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INVESTIGATION ON CORROSION BEHAVIOR OF HIGH-LEVEL WASTE CONTAINER MATERIALS

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ABSTRACT

The proper high-level waste container materials in China are still under research. In the consideration of availability of carbon steel and low-alloy steel, the corrosion behaviors of four kinds of commercial steels in simulated groundwater of Beishan, a candidate place for the geological disposal of high level waste in china, were investigated (which is the preselected area for building geologic disposal repository to store high-level nuclear waste) groundwater in the presence of different immersion time, temperature and oxygen content. The morphology and chemical compositions of corrosion products were investigated by means of Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) and Energy Disperse Spectroscopy (EDS). The corrosion behaviors of these four steels were compared, and the most potential candidate steel based on the present immersed corrosion test results was recommended.

1. Introduction

At present, many countries have investigated the selection of high-level waste (HLW) container materials, and corrosion behaviors and mechanism of them in contact with potential disposal environments (*e.g.* salt, clay and granite). The design of different containers for HLW would vary according to the nature of the geologic formation at the site of the repository. It has been researched widely that carbon steels, stainless steels, nickel-based alloys, titanium-based alloys and copper can be potential container materials for particular host rock formations. The results indicate that Ti99.8-Pd is the primary choice for the thin-walled corrosion-resistant material in salt rock; stainless steels, Ni-based alloys and Ti-based alloys are the most important candidate materials for thin-walled containers in clay environment; copper containers provide an excellent corrosion barrier in granitic environments; and carbon steel is considered the main choice for the thick-walled corrosion-allowance concept in granite and salt rock [1-3].

The waste container sometimes may be a single vessel, but most programs generally call for concentric double walled vessels of dissimilar metals. Table 1 shows a list of nations, the intended geologic formation, the type of environment, and the current proposed design for the containers [2].

China has planed to build a HLW geologic disposal repository in Beishan, Gansu province, in where the preselected geological formations of granite are distributed in a large area. Beishan is a typically arid area and rainfall usually happens in June, July and August by rainstorm, which is relatively favorable for recharging groundwater [4]. The main type of groundwater in this area is bedrock fracture water. The recent researchers of the preselected area are mainly about hydrology, the characteristics of granite, seismic geological environment, structural geology, and engineering geology and so on [5]. China preselects benonite as backfill material to delay the release of radionuclides to the environment and retard the diffusion of oxygen towards the containers. The suitable materials of HLW containers for Beishan' disposal environments are shifting through numerous materials. According to the selection of Sweden, Spain, Korean and Japan which have the similar disposal environment (the geological formations of granite and backfill material of benonite) and choose steels as one of the important candidate materials, it is necessary to research the corrosion behaviors of steels in Beishan underground environment. Based on previous comprehensive corrosion studies on a wide range of materials [6-9], carbon steels were identified as promising for the manufacture of long-lived containers.

Table 1 Different Types of Repository Design Mainly for HLW [2]

Country	Geologic Formation	Type of Environment	Current Materials Container
Japan	to be determined	Bentonite and Sand	Carbon Steel, Copper overpacks
Korean	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

This paper aims at researching the corrosion behaviors of four kinds of steels in simulated Beishan groundwater in the presence of different immersion time, temperature and oxygen content. In consideration of the change of the HLW disposal in initial and later stages, room temperature and 90℃ were studied. This work intended to offer the evidence report of the selection of container materials for Beishan disposal repository.

The four kinds of steels which are chosen in this paper are popular for the commercial using in China as structure materials and the cost of them is low, which are the reasons of choosing them as test subjects.

2. Experimental procedure

2.1 Materials and solutions

A kind of carbon steel, E235B and three kinds of low alloy steel sheet, E355CC, Corten A and Corten B were used in this study. Table 2 shows the compositions of all steels. The size of specimen was 50 mm in length, 25 mm in width, and 3 mm in thickness. Prior to the experiment, the specimens were ground with wet silicon carbide paper to 150 grade, degreased with acetone, cleansed with distilled water and dried in a compressed hot air flow. The specimens were immersed into the simulated Beishan groundwater whose composition was shown in Table 3. All the corrosion tests were performed in the solution that was refreshed weekly during long term measurements.

