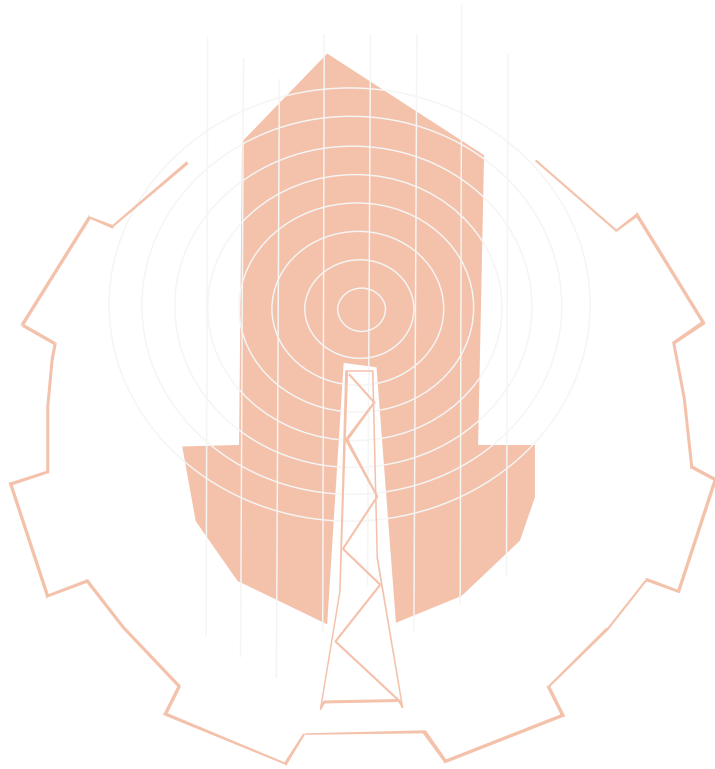




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ROLE OF Na-THIOSULFATE IN PITTING AND REPASSIVATION BEHAVIOR OF 304 STAINLESS STEEL IN CHLORIDE-CONTAINING MEDIA

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المخلص

تم في هذا البحث دراسة التآكل النقري للصلب الأوستينيقي المقاوم للصدأ صنف 304 في أوساط مائية ملوثة بأيونات الكلوريد (Cl-) تركيز 200 جزء في المليون، في وجود وغياب تراكيز لأيونات سلفات الصوديوم ($S_2O_3^{2-}$) باستخدام طرق الاستقطاب الكهروكيميائي المتردد والثابت. ولضمان منع حدوث التآكل النقري والجويبي أنياً على سطح عينة الاختبار، صممت خلية تآكل خاصة محتوية على ثلاثة أقطاب مغمورة في حمام مائي لضبط درجة حرارة الاختبار. وقد مكن هذا النظام من قياس الجهود الحرجة (E_p & E_{prot}) لحدوث التآكل النقري على أسطح عينات الصلب المختبرة. كان من ضمن أهم متغيرات الدراسة تعيين تأثير درجة الحرارة، وتركيز أيونات سلفات الصوديوم على مقاومة التآكل النقري. لوحظ بناءً على نتائج القياسات المعملية أن وجود أيونات سلفات الصوديوم ($S_2O_3^{2-}$) بالتزامن مع أيونات الكلوريد (Cl-) يؤدي إلى نقص في مقاومة التآكل النقري للصلب الأوستينيقي صنف 304 قيد الدراسة. كما تم توكيد التأثير الضار لأيونات سلفات الصوديوم على مقاومة الصلب للتآكل النقري من خلال نتائج قياس جهد الحماية (E_{prot})، وكثافة تيار الممانعة (i_p) أثبتت نتائج البحث أن لنسبة تركيز أيونات الكلوريد/سلفات $[Cl^-/S_2O_3^{2-}]$ تأثير ملحوظ على جهد الحماية (E_{prot}) وكثافة تيار الممانعة (i_p) خاصة عند نسبة تركيز $[Cl^-/S_2O_3^{2-}] = 1.5$ ، وتبين أن نشؤ النقور يحدث تحت تأثير الكلوريد، بينما تعمل أيونات سلفات الصوديوم على اتساع مجال الجهد الذي يسمح بنمو النقور، وذلك بخفض قيم جهد الحماية (E_{prot}).

