



## Pit Transition Potential and Repassivation Potential of Stainless Steel in Thiosulfate Solution

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The transition potential and the repassivation potential of AISI type 316 stainless steel was investigated in the absence and the presence of 0.01 M thiosulfate in chloride containing media. The pencil electrode method was employed to explore the key factors affecting the pit transition potential and the repassivation potential in thiosulfate containing solution. Using this method the pit chemistry at various temperatures was also evaluated. A good correlation was found between the pitting potential and the pit transition potential at various temperatures. Moreover, there was a significant decrease in the repassivation potential by addition of 0.01 M thiosulfate. The results were in accordance with the theory suggesting that the chemistry of the pit governs the pit repassivation potential. © 2016 The Electrochemical Society. [DOI: 10.1149/2.0381606jes] All rights reserved.

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The wide application of thiosulfate in industrial environments, particularly in the pulp and paper industries and in refinery plants makes the study the role of thiosulfate on corrosion of alloys necessary.<sup>1-4</sup> Moreover, the thiosulfate leaching process has been introduced as an alternative approach to cyanide leaching for gold and silver extraction.<sup>5</sup> The action of thiosulfate on pitting corrosion has been extensively studied.<sup>1-3,6-13</sup> Localized corrosion of stainless steels and nickel alloys in thiosulfate containing solutions strongly depends on the thiosulfate to chloride ratio.<sup>6,7,14</sup> The presence of a small amount of thiosulfate enhances the localized corrosion in chloride solutions.<sup>11,13,14</sup> However, thiosulfate addition does not affect the pitting corrosion until the chloride ions lead to breakdown of the passive layer.<sup>14</sup> Addition of thiosulfate promotes both the initiation and the growth of metastable pitting on the surface of stainless steels.<sup>13,15,16</sup> Thiosulfate ions enhance the frequency, growth rate, pit stability product, and pit current of metastable events on 316 SS. The survival probability of stable pits is also found to be decreased by thiosulfate addition to chloride solution.<sup>13</sup> It has been reported that thiosulfate promotes both metastable pit occurrence and growth on 304L and LDX2101.<sup>15</sup> At low thiosulfate to chloride concentrations, adsorbed sulfur may have combined effects with chloride ions on increasing oxygen vacancies in the passive layer.<sup>17</sup> The catalytic effect of adsorbed sulfur on lowering the activation energy of metal dissolution of stainless steels has been reported in the literature.<sup>3,16,18,19</sup> In addition, when molybdenum is present in the alloy composition, sulfur is unstable as S<sup>0</sup>, and is reduced to aqueous hydrogen sulfide.<sup>20</sup> Thiosulfate ion is quite stable in neutral solutions. However, in the pit environment, which is under low pH conditions,<sup>21</sup> thiosulfate has a thermodynamic tendency for chemical disproportionation and is reduced into adsorbed sulfur and sulfide on the bare metallic surface.<sup>22</sup> The disproportion of thiosulfate ions to sulfur ions may also give hydrogen sulfide (H<sub>2</sub>S or HS<sup>-</sup>), which has been demonstrated to be a catalyst for dissolution of iron.<sup>23</sup> The adsorbed sulfur (or sulfide) is produced on the bare metal surface thus hinders the repassivation of metal. Following the sulfur adsorption, the pH decreases to a value low enough to sustain the very high rate of anodic dissolution.<sup>2</sup>

Some particular experiments have been reported for the development of a single corrosion pit in order to understand the mechanisms involving the pitting corrosion.<sup>12,24-27</sup> Recently, the pencil electrode has been employed to study the pitting phenomenon and to extract the kinetic parameters required for determining the critical conditions for pit stability and repassivation.<sup>28,29</sup> Assessment of the anodic current density required to maintain acidity via the metal ions concentration in the pit solution (C<sub>S</sub>) provides a valuable interpretation of the transition from metastable to stable pitting. Using a single corrosion pit, it has been shown that the thiosulfate may enhance the pit stability either

through the presence of a salt film or through a cathodic side-reaction.<sup>6</sup> In our related work,<sup>12</sup> evaluation of pit anolyte by the pencil electrode method revealed that thiosulfate causes a decrease in both saturation and critical concentration of metal salt within the pit solution.

It is believed that the presence of salt film is necessary for a pit to sustain stable growth after the pit cover ruptures.<sup>30</sup> For an open cavity, when the pit cover collapses, a model developed by Laycock and Newman<sup>31</sup> describes the transition from metastable to stable pitting with regard to the pit transition potential, E<sub>T</sub>, which is the potential between bare and salt covered state. In other words, the E<sub>T</sub> is a potential above which diffusion control dominates.<sup>31,32</sup> At potentials above E<sub>T</sub>, the change of current density with time is representative of diffusional control current density.<sup>33</sup> In this stage, the dissolution rate is controlled by diffusion of metal cations from the salt/pit solution interface into the bulk solution. In this stage of pit growth, the relation between the square of current density and reciprocal of time, i<sup>2</sup> ~ t<sup>-1</sup>, which is an indication of the anodic diffusion control, was confirmed.<sup>34,35</sup> Back scanning however, causes the salt film thickness to decrease.<sup>36</sup> Once the potential reaches the period at which the cation concentration decreases below the saturated concentration (C<sub>S</sub>), precipitated salt would no longer be stable. Thereby, the metal salt film would be dissolved and afterward the pit bottom will be salt film free. This event results in an ohmic/activation control regime to be established.<sup>37</sup> In this region, current density decreases linearly with potential.

