Effects of Corrosion Products Deposited on 304 Stainless Steel on Reduction of Se (IV/VI) in Simulated Groundwater

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Abstract: Selenium (Se) is a key mobile fission product in the geological disposal of nuclear waste. It is necessary to analyze the reductive deposition behavior of iron-based materials to Se(IV) and Se(VI) in groundwater. In the present work, the corrosion behavior of 304 stainless steel in simulated groundwater (SG) and the effects of corrosion products on the dissolution of Se were investigated by electrochemical and immersion tests. Experimental results revealed that passivation films formed on 304 stainless-steel samples were destroyed by polarization measurements, forming corrosion products consisting of Fe(II) compounds, such as FeO and FeO. Corrosion products deposited on the surface of steel samples previously treated by polarization measurements in SG + CaCl2/Na2CO3/Na2SiO3 solutions effectively reduced soluble Se(IV) and Se(VI) during immersion tests, depositing FeSe2 on sample surfaces.

Keywords: 304 stainless steel; simulated groundwater; selenium; corrosion behavior; reduction rate

1. Introduction

Deep geological disposal is widely accepted by major nuclear power countries in the world to isolate radionuclides permanently from the biosphere [1,2]. 79Se is considered a key mobile fission product for the geological disposal of nuclear waste. Selenium (Se) is a high-level radioactive waste (HLW) and exists in the form of 79Se (unstable isotope) with a half-life of 3.77 × 10^5 years [3–5]. In the process of geological disposal of HLW, nuclides are isolated by multiple barriers; moreover, nuclides can react with corrosion products when the leakage of nuclides is caused by corrosion perforation of geological disposal containers. Therefore, the mobility of Se is a key factor for the safe disposal of HLW.

Se exists in the form of different valence compounds (−II, −I, 0, +IV, +VI) [5]. The solubility of Se is influenced by its oxidation state to some extent, and its oxidation state compounds (selenite (SeO3^2−) and selenate (SeO4^2−)) are highly soluble under different chemical conditions, whereas Se and its selenides have very low solubility [5,6]. It has been proven that Fe(II)-containing minerals, such as green rust [7], magnetite [8–12], pyrite [13,14], and troilite [14], can reduce SeO4^2− and SeO3^2−, and the abiotic reduction of Fe(II)-containing minerals is very high. Se is the main reduction product of several Fe(II)-containing minerals. Iron selenide (FeSe) was found to be the main reduction product of magnetite and green rust selenite [4].

Fe(II)-containing minerals generally exist in deep geological media, and abiotic reduction has an important effect on the mobility of Se in groundwater [15]. Mingliang Kang et al. [6] investigated the interaction of aqueous Se(IV) with pyrite under O2-free
conditions at pH ranging from 4.5 to 6.6; they found that pH and iron concentration have a significant effect on the Se(IV) reaction rate and reaction product. Mingliang Kang et al. [5] investigated the influence of pH and reaction time on the formation of FeSe₂ by reductive precipitation of Se(IV) with nanosized pyrite–greigite; they found that FeSe₂ was formed at pH > 6.07. Teng Li et al. [2] found that an Fe(II) compound-containing passivation film was formed on the surface of pure iron in simulated groundwater containing carbonate, silicate, and calcium ions.

Fe + 2H₂O → Fe(OH)₂ + H₂. \hspace{2cm} (1)

Fe²⁺ + CO₃²⁻ → FeCO₃. \hspace{2cm} (2)

2Fe²⁺ + SiO₃²⁻ + 2OH⁻ → Fe₂SiO₄ + H₂O. \hspace{2cm} (3)

In order to investigate the effect of corrosion products on the migration of Se in a deep geological disposal repository after the corrosion failure of the disposal vessel, 304 stainless steel was selected as the research object to analyze the reduction adsorption and deposition behavior of Se(IV) and Se(VI) by corrosion products.

