# Investigation of corrosion behaviours of high level waste container materials in simulated groundwater in China

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Appropriate high level radioactive waste container materials in China are still under investigation. The corrosion behaviours of four types of materials (carbon steel Q235, aluminium alloy 2024, copper and stainless steel SUS 304) in simulated groundwater at room temperature were investigated. The corrosion rate was measured through the weight loss method. The chemical composition of corrosion product films formed on the surface of materials was investigated by means of X-ray diffraction and energy dispersive X-ray spectroscopy. The results showed that there was no crevice and pitting corrosion for carbon steel after one year of immersion; the corrosion was dominated by general corrosion, the composition of the corrosion product film being mainly $\gamma$-FeOOH, as well as $Fe_3O_4$. Copper underwent slight crevice corrosion, but aluminium alloy 2024 suffered serious localised corrosion. No corrosion was observed on stainless steel SUS 304. The presence of oxygen promoted crevice corrosion of copper and aluminium alloy 2024.

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## Introduction

Nuclear power as a clean and efficient energy source is widely used in many countries. China, as a developing country, started its nuclear industry relatively late. China announced its first nuclear power plan in 1970, and the first nuclear engineering research and design institute was founded in Shanghai.[1] China's first nuclear power reactor was connected to the grid at Qinshan Nuclear Power Plant in 1991. At present, China has 15 running nuclear power units spread out over six separate sites, accounting for 2% of current power generation in China. There are another 26 units under construction. The percentage of China's electricity produced by nuclear power is expected to rise from the current $\sim 2\%$ to 6% by 2020. This will require the current installed capacity of 13·8 GW to be increased to 80·6 GW.

The use of nuclear energy produces a large amount of high level radioactive waste (HLW); how to deal with this nuclear waste has raised security concerns and restricted the development of nuclear energy. The generally accepted strategy for dealing with HLW is deep underground burial in stable geological formations.[2] Since 1985, China has chosen deep geological disposal as the main approach by which to address the HLW issue. According to the preliminary siting criteria, five regions were identified as pre-selected regions for China's HLW repository: southwestern region, eastern region, inner Mongolia region, southern region and northwestern region. After years of investigation and debate, the northwestern region located in the Gobi Desert area is expected to be the first site for China's HLW repository, due to its several advantages, such as low population density, low precipitation, no earthquakes, favourable hydrogeological conditions, etc.

The container is one of several barriers to the release of radioactive products to the environment. The container provides the primary anticorrosion protection as well as some structural support for the waste package. Based on the particular geological conditions, different countries choose different materials as packaging containers. Table 1 shows a list of different types of repository design for HLW in different countries.[3,4] Carbon steel, cast iron, stainless steel, copper and titanium, as well as Ni based alloy, have been chosen as candidate materials of packaging containers for geological disposal in different countries. China's nuclear waste packaging material has not been determined. It is necessary to evaluate the in-service behaviour of different materials in underground conditions in the northwestern region of China. Corrosion, especially localised corrosion, such as crevice or pitting corrosion, is the main damage which limits the lifetime of a container. Crevice corrosion may occur due to contact of the packaging container with other objects and the presence of deposits, corrosion products, etc.[5]

The aim of the work reported here has been to research the crevice corrosion behaviours of four kinds

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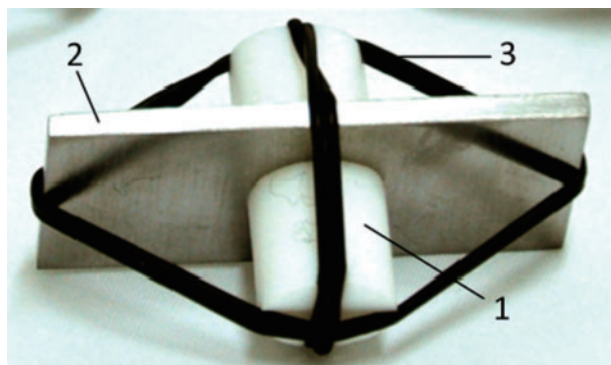
*1* PTFE; *2* metal; *3* low-sulphur rubber ring
**1 A view of crevice sample for immersion test**

of materials in simulated groundwater in the north-western region of China, with the objective of providing a basis for the selection of materials for the construction of HLW containers in China.