Based on the model proposed by Laycock and Newman,<sup>31</sup> the pit transition potential (E<sub>T</sub>) is the summation of E<sub>corr</sub> in the pit solution, activation overpotential (η<sub>act</sub> = b<sub>a</sub> log( $\frac{i_{lim}}{i_{corr}}$ )) relative to E<sub>corr</sub> in the saturated pit, and IR drop. This potential is expressed in Equation 1.

$$E_T = E_{corr} + b_a \log \left( \frac{i_{lim}}{i_{corr}} \right) + I_{lim} R_S \quad [1]$$

where b<sub>a</sub> is the anodic Tafel slope in the pit solution, i<sub>corr</sub> is the corrosion current density in the pit solution, i<sub>lim</sub> is the limiting current density, and I<sub>lim</sub> is the limiting current. In this equation, R<sub>S</sub> represents the total solution resistance. Measurement of the pit transition potential as a function of the anodic limiting current density, aids to precise prediction of the pitting potential. By an extrapolation of this potential to very small length scales, Laycock and Newman<sup>32</sup> have predicted the variation of pitting potential with chloride concentration, Mo alloying, etc.

The repassivation potential, E<sub>rep</sub>, is a characteristic potential below which, no pit could grow. In other words, at potentials less than the repassivation potential, pitting corrosion, once begun, will stop. After the passage of large charge densities, E<sub>rep</sub> is practically independent of the amount of charge passed in a localized corrosion process.<sup>38-40</sup> At high pit depths, the repassivation potential for pitting and the repassivation potential for crevice corrosion coincide. Thus, the repassivation potential for deep pits or crevices could be utilized as a conservative threshold for the occurrence of localized corrosion.<sup>39,40</sup>

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**Table I. The chemical composition of experimented 316 SS stainless steel (in wt %).**

Metal	C	S	P	Si	Mn	Ni	Cr	Mo	Fe
Bulk alloy	0.05	0.012	0.02	0.4	1.9	10.5	18.1	2.1	Bal.
50 $\mu\text{m}$ dia. wire	0.045	0.015	0.019	0.5	2.1	10.8	18.7	2.05	Bal.

Newman<sup>41</sup> has paralleled the protection to passivation at a critical metal cations concentration ( $M^{n+}$ ), which is equivalent to a critical pH, and approximately equal to a critical current density for a given pit geometry. The concentration of metal cations in a growing pit is a mass balance between the diffusion plus electro-migration from the pit and the dissolution rate of the pit walls.<sup>42</sup> Replacement of concentration losses from the pit by the metal cations produced through the metal dissolution is the critical factor in sustaining the pit growth.<sup>42-47</sup>

In this study, we focused on the pit transition potential and the repassivation potential as two important pitting corrosion criteria. First, the influence of thiosulfate on the pit transition potential and the correlation between  $E_T$  and  $E_{pit}$  was studied in 0.1 M chloride containing solution by the pencil electrode technique. We implemented the model introduced by Laycock and Newman<sup>31</sup> to find out how thiosulfate influences the parameters affecting the pitting potential of 316 stainless steel in sodium chloride solution. The next measurements conducted in this work concern the repassivation of growing pits. In this part of the work, we investigated the mechanism by which thiosulfate may affect the repassivation potential. The possible mechanisms of the influence of thiosulfate on the repassivation potential are also discussed.

### Experimental

Two types of specimens were prepared for electrochemical experiments. Pitting potential measurements were performed on AISI 316 stainless steel flat samples with 0.8  $\text{cm}^2$  exposed surface area. Flat samples were initially pre-passivated at anodic potential of 950 mV (SCE) in 0.1 M sodium sulfate to avoid crevice corrosion at the metal/insulator interface.<sup>48</sup> To make the electrical connection, the other end of each electrode was connected to a shielded copper wire which was inserted into a rigid plastic tube. Before each test, specimens were wet ground to 1200 grit silicon carbide paper. For artificial pit experiments, 50  $\mu\text{m}$  diameter 316 stainless steel wire embedded in epoxy resin was used. The compositions of the materials used in this study are listed in Table I. For each test, fresh solution was prepared from analytical grade chemicals and distilled water. A conventional three electrode cell including a saturated calomel electrode (SCE) as the reference electrode and a platinum foil as the counter electrode were used. The electrochemical cell was a 200 ml open to air beaker. Before each electrochemical test, the open circuit potential was monitored for 30 min, which was sufficient to approach the steady state condition.

The pitting potential of alloy in 0.1 M sodium chloride solution with and without 0.01 M sodium thiosulfate was assessed in the temperature range from 20°C to 40°C in 5°C intervals. The potential was swept from 50 mV below the rest potential, at a given scan rate (30  $\text{mV min}^{-1}$ ) until the current density exceeded 0.3  $\text{mA cm}^{-2}$ . In the present study, the pitting potential was defined as the potential at which the current density started to increase progressively, i.e. the stable pitting occurred.<sup>49</sup> Potentiodynamic polarization with the sweep rate of 100  $\text{mV min}^{-1}$  in simulated pit solution (i.e. 5 M HCl and 5 M HCl + 0.01 M  $\text{Na}_2\text{S}_2\text{O}_3$ ) was performed to estimate the corrosion potential and corrosion current density within a real growing pit.<sup>25,27,50,51</sup>

The probability of the repassivation potential in 0.1 M sodium chloride solution with and without 0.01 M thiosulfate was assessed by cyclic potentiodynamic polarization measurement using flat samples at 25°C. The repassivation potential was determined to be the point where the hysteresis loop was completed and the reversed scan crossed the forward scan.<sup>52</sup> The cyclic polarization test was repeated 15 times

for each solution at the identical condition, then the pitting probability distribution was calculated using Equation 2.<sup>53</sup>

$$P(E) = \frac{n}{(N + 1)} \quad [2]$$

where  $n$  is the  $n^{\text{th}}$  sample on which pitting occurred and  $N$  is the total number of the experiments.

The pencil electrode method was employed to study the effect of thiosulfate on the pit transition potential, the IR drop, the repassivation potential and the critical chemistry necessary for passivation of 316 SS. For creating single corrosion pits, pencil electrodes were potentiostatically polarized in 0.1 M sodium chloride solution with and without 0.01 M sodium thiosulfate at 750 mV (SCE) for 600 s followed by 120 s potentiostatic polarization at 400 mV (SCE). Subsequently, the potential was reversely swept to the passive region potentiodynamically at a sweep rate of 60  $\text{mV min}^{-1}$  until passivity set in.

