

Experimental Study on the pH of Pore water in Compacted Bentonite under Reducing Conditions with Electromigration

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ABSTRACT

Compacted bentonite and carbon steel are considered a good buffer and over-pack materials in the repositories of high-level radioactive waste disposal. Sodium bentonite, Kunipia-F contains approximately 95wt% of montmorillonite. Bentonites prominent properties of high swelling, sealing ability and cation exchange capacity provide retardation against the transport of radionuclides from the waste into the surrounding rocks in the repository and its properties determine the behavior of bentonite. In this regards, the pH of pore water in compacted bentonite is measured with pH test paper wrapped with semi-permeable membrane of collodion sheet under reducing conditions. On 30 days, the pH test paper in the experimental apparatus indicated that the pH of pore water in compacted bentonite is around 8.0 at saturated state. The carbon steel coupon is connected as the working electrode to the potentiostat and is held at a constant supplied potential between +300 and -300 mV vs. Ag/AgCl electrode for up to 7days. During applying electromigration the pH of pore water in bentonite decreased and it reached 6.0~6.0 on 7 days. The concentration of iron and sodium showed nearly complementary distribution in the bentonite specimen after electromigration. It is expected that iron could migrate as ferrous ion through the interlayer of montmorillonite replacing exchangeable sodium ions in the interlayer. Semi-permeable membrane of collodion sheet does not affect the color change of pH test paper during the experiment.

INTRODUCTION

Bentonite and carbon steel are considered a good buffer and over-pack materials in the repositories of high-level radioactive waste disposal [1]. Bentonites prominent properties of high swelling capacity, high plasticity, low permeability, and cation exchange capacity provide retardation against the transport of radionuclides from the waste into the surrounding rocks in the repository. However, as a porous media, it is possible that radionuclides migrate through the buffer into the geosphere by diffusion process [2]. Physico-chemical properties of the buffer play an important role in the solubility of nuclides in the pore water of montmorillonite [3]. Solubility of radionuclides in an oxidized state is affected by pH of bentonite [4]. Bentonite changes the chemical characteristics of infiltrating ground water by means of mineral water chemical interactions. The interactions controlling pore-water chemistry include ion-exchange reactions of smectite, protonation/deprotonation reactions due to surface hydroxyl group of smectite, as well as dissolution/precipitation reaction and redox reactions of accessory minerals, and dissolution of soluble impurities. The protonation/deprotonation reactions of the smectite tend to decrease pH under initially slightly alkaline conditions and this reaction causes a certain dependence of pH on solid/liquid ratio in bentonite-water systems under anaerobic conditions. Wieland et al. suggested that the pore-water chemistry is affected by deprotonation of surface OH groups in montmorillonite [5]. According to their study, the deprotonation of OH groups would cause a drop of pore waters pH, which is expected to be remarkable in highly compacted bentonite. One of the important factors, which affect the passive behavior of carbon steel, may be the pH of the pore water in the compacted bentonite [6]. Therefore, the pH of pore water in bentonite is important to express the passivation of carbon steel in compacted bentonite. Although efforts to accumulate the theoretical modeling evidence and thermodynamic data are accomplished so far, direct measurements of the pH of pore water in saturated bentonite are not reported yet.

The purpose of this study is to measure the pH of pore water in compacted bentonite under the reducing conditions with pH test paper wrapped by collodion sheet.

MATERIALS AND METHODS

Pre- Experiment

The collodion sheet is used to wrap pH test paper in order to protect the color disappearance of pH test paper in this study. Collodion is a solution of nitrocellulose in ether or acetone. Its generic name is pyroxylin solution. As the solvent evaporated, it dries to celluloid like film. The surface of this membrane does not react with the pore water of compacted bentonite. However, this membrane has the capacity to allow the migration of the pore water from compacted bentonite to the pH test paper. Moreover, three experiments are carried out at different pH standard solutions to examine the effect of collodion sheet on pH change. Photographs (1), (2), and (3) which are taken with soaking of Phthalate pH Standard Solution, Phosphate pH Standard solution and Tetraborate pH Standard Solution respectively, and (4) shows the photograph of pH indicator.

