure 2 shows the variation of the solution containing copper ions. The concentration of copper ions at each temperature are greatly decreased. Sodium ions are increased similarly to the case of Fe, Cr and Ni, however,

INITIAL CONC. OF ELEMENTS (mg/L)						
Ca	Mg	Na	K	Fe	Cr	Ni
9.5	2.0	55.5	53.5	49.5	45.1	72.1

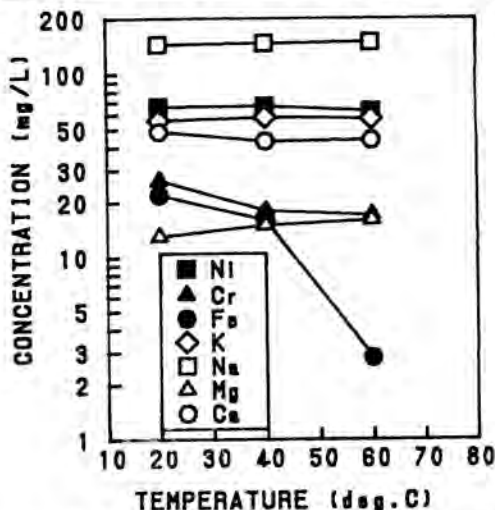


Fig. 1. Variations of the Concentration of Cations in the Solution Containing Fe, Cr and Ni ions.

INITIAL CONC. OF ELEMENTS (mg/L)						
Ca	Mg	Na	K	Cu	-	-
20.2	4.2	93.5	4.8	45.0	-	-

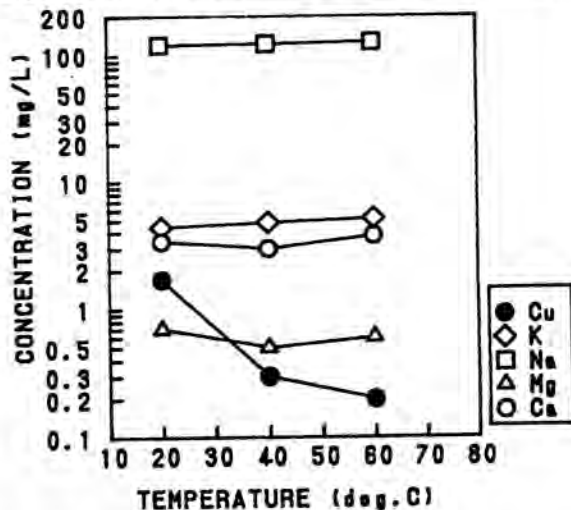


Fig. 2. Variations of the Concentration of Cations in the Solution Containing Cu ions.

contrary to the former case, calcium and magnesium ions are decreased. Results on the solution containing titanium ions are shown in Fig. 3. In this case, sodium, calcium and magnesium ions are increased similarly to the case of Fe, Cr and Ni.

The pH and Eh values of these initial solutions were set as follows:

Fe, Cr, Ni solution: 2.00 pH, 572 Eh(mV)

INITIAL CONC. OF ELEMENTS (mg/L)						
Ca	Mg	Na	K	Ti	-	-
16.0	4.8	55.0	5.1	43.6	-	-

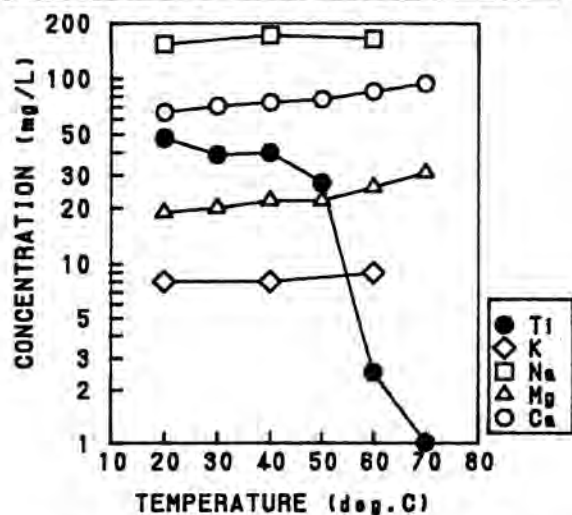


Fig. 3. Variations of the Concentration of Cations in the Solution Containing Ti ions.