Table 2　Compositions of four kinds of steels

	Chemical composition (wt.%)										
	C	Si	Mn	P	S	Cr	Ni	Cu	Al	V	Fe
E235B	0.18	0.25	0.5	0.016	0.018	0.01	0.02	0.01	0.02		Bal.
E355CC	0.16	0.29	1.39	0.019	0.007						Bal.
Corten A	≦0.12	0.25～0.75	0.2～0.5	0.07～0.15	≦0.04	0.3～1.25	≦0.65	0.25～0.55			Bal.
Corten B	≦0.19	0.30～0.65	0.8～1.25	≦0.03	≦0.02	0.4～0.65	≦0.40	0.25～0.40		0.02～0.10	Bal.

2.2 Experimental conditions

The specimens were immersed into the solution at room temperature and in aerated environment for 15 days, one month, three months and six month, respectively, to understand the effect of immersion time on corrosion behaviors of steels. At the meantime, the corrosion tests were performed in simulated groundwater at room temperature or 90℃ in aerated or deaerated environment for 15 days to research the influences of temperature and oxygen on the corrosion behavior in the groundwater.

2.3 Weight loss test

After immersion, the corroded specimens were taken out from the solution, and cleaned with distilled water. The corrosion products on the specimen's surface were removed using the chemical product-cleanup method [10]. Afterward, the samples were rinsed with water, dried and weight loss values were recorded.

2.4 Surface morphology observation and corrosion product analysis

The corrosion morphology of steels was characterized by a digital camera and SEM. Corrosion products on the corroded samples were analyzed using X-ray diffractometer with a Cu Kα X-ray source to determine the phases. After the corrosion products were removed, the morphology of the corroded specimens was recorded by digital cameras.

Table 3 Composition of simulated Beishan groundwater (mg/L)

Elements	Na^+	K^+	F^-	CO_3^{2-}	NO_3^-	Ca^{2+}	Mg^{2+}	Cl^-	Br^{--}	SO_4^{2-}	SiO_2
Concentration	1027	16.1	1.89	138	30.2	206	51.2	1155	0.057	1074	13.1

3. Results and discussion

3.1 Influence of the immersion time

Weight loss measurements can provide the most reliable results concerning the corrosion rates, so that the corresponding corrosion data obtained from them in experimental environment are more accurately than that obtained from any other test [9, 10]. The average corrosion rates of steels that immersed for different time at room temperature and in aerated simulated groundwater are shown in Fig.1. The corrosion rates of E235B decreased with increasing immersion time. The corrosion rates of E355CC and Corten A increased with time to three months, and then decreased to one year. The whole trend of corrosion rate of Corten B was decline while it had a sudden rise after three months of immersion. The phenomena can be understood by the analysis of corrosion products and corrosion behaviors of different steels. Results indicated that the final trend of corrosion rates of steels reduced in general with the increase of immersion time, which was caused by the protection of corrosion products.

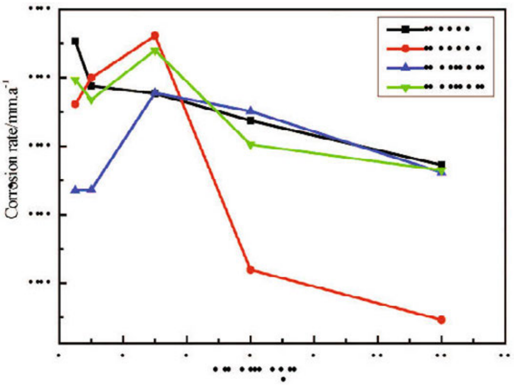


Fig.1 The average corrosion rates of all steels that immersed into simulated groundwater for different time at room temperature and in aerated environment

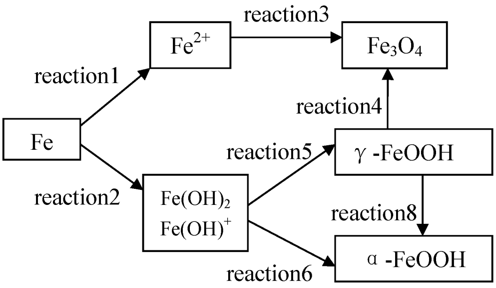


Fig.2 A possible formation and transformation mechanism of corrosion products on steels in groundwater [13, 14]

