Sulfide Corrosion by Sulphate-Reducing Bacteria in MX-80 Bentonites

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Abstract

In the safety assessment of the Spent Nuclear Fuel Final Disposal Program, the corrosion behavior of copper canister caused by the sulfide is an important issue. Bentonite is one of the engineered barrier materials adjoining the canisters to prevent the harmful substances from the outside to be in contact with the canisters; however, the corrosive sulfide could exist in bentonites, and corrosion of the copper canisters could happen. One of the important sources of sulfide comes from the sulphate-reducing bacteria (SRB) group, which live naturally in underground water and clays. When active, the bacteria will reduce sulfate and produce sulfide; therefore, the knowledge of the SRB sulfide production and canister corrosion mechanisms, and relevant tests should be developed.

One of the strong restrictions against the microbial activity is the swelling pressure of the bentonite, which is dependent on compacted density of it. The investigation of how well the SRB activity is inhibited by the increasing density of MX-80 bentonite is developed, and related works are done in progress. In addition, the diffusion experiments of sulfate are set up to obtain diffusion coefficients in the saturated MX-80 compacted bentonite.

1. Introduction

Sulphate-reducing bacteria (SRB) can obtain energy by oxidizing organic compounds or molecular hydrogen (H_2) while reducing sulfate (SO_4^{2-}) to hydrogen sulfide (H_2S). Sulphide is a very corrosive molecule that can corrode the copper canister; on the other hand, microbes can withstand harsh conditions generally, and it is no exception to SRBs: they are very common in deep soil and groundwater. Therefore, sulphide production and possible effects on the repository function must be considered in the safety assessment.

Due to the fact that sulphide is usually precipitated with ferrous iron, high concentrations do not occur in groundwater. In addition, its diffusive transport capacity is very low in bentonite buffer. Thus, sulphide formation must take place in the buffer, near the canister and be of considerable extent for corrosion to be a threat to canister integrity [1].

In the SR-Can safety assessment, the low limit of clay saturation density for microbial sulphide production was set at 1,800 kg/m^3, based on the experiments of microbial survivability. Microbial activity was assumed not to occur at densities above this limit [2].

Test of SRB activity against the change of buffer density is designed based on the previous work done by Swedish Nuclear Fuel and Waste Management Company (SKB) [3]. In the experiment, test cells are designed to hold the bentonite clay in a constant volume, with isolated and anaerobic environments. Different conditions of cells are set with different saturation density, different treatments of bentonite, and experiment time. In addition, the anaerobic SRB growth medium is used in saturation process. After saturation, radioactive tracers, $^{35}SO_4^{2-}$, is added at one side of bentonite clay, and copper disc is installed at another side. It is expected that $^{35}SO_4^{2-}$ is diffused through the bentonite clays and at the same time consumed by actived SRB to produce $^{35}S^{2-}$.when $^{35}S^{2-}$ is diffused and reaches copper discs, reaction occurs and Cux^{35}S is formed on the disc. When the cells are disassembled, the amount of $^{35}S^{2-}$ can be detected by radiation testing equipment. Using computer simulation program, evaluation of how microbial activity decreases as buffer density and swelling pressure increase will be obtained.

In addition, the diffusion experiments are set up to obtain apparent diffusion coefficients of sulfate in the saturated MX-80 compacted bentonite with different compacted density. The data, as a characteristic of sulfate in MX-80 bentonite, can be used in the SRB activity experiment as well as other related experiments. In this experiment, the diffusion cells are designed to hold the bentonite clay in a constant volume, and through-diffusion test is done with constant concentration in the both sides [4]. Based on the diffusion theory, the setting initial conditions and the boundary conditions, the apparent diffusion coefficients can be evaluated.

2. Materials and Methods

2.1 SRB activity experiment

In this experiment, six test cells are designed with the inside volume, a cylinder with 50 mm in diameter and 20 mm in height, and are set to seal bentonite clays (Figure 2-1). These cells are made of stainless steel 316, which has high corrosion resistant properties, for the purpose of limiting the interaction of sulfide and the cell inner wall. The test cell is consisted of a top lid, a bottom lid, a cylinder, and a piston. A tunnel through the piston is designed to link the cell with the air vacuum system, and the other tunnel through the bottom lid is designed to link with the water saturation system. Swelling pressure of bentonite can be monitored and recorded through the force transducer, which is set between the top lid and the piston, by a data logger. A 40 µm pore size stainless steel filter accompanied by a support disc and a copper disc with the same size are designed to be installed at the bottom lid.