Cu solution : 5.57 pH, 586 Eh(mV)

Ti solution : 1.61 pH, 641 Eh(mV)

In these static sorption tests, pH values were all increased while Eh values were varied very little. In the case of the Fe, Cr and Ni solutions, pH was increased to 2.58, 2.57 and 2.47 at the temperatures of 20, 40 and 60 degrees Celsius, respectively. Similarly, in the case of the Cu solution, pH was increased to 6.75, 7.21 and 7.94 at the same temperatures as the Fe, Cr and Ni solutions. And in the Ti solution, pH was slightly increased to 1.62, 1.63 and 1.65 at the same temperatures.

Figures 4, 5 and 6 show the variations of the metallic ions added to the simulated groundwater in these tests; that is, Fe, Cr, Ni, Cu and Ti. On the vertical axis of the figures, concentration ratios ( $C/C_0$ ) are taken:

where

$C_0$  - initial concentration of each ion

$C$  - concentration of each ion in the solutions contacted with bentonite for 48 hours.

As shown in Fig. 4, the sorption amounts of Fe, Cr and Ni ions are increased as the temperature rises. Among these three elements, the sorption amount of Fe ions is larger than those of Cr and Ni. Ni ions were little sorbed. The cases of copper and titanium are shown in Figs. 5 and 6. The sorption amounts of Cu ions were great even in a low temperature range. In case of titanium, the sorption amount showed very sensitive characteristics to temperature. It decreased sharply from 40 to 60 degrees Celsius.

In these tests, pH values of solutions were increased. It is considered hydrogen ions were exchanged with sodium, magnesium and calcium ions. For example, in the case of Fe,

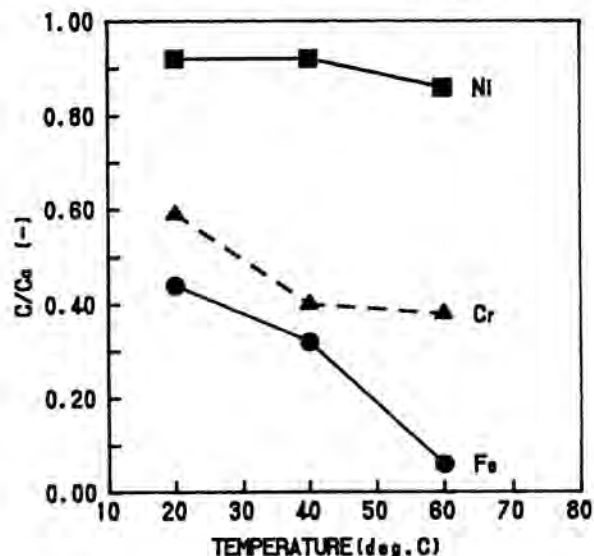


Fig. 4. Decrease in Fe, Cr and Ni Concentration.

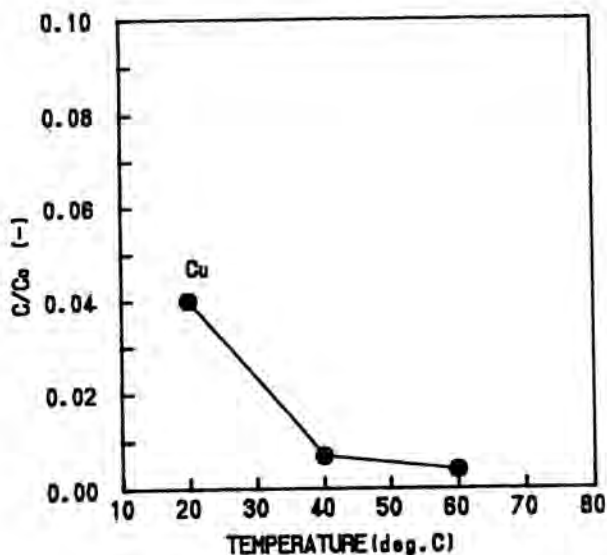


Fig. 5. Decrease in Cu Concentration.

