CORROSION BEHAVIOUR OF AUSTENITIC STEELS IN BASIC THIOSULFATE GOLD LEACHING ENVIRONMENTS

by

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Abstract

Thiosulfate leaching of gold is being proposed as an environmentally friendly alternative to the dominant cyanide-leaching technology. Thiosulfate leaching is, to a large extent, dependent on the availability of materials of construction. There are indications that materials of construction could be a major issue if not addressed; particularly their corrosion resistance. Therefore, understanding the corrosion behaviour of materials of construction, such as stainless steels, in this medium is critical to the future development and acceleration of industrial implementation of this new technology.

The debate surrounding the use of cyanide in the mining industry has fuelled considerable investigation into the development of some more environmentally benign alternatives. The thiosulfate process has been widely accepted by researchers around the world as a potential alternative lixiviant for the leaching and recovery of gold. Moreover, sodium thiosulfate is relatively nontoxic and, consequently, from an environmental standpoint, has a definite advantage over cyanide. Comparing reagent unit costs, sodium thiosulfate is far cheaper than sodium cyanide. Thus, with similar or even slightly higher lixiviant consumption, the application of thiosulfate for gold recovery can be economical and compete directly with cyanidation.

‘Rust never sleeps!’, so says a popular song. In a broad sense, corrosion appears to be the reverse process of extraction. In this process, most metals tend to presume a chemically-combined state rather than a pure metallic form achieving, in the process, the most energy stable
form possible. Thus, freshly-extracted metals, as well as finished metallic products, tend to deteriorate when exposed to certain environments. Thiosulfate has been identified as such an environment in mining and other industries, where thiosulfate-dominated processes, such as thiosulfate gold leaching, are strongly believed to highly promote localized corrosion.

In this work, the pitting corrosion behaviour of 304- and 316-type stainless steels were studied using cyclic polarization techniques and electrochemical impedance spectroscopy (EIS) run on a thiosulfate system at several pH and temperature levels in the presence and absence of chloride ions. The stainless steels studied were found to show similar general corrosion behaviour with varying degrees of corrosion resistance to pitting as control variables were regularly perturbed. The results indicate that SS316 has a relatively lower corrosion rate and is more resistant to localized corrosion than SS304 under the conditions considered.

The presence of thiosulfate seems to activate both anodic and cathodic current densities of steel in chloride solutions. The higher the thiosulfate concentration is, the greater the current densities. In addition, for both alloys, the corrosion rate generally increases as the magnitude of the variables is increased; except when the content of chloride ions is altered. Thiosulfate seems to promote passivation in the presence of chloride ions and deter interaction of those ions with the surface of the metal alloys by the formation of an adsorption layer of sulfur that seems to protect the metal surface.
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1. Introduction

The conventional hydrometallurgical route of the extraction of gold from its ores is universally described as the entrenched leaching process known as “cyanidation”; where the dissolution of gold involves the formation of a cyanide (CN⁻) complex of gold, and the gold recovery is then usually achieved through the well-established carbon-in-pulp (CIP) process.

The cyanidation process, as it stands, incorporates a number of advantages including simplicity, rapid leaching kinetics and ease of gold recovery. However, due to the rising environmental concern, especially where excessive amounts of cyanide are required when treating resistant ores, thiosulfate as an environmentally friendly alternative lixiviant, has received most of the attention as the most economically promising and technically viable option.

The process, according to some dedicated studies [Breuer and Jeffrey, 2002], involves the oxidation of gold which is believed to occur at a standard potential of 150 mV, and thus, dissolved oxygen (E⁰ = 400 mV) in alkaline solutions is expected to oxidize gold to gold thiosulfate. Those studies of the system describe the dissolution of gold; where oxygen is the oxidant and thiosulfate is the ligand, as follows:

\[ 4\text{Au} + 8\text{S}_2\text{O}_3^{2-} + \text{O}_2 + 2\text{H}_2\text{O} \leftrightarrow 4[\text{Au(S}_2\text{O}_3)_2]^{3-} + 4\text{OH}^- \]

In solutions containing Cu (II), ammonia, and thiosulfate, there is also the possibility of an additional cathodic reaction: the reduction of Cu (II) to Cu (I). Breuer and Jeffrey state that the standard potential for this reaction has been determined to be 220 mV. In a review of the prospects of the technology [Hilson and Monhemius, 2006], cupric tetramine was expected to
oxidize gold to gold thiosulfate with the rate of dissolution being highly influenced by the concentrations of thiosulfate and dissolved oxygen, and the process temperature.

The thiosulfate leaching of gold has been viewed [Breuer and Jeffrey, 2002] as a corrosion reaction, since it can be studied using standard electrochemical techniques. This aspect of the system further merits the study of corrosion behaviour of construction materials as these are generally known to be much less noble than gold, and hence, expected to be highly susceptible to dissolution and corrosion attack in this environment.

Thiosulfate-dominated environments are observed in various applications such as the pulp and paper industry [Tarja Laitinin, 2000], where the bleaching agent may contain sulfide species including thiosulfate and possibly a combination of thiosulfate and chloride ions, which are known to act synergistically to inflict severe damage in the form of pitting corrosion of alloys. This is also the case observed in high-temperature, aqueous solutions common in power plants [Jin-Ju Park and Su-II Pyun, 2003]. In these media, thiosulfate contamination at high temperature and pressure can significantly alter the sensitivity of alloys to localized corrosion. Another well-known issue is the role that thiosulfates may have in initiating and/or accelerating crack growth in stress corrosion cracking (SCC) cases.

The development of a large-scale gold-processing plant based on this new technology largely depends on a number of factors, the most significant of which may be the selection of corrosion-resistant constructional materials compatible with the process environment. The corrosion behaviour of a number of alloys has been evaluated in dilute-acidic and mildly-acidic,
thiosulfate solutions, while this new gold leaching technology of thiosulfate, using more concentrated solutions of thiosulfates under considerably higher pH conditions has, to the best knowledge of the author, not been considered in any other academic study or investigation concerning the corrosion behaviour of alloys. Therefore, there seems to be a considerable knowledge gap existing in corrosion science as far as this system is concerned, and it is the sole and primary purpose of this study to help bridge it up.

Stainless steel alloys, used as construction materials, are susceptible to pitting corrosion in the presence of both chloride and thiosulfate ions. Thus, investigating the combined effect of these two species provides insight into the mechanism of pitting corrosion of stainless steels. It has already been shown [Kuo et al, 1999] that thiosulfate levels between 3 and 75 ppm can result in the pitting corrosion of SS316L.

Another study investigating the localized corrosion of steel alloys in environments containing thiosulfate, chlorides, and sulfate [Ehrnst et al, 1996] reports thiosulfate ions as being high promoters of localized corrosion. Based on these studies, the susceptibility of alloys to localized corrosion in such environments is largely determined by the electrochemical potential and ionic strength of the solution; having to be within a certain proportion and range for corrosion to occur.

Stainless steel is resistant to corrosion due to the formation of a passive film; however, localized corrosion can occur in the presence of an aggressive anionic species. Chloride (Cl⁻) ions are usually, although not always, the main cause. The aggressiveness of the Cl⁻ is due to its
small size, high diffusivity, and strong acidic anionic nature \cite{J.R. Galvele, 1981}. Thiosulfate ions ($S_2O_3^{2-}$) have also been reported as potentially detrimental to the stability of the passive film \cite{Abd El Meguid, et al., 1998}. It has been found that $S_2O_3^{2-}$ alone is not enough to cause pitting of stainless steel. In conjugation with chloride or sulfate ions, localized corrosion has been reported \cite{Roberge, et al., 1996}.

The stability of the passive film formed on stainless steel and its susceptibility to breakdown depends on certain parameters such as applied potential, pH, temperature, and solution composition \cite{El-Egamy, et al., 2000}. Studies of AISI 304L and AISI 316L in a chloride/thiosulfate solution have revealed that the ratio of these ions concentration controls pitting behaviour because of the variation in overall ionic strength \cite{Newman et al., 1983}.

The presence of chemical or physical heterogeneities at the surface of the metal, such as sulfur inclusions, second phase particles, flaws, mechanical damage, or dislocations in alloys adds to the propensity of materials to corrosion \cite{Pidaparti and Rao, 2008}. Sulfur inclusions in particular are reported to play a significant role in initiating pits under the conditions prevailing in thiosulfate environments. Using the cyclic polarization technique to measure the tendency of alloys to form pits, studies \cite{Danaduri et al., 1999} have shown that the pitting corrosion resistance may be greatly improved with titanium stabilization of alloys as compared to molybdenum stabilized steels, such as SS316.

To probe deeper into the understanding of pit initiation and propagation, \textit{Park et al.} conducted a study on the behaviour of single corrosion pits in a thiosulfate system containing
NaCl to report that the local chemical environment which arises in the vicinity of such heterogeneities is different from that of the external bulk solution [Park et al., 1991], and is thus critical for determining whether or not a corrosion pit propagates or repassivates. The passive film is often drawn schematically (Figure – 1.1) as a simple inert layer covering the underlying metal and blocking access of the environment to the metal.