## Experimental

Four kinds of materials were used. Their chemical compositions were as follows (wt-%): carbon steel Q235 (C 0·36, Si 0·08, Mn 0·41, P 0·36, S 0·009, N 0·05, Fe bal.), aluminium alloy 2024 (Cu 3·8–3·9, Mg 1·2–1·8, Mn 0·3–0·9, Fe $\geq$0·3, Si $\geq$0·2, Zn $\geq$0·1, Al bal.), stainless steel SUS 304 (C $\leq$07, Mn $\leq$2·0, Ni 8·0–11·0, Si $\leq$1·0, P $\leq$0·035, S $\leq$0·030, Cr 17·0–19·0, Fe bal.) and pure copper. Samples were machined into dimensions of $50 \times 25 \times 3$ mm. Before the experiments, the sample surface was mechanically polished by silicon carbide paper progressively up to 150 grit. After drying in hot air, samples were weighed and then stored in a desiccator. The immersion experiments were conducted according to Chinese standard GB/T10127-2002 (ferric chloride crevice corrosion test of stainless steel). A crevice sample was created by a sample plate and two cylinders of polytetrafluoroethene, as shown in Fig. 1. Three samples were run for each experiment.

The chemical composition of the immersion solution simulating the groundwater in the northwestern region of China is shown in Table 2. The pH value of the solution was adjusted with $H_2SO_4$ to 7 before the immersion tests. The immersion tests were performed for one year at room temperature. After the immersion tests the pH value was about 7·8. In order to simulate
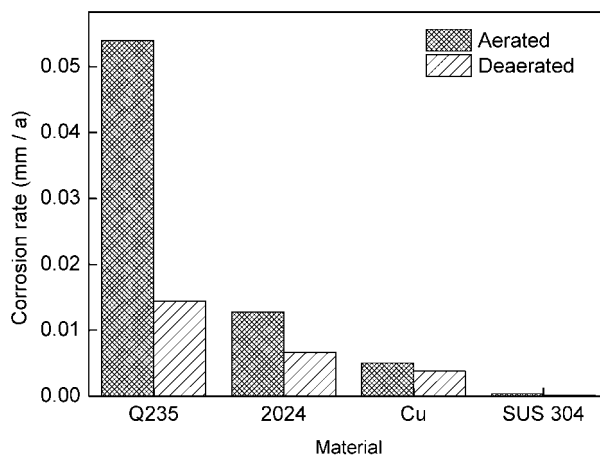


**2 The corrosion rates of the four materials**

the deaerated conditions at the later geological disposal stage and to study the effect of oxygen, the solution was divided into oxygen-containing solution (hereafter referred to as aerated) and solution from which the oxygen had been removed (deaerated). The deaerated solution had been deoxygenated by purging with nitrogen gas for 1 h.

After the immersion experiments, X-ray diffraction and energy dispersive X-ray spectroscopy analyses were employed to determine the composition of corrosion products. The corrosion rates were measured by the weight-loss method. The corrosion products were removed completely, using different solutions, as follows: carbon steel Q235, 500 mL HCl+500 mL $H_2O$+20 g $C_6H_{12}N_4$; aluminium alloy 2024, $HNO_3$; Cu, 500 mL HCl+500 mL $H_2O$; SUS 304, 100 mL $HNO_3$+900 mL $H_2O$. The crevice corrosion depth was measured by a Dektak 150 Surface Profiler.

