

## Peculiar Corrosion Behavior of Type 316L SS in Simulated Cooling Water at Various pH Values

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*The effect of pH on the corrosion behavior of Type 316L stainless steel (SS) (UNS S31603) in simulated cooling water was studied using corrosion potential and potentiodynamic polarization techniques. The fundamental result is that corrosion is very effectively controlled within a relatively narrow range of neutral to near-neutral pH values with increased corrosion rates outside that range in either direction. The negative (active) open circuit potential at pH values lower and higher than neutral ( $6 \leq \text{pH} \leq 8$ ) was due to dissolution of the passive film by a hydrogen reduction reaction and oxidation of hydroxyl ions by oxygen evolution in the presence of chloride ions. It was also found that the corrosion potential was relatively positive (noble) when the concentration of hydrogen and hydroxyl ions was balanced ( $\text{pH} = 7$ ), which depicted excellent corrosion protection of SS.*

of a passive film, which is composed of an inner chromium oxide ( $\text{Cr}_2\text{O}_3$ ) layer with ferrous hydroxide [ $\text{Fe}(\text{OH})_2$ ] at the top. The passive film remains stable in the presence of oxidizing constituents in the environment.<sup>4</sup>

Water is a good solvent and has the ability to dissolve salts and oxygen. The presence of chlorides above specific limits can negatively affect the integrity of the passive film.<sup>4</sup> Most commonly, corrosion, fouling, and scaling problems arise in cooling tower systems due to soluble impurities in the water, which increase operational and maintenance costs.<sup>5</sup> Major failures in cooling towers occur due to localized corrosion of metallic structures in contact with circulating water. The water corrosiveness, however, depends largely on composition and on the alloy exposed to the aqueous environment.<sup>6</sup> Cooling water that contains large amounts of dissolved oxygen (DO) and aggressive ions, such as chlorides and sulfates, can break down passive films on the SS.<sup>3,6</sup> In order to minimize corrosion problems in the cooling towers, the present study was carried out to understand the mechanism of passive film dissolution by the aggressive ions in cooling water with pH values between 6 and 8.

**Water is commonly used in cooling systems as a heat transfer medium to remove heat from surfaces and dissipate heat into the atmosphere through evaporation inside cooling towers. Evaporative cooling towers offer the most cost-effective cooling technology for commercial air conditioning and industrial processes.<sup>1-3</sup>**

Stainless steel (SS) has inherently good corrosion resistance due to the formation

### Experimental Procedures

The chemical composition of the specimens was determined by an x-ray fluorescence (XRF) spectrometer, which confirmed the SS as AISI 316L (UNS S31603).

The electrochemical behavior of this steel was measured in simulated cooling water, which was prepared by adding sodium chloride (NaCl) (500 ppm), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) (520 ppm), sodium bicarbonate (NaHCO<sub>3</sub>) (170 ppm), and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) (66 ppm) to distilled water.<sup>7</sup> This simulated cooling water had a pH value of 8. The specimens were analyzed in this solution at various pH values from 8 to 6 (adjusted by the addition of sulfuric acid [H<sub>2</sub>SO<sub>4</sub>]). The specimens were mechanically polished with 1000 grit silicon carbide (SiC) papers, degreased in acetone, and rinsed with deionized water before electrochemical analysis. Corrosion potential and potentiodynamic polarization scans of the SS specimens were obtained in a three-electrode cell coupled with the Gamry Potentiostat PC14/750<sup>†</sup> to evaluate the surface stability and corrosion kinetics against these electrolytes, respectively.

## Results and Discussion

### Open Circuit Potential Measurements

The open circuit potential (OCP) of Type 316L SS (UNS S31603) in simulated cooling water is highly dependent on pH and the composition of anions and cations. The OCP for Type 316L SS in simulated cooling water at different pH values, as measured with reference to a saturated calomel electrode (SCE), are shown in Figure 1. The variations in the OCP of SS samples in simulated cooling water at various pH values are given quantitatively in Table 1 for comparison.