Different conditions of cells are set, shown as table 2-1. Two different saturation densities of bentonite are prepared, 1,750 kg/m^3 and 2,000 kg/m^3, to verify how microbial activity decreases as bentonite density increases. In one set of three cells with same bentonite density, different experiment time, 47 days and 77 days, is designed; one cell is installed with sterilized bentonite as negative controls; others are pre-mixed with SRB.

In saturation process, the anaerobic SRB growth medium without lactate and sulfur is used. The recipe is shown as table 2-2. In consequence, clays in the cells are kept in the better surroundings for microbes, and rich of SRB. After saturation, the sulfur radiotracers $^{35}SO_4^{2-}$ and the copper disc will be added. First of all, the top lid is unscrewed, and the piston is removed from the cells. $^{35}SO_4^{2-}$ is added at the surface of clays by pipette, with the concentration and the points of addition recorded. Secondly, the bottom lid is unscrewed, filter and support disc are removed, and the space is replaced with a cleaned copper disc with the same size. Finally, the test cell is reassembled, and the screws are adjusted to keep the swelling pressure same as the recorded pressure when the test cell is opened.

After several days, based on the settings, the test cells are disassembled. The copper discs are removed from the bottom lids and carefully washed. Using radiation testing equipment, radioactivity counts and the distribution at different points of the disc can be gained with final amount of the sulfur tracers, which is adjusted for the half-life of the ^{35}S isotope (87.4 days).

A computer program will be used to simulate the diffusion and the reactions of the sulfur tracers. In the program model, space of the clay will be divided into serval parts, and concentrations of $^{35}SO_4^{2-}$ and $^{35}S^{2-}$ at each small space. With the simulation of a short time interval, molecules will diffuse to adjacent space, and in each space, $^{35}SO_4^{2-}$ will be reduced into $^{35}S^{2-}$ by SRB. By iterative calculations, complete experiment time can thus be simulated through accumulations of each computed short time interval. The diffusion process is computed with Fick's law [5], shown as below; sulfate reduction rate is computed as equation below.

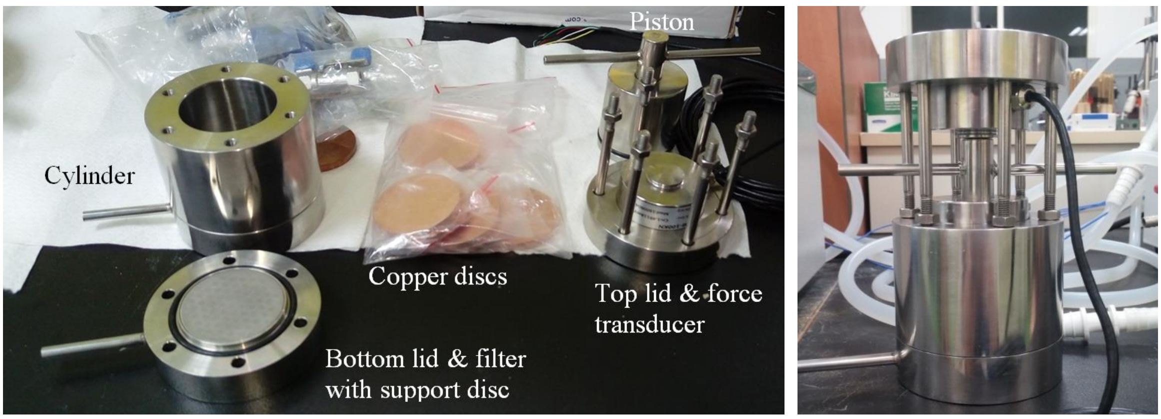


Figure 2-1 Left: Exploded view of the test cell. Right: Assembled form of the test cell.