![Figure – 1.1 Schematics of a passive film](image)

The view of the passive film as being a dynamic, rather than static, structure is critical to the proposed mechanisms of passive film breakdown and pit initiation. It is often assumed that the alloying regime affects localized corrosion via changes in the composition and structure of the passive film [Shibata and Takeyama, 1977]. According to this view, pit growth is considered to be well understood and to offer little in the way of fundamental understanding of the phenomenon of pitting. On the other hand, others feel that pit growth is pivotal and often controls the pitting process, since pits will not initiate if they cannot grow at least for a short while [Laycock et al., 1995] It is considered that the passive state is required for pitting to occur,
but details of the passive film composition and structure play a minor role in the pitting process.

The breakdown of the passive film and the very initiation of the pitting process is probably the least understood aspect of the pitting phenomenon. Breakdown occurs extremely rapidly on a very small scale, making direct observation extraordinarily difficult. Depending on alloy composition, corrosion environment, potential, and exposure history, this film can have a range of thickness, structure, composition, and protectiveness. Typical passive films are quite thin, and support an extremely high electric field ($10^6$ to $10^7$ V/cm) [Baroux, 1995]. The passage of a finite passive current density is evidence of continual reaction of the metal to result in film thickening, dissolution into the environment, or some combination of the two.

Theories for passive film breakdown and pit initiation have been categorized in three main mechanisms that focus on passive film penetration, film breaking, or adsorption, as illustrated in Figure 1.2. As with most such situations, different mechanisms or combinations of these mechanisms may be valid for different metal/environmental systems. However, pits in real alloys are most often associated with inclusions or second-phase particles.

Penetration mechanisms for pit initiation (Figure 1.2a) involve the transport of the aggressive anion through the passive film to the metal/oxide interface where aggressive dissolution is promoted [Hoar, 1965]. Anion migration would be assisted by the high electric field in the film. The penetration mechanism is supported by the existence of an induction time for pitting following the introduction of chloride ions into an electrolyte. On the other hand, estimated induction times based on expected values of anion transport rates exceeded measured values by many orders of magnitude. Marcus and Herbelin [1993] found chloride present in
passive films on Ni using careful XPS and radiotracer measurements. A critical concentration of chloride ion concentration in the inner oxide portion of the passive film was associated with film breakdown and pit initiation [Graham M. J, 1992].

![Diagram of passive film breakdown mechanisms]

**Figure – 1.2 Passive film breakdown mechanisms**

a) Penetration    b) Adsorption    c) Breakdown

A related model for passive film breakdown is the outgrowth of the point-defect model developed by Chao and coworkers to describe passive film growth by the movement of point
defects under the influence of an electrostatic field [Chao et al., 1981]. The major point defects in an oxide film are assumed to be electrons, holes, and metal and oxide vacancies. Transport of vacancies across the film controls the film growth according to this view.

The point-defect model has been used to explain pit initiation by assuming that the adsorption and incorporation of the aggressive chloride ions at the outer surface of the barrier oxide layer results in the formation of cationic vacancies [Lin et al., 1981]. These vacancies diffuse to the metal/oxide surface where they are annihilated by the oxidative injection of cations from the metal. However, if the flux of vacancies is larger than can be accommodated by oxidation, the vacancies will condense at the metal/film interface to form a void that is the first step in the pitting process according to this model [Urquidi and Macdonald, 1985]. The point-defect model has been fitted to experimental data describing the statistical distribution of pitting potentials, the induction time for pitting, and the influence of alloying on the pitting potential.

Interestingly, the pitting potential and induction time relate to pit stability and growth rather than pit initiation, since it is well known that metastable pits initiate at potentials far below the pitting potential and during the induction time prior to stable pit growth. Predictions from the point-defect model have yet to be compared to experimental measurements of the earliest stages of pit formation despite the fact that the model is based on phenomena occurring at the nanometer level [Sterhblow, 1995]. Other criticisms of the point-defect model have focused on the handling of the electrode potential and its influence on vacancy concentration and migration.

Adsorption theories of initiation, Figure - 1.2b, were first based on the notion of competitive
adsorption of chloride ions and oxygen [Hoar, 1965]. It is now known that the passive film is at least several mono-layers thick rather than just an adsorbed oxygen layer. However, aspects of the adsorption model are still relevant. For instance, exposure of Fe to chloride and other halides caused thinning of the passive film based on XPS measurements, even under conditions where a pit had not formed, as a result of what was described as catalytically enhanced transfer of cations from the oxide to the electrolyte [Sterhblow, 1995].

On the other hand, another study using SIMS found that there was no difference in oxide thickness on Fe samples pre-passivated in borate solution and then galvanostatically anodized at 5A/cm² in solutions with or without Cl⁻ [Bardwell, 1989]. Interestingly, no Cl⁻ was found to be incorporated into the oxide during this treatment either. When thinning occurs locally because of some local adsorbed species, the local electric field strength will increase, which may eventually lead to complete breakdown and the formation of a pit.

Pit initiation by a film-breaking mechanism, Figure - 1.2c, considers that the thin passive film is in a continual state of breakdown and repair [Sato, 1971]. Mechanical stresses at weak sites or flaws resulting from electrostriction and surface tension effects may cause the local breakdown events, which rapidly heal in nonaggressive environments. In fact, the background passive current density may come from a summation of many such breakdown and repair events. In chloride-containing solutions, however, there would be a lower likelihood for such a breakdown to heal because of the inhibition of repassivation by chloride.

The film-breaking model really involves initiation based on pit growth stability. It assumes
that breakdown will always occur, albeit at a rate that depends on many factors related to the passive film properties. However, according to this model, breakdown will only lead to pitting under conditions where pit growth is possible.

Several techniques based on electrochemical measurements at the metal surface have been applied to estimate the propensity of alloys for localized corrosion in thiosulfate media and to quantify the corrosion rate. The findings of studies [Park et al., 1991] employing such techniques support the conclusion proposed by Williams *et al.* that thiosulfate influences the propagation of pits in stainless steels; although others suggest that thiosulfate has to first be reduced to sulfur on the surface of the dissolving metal in order to inflict any measurable corrosion damage.

Characteristic features critical in determining the propensities of alloys for localized corrosion are identified as the “protection” or “repassivation” potentials and “pitting” potentials. These two parameters are extremely important and sensitive to changes in experimental variables such as scan rate and point of scan reversal. Figure – 1.3 illustrates some typical generalized polarization scans emphasizing such features.

A traditional interpretation is that pitting would occur if the hysteresis between the forward and reverse scan appears as in Figure – 1.3(a) and the corrosion potential is at least 100 mV more active (more cathodic) than the pitting potential. Pits are expected to propagate and grow if the corrosion potential lies between the pitting and repassivation potentials. On the other hand, the alloy would be expected to resist localized corrosion if the corrosion potential is cathodic (active)
with respect to the repassivation potential, or if the scan appears as in Figure – 1.3(b). A general rule is to require corrosion potential to be ~ 200mV more active than repassivation potential for risk of localized corrosion to be trivial or insignificant.

Hysteresis is another feature of the cyclic polarization scans in which the forward and reverse portions do not overlay one another. It is usually the result of the difference between the current density of the forward and reverse scans which, in turn, is a result of disruption of the passivation layer on the surface induced by the increase of applied potential. This feature reflects the ease with which passivation is restored as potential is decreased on the reverse loop. The greater the current on the reverse loop, the greater the disruption of passivity and, consequently, the greater the difficulty to repassivate. Hence, the greater risk to pit.

Hysteresis can be “negative”, an illustration of which is shown in Figure – 1.3(a), indicating an alloy with great difficulty to repassivate. Figure – 1.3(b), on the other hand, shows a “positive” hysteresis, where the current decreases rapidly during the reverse loop indicating an alloy that passivates very easily, suggesting high resistance to localized corrosion.

The difference between anodic-cathodic transition potential and the corrosion potential provides evidence of persistence of passivity; at least until transpassivation is hit. When this potential is cathodic (i.e. active) with respect to corrosion potential, the suggestion is that passivity persists (stable) as the scan reverses back toward the corrosion potential indicating low general corrosion (figures – 1.3(a) & 1.3(b)). On the contrary, if this potential is anodic (noble), the passive layer is not stable at the corrosion potential (figure – 1.3(d)); and general corrosion in
this case is measurable.

(a)

(b)

(c)

(d)

Figure – 1.3 Illustrative polarization scans

(D. C. Silverman, 1998)

The conducted literature survey presented in the following chapter summarizes a significant
number of papers dealing with the influence of thiosulfates on the corrosion of steel alloys, where it is felt that the main focus was generally placed on the understanding of the mechanism of localized attack of thiosulfates and developing models that describe the initiation and propagation aspects of the process.

However, these studies were not directly related to the thiosulfate-assisted gold leaching environments as the range of thiosulfate concentration concerned and the pH conditions are widely different. It is reported [Aylmore and Muir, 2001] that gold leaching using thiosulfates is performed at the concentration range of 0.1 – 0.2 M thiosulfate, and at a pH range of 9 – 11. Those settings were laid down in lieu of the stability of gold-thiosulfate complex under these conditions.

Systematic work on the effect of thiosulfate ions together with chloride ions on the corrosion behaviour of the selected materials is limited. Therefore, there exists a significant amount of interest in conducting corrosion studies under these conditions known to be prevailing in this system, with the primary aim being to assist in making the selection of the appropriate materials for gold leaching plants much more informative.

The present study is therefore intended to investigate the behaviour and systematically evaluate the susceptibility to localized corrosion and determine how resistant those materials are to pitting under the thiosulfate gold leaching conditions. The study, outlined in this specific notion, was conceptualized with all the aspects described so far taken into consideration as much as practically possible. Consequently, the study was structured in a way that was realized to best
demonstrate relevance and assure both efficiency and sufficiency of results.

