Factors Influencing Passivity Breakdown on UNS N08800 in Neutral Chloride and Thiosulfate Solutions

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In this work, the passivity degradation of UNS N08800 in solutions containing Cl− and S2O32− is studied by using polarization curve, electrochemical impedance spectroscopy (EIS), and X-ray photoelectron spectroscopy (XPS). Experimental results reveal that the passivity breakdown heavily depends on anodic potentials, concentration ratios of Cl− to S2O32−, and the composition of materials. A combined effect between Cl− and S2O32− on pitting corrosion is observed at high anodic potentials at which the passive film is broken down; in this situation, S2O32− ions can enter into the pits by electromigration, and they are reduced to S0ads and S2−, stabilizing the metastable pits and accelerate the pit growth rate. However, there is no such combined effect at low anodic potentials when the passive film is intact, on the contrary, S2O32− is beneficial to passivity in chloride solutions. At low anodic potentials, the interaction of S2O32− with an intact passive layer is weak, and the adsorption of S2O32− would mitigate the detrimental effect of Cl− ions.

This work aims to fully understand the factors influencing the passivity degradation of UNS N08800 in Cl− and S2O3− solutions. The effect of CTCR on passivity of UNS N08800 is studied by polarization curve and electrochemical impedance spectroscopy (EIS). Eventually, how CTCR and electrochemical potential affect the passivity breakdown on UNS N08800 is elucidated, and a mechanism is proposed to fully understand the corrosion degradation process.

Passivity degradation of steam generator (SG) alloys in solutions containing chloride and thiosulfate ions has received much attention in recent years due to the rapidly developed nuclear power around the world.14 SGs, which is used in pressurized water reactor (PWR) between the primary and secondary loops, are heat exchangers used to convert secondary-loop water into steam.5 UNS N08800 is one of the most frequently used SG tubing materials, which has shown excellent performance in CANDU (CANada Deuterium Uranium) system without serious problems during long term service for almost 30 years. Nevertheless, a few flaws have been found on some UNS N08800 tube sheet in two power plants designed by Siemens.7 Because CANDU power plants are approaching a designed life of 30-years, life extension of non-refurbishable nuclear components such as SGs to a target life time of 60-years is being undertaken. Therefore, it is urgently needed to comprehensively understand corrosion degradation mechanism of the SG tubing under the simulated service conditions, for managing the corrosion degradation of SG in a proactive manner.8,9

The locations that corrosion degradation most possibly occurs are the crevices where are usually located between the tube-to-support plate and tube-to-tube sheet, or under deposits including thick freespan deposits and tubeshell sludge piles.5,10 Some impurities including SO2−, Cl− in the secondary loop water can concentrate within these crevices.11,12 In order to avoid elevated corrosion potential of SG alloy and minimize oxygen content, hydrazine is intentionally added to the secondary loop of SGs, leading to a reduction of sulfate to HS−, H2S or S2O32−.13,14 HS−, H2S and S2O32− are generally termed “reduced and intermediate oxidation level sulfur”,15 which have been recognized to enhance active dissolution of metal, increase stress corrosion cracking and pitting susceptibility.16–17 As pointed out by Newman,2 some corrosion phenomena in SG tubing with the presence of “reduced” sulfur species and oxygen have been recognized to occur at low temperature. Therefore, it is necessary to investigate corrosion degradation of SG tubing at low temperature.

The passivity degradation of SG in Cl− and S2O32− solutions has been extensively studied in recent years.14,18–29 It is generally accepted that, in neutral solutions, chloride-to-thiosulfate concentration ratio (CTCR) had a remarkable impact on the breakdown potential of SG alloys.30 The breakdown potential decreases first and then increases as CTCR decreases.31,32 Generally, two situations regarding to the passivity degradation are summarized below:

1. At high CTCR, the breakdown potential is significantly lowered, compared with breakdown potential in chloride-only solution.15 For instance, previous experiments have indicated that S2O32− lowered the pitting potential of Alloy 690,26,33 Type 304 stainless steel,37,38 UNS N0880028,34,35 and Alloy 60029 in solutions containing Cl−. The mechanism has been fused together by Newman27 and Marcus36 who claimed that, at higher CTCR, the passive film was damaged by Cl− and stabilized by the reduction of S2O32− ions. They claimed that S2O3− can be enriched within the pits by electromigration, and delivered adsorbed sulfur with 0 valence (S0ads) by electroreduction. S0ads would activate the anodic dissolution of metal within the pits. They27,29 suggested a mechanism consisting of local breakdown of the passive film by Cl−, subsequent adsorption of S0ads on these sites, weakening of metal-metal bonds to form metal sulfide. This mechanism can interpret the dependence of pitting potential on CTCR. However, this combined effect of Cl− and S2O3− is always observed at high anodic potentials, whether a combined effect is existed at low potentials and on an intact the passive film is unknown and therefore need to clarify.

