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# Temperature dependence of passivity degradation on UNS N08800 in near neutral crevice chemistries containing thiosulphate

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ABSTRACT

Reduced sulphur induced corrosion of steam generator (SG) tubing in pressurized water reactor (PWR) is assumed to occur at low temperature. Corrosion of UNS N08800 in chloride and thiosulphate solutions at 20, 40 and 90 °C is systemically investigated by using polarization technique, electrochemical impedance spectroscopy (EIS), and X-ray photoelectron spectroscopy (XPS). It is concluded that thiosulphate can be reduced to $S^{\circ}$, $S_2^{2-}$ and $S^{2-}$, and incorporate into the passive film, which significantly depends on temperature. The evolution on pitting potentials in chloride + thiosulphate solution can be ascribed to the competitive adsorption of these two ions on the passive surface.

## 1. Introduction

Some corrosion phenomena in pressurized water reactor (PWR) are assumed to occur at low temperature during the shutdown and start-up transient conditions [1,2], and this is regarded as the situation for reduced sulphur-induced corrosion degradation on steam generator (SG) alloys. Many researches in recent years have focused on corrosion and electrochemical behavior of SG tubing alloys in reduced sulphur - containing environment [3,4].

Sulphate concentration is up to 10 ppb (by weight) in the feedwater of the secondary loop, and its concentration can be increased by several times in the heat - transfer crevices. Sulphate is not very aggressive to SG tubing alloys unless it is reduced to “reduced and intermediate oxidation level sulphur” (designated as $S^x$) [3]. $S^x$ is regarded as one of the most aggressive species, which is well known to increase pitting and stress corrosion cracking (SCC) susceptibility [4]. Thiosulphate is one typical $S^x$ existing in the heat - transfer crevices between the SG tubing and tubing support. Thiosulphate stems from the reduction of sulphate caused by hydrazine which is intentionally added into the feedwater of the secondary loop aiming at eliminating oxygen and maintain the electrochemical potential of SG tubing.

Besides $S^x$, other impurity ions such as chloride ions also concentrate within the crevices. Chloride and thiosulphate ions can jointly interact with passive film in a quite complicated way, depending on the concentration ratio of these two ions, electrode potential and pH [5–7]. At room temperature, chloride ions have a combined effect with thiosulphate on pitting corrosion in the case that the thiosulphate concentration is low. However, further increasing thiosulphate concentration would inhibit pitting corrosion. This “dual effect” of thiosulphate and the underlying mechanism on pitting corrosion has been fused together [2,8–10]: thiosulphate itself cannot break down the passive film easily, a sufficient concentration of chloride ions is necessary to break down the passive film, and a small amount of thiosulphate would stabilize and accelerate the pitting corrosion via reduction to $S^{\circ}$ within the pits [5]; further increasing thiosulphate concentration would mitigate the adsorption of chloride ions, and then, there are not enough chloride ions available to break down the passive layer [11].

Passive film breakdown can be enhanced by increasing electrolyte

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temperature. The species distribution and concentration ratio of $S^x$ are highly dependent on temperature according to the *E*−pH diagrams [12–15]. For instance, thiosulphate exists at room temperature in the absence of oxygen, but it can interact with metal surface and be reduced to other $S^x$ species on these metals. Unfortunately, the relevant researches are lacking.

This work aims to clarify how solution temperature affects the $S^x$ species distribution and their influence on the electrochemical behavior of UNS N08800 which is one of the preferred SG tube materials for CANDU™[2] (CANada Deuterium Uranium) reactors and the reactors in Germany and China. Passive film composition under various temperature with/without $S^x$ are analyzed, and the correlation between film properties and passivity breakdown is established.

## 2. Experimental procedures

### 2.1. Materials

UNS N08800 SG tube materials, with inner and outer diameters were 13.4 and 15.8 mm respectively, were supplied from the Sandvik Company, Sweden. The materials were cut in 10 mm length and embedded in an epoxy resin, the outer surface was ground by 300, 600, 1200, 1500 and 2000 - grit SiC paper, and then cleaned in distilled water, ethanol and acetone. The prepared specimen was placed in a desiccator for 24 h and then was taken out to conduct electrochemical tests. The chemical compositions of UNS N08800, which are given by the manufacturer, are as follows: Ni 32.78, Fe 43.20, Mn 0.50, Cr 21.78, Ti 0.48, Al 0.29, Si 0.46, Cu 0.02, Co 0.01, N 0.016, P 0.012, C 0.017, and S 0.001 wt. %.

### 2.2. Electrolytes

The used electrolytes were prepared according to the suggestion of Atomic Energy of Canada Limited (AECL), which were shown in Table 1. All the solutions were freshly prepared by dissolving various chemicals into the deionized water with resistivity of 18.2 MΩ•cm. The pH values at 20, 40 and 90 °C were measured by a pH meter. Various concentrations of chloride and thiosulphate are used as the simulated crevice chemistries.

