Heating impact on corrosion mechanism of carbon steel surrounded by bentonite

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Received: 24 November 2020; Revised: 6 May 2021; Accepted: 30 July 2021

Abstract
The long-term safety of geological disposal of radioactive waste is studied through several simulations. Before underground disposal, radioactive waste is stored for 30 to 50 years at facilities near nuclear power plants to cool it down to around 100 degrees Celsius. It is then placed in steel canisters surrounded by artificial materials such as bentonite and concrete. To determine the long-term safety and stability of this disposal method, we’ve studied the corrosion rate of the steel canisters under different conditions using electro-chemical impedance spectroscopy (EIS). This paper describes the corrosion of the carbon steel and elucidates the corroded condition using EIS measurement. EIS was adopted to estimate the corrosion condition from the impedance frequency characteristic. In our experiment, samples of bentonite and carbon steel were Kunigel V1 compacted to 1.37 Mg/m$^3$ dry density with several different water contents, and SM400 as a low carbon steel. An electric heater was set inside the steel canister to maintain the temperature at 100 degrees Celsius. This model was made to a scale of around 1/120 as a current concept of a vertical disposal plan and reproduced the enclosed situation after underground emplacement of the radioactive waste. During heating, we conducted EIS measurements and set this data result as an equivalent circuit. We noted some different trends of impedance frequency characteristic depending on the bentonite’s water content and the heating time. From this result, we estimated the corrosion condition to analyze the corrosion products.

Keywords: Radioactive waste, Corrosion, Carbon steel, Bentonite, EIS

1. Introduction
Several type experiments have been conducted on any materials used for the disposal of radioactive waste to date. One of them was conducted on engineered barrier materials comprising steel, bentonite and concrete, shown in Figure 1. Others targeted a natural barrier material were a host rock in the disposal tunnel, which are sedimentary or crystal rock in Japan. Some mockup tests and full-scale experiments were conducted using an engineered barrier material and were continued at the tunnel site in order to determine the characteristics of each material and observe the time course of the interface reaction between different materials (NUMO, 2021). As an example, the FEBEX experiment (Full-scale Engineered Barrier Experiment) carried out in Switzerland can be considered as the most recent extensive experiment (ENRESA, 1998). In this experiment, the behaviors of each engineered material were measured by large number of sensors. Several types of materials were then extracted from this site and analyzed using the latest technical methods (Uyama et al., 2019). After this experiment, in order to define the behavior of the materials after the disposal, many scientist and engineer performed laboratory experiments. Our target of material was a metal corrosion surrounded by the bentonite material.

Electro-chemical experiments (Saito et al., 1999) have been conducted at many R&D institutes around the world to determine the corrosion condition and to realize repeatability at different disposal sites (Uyama et al., 2019; Wersin et al., 2015). The corrosion potential or current density from polarization tests and the impedance from EIS tests can be...
associated with a present corrosion status. Other experiments focused on current density, which reflected the corrosion rate. In short, the corrosion mechanism can be demonstrated by the electrical reaction.

There are several different surrounding environments of the steel container, and they continue to change. Typical examples are differences of water and oxygen volume. More specifically, they are water content ratio and density of the surrounding material. Although the oxygen and moisture content after disposal decreases, they are the main reason for corrosion after the tunnel is backfilled, and the surrounding environment may change in the long term. Moreover, the temperature of the container before disposal in the disposal tunnel is approximately 100 degrees Celsius. We also need to consider this situation, which has been complicated and little has been reported on this phenomenon. We conducted some laboratory experiments to determine the corrosion rate at this high temperature using the electro-chemical test.

Fig. 1 Disposal concept in Japan (Overpack of horizontal emplacement in deep underground tunnels)

2. Materials and methods

To simulate the underground situation after the disposal, a carbon steel rod as the workings electrode (WE) with a heater and a steal sheet with compacted bentonite as the reference electrode (RE) was used for this experiment (shown on Figure 2). These type of each steel as WE and RE were SM400 (JIS G 3106) and SPCC (JIS G 3141) shown table 1. The steel type of them is that SM400 is “Rolled steel for welded structures”. On the other hand, SPCC is “Steel Plate Cold Commercial” shown in Table 1. The engineered materials currently used in Japan comprise a carbon steel and bentonite to one of the standards SM400A and Kunigel V1. We prepared compacted bentonite samples of 3 water content ratios: 14, 17, and 21 %. And, the dry density was 1.37 Mg/m³. In order to reproduce a closed situation such as the geological disposal, these samples enclosed the outside of samples using an epoxy resin material. The maximum temperature of the carbon steel rod during the corrosion test was maintained at 100 degrees Celsius using a heating wire. And, the outside of temperature was maintained 20 degrees Celsius.