2. Experimental

2.1. Materials

Sodium chloride (NaCl; AR; Sinopharm Chemical Reagent Co. LTD. (Shanghai, China)), calcium chloride anhydrous (CaCl₂; AR; Sinopharm Chemical Reagent Co. LTD. (Shanghai, China)), sodium hydrogen carbonate (NaHCO₃; AR; Sinopharm Chemical Reagent Co. LTD. (Shanghai, China)), sodium carbonate (Na₂CO₃; AR; Sinopharm Chemical Reagent Co. LTD. (Shanghai, China)), sodium metasilicate nonahydrate (Na₂SiO₃·9H₂O; AR; Sinopharm Chemical Reagent Co. LTD. (Shanghai, China)), ethanol absolute (C₂H₆O; AR; Sinopharm Chemical Reagent Co. LTD. (Shanghai, China)), sodium selenite (Na₂SeO₃; AR; Chengdu Huaxia Chemical Reagent Co. LTD. (Chengdu, China)), and sodium selenate (Na₂SeO₄; AR; Chengdu Huaxia Chemical Reagent Co. LTD. (Chengdu, China)) were the main chemicals of this experiment.

The chemical composition of the commercial 304 stainless steel used in this experiment is presented in Table 1. For the immersion test, the 304 stainless-steel plate was cut into samples of 20 mm × 10 mm × 2 mm size. Each sample was mechanically ground to 2000 grit with silicon carbide papers, washed with ethanol, and dried. For the electrochemical experiment, the 304 stainless-steel plate was cut into specimens of 10 mm × 10 mm × 2 mm size to prepare electrodes. These working electrodes were ground to 2000 grit, polished to a mirror surface, washed with ethanol, and dried.

![Table 1. Chemical composition of the 304 stainless steel.](image)

| Composition (wt.%) |
|-------------------|
| C     | S       | P       | Si | Sn | Mn | Ni | Cr | Fe |
| 304 stainless steel | 0.08 | 0.003 | 0.04 | - | 0.8 | 1.8 | 9 | 19 | balance |

2.2. Simulated Groundwater Solution

The simulated groundwater (SG) solutions used in this experiment contained SG (10 mM NaCl + 2 mM NaHCO₃) and different ions (Ca²⁺, CO₃²⁻, SiO₃²⁻). The concentrations of Ca²⁺, CO₃²⁻, and SiO₃²⁻ ions were set to 0 mM, 1 mM, 5 mM, 10 mM, or 20 mM by adding CaCl₂, Na₂CO₃, and Na₂SiO₃, respectively. The chemical compositions of the as-prepared simulated groundwater solutions are listed in Table 2.

2.3. Immersion Solutions

The immersion solutions used in this experiment contained SG and different valence states of Se solution (Se(IV/VI)). The concentrations of Se solution were set to 30 mg/L and
100 mg/L by adding Na$_2$SeO$_3$ or Na$_2$SeO$_4$. The chemical compositions of the as-prepared immersion solutions are listed in Table 3.

Table 2. Chemical composition of simulated groundwater.

| Solution     | NaCl | NaHCO$_3$ | CaCl$_2$ | Na$_2$CO$_3$ | Na$_2$SiO$_3$ |
|--------------|------|-----------|----------|--------------|---------------|
| SG           | 10   | 2         | 0        | 0            | 0             |
| SG + CaCl$_2$| 10   | 2         | 1        | 0            | 0             |
|              | 10   | 2         | 5        | 0            | 0             |
|              | 10   | 2         | 10       | 0            | 0             |
|              | 10   | 2         | 20       | 0            | 0             |
| SG + Na$_2$CO$_3$ | 10 | 2 | 0 | 1 | 0 |
|              | 10 | 2 | 0 | 5 | 0 |
|              | 10 | 2 | 0 | 10 | 0 |
|              | 10 | 2 | 0 | 20 | 0 |
| SG + Na$_2$SiO$_3$ | 10 | 2 | 0 | 0 | 1 |
|              | 10 | 2 | 0 | 0 | 5 |
|              | 10 | 2 | 0 | 0 | 10 |
|              | 10 | 2 | 0 | 0 | 20 |

Table 3. Chemical composition of the solution for the immersion test.