## Results and discussion

### Corrosion rate

Figure 2 shows the corrosion rates of the four materials immersed in the simulated groundwater at room temperature. It can be seen that the presence of oxygen increased the corrosion rate. The corrosion rate of Q235 was the greatest, followed by 2024, Cu and SUS 304. Normally, a dense layer of oxide film can form on the surface of copper, 2024 and SUS 304, and provide protection to the substrates, so the corrosion rates of

**Table 1 Different types of repository design for HLW in different countries**

| Country | Geologic formation | Type of environment | Container materials |
|---|---|---|---|
| Japan | Granite | Bentonite and sand | Carbon steel, copper over packs |
| Korea | Plutonic rock | Bentonite, sand | Copper or stainless steel on carbon steel |
| Finland | Crystalline | Bentonite, crushed rock | Copper on cast iron |
| Sweden | Crystalline bedrock | Bentonite | Copper on cast iron |
| USA | Unsaturated volcanic tuff | Unsaturated (dry) | Ni–Cr–Mo alloy type 316SS |
| Canada | Granite | Bentonite, sand, crushed rock | Titanium, copper |
| Spain | Granite or clay | Bentonite | Carbon steel |
| Switzerland | Crystalline and clay | Bentonite | Steel |

**Table 2 Chemical composition of immersion solution**

| Component | $Na^+$ | $K^+$ | $F^-$ | $CO_3^{2-}$ | $NO_3^-$ | $Ca^{2+}$ | $Mg^{2+}$ | $Cl^-$ | $Br^-$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Concentration/mg L$^{-1}$ | 1027 | 16·1 | 1·9 | 138 | 30·2 | 206 | 51·2 | 1155 | 0·057 | 1074 |
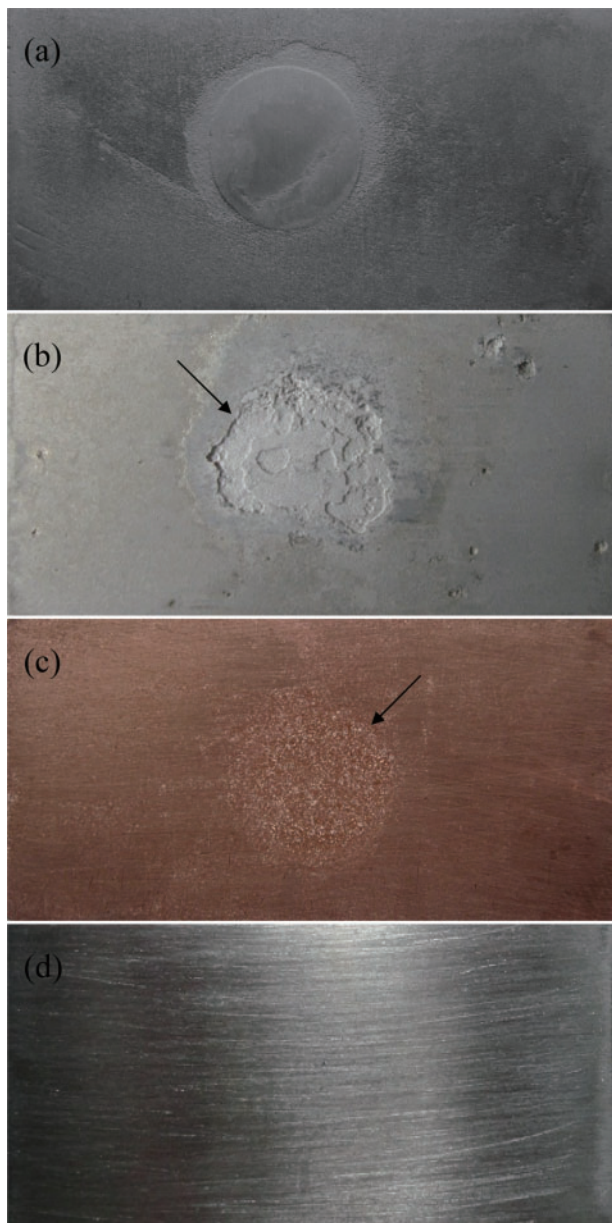
*a* Q235; *b* 2024; *c* Cu; *d* SUS 304