2. Literature Review

Thiosulfates, as well as other reactive sulfur species, are well known for their deleterious effect on the resistance of sensitized stainless steel alloys to localized corrosion. The role played by these reactive sulfur species is considered an important aspect in pitting mechanisms as pit initiation is often related to the presence of sulfide inclusions in industrial stainless steels. Thiosulfates (S$_2$O$_3^{2-}$) have been shown to act synergistically with other common ions, such as chlorides (Cl$^-$) or sulfates (SO$_4^{2-}$), to cause severe localized corrosion. This was observed to be the case in many different processes involving thiosulfates as a reagent or as a contaminant.

In the pulp and paper industry, for instance, the bleaching agent is believed to be comprised of various sulfur species including thiosulfates [Arima et al., 2004]. Combined with chloride ions, the environment is considered to cause severe pitting damage to the alloys making up the process equipment and structure [Laitinin, 2000]. In power plants the case is similar, where thiosulfate contamination at high temperature and pressure appears to significantly affect the propensity of the used alloys to localized corrosion [Ho and Yu, 1992]. It has been conceived that the formation of sulfur is the main cause for the observed detrimental effect.

In sea water environments having low amounts of thiosulfate ions originating from the bi-oxidation of sulfur by organic species, the corrosion behaviour of some alloys, such as copper-nickel alloys and stainless steels, shows that the presence of thiosulfates accelerates the anodic dissolution at early pit initiation stages [Geesey et al., 2000], while on a long time span, the corrosion rate decreases due to the formation of sulfur-containing barrier films.
Thiosulfates also affect the corrosion integrity of materials involved in processes relevant to the oil industry. The sulfur present in sour crude oil, which is sometimes used as feedstock for hydrocrackers, produces iron sulfide scale. The scale subsequently reacts with water and oxygen during shutdowns to form polythionic acids and other oxyanions, such as thiosulfate.

Sulfur species can also be present due to contamination of the oil by atmospheric sulfuric oxide, via antifraction and deoxidizing agents, through the degradation of ion exchange resins, or even by air oxidation of iron sulfide produced by sulfate-reducing bacteria present in the system. In this environment, the main corrosion-controlling factor is carbon dioxide. Studies relevant to the effect of thiosulfates on pitting corrosion in the presence of CO$_2$ [Ezuber, 2009] show that thiosulfates increase the chloride corrosion in the presence of CO$_2$.

The following literature review draws a broad general picture of the main course of developments in this subject and the progress in research studies conducted relevant to thiosulfate corrosion. Particular emphasis is intentionally placed on the research work devoted for the study and investigation of pitting corrosion in basic solutions of thiosulfates, and the major influential factors that affect the corrosion behaviour of stainless steel alloys and the electrochemical performance of similar materials in common industrial use in thiosulfate-dominated environments. Specific attention is paid to the passivation and prevailing behaviour at the passive regions, and any instability in the current densities and/or formation of anodic peaks within those regions are of particular interest in the evaluation of pitting resistance.
2.1. Electrochemistry of Thiosulfates

The unique chemistry of the thiosulfate ion, $S_2O_3^{2-}$ or $SSO_3^{2-}$, is dominated by the sulfide-like sulfur atom, which is responsible for the reducing properties and complexing abilities of thiosulfates [Koh, 1990]. Thiosulfate ions are metastable and tend to undergo chemical decompositions in aqueous solutions, especially in the presence of copper. The factors that influence the thiosulfate stability are reported [Wan and LeVier, 2003] to be the concentration and pH of solutions and the presence of certain metals.

Some general chemical properties of thiosulfates were stated [Ellen and David, 2002] as:

- Tendency to be oxidized (by $O_2$, $Cu^{2+}$, etc.),
- Tendency to hydrolyze at pH < 5.5 to $S^0$ and $HSO_3^{2-}$ at mildly acidic pH and to more complex mixtures in stronger acidic pH,
- Moderately good hydrolytic stability in basic solution,
- Ability to form complexes with a variety of metals, e.g. gold, silver, copper ($Cu^+$ and $Cu^{2+}$), iron ($Fe^{3+}$), etc.,
- Formation of metal sulfides, e.g. with copper, silver, and mercury, and
- Stability toward reduction to free sulfide,

The thiosulfate solutions used for gold leaching were reported to be very complicated systems. Many interactions may occur among the system constituents, not to mention that the system itself is thermodynamically not very stable. The complexity of the leaching chemistry is reported [Gamini, 2004] to be due to:
- Involvement of a number of metal–ligand complexes, including mixed ligand complexes,
- Simultaneous oxidation of gold and thiosulfate by copper(II) and oxygen,
- Degradation of thiosulfate to polythionates and a decrease in copper(II) activity,
- Precipitation of solids such as S, Au₂S, Cu₂S, and CuS, and
- Reactivity of host minerals towards gold lixiviant.

2.2. Thiosulfate Gold Leaching System

Leaching of gold in thiosulfate solutions is believed to be a corrosion reaction in the sense that it can be studied using standard electrochemical techniques. The presence of Cu(I) and Cu(II) species complicates an electrochemical study since, in particular, the oxidation of Cu(I) occurs simultaneously with gold oxidation which is dependent on the solution chemistry generated by the addition of copper(II) to the solution.

Chandra and Jeffrey in a study conducted in 2004 described the leaching of gold in thiosulfate solutions as an electrochemical reaction involving the oxidation of gold to gold thiosulfate. It was indicated in this study that the copper–ammonia–thiosulfate system is further complicated by the homogenous reduction of copper(II) by thiosulfate, and that the requirement of oxygen to regenerate copper(II) from copper(I) results in the consumption of thiosulfate at a significant rate.

Another difficulty encountered when using thiosulfates as a lixiviant in the gold leaching
system is the decrease in the leaching rate after prolonged exposure of the gold surface to the thiosulfate solution. Reporting on the impact of thiosulfate oxidation products on the leaching rate, Chu et al. [2003] refers to the leaching reaction as being severely hindered as the reaction between thiosulfate and copper(II) occurs in the presence of oxygen and hence suggests that an intermediate product of the oxidation of thiosulfate by copper(II) in the presence of oxygen could be responsible for the slow leaching kinetics.

Baron et al. [2011] relate this decrease to the formation of a passive layer on the gold surface produced by the decomposition of thiosulfate preventing the further dissolution of gold. This passive layer, they further describe, is composed of surface sulfur species that are the result of gold interaction with thiosulfate and are different from the electrochemical oxidation of thiosulfate products.

According to an Eₜ–pH diagram constructed by Wan et al. [2003], and reproduced below in Figure – 2.1, desirable working conditions, such as solution oxidizing potential and pH in the presence of ammonia and oxygen are recommended to be maintained so as to eliminate sulfur/sulfide formation while decelerating the thiosulfate decomposition [Wan and LeVier, 2003]. Some typical conditions are given by Aylmore [2001] in Table – 2.1 below.

The mechanism by which thiosulfate influences the corrosion of stainless steel is of particular interest in the thiosulfate leaching process of gold. Sulfur particles in stainless steel alloys are known to be the preferred sites for the initiation of localized corrosion. The thiosulfate ion, being an aggressive species which chemisorbs on the stainless steel passive film, is well
known to cause the breakdown of the passive film when present above a critical concentration.

![Diagram of Eh–pH diagram of gold – ammonia – thiosulfate system at 25°C](image)

*Figure – 2.1 Eh–pH diagram of gold – ammonia – thiosulfate system at 25°C (Wan, et al., 2003)*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Thiosulfate Leaches</th>
<th>In-situ Thiosulfate Leach</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall Leaching Period (hrs)</td>
<td>96</td>
<td>Up to 96</td>
</tr>
<tr>
<td>Sample Weight (g)</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>Total Solution Volume (mL)</td>
<td>1200</td>
<td>1000</td>
</tr>
<tr>
<td>Thiosulfate Concentration (M)</td>
<td>0.1 – 0.8</td>
<td>Up to 1.2</td>
</tr>
<tr>
<td>SO₂ Rate (mL/min)</td>
<td>–</td>
<td>500 or 200</td>
</tr>
<tr>
<td>Ammonia Concentration (M)</td>
<td>1.5 – 4</td>
<td>Up to 4</td>
</tr>
<tr>
<td>Copper II Concentration (M)</td>
<td>0.0125 – 0.0625</td>
<td>0.24</td>
</tr>
<tr>
<td>Sulfur Addition (g)</td>
<td>–</td>
<td>30</td>
</tr>
<tr>
<td>pH</td>
<td>10.2</td>
<td>9 – 9.2</td>
</tr>
</tbody>
</table>
2.3. Thiosulfates-induced Corrosion

Although thiosulfate anions alone have not been found aggressive enough to cause damage to stainless steel, they have been shown (figure – 2.2) to act synergistically with other common ions, such as chlorides or sulfates to cause severe localized corrosion [Kuo, et al., 1999]. Therefore, investigation of this synergic effect is hoped to provide deeper insight into the mechanism of pitting corrosion in stainless steel alloys.

