Electricity has played an important role in the history of human civilization and greatly influences the quality of life in modern society. The ever-increasing demand for electricity and environmental concerns warrant the need to seek safer, cleaner and more efficient methods to generate electricity, especially in the developing countries such as China and India where local economies are booming. However, the air pollution from coal-fired plants in China, for example, is deteriorating the environment and negatively affecting human health, thus validating the necessity to generate power in a more environmentally friendly manner. Nuclear power generation can provide a reliable supply of electricity, with low carbon emissions and relatively small amounts of waste that can be safely stored and eventually disposed of. Pressurized water reactors (PWRs) are used in the large majority of nuclear plants worldwide. Fig.1 shows a pictorial explanation of a PWR which mainly includes two loops—primary coolant loop (also called primary side) and secondary coolant loop (also termed as secondary side). The primary side refers to the heat generation system to make steam in the secondary side (shown as the orange loop in Fig. 1), and the secondary side denotes the Turbo-generator system (shown as the blue loop in Fig. 1).

The steam generator (SG) shown in Fig. 1 is one of the core components in PWRs, it facilitates heat transfer from the primary to secondary side. The main metallic components in a SG includes SG tubing, tube support plate (TSP) and tubesheet (TST). Primary coolant flows through the inside of the SG tubes and secondary water and steam are heated outside the SG tubes. Several early PWRs used austenitic stainless steel (SS) as SG tubing materials, but later changed to Alloy 600MA (“MA” means mill annealed) due to the alkaline and Cl−-induced stress corrosion cracking (SCC) of SS, then changed to use Alloy 600TT (“TT” means thermally treated) and generally to Alloy 690TT and Alloy 800NG (UNS N08800). Carbon steel was initially used for the tube supports but was found to be prone to corrosion,2 so was later changed to SS of various grades (Types 304, 316, 405, 409, 410).2 All the SG tubing, TSP and TST materials are of interest in this review paper, and are listed in Table I. It is worth noting that from batch to batch, their chemical compositions may vary slightly.

As SGs operate with high temperature and high pressure water, corrosion is an issue that threatens safe operation and causes reactor outages. On the primary side, primary water SCC, although historically important, does not fall within the main scope of this review paper because corrosion induced by sulfur is not a problem in the primary side. On the secondary side, corrosion is most likely to occur in the heat-transfer crevice (HTC)4 that is formed, for instance, between SG tubing and TSP at the secondary side.2,5,6 Inside the HTCs, some impurities from the bulk environment can concentrate and deposit, producing an often aggressive local environment and leading to sharp gradients in temperature, electrochemical potential, temperature, Sx species, alloy compositions and other impurity ions like Cl−. © The Author(s) 2019. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0531902jes]
Figure 1. Pictorial explanation of a commercial PWR. Primary coolant loop (primary side) is in orange and the secondary coolant loop (secondary side) is in blue. (Reproduced from Ref. 1).

Table I. Composition of Alloys Used in SG Tubing and Tube Supports.

| Element | Type 304A | Type 316A | Alloy 600 EPRI GuidanceB | Alloy 690 EPRI GuidanceC | Alloy 800 EPRI GuidanceD | Carbon steel ASTM A285 Gr C4A | Type 405 ASME SA479A | Type 410 ASME SA479A |
|---------|-----------|-----------|--------------------------|--------------------------|--------------------------|-----------------------------|------------------------|------------------------|
| C       | 0.08 max  | 0.08 max  | 0.025–0.05               | 0.015–0.025               | 0.03                      | 0.28                        | 0.15                   | 0.08                   | 0.15                   |
| Mn      | 2.00 max  | 2.00 max  | 1.00 max                 | 0.50                      | 0.4–1.0                   | 0.90                        | 1.00                   | 1.00                   | 1.00                   |
| P       | 0.045 max | 0.045 max | 0.015                    | 0.015                     | 0.020                     | 0.035                       | 0.040                  | 0.045                  | 0.040                  |
| S       | 0.03 max  | 0.03 max  | 0.010 max                | 0.003                     | 0.015                     | 0.035                       | 0.030                  | 0.045                  | 0.030                  |
| Si      | 1.00 max  | 1.00 max  | 0.50 max                 | 0.50                      | 0.3–0.7                   | -                           | 0.50                   | 1.00                   | 1.00                   |
| Cr      | 18–20     | 16–18     | 15.0–17.0                | 28.5–31                   | 20–23                     | -                           | 11.5–13.0              | 10.5–11.75             | 11.5–13.5              |
| Ni      | 8.0–10.5  | 10–14     | 10–14                    | 32–35                     | -                         | -                           | 0.50                   | -                      | -                      |
| Mo      | 0.2       | 0.2       | 0.2                      | 0.2                       | -                         | -                           | -                      | -                      | -                      |
| Fe      | Bal. *    | Bal.      | Bal.                     | Bal.                     | Bal.                      | Bal.                        | Bal.                   | Bal.                   | Bal.                   |
| Cu      | -         | -         | 0.50 max                 | 0.10                      | 0.75                      | -                           | -                      | -                      | -                      |
| Co      | -         | -         | 0.014 avg.               | 0.10                      | -                         | -                           | -                      | -                      | -                      |
| Al      | -         | -         | 0.40                     | 0.15–0.45                 | -                         | -                           | -                      | -                      | -                      |
| Ti      | -         | -         | 0.40                     | 0.60                      | -                         | 6xC to 0.75                 | -                      | -                      | -                      |
| other   | -         | -         | N = 0.050                | TiC≥12                    | -                         | -                           | -                      | -                      | -                      |
|         |           |           | B = 0.005                | Ti(C+N) ≥8                | -                         | -                           | -                      | -                      | -                      |
|         |           |           | Nb = 0.1                 | N≥0.03                    | -                         | -                           | -                      | -                      | -                      |

*a Bal. = balance.

*From ASM Handbook.174

*From EPRI.175

*From Gorman.176

*From Stellwag, et al.177

The Source of S⁺ Species in the Heat-Transfer Crevice

Sulfate \((SO_4^{2−})\) at ppb or ppt levels is present on the secondary side of SG tubing.2,13 Also, \(SO_4^{2−}\) can leak from the resin beads in the condensate polisher into the SG tubing.2,13 The purposeful addition of hydrazine \((N_2H_4)\) (e.g. ~100 ppb)4 to maintain the corrosion potential of SG within a safe region can cause a reduction of \(SO_4^{2−}\) to other \(S^+\) species, which are detrimental to the passivity of SG alloys.

\(S^+\) species in deposits in heated crevices is of primary importance, since some \(S^+\) species can promote SCC and pitting corrosion of SS and Alloy 600,4 which has been often reported in field inspections and in laboratory tests. The Canadian Bruce Unit 4 SGs5 experienced IGA/SCC of sensitized Alloy 600 at the top of TST since it restarted in late 2003, and the degradation was likely caused by \(S_2O_3^{2−}\) and \(S_4O_6^{2−}\) compounds that were found in the TTS sludge material.15 This kind of attack in Bruce Unit 4 most likely occurred during startup situations where oxidizing conditions developed during the shutdown. The IGA identified in Alloy 600 SG tubes and the TSP at the Palisades Nuclear Power Plant6 and Arkansas Nuclear One-1 in 1983 was also associated with \(S^+\) at low temperatures.16 Sulfur and chloride species were found in the pits of Alloy 600 tubes removed from Millstone 2, indicating that the sulfur species are likely involved in the pitting process.16 Alloys 800 and 690 have not been reported to have the occurrence of \(S^+\)-SCC and pitting corrosion under service conditions, but they have been extensively reported in laboratory tests.

\(\begin{array}{l}
\text{a nuclear power station in Ontario, Canada.} \\
\text{b nuclear power plant in Michigan, USA.} \\
\text{c nuclear power plant in Connecticut, USA.}
\end{array}\)
In this section, we will discuss the source of $S^i$ species in the HTC. The HTC can be found in three common types: (1) TSP/SG tubing crevice, (2) TST/SG tubing crevice, and (3) sludge/SG tubing crevice. $S^{2−}$ species are present in the HTC due to the reduction of $SO_4^{2−}$ by $H_2N_4$ within the crevice during full power operation, and $S^{2−}$ can be oxidized to $S_2O_3^{2−}$ and polythionate under the oxidizing conditions that occur during shutdown. The reduction of $SO_4^{2−}$ to lower valence $S^i$ (e.g. $S^{2−}$), which has been confirmed experimentally by Sakai et al., Sala et al., and Allmon et al., is thermodynamically feasible since the $N_2/N_2H_4$ half-cell equilibrium is very negative relative to the $S^6+/S^2−$ half-cell equilibrium. For instance, 0.9−21.3% $SO_4^{2−}$ was reduced to $S^i$ in the presence of $N_2H_4$ and ferrous ions at 345°C and 155°C within one month. Carbon steel 508 and 410 SS also significantly catalyze the reduction of $SO_4^{2−}$ under SG operating conditions. The Alloy 800 SG tubing material is much more inert to reduction of $SO_4^{2−}$ than both materials mentioned above. Unfortunately, the reaction kinetics of $H_2N_4$ under secondary side conditions and the reaction rates between $H_2N_4$ and $SO_4^{2−}$ or oxygen have not been measured and should be investigated in future work. These reactions within the HTC may be primarily heterogeneous because the crevice is actually a system involving at least steam and water, as schematically shown in Fig. 2.

The temperature of the outside circumference surface of the SG tube within HTC is close to the primary temperature $T_P$, but lower than the temperature of the secondary water ($T_S$). Therefore, there is a superheat temperature of $(T_P - T_S)$. The superheat in HTCs is the primary factor affecting $S^i$ concentration and the valence state of $S^i$ species. The condition within the crevice is very complicated, because it is filled with many deposits other than $S^i$, including Cu, Pb, Cl, iron oxide, silicate, organic species (as schematically shown in Fig. 2). Due to the sharp gradients in temperature, electrode potential, fluid density and concentration of impurities, the environment in the crevice is likely to be very aggressive. However, not all the reactions within the crevice are associated with degradation in-service, because the complex environment results in precipitation of stable and relatively nonthreatening species (many ionic species precipitate out due to loss of water polarity). This is one reason why degradation is not often observed in-service. Also, corrosion product, such as magnetite, in the HTC may play an important role in corrosion, but is seldom studied. The concentrations of the various deposits are significantly different, depending on their vapor pressures because of higher concentrating species having lower vapor pressures. The pH and electrochemical potential with in the crevice can significantly affect the $S^i$ species distribution. However, the concentrations of $S^i$ species within the crevice are not well determined.