3 **Surface morphologies of the substrates after immersion in the aerated groundwater for one year**
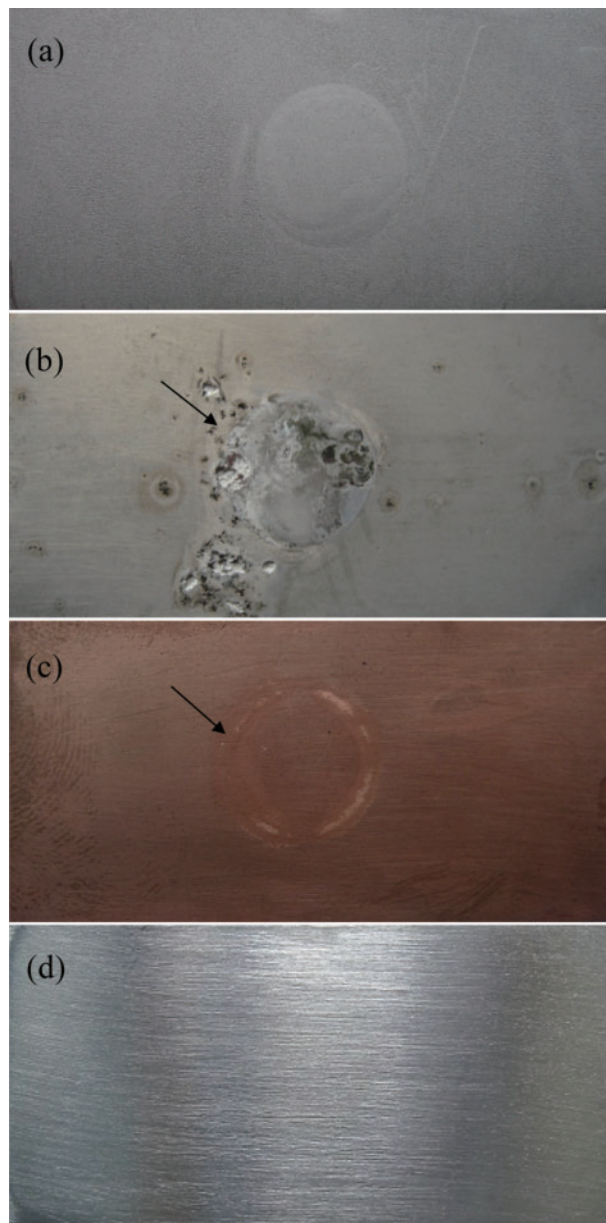


*a* Q235; *b* 2024; *c* Cu; *d* SUS 304
4 **Surface morphologies of the substrates after immersion in the deaerated solution for one year**

these materials were significantly smaller than that of the carbon steel Q235.

## Surface morphology and crevice depth

The surface morphologies of the materials after corrosion product removal are shown in Fig. 3. These samples were immersed in the aerated solution for one year. No localised corrosion was observed inside and outside of the crevice on carbon steel Q235. A higher inside and lower outside step indicated that crevice corrosion had not occurred on Q235. This phenomenon implies that the inside of the crevice was protected by polytetrafluoroethene and the acidification inside the crevice was not serious. On the contrary, both aluminium alloy 2024 and copper underwent obvious crevice corrosion. The average crevice depths on 2024 and copper were 0·302 and 0·0261 mm, respectively. The surface of SUS 304 was observed to lack any damage.

The corrosion behaviours of the materials in the deaerated solution were similar to those in the aerated condition, as shown in Fig. 4. No crevice corrosion was observed on Q235 and SUS 304, whereas aluminium alloy 2024 and copper underwent crevice corrosion. The greatest depths of crevices on aluminium alloy 2024 and copper were 0·153 and 0·00639 mm, respectively. From a comparison with the results shown in Fig. 3, it can be concluded that the presence of oxygen promoted the development of crevice corrosion of aluminium alloy 2024 and copper.