The depth of each pit, was calculated by measuring the total charge passed during the current density vs. time curve.<sup>12,25,54</sup> In this set of experiments, to eliminate the effect of pit depth, only the results of single corrosion pits with depth of about 190  $\mu\text{m}$  were considered.

The potential at which the transition from diffusion control to activation/ohmic control occurs was defined as the pit transition potential.<sup>31,32</sup> The repassivation potential was defined as the potential at which a sudden drop in current density was observed.<sup>55</sup>

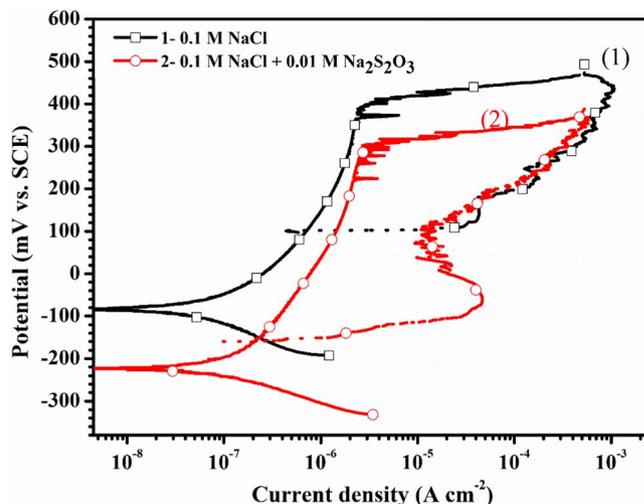
In order to investigate the effect of temperature on the transition potential, pencil electrode experiments were performed in 0.1 M NaCl and 0.1 M NaCl + 0.01 M  $\text{Na}_2\text{S}_2\text{O}_3$  solutions at temperature range from 20°C to 40°C at 5°C intervals.

Furthermore, a set of experiments were conducted to study the variation of pit transition potential with limiting current density. In these experiments, the potentiostatic polarization time was varied from 50 s to 2000 s to obtain pits with depth ranged from ca. 80  $\mu\text{m}$  to ca. 190  $\mu\text{m}$ . The results of these experiments were used to evaluate the repassivation potential and the chemistry of single growing pits with different pit depths in 0.1 M NaCl and 0.1 M NaCl + 0.01 M  $\text{Na}_2\text{S}_2\text{O}_3$  solutions.

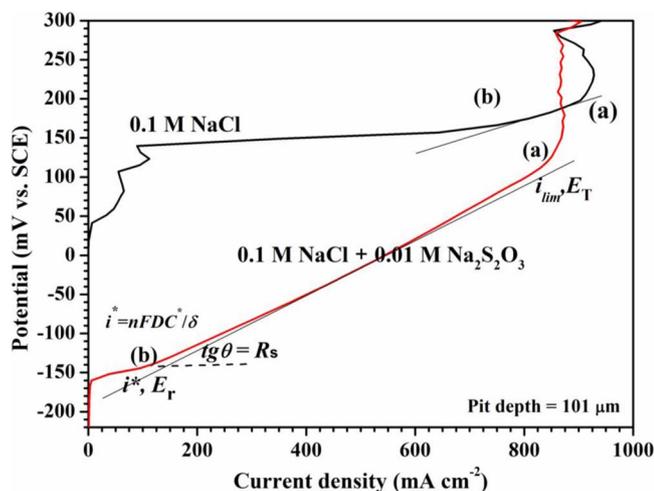
### Results

#### The influence of thiosulfate on 316 SS pit transition potential.—

The pitting potential of the alloy was assessed using a flat sample at various temperatures in 0.1 M NaCl solution in the absence and the presence of 0.01 M thiosulfate at temperatures above the critical pitting potential (CPT).<sup>12</sup> Figure 1 shows typical polarization curves

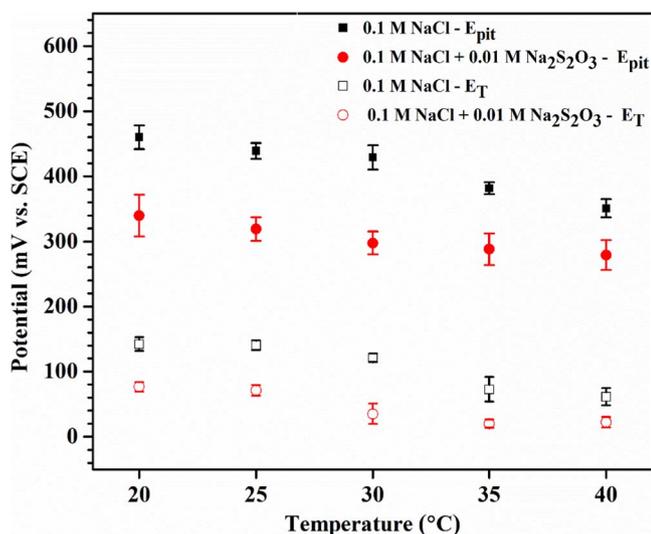


**Figure 1.** Typical cyclic polarization curves for 316 SS in 0.1 M chloride solution with and without 0.01 M thiosulfate at 25°C. The sweep rate was 30  $\text{mV min}^{-1}$  at 25°C.