Cr and Ni solutions at the temperature of 60 degrees Celsius (Fig. 1), the increments of sodium, magnesium and calcium ions in the solution were 0.82, 0.17 and 0.12 mmol respectively, while the decreased amount of hydrogen ions was 1.32 mmol. The summation of products of the valency and the increased amount of Na, Mg and Ca is 1.04 mmol.

The mechanism of the sorption of metallic ions in this study has not been determined at this time. It is considered the sorption of bentonite clays consists of ion exchange, adsorption, the formation of slightly soluble precipitates

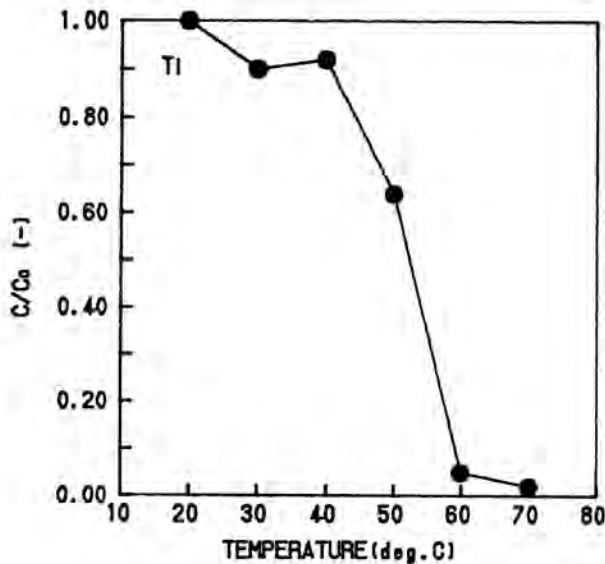


Fig. 6. Decrease in Ti Concentration.

and so on. In this case, exchangeable cations of bentonite, such as sodium, are substituted by hydrogen ions as described above, so pH values were increased. By the Eh-pH diagram of each metal, the sorption is considered due to the precipitation of hydroxide or hydrated oxide; that is,  $Fe(OH)_3$ ,  $Cr(OH)_3$ ,  $Cr(OH)_3$ ,  $Cu(OH)_2$  and  $TiO_2 \cdot H_2O$ . As far as nickel is concerned, the concentration of nickel ions was slightly decreased as shown in Figs. 1 and 4. Since the nickel ion is stable in water with a low pH, the sorption of nickel is considered to occur by coprecipitation. However, further study using an X-ray diffraction analysis or a differential thermal analysis (D.T.A.) will be required to determine the sorption mechanism.

The permeability test using desalted water was carried out at room temperature conditions (ca. 20 degrees Celsius). Cumulative permeated water volume in this test is shown in Fig. 7. We got a straight line using the least squares method. The calculated result of hydraulic conductivity of this test piece was  $1.69 \times 10^{-13}$  m/sec. By the chemical buffering effects of this bentonite, the pH-value shifted above 8 at the time of 17 days, as shown in Fig. 7. Sodium and potassium concentration data in the permeation solution is shown in Fig. 7.

Permeated water volume data in tests for the solution containing Fe, Cr and Ni is shown in Fig. 8. The tests were carried out at the temperatures of 20, 30, 40 and 60 degrees Celsius. The broken line in Fig. 8 shows the result of desalted water described above. Compared with this line, permeation amounts of the solutions were small. They were about one-third or one-half of that of desalted water. There were small differences among data at temperatures of 20, 30 and 40°C. However, at 60°C, the permeation amount was larger than those for other temperature conditions. Analytical values of the test at the temperature of 40° C are sum-