### The Stability of Sulfur Species

**Sulfur compounds.**—Sulfur compounds ($S^i$) found in the HTCs of secondary side of PWR are expected to be present as various of species with oxidation states from $−2$ to $+6$. Some species can adsorb (chemisorb) on the SG tubing surface, and may further be electro-reduced or electro-oxidized. In fact, the environment in the HTCs is very complicated and it contains solid particles, steam, and water; of more concern is the complexity of the chemistry in the crevice itself and the wide variation of pH ($∼4$ to $9$), cations (Na, Cu, Ca, Mg, Pb, etc.) and anions (e.g. $S$, $Cl$, etc.) possibly present. Fig. 3 schematically shows the diversity and formation conditions of chemical reactions of $S^i$ species and their interconversion under specific conditions. Most of them are unstable or metastable except $SO_4^{2−}$, $S^{2−}$, and $S^{6−}$. The oxidation states of $S$ can be fractional because $S$ atoms can be present different oxidation states in a compound. Table II shows the structures and space-filling models of some common sulfur species. The complicated condition in the HTC may change the course of
Table II. The structure and space-filling model of some common sulfur species.

| Sulfur-species       | Valence of sulfur | Structure | Space-filling model |
|----------------------|-------------------|-----------|---------------------|
| Sulfate (SO$_4^{2-}$) | +6                | ![Structure](image1) | ![Space-filling](image2) |
| Dithionate (S$_2$O$_6^{2-}$) | +5               | ![Structure](image3) | ![Space-filling](image4) |
| Sulfite (SO$_3^{2-}$) | +4                | ![Structure](image5) | ![Space-filling](image6) |
| Tetrathionate (S$_4$O$_6^{2-}$) | +2.5              | ![Structure](image7) | ![Space-filling](image8) |
| Dithionite (S$_2$O$_4^{2-}$) | +3                | ![Structure](image9) | ![Space-filling](image10) |
| Thiosulfate (S$_2$O$_3^{2-}$) | +2               | ![Structure](image11) | ![Space-filling](image12) |
| Elemental sulfur (S) | 0                 | ![Structure](image13) | ![Space-filling](image14) |
| Elemental sulfur (S$_8$) |                  | ![Structure](image15) | ![Space-filling](image16) |
| Sulfide (S$_2^{2-}$)   | −2                | ![Structure](image17) | ![Space-filling](image18) |
| Hydrogen sulfide (H$_2$S) |                | ![Structure](image19) | ![Space-filling](image20) |

Aqueous solutions of S$_2$O$_4^{2-}$ with low concentrations are stable and can be boiled without decomposition. When the concentration of S$_2$O$_4^{2-}$ is increased, a disproportionation into SO$_4^{2-}$ and SO$_3^{2-}$ will occur as shown in Equation 2.

$$S_2O_4^{2-} + H_2O \rightarrow H_2SO_3 + SO_3^{2-}$$ [2]

In laboratory test, during the anodic polarization of metal during immersion in aqueous solution containing S$^-$, S$_2$O$_6^{2-}$ can be generated at high potential due to the oxidation of low valence S$^-$.

Sulfite (SO$_3^{2-}$).—Sulfite (SO$_3^{2-}$) is not present in the feed water of secondary side of PWR, but it may stem from the oxidation of S$^-$ in the presence of oxygen during PWR shutdown, thus occurring at HTC occluded sites.

$$2S^- + 3O_2 \rightarrow 2SO_3^{2-}$$ [3]

SO$_3^{2-}$ undergoes hydrolysates to generate H$_2$SO$_3$ and HSO$_3^{-}$:

$$SO_3^{2-} + H_2O \rightarrow HSO_3^{-} + OH^-$$ [4]

$$HSO_3^{-} + H_2O \rightarrow H_2SO_3 + OH^-$$ [5]

Tetrathionate (S$_4$O$_6^{2-}$).—S$_4$O$_6^{2-}$ has been reported to be found in TTS sludge material, due to the oxidation of S$_2$O$_3^{2-}$.

$$2S_2O_3^{2-} \rightarrow 2e^- \rightarrow S_4O_6^{2-}$$ [6]

Surface reactions occurring on SG tubing, with potential consequences in pitting corrosion, uniform corrosion, passivity degradation, and SCC. Therefore, the analysis of the stability of sulphur species is useful when identifying their roles on uniform corrosion and localized corrosion.

Sulfate (SO$_4^{2-}$).—Sulfate (SO$_4^{2-}$) at ppb or ppt levels can be detected in the secondary side feedwater. SO$_4^{2-}$ is a stable anion because the S atom is surrounded symmetrically by four oxygen atoms, thus it can be reduced only in a strong reducing environment. The reducing agent hydrazine (N$_2$H$_4$) that is present on the secondary side of SG tubing can reduce SO$_4^{2-}$ to S$^2^-$. This reaction does not happen readily at room temperature and likely, is highly dependent on temperature although this is still unclear. Experimental evidence has confirmed that Fe, Ni, Cr and their alloys can act as catalysts for SO$_4^{2-}$ reduction reactions at high temperature. In addition to PWR condition, SO$_4^{2-}$ can be reduced to S$^2-$ by sulfate-reducing bacteria that is extensively present in soil or petroleum.

$$2Fe_2(SO_3)_3 \rightarrow 2FeS_2O_6 + 2FeS + 3O_2$$ [1]

$S_2O_3^{2-}$ undergoes hydrolysates to generate H$_2$SO$_3$ and HSO$_3^{-}$:

$$SO_3^{2-} + H_2O \rightarrow HSO_3^{-} + OH^-$$ [4]

$$HSO_3^{-} + H_2O \rightarrow H_2SO_3 + OH^-$$ [5]

Tetrathionate (S$_4$O$_6^{2-}$).—S$_4$O$_6^{2-}$ has been reported to be found in TTS sludge material, due to the oxidation of S$_2$O$_3^{2-}$.23

$$2S_2O_3^{2-} \rightarrow 2e^- \rightarrow S_4O_6^{2-}$$ [6]
It should be stored at low temperature (2–8°C), as it is not stable at high temperature.13 In acidic solutions, it can be reduced to form S0.13

\[ \text{S}_4\text{O}_6^{2-} + 12\text{H}^+ + 10\text{e}^- \rightarrow 4\text{S} + 6\text{H}_2\text{O} \]  

\[ \text{S}_2\text{O}_3^{2-} + \text{H}^+ \rightarrow \text{S}_0 + \text{HSO}_3^- \]  

**Thiosulfate (S_2O_3^{2-}).**—The pH value of the HTC is, in most cases, near neutral,12 therefore, thiosulfate (S_2O_3^{2-}) is present because S_2O_3^{2-} is metastable only in neutral or alkaline solution.13 In acidic solution S_2O_3^{2-} decomposes to HSO_3^- , S^-, and SO_2:13

\[ \text{S}_2\text{O}_3^{2-} + 2\text{H}^+ \rightarrow \text{SO}_2 + \text{S}^0 + \text{H}_2\text{O} \]  

\[ \text{S}_2\text{O}_3^{2-} + 2\text{H}^+ \rightarrow \text{SO}_2 + \text{S}^0 + \text{H}_2\text{O} \]  

\[ \text{S}_2\text{O}_3^{2-} + 2\text{H}^+ \rightarrow \text{SO}_2 + \text{S}^0 + \text{H}_2\text{O} \]  

\[ \text{S}_2\text{O}_3^{2-} + 2\text{H}^+ \rightarrow \text{SO}_2 + \text{S}^0 + \text{H}_2\text{O} \]  

\[ \text{S}_2\text{O}_3^{2-} + 2\text{H}^+ \rightarrow \text{SO}_2 + \text{S}^0 + \text{H}_2\text{O} \]  

\[ \text{S}_2\text{O}_3^{2-} + 2\text{H}^+ \rightarrow \text{SO}_2 + \text{S}^0 + \text{H}_2\text{O} \]  

**Thermodynamics of corrosion in environments containing S_x**.—Corrosion thermodynamics provides the framework for bounding sub-modes of SCC and passivity degradation on the secondary side of SG tube materials. The corrosion thermodynamics can be shown in forms of Pourbaix diagrams, volt-equivalent diagrams (VEDs) and E–temperature (E–T) diagrams. Calculations of S–H_2O and S–metal–H_2O thermodynamics are not easy as S exists in a variety of oxidation states (including fractional states) from −2 to 6, and more importantly, S can adsorb on Fe, Ni and Cr with a broad pH range and play a role in corrosion acceleration14 (the mechanism will be discussed in details in S^0 section).

**Potential–pH (E–pH) and E–temperature (E–T) diagrams.**—Potential–pH (E–pH) and E–temperature (E–T) diagrams are maps from which corrosion tendencies can be identified. Below, E–pH and E–T relations are described for S–H_2O and S–metal–H_2O systems.

1. **S–H_2O**

   To investigate the electrochemical behaviors of alloys in S^0–containing solutions, the valence of S^0 as functions of the electrode potential and the solution pH has been studied with an E–pH diagram of the S–H_2O system.37–39 This type of E–pH diagram and distribution curves of aqueous species are of theoretical and practical importance for understanding the secondary side environment. Such diagrams involving H_2S, H_2O, S^2-, S^0, HSO_3^-, SO_3^{2-}, and SO_4^{2-} (some of them are metastable in solution) have been reported at 25°C,25,30,31,200°C,32 and 300°C.33 Some metastable ions were also included in the studies, because E–pH diagrams can predict the metastability of those species, including S_2O_3^{2-}, SO_4^{2-}, and S_2O_6^{2-}.33,33 However, the E–pH diagram of S–H_2O system gives no information on the corrosion of alloy elements in the SG tubing materials. Therefore, there is a need to develop E–pH diagram of S–Metal–H_2O.

2. **S–Metal–H_2O**

   The E–pH diagram of S–Metal–H_2O gives a framework for bounding sub-modes of SCC and passivity degradation on the secondary side of SG tube materials. Theoretical calculations made by Marcus and Protopopoff31,36–38 considered S adsorbed on Fe, Ni, Cr, or Cu in water at 25 and 300°C, as shown in Fig. 4. They described the stability regions of metal, metal oxides, metal hydroxides and the formation of metal sulfide. It should be noted that Cr is very resistant in near-neutral pH S^0-containing environments due to the formation of Cr_2O_3, but Fe and Ni are not so resistant because the formation of sulfide in certain potential range. As seen from Figs. 4e and 4f, the presence of sulfur has limited effect on Cr, at 25°C and 300°C, and no metal sulfides are formed. In addition, S^0 can adsorb on Fe, Ni, Cr surface in a wide potential range to catalyze anodic dissolution. It is a chemisorption process on metal surfaces due to an electronegative attraction, with partial charge transfer, resulting in a partial dipole (+) charge on the metal surface.31,39,40 This leads to increased activation energy necessary needed for metal dissolution, thus accelerating anodic corrosion reactions.31,39,40

E–Temperature (E–T) diagrams were recently developed by Nickchi and Alfantazi41 who used them to evaluate the thermodynamic stability of metal (Fe, Ni, Cr)-H_2O systems at temperatures up to 200°C, and studied the corrosion behavior of high purity Fe, Ni, and Cr in NaSO_4 solutions. The advantages of these diagrams are their capabilities of presenting the phase stability as a function of temperature. However, only SO_3^{2-} was considered in the work,31 and no other important S^x species were taken into consideration.