It can be seen from Figure 1 that the OCP of the substrate is more negative (-540.75 mV) at pH 8 than those at lower pH values. With the addition of small amounts of H<sub>2</sub>SO<sub>4</sub> to adjust the pH to 7.5, there is an appreciable shift in potential from the more negative value to -129.8 mV vs. SCE, reflecting a decrease in surface activity corresponding to the reduced pH value.

<sup>†</sup>Trade name.

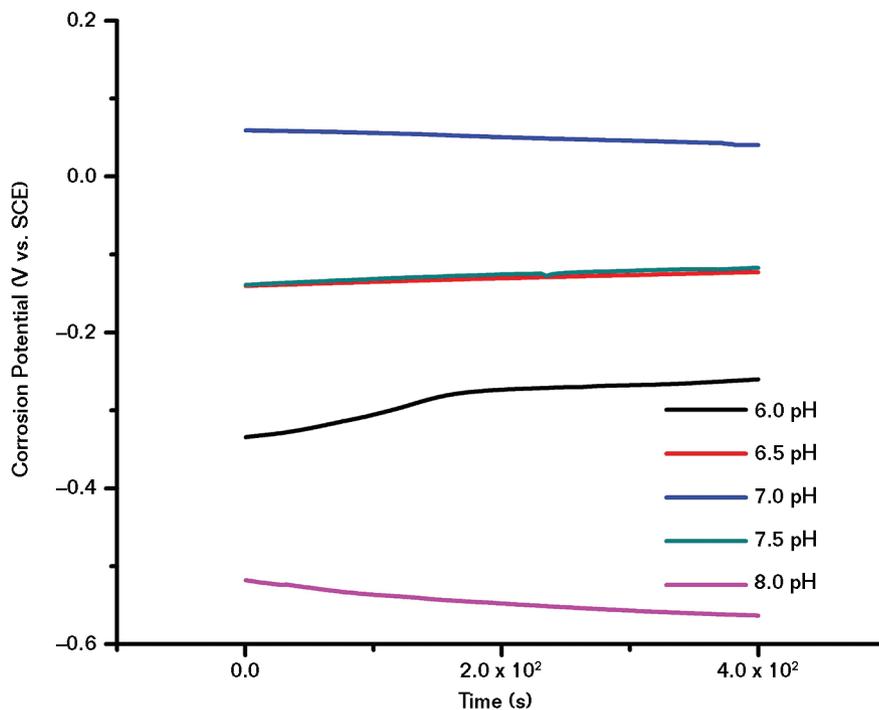


FIGURE 1 OCP of SS specimens at different pH values.

Interestingly, with a neutral pH value (pH 7), the OCP becomes strongly positive (49.73 mV vs. SCE), suggesting high stability of SS in the neutral environment. With decreasing pH values, the OCP again shifts to more negative potentials, reaching -261.0 mV at pH 6 (Figure 1). However, in apparent symmetry, the OCP at pH 6.5 (-125.85 mV vs. SCE) is nearly equal to the OCP at pH 7.5.

### Understanding the Reactions Mechanism

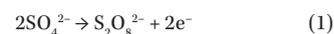
This corrosion potential study shows that the interesting behavior of SS under alkaline and/or acidic conditions at a constant chloride level (500 ppm NaCl) has greatly influenced the depolarization tendency of the surface. The increase in H<sup>+</sup> or OH<sup>-</sup> ion concentration in simulated cooling water might have inhibited the formation of passive films on the surface according to Equations (1) and (2).<sup>3,8</sup>

In acidic conditions (at pH values <7), the incorporation of sulfate (SO<sub>4</sub><sup>2-</sup>) in the electrolyte enhanced the depolarizing ten-