| Chemicals Concentration | NaCl | NaHCO$_3$ | Na$_2$SeO$_3$ | Na$_2$SeO$_4$ |
|-------------------------|------|-----------|---------------|---------------|
| SG + Na$_2$SeO$_3$      | 10 mM| 2 mM      | 30 mg/L       | 0             |
|                         | 10 mM| 2 mM      | 100 mg/L      | 0             |
| SG + Na$_2$SeO$_4$      | 10 mM| 2 mM      | 0             | 30 mg/L       |
|                         | 10 mM| 2 mM      | 0             | 100 mg/L      |

2.4. Electrochemical Measurements

In order to analyze the corrosion behavior of 304 stainless steel in anoxic SG, the potentiodynamic polarization curves of 304 stainless-steel samples at different ion concentrations were plotted by a Zahner electrochemical workstation (Germany) at 40 °C. An electrochemical cell consisting of three electrodes was used in this experiment; 304 stainless-steel samples acted as working electrodes, a saturated Hg/HgCl$_2$ electrode worked as the reference electrode, and a platinum foil served as the counter electrode. Each solution was purged with argon gas containing 0.03% CO$_2$ for 20 min to obtain a H$_2$- and O$_2$-free solution. The open-circuit potential of each solution was tested for 30 min. The potentiodynamic polarization curve of each solution was tested in a potential range of $-0.3$ to $1.6$ V relative to the open-circuit potential. The potential sweep rate was set to 0.5 mV/s.

2.5. Immersion Test

In order to explore the corrosion behavior of 304 stainless steel, a CHI 660E electrochemical workstation was used for pitting 304 stainless steel in SG + 20 mM CaCl$_2$/Na$_2$CO$_3$/Na$_2$SiO$_3$ solutions by polarization measurements. Subsequently, the 304 stainless-steel samples treated by polarization measurements were immersed in SG solutions (Table 2) for 4 weeks. The concentrations of Se in these solutions after different immersion times were determined.

2.6. Surface Characterization

The concentrations of Se in immersion solutions were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES; Prodigy 7/Prodigy 7, Hudson, NH, USA). The surface morphology and elemental composition of corrosion products
deposited on the surface of 304 stainless-steel samples after the 4 week immersion test were analyzed by a scanning electron microscope equipped with an energy-dispersive spectrometer (SEM/EDS; Zeiss Auriga FEI Quanta FEG 250 SEM/Oxford Inca X-act 2000 EDS, Hillsboro, OR, USA). The formation mechanism of corrosion products deposited on the surface of 304 stainless-steel samples after the 4 week immersion test was analyzed by a confocal Raman microscope (CRM, Renishaw, London, UK). Corrosion products deposited on the surface of 304 stainless-steel samples after the 4 week immersion test were characterized by an X-ray photoelectron spectrometer (XPS, Kratos, Manchester, UK) equipped with a monochromated Al K-α X-ray source (HV = 1486.69 eV) at 150 W.

3. Result and Discussion

3.1. Potentiodynamic Polarization Curves

The electrochemical corrosion behavior of 304 stainless steel in different SG solutions was analyzed by potentiodynamic polarization measurements at 40 °C. The polarization curves of 304 stainless steel in different SG solutions are displayed in Figure 1, and electrochemical parameters obtained from the fitted curves are listed in Table 3.

![Polarization curves of 304 stainless steel in different simulated groundwater at 40 °C: (a) SG + CaCl₂; (b) SG + Na₂CO₃; (c) SG + Na₂SiO₃.](image)

It is noticeable from Figure 1 that, in SG + CaCl₂ solutions, the polarization curves had a similar shape, indicating that the corrosion behaviors of 304 stainless-steel samples were similar under the influence of different concentrations of CaCl₂. The anodic polarization curve only had an activation dissolution zone. When the potential reached the pitting potential, the passivation film on the steel surface ruptured, and the corrosion current density dramatically increased. In the SG + Na₂CO₃/Na₂SiO₃ solutions, the polarization curves of 304 stainless steel had different forms. When the ion concentration was 0 mmol/L, the anodic polarization curve only had an activated dissolution zone. When the ion concentration continued to increase, the anodic polarization curve had a stable passivation zone. When the potential reached the pitting potential (Epp), the passivation film on the steel surface ruptured, and the corrosion current density dramatically increased. The Epp
of 304 stainless steel was more positive as compared to the pitting potential of the steel in low-concentration solutions.