After the set-up of each samples, the electro-chemical impedance spectroscopy test (EIS) was conducted in order to conform a corrosion status using a potentiostat of HZ-400, Hokuto denko corporation. A conducted frequency and AC voltage width were 1 m – 20 kHz and ±50 mV using a two-electrode system.

Fig. 2 Illustration of heating test sample
Table 1 Chemical component of SM400A and SPCC (Mass %)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>SM400A</td>
<td>0.23 or less</td>
<td>-</td>
<td>2.5 over</td>
<td>0.035 or less</td>
<td>0.035 or less</td>
</tr>
<tr>
<td>SPCC</td>
<td>0.15 or less</td>
<td>-</td>
<td>0.60 or less</td>
<td>0.100 or less</td>
<td>0.035 or less</td>
</tr>
</tbody>
</table>

3. Results and discussion
3.1 Corrosion status and rate

Figures 3 and 4 show results of the EIS experiment and the corrosion rate. Adapted equivalent circuit was set as RC parallel circuits as a high and low frequency side were a solution and charge transfer resistance. Fig.3 shows that the charge transfer resistances increased as the bentonite’s water content decreased after heating. This result indicates that the corrosiveness depends on the water content of the compacted bentonite, as shown in previous reports (Uyama et al., 2019; Uyama et al., 2017). However, there were changes in the charge transfer resistance. Heating is considered one of the triggers of this phenomenon, which we’ll discuss chapter 3.2.

Next, the corrosion rate shown as Figure 4 is calculated by the following Equation (1) using Faraday’s law (McCafferty, 2010).

\[ D = \frac{I \cdot t \cdot m}{n \cdot F \cdot \rho} \]  

where D: corrosion depth, I: current density, n: ionic valence, t: time, m: Fe molar mass, \( \rho \): density of carbon steel and F: faraday’s constant.

In order to obtain the current density, using the value of K, the ratio of polarization resistance (R_{ct}) to corrosion current defined (I_{corr}) by the equation (2) of Stern-Geary, we adapted the value of K=26 mV as an active state of corrosion (Andrade, et al., 1978).

\[ i_{corr} = \frac{K}{R_{ct}} \]  

(1 = i_{corr}/A), where A: surface area of working electrode.

Next, this corrosion rate is larger than those in other reports, most of which are under 0.01 mm/y (NUMO and JAEA, 2012). Especially, because some high corrosion rates were found with high water contents, we confirmed that the corrosion rate inside the samples after the heating experiment was like localized corrosion. As for this corrosion status, we analyzed inside of the carbon steel rod by several type of analytical methods in order to check situation after the heating test and describe on the chapter 3.4. The result of the high frequency was adapted as a solution resistance, whereas that of the low frequency is a charge transfer resistance. Figure 5 is a graph that compares the average charge transfer resistance after heating, which is one of the factors defining the corrosion rate.
3.2 Heat conductivity in bentonite

We should be considered the heat diffusion in bentonite. Figure 6 is one-dimensional model of the unsteady state of heat conductivity. The rising temperature inside the bentonite given by Equation (3) is shown in Figure 7. The values of specific heat and thermal conductivity of the compacted bentonite were obtained from JAEA reports (Kikuchi et al., 2003). The temperature of the sample surface was set by the measured value during the heating test inside of bentonite as a boundary condition.

As a result of calculation, the temperatures inside the bentonite were over 50 degrees Celsius and resulted from heat transfer from the metal at the beginning of the test. States over 50 degrees Celsius have been reported to cause some
changes as like movement of water inside the material (Smits et al., 2012).

\[
\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2}, \quad \left( \alpha = \frac{\lambda}{\rho C_p} \right)
\]  

(3)

where T: temperature, t: time, x: distance from center, \( \alpha \): thermal diffusivity of bentonite, \( \lambda \): heat conductivity of bentonite, \( \rho \): density of bentonite and \( C_p \): specific heat of bentonite.

Based on the result of temperature change in the bentonite after the heating, the next gives considerations the result of the measured charge transfer resistance. As a reason why the values of charge transfer resistance about the low-water-content bentonite tended to be changed continuingly after the heating, some liquids island in bentonite had been in unstable situations by the heat. It is because that the space inside of the low water content bentonite in order to transfer was bigger than the higher water content one. However, as for the reason of limited space in samples, it was difficult to make a change of the charge transfer resistance at the before and after the heating. On the other hand, in the case of 21 % water content bentonite, the value of charge transfer resistance was, however, almost as same as the value after the heating. The limited space in the bentonite was a difficult to transfer. Next, as a reason why the situation changed to be corroded status after the heating in the case of 21% water content bentonite, the condition of the high temperature become the reason of the increase of the oxygen diffusion rate. And, this situation caused a high corrosion rate in case of the high-water content bentonite after the heating (F. Speller, 1961).