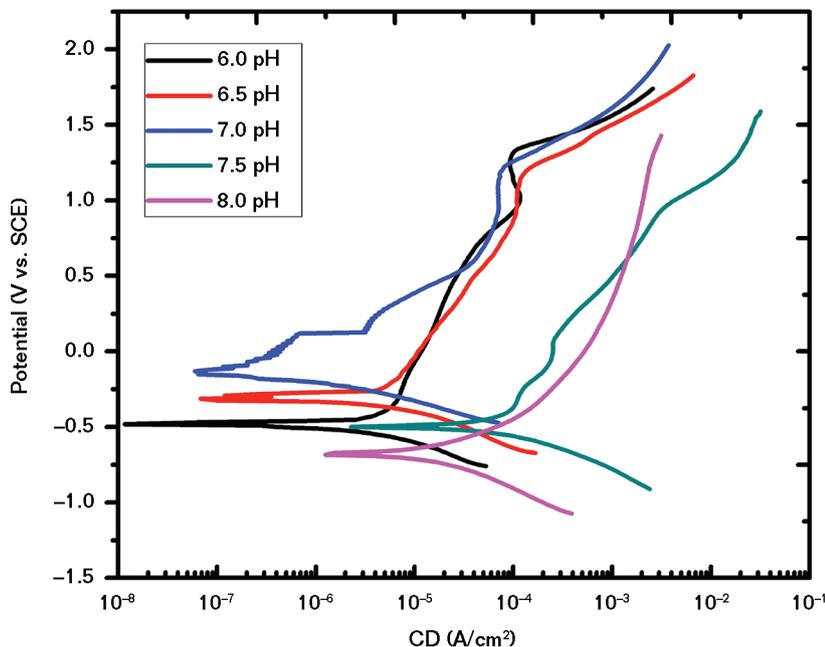
TABLE 1. OCP VALUES OF SS SAMPLES IN SIMULATED COOLING WATER OBTAINED AT VARIOUS pH VALUES

pH	Corrosion Potential (mV vs. SCE)
6.0	-261.01
6.5	-125.85
7.0	+49.73
7.5	-129.80
8.0	-540.75

dency of DO. The mechanism of depassivation of SS can be described according to the following reactions:



The oxidation of sulfate ions will limit the availability of oxygen for passivation.

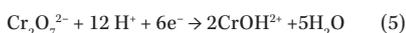
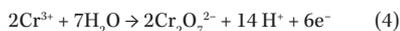
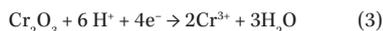


**FIGURE 2** Potentiodynamic polarization of SS specimens in simulated cooling water at various pH values.

**TABLE 2.**  $I_{corr}$  AND  $E_{corr}$  VALUES OF SS IN SIMULATED COOLING WATER

pH	$E_{corr}$ (mV vs. SCE)	$I_{corr}$ ( $\mu\text{A}/\text{cm}^2$ )
6.0	-494.0	9.55
6.5	-312.0	6.33
7.0	-142.0	0.19
7.5	-499.0	160.0
8.0	-677.0	20.0

On the other hand, the increase in  $\text{H}^+$  ions will produce more deleterious effects on the passivation of Type 316L SS in combination with sulfate ion oxidation. The mechanism of deterioration of the  $\text{Cr}_2\text{O}_3$  passive film at the SS surface can be explained as follows:



The oxidation of  $\text{Cr}^{+3}$  will produce hexavalent chromium oxide ( $\text{Cr}_2\text{O}_7^{-2}$ ), which produces  $\text{CrOH}^{2+}$  ions in an acidic condition (Equation [5]). This can be explained on the basis that the specific interaction of chlorine ( $\text{Cl}^-$ ) and  $\text{SO}_4^{2-}$  ions with  $\text{CrOH}^{2+}$  could dissolve the passive film on SS.<sup>4</sup>

At the neutral condition ( $\text{pH} = 7$ ), the positive potential might have resulted due to the retardation of  $\text{Cr}_2\text{O}_3$  dissolution because of the balance of  $\text{H}^+/\text{OH}^-$  ions at  $\text{pH} = 7$ . In this condition, the mechanism of  $\text{Cr}_2\text{O}_3$  dissolution might reverse (Equations [1] through [4]) and would promote formation of the passive film.