**Volt equivalent diagrams.**—The E–pH diagram in Fig. 4 includes several S^x species only, because it is too complex to convey useful information if all the S^x species are included. Volt equivalent diagrams (VEDs) developed by Macdonald and Sharifi-Asl,42 were used to represent thermodynamic stability of S^x in a convenient way. In VEDs, equilibrium information for any given S^x species is represented as a
Figure 4. Equilibrium $E$-$pH$ diagrams for the system $S_{ads}$ (Fe, Ni, Cr)-$O_{ads}$ (Fe, Ni, Cr)-$S$-(Fe, Ni, Cr)-$H_2O$ at 25°C (a, c, e) and 300°C (b, d, f) (The activities of dissolved sulfur and nickel species are, on the molar scale: dissolved $S = 10^{-4}$ mol/kg; dissolved metal $= 10^{-6}$ mol/kg. The stability domains are limited by the lines: (... ...) $H_2O$ system; (- - -) $S$-(Fe, Ni, Cr)-$H_2O$ systems; (- - - -) $S_{ads}$ (Fe, Ni, Cr)-$O_{ads}$ (Fe, Ni, Cr)-S-Ni-$H_2O$ systems. $\theta_0$ and $\theta_0$ are the relative surface coverage of adsorbed sulfur and oxygen, relatively $^{37}$ (a) $S_{ads}$ (Fe)-$O_{ads}$ (Fe) -$S$-Fe-$H_2O$ (b) $S_{ads}$ (Fe)-$O_{ads}$ (Fe) -S-Fe-$H_2O$ (c) $S_{ads}$ (Ni)-$O_{ads}$ (Ni) -S-Ni-$H_2O$ (d) $S_{ads}$ (Ni)-$O_{ads}$ (Ni) -S-Ni-$H_2O$ (e) $S_{ads}$ (Cr)-$O_{ads}$ (Cr)-S-Cr-$H_2O$ (f) $S_{ads}$ (Cr)$-O_{ads}$ (Cr)-S-Cr-$H_2O$ (Reprinted with permission from Ref. 37).
function of average sulfur oxidation state. Figs. 5a and 5b shows VEDs for the S–H₂O system at pH = 0 and 10.5, respectively, at 25°C (the activity of all S⁰ species is 1), with positive slopes in acidic solutions and negative slopes in alkaline solutions. One can judge the stability of S⁰ species by these rules; if a species A, for instance, lies above a line joining any two or more other compounds (B and C), A will tend to be decomposed into B and C; If A lies below B and C, B and C will tend to react to form A.

VEDs are useful tools to evaluate the thermodynamic stability of almost all S⁰ species in S–H₂O system, but they do not give information in S– Metal–H₂O systems.

Summary of S thermodynamics.—Thermodynamic calculations such as E–pH and E–T diagrams provide a holistic picture of the stability of metal (including their dissolved anions or cations) and S⁰ species as functions of temperature, solution pH, and electrode potential. Species distributions and VEDs depict the thermodynamic stability of S⁰ species. Combined use of these diagrams can present visual information about corrosion state and stability of species. The information that is not provided in E–pH and VED diagrams includes the following:

1. Thermodynamic calculations offer little information about the corrosion process and the underlying mechanism of corrosion. Besides, the reaction kinetics are also not provided, but the kinetics of SO₄²⁻ reduction is particularly important in enabling corrosion occurrence on SG, TSP and TTS materials.
2. Most developed diagrams are representative of a pure metal, but are not valid for alloys that contain more than one alloy element. A recent important work has focused on E–pH diagrams for Ni–Cr–Fe alloys and Pb adsorption on Ni–Cr–Fe alloy surfaces in aqueous solutions in a temperature range of 25–300°C, and such diagrams in S⁰-containing environment are needed.
3. During the corrosion process, some intermediate products are formed that are not considered in the thermodynamic calculations.
4. Thermodynamic calculations are performed based on the equilibrium state of metal and its corresponding cations in solution only, but the effects of other soluble ions on the equilibrium are neglected. When conducting metal corrosion experiments in high temperature and high pressure water to simulate the secondary side condition, the results are greatly affected by Fe²⁺, Ni²⁺, Cr³⁺, and S⁰ concentrations, temperature, complexing agents and pH. These variables usually change over time as corrosion reactions progress, therefore, the thermodynamic stability range of ions and compounds also change with time, which should be taken into consideration in the experiment. In addition, localized corrosion such as pitting corrosion and SCC is often the primary concern and local chemistry conditions in pits and cracks are also constantly in flux. Recently, Santucci Jr. et al. developed chemical stability diagrams (CSDs) to present the relative stabilities of ions, chemical compounds, and complexes of an element as a function of bulk solution chemistry (pH and metal ion concentration). With the help of CSDs, data interpretation and experimental design in simulated secondary side conditions can be improved.
5. In real situations, the corrosion may significantly be inhibited by solid deposition on the tubing surface. As shown in Fig. 2, these depositions may include iron oxide, silicate, and organic species, which are not considered in the thermodynamic calculations.
6. In E–pH diagrams, the average pH value in bulk solution, not the pH on the anodic and cathodic reaction sites, is used. However, in real corrosion systems, the pH in anodic and cathodic regions is likely different from the one in the bulk solution.

Factors That Influence S⁰–Induced Passivity Degradation

pH.—As SG tubing alloy and TSP materials are in passive state (a metal protected with an oxide film), the outermost surface of the passive film interacts with H⁺ or OH⁻ in the solution when it is exposed to an aqueous solution, resulting in dissolution of the passive layer. The formation and dissolution kinetics of passive film and other film properties are mainly governed by the solution pH and potential, which influences the level of protection the passive layer provides to the metal in direct and indirect ways. The TSP material used in early times was carbon steel, which is also in passive state in the bulk secondary side water. In this part, we mainly discuss the effect of solution pH on the degradation of passive metal/alloys.

pH and S⁰ species distribution.—The effect of pH on the S⁰ distribution in an aqueous solution can be expected in Fig. 4. S₂O₄²⁻ is present only in near neutral or alkaline solutions whereas H₂S exists only in the solutions where the pH is lower than 7 (S₂O₄²⁻ is a metastable species, as discussed in Thiosulfate (S₂O₄²⁻) section). Solution pH, on the one hand, affects the S⁰ species that is present in solution, and on the other hand, it also determines the H⁺ and OH⁻ concentrations. These factors ultimately determine the electrochemical behavior of the metal in a complex way.
pH and surface charge.—Solution pH determines the surface charge of a passive film, therefore, there exists a critical pH at which the surface of the adsorbent is neutral, i.e., the point of zero charge (PZC) (also called pH_{PZC}).46-48 Because the ions with the same charge are repulsive,45 solution pH significantly influences the passivity breakdown via changing the surface charge. When the pH is lower than the pH_{PZC}, such as in acidic solutions, the surface is positively charged. The dissolution products of the passive film are Fe(H_{2}O)_{6}^{2+}, Cr_{2} (OH)_{3}^{2+}, and Cr(OH)_{2}^{+}, which accumulate in the interfacial layer, and Cl^{-} and S_{2}O_{3}^{2-} appear to reach the film surface due to anion-selective Reactions 20–22.49

\[
\text{FeO}_{3} + 12\text{H}_{2}O + 6\text{H}^{+} + 2e^{-} \rightarrow 2\text{Fe}^{2+} + 6\text{H}_{2}O
\]  [20]

\[
3\text{Cr}_{2}O_{3} + 10\text{H}^{+} \rightarrow 2\text{Cr}^{3+} + 5\text{H}_{2}O
\]  [21]

\[
\text{Cr}_{2}O_{3} + \text{H}_{2}O + 2\text{H}^{+} \rightarrow 2\text{Cr}^{3+} + \text{H}_{2}O
\]  [22]

When the passive film surface is negatively charged, as in alkaline solution, film dissolution reactions are shown in Equations 23 and 24. The Cl^{-} and S_{2}O_{3}^{2-} attack on the passivated alloy surface is significantly limited.49

\[
\text{CrO}_{4}^{2-} + \text{OH}^{-} + 4\text{H}_{2}O \rightarrow 2\text{Cr}^{3+} + 4\text{OH}^{-}
\]  [23]

\[
\text{FeO}_{3} + 3\text{H}_{2}O + 2e^{-} \rightarrow 2\text{Fe}^{2+} + 3\text{OH}^{-}
\]  [24]

pH effect on film dissolution.—The pH effect on film dissolution can be estimated from the E–pH diagrams as shown in Fig. 4. The Fe-Cr-Ni alloy may undergo dealloying in caustic conditions due to the formation of soluble CrO_{2}^{2-}50 as shown in Fig. 4f. For instance, Cr was depleted while Fe was enriched in the passive film formed on alloy 800 in alkaline solution at 300°C.31 This observation agrees with other results52 that a Cr-depleted and Fe-enriched anodic film formed on a Cr-depleted Fe-Cr-Ni alloy may undergo dealloying in caustic conditions due to a lack of experimental evidence. Unfortunately, the underlying mechanism was not interpreted in depth due to a lack of experimental evidence.

The metal cation transport rates during film formation also have significant effects on film composition.54,55 Faster diffusing species will pass through to the outer layer, while slower diffusing components, such as Cr, will be oxidized due to their stagnant movement and remain in the inner layer. The diffusion rates of these alloy ions in the oxide have been measured54,55 and show a well defined order:

\[
\text{Fe}^{2+} > \text{Ni}^{2+} >> \text{Cr}^{3+}
\]  [25]

Therefore, film compositions are mainly influenced by these two aspects: (1) solution pH, and (2) metal cation transport rate through the oxide film. With respect to the S^{2-} effect on film dissolution, especially at high temperature, the mechanism is poorly understood. Atomic modeling and calculations regarding the interaction of S^{2-} with the passive film are needed to assist clarification of the film dissolution mechanism at the atomic scale.

Electrode potential.—As shown in the E–pH diagrams (Fig. 4), the electrode potential can significantly affect the S^{2-} species distribution as well as the film composition. Under the fully deaerated secondary side conditions, the electrochemical potential of the cathode reaction is dominated by the H_{2}OH_{2} equilibrium, depending on the pH and the pressure of H_{2}O.11 In the HTC, the electrochemical potential of SG tube is influenced by the deposits including S^{2-} species, iron oxide, silicate and organic species. During PWR shutdown, sometimes O_{2} is admitted to the secondary side and it can oxidize some S^{2-} species to higher valence species.13 As a result, the electrochemical potential of SG tube is changed due to a change in environmental conditions.