2. At low CTCR, the combined effect between Cl− and S2O32− becomes less significant.28 In this situation, Newman et al. claimed that the decomposition of S2O32− within the pits would tend to neutralize any acid generation (S2O32− + 2H+ = S + H2SO3, S2O32− + 6H+ + 4e− = 2S + 3H2O).37 However, this conflicts with Xia’s investigation,39 who found that there is no pits formed on UNS N08800 if the S2O32− concentration in Cl− solutions is sufficiently high. Therefore, the relevant mechanism is needed to clarify.
Table I. Chemical compositions of UNS N08800 (wt.%).

|   | C  | Si | Mn | P  | S  | Cr | Ni | Co | Ti | Cu | Al | N  | Fe |
|---|----|----|----|----|----|----|----|----|----|----|----|----|----|
|   | 0.017 | 0.46 | 0.5 | 0.012 | 0.001 | 21.87 | 32.78 | 0.01 | 0.48 | 0.02 | 0.29 | 0.016 | 43.2 |

Experimental

Materials and electrolytes.—Samples of the nickel-based UNS N08800 were cut from tubing (Sandvik, heat number 516809) with an average wall thickness of 1.13 mm and outer diameter of 15.88 mm. The composition of UNS N08800 is listed in Table I. The cut specimens were connected to copper wires and were sealed with epoxy resin. The outer surface of the tube was polished flat and used as exposed surface to the electrolyte. The exposed surface was ground by SiC paper in the following sequence: 320, 600, 800, and 1200 grit, rinsed copiously with deionized water, degreased by acetone and ethanol, then kept in a desiccator for 24 h. The exposed area for electrochemical tests was about 4 cm² except the samples used in the corrosion morphology monitoring by using an optical microscope (part 3.3).

The test solutions are listed in Table II, and the CTCR values are also given. All chemicals used in the experiments were reagent grade (ACS reagent, +99%, Aldrich). Test solutions were freshly prepared with deionized water prior to each electrochemical test.

Electrochemical measurements.—Prior to each electrochemical experiments including polarization curve and EIS, the solutions were deaerated with high purity (99.99%) N₂ for 1 hour. The electrochemical measurements were conducted using a PARSTAT2273 electrochemical workstation (Princeton Applied Research, USA). A three-electrode cell was used with UNS N08800 as the working electrode (WE), a saturated calomel electrode (SCE) as the reference electrode (RE), and a platinum electrode as the counter electrode (CE). Each test was repeated at least 4 times and were conducted on separate specimens.

Before polarization and EIS test, a constant-cathodic polarization of −1.0 V (versus SCE) was applied for 15 min to reduce the oxide film, then the specimens were then kept at an open-circuit potential for 30 min. An electrochemical equivalent circuit (EEC) was used to model EIS data. Potentiodynamic polarization was conducted by sweeping the electrode potential in the positive direction at 10 mV amplitude signal, and the applied frequency was ranged from 100 kHz to 0.01 Hz. For the EIS test at a certain anodic potential, the passive current densities stay around 10⁻⁶ A cm⁻².

Corrosion morphology.—Corrosion morphology, including the in-situ morphology observation in electrolyte (part 3.3), was characterized by an optical microscopy (KEYENCE VHX-5000) or a field-emission scanning electron microscope (FE-SEM, Hitachi, Japan).

X-ray photoelectron spectroscopy.—X-ray photoelectron spectroscopy (XPS) measurements were performed using an Axis-ULTRA spectrometer (Kratos Analytical) controlled by a SUN workstation to test the valance of main elements in the corrosion product formed in solutions containing Cl⁻ and S₂O₃²⁻. Photoelectron emission was excited by an aluminum (monochromatized) source operated at 210 W with initial photon energy of 1486.71 eV. The survey spectra were recorded in steps of 0.33 eV using 160 eV pass energy, and high-resolution spectra were taken in steps of 0.1 eV using 20 eV pass energy. The base pressure was approximately 5 × 10⁻¹⁰ Torr. The photoelectrons were collected at a take-off angle of 90° with respect to the sample surface. The Cl peak at 284.6 eV from adventitious carbon was used as a reference to correct for charging shifts. Specimens were cleaned using distilled water, before each test.

Table II. Test solutions and the corresponding concentration ratio of chloride to thiosulfate.

| Concentration of chloride (C_Cl⁻) (mol · L⁻¹) | Concentration of thiosulfate (C_S₂O₃²⁻) (mol · L⁻¹) | C_Cl⁻/C_S₂O₃²⁻ | pH |
|-----------------------------------------------|-----------------------------------------------|-----------------|----|
| 0.6                                          | 0.5                                          | 1.2             | 6.98 |
| 0.6                                          | 0.075                                        | 8               | 6.99 |
| 0.6                                          | 0.01                                         | 60              | 6.98 |
| 0.6                                          | 0.001                                        | 600             | 6.97 |
| 0.6                                          | 0                     | +∞              | 6.98 |

Results

Breakdown potential.—Fig. 1 shows polarization curves of UNS N08800 in 0.6 mol · L⁻¹ NaCl solution containing various S₂O₃²⁻ concentrations ranging from 0 to 0.5 mol · L⁻¹. The corrosion potential is in the range of −0.24~−0.16 V_SCE. UNS N08800 is self-passive in all solutions even when the S₂O₃²⁻ concentration is 0.5 mol · L⁻¹, and the passive current densities stay around 10⁻⁶ A cm⁻². The passive current density increases as the potential increases for all solutions, indicating that the corrosion resistance of the passive layer is weakened. In other words, the dissolution rate of the passive layer is believed to be increase, as a result, the film thickness becomes thinner. Its smaller thickness yields an increased electrical field strength for the same potentiostatically fixed potential drop, which in turn causes faster migration of the cations through the layer to compensate for the faster passive corrosion reaction at the film–electrolyte interface. From Fig. 1, it is seen that the current abruptly increases at a certain potential, corresponding to passive film breakdown or oxidation of some ions in the solution. In thiosulfate-only solution, the current increases may attributed to thiosulfate species to oxidize to tetrathionates or other high oxidation state sulfur species. The oxidation potential of thiosulfate begins at around 0.5 V_SCE, which is observed from the cyclic voltammetry of thiosulfate on Pt electrode. Therefore, in thiosulfate-only solution, the increased current may attributed to thiosulfate species to oxidize to tetrathionates or other high oxidation state sulfur species. In addition, the E-pH diagram of S-H₂O system shows that thiosulfate species may oxidize to HSO₃⁻ at high potential.¹⁷