ABSTRACT

The pitting corrosion behavior of type 304 stainless steel in 200 ppm chloride solution in the presence and absence of thiosulfate ions was studied using cyclic polarization and potentiostatic polarization methods. Three-electrode cell arrangement was designed and constructed to ensure crevice-free test conditions for the measurement of pitting and repassivation potentials. The influence of temperature and thiosulfate ion concentration on pitting was investigated. It was found that the presence of thiosulfate combined with chloride ions led to a notable decrease in corrosion resistance of tested steel. Moreover, the deleterious effect of thiosulfate ion addition was confirmed by measurement of passive current density and the repassivation potential. At 0.5 to 1.5 chloride/thiosulfate ion ratio, thiosulfate had a remarkable effect on repassivation potential and the passive current density, particularly at $Cl^-/S_2O_3^{2-}$ ratio of 1.5. The role of chloride was to initiate corrosion pits, whereas thiosulfate increases the possible potential range of corrosion pits to grow by lowering the repassivation potential.

KEYWORDS: Thiosulfate; Repassivation Potential; Passive Current Density; Stainless Steel; Pitting Potential

INTRODUCTION

Austenitic stainless steels are widely used as a material of construction in chemical, petrochemical, desalination and many other industries due to their good formability and corrosion resistance in particular [1,2]. However, they do fail by localized corrosion attack under certain condition and in presence of aggressive anions such as chlorides and thiosulfates. Over the years, many failure incidences have been reported in the literature in the presence of these aggressive anions [3-5]. Similar to other aggressive anions such as chlorides, bromides and hypochlorites, thiosulfate ions are known as corrosion promoters of many important structural materials such as stainless steel. For instance, thiosulfate ions had bad effects on equipment in oil and petrochemical systems because sulfur and chloride ions present in crude oil with relatively high concentration. The corrosion behavior of stainless steel in chloride solutions containing thiosulfate ions has been extensively studied since early eighties [6-9]. The influence of major factors which affect the pitting corrosion behavior of type 316 stainless steel in thiosulfate solutions with presence & absence of various concentration of chloride ions was studied by Almarshad and Jamal [10]. They found that type 316 austenitic stainless steel is more susceptible to pitting corrosion at higher ($S_2O_3^{2-}$) concentrations. Using cyclic polarization scans and a novel technique known as contact electric resistance, Laitinen [11] was able to prove the enhanced anodic dissolution of type 304 stainless steel caused by thiosulfate solutions. He further added that thiosulfate and chloride ions have a synergistic effect in inducing localized corrosion of stainless steel. In a recent study carried out by Zakeri and co-workers [12] it was reported that the pitting & repassivation potentials decrease with thiosulfate addition due to significant drop in the critical concentration of cations within single corrosion pits on 316 stainless steel surface.

Most of the above mentioned studies were conducted in industrial environments found in pulp & paper or in hydrometallurgy processing of gold or aluminum metals. However, the action of thiosulfates does not seem to be restricted to these cases. Thiosulfate ions do exist in refinery, chemical & petrochemical, nuclear power and agricultural industries as well. In a review paper on the role of thiosulfate in the corrosion of steels, Choudhary, MacDonald and Alfantazi [13] reported that four main forms of corrosion that have been observed in the presence of thiosulfate ions in solutions. These are: pitting, stress corrosion cracking [14] corrosion fatigue [15] and crevice corrosion [16]. All these types of corrosion are localized; thus dangerous and frequently lead to equipment failure under a wide range of service conditions. It is well known that stainless steel material, most often, fail by localized forms of corrosion. Also, thiosulfate ($S_2O_3^{2-}$) ions exist together with other corrosive anions such as chlorides and sulfates. Therefore, this study attempts to investigate the effect of temperature and thiosulfate content of chloride-containing solutions on susceptibility of 304 stainless steel to pitting corrosion using cyclic and potentiostatic polarization methods. Data compilation on stainless steel corrosion behavior in thiosulfate-containing environments prevailing in oil refinery systems is required to make material selection much more informative.