It is evident from Table 4 that, in the SG solution containing CaCl$_2$, the current density was $1.72 \times 10^{-6}$ A·cm$^{-2}$ and the Epp was around 0.5 V. In the SG solutions containing Na$_2$CO$_3$ and Na$_2$SiO$_3$, a larger passivation region led to a more positive Epp. Corrosion products only existed in pitting pits at different concentrations of CaCl$_2$ (Figure 2); thus, the corrosion resistance of the steel was the same in different SG solutions. When different concentrations of Na$_2$CO$_3$/Na$_2$SiO$_3$ were added, corrosion products accumulated in a layer (Figure 2), increasing the corrosion resistance of the steel in the solutions.

Table 4. Electrochemical parameters obtained from the fitted curves.

| 40 °C | mM | $i/E_{pp}$ | 0  | 1  | 5  | 10 | 20 |
|-------|----|------------|----|----|----|----|----|
| CaCl$_2$ |  | i/A·cm$^{-2}$ | $1.72 \times 10^{-6}$ | $2.67 \times 10^{-6}$ | $1.91 \times 10^{-6}$ | $1.36 \times 10^{-6}$ | $1.66 \times 10^{-6}$ |
|  |  | Epp/V | 0.545 | 0.498 | 0.524 | 0.400 | 0.487 |
| Na$_2$CO$_3$ |  | i/A·cm$^{-2}$ | $1.72 \times 10^{-6}$ | $3.03 \times 10^{-6}$ | $2.74 \times 10^{-6}$ | $2.37 \times 10^{-6}$ | $2.46 \times 10^{-6}$ |
|  |  | Epp/V | 0.545 | 0.528 | 0.645 | 0.703 | 0.969 |
| Na$_2$SiO$_3$ |  | i/A·cm$^{-2}$ | $1.72 \times 10^{-6}$ | $1.98 \times 10^{-6}$ | $2.11 \times 10^{-6}$ | $2.67 \times 10^{-6}$ | $2.77 \times 10^{-6}$ |
|  |  | Epp/V | 0.545 | 0.572 | 0.988 | 0.981 | 0.908 |

3.2. Characterization of Corrosion Products and the Passivation Film

In order to analyze the morphology and composition of the corrosion products and passivation film, SEM/EDS measurements were performed on the surface of 304 stainless steel treated by polarization measurement in SG, SG + 20 mmol/L CaCl$_2$, SG + 20 mmol/L Na$_2$CO$_3$, and SG + 20 mmol/L Na$_2$SiO$_3$ solutions.

It is clear from Figure 2 that the nontreated sample surface did not have any corrosion products and pits. In the SG solution, the presence of a small number of granular corrosion products was found near the pit. In the SG + 20 mmol/L CaCl$_2$ solution, granular corrosion products only existed in pits. In the SG + 20 mmol/L Na$_2$CO$_3$ solution, the number of granular corrosion products increased greatly, and they existed as clusters. In the SG + 20 mmol/L Na$_2$SiO$_3$ solution, the number of corrosion products dramatically increased, and they existed as agglomerates, forming a thin corrosion product layer. Corrosion products generated by the reaction of CO$_3^{2-}$/SiO$_3^{2-}$ with the steel formed a dense passivation film on the steel surface, generating a protective effect on the steel matrix.

Figure 2. The SEM images of 304 stainless steel treated by polarization measurement in different solutions: (a) nontreated; (b) SG; (c) SG + CaCl$_2$; (d) SG + Na$_2$CO$_3$; (e) SG + Na$_2$SiO$_3$. 
It is noticeable from Figures 3 and 4 that, after being treated by polarization measurements in the SG solution, corrosion products were mainly composed of Fe and O. After being treated by polarization measurements in the SG + CaCl₂ solution, corrosion products generated on the steel surface were mainly calcium-rich products and Fe-based compounds, indicating that Ca²⁺ ions were involved in the corrosion reaction. After being treated by polarization measurements in the SG + Na₂CO₃/Na₂SiO₃ solutions, corrosion products were also Fe-based compounds. After the addition of Na₂SiO₃, corrosion products were mainly composed of Fe, O, and Si, indicating that SiO₃²⁻ was involved in the corrosion reaction. Moreover, Fe-based compounds in the corrosion products mainly contained Fe(II) and Fe(III) elements, such as FeO and Fe₃O₄ [2].