Fig. 2 shows the evolution of breakdown potential as a function of S₂O₃²⁻ concentrations in Cl⁻ and S₂O₃²⁻ solutions. For comparison, the breakdown potentials in chloride-only and S₂O₃²⁻-only solutions are also presented. It is clear that the breakdown potential varies greatly with solution chemistries. In chloride-only solution (Cl⁻ concentration is 0.6 mol · L⁻¹), the breakdown potential is 0.466 V_SCE. The addition of 0.001 mol · L⁻¹ S₂O₃²⁻ ions into 0.6 mol · L⁻¹ Cl⁻ solution

Fig. 1. Polarization curves of UNS N08800 in various solutions containing chloride and thiosulfate ions.

Table II. Test solutions and the corresponding concentration ratio of chloride to thiosulfate.
Cl\(^{-}\) solution leads to the breakdown potential decreases from 0.466 V\(_{\text{SCE}}\) to 0.369 V\(_{\text{SCE}}\), indicating that S\(_2\)O\(_3\)\(^{2-}\) plays a detrimental effect on passive film breakdown. The breakdown potential continues to decrease from 0.369 to 0.22 V\(_{\text{SCE}}\), and to −0.012 V\(_{\text{SCE}}\) as S\(_2\)O\(_3\)\(^{2-}\) concentrations increases from 0.001 to 0.01, and to 0.075 mol·L\(^{-1}\) respectively. In this case, S\(_2\)O\(_3\)\(^{2-}\) is detrimental to film breakdown. However, as S\(_2\)O\(_3\)\(^{2-}\) concentration further increases, the breakdown potential increases from −0.012 to 0.148 V\(_{\text{SCE}}\). The results reveal that abundant S\(_2\)O\(_3\)\(^{2-}\) ions may mitigate passive film breakdown. In thiosulfate-only solution (thiosulfate concentration is 0.5 mol·L\(^{-1}\)), the breakdown potential is as high as 0.734 V\(_{\text{SCE}}\) or even higher, demonstrating that S\(_2\)O\(_3\)\(^{2-}\) cannot significantly damage the passive layer without the existence of Cl\(^{-}\) ions.

Surface images of the passive film after breakdown.—Fig. 3 shows surface morphology of the passive film on UNS N08800 after the polarization curve. For comparison, all the samples are taken out as the current density reach to 1 mA·cm\(^{-2}\). Fig. 3a shows surface image of the passive film after breakdown in 0.6 mol·L\(^{-1}\) Cl\(^{-}\) solution. No visible pits can be found on the surface. The enlarged view shown in Fig. 3b shows that the pit size formed in this solution is extremely small, with diameters 0.2 to 4 μm. Nevertheless, the pit number in Cl\(^{-}\)-only solution is numerous. From Fig. 1, it is seen that there are many transient peaks in the polarization curve especially when the potential is close to the pitting potential. Each peak involves passive film breakdown and repassivation, which corresponds to a metastable pit process. The metastable pitting is not easy to propagate and to develop to stable pitting in chloride-only solution, therefore the pits size is very small in chloride-only solution. Fig. 3c shows surface image of the passive film after breakdown in 0.6 Cl\(^{-}\) + 0.01 mol·L\(^{-1}\) S\(_2\)O\(_3\)\(^{2-}\) solution. The pit size is much larger than that in Cl\(^{-}\)-only solution shown in Fig. 3b, however, the pit number is much less than that in Cl\(^{-}\)-only solution. Compared with chloride-only solution, not only the pitting potential decreases but also the number of transient peak decreases (Fig. 1). As the film breakdown induced by Cl\(^{-}\), S\(_2\)O\(_3\)\(^{2-}\) will adsorb on these sites, and stabilize the metastable pitting, leading to pitting propagates rapidly. As S\(_2\)O\(_3\)\(^{2-}\) concentrations increases from 0.01 to 0.075 mol·L\(^{-1}\), pit size becomes bigger and pit number also increases, as shown in Fig. 3d. This is due to abundant S\(_2\)O\(_3\)\(^{2-}\) ions adsorbing on metastable pitting sites to accelerate pit growth, leading to an increased pit number. As seen from Fig. 1, there is no transient peaks in the polarization curve conducted in 0.6 Cl\(^{-}\) + 0.075 mol·L\(^{-1}\) S\(_2\)O\(_3\)\(^{2-}\) solution, illustrating that as long as the film is broken down, the stable pitting occurs. As S\(_2\)O\(_3\)\(^{2-}\) concentrations further increases from 0.075 to 0.5 mol·L\(^{-1}\), pits size becomes small due to the reduced chloride adsorption, as shown in Fig. 3e. In summary, when the Cl\(^{-}\) adsorption is dominant, increasing S\(_2\)O\(_3\)\(^{2-}\) concentration would lower the pitting potential and produces more corrosion pits (Figs. 3c and 3d). However, further increase S\(_2\)O\(_3\)\(^{2-}\) concentration will mitigate the adsorption of Cl\(^{-}\) (Fig. 3e), therefore, retards the passivity breakdown and increases the pitting potential (see Fig. 1). Fig. 3f shows the corrosion morphology of UNS N08800 after passive film breakdown in 0.5 mol·L\(^{-1}\) S\(_2\)O\(_3\)\(^{2-}\) solution, which is obviously different from the situations shown above. No pits can be found on the whole surface, this is because the increased current is possibly due to oxidation of thiosulfate species to tetrathionates or other high oxidation state sulfur species.