<table>
<thead>
<tr>
<th>$E_h$ (mV SHE)</th>
<th>+ 80 – + 180</th>
<th>+ 50 – + 250</th>
</tr>
</thead>
</table>

![Thiosulfate (0.01M) vs. No Thiosulfate](image)

**Figure – 2.2 Potentiodynamic polarization curves of steel in a chloride solution with and without thiosulfates**

*(Kuo et al., 1998)*

In a study by Laitinen conducted in 2000, thiosulfates were reported to reduce the surface...
film resistance to negligible values provoking an active surface or a weak surface film. In the same study [Laitinen, 2000], the author concludes that, despite thiosulfate being not able to initiate corrosion by itself, it makes it easier for other anions, such as chlorides and sulfates, to initiate localized corrosion much faster by weakening the passive surface film or accelerate corrosion that was already initiated.

It is presently known that the thiosulfate ion itself does not directly cause pitting corrosion of stainless steels in aqueous environments. However, with the presence of a pitting agent such as Cl\textsuperscript{−}, an acceleration of pitting corrosion would occur. The presence of the thiosulfate ion causes a decrease in pitting corrosion potential; and the critical concentration of Cl\textsuperscript{−} to induce pitting corrosion decreases as the concentration of the thiosulfate ion increases [Tsai and Wu, 2000]. Interestingly, this enhanced pitting corrosion effect disappears as the concentration of thiosulfates increases further [Tsai and Wu, 2000]. These observations indicate that thiosulfate ions could either act as a promoter or an inhibitor for pitting corrosion depending on its concentration.

Thiosulfate-containing environments are thus detrimental to the corrosion resistance of alloys such as stainless steels. It has been proposed that the formation of adsorbed sulfur could cause the observed detrimental effect. Marcus and Protopopoff in an XPS study [1997] found evidence that thiosulfates can be reduced by direct reaction with the metallic surface of iron-chromium alloys, and then prevent passivation or repassivation to stabilize otherwise metastable pits.
Comparing the behaviour of the different metals in the presence of dissolved sulfur species, Marcus and Protopopoff in the same study also found that the extent of the overlap of adsorbed sulfur with the stable metals appears to decrease in the sequence Ni, Fe, Cr, and so the effect of thiosulfates on corrosion of the metals is expected to decrease in the same order.

Marcus and Protopopoff go on in this study to assert that sulfur adsorption in the active domains (i.e. during anodic dissolution) is a very important factor because that is the condition in which sulfur-enhanced dissolution is experimentally observed. Thus, another effect of thiosulfates expected from the stability of adsorbed sulfur in the passive domain is the blocking or retarding of passivation (or repassivation) of stainless steels.

The effect of thiosulfates is greatly magnified in the presence of inclusions containing sulfur species in the alloy [Donik, et al., 2010]. The reduction of thiosulfates on the emerging sulfide inclusions may explain the role of the inclusions observed in the pitting initiation in thiosulfate solutions. The reduced forms of sulfur, such as sulfides incorporated in the oxide layer of alloys, or free sulfur adsorbed at the metal/oxide interface, end up being oxidized at the metal surface. Furthermore, thiosulfate is well known to cause the breakdown of the passive film when present above a critical concentration.

Various mechanisms were proposed to account for the role of thiosulfates in inducing corrosion. The mechanism by which all sulfur species were proposed to operate, as proposed by Marcus and co-workers [Brossia and Kelly, 1998], was via the formation of a surface sulfur layer that prevents repassivation and enhances the dissolution kinetics of the alloy.
According to a study by Duret-Thual et al., the most widely accepted mechanism is the one based on the well characterized role of this adsorbed sulfur on the corrosion resistance of alloys, which suggests that thiosulfates normally reduce to free adsorbed sulfur, which inhibits the repassivation process once pitting has initiated [Duret-Thual et al., 1997]. In another study [Ezuber, 2009], the anodic dissolution reaction facilitating the corrosion process was related to the reaction of this adsorbed sulfur with Fe$^{2+}$ to form ferrous sulfides, a product which is quite cathodic to steel and causes galvanic coupling.

_Duret-Thual et al._ suggest in their study [1997] that the mechanism for the reduction of thiosulfates involves the reduction of thiosulfates on the non-oxidized iron, forming iron sulfide islands. The lateral growth of those sulfide islands and the further increase in their thickness with time indicate that the reduction reaction may take place on the alloy surface at the edge of the sulfide islands and/or on the sulfide islands surface.

_Ezuber_ stipulates that steel corrosion rate increases linearly with the logarithm of the thiosulfate concentration. The presence of thiosulfates, according to his study [Ezuber, 2009], seems to activate both anodic and cathodic current densities of steel in chloride solutions. The study further proposed that the higher the thiosulfate concentration becomes, the greater the anodic/cathodic current densities go, and thus, solutions containing the thiosulfate species obviously yield the highest corrosion anodic and cathodic current densities.
2.4. Thiosulfate Corrosion Mechanisms

*Laitinen, [2000]* summarized the role of thiosulfate on localized corrosion as being played in two different broad mechanisms; mainly:

- The thiosulfate ion is reduced to elemental sulfur, which adsorbs on bare metallic surface preventing passivation, or
- The thiosulfate ion is reduced to hydrogen sulfide which catalyzes the anodic dissolution of stainless steel.

*Kuo et al. [1999]* emphasized the fact that, regardless of the thiosulfate anion being found to be not aggressive enough on its own to cause damage to stainless steel, their study has shown that these anions act synergistically with other common ions, such as chlorides or sulfates, to cause severe localized corrosion *[Kuo, et al., 1999]*.

In close agreement, *Laitinen* reports that thiosulfate reduces the surface film resistance to negligible values indicating an active surface or a weak surface film. So, even though thiosulfate is not able to initiate corrosion by itself, it makes it easier for some other anions, such as chlorides and sulfates, to initiate localized corrosion by weakening the passive surface film. Consequently, thiosulfates would also accelerate corrosion already initiated *[Laitinen, 2000]*.

According to the competitive adsorption mechanism proposed by Leckie and Uhlig *[1996]*, the thiosulfate ion might compete for surface site with Cl$^-$ ions. At low concentrations of
thiosulfates, the surface sites are mainly occupied by Cl⁻ ions and pitting corrosion initiates. Under such conditions, the formation of S due to the reduction of thiosulfates occurs, subsequently reducing to form H₂S. The adsorbed H₂S on the metal surface could cause an increase in metal dissolution. If H₂S was adsorbed on the fresh pit surface, enhanced pitting corrosion would be possible. A decrease in Eₚᵢᵗ with the addition of the thiosulfate ion would be observed. At high concentrations of Na₂S₂O₅, on the other hand, the surface sites are almost totally covered by thiosulfate ions, and Cl⁻ ions are expelled from the surface. This is presumably why pitting corrosion would be retarded giving rise to an increase in Eₚᵢᵗ.

### 2.5. Factors Influencing Thiosulfate Corrosion

As has already been indicated, localized corrosion observed on metals and alloys in aqueous solutions containing dissolved sulfur species such as thiosulfates, according to Protopopoff and Marcus [2003], is due largely to chemisorbed sulfur accelerating metal dissolution and hindering its formation of a passive film. Effect of factors such as solution pH, temperature, chemical composition and electrochemical potential on the corrosion resistance and susceptibility of common steel alloys to familiar types of localized corrosion promoted by the presence of thiosulfate ions are detrimental to the understanding of these corrosion processes and the alloys corrosion behaviour in such environments.

Protopopoff and Marcus explain that the conditions of adsorption of sulfur or oxygen species on metal surfaces in water may be predicted from thermodynamic calculations of the equilibrium potentials of the couples dissolved/adsorbed species and drawing of Eₗₚ pH diagrams [2003]. In another report, Protopopoff and Marcus [1997] used Eₗₚ-pH diagrams to predict the
domains of thermodynamic stability of the adsorbed species on iron surfaces in solutions containing sulfides or thiosulfates. Such diagrams allow assessing the risk of corrosion of stainless steels induced by adsorbed sulfur produced by electro-oxidation of sulfides or electro-reduction of thiosulfates.

According to Tsai and Wu, the value of pitting nucleation potential (E_{pit}) increases with increasing the solution pH value in the range of 2-10. The increase in solution pH, they further add, usually results in a considerable decrease in corrosion rate [Tsai and Wu, 2000]. Discussing the effect of temperature, Ezuber [2009] explains that corrosion increases with increasing temperature and the scale formed on steel surface is regarded as non-protective. At higher temperatures, he continues, protective films are formed more easily and the corrosion rate goes through a maximum. He further indicates that the protectiveness of the surface film depends on the nature of the base alloy (i.e. composition & heat treatment).

According to Ezuber, an increase in solution temperature will lead to an increase in the equilibrium constants reflecting greater amounts of H^+ ions present in the system and, subsequently, increasing the corrosion rate. The increased amount of H^+ as a result of raising the test temperature may well provide additional source of H^+ ions and consequently increase both cathodic and anodic reaction rates. Furthermore, raising the solution temperature, he adds, results in an increase in the rate of transport or reduction of thiosulfate ions. Consequently, the adsorption process (surface coverage of S_{ads}) might become more efficient at higher temperatures, therefore increasing the corrosion rate [Ezuber, 2009].
Discussing the influence of the solution chemistry and corrosion environment, Kuo et al. [1999] describes the role of ionic species present in terms of potential change as being associated with the cations present in solutions. In saturated ammonium chloride solutions, he presumes that the higher corrosion potential observed is due to the higher solution pH. On the other hand, the adsorption of ammonium ions on the stainless steel surface may reduce the surface concentration of the chloride ion and eventually causes a delay in the pitting corrosion.