EXPERIMENTAL

This study was conducted in chloride solutions in which thiosulfate salts were intentionally added to simulate industrial environments. In particular, those found in refinery equipment. It is required to investigate the effect of temperature and thiosulfate content of chloride-containing solutions on susceptibility of 304 stainless steel to pitting and repassivation behavior. The specimens were small discs 24 mm in diameter, 10 mm

thick. The surface preparation involved grinding on emery paper down to grade 1000, then ultrasonic cleaned in distilled water. Finally, specimens were rinsed in acetone and dried in air. The working surface of the specimen was partially masked with an anti-acid tape leaving 1 cm² exposed area. Test solutions were prepared from reagent grade chemicals and distilled water.

All electrochemical experiments were carried out in a conventional three-electrode glass cell with a saturated calomel electrode (SCE) as the reference electrode and a graphite rod as the counter electrode. The working electrode (sample) was in the shape of a disc 24 mm in diameter, 10 mm thick mounted in PTFE sample holder. All potentials were measured against the saturated calomel electrode. Specimens were first polarized to -250 mV versus corrosion potential (E_{corr}) for 15 seconds conditioning, then cyclic polarization scan was started below E_{corr} to vertex potential and then back to final potential at a scan rate of 0.1 mV/s. No IR-drop compensation was used during test run. Pitting potentials were determined to be the potentials where the current density exceeds 100 $\mu\text{A}/\text{cm}^2$. Repassivation potentials were determined to be the point where the hysteresis loop was completed and the reverse scan crossed the forward scan.

RESULTS and DISCUSSION

Effect of $\text{S}_2\text{O}_3^{2-}$ on Corrosion Potential:

The upper curve of Figure (1) illustrates the open circuit potential of 304 stainless steel in 200 ppm chloride solution at 30 °C. The lower curve in the same figure is the corrosion behavior diagram of the thiosulfates-containing solution, i.e, 200 ppm Cl^- plus 0.1 M $\text{S}_2\text{O}_3^{2-}$ solution at 30 °C. In both curves, the corrosion potential (E_{corr}) shifts rapidly in the active direction at the beginning of measurement. Following this rapid shift, E_{corr} remains fairly constant indicating the approach to a steady state process. By the end of measurement, E_{corr} approaches -95 mV (SCE) in thiosulfate-free electrolyte and about -330 mV(SCE) in chloride plus thiosulfate solution. This shift of stainless steel corrosion potential in the active direction means greater tendency for corrosion since the passive film is destabilized.

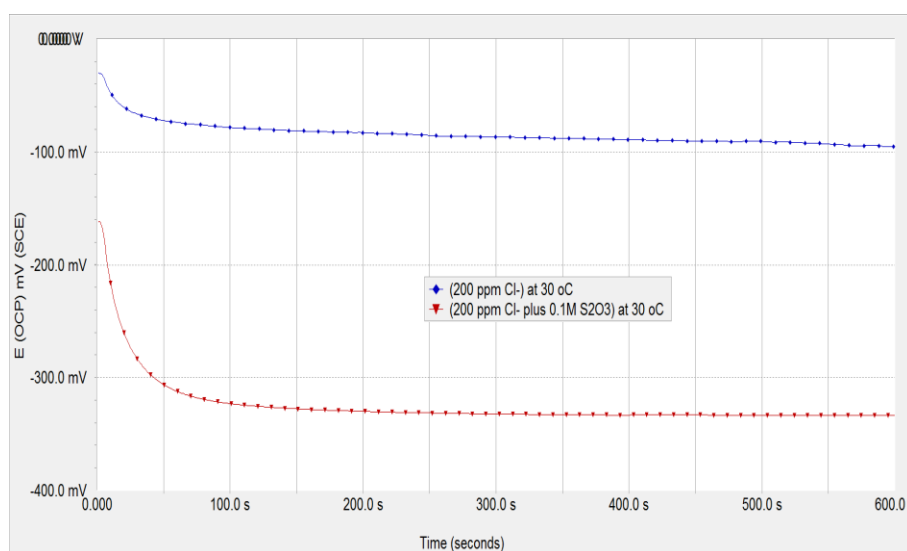


Figure 1: Effect of thiosulfate ions addition on open circuit potential of 304 stainless steel at 30 °C