Pit growth rate.—In order to elucidate the effect of thiosulfate on pitting growth rate, two sample were placed in an electrochemical cell and was polarized under a certain potential, and the corrosion morphology was monitored by using an optical microscope, the results is shown in Fig. 4. Figs. 4a–4e show corrosion morphology evolution of UNS N08800 in 0.6 mol·L\(^{-1}\) chloride + 0.075 mol·L\(^{-1}\) thiosulfate solution and under a potentiotostatic polarization of 0.2 V\(_{\text{SCE}}\) (~0.2 V higher than the pitting potential), some visible pits form on electrode surface at 5s (Fig. 4b), and more pits can be seen at 10s (Fig. 4c). At 30s, some pits continue to propagate whereas the other pits no not propagate (Fig. 5d). At 60s, some new pits generate while most of the old pits do not grow (Fig. 4e). It seems like the pit will no longer propagate when the pit size is big enough. This can be explained by the conditions for pitting propagates: an acidic environment is need for pit growth, the local environment do not maintain acidic if the pit size is big because big pits permit the fast mass transfer of ions from the bulk solutions to the pits. Figs. 4f–4j show corrosion morphology evolution in 0.6 mol·L\(^{-1}\) chloride solution and under a potentiostatic polarization of 0.8 V\(_{\text{SCE}}\) (~0.2 V higher than the pitting potential). The corrosion morphology evolution is remarkably different from the above one. In chloride-only solution, no visible pits can be found on
Electrochemical impedance spectroscopy.—In order to fully understand the passivity degradation mechanism, EIS was conducted at various passive potentials (including corrosion potential), and the results are shown in Fig. 5. Three test solutions are used in the EIS, they are Cl−-only solution, Cl− + S2O32− solution, and S2O32−-only solution. Overall, the Nyquist plots present incomplete capacitance arcs, which is consistent with the EIS characteristics of the passive systems. From the Nyquist plot, it is seen that the radius of the capacitance arc decreases as the polarization potential moves toward 0.24 to 0.44 V SCE. The decreased capacitance arc radius represents a decreased corrosion resistance of the passive layer, which is possibly due to the thinning passive layer and the increased dissolution rate of the passive layer. In Cl−-only solution, it is believed that the passive film degrades as the potential moves toward the anodic direction. In other words, the detrimental effect of Cl− ions on passive film degradation is more remarkable as the passive potential becomes more positive.

Fig. 5b shows Nyquist plots of UNS N08800 obtained at various passive potentials in 0.6 mol · L−1 Cl− solution with an addition of 0.075 mol · L−1 S2O32−. It is interesting that the capacitance arc radius increases first and then decreases, indicating that the detrimental effect of S2O322− is strongly dependent on the anodic potential. S2O32− is not detrimental to passivity when the potential locates within −0.223 to −0.123 V SCE. However, the detrimental effect becomes apparent as the potential is close to the pitting potential (0.043 V SCE). Fig. 5c shows Nyquist plots of UNS N08800 obtained at various passive potentials in 0.5 mol · L−1 S2O32− solution. Similar to the situation shown in Fig. 5b, the capacitance arc radius increases first and then decrease as the polarization potential becomes positive. The results reveal that S2O32− is beneficial to passivity in the potential range of −0.25 to −0.1 V SCE. In other words, S2O32− is only very harmful in the case that the test solution containing Cl− ions and, at the same time, the polarization potential must be sufficiently high.

The EIS data for an intact passive layer is modelled with electrochemical equivalent circuit 1 (EEC1) (Figure 6a) with one time constant. An EEC with two time constants (EEC2, Figure 6b) is used to model the EIS data for a passive film containing pits. In the EEC1, Rp represents the polarization resistance, and Qp is the constant phase element (CPE) related to the capacitance of the barrier layer. In the EEC2, the passive film is characterized by the capacitance of the barrier layer (Qp) and a film resistance (Rp). The second time constant describing the response of the substrate/electrolyte interface, is represented by a parallel combination related to the double layer, consisting of another CPE (Qdl) and a corresponding charge transfer resistance (Rct).

Fig. 6c presents the Nyquist plot for Rp as functions of potential and solution chemistries. At corrosion potential, Rp in S2O32−-only solution is significantly higher than Cl−-containing solution, indicating that Cl− ions are very aggressive in enhancing film degradation. In Cl− + S2O32− solution, Rp increases first and then decreases. Since Rp is related to charge transfer resistance at the film/solution interface, the increased Rp value indicates that charge transfer becomes tough. In thiosulfate-only solution, Rp increases first and then decreases, which is possible due to a change in film structure. This trend is also found in Cl− + S2O32− solution, indicating that the addition of thiosulfate into chloride solution will enhance the passivity in the potential range of −0.25 ~ −0.1 V SCE. In chloride-only solution, Rp keeps decreasing as the potential goes high, meaning that chloride ions enhance the charge transfer reaction rate at the film/solution interface. Overall, S2O32− is always beneficial to passivity when the potential is within −0.25 ~ −0.1 V SCE; but when the potential is higher than 0 V SCE, it has a combined effect with Cl− ions on film degradation.