Table 2-1 Setting conditions of each test cell

saturation density (kg/m^3)	Bentonite clays treatment		
	sterilized	pre-mixed with SRB	
1,750	Cell 1	Cell 2	Cell 3
2,000	Cell 4	Cell 5	Cell 6
Experiment Time (day)	77	47	77

Table 2-2 SRB growth medium for saturation

composition	amount
Analytical grade water	1,000 mL
NaCl	7.0 g/L
$CaCl_2 \cdot 2H_2O$	1.0 g/L
KCl	0.67 g/L
NH_4Cl	1.0 g/L
KH_2PO_4	0.15 g/L
$MgCl_2 \cdot 6H_2O$	0.5 g/L

$$m' = \Delta C \times D \times A/d \text{ (Fick's law)} \quad (1)$$

m' = transport rate (mol/s)
ΔC = concentration difference (mol/m^3)
D = diffusion coefficient (m^2/s)
A = boundary area between two adjacent space (m^2)
d = distance between space centers (m)

$$dSO4Red = RedRate \times V \times dT \quad (2)$$

dSO4Red = amount of reduced SO_4^{2-} to S^{2-} during a time interval (mol)
RedRate = SO_4^{2-} reduction rate (mol/m^3 s)
V = volume of a small space (m^3)
dT = time interval (s)

In consequence, with the simulation conditions same as the experiment, when proper reduction rate is chosen, result amounts of the $^{35}S^{2-}$ at the bottom space of the clay will match the results gained on the copper disc. Illustrations of concept of the model are shown as figure 2-2. Using computer programs to simulate the diffusion of sulfate tracers and the reduction of $^{35}SO_4^{2-}$ to $^{35}S^{2-}$ done by SRB, and then comparing the resulting amounts of $^{35}S^{2-}$ at the copper side with amounts found in the experiment, reduction rates can be calculated.

2.2 Diffusion experiment of sulfate

In this experiment, the diffusion cells are designed to hold the bentonite clay in a constant volume, a cylinder with 50 mm in diameter and a fixed height based on the chosen porous supports (Figure 2-3). These cells are made of Polytetrafluoroethylene (PTFE), which has high corrosion resistant properties, for the purpose of limiting the interaction of salt and the cell inner wall. The diffusion cell is consisted of 2 opposite reservoirs; changeable porous supports with different length; a central cylinder. Bentonite can be compacted directly in the central cylinder. After compaction, a filter paper and a stainless steel filter is installed at each side of the bentonite clays, and porous supports with proper size is installed to fill the rest of the space of the central cylinder.

(a)
(b)
(c)

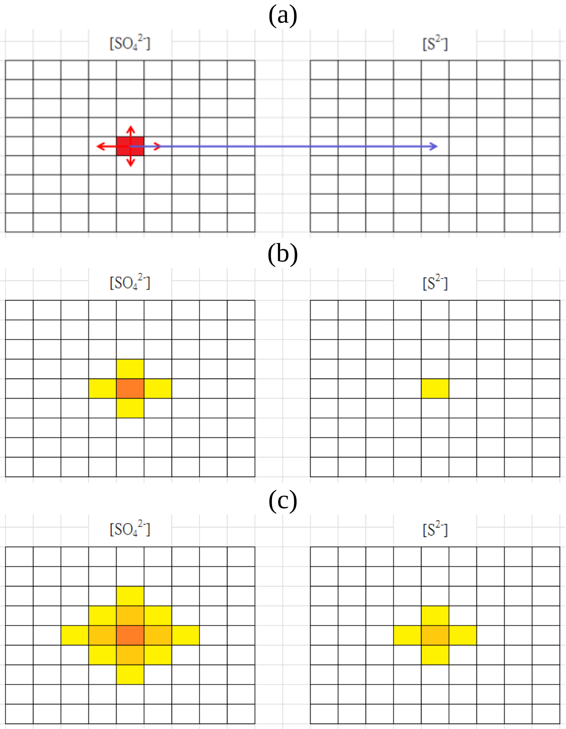
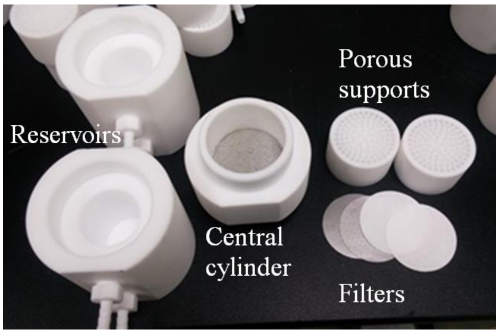


Figure 2-2 Illustrations of concept of the model. (a) Initial concentration contribution. Red arrows represent the transportation through diffusion; blue arrow represents SO_4^{2-} reduction. (b) Concentration contribution after a time interval. (c) Concentration contribution after another time interval.