For E235B, the corrosion rates gradually reduced with the increase of immersion time, which were in the agreement with the general rule for corrosion. According to CHEN Huiling et al. [13] and ZHENG Yingying et al. [14], a possible formation and transformation mechanism of corrosion products on steels in groundwater is shown in Fig.2. Moreover, Fig.3 shows XRD results of corrosion products of E235B at room temperature and in aerated environment. The rates of reaction 1 and 3 were high and the environment reached to a hypoxia condition quickly, so Fe_3O_4 formed in the inner layer of the product quickly which led to the products with low protective ability. $Fe(OH)^+$ and $Fe(OH)_2$ were the major products when Fe dissolved, especially in the near-neutral groundwater. The reaction 5 and 6 took place in the process that $Fe(OH)^+$ and $Fe(OH)_2$ transformed into γ-FeOOH and α-FeOOH, the former reaction needed shorter time and the latter was slow whose products could protect the metal. As mentioned above, reaction 4 and 8 were useful to form protective products. Therefore, Fe_3O_4 formed quickly at first had little protection, leading to the high corrosion rates, and γ-FeOOH with some protective ability formed gradually which slowed down the corrosion rate, then dense and stable α-FeOOH and Fe_3O_4 generated in the products gradually to reduce the corrosion rate further. Further, the products were becoming thicker and prevented the corrosion of substrate. And known from Fig.3, γ-FeOOH and Fe_3O_4 existed in the first 3 months while α-FeOOH began to form in the corrosion time of 6 months, which is consistent with the above analysis. That was why the corrosion rates of E235B reduced gradually.

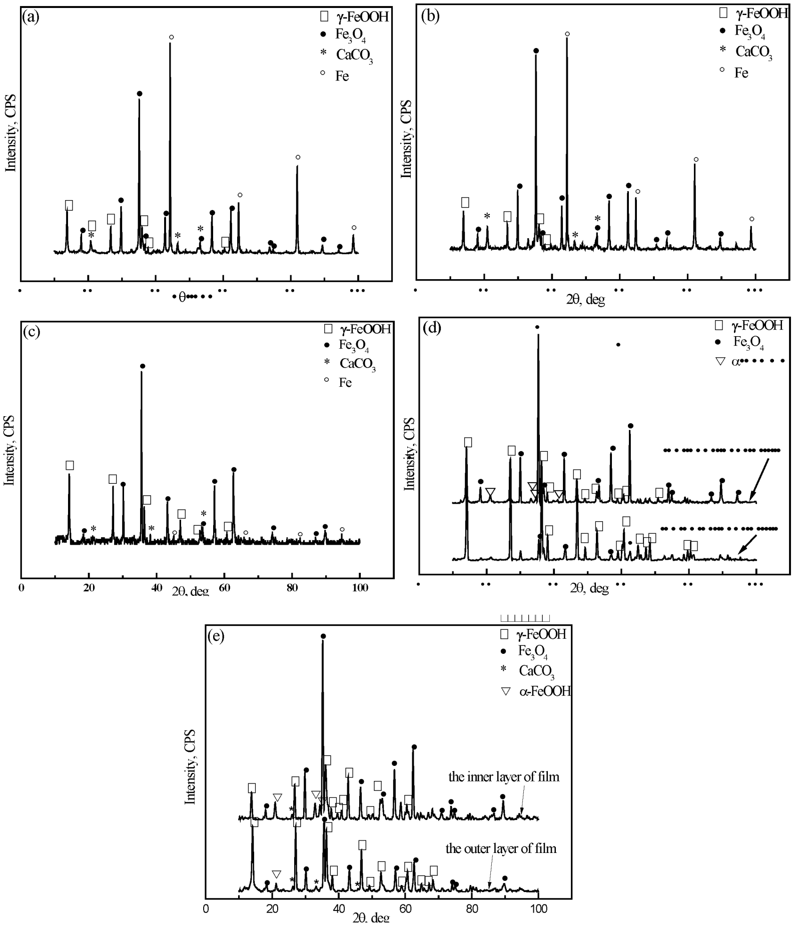


Fig.3 XRD pattern of corrosion product film formed on the surface of E235B at room temperature and in aerated environment for different time (a:15 days; b: one month; c: three months; d: six months; e: one year)