It is interesting to note that these cations may also affect the corrosion behaviour of austenitic stainless steel. According to Kuo et al, the presence of ammonium ions could assist the passivation at almost the same chloride ion concentrations by expanding the passive region more than 500 mV. This expanded passivation region could mainly be due to the preferential adsorption of ammonium ions on the specimen surface [Kuo et al., 1999].

Furthermore, the ratios of the ionic species also are important for corrosion to proceed. Uutela et al. [2003] reported that, according to Newman et al. [1989], pitting of UNSS30400 and AISI 316L, for instance, is worst at molar ratios of ([SO$_{2}^{-4}$] + [Cl$^{-}$]) to [S$_{2}$O$_{3}^{2-}$] from 10 to 30. Newman further reported that stainless steel AISI 316L requires higher total ion concentration and higher temperature than UNSS30400, and that chlorides had to be the predominant ions.

Thus, corrosion of steel alloys in thiosulfate environments is greatly affected by many factors, primarily the pH, potential, solution chemistry, and temperature. Full understanding of the mechanism of initiation and propagation is seen to be highly driven by the degree of
understanding of the effect of such factors on the corrosion process and the susceptibility of alloys to localized corrosion.

2.6. Forms Of Thiosulfate-induced Corrosion

Steel alloys, being the most selected materials for equipment in common use in industrial processes, are highly susceptible to most forms of localized corrosion. In particular, stress cracking, pitting, and crevice corrosions are commonplace among which the most common feature is probably the mode of initiation. As has already been pointed out, those three forms of corrosion usually initiate with pitting and thereafter propagate in different modes distinguished by mechanisms respective to each type, depending on the prevailing conditions of the environment.

The probabilistic nature of localized corrosion is a concept widely accepted; and new probabilistic approaches to the problem are constantly introduced. Salvago et al [2002], introducing one of those approaches, postulated that the scattering of results in localized corrosion is related to the nature of the involved electrochemical processes, and to the stochastic characteristics of the metal/environment design system.

In fact, it is well known that the corrosion potential and the corrosion current density do not properly describe the localized mechanism; and experimentally-evaluated parameters (i.e. pitting potential, crevice potential, critical pitting temperature, critical crevice temperature, depassivation pH, passivation potential, passivation current, electrochemical noise, etc.) are usually only proposed.
With the known close similarities and links between those three different forms of localized corrosion, it is not all surprising to see persistently growing trends in research work directed at establishing a collective mechanism for understanding at least the initiation part of the process which would then hopefully lead to understanding the part concerning propagation, culminating finally in proposing the most effective routes for mitigation and prevention.

2.6.1. Crevice Corrosion

Crevice corrosion is a form of localized attack, which can quickly induce metal perforation when the protective chromium oxide film is damaged even with high grade stainless steels like 316L. Danadurai, et al. [2000] describes crevice corrosion as one of the most detrimental forms for stainless steel corrosion. It is considered to be the most deleterious form of corrosion as it occurs on shielded areas of a metal surface where it is difficult to visually examine the underlying metal resulting in unpredicted catastrophic failures. Danadurai et al. continues to explain that factors such as solution composition, surface preparation and stagnation time are detrimental for the initiation and propagation of crevice corrosion [Danadurai et al., 2000].

Laycock et al. draws many similarities displayed by crevice corrosion with pitting such as an increase in likelihood with increasing potential or chloride concentration, and the existence of critical crevice temperatures (CCT) analogous to the critical pitting temperature (CPT) [Laycock et al., 1997]. Pitting and crevice are similar in the initiation conditions (in the presence of inclusions as impurities or as alloying components). Given the similarities between these two forms of localized corrosion, it is not surprising that some authors have considered pitting to be a special case of crevice corrosion, while others have thought of corroding crevices simply as large
A commonly accepted model for the initiation of crevice corrosion in stainless steels is the passive dissolution model in which thiosulfate entrapment is proposed to account for the role of the thiosulfate ion \cite{Laycocketal1997}. Based on this model, crevice corrosion initiation is based on dissolution of MnS inclusions within the crevice. Anodically dissolving bulk samples of MnS, the electrochemical oxidation of MnS was shown to produce both thiosulfate ions ($S_2O_3^{2-}$) and protons, and that further dissolution of MnS also occurred to produce elemental sulfur.

Earlier studies \cite{GadandEl-Sayed2008} showed that the enhanced crevice corrosion of stainless steels exposed to chloride solutions containing thiosulfate species results from the catalytic dissolution of the iron component by reduced sulfur species; probably $H_2S$, and hence the presence of chloride ions was necessary to initiate the crevice corrosion. The decrease in pH within the crevice resulting from localized hydrolysis reactions with the decrease in potential that accompanied the onset of crevice corrosion produced thermodynamic conditions within the crevice that were conducive to the reduction of thiosulfate ions to $H_2S$.

\cite{LottandAlkire1989} presume that the presence of both chloride and thiosulfate ions above a critical level of concentration is to cause rapid depassivation of stainless steel, and thus, the initiation of crevice corrosion in such a system is a result of entrapped thiosulfate ions \cite{LottandAlkire1989}. They further discuss active crevice corrosion as being characterized by a large anodic current density and a corresponding increase in potential drop along the crevice. For
stainless steel crevices that have already become active, the crevice solution pH, they further stipulate, remains low owing to the hydrolysis of Cr(III) and its complexes and would change only at the onset of breakdown of passivity, indicated by a developing crevice potential drop.

The initiation of crevice corrosion according to Lott and Alkire would be expected to be significantly influenced by three major factors; sulfide ion inclusion density, applied potential and crevice geometry. If the inclusion surface density is low, the rate of thiosulfate production within the crevice would be reduced and, therefore, the breakdown time would be longer. Lower bulk sulfur content may, therefore, be correlated with the increase in resistance to active corrosion of stainless steel. In particular, stainless steels with lower bulk sulfur contents have a lower critical anodic current density [Lott and Alkire, 1989]. Decreasing the bulk sulfur content in steels serves to decrease the build up of thiosulfate ions in the crevice during the initiation stage.

As the cathodic potential is applied to a crevice, Lott and Alkire further stipulate that the potential within the crevice would decrease throughout and that the thiosulfate ion build up would decrease below the critical concentration. Thus, a critical applied cathodic potential at which the critical thiosulfate concentration required for breakdown is not realized would exist based on these analyses [Lott and Alkire, 1989]. Owing to the potential distribution, the solution potential at the edge of a crevice is more negative as compared to the center of the crevice. Thus, the inclusion dissolution rate or the production rate of thiosulfates is consequently highest at the edge of the crevice. Lott and Alkire therefore conclude that thiosulfate ions produced near the crevice mouth diffuses into the crevice as well as to the outside, and as a consequence, the
thiosulfate ion concentration profile exhibits a maximum.

2.6.2. Stress Corrosion Cracking (SCC)

Stress corrosion cracking (SCC) is one of the most important causes of failure of stainless steel equipment in industrial plants. Stress corrosion cracking (SCC) initiates in a pit that may propagate into a crack under conditions of static stress load. It is well known that steel alloys are susceptible to SCC in oxidizing environments. In thiosulfate solutions, it is postulated [Tsai et al., 1996] that the susceptibility is dependent upon grain boundary chromium depletion, solution concentration, solution pH, and applied potential.

According to Mariano and Spinelli, the susceptibility of steels to stress corrosion cracking is determined by imposing stresses on test specimens and determining the time elapsed for cracks to propagate [Mariano and Spinelli, 2004]. The failure time, according to their study, increases as the severity of imposed stress decreases. Thus, stress values should be imposed until such time when no failure occurs, thereby determining the maximum stress value that can be applied to prevent crack propagation by SCC.

Although the chemistry of sulfur oxy-anion compounds is somewhat complicated, Wells et al. suggest through a simplified Pourbaix diagram of the metastable Fe-S-H₂O system at STP that the cracking environment can be related to the Fe²⁺ + S stability field [Wells et al., 1992]. Thus, they presumed that metastable sulfur oxy-anions act in an identical manner by releasing sulfur either by disproportionation reaction or electroreduction; thereby stimulating anodic dissolution of chromium depleted regions.
The SCC mechanism in thiosulfate-dominated environments can be predicted from the morphology of the tested specimen examined in a scanning electron microscope (SEM). The SCC mechanism can also be elucidated from an experimental E–pH diagrams constructed using the electrochemical hysteresis method [Chen et al, 2005]. Furthermore, the SCC behaviour of structural steels under the influence of a static strain (pre-stress) in the same environment can also be investigated using U-bend tests (figure – 2.3). Finally, the morphology and the chemistry of the corrosion products may be analyzed using SEM, X-ray diffraction (XRD) and other specialized techniques [Chen et al, 2005].

![Figure 2.3 Stress/strain curves in Na₂S₂O₃-NaCl solutions at 25°C. (Chen, et al., 2005)](image)

Classic electrochemical models for SCC assume that, under the influence of mechanical tensile stresses, the passive films are disrupted leading to the formation of anodic sites. Anodic
dissolution at the bottom of the crack becomes rate controlling and is quantitatively related to crack advance which depends upon the balance between the bare surface dissolution rate at the crack tip and the repassivation rate at the crack walls. Thus, the role of the passive film on stainless steels during crack growth and repassivation is considered of utmost importance for the understanding of the SCC phenomenon [Rangel, et al., 2005].