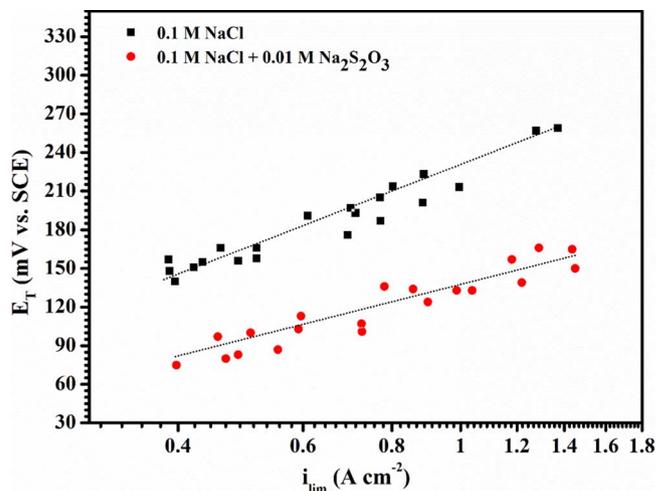


**Figure 2.** Typical potential vs. current density curves obtained from pencil electrode tests for 316 SS in 0.1 M chloride solution with and without 0.01 M thiosulfate at 25°C. The pit depth was ca. 101  $\mu\text{m}$ , and the sweep rate was  $-60 \text{ mV min}^{-1}$ .

used for assessment of pitting potential representing lower pitting potential in the presence of thiosulfate ions. Figure 2 shows typical potential vs. current density curves obtained from pencil electrode tests in 0.1 M chloride solution with and without 0.01 M thiosulfate at 25°C. In Figure 2, point (a) is the potential between diffusion controlled and activation/ohmic control, i.e. the transition potential. Obtained values of  $E_T$  and  $E_{\text{pit}}$  are plotted vs. temperature in Figure 3. It is shown that the pitting potential decreased with increasing temperature. In the absence of thiosulfate ions, the average of pitting potential was 468 mV (SCE) at 20°C. At this temperature, the average pit transition potential of alloy in 0.1 M NaCl solution was 142 mV (SCE). An increase in the temperature decreased both the pitting potential and the pit transition potential. In pure NaCl solution, the pitting potential changed from 468 to 351 mV (SCE) and the transition potential decreased from 142 to 61 mV (SCE) over 20°C to 40°C. Comparison of the  $E_{\text{pit}}$  and  $E_T$  shows a decrease in both parameters



**Figure 3.** Pit transition potential (obtained from artificial pit experiments) and pitting potential (obtained from potentiodynamic polarization) of 316 SS as a function of temperature, in 0.1 M chloride solution with and without 0.01 M thiosulfate. (The pit depth was ca. 190  $\mu\text{m}$ ). Error bars represent 95% confidence limits measured from at least five experimental tests under identical conditions.



**Figure 4.** Pit transition potential as a function of limiting current density, obtained from pencil electrode studies on 316 SS in 0.1 M chloride solution with and without 0.01 M thiosulfate at 25°C.

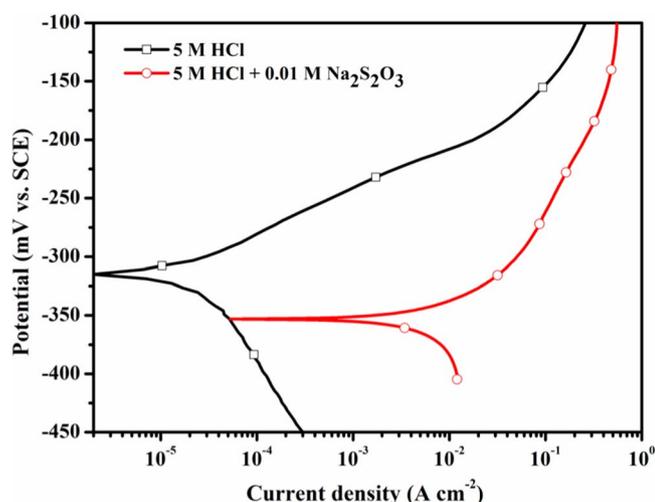
by thiosulfate addition. Apparently, the addition of thiosulfate shifted the pitting potentials to lower values than that of in pure chloride solution. In the presence of 0.01 M thiosulfate,  $E_{\text{pit}}$  ranged from 340 mV (SCE) to 279 mV (SCE) and  $E_T$  ranged between 76 mV (SCE) and 22 mV (SCE) when temperature was between 20°C and 40°C. Based on these experimental results, there is a good correlation between the pit transition potential and the pitting potential. Such correlation between the  $E_{\text{pit}}$  and the  $E_T$  has been previously reported by Laycock and Newman.<sup>32</sup>

Figure 4 shows the plot of  $E_T$  vs.  $\log i_{\text{lim}}$  for the artificial pits growing in NaCl solution in the absence and the presence of 0.01 M thiosulfate. Clearly, the addition of 0.01 M thiosulfate decreased the pit transition potential of 316 SS at limiting currents. Furthermore, the  $E_T$  values obtained in both solutions are increased with limiting current increase. In comparison to deeper pits, shallower pits have higher limiting current. The best linear trend line was fitted on the results obtained in each solution. The slope is larger in pure chloride solution than in the thiosulfate solution, ca. 119 mV per decade and ca. 76 mV per decade in the absence and the presence of thiosulfate, respectively. Based on the model of dissolution kinetics introduced by Laycock and Newman,<sup>31</sup> the plot of pit transition potential vs. logarithm of limiting current density can be used to evaluate the slope of anodic dissolution curve, i.e. the Tafel slope in the pit solution. Shown in Figure 5, potentiodynamic polarization of the alloy in simulated pit solution revealed a decrease (about 40 mV) in corrosion potential and an intense increase (by a factor of ca. 100) in corrosion current density in the presence of thiosulfate ion.

The IR drop was assessed in 0.1 M NaCl and 0.1 M NaCl + 0.01 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution for different pit depths. The IR drop was defined as the product of limiting current ( $I_{\text{lim}}$ ) and the pit solution resistance ( $R_S$ ). The limiting current is the current corresponding to the pit transition potential. The reciprocal of the slope of potential vs. current curve in the activation/ohmic region was taken into account as the pit solution resistance.<sup>31</sup> The addition of thiosulfate increased the IR drop on the order of 100 mV (see Figure 6).