## Analysis of corrosion products at the edge of crevices

Figure 5 shows the surface morphologies with corrosion products of the four materials after one year of immersion in the aerated solution. It can be seen that the corrosion product scale on Q235 was composed of two layers at the edge of the crevice. The colour of the outer layer was yellow and that of the inner layer was black. Energy dispersive X-ray spectroscopy analysis showed that both the outer and inner layers of corrosion product contained
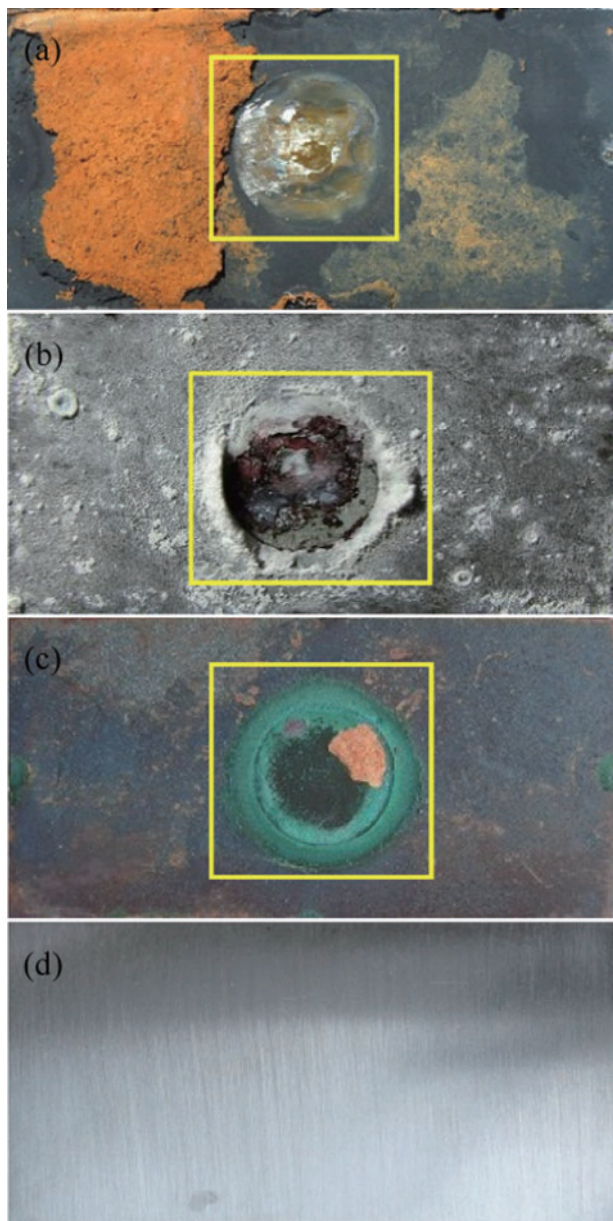
*a* Q235; *b* 2024; *c* Cu; *d* SUS 304