Fig. 6d presents the obtained Qp values as functions of potential in three typical solutions. It is clear that the capacitance of the barrier layer in thiosulfate-only is lowest. The capacitance values decrease a little bit and then increase, which is possibly due to a changed film structure and composition. Similar phenomenon is seen in Cl− + S2O32− solution. In plain chloride solutions, the Qp values keep increasing. Table III lists the fitting results using EEC2 for passive film containing pits. When the potentials are close to the pitting potential, the Rp and Rct in Cl− + S2O32− solution are significantly lowered whereas the capacitance of the barrier layer goes high, compared with those in plain chloride solution. In thiosulfate-only solution, though the Rp and Rct are very low, this cannot be attributed to poor film properties, because at such a high anodic potential, part of the anodic...
Figure 5. EIS spectra of UNS N08800 polarized at various potentials (a) in 0.6 mol·L⁻¹ chloride solution (b) in 0.6 mol·L⁻¹ chloride + 0.075 mol·L⁻¹ thiosulfate solution (c) in 0.5 mol·L⁻¹ thiosulfate solution (fitting results are shown as lines on top of the data).

Figure 6. EIS fitting results (a) the electrochemical equivalent circuit for intact passive films (b) the electrochemical equivalent circuit for passive films containing pits (c) the polarization resistance as a function of anodic potential (d) the capacitance of the barrier layer as a function of anodic potential.

Current stems from thiosulfate species to oxidize to tetrathionates or other high oxidation state sulfur species.

X-ray photoelectron spectroscopy.—The corrosion product formed on UNS N08800 at the pitting potential and in 0.6 mol·L⁻¹ Cl⁻ together with 0.075 mol·L⁻¹ S₂O₃²⁻ was analyzed by XPS. The corrosion product is a complex mixture of sulfur and chlorine containing species.

### Table III. Parametric values of impedance parameters after simulation using nested EEC 2 for a passive layer containing pits.

| Solution          | Polarization potential (V SCE) | \( R_i \) (Ω·cm²) | \( Q_f \) (s⁰/Ω·cm²) | \( R_f \) (Ω·cm²) | \( n_f \) | \( Q_{dl} \) (s⁰/Ω·cm²) | \( R_{dl} \) (Ω·cm²) | \( n_{dl} \) |
|-------------------|-------------------------------|------------------|---------------------|------------------|---------|---------------------|------------------|---------|
| 0.6 Cl⁻           | 0.440                         | 12.3 ± 1.2       | 6.9 × 10⁻⁵ ± 1.2 × 10⁻⁶ | 1254 ± 351       | 0.84 ± 0.04 | 6.8 × 10⁻⁵ ± 2.1 × 10⁻⁶ | 2341 ± 1275     | 0.79 ± 0.02 |
| 0.6 M Cl⁻ + 0.075 M S₂O₃²⁻ | 0.142                         | 11.2 ± 1.6       | 8.7 × 10⁻⁵ ± 2.5 × 10⁻⁶ | 845 ± 198        | 0.78 ± 0.01 | 7.2 × 10⁻⁵ ± 1.8 × 10⁻⁶ | 899 ± 187       | 0.78 ± 0.03 |
| 0.5 M S₂O₃²⁻        | 0.6                           | 12.3 ± 2.2       | 10.1 × 10⁻⁵ ± 3.6 × 10⁻⁶ | 323 ± 98         | 0.86 ± 0.07 | 15.2 × 10⁻⁵ ± 2.4 × 10⁻⁶ | 458 ± 214       | 0.86 ± 0.02 |
Figure 7. The XPS detailed spectra for corrosion products form at the pitting potential and in 0.6 mol·L\(^{-1}\) chloride + 0.075 mol·L\(^{-1}\) thiosulfate (a) sulfur, (b) iron, (c) chromium, (d) nickel and (e) oxygen (f) the whole survey spectra.

spectra for S\(_2\)p, O1s, Fe2p3/2, Ni2p3/2, Cr2p3/2 are presented in Fig. 7. Fig. 7a shows the detailed spectra for the 2p level of S. It shows that the peak is composed of S\(^{2-}\), S\(^0\), SO\(^3\)\(^{2-}\), SO\(^4\)\(^{2-}\) peaks at energy level region of 160~172 eV, respectively. SO\(^3\)\(^{2-}\) and SO\(^4\)\(^{2-}\) is likely linked to the residual S\(_2\)O\(^3\)\(^{2-}\) in the solution, which contaminates the corrosion product and can be further oxidized in the air. S\(^{2-}\) and S\(^0\) refer to the electrochemically reduction of S\(_2\)O\(^3\)\(^{2-}\) within the pits to form sulfide and elemental sulfur. Fe\(^{3+}\) peak is observed at 710 eV, as shown in Fig. 7b. It is likely related to the well-known corrosion product formed on Fe-Cr-Ni alloys consisting of FeOOH. Fe\(^{2+}\) peak is observed at 711.5 eV, which is associated with FeS formed in the pits. Cr\(^{3+}\) peaks are observed at 577.6 and 576.1 eV (Fig. 7c), which refer to Cr(OH)\(_3\), and Cr\(_2\)S\(_3\) respectively. Fig. 7d shows Ni2p spectra, and the peaks corresponding to 862 and 855 eV refer to NiS and NiOH respectively. Also significant is the broad range of stability of NiS over the range of pH and potential, which means that NiS is stable in preference to NiO (similar to nature). The detailed spectra for the 1s level of O shown in Fig. 7e indicates that the peaks located in 529 and 531 eV are related to oxides and hydroxides. XPS results indicate that the corrosion product is mainly composed of sulfide and S\(^0\). Fig. 7f shows the whole XPS survey spectrum of the corrosion product in which Fe, Ni, Cr, S, C, Cl and Na are the main elements involved. Fe, Ni, Cr and S are the main composition of the corrosion product; Na and Cl come from the electrolyte we used; C is possibly from the contaminant in the air.