The crack growth rate, according to Tsai et al. is governed by the passive film rupture rate and the dissolution rate of the freshly exposed metal in the crack tip region. Under the same stress intensity factor, it is assumed that the film rupture rate is nearly the same. Furthermore, they continue, the metal dissolution rate increases exponentially with increasing potential for a film-free metal [Tsai et al., 1996].

Huang et al. [2010], on the other hand, recognize that nucleation and growth of corrosion cracking is strongly related to protective properties of passive films formed on the metal surface, therefore, an understanding of the composition and structure of the passive films formed on alloys can provide important information on their corrosion resistance [Huang, et al., 2010].

To correlate the composition and structure of the passive film with stress corrosion cracking, a variety of techniques ranging from X-ray diffraction, X-ray photoelectron spectroscopy, and Auger electron spectroscopy to AC impedance and photoelectrochemical studies are known to be employed and, in spite of vast research efforts, the understanding of SCC, particularly, of crack initiation needs further investigation [Rangel et al., 2005].
The behaviour of the steels in sodium chloride solutions containing thiosulfates will differ as a function of the stability of passive film and of the critical concentration of hydrogen ions absorbed which can modify the mechanical characteristics of the steels [Zucchi et al., 2000]. The influence of thiosulfate ions on SCC is concentration dependent and the crack propagation rate is a function of the stress concentration factor (K) [Tsai et al., 1989]. With an increase in thiosulfate concentration, the maximum load at failure, and correspondingly, the time to failure, gradually decreases due to SCC [E.A. Ashour and H.S. Hegazy, 2003].

The aggressiveness of the thiosulfate concentration is also an important factor in determining the degree of susceptibility to SCC. Slow strain rate tests under open circuit as well as under potential-controlled conditions suggest a film rupture anodic dissolution type of mechanism operative during SCC of sensitized steel in thiosulfate solutions [Roychowdhury et al., 2004].

Haruna et al. observed cracks that usually initiate from pits and propagate with the evolution of bubbles. According to their observations, the SCC occurs at thiosulfate concentrations > 10^{-3}M and the variation in the concentration from 10^{-3} M to 10^{-1} M has no marked difference in SCC susceptibility evaluated by maximum stress [Haruna et al., 1997]. They further noticed that crack propagation rates increased slightly with an increase in the concentration of thiosulfates. They considered the increase to be caused by the change in the corrosion potential with the concentration.

Decreasing chloride ion concentration causes the critical concentration of thiosulfate that
provokes SCC susceptibility to increase [Zucchi et al., 2000]. It appears that the distribution of secondary cracks gradually increases and secondary cracks become broader and longer with increasing chloride ion concentration.

The effect of lowering the solution pH on the SCC susceptibility is partly to provide an acidified environment for the pit growth and partly to accelerate the thiosulfate decomposition reactions [Chen et al., 2005]. Decreasing the pH thus causes the corrosion potential to shift slightly to a more positive value. The anodic current densities however increase drastically by one to two orders of magnitude above the corrosion potential until passivation was observed [Hsu et al, 1991]. Constant load tests under controlled potentials demonstrated that sensitized alloys were susceptible to SCC in thiosulfate only when pH was lowered indicating that passivation was a necessary but not sufficient condition for SCC.

The susceptibility of sensitized stainless steel to SCC was also found to increases with applied potentials. A critical potential was found to exist, below which no SCC took place [Roychowdhury et al., 2004]. The crack propagation rate slightly increases with increase in potential which rises as thiosulfate concentration increases. Therefore, it is concluded that the crack propagation rate depends on the potential [Haruna et al., 1997]. Potential fluctuations under open circuit conditions appear to be correlated with crack initiation and propagation during SCC. Current fluctuations under controlled potential gave indications of crack nucleation; however, at higher applied potentials such fluctuations were absent [Roychowdhury et al., 2004].

With the application of more positive potentials, the susceptibility to cracking increased,
with a gradual decrease in maximum load at failure. The frequency of fluctuations decreased with the increase in thiosulfate concentrations [Roychowdhury et al., 2004]. Such potential fluctuations could be correlated with crack initiation and propagation with a marked and continuous decrease in potential if cracking remained active and an increase in potential when cracks repassivate. Such current fluctuations were almost absent at higher applied potentials [Roychowdhury et al., 2004].

The SCC susceptibility; measured by such parameters as UTS, UEL, and RA, was reported to also decreases with increasing temperature in solutions [Chen et al., 2005]. In addition, the effect of solution pH on the SCC susceptibility becomes more marked with increasing temperature. Chen et al. further stipulate that the area of ductile fracture surface decreases with increasing temperature facilitating higher susceptibility to SCC.

This response to increasing temperature was attributed by Chen et al. to the increase of the chloride ions activity as well as to the acceleration of the thiosulfates decomposition reactions, causing the passive oxide film to become unstable with an associated decrease in the SCC resistance [Chen et al., 2005]; in the low-pH solution, susceptibility to pitting and SCC increase to an even greater extent. A decrease in temperature can therefore effectively prevent SCC since an increase in temperature will cause an increase in the SCC susceptibility and enhance the effects of chloride ions concentration and solution pH.

In summary, environmental factors such as chloride ions concentration, solution pH and temperature have certain degree of influence on the SCC susceptibility of steel alloys. However,
it is difficult to know which factor most affects the susceptibility to SCC and whether there are interactive effects among these factors based solely on the results of individual SSRT tests. The influence of these parameters on SCC susceptibility decreases in the order, temperature > solution pH > chloride ions concentration effect.

2.6.3. Pitting Corrosion in Thiosulfates

Stainless steel is frequently used as a construction material in various aggressive environments such as chemical plants, desalination plants, waste-water treatment plants, and the petroleum and mining industries. Stainless steel is resistant to corrosion due to the formation of a passive film; however, localized corrosion can occur in the presence of aggressive anionic species such as thiosulfates, sulfates, and chlorides.

Localized corrosion of stainless steels in environments containing thiosulfate ions, according to Laitinen [2000], is known to occur in a limited potential range and molar ration. The author emphasizes that, in mildly acidic media, the most sensitive potential range for thiosulfate pitting is the range extending from 0 mV to -400 mV combined with a molar ratio of 10 – 30. Pitting is considered to be autocatalytic in nature; once a pit starts to grow, the conditions developed are such that further pit growth is promoted [Frankel, 1998].

In agreement, Kamrunnahar et al. reported that the pitting corrosion of stainless steel is a localized phenomenon that may initiate at various types of surface sites including sulfide inclusions and that interest in pitting corrosion is high because it is often the first step in leading to crevice corrosion, corrosion fatigue, stress-corrosion cracking, and failure of coatings.
Pitting corrosion occurs at lower chloride concentrations when thiosulfate is present in pure chloride solutions. As pointed out by Ehrnsten et al, pre-absorbed sulfur on the surface of stainless steels accelerates the dissolution rate in the active region. According to Ehrnsten et al, sulfur can be produced in the pit in the presence of thiosulfate, and the surface layer formed in a thiosulfate-containing environment has a significantly lower electrical resistance as compared to the layer formed in a pure chloride solution, indicating that thiosulfates can hinder repassivation [Ehrnsten et al., 1996].

Local chloride-rich environments, together with thiosulfate ions hindering repassivation of the pit, may be very essential for the pit growth. As Ehrnsten et al. further explain, the role of the deposit in the pits can also be important, as it can affect, for example, the ionic flow between the electrolyte and the pit, enabling creation and preservation of the local acidic environment on the bottom of the pit needed for pit growth.

2.7. Factors Influencing Pitting

The stability of the passive film formed on stainless steel and its susceptibility to breakdown leading to the initiation of pitting corrosion would be expected to be significantly influenced by four major factors: pH, temperature, alloy composition, and ions concentration. Parameter sensitivity analysis was used by Kamrunnahar et al. to determine which of these factors are the most significant by determining the effect of perturbing the parameters on the process output. Such analysis aids in selecting those parameters to be estimated for further
examination using simulation and/or experimental data in designing future experiments [Kamrunnahar et al., 2004].

2.7.1. Effect of pH

Pitting corrosion is influenced by variations in pH. Almarshad and Jamal report that the resistance of steel to pitting corrosion decreases with an increase in pH (figure – 2.4) and that the pitting potential in very alkaline solutions is significantly displaced in the noble direction [Almarshad and Jamal, 2004]. In chloride-containing electrolytes, metastable pitting events, according to Webb and Alkire, cause rapid temporary periods during which the pH decreases to values as low as zero. However, sustained pH decreases, they further add, occur only with the onset of stable pitting.

![Figure 2.4 Variation of $E_{\text{pit}}$, $E_{\text{corr}}$, and $E_{\text{prot}}$ with pH](image)

*(Almarshad and Jamal, 2004)*

The decrease in the pH that occurs as a consequence of dissolution, they further explain, is
consistent with the view that electrochemical dissolution occurs with the production of hydrogen ions, such as would occur during the production of thiosulfates [Web and Alkire, 2002].

2.7.2. Effect of Temperature

The values of pitting and repassivation potentials move in the active direction with an increase in temperature (figure – 2.5). The decrease in pitting and repassivation potentials with increase in temperature, as explained by Almarshad and Jamal, may be attributed to the increased ionic activity of thiosulfate and chloride ions or their collective synergistic effect. The shift in pitting potential values in the noble direction is more pronounced at lower temperatures [Almarshad and Jamal, 2004].