A comparison between the steady state corrosion potential of tested steel in both solutions clearly shows that E_{corr} of thiosulfate-containing solution is less noble than E_{corr} of thiosulfate-free electrolyte. In other words, a metal sample with higher corrosion potential value means that its corrosion protection is better than a sample with lower E_{corr} value. Thus, adding $\text{S}_2\text{O}_3^{2-}$ to electrolytic solution makes it more aggressive to stainless steel surface.

This corrosion behavior persists at other test temperatures; namely 50 and 70 °C as shown in Figure (2) and in Figure (3).

Table (1) shows the magnitude of shift in corrosion potential as a result of adding 0.1 M $\text{Na}_2\text{S}_2\text{O}_3^{2-}$ to the 200 ppm chloride solution.

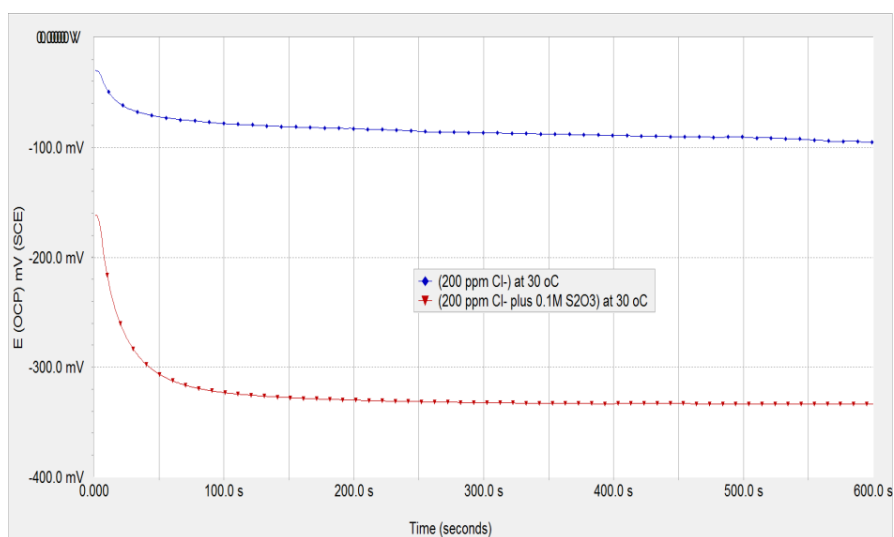


Figure 1: Effect of thiosulfate ions addition on open circuit potential of 304 stainless steel at 30 °C

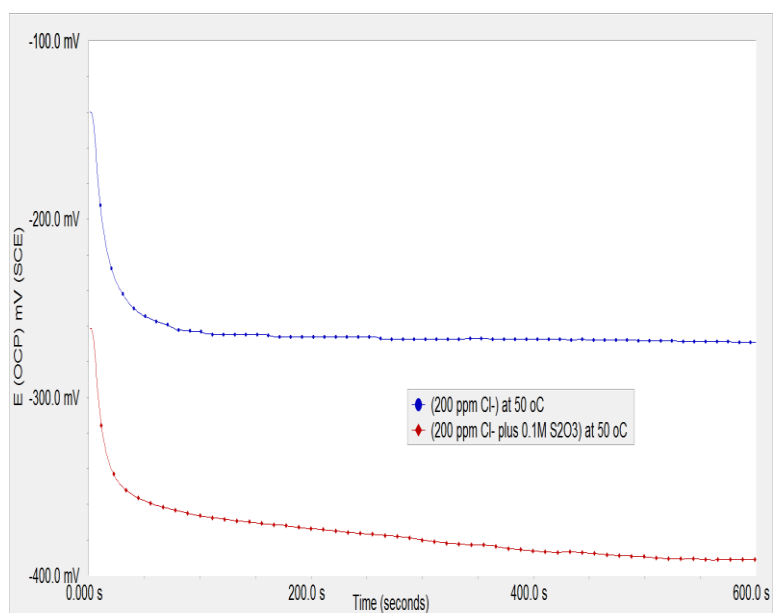


Figure 2: Effect of thiosulfate ions addition on open circuit potential of 304 stainless steel at 50 °C