S^{2-} species distribution.—As indicated both in the thermodynamic predictions (Fig. 4) and in laboratory tests,54,55 the electrode potential has a significant effect on the S^{2-} species: at high anodic potential, S^{2-} is present as the oxidized species, such as SO_{4}^{2-} and HSO_{4}^{2-}; at low potential, S^{2-} is reduced mainly to HS^{-} and H_{2}S. However, the kinetics of those reactions are poorly understood.

Film composition.—Film composition is significantly affected by the electrode potential, which can be estimated from the E–pH diagram in Fig. 4. The effect of electrode potential on film dissolution rate can be directly observed from the polarization curves. In most cases, the dissolution rate of a passive metal at the free corrosion potential is as low as nA·cm^{-2}. Driving the potential in the anodic direction, the film dissolution rate increases until the film breaks down. For SG tubing containing Cr (alloy 690 is an example), the polarization curves show two regions in simulated crevice chemistries containing S_{2}O_{3}^{2-} in alkaline solutions: a passivity region at low potential and a transpassivity region at high potential; the latter is ascribed to the dissolution of Cr_{2}O_{3} in the passive film to CrO_{4}^{2-}.50-57 (also termed as dealloying).

Alloy composition.—Iron/nickel/chromium.—SG tubing materials should be self-passive in normal service conditions of the secondary side. The contents of Fe, Ni, and Cr in alloys significantly affect their localized corrosion resistance in Cl^{-} + S_{2}O_{3}^{2-} solutions.58,59 Cr is considered to be beneficial for passivity in S^{2-} containing environments due to the formation of protective Cr_{2}O_{3} in near neutral conditions.60 The work of Marcus et al.61 claimed that excessive Fe and Ni contents in alloys will make the alloys more susceptible to accelerated anodic dissolution in the presence of reduced sulfur species, because the passivity can be impaired by the more thermodynamically favorable but less protective FeS, NiS, Ni_{3}S_{2}, leading to a high passive current density. In Cl^{-} only solutions, Alloys 600, 690 and 800 are all sensitive to pitting corrosion, but Alloy 600 is relatively less susceptible to pitting than 690.63 In the presence of S_{2}O_{3}^{2-} in chloride solutions, Alloys 600, 690 and 800 are all sensitive to pitting corrosion and pitting corrosion in chloride solutions.58,59 One of the most important issues of concern is the critical step for pitting corrosion. A recent perspective paper proposed that the critical step is pit growth stability under aggressive conditions.64 and Alloy 800 in 0.6 M CI^{-} + 0.075 M S_{2}O_{3}^{2-} solutions is an example. In this case, passive film is easy to breakdown, leading to a fast pitting growth rate. If the solutions are not harsh, e.g., Alloy 800 in 0.001 M Cl^{-} + 0.075 M S_{2}O_{3}^{2-} solutions, pits are not easy to initiate, the passive film breakdown becomes the critical step for pitting corrosion.

Other alloying elements.—(1) Molybdenum Mo, as an alloying element, is present in 316 SS and Alloy 690 (see Table I). TSP materials like 316 SS with higher molybdenum (Mo) content are more resistant to pitting corrosion than the Mo-free 304 SS.65,66 The role of Mo in solid solution in the pitting corrosion of metals was summarized in three points:56,67-70

(1) Mo-containing alloys are more resistant to pitting corrosion. This effect is likely provided by Mo^{5+} locally enriched on the film surface.
(2) Mo slows the kinetics of anodic dissolution after film breakdown and pitting initiation, as reported by Marcus and Olefeld.69
(3) Mo located on the surface binds adsorbed S and removes it from the surface (by dissolution), thus improving the corrosion resistance when S^{2-} species are present. This binding effect was originally reported for nickel alloys.70

(2) Nitrogen
Nitrogen (N) is present in solid solution as well as in precipitates in Alloy 800 and 690 (see Table I). N plays dual roles in the corrosion...
resistance of alloys. Alloying N is beneficial to the tensile property and corrosion resistance of the metal, and it also promotes the formation of TiN inclusions on the metal (which is usually harmful).\(^\text{71}\) The effect of solid solution N on increased corrosion resistance in acidic solutions is because the solid solution N can interact with \(\text{H}^+\) to form \(\text{NH}_4^+\) at the interface of the metal/passive film.\(^\text{71}\)

\[\text{[N]} + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NH}_4^+ \quad [26]\]

Equation 26 leads to higher pH. This mechanism may also be applied in localized corrosion, as the pH in the corrosion pits is acidic. However, in alkaline solution, the mechanism is not clear. Alloying N has a synergistic effect with Mo on increasing the pitting potential.\(^\text{72}\) Solid solution N obviously plays a role in corrosion resistance for Alloys 800 690 600, but it is hard to correlate N with the differences in corrosion resistance among them, because corrosion resistance is jointly impacted by many other factors. As of this writing, the role of N on S\(^{\circ}\)-induced corrosion has not been studied systematically.

TiN inclusions are present in alloys 690 and 800, mainly in square and rectangular shapes.\(^\text{73}\) The size generally varies from submicron to several microns. Broken TiN and TiN clusters may facilitate the corrosion fatigue of Alloy 690.\(^\text{74}\) However, their role in localized corrosion in simulated PWR conditions has not been investigated.

**Temperature.**—Increasing temperature leads to a change in S\(^{\circ}\) species distribution. Increasing solution temperature degrades the protectiveness of the passive film and increases the corrosion rates in S\(^{\circ}\) environment since corrosion is thermally activated.\(^\text{75}\) Each 10\(^\circ\)C increase in temperature corresponds to about 50 kcal mole/\(^\text{−}\) in activation energy for corrosion reaction, thus doubling the corrosion rate.\(^\text{76}\) Increasing operating temperatures have been regarded as the reason of increased uniform corrosion rates for Alloy 600MA tubes.\(^\text{4}\) At high temperature, the dissolution rate of the passive layer is higher than the dissolution rate at low temperature because the vacancy generation and transfer rate are enhanced.\(^\text{77}\) The corrosion of SG tubing alloys has been postulated to occur at low temperature due to the presence of both O\(^{2−}\) and S\(^{\circ}\) species during PWR shutdown or startup evolutions, as well as at high temperature during full power operation.\(^\text{78,79}\) Early work mainly investigated the pitting corrosion of Alloys 600, 690, and 800 in solutions containing Cl\(^{−}\) and S\(_2\)O\(_3^{2−}\) in low temperature ranges (below 100\(^\circ\)C).\(^\text{77-79}\) and recent work was conducted at elevated temperatures up to 315 \(^\circ\)C.\(^\text{51,60}\) Increasing temperature, the pitting potential of 304 SS and 316L SS decreased in Cl\(^{−}\)-only or Cl\(^{−}\) + S\(_2\)O\(_3^{2−}\) solutions.\(^\text{80}\)

**Valence of S\(^{\circ}\) species.**—The electrochemical reactions of S-oxygen compounds have been reviewed by Hemmingsen.\(^\text{81}\) Some S-oxygen compounds are presented in the order of oxidation state in Table 3. The impact of the valence of S\(^{\circ}\) species on corrosion degradation is briefly reviewed in the following sections.

S\(^{0}\).—S\(^{0}\) has been reported to significantly increase the corrosion of carbon steel under both aerated and deaerated conditions.\(^\text{82,83}\) Early TSP used carbon steel as the material. This type of materials is subjected to catalysis of cathodic and anodic reactions in acidic environments based on the following proposed reactions:\(^\text{82,83}\)

\[\text{S}_{n-1} \cdot \text{S}^{2−} + 2\text{H}^+ + 2(\text{x} - 1)\text{e}^- \rightarrow \text{xH}_2\text{S} + \text{S}_{n-x} \text{(cathodic)}, \quad [27]\]

\[(\text{x} - 1)\text{Fe} \rightarrow (\text{x} - 1)\text{Fe}^{2+} + 2(\text{x} - 1)\text{e}^-\]

\[(\text{x} - 1)\text{Fe}^{2+} + (\text{x} - 1)\text{H}_2\text{S} \rightarrow (\text{x} - 1)\text{FeS} + 2(\text{x} - 1)\text{H}^+ \text{(anodic)}, \quad [28]\]

which gives the overall corrosion reaction as:

\[(\text{x} - 1)\text{Fe} + \text{S}_{n-1} \cdot \text{S}^{2−} + 2\text{H}^+ \rightarrow (\text{x} - 1)\text{FeS} + \text{H}_2\text{S} + \text{S}_{n-x} \cdot \quad [29]\]

The additional cathodic reaction in acidic environment is:

\[\text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{ads} \rightarrow 1/2\text{H}_2 \quad [30]\]

In neutral conditions, the additional cathodic reactions are expected to be:

\[\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \quad [31]\]

\[2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2 \quad [32]\]

In the presence of Cu\(^{2+}\) in the HTC, the following cathodic reaction is also involved:\(^\text{13}\)

\[\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu} \quad [33]\]

Adsorbed S\(^{\circ}\) catalyzes anodic dissolution during which there is no change in the oxidation state during the dissolution process.\(^\text{84}\) This catalytic effect on the anodic dissolution has been reported on Fe, Ni, Fe–Cr, Fe–Ni, carbon steel, Fe–Ni–Cr alloys.\(^\text{85}\) The mechanism has been merged together by Marcus et al.\(^\text{86}\) the adsorbed S\(^{\circ}\) can disrupt oxide formation and block H\(_2\)O adsorption and dissociation, therefore inhibit the oxide film formation. Adsorbed S\(^{\circ}\) on metal surface results in a dipole (δ−) charge on the adsorbed S atom and a dipole (δ+) charge on metal surface, which reduces the activation energy necessary for active dissolution of metal.