![Figure 3](image_url)

**Figure 3.** The EDS analysis of 304 stainless steel treated by polarization measurements in different solutions: (a) SG; (b) SG + CaCl₂; (c) SG + Na₂CO₃; (d) SG + Na₂SiO₃.

Furthermore, the information of products deposited on the surface of 304 stainless steel samples immersed in SG and SG + 20 mmol/L CaCl₂/Na₂CO₃/Na₂SiO₃ solutions was obtained by high-resolution XPS spectroscopy, as shown in Figure 5.

The Cr 2p spectra in different solutions contained the peaks of Cr₂O₃ (576.1 eV/586.3 eV), CrO₂ (575.4 eV), and Cr(OH)₃ (577.4 eV) [16–19] (Figure 5a). Cr in the steel matrix was oxidized to Cr(II/III) compounds and formed a passivation film on the steel surface. The Fe 2p spectrum consisted of seven peaks [16–21] (Figure 5b); the peaks of FeOOH (711.8 eV) and Fe₂O₃ (710.8 eV/724.5 eV) were the most significant, while the peaks of FeO (709.8 eV) and Fe₃O₄ (729.5 eV) were relatively weak. The peaks of Fe (706.7 eV/719.9 eV) were the weakest, indicating that Fe in the steel matrix was oxidized to Fe(II/III) compounds and formed a passivation film on the steel surface. In the SG + 20 mmol/L Na₂CO₃ solution, the C 1s spectra of corrosion products contained the peaks of C–C (284.4 eV), C–O–C (285.7 eV), and O–C=O (289.1 eV) [21,22] (Figure 5c), indicating the possible presence of CO₃²⁻ ions. In the SG + 20 mmol/L Na₂SiO₃ solution, the Si 2p spectra of corrosion products contained the peaks of SiO₂ (102.6 eV) and SiO₃²⁻ (103.7 eV) [22–24] (Figure 5d), indicating that ferric carbonates and silicates were formed after the immersion test.
Figure 4. The EDS analysis of 304 stainless steel treated by polarization measurements in different solutions: (a) SG; (b) SG + CaCl$_2$; (c) SG + Na$_2$CO$_3$; (d) SG + Na$_2$SiO$_3$.

Furthermore, the information of products deposited on the surface of 304 stainless steel samples immersed in SG and SG + 20 mM CaCl$_2$/Na$_2$CO$_3$/Na$_2$SiO$_3$ solutions was obtained by high-resolution XPS spectroscopy, as shown in Figure 5.

Figure 5. The XPS spectra of 304 stainless steel surfaces obtained after 4 week immersion in SG, SG + 20 mM CaCl$_2$, SG + 20 mM Na$_2$CO$_3$, or SG + 20 mM Na$_2$SiO$_3$ solutions at 40 °C: (a) Cr 2p; (b) Fe 2p; (c) C 1s; (d) Si 2p.

From the above experiments and characterization analysis, it can be seen that the Fe(II) compounds produced by the corrosion of 304 stainless steel in SG solutions containing different concentrations of CaCl$_2$, Na$_2$CO$_3$, and Na$_2$SiO$_3$ were Fe$_3$O$_4$, FeCO$_3$, FeSiO$_3$, etc.
3.3. Analysis of the Dissolution Rate of Se after the Immersion Test

The 304 stainless-steel samples treated by polarization measurements were directly immersed in SG + 30 mg/L Na2SeO3 solution. It is clear from Figure 6a that the concentration of soluble Se in the solution decreased slightly in the initial stage due to the adsorption effect. As the adsorption effect weakened or disappeared, the amount of dissolved Se in the solution remained negligible during the immersion period. As 304 stainless steel is a self-passivating alloy, the passivation film formed on the surface prevented the steel from reacting with Na2SeO3 in the solution; hence, only adsorption reduced the concentration of soluble Se in the solution.