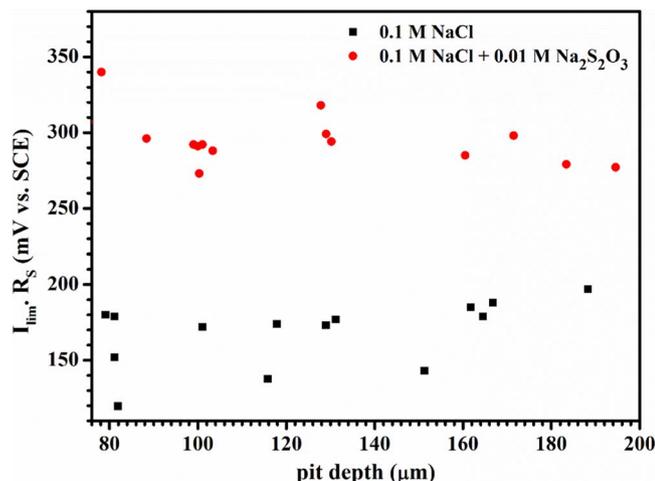
The plot of potential vs. current (shown in Figure 7) compares the current density in the activation/ohmic stage in the absence and the presence of thiosulfate ions. Data are extracted from the activation/ohmic stage of the tests obtained from single pits with various pit depths. Each point shown in this figure, is the middle point of the activation/ohmic region.

**Influence of thiosulfate on 316 SS repassivation potential.**—The repassivation potential is the potential at which a stable pit or crevice will cease to grow.<sup>56</sup> As the typical cyclic polarization curves for

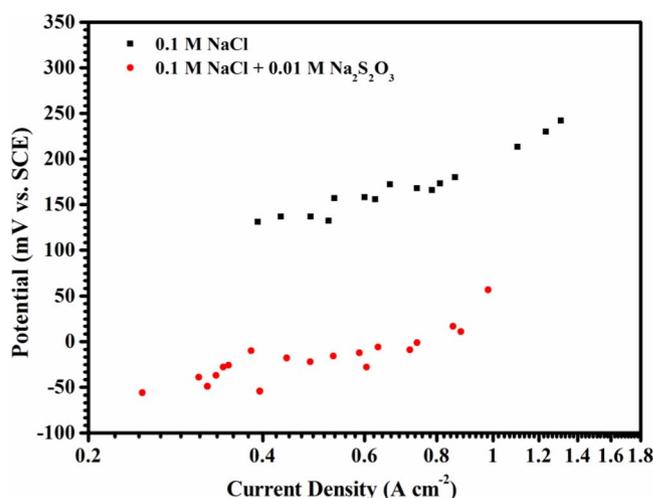


**Figure 5.** Potentiodynamic polarization curves of 316 SS in 5 M HCl with and without 0.01 M thiosulfate as simulated pit solutions. The sweep rate was  $100 \text{ mV min}^{-1}$ .

316 SS in chloride solution containing and non-containing 0.01 M thiosulfate shows (Figure 1), once the pit interfacial potential reaches the repassivation potential, the system controls the current by passivating the active pit surface. The potential at which the current returned to the passive condition was taken as the repassivation potential ( $E_{\text{rep}}$ ).<sup>52</sup> The probability distribution of repassivation potential in the absence and the presence of thiosulfate ions is shown in Figure 8. It can be seen from Figure 8 that thiosulfate addition led to a considerable decrease of the repassivation potential. The median value of the repassivation potentials obtained from cyclic polarization of 316 SS was 114 mV (SCE) in the pure chloride solution and is  $-89 \text{ mV (SCE)}$  in the presence of 0.01 M thiosulfate. The repassivation potentials measured from flat samples may come from the largest pit among several pits. The study of single pits, alleviates some of the uncertainty. The pit repassivation potential of a single growing pit may be obtained from pencil electrode results. Once the potential reaches to  $E_{\text{rep}}$ , current density starts decreasing dramatically, which indicates the onset of passivation (point (b) in Figure 2). Indeed, when the potential is lower than the repassivation potential, the pit stops growing and is not stable anymore. The results attributed to the pits with ca.  $190 \mu\text{m}$  pit depth were used for this purpose. Figure 9 represents the cumulative



**Figure 6.** IR drop as a function of pit depth, obtained from artificial pit experiments on 316 SS in 0.1 M chloride solution in the absence and the presence of 0.01 M thiosulfate at  $25^\circ\text{C}$ .

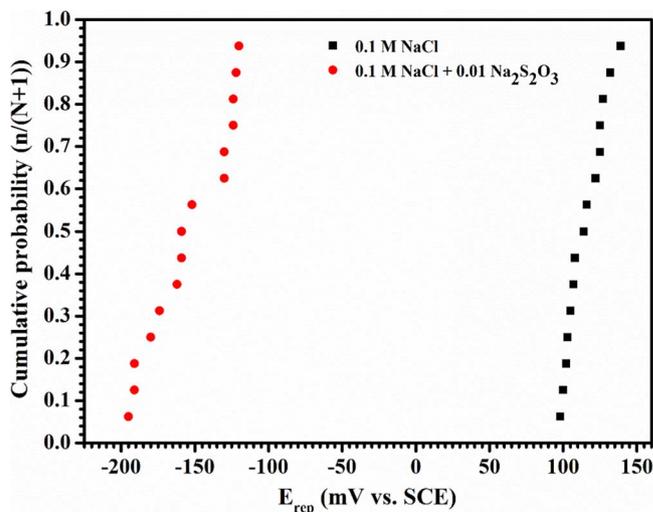


**Figure 7.** The middle points of activation/ohmic stage of curves obtained from the pencil electrode test results. The results obtained from a range of pit depths ( $80\text{--}190 \mu\text{m}$ ) were used.