Fig. 6 One dimensional model of unsteady heat state inside bentonite

![One dimensional model of unsteady heat state inside bentonite](image)

Fig. 7 Temperature calculation result inside bentonite by one dimensional heat conductivity model

![Temperature calculation result inside bentonite](image)
3.3 Corrosion amount

Figure 8 shows the corrosion state of the carbon steel rods and the corrosion products spread on the compacted bentonite after the EIS experiment. The areas of the corrosion influenced on the bentonite differed depending on the water contents. The higher the water content were the greater the spread of corrosion.

Figure 9 shows the relation between corrosion weight according to the water content inside bentonite. The corrosion weight loss and speed after the test show similar trends which are increasing according to the water content. In the case of the low water content rate, this corrosion weight trend is lower than the estimation of corrosion rate calculated from the result of the EIS experiment. One of the reasons is a difference of corrosion reaction between $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$. The corrosion rate is calculated based on equation (4). This corrosion products are shown in 3.4.

\[ Fe = \text{Fe}^{2+} + 2e^- \]  \hspace{1cm} (4)

![Fig. 8 Corrosion state of metal rod surrounded by compressed bentonite for each water content after heating test](image)

![Fig. 9 Relation between corrosion rate and weight according to the water content inside bentonite](image)
3.4 Corrosion products and mechanism

Raman spectroscopy and X-ray diffraction measurement (Hear after XRD) were conducted after removing the carbon steel rods from the bentonite to confirm the corrosion products after the heating test. Since the total volume of corrosion products for water content 14% was too little to analyze by XRD, Raman spectroscopy was conducted as alternative. The result showed that most of the corrosion products of the 14% and 17% samples were FeOOH (Goethite). In contrast, those of the 21% sample were a mixture of Fe$_3$O$_4$ (Magnetite) and Goethite. The colors on the surfaces of the carbon steel confirmed that nearly the same results were obtained for the 21 % water content, black indicating Magnetite, and the others showed some red rust, indicating Fe$_2$O$_3$ (Hematite) and Goethite. In regard this result confirming Hematite around the carbon steel, this bentonite also includes Fe$_2$O$_3$ as a major component and it is difficult to determine as a corrosion product.

As reported in several other studies, the corrosion products depend on the total oxygen volume before emplacement of the carbon steel in the bentonite in the case of an enclosed environment (Uyama et al., 2019; Wersin et al. 2015; Uyama et al., 2017). Magnetite is a mixture of ferrous and ferric corrosion product and Goethite is a ferric corrosion product. Based on these results, these corrosion reactions are an atmospheric corrosion and have a relation with the water film thickness (N. D. Tomashov, 1966). In the case of the moist atmospheric corrosion step before the saturation, the thicker the water thickness, the faster corrosion rate is. By the reason of mentioned above, the corrosion rate of the high-water content bentonite sample caused faster trends. After the heating, the water flow inside of bentonite start to move outside and this phenomenon is easier for a low water content bentonite. However, in the case of the closure space such as this sample, it was difficult to transfer outside and to be dry condition around carbon steel. As a reason of that, the charge transfer resistance constantly had changed during the heating rather than did not change much before and after the heating, as illustrated at Figure 10 (a). The higher oxygen content made a ferric corrosion product such as Goethite. On the other hand, for the 21 % water content bentonite, the water in the bentonite cannot easily transfer to the surface of sample after heating, as shown in Figure 10 (b). Thus, the moisture content is maintained, resulting in a low charge transfer resistance. Besides, the oxygen volume is low, and this corrosion reaction starts to change to the ferric corrosion product and ferric one such as Magnetite. If this sample has a higher density due to the limited space for oxygen, a ferrous corrosion product such as FeCO$_3$ would be found at the surface of metal as in the in-situ experiment, ABM1, in Sweden (Wersin et al., 2015).

Figure 11 is a microscope picture of the carbon steel rod surface after the test. The lower water content bentonite had thin corrosion products on their surface. This corroded condition is in the state of the oxide scale. The oxide scale on the metal surface usually suppresses the corrosion, however it held a corroded condition because of non-uniform corrosion occurred. As for the reason, microscopic ununiformed bentonite filter around the carbon steel has a character to make a uniform oxygen diffusing difficulty. Furthermore, the situation of the high temperature makes corrosion rate faster. this corrosion rate become faster in the case of high-water content. From such reason, high-water content sample had a pitting on the surface.

![Fig. 10 Schematic representation of moisture flow inside bentonite before and after heating](image-url)
4. Conclusion

In conclusion, the present study has demonstrated that:
- Corrosion rate was in proportion to water content bentonite after heating.
- Corrosion rate of lower water content bentonite sample was not stable because of the spaces allowing transfer of water after heating.
- Heating triggered corrosion growth immediately in the higher water content bentonite, and this the main reason for corrosion pitting.

Acknowledgements

The authors wish to acknowledge Shuji Miyamoto and Kanta Mori of Tokyo Denki University and Sayaka Hayagane of Obayashi Corporation for his contribution to the experiments.

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