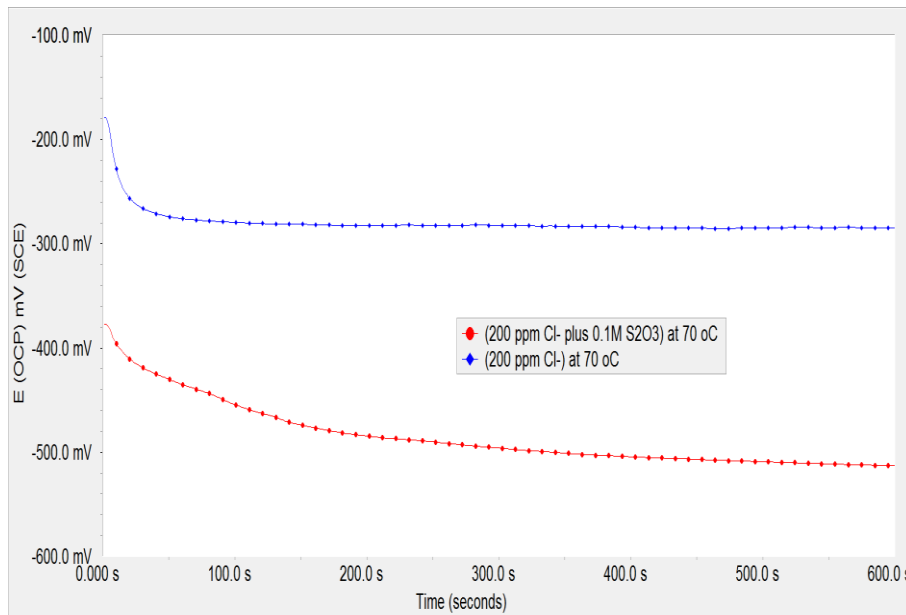


Figure 3: Effect of thiosulfate ions addition on open circuit potential of 304 stainless steel at 70 °C

The data in Table (1) also show the effect of temperature on the stability of passive layer formed on 304 stainless steel because the temperature has an influence on both anodic and Cathodic processes occurring on metal surface. As temperature decreases, E_{corr} shifts to less negative potential values indicating better resistance of the passive layer at lower temperatures.

Table 1: Effect of temperature on corrosion potential of 304 stainless steel

T (°C)	Open circuit potential (mV)		ΔE (mV)
	200 ppm Cl ⁻	200 ppm Cl ⁻ + 0.1M S ₂ O ₃	
30	-86	-332	246
50	-266	-380	114
70	-282	-496	214

Cyclic Polarization Scans:

The cyclic polarization scan of tested steel in 200 ppm chloride solution at 50 °C is shown in Figure (4). Starting from -250 mV below corrosion potential, the graph displayed an active/passive behavior with an average passive current density of 15 $\mu\text{A}/\text{cm}^2$. The most active potential where a considerable increase in passive current density (i_p) observed on the forward scan denotes the formation of stable non-repassivating pits and is referred to as pitting potential (E_p). In Figure (4) the measured value of E_p was equal to 451 mV (SCE). Pitting potential is a measure of how resistant the material against pitting corrosion. A high value means a high resistance to pitting. E_p is the potential value where the stable pitting stage is reached and depends on many parameters such as chloride concentration, surface finish, temperature and pH of solution. The potential where the reverse and forward scans intersect is referred to as the protection, or repassivation ($E_{prot.}$ or E_{rp}) potential. In this measurement, $E_{rp} = -80 \text{ mV(SCE)}$. A

negative hysteresis loop of this graph signifies active or stable pits growing between vertex potential of 1.5 V(OCP) and repassivation potential of -80 mV(SCE).