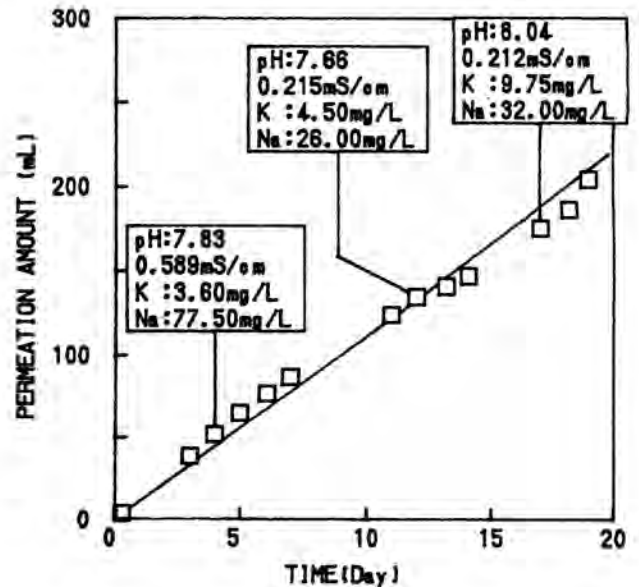


Fig. 7. Permeation Amount of Desalted Water Through Compacted Bentonite/Sand Block.

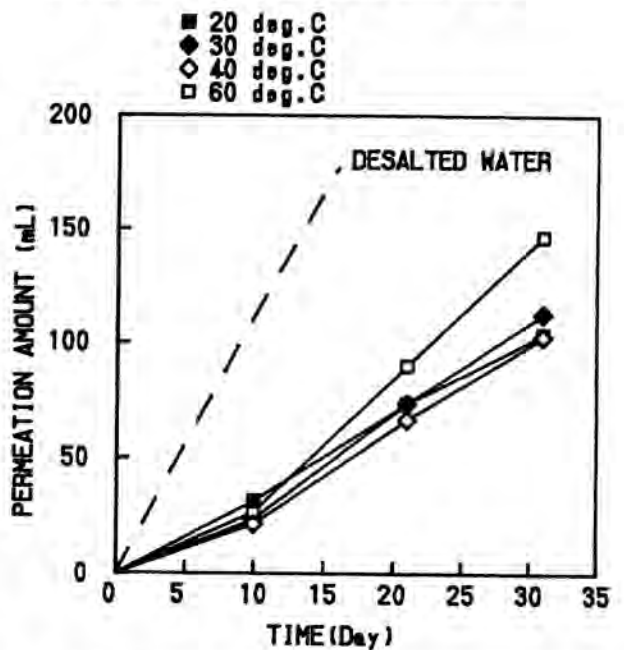


Fig. 8. Permeation Amount of Solution Containing Fe, Cr and Ni ions Through Compacted Bentonite/Sand Block.

marized in Table III. It is notable that the sodium concentration was decreased with the passage of time, while pH was stable at 8.4. The maximum concentration of nickel was 2.7 mg/L. Iron and chromium were little detected. In this case, these metals are considered to be precipitated as hydroxides or hydrated oxides within the pores of swelled bentonite and/or bound to the pore surfaces electrically.

TABLE III  
Results of Permeation Test  
(Containing Fe, Cr and Ni - 40°C)

Time (Day)	Concentration (mg/L)							pH	Electric Conductivity (mS/cm)
	Fe	Cr	Ni	Na	K	Ca	Mg		
10	1.1		1.1	632.5	7.2	9.5	2.2		
21	0.2	ND	2.6	460.0	9.2	3.0	1.2	8.4	2.2
31	ND	ND	2.7	300.0	7.4		1.8	8.4	2.5

As described above, the hydraulic conductivity in the cases using Fe, Cr and Ni solutions were a little lower than that in the case of desalted water. However, they were in the same order of magnitude, therefore, we may take these effects of sorption on hydraulic conductivity to be small, conservatively.

### CONCLUSION

In this study, some characteristics on static sorption behavior of bentonite clay and on permeability sorption behaviors of solutions through a compacted bentonite/quartz sand block are examined. The following four main conclusions are obtained from this study.

In the static sorption tests:

1. The sorption amount of Fe, Cr, Ni, Cu and Ti ions is increased with the increase in temperature.

2. The sorption amount of Fe, Cr and Ni are the following order.

Fe > Cr > Ni

In permeability tests:

1. Hydraulic conductivity of the compacted bentonite/quartz sand is  $1.69 \times 10^{-13}$  m/sec.

2. The permeation amount of the solution containing Fe, Cr and Ni ions through the compacted bentonite/quartz sand is lower than when using desalted water.

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