S\(^2−\).—S\(^2−\) and S\(_2\)O\(_3^{2−}\) have similar impacts on uniform corrosion and pitting corrosion.\(^\text{88,89}\) However, S\(^2−\) is only stable in alkaline solution. In acidic solution, S\(^2−\) can interact with H\(^+\) to form HS\(^−\) and H\(_2\)S, which are aggressive for SG and TTS material; in alkaline solutions, S\(^2−\) is also stable and the corrosion products on SS are FeS, FeS\(_2\), NiS, Ni\(_2\)S\(_3\), which are less protective.\(^\text{90}\) FeS deposit was reported to be electrochemically reactive and led to a large interfacial capacitance.\(^\text{90,91}\)

S\(_2\)O\(_3^{2−}\) is known to enhance uniform corrosion as well as pitting corrosion for many alloys. For example, in the presence of S\(_2\)O\(_3^{2−}\), the corrosion rate of plain carbon steel was greater than 1 cm per year in simulated pipeline water composition.\(^\text{92}\) In cases of pitting corrosion of 316 SS, S\(_2\)O\(_3^{2−}\) can damage the passive film seriously in the presence of Cl\(^−\), which has been extensively reported.\(^\text{93}\) A mechanism has been proposed: S\(_2\)O\(_3^{2−}\) can stabilize metastable pits during passive film breakdown induced by Cl\(^−\).\(^\text{94,95}\) The combined effect of Cl\(^−\) and S\(_2\)O\(_3^{2−}\) on localized corrosion occurs when the Cl\(^−\)/S\(_2\)O\(_3^{2−}\) concentration ratio is high, ensuring that Cl\(^−\) adsorption is dominant, and as a result, the initial film breakdown is induced by Cl\(^−\).\(^\text{97}\) If the Cl\(^−\)/S\(_2\)O\(_3^{2−}\) concentration ratio is low, insufficient amounts of Cl\(^−\) are available for breakdown of the passive film, therefore pitting corrosion is mitigated. Obviously, pitting does not occur in a solution containing only S\(_2\)O\(_3^{2−}\). These electrochemical behaviors mentioned above have been found on 304L and 316L.\(^\text{98}\) The interactions of Cl\(^−\) and S\(^\circ\) with passive film at high and low Cl\(^−\)/S\(_2\)O\(_3^{2−}\) concentration ratios is discussed later in details in Interactions of Cl\(^−\) and S\(^\circ\) with passive film at high and low Cl\(^−\)/S\(_2\)O\(_3^{2−}\) concentration ratios section.

The reason that S\(_2\)O\(_3^{2−}\) alone or S\(_2\)O\(_3^{2−}\) + small amount of Cl\(^−\) is not very detrimental to passivity is still in debate and the following three reasons have been proposed:

1) an excess of S\(_2\)O\(_3^{2−}\) can neutralize the acidic conditions within a pits, therefore retard pit growth.\(^\text{98}\)

2) under the condition where Cl\(^−\)/S\(_2\)O\(_3^{2−}\) concentration ratio is low, an excessive amount of S\(_2\)O\(_3^{2−}\) will retard the adsorption of Cl\(^−\), therefore passive film does not break down easily and no pitting corrosion is observed, as reported.\(^\text{99}\)
(3) possibly due to its large anion size, S$_2$O$_3^{2-}$ is unable to occupy the vacancies in the passive layer.$^{100}$ S$_2$O$_3^{2-}$ itself can hardly enter the lattice of oxygen vacancy unless it is reduced to S$^{2-}$. $^{99}$

In absence of Cl$^-$, S$_2$O$_3^{2-}$ may interact with the passive film and slightly alter the composition of the passive film, which has been confirmed by radioactive labeling and Auger electron and x-ray photoelectron spectroscopy. $^{101,102}$ It was found that S$_2$O$_3^{2-}$ accumulation on the 304SS surface is irreversible and occurs over a broad electrode potential range of −1.0 to −0.50 V$_{Ag/AgCl}$. $^{101,102}$ This irreversible surface behavior is attributed to S$_2$O$_3^{2-}$ incorporation into the passive film. However, the authors concluded that S$_2$O$_3^{2-}$ accumulation is reversible on 316 SS because the Mo content in 316 SS is higher than that in 304 SS. $^{101,102}$ Possibly, the Mo cation creates a barrier that makes S$_2$O$_3^{2-}$ penetration into the passive film of 316 SS energetically more difficult than into the passive film of 304 SS. A recent study conducted by Faichuk et al. $^{103}$ also showed that S$_2$O$_3^{2-}$ accumulation on Alloy 600 (Mo-free alloy) was irreversible because S is detected in the passive film.

It has been reported that S$_2$O$_3^{2-}$ may “facilitate” hydrogen adsorption and permeation into metallic materials in acidic solutions. $^{104,105}$ but these effects are attributed mainly to the decomposition products of S$_2$O$_3^{2-}$ (H$_2$SO$_3$, HSO$_3^-$, and S$^0$), as S$_2$O$_3^{2-}$ is readily decomposed in acidic environments to give the above products, and because experimental results obtained in the same acidic environment with SO$_3^{2-}$ showed much less hydrogen permeation. Although S$_2$O$_3^{2-}$ can facilitate hydrogen permeation into the passive film, the passive film of O$_2$ in the S$_2$O$_3^{2-}$ solution inhibits hydrogen permeation. $^{106}$ Hydrogen adsorption enhancement is lower in neutral solution where S$_2$O$_3^{2-}$ remains mainly undecomposed. Thus, the major effects of S$_2$O$_3^{2-}$ are caused by itself in neutral media and by its decomposition products in acidic media. It should be noted that the pitting potential of metal caused by itself in neutral media and by its decomposition products should not be neglected when conducting experiments and experimental results obtained in the same acidic environment with SO$_3^{2-}$ to decompose to yield S$_2$O$_3^{2-}$ incorporation into the passive film. However, the authors concluded that S$_2$O$_3^{2-}$ accumulation is reversible on 316 SS because the Mo content in 316 SS is higher than that in 304 SS. $^{101,102}$ Possibly, the Mo cation creates a barrier that makes S$_2$O$_3^{2-}$ penetration into the passive film of 316 SS energetically more difficult than into the passive film of 304 SS. A recent study conducted by Faichuk et al. $^{103}$ also showed that S$_2$O$_3^{2-}$ accumulation on Alloy 600 (Mo-free alloy) was irreversible because S is detected in the passive film.

It has been reported that S$_2$O$_3^{2-}$ may “facilitate” hydrogen adsorption and permeation into metallic materials in acidic solutions. $^{104,105}$ but these effects are attributed mainly to the decomposition products of S$_2$O$_3^{2-}$ (H$_2$SO$_3$, HSO$_3^-$, and S$^0$), as S$_2$O$_3^{2-}$ is readily decomposed in acidic environments to give the above products, and because experimental results obtained in the same acidic environment with SO$_3^{2-}$ showed much less hydrogen permeation. Although S$_2$O$_3^{2-}$ can facilitate hydrogen permeation into the passive film, the passive film of O$_2$ in the S$_2$O$_3^{2-}$ solution inhibits hydrogen permeation. $^{106}$ Hydrogen adsorption enhancement is lower in neutral solution where S$_2$O$_3^{2-}$ remains mainly undecomposed. Thus, the major effects of S$_2$O$_3^{2-}$ are caused by itself in neutral media and by its decomposition products in acidic media. It should be noted that the pitting potential of metal caused by itself in neutral media and by its decomposition products should not be neglected when conducting experiments and experimental results obtained in the same acidic environment with SO$_3^{2-}$ to decompose to yield S$_2$O$_3^{2-}$ incorporation into the passive film. However, the authors concluded that S$_2$O$_3^{2-}$ accumulation is reversible on 316 SS because the Mo content in 316 SS is higher than that in 304 SS. $^{101,102}$ Possibly, the Mo cation creates a barrier that makes S$_2$O$_3^{2-}$ penetration into the passive film of 316 SS energetically more difficult than into the passive film of 304 SS. A recent study conducted by Faichuk et al. $^{103}$ also showed that S$_2$O$_3^{2-}$ accumulation on Alloy 600 (Mo-free alloy) was irreversible because S is detected in the passive film.

It has been reported that S$_2$O$_3^{2-}$ may “facilitate” hydrogen adsorption and permeation into metallic materials in acidic solutions. $^{104,105}$ but these effects are attributed mainly to the decomposition products of S$_2$O$_3^{2-}$ (H$_2$SO$_3$, HSO$_3^-$, and S$^0$), as S$_2$O$_3^{2-}$ is readily decomposed in acidic environments to give the above products, and because experimental results obtained in the same acidic environment with SO$_3^{2-}$ showed much less hydrogen permeation. Although S$_2$O$_3^{2-}$ can facilitates hydrogen permeation into the passive film, the passive film of O$_2$ in the S$_2$O$_3^{2-}$ solution inhibits hydrogen permeation. $^{106}$ Hydrogen adsorption enhancement is lower in neutral solution where S$_2$O$_3^{2-}$ remains mainly undecomposed. Thus, the major effects of S$_2$O$_3^{2-}$ are caused by itself in neutral media and by its decomposition products in acidic media. It should be noted that the pitting potential of metal caused by itself in neutral media and by its decomposition products should not be neglected when conducting experiments and experimental results obtained in the same acidic environment with SO$_3^{2-}$ to decompose to yield S$_2$O$_3^{2-}$ incorporation into the passive film. However, the authors concluded that S$_2$O$_3^{2-}$ accumulation is reversible on 316 SS because the Mo content in 316 SS is higher than that in 304 SS. $^{101,102}$ Possibly, the Mo cation creates a barrier that makes S$_2$O$_3^{2-}$ penetration into the passive film of 316 SS energetically more difficult than into the passive film of 304 SS. A recent study conducted by Faichuk et al. $^{103}$ also showed that S$_2$O$_3^{2-}$ accumulation on Alloy 600 (Mo-free alloy) was irreversible because S is detected in the passive film.

| SO$_3^{2-}$ | SO$_2^{2-}$ | SO$_4^{2-}$ | SO$_3^{2-}$ | SO$_2^{2-}$ | SO$_4^{2-}$ |
|-----------|-----------|-----------|-----------|-----------|-----------|

$^{1}$Hideout and hideout return are impurities deposited during boiling and dissolved back to solution during shutdown. During boiling, the solutions accumulate in flow-restricted regions on the secondary side of the SG, such as crevices formed at the intersections between the SG tubes and the tube sheet, the support structure, and deposits have accumulated on the tube surface and on the tube sheet. These processes lead to the formation of concentrated solutions (hideout) in these flow-restricted regions. During shutdown and cooldown, steam voids collapse, areas are rewetted, and impurities are released back into the bulk steam generator water—a phenomenon known as hideout return. Hideout return studies correspond to water composition analysis in the HTC conducted at the shutdown or cooldown time.

H$_2$S.—H$_2$S as a weak acid in aqueous solution can affect anodic and cathodic reactions occurring on passive metal surfaces. $^{111,114}$ In H$_2$S containing solutions, cathodic reactions stem from reductions of H$^+$ and H$_2$S. $^{115,116}$ H$_2$S showed less detrimental effect than S$_2$O$_3^{2-}$ on the passive film degradation, $^{117}$ because H$_2$S showed a diffusion effect, not a migration effect during localized corrosion. At the acidic pH values in and near a pit in the passive film, H$_2$S is uncharged and will always be depleted inside the pit. S$_2$O$_3^{2-}$ is an anion, and although it is decomposed in acidic solutions, the decomposition is slow enough so that there is always pit enrichment of S$_2$O$_3^{2-}$ by electromigration.