Discussion

According to the experimental observations mentioned above, the factors influencing passivity degradation on UNS N08800 in Cl\(^-\) and S\(_2\)O\(^3\)\(^-\) solutions are summarized and discussed. It is concluded that the passivity degradation depends on anodic potentials, chloride/thiosulfate concentration ratios, as well as the composition of the materials. Consequently, the breakdown mechanism is proposed based on the observed phenomenon.
Factors influencing passivity on UNS N08800 in chloride and thiosulfate solutions.—Potential.—From the EIS results, it is clear that the corrosion resistance of the passive film depends on the anodic potentials. At low anodic potentials, the addition of $S_2O_3^{2-}$ ions into chloride solution leads to an increased corrosion resistance of the passive layer. This can be explained by the competitive adsorption of $S_2O_3^{2-}$ and chloride ions on passive film surface. As long as there is some $S_2O_3^{2-}$ ions adsorb on film surface, it will mitigate the detrimental effect of $Cl^-$ ions, and therefore is beneficial to passivity within the potential ranging from to $-0.25$ to $-0.1$ V$_{SCe}$. The EIS and fitting results shown in Fig. 6 and Table III support this conclusion.

However, this beneficial effect does not exist at high anodic potential. On the contrary, a combined effect of $S_2O_3^{2-}$ ion and $Cl^-$ ion on film degradation is observed. Because $Cl^-$ ions in the solution are very aggressive, they will attack the passive layer at high anodic potential, leading to film breakdown and metastable pits forming on the surface. If the film is broken down, $S_2O_3^{2-}$ can adsorb on the fresh surface, reduce to $S^2-$ and form FeS, CrS$_2$ and NiS (see Fig. 7). The mechanism is well discussed and understood, which is generally believed that sufficient amount of $Cl^-$ ions are necessary to induce film breakdown and metastable pitting, and the subsequently adsorption and electrochemical reduction of $S_2O_3^{2-}$ within the metastable pits would stabilize the metastable pits, as a result, pits are formed and propagated.

Chloride-to-thiosulfate concentration ratio (CTCR).—CTCR is another important factor that influencing passivity breakdown. In this part, we only discuss the ion ratio effect on the high anodic potential or pitting potential. Because at low potential, i.e. at free corrosion potential, $S_2O_3^{2-}$ is always considered beneficial to passivity. At higher chloride/thiosulfate concentration ratio, $Cl^-$ adsorption is dominant, and therefore sufficient amount of $Cl^-$ ions would damage the passive layer to induce metastable pitting. The addition of $S_2O_3^{2-}$ ions into $Cl^-$ solutions would lower the pitting potential significantly. This phenomenon have been reported recently. For example, Singh et al. studied effect of $S_2O_3^{2-}$ addition on the metastable pitting of UNS S30403 and lean duplex stainless steel (LDX2101, UNS S32101) in 0.6 mol·L$^{-1}$ NaCl, and they found that the addition of $S_2O_3^{2-}$ stabilizes metastable pit growth and promotes pitting kinetics in $Cl^-$ solution. Moayed et al. studied the effect of $S_2O_3^{2-}$ ion on pitting corrosion of AISI 316 stainless steel in 0.1 mol·L$^{-1}$ NaCl solution, and they claimed that the $S_2O_3^{2-}$ addition increased pit initiation susceptibility and facilitated the transition of metastable pitting to stable pitting. From Fig. 1, it is found that in 0.6 mol·L$^{-1}$ NaCl solution, the addition of 0.001 to 0.5 mol·L$^{-1}$ $S_2O_3^{2-}$ would lower pitting potential, but the pitting potential reach to a minimum value when the $S_2O_3^{2-}$ concentration is 0.075 mol·L$^{-1}$. When $Cl^-$ adsorption is dominant, increase $S_2O_3^{2-}$ concentrations from 0.001 to 0.075 mol·L$^{-1}$ would lower the pitting potential; as $S_2O_3^{2-}$ concentration further increase to 0.5 mol·L$^{-1}$, the adsorption of $Cl^-$ ions is weakened, consequently, pitting potential increases accordingly. Similar phenomenon has been reported by Newman previously.

At lower chloride/thiosulfate concentration ratio, it is believed that $S_2O_3^{2-}$ adsorption is dominant and the adsorption of $Cl^-$ is weakened. As a result, the passive film cannot be broken down in this situation. In our previous work, we found that there is no pits formed on UNS N08800 surface after the polarization curve conducted in solution containing 0.1 mol·L$^{-1}$ + 0.5 mol·L$^{-1}$ $S_2O_3^{2-}$. The experimental observation verified that there is no pitting corrosion occurred if the chloride/thiosulfate concentration ratio is very low.

More important, the chloride/thiosulfate concentration ratio influences pit growth rate, as mentioned in part 3.3. In our previous work, we also found that the pit size in $Cl^-$ only solution is very small but the pit quantity is mass. This is because the pit growth rate in $Cl^-$ only solution is slow, which permit pit initiation on other sites of the passive layer. Comparatively, in $Cl^-$ + $S_2O_3^{2-}$ solutions, the pit size is much larger than that in $Cl^-$ only solution. This is related to the role of $S_2O_3^{2-}$ on pit propagation. The electrochemically reduction of $S_2O_3^{2-}$ within the pits and the subsequently formation of S$_{ads}$ is the main reason for accelerated pit growth rate.