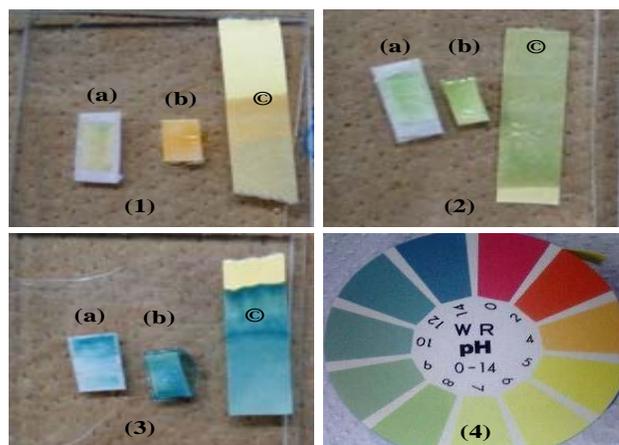


Fig. 1. Typical photographs illustrating the color of pH test paper at different pH standard solutions, where (a): pH test paper wrapped with eggshell membrane, (b): pH test paper wrapped with collodion sheet and (c): unwrapped pH test paper.

The photographs (1), (2) and (3) in Fig. 1 contains three pH papers (a), (b), and (c), which are wrapped with eggshell membrane, collodion sheet, and unwrapped one, respectively. The pH test paper wrapped with collodion sheet and unwrapped pH test paper shows the same color and does not affect the color of pH test paper. On the other hand, pH paper wrapped with eggshell membrane shows foggy. So, the collodion sheet is used in this study.

Experiment

Typical Japanese sodium bentonite, Kunipia-F is used in this experiment. It contains approximately 95wt% of montmorillonite. Kunipia-F contains 98-99% montmorillonite. The chemical composition of Kunipia-F is shown in Tables 1 and its as $(\text{Na}_{0.4}\text{Ca}_{0.03}\text{K}_{0.01})(\text{Al}_{1.6}\text{Mg}_{0.3}\text{Fe}_{0.1})\text{Si}_4\text{O}_{10}(\text{OH})_2$. Approximately 372 of the molecular weight and ca. 1 eq/kg of cation exchange capacity are estimated from the chemical composition. Bentonite powder was compacted into cylinders of 10 mm in diameter and 10 mm in height with the dry density of 1.4 Mg/m^3 . The compacted bentonite is inserted in an acrylic resin column with four pieces pH test paper of 1.5 mm in length and 1.5mm wide, which are wrapped with collodion sheet and soaked in NaCl aqueous solution of 0.01M for one month. Carbon steel, JIS SM41B is cut into cylindrical coupons of 18 mm in diameter and 3 mm in thickness. The surface of the coupon was wet-polished with # 1500-emery paper.

Table 1. Chemical Composition of Kunipia-F used in this Study.

Constituent	Content, wt %
SiO ₂	58.36
Al ₂ O ₃	20.36
Fe ₂ O ₃	1.34
FeO	0.51
TiO ₂	0.13
MnO	<0.01

Na ₂ O	2.93
K ₂ O	0.09
CaO	0.42
MgO	2.97
P ₂ O ₃	<0.01

pH Test with Electromigration

After one month, the color of pH test paper in the experimental apparatus is changed. The pH test paper that is wrapped with collodion sheet became green. After that, a carbon steel coupon is assembled with water-saturated bentonite; they are put into an apparatus for conducting an electromigration experiment as shown in Fig. 2. There are a reference electrode of Ag/AgCl and a counter electrode of platinum foil in upper part of the apparatus with 0.01 M of NaCl aqueous solution. The carbon steel coupon is connected with potentiostat as a working electrode and is supplied electrical potential of + 300 mV and -300mV vs. Ag/AgCl electrode at 25 °C for up to 7 days. During supplying the electrical potential, the color of pH test paper in the experimental apparatus is rapidly changed. After supplying electrical potential, the bentonite specimen is taken out from the column and is sliced into thin leaves of 1~2 mm in thickness. Iron and sodium in each slice are extracted with 1N HCl, and the concentration of iron and sodium in each extracting solution are measured with atomic absorption spectrophotometer.