Through-diffusion with constant concentration in both sides is adopted as the experimental method [4]. Based on the diffusion theory, using Fick's 2nd law, considering 1-D unsteady state diffusion, the initial condition and the boundary conditions, the concentration profile can be determined. Expression of the cumulative mass of diffused solute verse diffusion time is shown as figure 2-4. When the system reaches steady-state conditions, the expression can be simplified, and the diffusion coefficient can be calculated from the slope of the straight line fitting in the steady-state region on the figure. The intercept of fitting line with the time axis is denoted as time-lag (t_e) [6]:



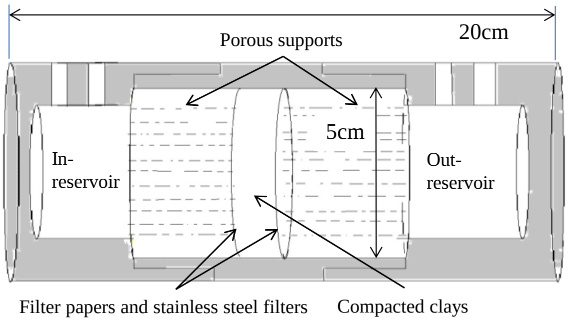


Figure 2-3 Left: Exploded view of the diffusion cell. Right: Assembled diagram of the diffusion cell.

$$D_a = d^2/6t_e \quad (3)$$

D_a = apparent diffusion coefficient
d = thickness of the clay
t_e = time-lag

The dimensionless time can be used for evaluation of experiment time [6]:

$$t_d = D_a t/d^2 \quad (4)$$

t_d = dimensionless time
D_a = apparent diffusion coefficient
d = thickness of the clay
t = experiment time

When t_d reaches 0.45, the system can be seen reaching steady state at referring experiment time. Distilled water is used to fill both reservoirs and circulated to saturate the clay. Saturation process takes about 30 days to ensure the full saturation of clays, as well as for the dissolution of small amounts of resident sulfate in the clays to some extent. After saturation process, the solution at in-reservoir is replaced with sodium sulfate solution with concentration of 0.1M. Then the in-reservoir is linked with the container which has a large volume of solution (4L), and a pump is used to circulate the solution to minimize the concentration change; in the

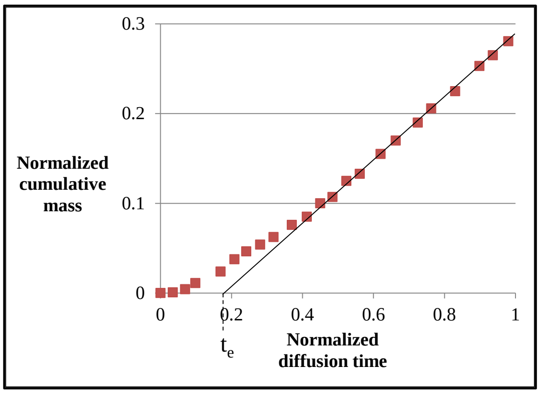


Fig 2-4 Normalized cumulative mass of diffused solute verse normalized solute diffusion time. Time-lag can be gain by the fitting line at the steady-state region.

out-reservoir, the solution is sampled and changed periodically to maintain the concentration near to zero. Experiment time lasts no less than the expected time to reach steady state for each cell.

3. Results and Discussion

3.1 Results of SRB activity experiment

Several instruments and standard operating procedures have been being established including the testing of six test cells, compaction method of bentonite clays, chemical cleaning process of copper disc, and the detection method of tracers on the copper discs using white image plate, etc.

Incubation of microbes is done by Nuclear Science and Technology Development Center at National Tsing Hua University, Taiwan. Three different species of SRB is chosen following the experiments done by SKB[3], *Desulfotomaculum nigrificans* (DSM 574) *Desulfosporosinus orientis* (DSM 765) and *Desulfovibrio aespoeensis* (DSM 10631), and are well cultivated following the instructions by German Collection of Microorganisms and Cell Cultures (DSMZ). Method of pre-mixing bentonite clays with SRB before compaction is established as well.