For E355CC, the result showed that corrosion rates increased at first and decreased then, that can be explained from the macro-morphology and XRD analysis of corrosion products of E355CC as shown in Fig.4 and Fig.5. From Fig.4, the corrosion products formed on the surface of E355CC steel were loose, flimsy and easily to fall off, especially before six months, so it could not protect the substrate from corrosion. That may be the reason of the corrosion rates increasing firstly. Fig.5 shows the compositions of the corrosion products were γ-FeOOH and Fe_3O_4 when the immersion time was less than six months, while α-FeOOH arose when the immersion time was longer than or equal to six months. According to Wei Ke et al. [15], the stability of γ-FeOOH was lower than that of α-FeOOH, which might lead to the reaction that γ-FeOOH transformed into α-FeOOH when the corrosion products were forming. Moreover, the electrochemical activity of γ-FeOOH was high, so it was possible that Fe^{2+} would react chemically with γ-FeOOH（$Fe^{2+} + 8\gamma\text{-}FeOOH + 2e = 3Fe_3O_4 + H_2O$）and formed Fe_3O_4 which was dense and stable in later process. All of the reactions or transformation would result in the more protective products film, which made the corrosion rates decrease. Likewise, the result also indicated that the rule of corrosion rates of Corten A was similar to that of E355CC, which showed that the corrosion rates increased at first and decreased then.

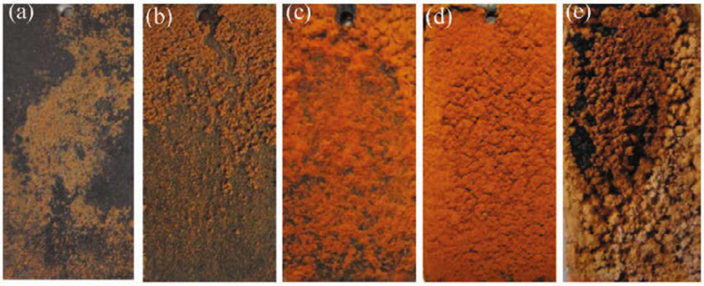
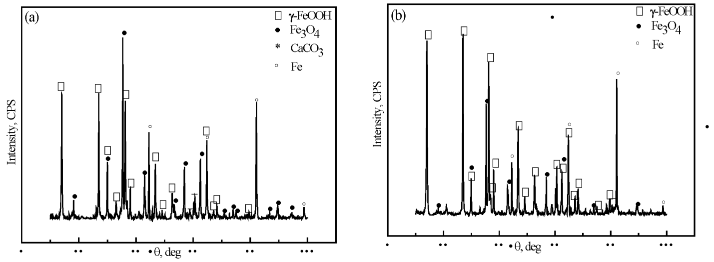


Fig.4 Macro-morphology of corrosion product film of E355CC steel immersed in groundwater for different time at room temperature and in aerated environment(a:15 days; b: one month; c: three months; d: six months; e: one year)



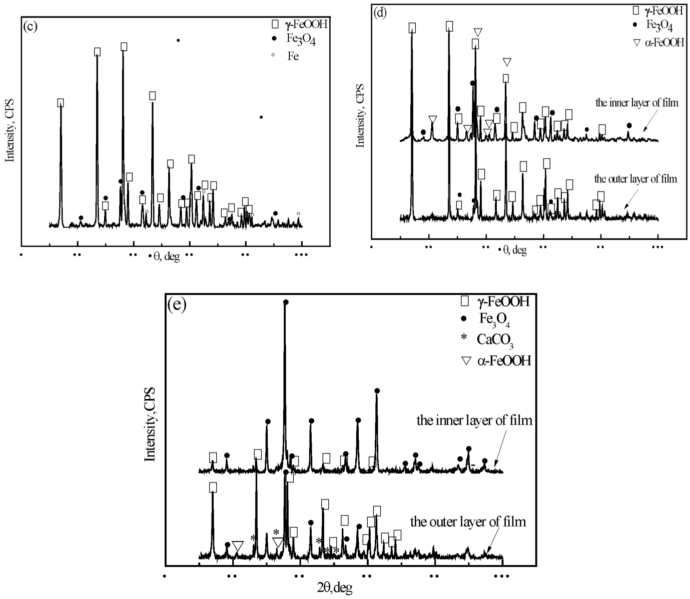


Fig.5 XRD pattern of corrosion products formed on the surface of E355CC at room temperature and in aerated environment for different time (a:15 days; b: one month; c: three months; d: six months; e: one year)

This article also lists the XRD analysis results of corrosion products of all steels at room temperature and in aerated environment for different time shown in Table 4. The compositions of corrosion products of all steels almost included the Fe_3O_4, FeOOH and $CaCO_3$, which is similar among four kinds of steels, but it is obvious that the compositions of products formed for six months and one year of E235B, E355CC and Corten A contained α-FeOOH while that of Corten B didn't have α-FeOOH.