![Graph](image)

*Figure – 2.5 Variations of \(E_{\text{pit}}\), \(E_{\text{corr}}\), \(E_{\text{prot}}\), and \(i_p\) with temperature (Almarshad and Jamal, 2004)*

Pitting potential changes insensitively with temperature, increasing when the temperature decreases. El Meguid et al. [2000] report that, in the presence of thiosulfates, the pitting potential
values drop in the active direction while in the presence of sulfates, pitting potential values shift to nobler values.

*Frankel* emphasizes that temperature is a critical factor in pitting corrosion since many materials will not pit at a temperature below a certain value, which may be extremely sharp and reproducible. This effect, he continues, can be seen either by varying the temperature at a range of fixed applied potentials, or varying the potential for a range of constant temperature experiments. At low temperatures, he concludes, extremely high breakdown potentials are observed, corresponding to transpassive dissolution [*Frankel, 1998*].

Just above the critical pitting temperature (CPT), *Frankel* further expands, pitting corrosion occurs at a potential that is far below the transpassive breakdown potential. This value of CPT is independent of environmental parameters and applied potential over a wide range and is a measure of the resistance to stable pit propagation. At higher temperatures, pitting potential decreases with increasing temperature and chloride concentration. *Frankel* postulates that critical pitting temperatures for many stainless steels are in the range of 10-100°C and that CPT can be used as a criterion for ranking susceptibility to pitting corrosion; the higher the CPT, the more resistant the alloy is to pitting [*Frankel, 1998*].

Furthermore, potentiostatic current transients revealed that the time necessary for pit embryo formation, decreased with increasing solution temperature. Analysis of the statistical distribution of pit embryo formation time carried out by *Park and Pyun* demonstrated that the pit embryo formation rate function at higher solution temperatures exhibits a weaker dependence on exposure time compared with that at lower solution temperatures [*Park and Pyun, 2004*]. This,
as they further explain, is attributable to the increase in the active sites necessary for pit embryo formation due to the increase of the defects in oxide film grown at higher solution temperatures. Moreover, it was found that the rate growth decreases with increasing solution temperature [Park and Pyun, 2004].

2.7.3. Effect of Alloy Composition

The alloy composition and microstructure can have strong effects on the tendency of an alloy to pit. Cr concentration, for instance, is found [Frankel, 1998] to play a dominant role in conferring passivity to ferrous alloys. The pitting potential is correspondingly observed to increase dramatically as the Cr content increases above the critical 13% value needed to create stainless steel. Increasing concentration of Ni, which stabilizes the austenitic phase, on the other hand, moderately improves the pitting resistance of Fe-Cr alloys. According to Frankel, small increases in certain minor alloying elements, such as Mo and N in stainless steels, can greatly reduce pitting susceptibility; with Mo being particularly effective, but only in the presence of chromium.

Frankel also suggested that Mo acts by adsorbing on the surface as molybdates or by blocking active sites during active dissolution. Other theories include enhancement of the cation-selective properties of the passive film and reducing the flux of cationic vacancies. Mo ennobles the pit dissolution kinetics, effectively decreasing the pit current density at a given potential. It has also been suggested that Mo counteracts the deleterious effect of sulfur by enriching at the surface, bonding to adsorbed sulfur, and then dissolving. According to Frankel, the majority of researchers seem to favour the notion that Mo influences localized corrosion via some kind of
dissolution and pit growth consideration. Small amounts of other elements, such as N and W, he continues, also have a strong influence on the pitting resistance of stainless steels.

MnS particles in stainless steel are known to be sites for the initiation of pitting corrosion. Lott demonstrated that thiosulfate produced upon the dissolution of manganese sulfide (MnS) inclusions caused the breakdown of the passive film adjacent to the pit when present above a critical concentration in the presence of chloride ions. Thiosulfate was noted to be an aggressive species which chemisorbs on the stainless steel passive film. In addition, pits were found not to initiate adjacent to MnS inclusions that were below a certain critical size, which was found to be approximately 0.7 μm [Park et al., 1991]. It is thought that only at MnS inclusions of sufficient size does the concentration of the sulfur species that is produced by the MnS dissolution increase above the critical concentration.

2.7.4. Effect of Concentration

Thiosulfate pitting corrosion varies depending on concentration. According to Meguid [2000], pits are usually found to contain very high amounts of sulfur when thiosulfates are present, whereas in the absence of thiosulfates, the pits only contain small amounts of sulfur. Sulfur, according to Ehrnsten et al., can be produced in the pit in the presence of thiosulfate.

Ehrnsten et al. stipulate that a surface layer formed in thiosulfate environments has a significantly lower electrical resistance compared to the layer formed in pure chloride solutions, indicating that thiosulfates can hinder repassivation [Ehrnsten et al., 1996]. Almarshad and Jamal report that pitting potential decreases with an increase in chloride concentration (figure – 2.6), and corrosion potential values change slightly toward active direction with an increase in
chloride ion concentration [Almarshad and Jamal, 2004]. While the increase in the value of current density in chloride solution is thought to arise from the increase in the passive current density below the pitting potential, Park and Pyun [2003] have a different opinion, attributing this increase mainly to the formation and growth of a stable pit on the surface above the pitting potential. This implies that increasing solution temperature is destructive to the passivity of oxide films formed on the specimen, leading to the occurrence of pitting corrosion.

![Figure – 2.6 E_pit and E_prot as a function of Cl⁻ concentration at 25°C](image)

*(Almarshad and Jamal, 2004)*

### 2.8. Summary of Literature Review

Thiosulfate leaching of gold is a promising alternative to the cyanide-based process, applicable to refractory ores and to the environmentally sensitive sites. The main advantage of thiosulfate leaching over the conventional cyanidation is its being a non–toxic alternative
permitting a decrease in interference by cations such as zinc, lead, and copper. Furthermore, gold dissolution rates can be higher than those for other options, including cyanide. The main disadvantages of the process, however, are the possible high consumption of reagent and the lack of a suitable gold recovery mechanism.

Steel alloys, being the most selected materials for equipment in common use in such processes, are highly susceptible to most forms of localized corrosion. In particular, stress cracking, pitting, and crevice corrosion are commonplace among which the most common feature is likely mode of initiation. These three forms of corrosion usually initiate with pitting and thereafter propagate in different modes distinguished by mechanisms respective to each type, depending on the prevailing conditions of the environment.

Thiosulfate has been identified as a corrosive environment in mining, oil and gas, pulp and paper, and other industries where a thiosulfate-dominated process, such as thiosulfate gold leaching, is strongly believed to highly promote localized corrosion. Localized corrosion of steel alloys in thiosulfate environments is greatly affected by many factors, primarily the pH, potential, chemical environment, and temperature.

This literature review has revealed a significant amount of research work conducted on the electrochemical behaviour of a variety of engineering materials, including stainless steels, in thiosulfate-dominated environments. The general trend in this research work is to focus on understanding the mechanism of the localized attack in such environments providing a balanced view of the critical factors influencing this type of attack and strategies for developing the
appropriate models for understanding and predicting the various corrosion behaviours involved.

The studies reviewed, nevertheless, have exposed a great deal of trends and fashions that delineate the main course of research. Those trends may be summarized in the following:

- Thiosulfates dissolved in aqueous solutions are known to be detrimental to the corrosion resistance of alloys such as stainless steels. It has been hypothesized that the formation of adsorbed sulfur could cause the observed detrimental effect. XPS studies gave evidence that thiosulfates can be reduced by direct reaction with the metallic surface of iron-chromium alloys, and then prevent passivation or repassivation and stabilize otherwise metastable pits [Marcus and Protopoff, 1997].

- Thiosulfates reduce the surface film resistance to negligible values resulting in active surfaces or weak surface films. So, although thiosulfate is not able to initiate corrosion by itself, it makes it easier for other anions, such as chlorides and sulfates, to initiate localized corrosion by weakening the passive surface film [Laitinen, 2000].

- Thiosulfates exert their effect in a reduced form. This reduced form may be a sulfide incorporated into the oxide layer or sulfur adsorbed at the metal/oxide interface. The mechanism for the reduction of thiosulfates involves reduction of thiosulfates on the non-oxidized iron forming iron sulfide islands [Duret-Thual, et al., 1997].

- Steel corrosion rate increases linearly with increasing thiosulfate concentration. The presence of thiosulfate seems to activate both anodic and cathodic current densities of steel in chloride solutions. The higher the thiosulfate concentration, the greater the
anodic/cathodic current densities. Thus, solutions containing thiosulfate species obviously yield the highest corrosion anodic and cathodic current densities [Ezuber, 2009].

- The effect of solution pH, temperature, chemical environment, and electrochemical potential on the corrosion resistance and the susceptibility of common steel alloys to the most familiar types of localized corrosion promoted by the presence of thiosulfate ions are detrimental to the understanding of the corrosion behaviour of such alloys in such environments.

The studies reviewed, although generally not directly applicable to the currently developed thiosulfate-assisted gold leaching technology due to disagreements in stated operating conditions, they nevertheless broadly agree on the basics and the phenomenology of the pitting process and the factors controlling its initiation and propagation where the general consensus is that the process may be controlled by the same factors controlling any electrochemical reaction; mainly, charge transfer, ohmic effect, and mass transfer considerations.

The role of many of the environmental and material parameters that are critical to the corrosion process such as potential, alloy composition, electrolyte concentration, pH, and temperature were explained in many of these studies by their influence on the growth and stability of the corrosion process under consideration.