Figure 6. The curve of concentration of dissolved Se plotted against time after treating the 304 stainless steel by polarization measurements in different solutions: (a) SG + Na2SeO3; (b) SG + Na2SeO4.

Furthermore, macroscopically, no corrosion products were found on the surface of 304 stainless-steel samples treated by polarization measurements in the SG + 20 mM CaCl2 solution; however, a large number of corrosion products were attached to the steel surface after polarization measurements in the SG + 20 mM Na2CO3 and SG + 20 mM Na2SiO3 solutions. In addition, a large number of pits and corrosion products existed on the steel surface, as observed by SEM and shown in Figure 2, during polarization measurements. Some of the corrosion products deposited on the steel surface fell off naturally, and the loss of corrosion products in the SG solution containing Na2SiO3 was more serious. These samples were subsequently immersed in the solutions in Table 3.

It is observable from Figure 6 that, at the initial stage of immersion, the concentration of soluble Se in the solution decreased rapidly, whereas, at the later stage, the concentration of soluble Se decreased slowly. After treating the steel by polarization measurements in SG + 20 mM Na2SiO3 solution, some of the corrosion products fell off naturally, which lowered the reduction rate of soluble Se in the solution of the sample participating in the immersion test. It is clear from Table 5 that the reduction rate of soluble Se was different when the samples were treated by polarization measurements in different solutions. When the samples were treated in the SG solution containing CaCl2, the reduction rates of Se(IV) and Se(VI) were about 40% and 45%, respectively. When the samples were treated in the SG solution containing Na2CO3, the reduction rates of Se(IV) and Se(VI) were about 60% and 65%, respectively. When the samples were treated in the SG solution containing Na2SiO3, the values were about 50% and 50%, respectively. After polarization measurements, corrosion products were generated on the steel surface and existed in pits. Fe(II) compounds in corrosion products reduced soluble Se(VI) to soluble Se(IV) and then reacted with soluble Se(IV) through a redox reaction. As the samples were adsorbed, the concentration of soluble Se in the solution decreased rapidly in the initial immersion stage. During immersion, the adsorption process weakened, and the presence of the passivation film formed by corrosion products on the surface of the sample weakened the reaction between Fe(II) compounds and Na2SeO3, resulting in a slight decrease in the concentration of soluble Se.
Table 5. The soluble Se reduction rate in the immersion test.

|                         | Reduction Rate (%) |
|-------------------------|--------------------|
|                         | SG + 20 mM CaCl₂   | SG + 20 mM Na₂CO₃ | SG + 20 mM Na₂SiO₃ |
| SG + 30mg/L Na₂SeO₃     | 39.48              | 48.32             | 67.36              |
| SG + 100mg/L Na₂SeO₃    | 37.98              | 72.46             | 41.86              |
| SG + 30mg/L Na₂SeO₄     | 46.28              | 70.76             | 53.08              |
| SG + 100mg/L Na₂SeO₄    | 47.98              | 60.22             | 50.02              |

The above results indicate that the samples treated by polarization measurements in different solutions led to different corrosion conditions on the surface of steel samples. In comparison to the samples not treated by polarization measurements, the treated steel samples could continuously reduce the concentration of soluble Se in the solution, indicating that the concentration of soluble Se in the solution was reduced in two ways: the adsorption process and the redox reaction between Fe(II) compounds in corrosion products and soluble Se. The number of corrosion products greatly affected the reduction of soluble Se.

3.4. Characterization of Corrosion Products after the Immersion Test

The surface morphologies of corrosion products deposited on the surface of 304 stainless steel after the 4 week immersion test in SG + Na₂SeO₃ solutions were similar (Figure 7). Granular corrosion products formed a dense layer and existed as clusters. The corrosion products deposited on the surface of the 304 stainless-steel samples treated by polarization measurement in the SG solution containing CaCl₂ were the lowest in number, while the corrosion products deposited on the surface of the 304 stainless-steel samples treated by polarization measurement in the SG solution containing Na₂SiO₃ were the greatest in number.