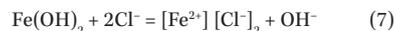
At higher pH values ( $\text{pH} > 7$ ), the oxidation of  $\text{OH}^-$  will be accelerated by Equation (6):



This suggests that in alkaline conditions ( $\text{pH} > 7$ ), the oxygen adsorption can induce severe deterioration of the passive film.

The constant value of  $\text{Cl}^-$  ions in simulated cooling water will have a strong depo-

larizing tendency due to the unavailability of DO (evolution of oxygen). The increase in pH results in an increased evolution of oxygen (Equation [6]), whereas the hydroxide could be hydrolyzed by the chlorides in the solution as shown in Equation (7):



### Potentiodynamic Polarization

Potentiodynamic polarization curves for Type 316L SS in simulated cooling water at different pH values are shown in Figure 2. The potentiodynamic polarization curve of SS samples at  $\text{pH} = 7$  demonstrated very low corrosion current ( $I_{corr}$ ) compared to those at lower and higher pH values, which agrees with the more positive corrosion potentials seen in Figure 1.

During the cathodic polarization scans (Figure 2), the cathodic current—because of the reduction of  $\text{H}^+$  ions (Equation [2])—is less sensitive than in the anodic range, where a significant increase in anodic current densities (CDs) leads to a shift in the corrosion potential ( $E_{corr}$ ) toward the more active direction. Hence, increase in the activity of hydrogen ions will promote the reduction of  $\text{Cr}_2\text{O}_3$  (Equation [3] through [5]). Table 2 gives the values of the corrosion potential ( $E_{corr}$ ) and corrosion CD ( $I_{corr}$ ) calculated from the potentiodynamic scans.

The CD and corrosion potential of specimens at  $\text{pH} 8$  are  $20.0 \mu\text{A}/\text{cm}^2$  and  $-677.0 \text{ mV}$ , respectively, which markedly increase to  $160 \mu\text{A}/\text{cm}^2$  and  $-499 \text{ mV}$  at a pH value of 7.5. The corrosion potential was appreciably increased from  $-129.8 \text{ mV}$  before cathodic polarization (Table 1) to  $-499 \text{ mV}$  after cathodic polarization. This change can be attributed to the hydrogen reduction reaction, which accelerated the dissolution of the  $\text{Cr}_2\text{O}_3$  passive film. The increase in corrosion CD from 6.330 to  $9.55 \mu\text{A}/\text{cm}^2$  at lower pH values (from 6.5 to 6.0, respectively) validated the mechanism of  $\text{Cr}_2\text{O}_3$  dissolution due to increasing activity of hydrogen ions in the presence of chloride ions as discussed earlier. Similarly, the  $E_{corr}$  shift from  $-312$  to  $-494 \text{ mV}$  (at lower pH values) is also in agreement with the proposed phenomenon.

## Conclusion

It is obvious that the presence of anions (i.e.,  $\text{OH}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ) and DO have complex electrochemical reaction mechanisms. The pH has great influence on the activity of specific cations, which may cause severe uniform corrosion of SS or local dissolution of the  $\text{Cr}_2\text{O}_3$  passive layer. SS remains in the immunity zone (noncorrosive) at a neutral pH when it comes into contact with fresh or saline water. However, a slight increase or decrease in pH in combination with  $\text{Cl}^-$  ions can cause localized attack on SS in the form of pitting or crevice corrosion followed by breakdown of the protective  $\text{Cr}_2\text{O}_3$  film. There is always a competitive and complex mechanism involved between the adsorption of oxygen, ingress of chlorides, and reduction of hydrogen ions to promote dissolution of passive films on SS.

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