H$_2$S in aqueous solution significantly enhanced the uniform corrosion rate of many metallic materials including SG TSP (carbon steel and SS), and the corrosion product was FeS (sometimes polymorphous) and Fe$_{1-x}$S (hexagonal crystal). $^{118-120}$ FeS mainly forms at low temperature and low H$_2$S partial pressure while Fe$_{1-x}$S is formed at high temperature and high H$_2$S partial pressure. Solution pH and temperature have significant effects on the protection of FeS, $^{119}$ increases in pH and temperature lead to increased corrosion resistance of FeS film due to its compact structure. $^{120}$ In a review of corrosion products of steels in H$_2$S environments, $^{19}$ it was pointed out that thermodynamics and detailed kinetics of the corrosion product formation and transformation are not well understood.

Experiments involving H$_2$S are complicated and dangerous because (1) H$_2$S is toxic and corrosive, (2) H$_2$S can contribute to the currents measured using electrochemical techniques (similar to S$_2$O$_3^{2-}$), because of the oxidation and reduction of H$_2$S $^{121}$ and (3) reactive and porous ferrous sulfide films increase the interfacial capacitance and introduce diffusional effects. $^{122}$ Tsukijawa, et al. $^{123}$ and Kappes et al. $^{124}$ developed a solution containing S$_2$O$_3^{2-}$ ions, which can be used to mimic the sour gas environments that are generally found in the petroleum industry.

**Summary of S$^-$ effects on corrosion.—** All S$^-$ species should be considered when investigating corrosion mechanisms of metals in S$^-$ containing environments in the lab. For instance, the initial added S$_2$O$_3^{2-}$ will be decomposed to many other species via electrochemical reductions or oxidations, complicating the determination of corrosion processes. The decomposition of S$^-$ species is dependent on the functions of electrode potential, solution pH, temperature, and oxygen concentration, and the compositions of the materials under investigation. $^{59}$ S$^-$ species can transform to higher or lower valences, complicating the determination of corrosion processes. 

**Interactions of Cl$^-$ and S$^-$ with passive film.—** Cl$^-$ is considered to be a detrimental ion for many alloys, including Fe-Ni-Cr alloys used in PWRs. Cl$^-$-induced pitting corrosion of Fe-Ni-Cr alloys has been extensively explored in the past decades, and the effect of S$^-$ on Cl$^-$-induced corrosion has been well documented. $^{51,124-130}$ This section will begin with the effects of Cl$^-$ on film degradation at high and low Cl$^-$/S$_2$O$_3^{2-}$ concentration ratios.
Interactions of Cl\(^-\) and S\(^x\) with passive film at high and low Cl\(^-/S_2O_3^{2-}\) concentration ratios.—The combined effect of S\(_2O_3^{2-}\) and Cl\(^-\) on passive film degradation has been reported on alloys 690, 304 SS, and Alloy 600, as a decreased pitting potential is observed in Cl\(^-\)-S\(_2O_3^{2-}\) solutions, compared with Cl\(^-\)-only or S\(_2O_3^{2-}\)-only solutions. The combined effect of S\(_2O_3^{2-}\) and Cl\(^-\) is observed in cases where Cl\(^-\) S\(_2O_3^{2-}\) concentration ratio is high, as discussed in S\(_2O_3^{2-}\)-section. Newman et al. and Marcus et al. claimed that if sufficient Cl\(^-\) ions were available to breakdown the passive layer, the adsorption of S\(_2O_3^{2-}\) within the pits and the electrochemical reduction of S\(_2O_3^{2-}\) would stabilize the metastable pits and catalyze the pitting growth. A critical concentration ratio at which pit growth rate reached a maximum value was defined as the Cl\(^-\)-S\(_2O_3^{2-}\) ratio = 250:1 for type 304 SS at 20 C in 1 M NaCl. This critical ratio is highly dependent on materials and temperature.

If the Cl\(^-\)/S\(_2O_3^{2-}\) concentration ratio is low, the ions have no combined effect, and pits are not initiated. One reasonable reason is that there is not enough Cl\(^-\) to break down the passive film, as discussed in S\(_2O_3^{2-}\)-section.

**Impact of sulfate.**—S\(_2O_3^{2-}\) alone cannot trigger localized corrosion of Alloys 600, 690 and 800 at temperatures below 100 C; however, it can induce localized corrosion of Alloys 600, 690 and 800 in the presence of S\(_2O_3^{2-}\) and Cl\(^-\). The presence of 8000 ppm S\(_2O_3^{2-}\) suppressed anodic dissolution reactions of alloy 600 in Cl\(^-\) solution, perhaps through the formation of S\(_2O_3^{2-}\)-salts. The sulfate anion is much more likely to precipitate out with stable ionic species in reaction with cations at low temperature. Pitting corrosion occurred in solutions where S\(_2O_3^{2-}\)/S\(_2O_3^{2-}\) concentration ratios ranged from 1.6 to 58. Newman claimed that S\(_2O_3^{2-}\)-induced pitting of commercial Aisi 304 SS occurred readily when \([S_2O_3^{2-}] + [Cl^-] /[S_2O_3^{2-}] = 1\) in the range of 10 to 30. Cl\(^-\) was not necessary for pitting; the right proportion of S\(_2O_3^{2-}\) and S\(_2O_3^{2-}\) ions could take part in an acidification process that leads to pitting. Ag\(_2S_2O_3\) may be used as a localized corrosion inhibitor for alloy 690 in NaCl solution at room temperature because Ag\(_2S_2O_3\) could interact with Cl\(^-\) to form AgCl of low solubility (see Equation 34), altering the interface of the double layer structure and mitigating anodic dissolution.

\[
\text{Ag}_2\text{SO}_4 + 2\text{NaCl} \rightarrow 2\text{AgCl} + \text{Na}_2\text{SO}_4 \quad [34]
\]

However, Ag\(_2S_2O_3\) has not been used in real PWRs at the temperature of 300 C because S\(_2O_3^{2-}\) is considered detrimental to passivity at high temperature, due to the formation of reduced species. The addition of a relatively small amount of SO\(_4^{2-}\) to a 0.1 M Cl\(^-\) solution results in a significant increase in current density in the anodic range of Ni and Ni alloys at 315 C, suggesting that SO\(_4^{2-}\) is detrimental to Ni-based alloys. Cullen also reported a similar phenomenon: there was a combined effect of SO\(_4^{2-}\) and Cl\(^-\) at high temperatures on nickel-based alloys, and the role of Cl\(^-\) is to breakdown the passive film, and reduced sulfur species (from SO\(_4^{2-}\)-reduction) adsorbed on these sites to promote pit growth.

**Oxygen (O\(_2\)) concentration.**—O\(_2\) contamination should be avoided during pressurized water reactor (PWR) startup and wet layup conditions, because O\(_2\) significantly increases the corrosion potential, and changes the chemical conditions on the secondary side of the SG tubing. The possible ingress of O\(_2\) during startup and shutdown should be prevented or greatly minimized. The role of O\(_2\) on corrosion can be summarized as the following three aspects:

1. O\(_2\) can oxidize the lower valence of S\(^x\), i.e. S\(^2-\), to high valence species S\(_x\) which is more aggressive to passivity.
2. O\(_2\) contributes to the cathodic reaction, therefore increases the cathodic current density, causing the increase in the anodic dissolution rate of carbon steel.
3. O\(_2\) can oxidize Fe\(^{3+}\) and Cu to form Fe\(^{3+}\) and Cu\(^{2+}\). These species are detrimental to passivity of SG tube and tube support materials.

**S\(^x\) Influences on Passive Film Properties**

**Film thickness.**—Passive film thickness in SG tubing is mainly influenced by the exposure temperature, and increases as the temperature rises. At room temperature, the passive film thickness is in the range of several nm, but the thickness can increase to hundreds of nm at 300 C. As the temperature in a PWR rises, anion vacancy generation rate increases at the metal/film interface, film dissolution increases at the film/solution interface, and the transport rates of oxygen vacancies and cation vacancies are enhanced. Anion and cation vacancies generation rate at the metal/film interface is faster than the film dissolution rate and as a result, film thickness increases. Film thickness cannot be correlated with the corrosion resistance of the passive film because corrosion resistance is mainly determined by the composition, defect level, and structure of the passive film.

**Film structure.**—Film structure greatly influences the SCC susceptibility of a passive metal. Passive film with a crystalline structure is superior to the passive film with an amorphous structure. In most cases, Ni and Fe hydroxides form the outer layer of the passive film whereas the inner layer contains oxides that protect the film from corrosion. A film enriched with crystallite CrO\(_3\) is beneficial for passivity. The heat treatment process of nickel-based alloys is important, because it highly influence the chromium depletion, precipitate evolution, and resistance to IGA. It is unknown whether the presence of S\(^x\) can change the structure of the passive layer on an alloy, and an atomic-scale mechanism is needed for clarification in future work. A recent paper reported the effect of Cl\(^-\) on the structure of the passive film formed on a FeCr15Ni15 single crystal, and confirmed that Cl\(^-\) was accumulated at the metal/film interface, leading to a lattice expansion on the metal substrate, undulations at the film/substrate interface, and structural inhomogeneity on the film side. What should be investigated in the future is whether S has the similar effect as Cl\(^-\) on film structure.

**Semiconductivity.**—Most metallic materials used on the secondary side of steam generator tubing in PWRs are in a passive state, i.e., a passive layer is formed on them. In most cases, the passive layers are a p-type, n-type, or n-p-type semiconductor. Metal oxides of Fe and Cr are n-type whereas Ni is p-type. The n-type oxide can be reduced easily, which is detrimental to passivity. Some results reported so far seem to be contradictory, as the nickel-based Alloy 600 shows either n-type or p-type semiconducting properties. This is possibly due to the limitations of the techniques in determining the semiconductivity. As the semiconductivity is usually experimentally determined by Mott–Schottky technique, during the potential scan, the results are always influenced by the Faradic current generated by the dissolution of a passive film, casting a dubious light on the experimental evidence. Semiconductivity influenced by S\(^x\) is not well understood yet. Recent investigations on Alloy 800 and 690 show that the adsorbed S\(^0\) on passive film surface can accept electrons to form S\(^2-\) by occupying the oxygen vacancies v\(_{0}^-\), as shown in Equation 35. However, a direct evidence is still needed to confirm this.

\[
V_{0}^- + S^0 + 2e^- \rightarrow S_2^- \quad [35]
\]

**Pit growth rate.**—Pit growth in an alloy leads to rapid material failure. S\(_2O_3^{2-}\) accelerates pit growth rate in Cl\(^-\) solution when the Cl\(^-\)/S\(_2O_3^{2-}\) concentration ratio is high. As discussed in Interactions of Cl\(^-\) and S\(^x\) with passive film at high and low Cl\(^-/S_2O_3^{2-}\) concentration ratios section, there is a critical Cl\(^-\)/S\(_2O_3^{2-}\) ratio at which the pit growth rate reaches a maximum. Increasing or lowering this ratio led to a decreased pit growth rate or no pit initiation. For instance, in the case of 316 SS and 304 SS in solutions containing S\(_2O_3^{2-}\) (0.01 to 500 ppm) and Cl\(^-\) (1 to 1000 ppm) the pit growth rate was around 10 to 50. Concentration ratios lower than 1 and higher than 1000 prevented pit formation. A similar phenomenon was reported by Wang et al. who used image analyses to study pit growth on alloy
Sx-Induced Stress Corrosion Cracking (Sx-SCC)

Sx—SCC is one important SCC submode owing to the concentrated Sx species in the HTC, which has been measured during shutdown return studies. As discussed in Valence of Sx species section, many Sx species are detrimental to passivity, therefore it is not surprising that these species can promote SCC. For instance, SCC of SG tube materials at some CANDU stations have been attributed to a low-temperature attack by S₂O₆²⁻ and S₄O₆²⁻. SCC of sensitized Alloy 600 SG tubes was detected in Three-Mile Island PWR under wet—layup conditions in the mid-1990s. Sensitized TSP materials such as 304 SS and 316 SS have shown great Sx—SCC susceptibility. Summary of SCC initiation work on metallic materials in Sx-containing solutions is shown in Table III. In this part, we discuss the factors affecting Sx—SCC and the possible remedies.