Table 4 The compositions of corrosion products of four kinds of steels at room temperature and in aerated environment for different time by XRD analysis

	15 days	One month	Three months	Six months	One year
E235B	Fe_3O_4, γ-FeOOH, $CaCO_3$	Fe_3O_4, γ-FeOOH, $CaCO_3$	Fe_3O_4, γ-FeOOH, $CaCO_3$	Fe_3O_4, γ-FeOOH, α-FeOOH,	Fe_3O_4, γ-FeOOH, $CaCO_3$ α-FeOOH,
E355CC	Fe_3O_4, γ-FeOOH	Fe_3O_4, γ-FeOOH	Fe_3O_4, γ-FeOOH	Fe_3O_4, γ-FeOOH, α-FeOOH,	Fe_3O_4, γ-FeOOH, α-FeOOH,
Corten A	γ-FeOOH	Fe_3O_4, γ-FeOOH	Fe_3O_4, γ-FeOOH,	Fe_3O_4, γ-FeOOH,	Fe_3O_4, γ-FeOOH,

Corten B	Fe_3O_4	Fe_3O_4, γ-FeOOH	$CaCO_3$ γ-FeOOH	$CaCO_3$ α-FeOOH, Fe_3O_4, γ-FeOOH, $CaCO_3$	α-FeOOH, Fe_3O_4, γ-FeOOH, $CaCO_3$

From the Fig.1, it is obvious that the corrosion rates of four steels of six months were : E235B > Corten B > Corten A > E355CC, and the difference of corrosion rates of E235B, Corten A and Corten B was small, which meant that the corrosion resistance of E355CC was better than that of the other steels immersed in groundwater for one year at room temperature and in aerated environment. In addition, from the surface observation of four steels shown in Fig.6, it is found that the surface roughness of E235B and E355CC were smaller, so that the possibility of pitting of E235B and E355CC were smaller when they corroded in this environment. Further, Fig.1 reveals that, the corrosion rates of E235B and Corten A in the later period of corrosion decreased slowly, while the volatility of that of Corten B was larger relatively. As shown above, E355CC is suitable for the aerated environment at room temperature from the perspective of uniform corrosion.

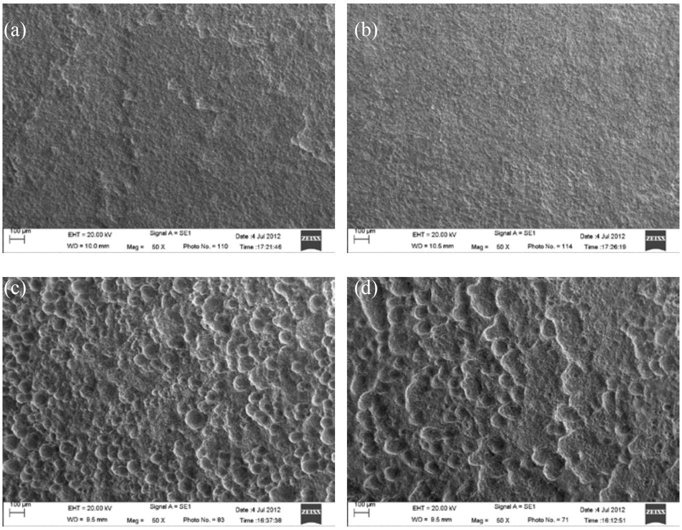


Fig.6 Surface observations of the steels tested in groundwater for one year at room temperature and in aerated environment

(a: E235B; b: E355CC; c: Corten A; d: Corten B)

3.2 Influence of temperature

Fig.7 shows the corrosion rates of all steels that were tested at different temperature and oxygen content. The results of corrosion rates of steels immersed into the simulated groundwater at room temperature or 90℃ in deaerated environment for 15 days indicated that increasing temperature promoted the corrosion process of all tests. Temperature had two opposing effects on the corrosion process: one was improving the diffusion rate of oxygen which increased the reaction rate, and the other was reducing the solubility of oxygen in solutions which weakened the effect of temperature [14]. In this case, temperature promotes the corrosion process evidently.