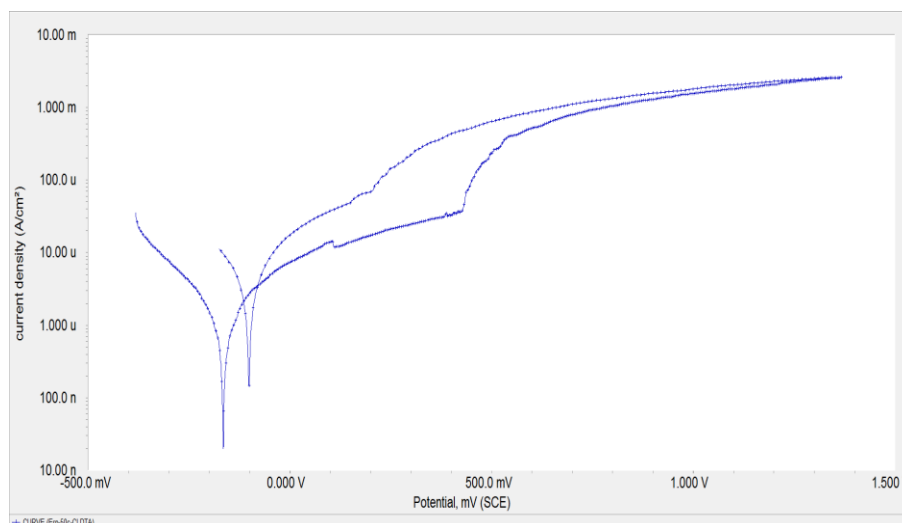


Figure 4: Cyclic polarization scan of 304 stainless steel in 200 ppm chloride solution at 50 °C

When thiosulfates ions ($0.1 \text{ M S}_2\text{O}_3^{2-}$) were added to the chloride solution, the cyclic polarization test results of 304 stainless steel are presented in figure (5). Here, the presence of a negative hysteresis loop signifies a material suffering some degree of pitting due to reaction between reduced sulfur species with Ni and/or Fe ions at the metal electrolyte interface; this result is similar to Tsai and Wong findings [5]

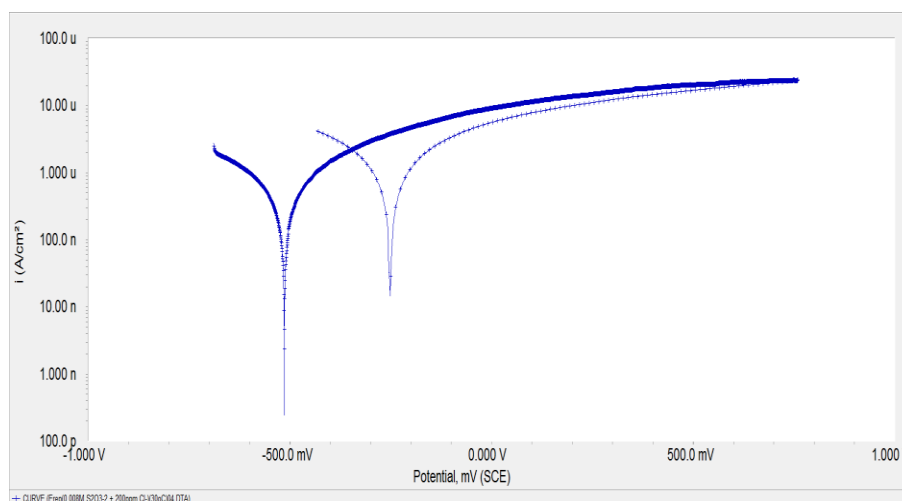


Figure 5: Cyclic polarization scan of 304 stainless steel in 200 ppm chloride plus 0.1 M thiosulfate solution at 50 °C

