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A long-term corrosion measurement of copper materials

Minsoo Lee*, Heui-Joo Choi, Jong Won Choi, Ji Hyeon Lee
Korea Atomic Energy Research Institute, 150 Deokjin-dong, Yuseong, Daejeon, 305-353 Korea
*Corresponding author: minm@kaeri.re.kr

1. Introduction

Copper is well known for its high corrosion resistance in natural environment, because it has a very strong oxide film on its surface to prevent a further oxidation from an environmental oxidant [1]. Thus we have a plan to use copper as a canister material on a HLW disposal plan of KAERI. Generally the disposal canister has to be huge to contain a whole assembly of spent nuclear fuels. The value is less than 1 um/yr in a natural environment according to previous reports [2]. Therefore only a 10 mm thickness is enough for the design of a Cu canister with ten thousand years validity. But a thin-walled copper canister with a large radius is hard to make mechanically because of its native flexibility.

To make a thin-walled copper canister, we adopted a cold spray coating (CSC). The merit of this technique is that the coating layer is rigid, easy to control regarding its thickness, and free from an oxidation.

To confirm that the CSC copper is suitable for a disposal canister, it is necessary to measure the corrosion rate of it at a real underground environment. A disposal canister will be placed in a 500 m underground rock hole and surrounded by a compacted Bentonite which minimizing the intrusion of a underground water. Korean underground water serves as a reductive condition and has little oxidants. Therefore a long-term corrosion test is essential for the measuring of the corrosion rate because of a harsh corrosion environment.

To perform a long-term corrosion test, we tried a laboratory test at small scale first using underground water from KURT (KAERI Underground Research Tunnel). The module is composed of a copper specimen, two compacted Bentonite blocks, a Ti vessel, and sealed glass bottle with underground water. Besides, the swelling pressure of compact Bentonite in the module was measured to justify a corrosion condition. But in laboratory test, it is hard to sustain an oxygen-free condition like an underground for a long period since the outside oxygen is slowly diffuse in the test module constantly through the barrier. To solve that, we designed and set up a long term corrosion apparatus for the field test at KURT. And the preliminary operation is now underway at KURT.

2. Experiment

The used copper materials were summarized in Table 1. The Cold sprayed Coppers were #2 and #3, and the common coppers were #4 and #5 from an extrusion and forging respectively. The copper specimen had 15 mm in diameter and 1mm in thickness. And a specimen surface was polished with a No.2,000 sand paper and finished with a 0.3 μm alumina slurry and its surface area was about 400mm^2.

Table 1. Characteristics of copper specimens.

Number	Description	Density (g/cm^3)	Oxygen content (%)
#2	Tafa on Stainless steel 304	8.90	0.019
#3	Changsung on Nodular Cast iron	8.72	0.32
#4	Extruded Copper	8.86	0.065
#5	Forged Copper	8.9*	0.06*

* Estimated value from a extruded copper

As a buffer material, a Ca-type Kyeungjoo Bentonite was used. The Bentonite was compacted using a press into a dry density of 1.6 g/cm^3, which size was about 30 mm in a diameter and 10 mm in a height.

And the used underground water was from a 100m deep aquifer at KURT. Its pH was 8.1 and oxygen content was 0.02 mg/L. The impurities in the water were summarized in table 2. The main contaminant was a carbonate. And it had 6.96 mg/L of SO_4^{2-} and 2.18 ml/L of Cl^- which are likely to be a strong oxidant for copper in an underground environment.

Table 2. Principal impurities in KURT underground water.
(Unit: mg/L)

Na	K	Ca	Mg	SiO_2	Cl^-
16.5	0.38	17.2	1.72	41.3	2.18
SO_4^{2-}	NO_3^-	F^-	HCO_3^-	CO_3^{2-}	
6.97	0.23	3.41	78.4	0.00	

We made a corrosion module simulating a real underground disposal condition (Figure 1). A copper specimen was placed between two compact Bentonite blocks. And then, those blocks are put in a Ti vessel. The inner dimension of it was adjusted to the volume of two blocks. The closing of Ti vessel was done by screw-type caps on both sides, which had several holes on them together with porous Ti filter. The assembled vessel was put in a glass bottle together with 350 ml underground water. Then the glass bottle was sealed and stored in a 70^{o}C environmental chamber for several months.

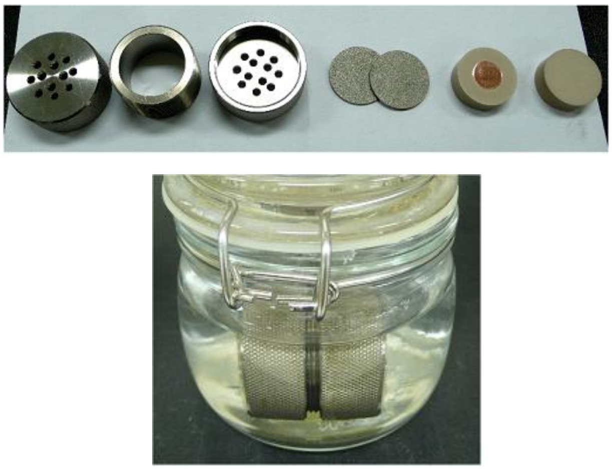

Figure 1. The module of a copper corrosion test.

Finishing a corrosion test, the module was dissembled and Ti vessel was dried for 1 day because it is hard to remove the closing cap at a Bentonite-swelled condition. The specimen was cleaned by a 2.5wt% HCl solution to remove the rust on its surface, and we calculated the corrosion rate from a weight measurement (Figure 2).

Figure 2. Copper specimen after a 9 month corrosion test.

Figure 3 shows the test result during 9 months. The #3 copper showed highest corrosion rate comparing with the others, but the value is much low that it could withstand for above million years. This test was scheduled for 2 years at a laboratory, so it is still ongoing.

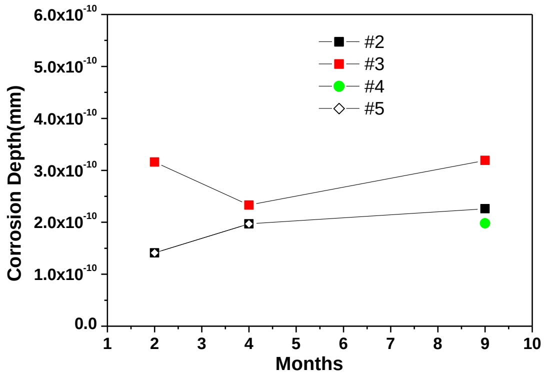

Figure 3. Copper corrosion depth using an underground simulated module.

3. Conclusions

From the simulated long-term corrosion test, we could understand the corrosion rate of a CSC copper was low enough to meet our requirement. Based on the laboratory long-term test, currently we have another plan to perform a KURT field test of it because the laboratory environment is somehow apart from real environment. Our final aim is evaluating the life time of a copper canister for a safe disposal of a high level radioactive waste.

Acknowledgement

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