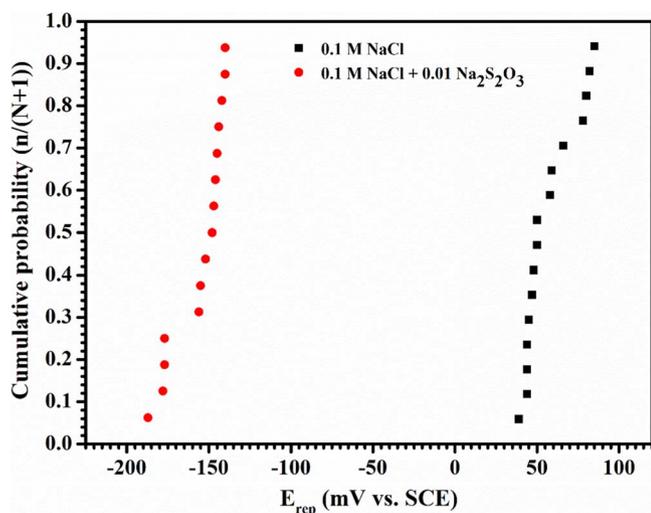
distribution of  $E_{\text{rep}}$  obtained from almost  $190 \mu\text{m}$  pits by the pencil electrode method. In the absence of thiosulfate, the median of the repassivation potential was  $50 \text{ mV (SCE)}$ . By addition of 0.01 M thiosulfate, the median value of  $E_{\text{rep}}$  was determined as ca.  $-200 \text{ mV}$  lower than the corresponding potentials in similar solutions without the thiosulfate addition.

Figure 10 presents the plot of  $E_{\text{rep}}$  vs.  $\ln(\text{pit depth})$ , showing a downward trend in both solutions. In other words, deeper pits repassivate at lower potentials. The  $E_{\text{rep}}$  value ranged from ca.  $222 \text{ mV (SCE)}$  to ca.  $-10 \text{ mV (SCE)}$  in 0.1 M NaCl solution and ranges from  $-128 \text{ mV (SCE)}$  to  $-183 \text{ mV (SCE)}$  in 0.1 M NaCl + 0.01 M  $\text{Na}_2\text{S}_2\text{O}_3$ . When, thiosulfate was present, the value of  $E_{\text{rep}}$  for any given pit depth was significantly lower. Furthermore, the linear trend of  $E_{\text{rep}}$  with pit depth is decreased in thiosulfate containing solution, and the difference between the results obtained in pure chloride solution and thiosulfate containing solution decreased with pit depth increase.

It is known that repassivation of a propagating pit occurs when the dissolution rate is outbalanced by diffusion of species out of the pit.<sup>57</sup> To investigate for correlation between  $E_{\text{rep}}$  and the critical concentration of cations within the pit, values of  $DC^*$  for various pit depths



**Figure 8.** Cumulative distribution of the repassivation potentials, obtained from cyclic polarization of 316 SS flat samples in chloride solution with and without 0.01 M thiosulfate at  $25^\circ\text{C}$ .



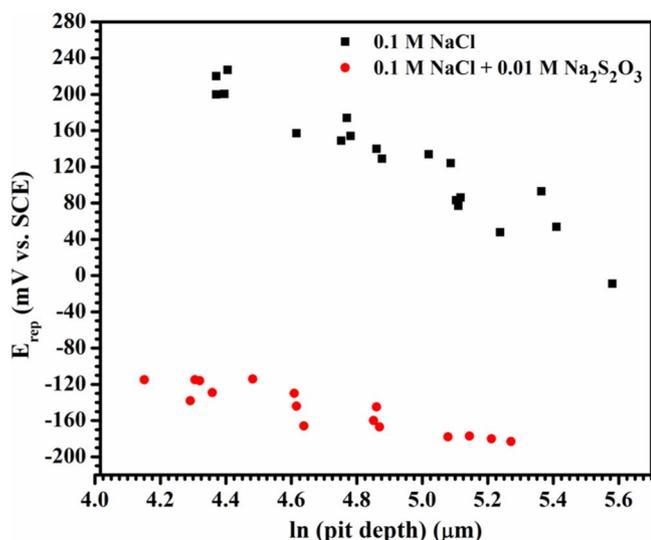
**Figure 9.** Cumulative distribution of the repassivation potentials, obtained from artificial pit experiments on 316 SS in 0.1 M chloride solution with and without 0.01 M thiosulfate at 25°C. (The pit depth was ca. 190  $\mu\text{m}$ ).

were determined in chloride solution in the absence and the presence of thiosulfate. The critical concentration of metal ions was derived from Fick's First Law (Equation 3)<sup>37</sup> and by substitution of current density attributed to the potential of repassivation.

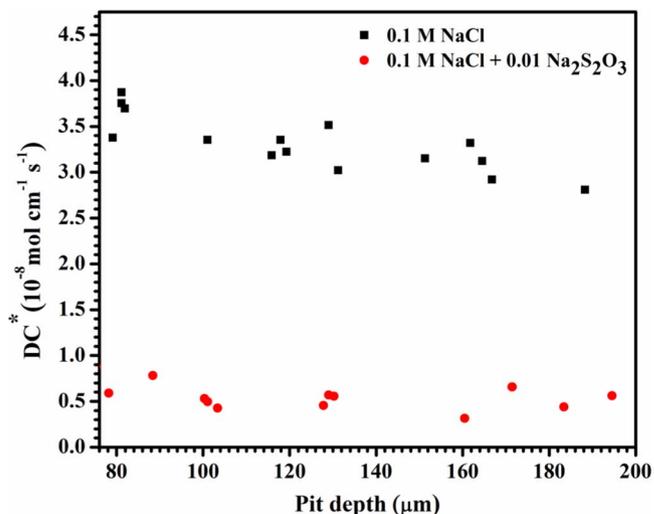
$$C^* = i_p \delta_p / zFD \quad [3]$$

where  $C^*$  is metal cation concentration,  $\delta_p$  is the pit depth attributed to the repassivation potential, and  $D$  is the dissolved cations diffusivity. For further investigation, the repassivation potential of 316 SS was assessed for pits with various depths in chloride solution with and without thiosulfate addition.

The plot of  $DC^*$  values against the pit depth is shown in Figure 11. In the range of experimented pit depths (ca. 80  $\mu\text{m}$  to 190  $\mu\text{m}$ ), the  $DC^*$  value was between  $3.9 \times 10^{-8} \text{ mol cm}^{-1} \text{ s}^{-1}$  and  $2.8 \times 10^{-8} \text{ mol cm}^{-1} \text{ s}^{-1}$  in pure chloride solution and between  $6.1 \times 10^{-9} \text{ mol cm}^{-1} \text{ s}^{-1}$  and  $5.7 \times 10^{-9} \text{ mol cm}^{-1} \text{ s}^{-1}$  in the presence of 0.01 M thiosulfate. Apparently, the trends of  $DC^*$  values vs. the pit depth are consistent with the descending trends found in Figure 10. Thus, it is



**Figure 10.** The repassivation potential as a function of  $\ln$  (pit depth), obtained from artificial pit experiments on 316 SS in 0.1 M chloride solution with and without 0.01 M thiosulfate at 25°C.