Effect of Temperatures on Critical Pitting Potentials:

A set of experiments were done to evaluate the effect of temperature on stainless steel corrosion behavior in chloride-containing environment. Thus, cyclic potentiodynamic polarization measurements were carried in solutions containing 200 ppm Cl^- at 30, 40, 50, 60, 70 and 80 °C. The measured pitting (E_p) and repassivation or

protection (E_{rp}) potentials are given in Table (2) and are graphically displayed in Figure (6). Pitting or breakdown potentials were taken at a current density of $200 \mu\text{A}/\text{cm}^2$

Table 2: Effect of temperature on critical potentials of 304 stainless steel in 200 ppm chloride solution

Temperature (°C)	Critical pitting potentials, mV (SCE)	
	E_p	E_{rp}
30	645	12
40	489	-33
50	490	-79
60	414	-110
70	339	-239
80	330	ND

ND: not determined; experimental difficulties

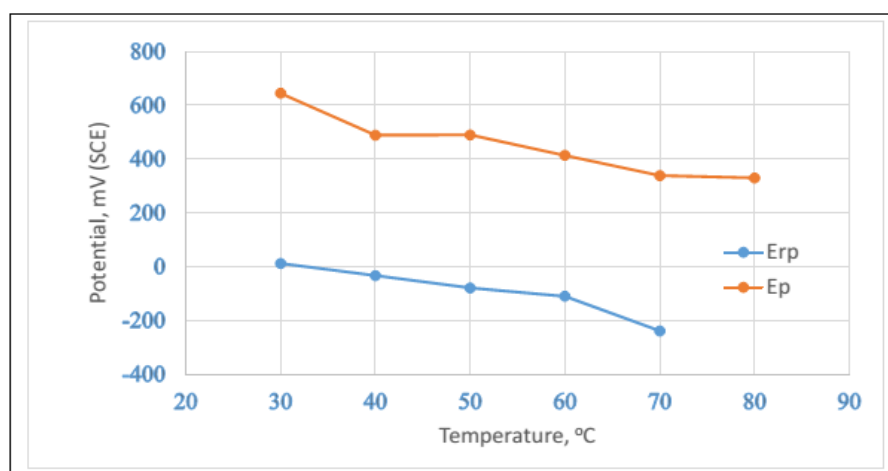


Figure 6: Critical pitting potentials of 304 stainless steel in 200 ppm chloride solution at different temperatures

As can be seen in Figure (6), temperature influences both pitting and repassivation or protection potentials. The general trend is that as the temperature increases, both pitting and repassivation potentials of 304 stainless steel decrease. However, the effect of temperature on critical potentials is quite similar, i.e, both potentials were affected in the same manner for this steel. This can be explained by the temperature effect on the solubility of chloride salts which hydrolyze to create an aggressive environment. The higher the temperature, the higher the solubility and more aggressive is the environment inside pits. Thus, lower repassivation and/or pitting potentials. Also, the temperature rise affects the diffusion and ions transport involved in the pitting process.

Effect of thiosulfate on repassivation potential

The measured values of the repassivation potentials for 304 stainless steel, at different temperatures between 30 and 70 °C, are reported in Table (3). These potential values are inferred from the cyclic polarization curves; a sample of which is presented in Figure (7).

Table 3: Independent measurement of repassivation potentials in thiosulfate and chloride-containing environments

Temperature(°C)	Repassivation potential, mV(SCE)		ΔE (mV)
	in chloride	in thiosulfate	
30	12	-325	337
40	-33	-374	341
50	-79	-255	176
60	-110	-400	290
70	-239	-300	61

As can be seen in Table (3) the main effect of thiosulfate is lowering the repassivation potential (E_{rp}). At 30 °C, the repassivation potential is 12 mV(SCE) in presence of chloride anions whereas the repassivation potential in presence of thiosulfate anions is -325 mV(SCE), a margin of more than 300 mV. According to Duret-Thual and co-workers (17) thiosulfate is not thermodynamically stable species. If localized breakdown of the thin film on the stainless steel surface result in exposing bare metal surface to the electrolyte, thiosulfate may be reduced to sulfur species. Thus, thiosulfate is able to prevent repassivation of the active stainless-steel surface and may stabilize metastable pits initiated.