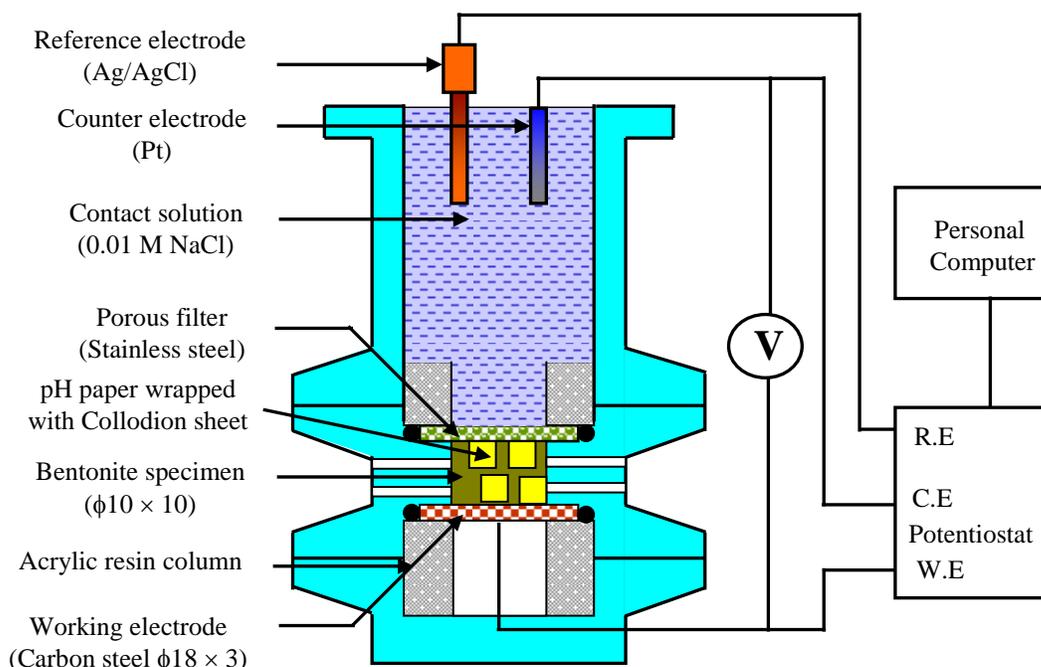


Fig. 2. Schematic diagram of experimental apparatus used in the present study.

RESULTS AND DISCUSSION

Observation of pH Test Paper

The color of pH test paper wrapped with collodion sheet attached to the bentonite specimen in the experimental apparatus became greenish on 15 days and finally reached green on 30 days. This green color indicated that the pH of pore water in saturated bentonite is around 8.0 on 30 days before electromigration. The carbon steel coupon connected with potentiostat as a working electrode and is supplied electrical potential of +300 mV vs. Ag/AgCl electrode for 7 days. During electro-migration, the color of pH test paper changed to yellow on 7 days. Photographs (a) and (b) in Fig. 3 showed the color change of pH of pore water in bentonite before electro-migration at 30 days and after electro-migration at 7 days, respectively.

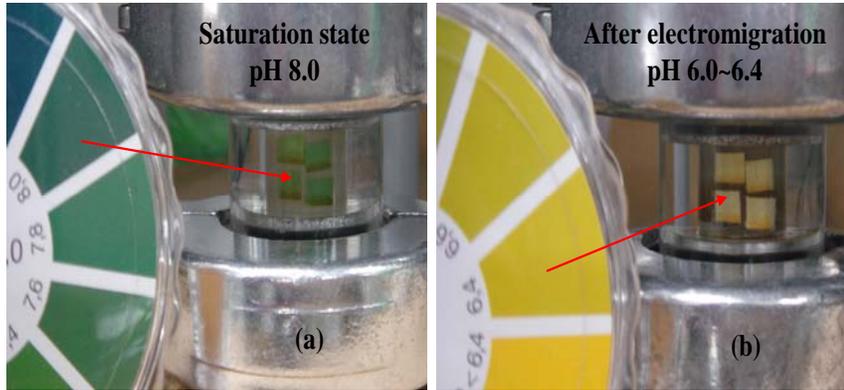


Fig. 3. Typical photographs (a) and (b) are indicating the pH of pore water in compacted bentonite before electromigration at saturated state and after electromigration at 7 days, respectively.