**Figure 11.** The values of  $DC^*$  as a function of pit depth, obtained from artificial pit experiments on 316 SS in 0.1 M chloride solution with and without 0.01 M thiosulfate at 25°C.

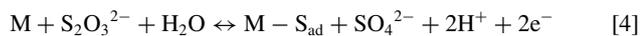
reasonable to correlate between the repassivation potential and the critical concentration of metal cations within the pit cavity.

## Discussion

**Influence of thiosulfate on 316 SS pit transition potential.**—It was observed that, in the range of pit depths at which the experiments were performed, both the transition potential and the pitting potential in comparable temperatures are decreased in the presence of thiosulfate ions. Comparing the results of the pitting potentials and the pit transition potentials in the absence and the presence of 0.01 M thiosulfate demonstrated that the decreasing trend of  $E_{\text{pit}}$  and  $E_T$  is similar and there is a correlation between the transition potentials and the pitting potentials. In other words, the relation of  $E_{\text{pit}}$  and  $E_T$  with temperature are parallel, which is in agreement with the result reported for 904L SS in 0.1 M sodium chloride solution.<sup>32</sup> This is consistent with the notion that precipitation of salt film on the pit surface is necessary for sustaining the growth of a pit when the pit cover ruptures. Since the  $E_T$  is the potential between the bare and salt-covered state, a decrease in the  $E_T$  represents the lower potential necessary for salt film precipitation. Based on the view that the presence of a salt layer is required for pit stability after the pit cover collapses,<sup>32</sup> and considering the definition presented for pitting potential as the potential at which metastable pitting transitions to stable pitting,<sup>31</sup> the lower  $E_T$  in the presence of thiosulfate could be a demonstration of the lower pitting potential. The addition of thiosulfate possibly accelerates anodic dissolution within the cavity in such a way that the potential necessary for reaching the same current density would be decreased. Thus, in a given condition, a lower potential is required for a pit to precipitate a salt film and stabilize the pit growth in thiosulfate medium.<sup>31</sup>

According to Equation 1, one factor affecting the transition potential is the activation overpotential. The slope of  $E_T$  vs.  $\log$  of  $i_{\text{lim}}$  plot is equal to anodic Tafel slope,  $b_a$ .<sup>32</sup> Tafel slopes of anodic reaction in pit solution environments obtained from the gradient of  $E_T$  vs.  $\log$   $i_{\text{lim}}$  plots are reasonably consistent with the measured Tafel slope for pure iron (100–120 mV per decade)<sup>58,59</sup> and also with the anodic Tafel slope of 302 SS<sup>32</sup> at ambient temperature in highly acidic, chloride concentrated solution. As observed in Figure 4, in comparison to thiosulfate free solution, there is a decrease in the slope of the increasing trend of  $E_T$  in the presence of thiosulfate. When thiosulfate is present, depolarizing of anodic dissolution causes a decrease in the anodic Tafel slope, thus, decreasing the corrosion potential (facilitation of anodic dissolution is evident in Figure 4 which shows the Tafel slope has been decreased). According to Equation 4, acidification of

the pit solution via decomposition of thiosulfate ions could result in depolarization of the cathodic reaction as well. However, as the results of potentiodynamic polarization in simulated pit solution show, depolarization of the anodic branch may be more intense. Therefore, a decrease in the corrosion potential in the pit solution is likely to occur in the presence of thiosulfate ions.



Furthermore, the results of potentiodynamic polarization in simulated pit solutions (Figure 5) revealed that the addition of thiosulfate increases the corrosion current density almost by factor of 100. As a result, one may conclude that thiosulfate could decrease the activation overpotential ( $\eta_{act}$ ) (second term of the Equation 1).

Analysis of the IR drop in the absence and the presence of thiosulfate revealed that this factor (third term of the Equation 1) increased with thiosulfate addition. By extrapolation of data obtained in solution with thiosulfate (Figure 7) to higher potentials, it is likely that the current density at a given potential is higher in the presence of thiosulfate ions. According to this curve, the increase of IR drop in the presence of thiosulfate could be explained by the effect of this ion on increasing the current within the pit. However, the effect of thiosulfate ion on  $R_s$  should be investigated more.

In summary, considering the key factors influencing the  $E_T$ , the deleterious effect of thiosulfate on pitting resistance may be described by the effect of this ion on decreasing the transition potential through lowering the corrosion potential and the anodic dissolution kinetics within the pit. These factors outweigh the positive effect of thiosulfate via increasing the IR drop in the pit cavity. The decreasing trend of the pit transition potential with temperature (shown in Figure 3) is consistent with the results reported for 904L SS in 1 M NaCl.<sup>32</sup> 1.04 times the IR drop at 25°C. For single growing pits with similar pit depth, the decrease in solution resistivity is compensated by the increase in limiting current density with increasing temperature, thus the IR drop seems to remain constant with temperature.<sup>60</sup> The decrease of the activation overpotential by increasing the temperature was postulated for this effect.<sup>32,60</sup> It has been reported that the activation potential is likely to change with temperature as a result of the temperature dependencies of  $i_{lim}$  and  $i_{corr}$ .<sup>60</sup>

#### **Influence of thiosulfate on 316 SS repassivation potential.—**

Based on the cyclic polarization results, 0.01 M thiosulfate addition causes a decrease in the repassivation potential of 316 SS. The artificial pit results confirm this observation. The lower  $E_{rep}$ , the more difficult it is for the metal to be repassivated.<sup>6</sup> This means that the stable pits stopped growing at lower potentials in solution contain 0.01 M thiosulfate compared to pure NaCl solution. In other words, thiosulfate increases the potential range at which stable pits can propagate. Newman and Franz<sup>61</sup> have reported that corrosion pits grown on 304 stainless steel in chloride solution have no tendency toward spontaneous repassivation in the presence of thiosulfate. As the results show, there is a similar dependency of  $E_{rep}$  values obtained from cyclic polarization experiments and the repassivation potentials of single propagating pits with thiosulfate concentration. However, the values are not precisely equal. There are two probable reasons for unequal repassivation potential identified by different methods. Firstly, the repassivation potential value depends upon the sweep rate,<sup>56</sup> and the polarization sweep rates were different. Secondly, it has been found that the repassivation potential depends on the degree of pitting established, decreasing with increasing in pit depth.<sup>62</sup> The amount of pit growth or depth of pits formed in flat samples was less than that obtained in single pit studies.