![Figure 7. The SEM images of 304 stainless-steel samples after being treated by polarization measurements in different solutions and a 4 week immersion test in SG + Na₂SeO₃ solution: (a) SG + CaCl₂ solution; (b) SG + Na₂CO₃ solution; (c) SG + Na₂SiO₃ solution.](image)

It is noticeable from Figures 8 and 9 that the main components of the corrosion products were Fe and Se, indicating that, in the immersion test, Fe(II) compounds in the corrosion products deposited on the treated steel surface were involved in the corrosion reaction. A higher number of corrosion products generated during polarization measurements indicates a greater content of corrosion products generated by Fe–Se compounds on the sample surface during the immersion test. It is preliminarily speculated that the Fe–Se compound was FeSe₂.
The surface morphology of corrosion products deposited on the steel surface in the SG + Na₂SeO₄ solution after 4 weeks of immersion was similar to that in the SG + Na₂SeO₃ solution (Figure 10). Corrosion products were granular and existed as agglomerates. The main components of these corrosion products were Fe and Se (Figures 11 and 12).

Figure 8. The EDS analysis of 304 stainless-steel samples after being treated by polarization measurements in different solutions and a 4 week immersion test in SG + Na₂SeO₃ solution: (a) SG + CaCl₂ solution; (b) SG + Na₂CO₃ solution; (c) SG + Na₂SiO₃ solution.

Figure 9. The EDS analysis of 304 stainless-steel samples after being treated by polarization measurements in different solutions and a 4 week immersion test in SG + Na₂SeO₃ solution: (a) SG + CaCl₂ solution; (b) SG + Na₂CO₃ solution; (c) SG + Na₂SiO₃ solution.
Figure 10. The SEM images of 304 stainless-steel samples after being treated by polarization measurement in different solutions and a 4 week immersion test in SG + Na2SeO4 solution: (a) SG + CaCl2 solution; (b) SG + Na2CO3 solution; (c) SG + Na2SiO3 solution.

Figure 11. The EDS analysis of 304 stainless-steel samples after being treated by polarization measurements in different solutions and a 4 week immersion test in SG + Na2SeO4 solution: (a) SG + CaCl2 solution; (b) SG + Na2CO3 solution; (c) SG + Na2SiO3 solution.

Figure 12. The EDS analysis of 304 stainless-steel samples after being treated by polarization measurements in different solutions and a 4 week immersion test in SG + Na2SeO4 solution: (a) SG + CaCl2 solution; (b) SG + Na2CO3 solution; (c) SG + Na2SiO3 solution.
The Raman spectra of 304 stainless steel after the 4 week immersion test in different solutions are displayed in Figure 13. Corrosion products deposited on the steel surface were mainly composed of Fe–Cr spinel (689 cm\(^{-1}\)) and FeSe\(_2\) (214 cm\(^{-1}\), 263 cm\(^{-1}\), 212 cm\(^{-1}\), 279 cm\(^{-1}\)) [25].

![Raman spectra of 304 stainless steel](image)

**Figure 13.** The Raman spectra of 304 stainless-steel samples after a 4 week immersion test in different solutions: (a) SG+ Na\(_2\)SeO\(_4\); (b) SG+ Na\(_2\)SeO\(_3\).

The above results indicate that corrosion products containing Fe(II) compounds were generated on the 304 stainless-steel surface treated by polarization measurements in SG solutions containing CaCl\(_2\), Na\(_2\)CO\(_3\), and Na\(_2\)SiO\(_3\). Soluble Se(IV) and Se(VI) in the solutions were reduced to FeSe\(_2\) by corrosion products. Moreover, a greater number of corrosion products generated during polarization measurements led to a greater content of FeSe\(_2\) formed during the immersion test.

### 3.5. Summary

#### 3.5.1. Corrosion Behavior of 304 Stainless Steel in SG

Pits and corrosion products were generated on the surface of 304 stainless steel samples treated by polarization measurements in SG solutions containing different concentrations of CaCl\(_2\), Na\(_2\)CO\(_3\), and Na\(_2\)SiO\(_3\). In the SG solution containing CaCl\(_2\), granular corrosion products only existed in pits. In the SG solutions containing Na\(_2\)CO\(_3\) and Na\(_2\)SiO\(_3\), granular corrosion products accumulated into layers and increased the corrosion resistance of 304 stainless steel in the solutions. The main corrosion products were Fe\(_3\)O\(_4\) and FeO [2,26,27].