**Table 1**
Test solutions for degradation of SG tubing materials in reduced sulphur environments.

| Test ID | Chemical composition | | $pH_{20°C}$ | $pH_{40°C}$ | $pH_{90°C}$ |
|---|---|---|---|---|---|
| | NaCl (mol/L) | Thiosulphate (mol/L) | | | |
| 1 | 0.6 | 0 | 6.98 | 6.85 | 6.72 |
| 2 | 0.6 | 0.075 | 6.92 | 6.84 | 6.79 |
| 3 | 0.6 | 0.5 | 6.98 | 6.88 | 6.78 |
| 4 | 0 | 0.5 | 6.95 | 6.81 | 6.79 |

### 2.3. Electrochemical methods

The electrochemical tests at 20, 40 and 90 °C were performed in a glass cell by using a PARSTAT2273 electrochemical workstation (Princeton Applied Research, USA). The working electrode was UNS N08800, the reference electrode was Ag/AgCl/KCl (saturated KCl), with a potential of 0.197 V vs. standard hydrogen electrode (SHE) at 25 °C. The counter electrode was a platinum sheet with an area of 2 × 2 $cm^2$. All the solutions were deaerated by purging $N_2$ for 1 h before the electrochemical tests.

Electrochemical impedance spectroscopy (EIS) was measured at free corrosion potential. The scanned frequency range was $10^5$–$10^{-2}$ Hz with the amplitude of the sinusoidal potential perturbation of 10 mV, and the overall data points is 49. EIS data were fitted by electrochemical equivalent circuits (EECs).

For polarization technique, the scan rate was 0.1667 mV/s, and the potential was scanned from cathodic to anodic direction. The initial potential is −200 mV vs. open circuit potential, and the final potential terminated when the current density reached 1 $mA \cdot cm^{-2}$. For cyclic voltammetry technique, the scan rate was 100 mV/s with a potential scan range of −1.8 to 2.2 $V_{SHE}$.

### 2.4. X-ray photoelectron spectroscopy

UNS N08800 was immersed in solutions for 5 days and then was taken out, cleaned using distilled water and ethanol before the X-ray photoelectron spectroscopy (XPS) test. XPS was performed using an Axis−ULTRA spectrometer (Kratos Analytical) to determine the valance of Fe, Ni, Cr, O, S in the passive film formed in simulated crevice chemistries containing chloride and thiosulphate ions. An aluminium source operated at 210 W with initial photon energy of 1486.71 eV was used as the photoelectron emission exciting. XPS 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 $5 \times 10^{-10}$ Torr. The photoelectrons were collected at a take-off angle of 90° with respect to the specimen surface. The C1s peak at 284.6 eV from adventitious carbon was used as a reference to correct for charging shifts. For each sample, XPS was measured for two times: before the etching and after etching for 30 s. Etching for 30 s corresponds to an etching depth of about 3 nm. It should be noted that the surface sulphur depositions were removed by an alcohol pad before XPS analyses.

### 2.5. Corrosion morphology

To observe the corrosion morphology and sulphur depositions, UNS N08800 was immersed in solutions for 5 days and then was taken out for observing. Corrosion images were observed by the KEYENCE VHX−2000 3D optical microscopy and a field-emission scanning electron microscope (FE-SEM, Hitachi, Japan) combined with an Energy Dispers Spectroscope (EDS).

## 3. Results

### 3.1. Polarization technique

Fig. 1 shows a summary of the polarization curves in chloride solutions with/without thiosulphate and at temperatures of 20, 40 and 90 °C respectively. UNS N08800 is self-passive in all test conditions, though the corrosion potential and pitting potential is slightly different. At 20 °C, the corrosion potentials follow within the range of −0.5 ∼ −0.42 $V_{SHE}$. Solution chemistries do not affect the passive current density to a large extent, and the current densities are approximately $10^{-7}$ $A \cdot cm^{-2}$. Solution chemistries significantly influence the breakdown potentials. Here, the term “breakdown potential” is used instead of “pitting potential”, because there is no pitting formed in thiosulphate-only solution. In thiosulphate-only solution, the current density reaches to 1 $mA \cdot cm^{-2}$ as the anodic potential rises to about 1 $V_{SHE}$. This increased current is not attributed to the transpassive dissolution of the passive layer, but related to the oxidation of thiosulphate to $S_4O_6^{2-}$ and $S_3O_6^{2-}$ [16], which can be described by the reactions (1) and (2):

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^- \quad (1)$$

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[2] CANadian Deuterium Uranium is a registered trademark of Atomic Energy of Canada Limited (AECL).