The effect of thiosulfate on the corrosion behavior of 304 stainless steel can also be seen in Figure (7). Here, the average values of the passive current density in presence & absence of thiosulfate ions can be identified. In chloride-containing environment, the average value of the passive current density is about 10 to 20 $\mu\text{A}/\text{cm}^2$ whereas the average passive current density in thiosulfate-containing environment is over 400 $\mu\text{A}/\text{cm}^2$. A higher passive current value means higher corrosion rates under similar temperatures.

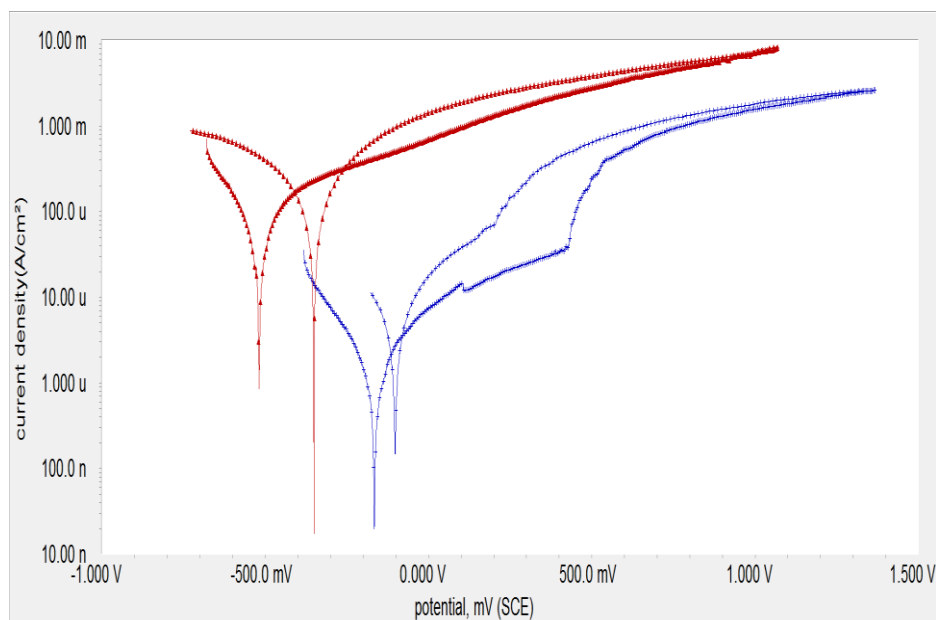


Figure 7: Cyclic polarization scan of 304 stainless steel at 50 °C, in presence & absence of thiosulfate ions

CONCLUSIONS

In the present study, the electrochemical corrosion behavior of 304 stainless steel was evaluated in thiosulfate-containing solutions using cyclic polarization and potentiostatic testing at different temperatures. On the basis of the results of this research, it can be concluded that:

1. The pitting resistance of 304 stainless steel as measured by pitting potential and repassivation potential decreases as the temperature increases
2. Thiosulfate is able to prevent repassivation of an active stainless-steel surface and able to stabilize the initiated metastable pits
3. At chloride/thiosulfate ion ratio between 0.5 to 1.5, thiosulfate have not been found aggressive enough to cause localized damage to standard 304 stainless steel. But they had a remarkable effect on repassivation potential and the passive current density, particularly at $\text{Cl}^-/\text{S}_2\text{O}_3^{2-}$ ratio of 1.5
4. The developed test method was found to be successful for determining critical potentials & corrosion behavior diagrams of tested stainless steel under crevice-free conditions
5. Electrochemical experiments have showed the deleterious effect of thiosulfate addition to chloride solutions; both on repassivation potential & passive current density
6. $\text{S}_2\text{O}_3^{2-}$ lowers repassivation potential down to -400 mV (SCE), thus thiosulfate stabilizes the metastable pits formed below actual pitting potential.

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