Profile of Iron and Sodium in Bentonite Specimen

Figure 4 shows the concentration profile of iron and sodium in bentonite specimen. The concentration of iron and sodium showed nearly complementary distributions in deeper part as reported in the previous study [7]. In other words, iron, as a ferrous ion, migrated in bentonite with exchanging it for two sodium ions in interlayer of montmorillonite.

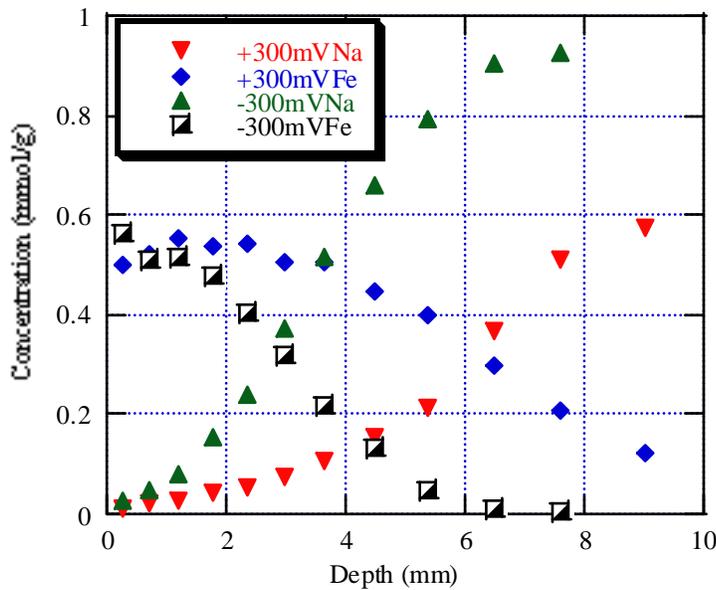


Fig. 4. Profiles of iron and sodium in compacted bentonite with electromigration up to 7 days.

The color change of pH test paper during electromigration at different times

The surface of montmorillonite clay platelets carry a permanent negative charge arising from isomorphous substitution of lattice cations by those with a lower valency. Charge neutrality is maintained by the presence of an excess amount of cations in solution. Since the areas within the interlayer space are predominant, the compensating cations reside mainly there. The electrostatically bound cations, which form the electrical double layer, can undergo stoichiometric exchange with the cations in solution [8, 9]. The color of pH test papers rapidly changed while

supplying electrical potential of +300 mV and -300 mV for 7 days. Photographs (a), (b) and (c) in Fig. 4 show the color changes of pH paper at 30 m, 70m and 7d, respectively during electromigration with +300 mV. On the other hand, photographs (d), (e) and (f) also show the color changes at -300 mV with same time differences. From these figures one can see that the color change of pH test paper start from lower part and gradually changed to upper lever. Because, when the carbon steel came into contact with bentonite specimen and applying electrical potential, the corrosion is occurred. Iron as a ferrous ion migrated in bentonite with exchanging it for two sodium ions in interlayer of montmorillonite.