**5 Morphologies of the corrosion products on the four materials after one year immersion in the aerated solution**
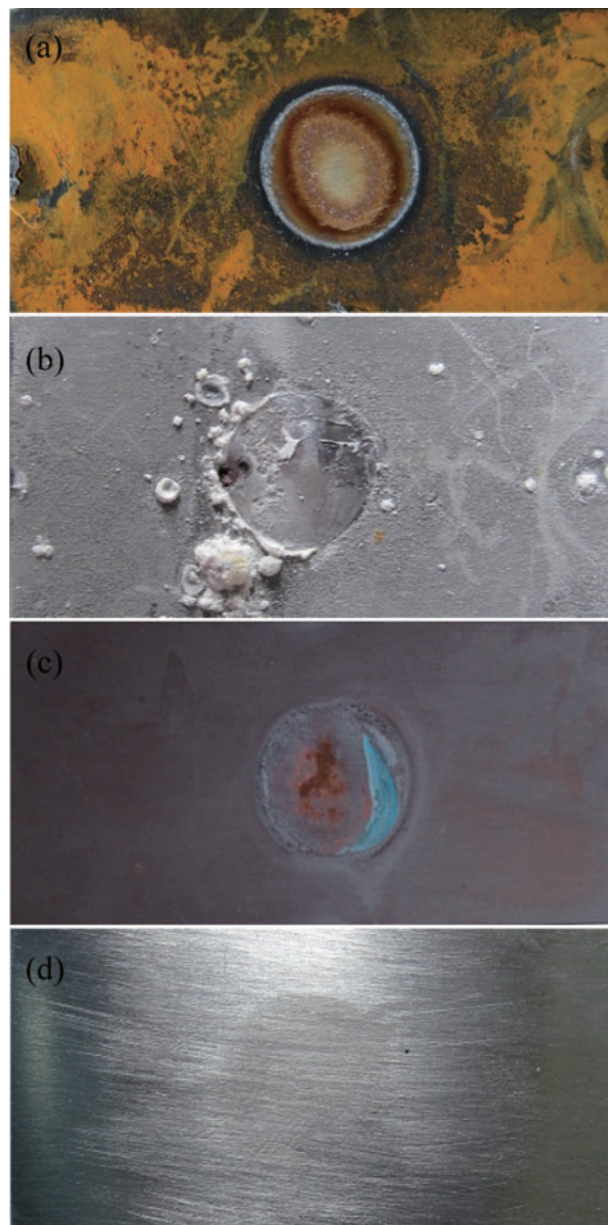