The saturation process is carefully test to maintain the system inside the cell in anaerobic conditions. First of all, all of the cells and the tubes in the experiment are sterilized before use. The compacted bentonite clays, a cylinder with 50 mm in diameter and 20 mm in height with different setting, are installed in the cells. The cells are assembled with the filters and support discs installed at bottom lids and linked with air vacuum system and water saturation system. Secondly, through the tunnels at the piston side, the cells are flushed by nitrogen, and then evacuated to < 10 Pa using a vacuum pump. This process is repeated several times in order to remove all O_2 in the system, and then the cells are kept at evacuated state. Finally, saturation medium (Table 2-2) is injected through the tunnels at the bottom side. A gas pressure of around 2 bars is added to a pressure-converted container made of stainless steel, and through a piston in the container, medium is pushed into the cells. Saturation process will lasts until the monitored swelling pressure reaches the Theoretical value, which depends on the clay density.

In addition, for the purpose of testing the experimental procedures, a blank test is done using bentonite clays with no extra treating, and saturated with distilled water. Experiment can start once all the procedures are set up completely.

3.2 Results of diffusion experiment

Two diffusion cells are installed with different conditions of compacted MX-80 bentonite clays, in consideration of the time each system takes to reach steady state. Settings of bentonite clays are shown as table 3-1. After experiment, samples are analyzed using ion chromatography system to detect the concentration of sulfate. Results are shown as figure 3-1.

The calculation results are shown as table 3-2. The resulting apparent diffusion coefficients are closed to other studies using similar situations [7].

4. Conclusions

In this report, instruments and procedures of the SRB activity experiment are introduced. The test cell is designed to seal the saturated clays pre-mixed with the well-incubated SRB in the anaerobic conditions; sulfur tracers $^{35}SO_4^{2-}$ are used as the reactant of microbial reduction reaction; computer programs are used to simulate the experiment and calculate the microbial activities. Related standard operating procedures have been being established.

Diffusion experiment of sulfate is done using two settings with different saturation density and thickness of the bentonite clays. Method of through-diffusion with constant concentration in both sides, and related initial and boundary conditions, are used in the experiment, and apparent diffusion coefficients are calculated using diffusion theories; the results are closed to other studies using similar situations. Further studies with this experiment will include uncertainty analysis, sensitivity analysis and the replication experiments.

Table 3-1 Settings of bentonite clays in diffusion experiment of sulfate.

Cell No.	Clay thickness (cm)	Clay saturation density (kg/m^3)	Estimated time to reach steady state (day)
1	0.5	1,750	10
2	0.25	2,000	15

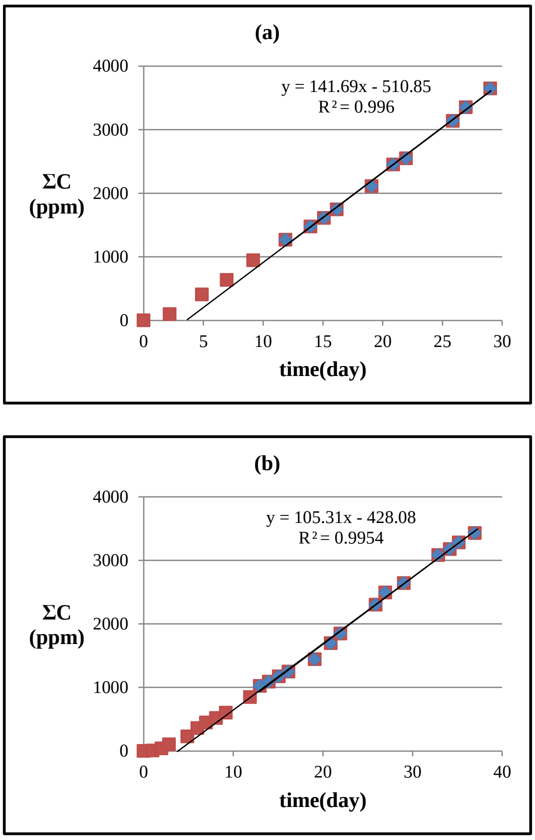


Figure 3-1 Cumulative concentrations of diffused sulfate verse diffusion time. (a) Cell No.1. (b) Cell No.2.

Table 3-2 Results of diffusion experiment of sulfate.

Cell No.	1	2
Clay saturation density (kg/m^3)	1,745	2,004
Time to reach steady state (day)	9.73	10.97
d (m)	0.00485	0.00215
t_e (day)	3.60	4.07
D_a(m^2/s)	1.26×10^{-11}	2.19×10^{-12}
D_a(theoretical value) (m^2/s)	1.2×10^{-11}	2×10^{-12}
Error	4.88%	9.68%

5. References

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