# Review of Anion Diffusion in Highly Compacted Montmorillonite for Copper Corrosion Modeling

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# 1. Introduction

KAERI has developed the geological disposal systems for high-level wastes (HLW). The main safety function of the disposal system is the isolation of HLW from the human environments for a very long period. Generally, the HLW is isolated with the engineered barrier system composed of a disposal canister and buffer.

The authors have developed the engineered barrier system consisting of a copper disposal canister and a Ca-bentonite buffer for the geological repository. The cold spray coating technique was used to manufacture a disposal canister, and a very long-term corrosion experiment is in progress at the KURT for ensuring the long-term performance of a copper canister.

Recently, the parts of long-term corrosion test results conducted at the KURT were published [1]. According to the report, the major corroding agent for copper is the dissolved oxygen in groundwater, since the water was taken from a borehole not too deep. The authors developed a numerical model for the corrosion test.

It is well-known that the corroding agents of copper under the repository condition are chloride ion, sulphide ion, and dissolved oxygen, which are all anionic ions. In the geological repository the disposal canister is surrounded by a bentonite buffer, in which no groundwater flow is allowed. Thus, the copper is corroded by the diffusion of corroding agents through a compacted montmorillonite buffer.

In general, the diffusion of anion in the compacted montmorillonite is explained by pore water diffusion and anion exclusion. In this study, the effect of anion diffusion on the copper corrosion was examined, and the diffusion of anion in compacted montmorillonite was reviewed and documented in detail to develop a copper corrosion model.

# 2. Copper corrosion

# 2.1 Corrosion test at the KURT

The long-term corrosion tests were performed under the simulated conditions at the KURT to verify the corrosion resistance of a copper canister. The column test (marked [B] in Fig. 1) at 70°C was carried out for approximately 3 years from 2009 to 2012. The groundwater from a borehole in the KURT was supplied at a flow rate of 15 cc/min. Fig. 2 shows the corrosion depth of copper specimens for three years.

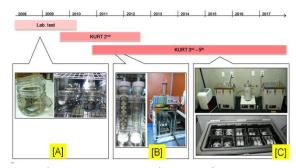


Fig. 1. Long-term corrosion test at the KURT.

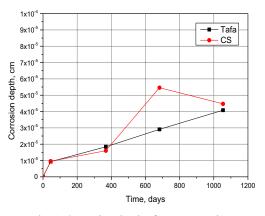


Fig. 2. Corrosion depth of copper specimens.

#### 2.2 Corrosion modeling

The transport mechanism of anions such as dissolved oxygen or sulphide through highly compacted bentonite buffer is mainly diffusion. Then, the one-dimensional diffusion equation in bentonite buffer is described in equation (1):

$$\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial x^2} \tag{1}$$

The apparent diffusion coefficient  $(D_a)$  of anion in equation (1) is generally identical to pore diffusion coefficient  $(D_p)$ . The corrosion depth of copper is proportional to the cumulative diffusive flux of corroding agent through the bentonite buffer, and the cumulative diffusive flux is given as follows:

$$Cf/ux = -D_{p} \cdot \varepsilon \cdot Area \cdot \int_{0}^{\tau} \frac{\partial C}{\partial t} dt$$
(2)

The porosity in equation (2) for anion is generally expressed as an effective porosity due to anion exclusion. There is a large difference between the effective porosity and total porosity for highly compacted montmorillonite.

### 3. Anion diffusion

#### 3.1 Previous Study on diffusion coefficients

J. O. Lee et al. measured the diffusion coefficient of Iodide for the domestic Ca-bentonite. The effective diffusion coefficient was  $1.25 \times 10^{-12}$  m<sup>2</sup> s<sup>-1</sup> at dry density of 1.7 Mg m<sup>-3</sup>, which was one order of magnitude lower than the apparent diffusion coefficient [2]. S.P. Yim et al. investigated the diffusion of iodide in compacted bentonite containing Ag<sub>2</sub>O [3]. They measured the diffusion coefficient of  $8.7 \times 10^{-12}$  m<sup>2</sup> s<sup>-1</sup> at dry density of 1.6 Mg m<sup>-3</sup> with no addition of Ag<sub>2</sub>O.

T. Kozaki et al. measured the diffusion of Chloride ions in sodium montmorillonite to understand the diffusion mechanism [4]. They reported the apparent diffusion coefficient of around  $3.7 \times 10^{-11}$  m<sup>2</sup> s<sup>-1</sup> at dry density of 1.6 Mg m<sup>-3</sup> at 25°C.

### 3.2 Anion Exclusion

It is well-known that anion transport through the stacks of montmorillonite does not take place because of Donnan exclusion [5]. This means that anion diffusion takes place through a part of total porosity in bentonite buffer.

According to the previous study by J.O. Lee et al., this ratio is around 9% of the total porosity at the dry density of 1.7 Mg m<sup>-3</sup>. Pusch et al. reported that the volume of interlayer water takes 10% of total water volume [5]. Also, it was reported that in case of a high ionic strength solution, the charges on the surface led to a lower exclusion effect [6].

As given in equation (2), the corrosion depth of copper depends only on the effective porosity,

through which anion can transport. It is very crucial to distinguish and estimate the interlayer porosity and inter-particle porosity.

#### 4. Conclusion

A copper disposal canister may be corroded under the geological repository conditions. It has been known that most of corroding agents are anions such as dissolved oxygen and sulphide. The corrosion depth of copper is proportional to the effective diffusion coefficients of anions in bentonite buffer, which were influenced much by the anion exclusion. To this end, a more sophisticate diffusion model should be developed to explain the anion exclusion in detail.

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