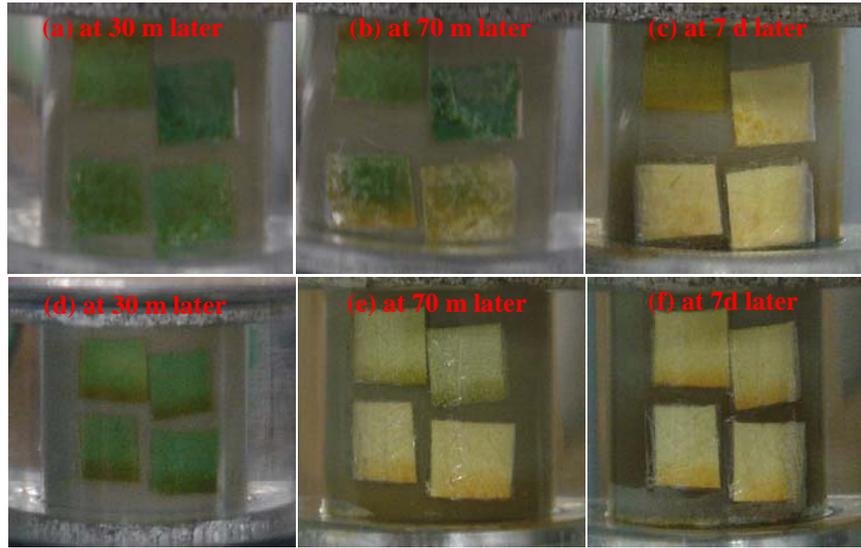


Fig. 4. Photographs (a), (b) and (c) show the color changes of pH test paper at different times during electromigration with +300 mV. In addition, photographs (d), (e) and (f) show the color changes at -300 mV with same time differences.

The experimental results shown in Fig. 4 indicated that concentration of ferrous ion decrease with increasing depth, however, the concentration of sodium ion increase with depth. Corrosion reaction can be written as follows:



$$E \text{ (mV)} = E^0 + \frac{59.1}{2} \log a_{\text{Fe}^{2+}} \quad (\text{Eq. 2})$$

CONCLUSION

The pH test paper wrapped with collodion sheet is used to measure the pH of pore water in compacted bentonite under reducing environment. Before electromigration at saturated state, the pH of pore water was around 8.0. When applying the electrical potential, the pH is changed rapidly and it reached around 6.0~6.4 on 7 days due to the corrosion occurred on the surface of carbon steel and iron as a ferrous ion migrated in bentonite by exchanging for two sodium ions in the interlayer of montmorillonite.

References

1. F.Bucher, M. Müller-Vonmoos, "Bentonite as a Containment Barrier for the Disposal of highly Radioactive Waste", Applied Clay Science, 4, 157 (1989).
2. Japan Nuclear Cycle Development Institute (JNC), JNC/TN1410, 2000-001 (2000).
3. Y. Torikai, S. Sato and H. Ohashi, "Thermodynamic Properties of Water in Compacted Sodium Montmorillonite", Nuclear Technology, 115, 73 (1996).

4. K. Idemitsu, H. Furuya, Y. Tachi and Y. Inagaki, "Diffusion of Uranium in Compacted Bentonite in the Presence of Carbon Steel", Scientific basis for Nuclear Waste Management XVII, edited by A. Barkatt and R.A. Van Konynenburg (Mater., Res. Soc. Proc. 333, Pittsburgh, PA.1994) 939-946.
5. E. Wieland, H. Wanner, Y. Albinsson, P. Werson and O. Karnland, SKB Technical Report, 94-26 (1994).
6. G.P. Marsh, I. W. Blend, J. A. Desport, C. Westcott and K.J. Taylor, European Applied Research report, Nucl. Sci. Techno., 5.2, 223 (1983).
7. K. Idemitsu, S. Yano, X. Xia, Y. Kikuchi, Y. Inagaki, T. Arima, "Migration Behavior of Iron in Compacted Bentonite under Reducing Condition by using Electromigration", Scientific Basis for Nuclear Waste Management XXVI, edited by R. J. Finch and D. B. Bullen (Mater. Res. Soc. Proc. 757, Pittsburgh, PA, 2003) 657-664.
8. R. E. Grim, "Clay Mineralogy", Mc Graw Hill (1953).
9. H. Van Olphen, "An Introduction to Clay Colloid Chemistry, Interscience Publishers", J. Wiley and Sons (1963).