Composition of the material.—Since Fe, Ni and Cr are the main composition of UNS N08800, the electrochemical behaviors of these pure metals are investigated in $Cl^-$ and $S_2O_3^{2-}$ solutions, the results are shown in Fig. 8. Fig. 8a shows polarization curves of Fe, Ni and Cr in 0.6 mol·L$^{-1}$ NaCl solution. It is apparent that Fe is active in $Cl^-$ solution. The corrosion potential of Fe in this solution is very negative, around $-0.7$ V$_{SCe}$. The corrosion current density is about 10$^{-4}$ Acm$^{-2}$, the current increases very fast as the potential goes high, and then increases slow due to the coverage of the corrosion product. Ni is more resistance to corrosion in $Cl^-$ solution than Fe, the corrosion potential is $-0.28$ V$_{SCe}$ and the corrosion current density would lower the pitting potential significantly. This phenomenon have been reported recently. For example, Singh et al. studied effect of $S_2O_3^{2-}$ addition on the metastable pitting of UNS S30403 and lean duplex stainless steel (LDX2101, UNS S32101) in 0.6 mol·L$^{-1}$ NaCl, and they found that the addition of $S_2O_3^{2-}$ stabilizes metastable pit growth and promotes pitting kinetics in $Cl^-$ solution. Moayed et al. studied the effect of $S_2O_3^{2-}$ ion on pitting corrosion of AISI 316 stainless steel in 0.1 mol·L$^{-1}$ NaCl solution, and they claimed that the $S_2O_3^{2-}$ addition increased pit initiation susceptibility and facilitated the transition of metastable pitting to stable pitting. From Fig. 1, it is found that in 0.6 mol·L$^{-1}$ NaCl solution, the addition of 0.001 to 0.5 mol·L$^{-1}$ $S_2O_3^{2-}$ would lower pitting potential, but the pitting potential reach to a minimum value when the $S_2O_3^{2-}$ concentration is 0.075 mol·L$^{-1}$. When $Cl^-$ adsorption is dominant, increase $S_2O_3^{2-}$ concentrations from 0.001 to 0.075 mol·L$^{-1}$ would lower the pitting potential; as $S_2O_3^{2-}$ concentration further increase to 0.5 mol·L$^{-1}$, the adsorption of $Cl^-$ ions is weakened, consequently, pitting potential increases accordingly. Similar phenomenon has been reported by Newman previously.

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is also much lower than that of Fe, and is about $10^{-6}$ Acm$^{-2}$. Cr is the most resistant metal among these three materials, showing wide passive region ranging from $-0.47$ to $0.72$ V
\text{SCE}$. or even higher (because the increased current is due to oxidation of thiosulfate). The passive current density of Cr in 0.6 mol $\cdot$ L$^{-1}$ NaCl solution is about $10^{-6}$ Acm$^{-2}$. The corrosion morphology of these three metals after polarization curves are shown in the insertion of Fig. 8a. Fe undergoes uniform corrosion and the corrosion locates in the grain boundary is extremely serious, and Ni suffers from localized corrosion whereas. Cr corrosion is not considered, because the increased current stems from the oxidation of thiosulfate, not corrosion of Cr.

Fig. 8b shows the polarization curves of Fe, Ni and Cr in 0.075 mol $\cdot$ L$^{-1}$ $\text{S}_2\text{O}_3^{2-}$ solution. Fe is active in this solution, which is similar to that shown in Fig. 8a. Both Ni and Cr is self-passive in $\text{S}_2\text{O}_3^{2-}$ solution. However, the passive current density of Ni is two order of magnitudes higher than that of Cr, indicating that $\text{S}_2\text{O}_3^{2-}$ is much detrimental to passivity degradation of Ni than Cr. The corrosion images after the polarization tests are shown in the insertion of Fig. 8b. Uniform corrosion occurs on Fe surface, and the corrosion degree at the grain boundary is much serious. Ni undergoes transpassive corrosion in $\text{S}_2\text{O}_3^{2-}$ solution, and Cr corrosion is not obvious. The acceleration corrosion of metal in solutions containing sulfur species is believed to be attributed to $\text{S}_ad_{S}$. Marcus et al.\textsuperscript{44} found that overlap of $\text{S}_{ad}$ with the stable metals decreases in the sequence Ni $>$ Fe $>$ Cr, so the effect of $\text{S}_2\text{O}_3^{2-}$ on the corrosion of these metals is expected to decrease in the same order Ni $>$ Fe $>$ Cr.

Fig. 8c shows the polarization of these three pure metals in 0.6 mol $\cdot$ L$^{-1}$ chloride $+0.075$ mol $\cdot$ L$^{-1}$ thiosulfate. Similar phenomena are presented, the most serious corrosion occurs on Fe, followed by Ni and Cr. In chloride $+$ thiosulfate solution, it seems that Ni undergoes uniform corrosion. However, in chloride-only solution, Ni suffers from localized corrosion. Previous investigation\textsuperscript{45,46} has been indicated that S-Fe and S-Ni bonds at metal surfaces are highly equal in character for submonolayer sulfur coverage although Ni and Fe sulfides are ionic solids, and the charge transfer from metal atom to sulfur is only $\approx 0.04$ electrons. This feature make the Fe and Ni more easily to dissolve from UNS N08800 substrate to solution. It should be noted that other factors may also affect the passivity breakdown, such as temperature, dissolved oxygen, pH value, etc. However, these factors are not considered in this work.

**Passivity degradation mechanism in chloride and thiosulfate solutions.**—Because Cl$^{-}$-induced passivity breakdown is extensively studied and the mechanism is discussed comprehensively though there has been some disputes on whether Cl$^{-}$ ions can enter into the passive layer.\textsuperscript{49-51} In this paper, we only discuss the possible mechanism of $\text{S}_2\text{O}_3^{2-}$-induced corrosion of UNS N08800 in Cl$^{-}$ solution, which is illustrated in Fig. 9.