Factors affecting Sx—SCC.—Seven factors that affect the Sx—SCC are: (1) stress, (2) electrode potential range, (3) solution pH, (4) temperature, (5) Sx species in solution, (6) alloy composition and (7) alloy structure.

Stress.—The stress may stem from the material itself or extraneous interference such as corrosion product. The corrosion product generated from carbon steel corrosion results in a slow straining and denting of the SG tube, which accelerate SCC of the SG tube. Stress induces film rupture, alters diffusion kinetics of atoms in the passive film, and oxidation kinetics on grain boundary. Both of these may greatly enhance SCC susceptibility. It is known that stress promotes the crack propagation rate of metals because film breakdown is easy in the presence of stress, as has been reported on sensitized Alloy 600. The repassivation of stressed Alloy 800 C-ring samples showed an increased maximum current and longer repair time when compared to unstressed sample. A recent work found that both tensile stress and compressive stress can lead to an increased surface reactivity of the passive film, and oxidation kinetics on grain boundary. The reason why the compressive stress leads to an increased surface reactivity of the passive film, needs to be further explored.

Electrode potential.—The effect of electrode potential on Sx—SCC can be estimated in the E—pH diagrams as shown in Fig. 4. The potential range in which the metal is active is also the region where metal is prone to Sx—SCC, while the relative minimum Sx susceptibility usually corresponds to good passivity of these alloys. For instance, heat sensitized nickel-based Alloy 600 underwent active dissolution between −300 mV_SCE and +400 mV_SCE in low temperature S₂O₆²⁻ solution, it also suffered from IGSSC susceptibility, because of the Ni-rich and chromium-depleted phase at the grain boundaries (see Table III).

Solution pH.—As can be estimated from E—pH diagrams shown in Fig. 4, iron based Alloy 800 and nickel-based Alloy 600 are active in acidic solutions, therefore Sx—SCC of Alloy 600 and 800 easily occurs in an acidic condition. Alloy 690 with more Cr content is susceptible to SCC in alkaline solutions since Cr is in the form of Cr₂O₇²⁻ as shown in Fig. 4f. There are different corrosion states shown in Figs. 4b, 4d, 4f: pitting and uniform corrosion occur below pH 3 (at 300°C) while pitting and SCC occur between pH 3 and 5 (at 300°C).

Temperature.—Sx—SCC susceptibility increases with temperature, which is not surprising since the passive region shrinks as the temperature elevates (see and compare the E—pH diagrams at 25°C and 300°C shown in Fig. 4). This is because Sx species distribution is changed at high temperature, therefore, the interaction of Sx with passive surface is totally different from the one at low temperature. In the case of sensitized Alloy 600 in 0.1 M S₂O₆²⁻ solution, the activation energy is as low as 3.5 kcal/mol. At high temperature, even ingress of SO₄²⁻ can accelerate the metal dissolution rate, particularly in Ni and Ni-rich alloys that may not form sufficiently compact oxide films in aggressive acid solutions. Severe SCC, IGA and pitting corrosion susceptibility of alloy 800 in acid SO₄²⁻ solutions at 280~320°C have been reported by Persaud et al. In laboratory experiments, traces of H₂S were detected and S was detected at the crack tip although oxide state was not reported.

Species.—Sx species with valences of −2, 0 and +4 are thermodynamically stable at low temperature, although other intermediate oxidation states of Sx can form via either reduction of SO₄²⁻ by H₂N₄ or oxidation of S²⁻ by O₂ introduced to the SG water during wet layup or startup. Sx—SCC mainly occurs in solutions containing S²⁻, S₂O₆²⁻, or SO₄²⁻ regardless of the low or high temperature, and Sx—SCC has been reported on 304 SS, Alloys 600 and 800, see the summary in Table III. SO₄²⁻ does not accelerate Sx—SCC at low temperature but can promote SCC at high temperature due to the electrochemical reduction of SO₄²⁻. The kinetics of all the reactions regarding Sx under startup and layup conditions are still not well understood. Additionally, whether magnetite and CuS have any synergistic effect with Sx on SCC should also be investigated.

Alloy composition.—Alloys 600MA and 800 are susceptible to Sx—SCC in near neutral conditions while Alloy 690 shows good Sx—SCC resistance. Almost all SG tube and SS materials are prone to Sx—SCC at 350°C in alkaline S₂O₆²⁻—containing solution. The results indicate that Sx—SCC occurs extensively on SG tubing materials as well as SS. In acidic solutions, where sulfur-species are most relevant, higher Cr content in Alloy 690 generally imparts more resistance to Sx—SCC due to the better ability to form and sustain a passive oxide after rupture or impairment (or in competition with sulfur), as compared to Alloy 600.

Alloy structure.—Some treatment methods for SG and TSP materials will significantly affect their structure. Sensitization treatment of Alloy 600 and 304 SS leads to an increased Sx—SCC susceptibility, but mill annealed Alloy 600 sustains no Sx—SCC susceptibility at low temperatures. This is because sensitization treatment generates a Ni-rich and chromium-depleted phase at the grain boundaries of Alloy 600 and 304 SS. Cold work of 316L SS led to an acceleration of SCC and a crack growth rate in oxygenated high temperature water, but whether cold work has the same effect on SG tubing and TSP materials in Sx environment is presently not known.

Prevention or amelioration of Sx—SCC.—Strategies that can prevent or ameliorate Sx—SCC are briefly discussed in this section, these methods including surface treatment, water chemistry optimization and SG structure design.

(1) Surface treatment is frequently used to enhance the SCC resistance of metallic materials. Laser shock peening and iterative thermomechanical processing have been reported to improve the resistance of Alloy 600 to SCC in S₂O₆²⁻ solution.

(2) The Sx concentrations in the secondary side can be lowered by exploring suitable strategies for water chemistry control, to minimize the formation of such species caused by the hydrazine reduction of SO₄²⁻.

kTwo types of iterative thermomechanical processing is shown here: (1) As received + Annealing at 1050°C, 10 min, WQ+SA + 3 cycles of (10% cold work + 1000°C, 10 min, water quenching) (2) As received + Annealing at 1050°C, 10 min, WQ+SA + 3 cycles of (10% cold work + 900°C, 10 min, water quenching).
### Table III. Summary of SCC initiation work on metallic materials in $S^\cdot$-containing solutions.

| Refs. | Material condition | Water chemistry | Test technique | Test duration | Results |
|-------|--------------------|-----------------|----------------|--------------|---------|
| 156   | Alloy 600          | ① 0.1 M thiosulfate, 22°C ② 0.1 M thiosulfate + 1.3% boric acid, 22°C ③ 0.1 M thiosulfate + 1.3% boric acid, up to 80°C ④ 0.1 M thiosulfate + 1.3% boric acid, held potentiostatically at 22°C at −100, −50, 0, +50, +100 mV_{SCE} at 22°C ⑤ 0.1 M thiosulfate + 1.3% boric acid, notched specimen, 22°C ⑥ 0.1 M tetrathionate, continuously purged with 99.999%, 22°C ⑦ 0.1 M thiosulfate + 1.3% boric acid at an initial pH 7.2 and continuously purged with 99.999% nitrogen, 22°C ⑧ 0.1 M thiosulfate + 1.3% boric acid at an initial pH 1.8, 22°C ⑨ 0.1 M tetrathionate, 22°C ⑩ 0.1 M tetrathionate, 22°C | Reverse U-Bend | ① 1000 h ② 1000 h ③ 72 h each at 40, 60, 80°C ④ 72 h each at potential ⑤ 1000 h ⑥ 48 h ⑦ 100 h ⑧ 200 h ⑨ 120 h ⑩ 18 h | ① NC* ② NC ③ NC ④ NC ⑤ NC ⑥ NC ⑦ NC ⑧ NC ⑨ NC ⑩ NC | GJA with crack initiation time | ① NC* ② NC ③ NC ④ NC ⑤ NC ⑥ NC ⑦ NC ⑧ NC ⑨ NC ⑩ NC | GJA with crack initiation time | ① NC* ② NC ③ NC ④ NC ⑤ NC ⑥ NC ⑦ NC ⑧ NC ⑨ NC ⑩ NC | GJA with crack initiation time |
| 77,167| Alloy 600, Solution annealing at 1095°C for 1 h followed by water quenching | Deaereated sodium thiosulfate solutions of various concentrations (0.003 to 0.1 M) at 95°C. The solution pH ranged from 6 to 7. | constant deflection test, Compact-tension (CT) specimens 12.7-mm thick | ① 0.1 and 0.03 M thiosulfate solution at 95°C, 1500 h at OCP ② 0.03 M thiosulfate solution at 95°C, −440 and +100 mV_{SCE} 72 h | ① NC ② IGSCC |
| 166   | Alloy 600 ① As-received (mill-annealed) ② Solution annealing (1100°C/1 h) ③ Solution annealing + sensitization (1100°C/1 h + 700°C/5 h) ④ Thermal stabilization (990°C/5 min+705°C/15 h) ⑤ Solution annealing + sensitization (1120°C/0.5 h + 700°C/15 h) | Deaereated 0.01 M Na$_2$S$_2$O$_3$ solution at 95°C | Reverse U-Bend | ① OCP (−300 mV_{SCE}) 1800 h, 100 mV_{SCE} 360 h, 150 mV_{SCE} 360 h, 250 mV_{SCE} 528 h, 500 mV_{SCE} 500 h ② OCP (−300 mV_{SCE}) 1800 h, 100 mV_{SCE} 360 h, 150 mV_{SCE} 360 h, 250 mV_{SCE} 480 h, 500 mV_{SCE} 20 h ③ OCP (−300 mV_{SCE}) 1100 h, 100 mV_{SCE} 5 h, 150 mV_{SCE} 2.5 h, 250 mV_{SCE} 4 h ④ OCP (−300 mV_{SCE}) 1100 h, 100 mV_{SCE} 7 h, 150 mV_{SCE} 2.5 h, 250 mV_{SCE} 1.7 h, 500 mV_{SCE} 0.33 h ⑤ OCP (−300 mV_{SCE}) 1800 h, 100 mV_{SCE} 408 h, −50 mV_{SCE} 290 h, 150 mV_{SCE} 190 h, 250 mV_{SCE} 8 h, 500 mV_{SCE} 2 h ⑥ OCP (−300 mV_{SCE}) 2 h, 150 mV_{SCE} 190 h, 250 mV_{SCE} 2 h | ① OCP ② OCP ③ OCP ④ OCP ⑤ OCP ⑥ OCP ⑦ OCP ⑧ OCP |
| 159   | Alloy 600, Solution sensitizing and 700°C/3 h and WQ | Deaereated sodium thiosulfate solutions of various concentrations (0.01 to 0.1 M) at 95°C. The solution pH ranged from 6 to 4.2. Some tests were performed in the thiosulfate solutions with pH of 3 for SAS specimen to study the effects of pH. | constant load (420 MPa) under potential control | Test at Ecorr, 50, 150, 200, 300, 400 mV_{SCE} in 0.01 M, 0.01M (pH = 3), 0.001M (pH = 3) up to 150 h | IGSCC depends on potential |
| 139   | Alloy 600, sensitized: annealing in solution at 1200°C for 30 min+ at 700°C for 3 h before water quenching | Deaereated 10$^{-1}$–10$^{-5}$ thiosulfate at 25°C | dog-bone tension specimens strain rate 2.5 × 10$^{-6}$/s 2.5 × 10$^{-7}$/s | 15–50 h depends on the polarization potential | IGSCC |
| 165   | Type-304 stainless steel sensitized at 650°C for more than 24 h | 0.1 mass% tetra-thionic potassium (K$_2$S$_4$O$_6$) at pH 2 at 25°C | three-point bending to induce a surface stress of 400 MPa C-ring, 2% plastic strain at the apex | 60 to 90 ks | IGSCC |
| 60,161| Alloy 800 tubing, and Alloy 600 tubing | 230 mL 0.55 M NaHSO$_4$ acid sulfate solutions, 315°C, deaereated with a 5%H$_2$–95%N$_2$ mixture for 12 h | Small dog-bone tensile specimens with blunt notch, slow rise-time cyclic loading | 60 h | Not known |
| 162   | Alloy 800NG, custom cast, hot-rolled and annealed, cold-rolled by 19% | 0.55 mol/kg SO$_4^{2−}$ solution, pH$_{250°C}$ = 3, at 280°C | 660 h | EAC and IGC |