The repassivation potential is determined by the buildup of ions in the pit electrolyte.<sup>41</sup> Thus, the analysis of the critical amount of metal cations by the pencil electrode technique can provide useful information on the effect of thiosulfate on the repassivation of 316 SS. It has been suggested that the surface of a pit cannot be passivated unless the pit environment is diluted.<sup>63</sup> The chemistry of the pit environment may be paralleled to a critical pH and in turn to a critical

current density for a given pit geometry.<sup>41</sup> It is suggested that a stable pit stops growing below a critical cations concentration,  $C^*$ .<sup>41</sup>

Regardless of the pit depth and the repassivation potential, the value of  $C^*$  is found to be almost constant.<sup>34</sup> It is well known that the pit dissolution rate is a function of potential. At potentials below the repassivation potential, the dissolution rate is too low and is unable to produce enough metal ions to exceed the critical concentration required for sustaining a stable pit, thus, pit would be repassivated. Based on our observations, in comparison to free thiosulfate solution, this potential is lower in the presence of thiosulfate.

As shown in Figure 10,  $E_{rep}$  is a function of  $\ln$  (pit depth) and deeper pits have less noble repassivation potential. These results are consistent with the observations of Yoshii and Hisamatsu<sup>64</sup> who found a correlation between the value of  $E_{rep}$  and occlusion of the pit. The effect of pit depth on  $E_{rep}$  may be due to the ohmic potential drop in the pit solution and/or the aggressiveness of pit electrolyte.<sup>56</sup> It has been stated that the contribution of ohmic potential drop to the influence of pit depth on the repassivation potential is negligible.<sup>31</sup> Moreover, it was argued that the deeper pits dissolve more slowly for a given chemistry. Therefore, the deeper pits are more tolerant of dilution of the pit electrolyte.<sup>34</sup> The critical concentration of metal salts in the pit electrolyte is equivalent to a critical product of the current density and the pit depth ( $i \cdot x$ ) for sustaining an aggressive pit electrolyte. Thus, the aggressiveness of the pit solution may be accounted for the dependence of the repassivation potential and the pit depth. The relation expressed in Equation 5 has been established for a one-dimensional pit:<sup>56</sup>

$$E_{rep}^{ext} = E_{rep}^{int} + \int i \cdot \rho dx \quad [5]$$

where  $E_{rep}^{ext}$  and  $E_{rep}^{int}$  denote to the measured repassivation potential at the pit entrance and the potential at the pit bottom, respectively. Assuming  $i \cdot x$  to be constant for sustained growth of a pit, and ignoring the dependence of the pit electrolyte resistivity ( $\rho$ ):<sup>56</sup>

$$E_{rep}^{ext} = E_{rep}^{int} + A \ln(x) \quad [6]$$

where  $x$  is the distance between the external part and a given point in the pit. This equation explains the logarithmic dependence of the repassivation potential on the pit depth,<sup>56</sup> and is accurately obeyed for 316 SS in the absence and the presence of thiosulfate ions (see Figure 10). The  $E_{rep}$  decreases vs.  $\ln$  (pit depth), however, with a steeper slope in pure chloride solution. This implies that the repassivation of pits in thiosulfate containing solution is less influenced by the pit depth, and the external and the internal surfaces of a pit would repassivate at relatively the same potential. The difference in the  $E_{rep}$  of deeper and shallower pits is negligible in thiosulfate containing solution. However, even the shallowest experimented single growing pit (80  $\mu\text{m}$  pit depth) in chloride solution containing 0.01 M thiosulfate repassivated at less noble potential than the deepest single growing pit in the absence of thiosulfate. At a low potential at which a deep pit stops growing in chloride solution, a shallow pit would continue to grow in the presence of 0.01 M concentrations of thiosulfate. Evaluation of the critical concentration of metal cations in different pit depths revealed a good correlation between the repassivation potential and the pit chemistry. Comparing the trend of both curves (Figures 10 and 11), it could be found that the difference in the pit chemistry throughout the pit depth is almost constant in the presence of 0.01 M thiosulfate, which is in accordance with the trend of the repassivation potential vs.  $\ln$  (pit depth). Similarly, the decreasing trend of the critical concentration of metal cations in pure chloride solution is the same as that observed for the values of the repassivation potential in this solution. In brief, the results of this part of study demonstrate that 0.01 M thiosulfate decreases the repassivation potential through a change in the pit chemistry.

## Conclusions

A good correlation between the pit transition potential and the pitting potential was observed in the absence and the presence of

0.01 M thiosulfate ions. The decrease in the corrosion potential and the activation overpotential in the saturated pit are found to be two factors in decreasing the transition potential in the presence of thiosulfate ions. These factors can outweigh the effect of thiosulfate ions on increasing the IR drop.

The pit repassivation potential decreases with thiosulfate addition. The significant drop in the critical concentration of cations within a single corrosion pit in the presence of thiosulfate could be an indication of its effect on the repassivation potential via lowering the critical concentration of the pit chemistry. Other factors may interfere when the amount of thiosulfate increases, which require a comprehensive study on the effect of thiosulfate/chloride ions ratio on the chemistry of pits and other factors affecting the pitting corrosion of stainless steels.

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