When UNS N08800 is immersed in solutions containing Cl$^{-}$ and $\text{S}_2\text{O}_3^{2-}$ ions and in the condition that Cl$^{-}$ adsorption is dominant, Cl$^{-}$ ions would attack the passive layer, leading to passive film breakdown. If there is no enough Cl$^{-}$ ions or the concentration ratio of Cl$^{-}$ to $\text{S}_2\text{O}_3^{2-}$ is low, no localized corrosion is observed. As long as the passive film breaks down to generate metastable pitting, $\text{S}_2\text{O}_3^{2-}$ can enter into this region by electromigration. After the passive film is broken down, a series of reactions occur in these regions, as shown in Fig. 9. Metallic elements including Fe, Ni and Cr can oxidized to form either complexes of $\text{S}_2\text{O}_3^{2-}$/$\text{Cl}^{-}$ or oxide in the pits. The localized pH value decreases within the pits. $\text{S}_2\text{O}_3^{2-}$ can be reduced to different sulfur species including $\text{S}_ad$ and $\text{S}^2$, as confirmed by the XPS results shown in Fig. 7. On the passive layer surface the $\text{O}_2$ in the solution can be protonated to form $\text{HO}_2^-$. The pitting propagates on these active regions and causes the UNS N08800 failure. In addition, previous work found that $\text{S}_2\text{O}_3^{2-}$ can facilitate hydrogen entering into the passive layer,\textsuperscript{48} therefore, $\text{S}_2\text{O}_3^{2-}$ also induces hydrogen embrittlement in some cases.\textsuperscript{17}

It has been reported that $\text{S}_2\text{O}_3^{2-}$ has two structures: structure A ($\text{S}_2\text{O}_3^{2-}$) and structure B ($\text{S}_2\text{O}_3^{2-}$).\textsuperscript{48} Structure B has a sulfur chain that is unapped, and the unapped ends are free-radicals containing lone, unpaired electrons, which render them very reactive, especially toward bare metal surfaces.\textsuperscript{49} Staehle et al.\textsuperscript{50} claims that $\text{SO}_4^{2-}$ and $\text{S}_2\text{O}_3^{2-}$ do not have a significant effect on corrosion. However, $\text{S}_2\text{O}_3^{2-}$ and $\text{S}_2\text{O}_4^{2-}$ do not have structure B so that the interaction of these two species with passive film is quite weak. However, the $\text{S}_2\text{O}_3^{2-}$ ions can be reduced readily to $\text{S}_2\text{O}_4^{2-}$ and sulfide readily.\textsuperscript{52,53} Zakeri et al.\textsuperscript{54} used polish Ni electrode to study the transition potential and the repassivation potential of AISI type 316 stainless steel in the absence and the presence of 0.01 M thiosulfate in chloride containing media, they claimed that there was a significant decrease in the repassivation potential by addition of 0.01 M thiosulfate. Lillard et al.\textsuperscript{55} investigated pit propagation at the boundary between manganese sulfide, and found that there was a preferential corrosion of the MnS inclusion to a depth that reaches a pre-existing trench.

It has been reported that FeS and Fe$_2$S$_2$ were found on the surface of stainless steel,\textsuperscript{34} Ni$_3$S and H$_2$S formed on Alloy 600 in $\text{S}_2\text{O}_3^{2-}$ solution at high temperature,\textsuperscript{54,55} and Ni-Cr-S particles formed on Alloy 690,\textsuperscript{56} each indicating the possibility of reduction of $\text{S}_2\text{O}_3^{2-}$ to intermediate oxidation level sulfur. However, the formation of either sulfide or oxide within the pits is really dependent on the localized conditions within the pits including pH, potential, and solubility of the corrosion products.\textsuperscript{12} The electrochemical/chemical reaction process may occur via the following steps:

1. $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$

2. $\text{S}_2\text{O}_3^{2-} + \text{HO-M-O-M} \rightarrow \text{S-M-O-M}$

3. $\text{S-M-O-M} \rightarrow \text{M-S-M-O-M} \rightarrow \text{M}_n\text{S}_y$

In addition, $\text{S}_2\text{O}_3^{2-}$ may hinder the repassivation process via regarding dehydration reaction. If $\text{S}_2\text{O}_3^{2-}$ is not present, the dehydration reaction is simple, as shown in Equation 4. In the presence of $\text{S}_2\text{O}_3^{2-}$, sulfur replaces the $\text{-OH}$ and inhibits the dehydration process.
Conclusions

In this work, the factors influencing the passive film breakdown in near-neutral Cl− and S2O3^2− solutions are summarized as the following:

(1) **Anodic potential, S2O3^2−** is beneficial to passivity at corrosion potential regardless of the chloride-to-thiosulfate concentration ratios. The adsorption of S2O3^2− ions on film surface would mitigate the aggressiveness of Cl− ions. At high anodic potential where the passive layer is broken down, S2O3^2− shows radically different role on film degradation, it would hinder the repassivation process by stabilizing the metastable pit via electrochemically reduction of S2O3^2−, which is the within the pits.

(2) **Chloride/thiosulfate concentration ratio.** At high concentration ratio, there is a combined effect between these two ions on film degradation. The mechanism is believed as Cl−−attacking the passive film and S2O3^2− stabilizing the metastable pits by electrochemically reduction to form elemental sulfur and S2O3^2−. However, at low concentration ratio, this combined effect is vanished, because there is no enough Cl− ions to attack the passive film.

(3) **Composition of the Material.** Cr is very resistant to passivity breakdown in Cl− and S2O3^2− solutions. Ni and Fe undergoes serious corrosion in chloride-thiosulfate solutions. Therefore, materials with more Cr content would be more beneficial to passivity breakdown in Cl− and S2O3^2− solutions.

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