*NC = No cracking.
(3) From an engineering perspective, it is better to avoid the formation of HTC. If the crevices between the SG tube and TSP cannot be eliminated, it should be designed so as to keep them as tight as possible in practice. Additionally, line contact arrangements, rather than surface to surface contact, should be used as the contact mode between the tube and tube support.

Future Work

(1) Exploring the passive film properties in Sx-containing environments at the nano and atomic scales.

The passivity degradation mechanism at the nanoscale is not clear, so a multiscale approach combining atomic modeling with advanced electrochemical and surface analyses techniques is needed to fully understand alloy corrosion mechanisms. The details of the film structure in an atomic scale, film thickness and semiconductivity influenced by Sx should be investigated. The roles of alloying elements with low concentrations such as Mo, S, and Cu in pitting and SCC initiation are not fully understood at the atomic scale, and this can be further investigated by in-situ techniques (such as Raman spectroscopy) that could be valuable to fill the knowledge gaps such as the small quantities of sulfur segregation and oxidation state information of sulfur. The electron transfer reactions occurring on a passive film influenced by Sx also need to be clarified. The repassivity kinetics of passive film at high temperature have been studied by in situ scratch electrode systems, but attention should also be paid to the reliability and data reproducibility of this technique.

(2) Environment at heat transfer crevice occluded sites

The specific condition in the HTC is very complicated because it is a two-phase system or steam blanketed. Unfortunately, the specific conditions are not well determined. The kinetics of the reduction of high valence Sx to low valence Sx is not known. There are various impurities in the HTC, the role of magnetite (Fe₃O₄) and Cu²⁺ on Sx−induced corrosion is not clear. Future work should be focused on systematically investigating the corrosion degradation of SG, TTS, and TSP materials in the simulated crevice chemistries.

(3) Sx-induced stress corrosion cracking (Sx-SCC) mechanism at the atomic scale

Sx is involved in SCC initiation and propagation. Sx− is detected in the crack tip on Alloy 800 at high temperature, but its valence is unknown. Our knowledge on how Sx influences the composition and fracture toughness of passive films at the atomic scale only remains at a superficial level, and should be expanded through future work. In addition, the roles of other impurities (Cu²⁺) on Sx−SCC should also be studied systematically.

(4) Simulated corrosion degradation in bulk boiling conditions, the nucleation boiling surface, and the flow boiling condition

Most corrosion experiments under simulated PWR conditions are conducted in a static autoclave, which is different from the environment on the secondary side of steam generator tubing. Future work should focus on the electrochemical behavior of SG tubing alloys in bulk boiling conditions or even at nucleation boiling surfaces and flow boiling conditions where the electrochemical reactions are significantly influenced by mass transfer. Bulk boiling condition refers to the situation where the electrolyte is heated to boiling (about 100°C). Nucleation boiling surface simulates the SG service condition where the inner temperature of SG is high, e.g., 150°C, and the outside of the SG is exposed to electrolyte, therefore the water at the SG tubing surface is boiled. The flow boiling condition simulates the real SG service condition which is similar to a nucleation boiling surface, i.e., the temperature inside SG tubing is as high as 300°C. Flow boiling is a complex condition involving elevated pressure and temperature which generate vapor and results in the flowing vapor-liquid two phases. Recently, Chen et al. established a novel experimental setup to simulate flow boiling condition and to study the solid-liquid mass transfer under flow boiling conditions. In such condition, the electrochemical process is governed by mass transfer, which has not been investigated previously.

Conclusions

This paper reviews the factors influencing Sx−-induced corrosion on the secondary side in PWRs. The following conclusions can be made:

(1) The stability of Sx species in aqueous solutions highly depends on pH, temperature and electrochemical potential. Sx species with valences of +6, 0, −2 are stable in the relevant pH and temperature ranges.

(2) pH, electrode potential, temperature, Sx species, alloy compositions and other impurity ions such as Cl− can significantly influence the uniform corrosion and localized corrosion of SG tubing and TSP materials in Sx environment.

(3) Sx−SCC can occur on Alloy 600, 800 and other SSs, but highly depends on solution pH, temperature and alloy compositions.

(4) Although great progress has been made regarding Sx-induced corrosion on the secondary side of PWRs, future work should focus on the corrosion mechanism at the atomic scale utilizing advanced surface analyses techniques and atomic modeling.

Acknowledgments

The authors acknowledge the National Natural Science Foundation of China (No. 51701140) and the open-ended fund of the CAS Key laboratory of Nuclear Materials and Safety Assessment (Institute of Metal Research, Chinese Academy of Sciences, China) (No. 2018NMSAF01).

ORCID

Da-Hai Xia https://orcid.org/0000-0003-2336-8564

Yashar Behnamian https://orcid.org/0000-0002-7313-4021

Jing-Li Luo https://orcid.org/0000-0002-2465-7280

References

1. https://www.nrc.gov/reading-rm/basic-ref/students/animated-pwr.html

2. R. W. Staehle and J. A. Gorman, Corrosion, 59, 931 (2003).

3. R. W. Staehle and J. A. Gorman, Corrosion, 60, 5 (2004).

4. R. W. Staehle and J. A. Gorman, Corrosion, 60, 115 (2004).

5. B. T. Lu, L. P. Tian, R. K. Zhu, N. Li, S. Q. Shi, and J. L. Luo, Corrosion Science, 100, 1 (2015).

6. B. T. Lu, J. L. Luo, and Y. C. Lu, Electrochimica Acta, 53, 4122 (2008).

7. R. W. Staehle, Bases for predicting the earliest penetrations due to SCC for alloy 600 on the secondary side of PWR steam generators, Division of Engineering Technology, Office of Nuclear Regulatory Research, US Nuclear Regulatory Commission, 2001.

8. D. B. Wells, J. Stewart, R. Davidson, P. M. Scott, and D. E. Williams, Corrosion Science, 33, 39 (1992).

9. L. Choudhary, D. D. Macdonald, and A. Alfattazi, Corrosion, 71, 1147 (2015).

10. W. Cullen, Review of IGA, GSCC and wastage of Alloys 600 and 600H in high-temperature acidified solutions, in, NACE International, Houston, TX (United States), 1996.

11. S. Persaud, J. Smith, and R. Newman, Corrosion, Just accepted (2018).

12. Z. Gao, Z. Wang, Y. Sun, S. Wu, C. Ma, Y. Zhu, and D.-H. Xia, Transactions of Tianjin University, 22, 189 (2016).

13. M. Huang, Degradation of SG tubing materials in reduced sulphur environments, in, AECL, 2009, pp. File No.153-3312-33401-33000.

14. C. Wood, Intern PWR Secondary Water Chemistry Recommendations for IGA/SCC Control, in, C. Wood, (Ed.), Palo Alto, CA: EPRI, 1992.

15. D. Durance, K. Sedman, J. Roberts, and J. Gorman, FFS issues for steam generator tube (top of tubesheet) intergranular attack/stress corrosion cracking, in: 17th International Conference on Nuclear Engineering, American Society of Mechanical Engineers, 2009, pp. 583.

16. U. E. Gustafsson and C. E. Shoemaker, Proceedings: Workshop on the Role of Sulfur Species on the Secondary-Stage Degradation of Alloy 600 and Related Alloys, in: U.E. Gustafsson and C.E. Shoemaker, (Eds.) EPRI-NP-6710-M, 1985.

17. T. Sakai, S. Okabayashi, K. Aoki, K. Matsumoto, F. Nakayasu, and Y. Kishi, Effect of Reduced Sulfur on High Temperature Aqueous Corrosion for Alloy 600, in: Proc. 4th Int. Symp. Environmental Degradation of Materials in Nuclear Power Systems—Water Reactors, ed. D. Cubicciotti, (Houston, TX: NACE, 1989), 1989, pp. 12.

18. B. Sala, P. Combrade, R. Erre, R. Benoit, and M. Le Calvar, Chemistry of sulfur in high temperature water reduction of sulfates, in: Proceedings of the fifth international symposium on environmental degradation of materials in nuclear power systems-water reactors, 1992.