3.3 Influence of oxygen

Analyzed the corrosion rates of all steels that were tested with different oxygen content environment from Fig.7, the corrosion rate in aerated environment was higher than that in deaerated environment at both room temperature and 90℃. It might be explained by the following reactions. The anode reaction both in aerated and deaerated environment was that Fe lost electrons and became Fe^{2+} while the cathodic reactions in different oxygen content were different. In aerated environment, the cathodic reaction was oxygen reduction reaction, which was controlled by oxygen content, so the corrosion rate in open system was greater due to adequate oxygen. The cathodic reaction was hydrogen evolution reaction in deaerated environment and it meant Fe would react chemically with H_2O and formed H_2 and ferrum oxide, which was usually quick at high temperature, so the corrosion rate in sealed system without oxygen at room temperature was lower.

$$\left.\begin{aligned} & Fe \rightarrow Fe^{2+} + 2e \\ & O_2 + 2H_2O \rightarrow 4OH^- + 2e \end{aligned}\right\} \text{(1) Main reactions occurred in aerated environment}$$

$$\left.\begin{aligned} & Fe \rightarrow Fe^{2+} + 2e \\ & H_2O \leftrightarrow 2H^+ + OH^- \\ & 2H^+ + 2e \rightarrow H_2 \end{aligned}\right\} \text{(2) Main reactions occurred in deaerated environment}$$

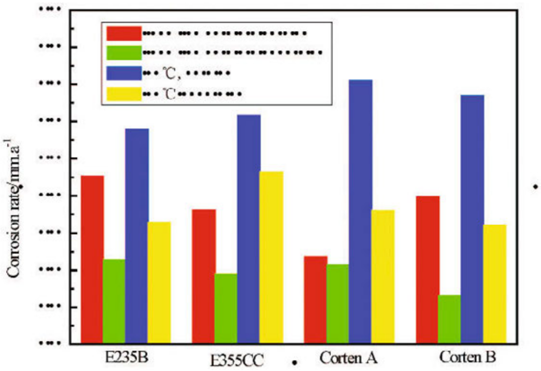


Fig.7 The corrosion rates of four kinds of steels under different conditions for 15 days

Table 5 gives the compositions using XRD analysis of corrosion products of all steels at different conditions for 15 days. It can be found that $CaCO_3$ formed in dearated definitely and the compositions of E235B, E355CC and Corten A at 90 ℃ were Fe_3O_4 and $CaCO_3$. Moreover, the products in deareated environment or at 90 ℃ almost have Fe_3O_4, $CaCO_3$ and γ-FeOOH only formed at room temperature and in aerated environment on the surface of E235B, E355CC and Corten A.

Table 5 The compositions of corrosion products of four kinds of steels at different conditions for 15 days by using XRD analysis

Conditions	Aerated, room temperature	Deaerated, room temperature	Aerated, 90℃	Deaerated, 90℃
E235B	Fe_3O_4, γ-FeOOH, $CaCO_3$	$CaCO_3$	Fe_3O_4, $CaCO_3$	Fe_3O_4, $CaCO_3$
E355CC	Fe_3O_4, γ-FeOOH	Fe_3O_4, $CaCO_3$	Fe_3O_4, $CaCO_3$	Fe_3O_4, $CaCO_3$
Corten A	γ-FeOOH	Fe_3O_4, $CaCO_3$	Fe_3O_4, $CaCO_3$	Fe_3O_4, $CaCO_3$
Corten B	Fe_3O_4	$CaCO_3$	Fe_3O_4	Fe_3O_4, $CaCO_3$

As known from the present result, it can reach the preliminary conclusion that selection of suitable material for HLW container is B from the perspective of uniform corrosion. We will continue carrying out a series of experiments, including pitting, crevice corrosion and galvanic corrosion, from which the final conclusion can be drawn

4. Conclusions

This paper aimed to investigate the corrosion behaviors of four kinds of commercial steels in simulated Beishan groundwater in the presence of different immersion time, temperature and oxygen content, in order to provide the primary data to the selection of container materials for HLW disposal in China. Results of the investigation are as follows:

1. The corrosion rates of E235B decreased with increasing immersion time. The corrosion rates of E355CC and Corten A increased with time to three months, and then decreased to one year. The whole trend of corrosion rate of Corten B was decline while it had a sudden rise after three months of immersion.
2. The increasing temperature of the solutions promoted the corrosion process of all tested steels.
3. The corrosion rate in aerated environment was higher than that in deaerated environment.
4. The preliminary immersed corrosion test results reveal that comparing to the other three steels, E355CC exhibits more potential possibility to be the material for HLW container in China.

Acknowledgement

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