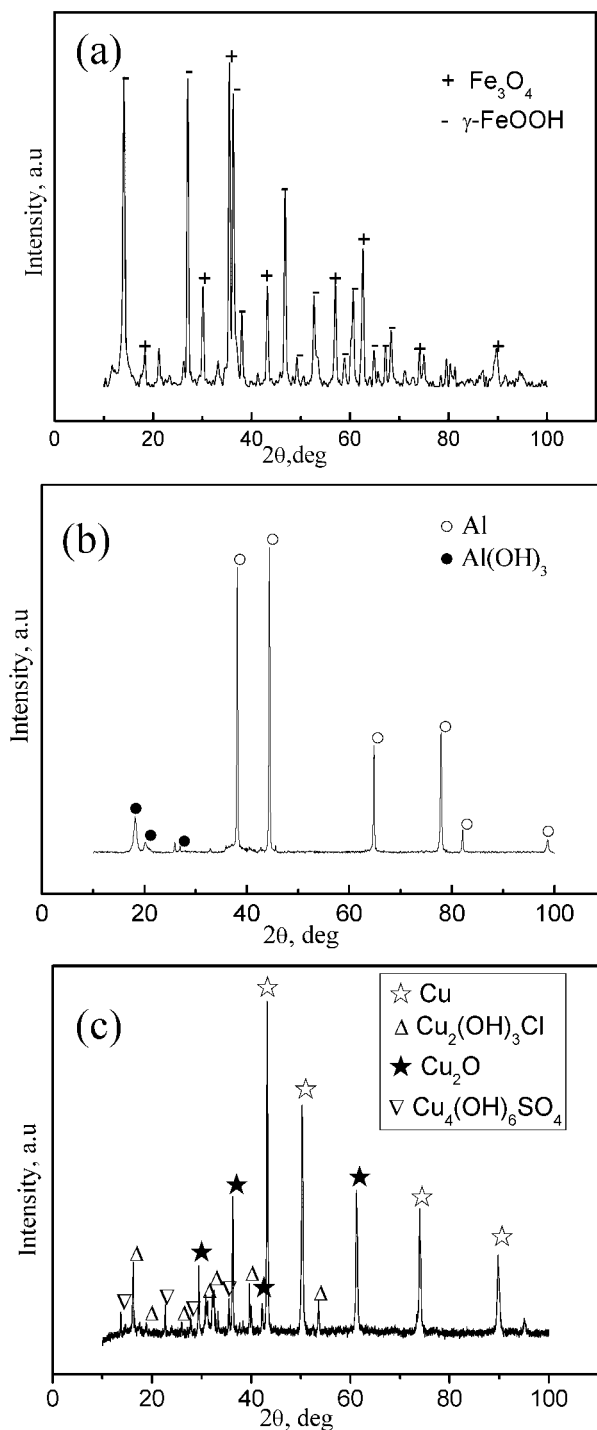*a* Q235; *b* 2024; *c* Cu; *d* SUS 304

**6 Morphologies of the corrosion products on the four materials after one year immersion in the deaerated solution**

Fe and O. At the crevice edge of 2024 there was a large amount of white corrosion product accumulated, which was dominated by two elements, Al and O. The corrosion product scale of copper exhibited a green colour at the crevice edge. Energy dispersive X-ray spectroscopy analysis showed that the green corrosion product contained Cu, O, Cl and S. Macro-corrosion product scale was not observed on the surface of SUS 304.

Energy dispersive X-ray spectroscopy analysis of the corrosion products formed on the four materials after immersion in the deaerated solution shown in Fig. 6 indicated that the compositions of corrosion products at the edge of crevices were the same as those formed in the aerated solution. These results imply that the oxygen did not change the composition of the corrosion product films.

The corrosion products inside the boxed sections in Fig. 5 were analysed by X-ray diffraction and the results are shown in Fig. 7. The yellow corrosion product on

Q235 was $\gamma$-FeOOH and the black corrosion product was $Fe_3O_4$. The white corrosion product on alloy 2024 was $Al(OH)_3$. $Al(OH)_3$ has colloidal properties and, when positively charged, it has been proven that the corrosion of aluminium is associated with it.[6] $Al(OH)_3$ attracts more anions from the bulk solution to the interior of the crevice that promotes the corrosion process of the metallic surface inside the crevice. The crevice corrosion mechanism of alloy 2024 is consistent with that of an oxygen concentration cell. That is, anodic dissolution of Al can cause a rise of anion concentrations inside the crevice, leading to hydrolysis of metal chloride and localised acidification inside the crevice, resulting in accelerated corrosion.[7] The corrosion product of copper was composed of $Cu_2O$, $Cu_2(OH)_3Cl$ and $Cu_4(OH)_6SO_4$. The green corrosion product on the crevice edge on copper was loose and porous, which can easily cause localised corrosion, so

a Q235; b 2024; c Cu
**7 XRD analysis of corrosion products after one year of immersion at room temperature**

the crevice corrosion of copper was observed.[8,9] SUS 304 contains alloying elements which cause surface passivation and improve its corrosion resistance. In this study, no crevice corrosion of SUS 304 was observed after one year of immersion in the simulated groundwater, which may imply that SUS 304 has a long crevice corrosion incubation period.

## Conclusions

This paper investigated the corrosion behaviours of four kinds of materials after one year of immersion at room temperature in a solution simulating the groundwater in the northwestern region in China, in order to provide primary data relating to the selection of container materials for HLW disposal in China. Results of the investigation are as follows.

1. Q235 did not undergo pitting and crevice corrosion. Only uniform corrosion was observed and the corrosion products were mainly $\gamma$-FeOOH and $Fe_3O_4$.

2. Copper underwent slight crevice corrosion; 2024 suffered serious crevice corrosion.

3. The crevice corrosion incubation period of SUS 304 was more than one year.

4. The presence of oxygen promoted the process of crevice corrosion of aluminium alloy 2024 and copper.

## Acknowledgement

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