**Anodic reaction:**

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^{-}. \quad (4)
\]

**Cathodic reaction:**

\[
2\text{H}_2\text{O} + 2e^{-} \rightarrow 2\text{OH}^- + \text{H}_2. \quad (5)
\]

**Total reaction:**

\[
\text{Fe} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + \text{H}_2, \quad (6)
\]

\[
\text{Fe}^{2+} + \text{CO}_3^{2-} \rightarrow \text{FeCO}_3, \quad (7)
\]

\[
2\text{Fe}^{2+} + \text{SiO}_3^{2-} + 2\text{OH}^- \rightarrow \text{Fe}_2\text{SiO}_4 + \text{H}_2\text{O}. \quad (8)
\]
3.5.2. Effects of Corrosion Products on the Dissolution of Se

Corrosion products deposited on the surface of 304 stainless-steel samples treated by polarization measurements in different SG solutions containing CaCl$_2$, Na$_2$CO$_3$, and Na$_2$SiO$_3$ contained different amounts of Fe(II) compounds, which reacted with soluble Se to produce FeSe$_2$ during the 4 week immersion test [6].

$$2\text{HSeO}_3^- + \text{Fe}^{2+} + 10\text{H}^+ + 10\text{e}^- \rightarrow \text{FeSe}_2 + 6\text{H}_2\text{O}.$$ (9)

It was found that Fe(II) compounds could reduce soluble Se at pH = 8.2.

$$\text{SeO}_4^{2-} + \text{Fe}^{2+} + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{SeO}_3^{2-} + \text{OH}^-,$$ (10)

$$2\text{SeO}_3^{2-} + \text{Fe}^{2+} + 6\text{H}^+ + 10\text{e}^- \rightarrow \text{FeSe}_2 + 6\text{OH}^-.$$ (11)

A greater number of corrosion products on the surface of 304 stainless steel led to a higher amount of reduced Se in the immersion solutions. The lowest number of corrosion products was deposited on the surface of 304 stainless steel treated by polarization measurements in the SG solution containing CaCl$_2$, and corrosion products only existed in pitting pits. The deposition amount of corrosion products on the surface of 304 stainless steel treated by polarization measurements in the SG solutions containing Na$_2$CO$_3$ and Na$_2$SiO$_3$ increased. However, during polarization measurements, some corrosion products deposited on the steel surface fell off, and the loss of corrosion products in the SG solution containing Na$_2$SiO$_3$ was more serious. The reduction rate $R$ of soluble Se was calculated as $R = 1 - C_1/C_0$, where $C_0$ is the initial concentration of soluble Se, and $C_1$ is the final Se concentration after the immersion test; the corresponding results are presented in Table 5.

4. Conclusions

1. Polarization measurements were executed on 304 stainless-steel samples in SG solutions containing CaCl$_2$, Na$_2$CO$_3$, and Na$_2$SiO$_3$. Corrosion products containing Fe(II) compounds, such as FeO and Fe$_3$O$_4$, were generated on the surface of steel samples.

2. The reduction rate of soluble Se was different when the samples were treated by polarization measurements in different solutions. When the samples were treated in the SG solution containing CaCl$_2$, the reduction rates of Se(IV) and Se(VI) were about 40% and 45%, respectively. When the samples were treated in the SG solution containing Na$_2$CO$_3$, the reduction rates of Se(IV) and Se(VI) were about 60% and 65%, respectively. When the samples were treated in the SG solution containing Na$_2$SiO$_3$, the reduction rates of Se(IV) and Se(VI) were about 50% and 50%, respectively.

3. In Se-containing solutions, Fe(II) compounds in corrosion products reduced soluble Se(VI) to soluble Se(IV), and Fe(II) compounds reacted with soluble Se(IV) through a redox reaction.

4. A large number of corrosion products were generated on the surface of 304 stainless-steel samples treated by polarization measurements. A large amount of FeSe$_2$ was produced on the surface of 304 stainless-steel samples by the 4 week immersion test, and the reduction rate of soluble Se was high.

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