These studies, however, are not directly relevant to the behaviour of these materials in the thiosulfate gold leaching environment, and cannot be directly applied therein. Therefore, there
seems to be a growing interest in conducting corrosion studies in such environment, especially in the wake of the building interest in thiosulfate as an alternative lixiviant for gold leaching.

A more detailed study on solution chemistry is one of many needed for further exploration of the topic since the complex electrochemical reactions in the solution will affect the electrochemical and corrosion response of construction materials in the thiosulfate environments. This includes studying the thermodynamics and kinetics of the thiosulfate gold leaching system which will help in anticipating the corrosivity of the solution at various pH, temperature, and thiosulfate concentration. Literature reviews of this type will further be enriched by searching for the potential alloys to be used in this medium. The materials of immediate interest would definitely include austenitic stainless steels 304 and 316, martensitic steels, and carbon steels.
3. Scope And Objectives

The approach of the study is to employ available electrochemical techniques to evaluate the pitting corrosion behaviour of the materials selected for the study under the influence of the critical factors described above. The effect of each factor is studied independently to avoid suspected confounding of their influences. In this way, the interpretation of results and the drawing of conclusions may be greatly facilitated and simplified.

The primary objectives of this study are summarized as follows:

- To investigate the electrochemical aspects of pitting corrosion in thiosulfate solutions for the two steel alloys selected for the study under a selected number of conditions involving solution strength, solution pH and temperature, and chloride ions content. This is carried out employing polarization techniques including cyclic polarizations.

- To study the passivation behaviour of these materials under the same conditions using cyclic polarization and electrochemical impedance techniques and establish the potentials at which pitting starts and that at which repassivation of pits occurs.

- Extract information and draw results that establish the full corrosion profile of the materials intended by the study.

The focus in this study is on the pitting susceptibility of a selected number of stainless steels conceived as possible construction materials for the thiosulfate gold leaching process currently
being developed on an industrial scale. The aim is to investigate the electrochemical performance of SS304 and SS316 in a laboratory environment simulating as close as possible the thiosulfate leaching system described to establish susceptibility to corrosion, specifically the localized type of corrosion.

Systematic work on the effect of thiosulfate ions together with chloride ions on the corrosion behaviour of the selected materials is limited. Therefore, there exists a significant amount of interest in conducting corrosion studies under these conditions known to be prevailing in this system, with the primary aim being to assist in making the selection of the appropriate materials for gold leaching plants much more informative.

The present study is therefore intended to investigate this behaviour to systematically evaluate the susceptibility of the materials selected to localized corrosion and determine how resistant those materials are to pitting under the conditions particularly specified by the thiosulfate gold leaching process under development. The study, defined with this scope, was planned with all the aspects described so far taken into consideration as much as practically possible. Consequently, the study was structured in a way that was realized to best demonstrate relevance and assure both efficiency and sufficiency of results.
4. EXPERIMENTAL

4.1. Tested Materials

4.1.1. Chemical Composition

Austenitic stainless steels are common steel alloys with high corrosion resistance that support their wide appliance in various industries. This demonstrated resistance is greatly owed to their composition. Chromium, molybdenum, and nitrogen normally constitute the principal portion of that composition which greatly improves resistance to corrosion. Test specimens in this study were fabricated from commercial rods of steel conforming to the AISI 304L having a diameter of 13 mm, and AISI 316L having a diameter of 8mm. The chemical composition of these materials was nominally taken as in Table 4.1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Nominal Composition (wt. %)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>SS304L</td>
<td>0.03</td>
</tr>
<tr>
<td>SS316L</td>
<td>0.03</td>
</tr>
</tbody>
</table>
Pitting Resistance Equivalent (PRE) index is generally defined [Renner et al, 1986] as follows:

\[ \text{PRE} = \text{wt}\% \text{ Cr} + 3.3 \text{ wt}\% \text{ Mo} + 13 \text{ wt}\% \text{ N} \]

Materials of higher PRE index are generally expected to exhibit higher corrosion resistance. The values calculated for the materials considered in this study based on the nominal compositions shown in Table – 4.1 above indicate that SS316L is to be expected to exhibit higher resistance with the PRE value of 24.26 versus 19 for SS304L.

4.1.2. Metallography

Specimens for metallographic examination were prepared according to standard procedures. Specimens were ground to a flat plane surface using silicon carbide (SiC) paper of grits ranging from 120 to 1200, and polished to a mirror-shine surface finish with 6µm and 1µm diamond pastes. The specimens were next etched with a glyceregia reagent (3 parts glycerine, 2 parts 37 vol. % hydrochloric acid (HCl), 1 part 68 vol. % nitric acid (HNO₃)) to reveal the microstructure. Qualitative metallographic inspection of the microstructures was then conducted on both materials using optical microscopy. The images obtained are displayed in Figures 5.1 and 5.2.

4.2. Electrochemical Tests

4.2.1. Specimen Preparation
Specimens were sectioned out into cylinders of cross-sectional areas of 13 and 8 mm in diameter from SS304L and SS316L steel rods, respectively. A nickel connection wire was welded to the rear of each specimen using a commercial cold-welding, metallic resin and covered with a tightly fitting transparent plastic tube. Specimens were then mounted in a cold-curing, epoxy resin to expose a working electrode area calculated based on the given diameters. Figure 4.1 shows a schematic diagram of the specimens.

The specimens were mechanically ground to 600 grit silicon carbide (SiC) paper followed by a fine polish on diamond (5μm and 1μm) wheels. Polishing of the specimens was carried out in order to minimize the effect of variation in surface roughness. The specimens were cleaned and degreased in methanol followed by a distilled water rinse and finally dried off using a dust buster prior to testing.

![Figure 4.1 Schematics of the specimens](image-url)
An aqueous solution of anhydrous sodium thiosulfate (Na$_2$O$_2$S$_3$) was prepared from deionized water and analytical grade chemicals. Table 4.2 lists the test environment composition corresponding to each test condition given in (g/L) concentrations along with the resulting pH. One litre of electrolyte was used for each test. The different working solutions were made up according to Table 4.2 below, which also includes the corresponding experimental conditions. A temperature-controlled bath was used to attain temperature at the required level. The pH was checked at random intervals during each experiment using a pH electrode specifically made for basic solutions applications. Adjustment of pH, whenever needed, was made using either NaOH or H$_2$SO$_4$ in minute quantities. For experiments conducted to investigate the effect of Cl$^-$, a gram of NaCl is deliberately added to the thiosulfate solution described above and the pH has again been adjusted to the defined level.

<table>
<thead>
<tr>
<th>Materials Studied</th>
<th>Electrochemical Tests Performed</th>
<th>Factors Considered</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Chemical</td>
</tr>
<tr>
<td>[Na$_2$S$_2$O$_3$]</td>
<td>[NaCl]</td>
<td>pH</td>
</tr>
<tr>
<td>SS304L</td>
<td>OCP</td>
<td>20 – 40 g/L</td>
</tr>
<tr>
<td></td>
<td>EIS</td>
<td>0 – 1 g/L</td>
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<tr>
<td></td>
<td>CP</td>
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</tr>
</tbody>
</table>

Table 4.2 Electrolyte composition and testing conditions
4.2.3. Corrosion Cell Setup

The electrochemical measurements were carried out in a three-electrode standard glass corrosion cell. The corrosion cell, containing the thiosulfate solution as the electrolyte, holds the working electrode (WE), a graphite rod counter (auxiliary) electrode (CE), and a saturated calomel electrode (SCE) mounted in an external compartment separated by a salt-bridge containing saturated potassium chloride (KCl) solution.

The working electrode (WE), prepared as a cylindrical section from the steel materials considered for testing (SS304L & SS316L), was centrally located in the cell facing the counter electrode. The counter electrode (CE) used was a carbon (graphite) rod, and all potentials were referenced to the saturated calomel electrode (SCE). All electrochemical measurements were conducted using a VersaStat4(R) potentiostat supplied by Princeton Applied Science.

4.3. Electrochemical Techniques

4.3.1. Open Circuit Potential

The potential an electrode develops relative to a reference electrode in a solution is a function of the surface condition of the metal and the composition of the solution and is referred to as the Corrosion Potential or the Open Circuit Potential. It is this potential and the effect of variations from it that is central to the electrochemical techniques employed in this study.
Prepared as described in section (4.2.1), the specimens were immersed in the indicated test solutions contained in the sealed corrosion cell. The specimens were then subjected to a cathodic potentiostatic polarization at $-1.5V_{SCE}$ potential for 120 seconds to remove any oxide films present on the surface of the specimen, and expose the metal surface to the electrolyte. The specimens were kept under open circuit for 1 hour to measure the open circuit potential ($E_{ocp}$) where no current is allowed to pass across.

This measurement made across the reference and the working electrodes was meant to determine the potential at which the anodic and cathodic reaction rates (currents) at the electrode/solution interface become equal, which indicates stability across the interface defined in corrosion experiments as the state of “equilibrium” or the “equilibrium potential”. This stability or stationary condition is needed to carry on with electrochemical polarization tests, including cyclic polarization. The potential value recorded at the end of the measurement is taken as the steady-state, open circuit potential.

4.3.2. Cyclic Polarization Scans

An indication of the susceptibility to initiation of localized corrosion is given by the potential at which the anodic current increases rapidly. The more positive this potential, obtained at a fixed scan rate, the less susceptible is the alloy to initiation of localized corrosion. The results of this test are not intended to correlate in a quantitative manner with the rate of propagation that might be observed when localized corrosion occurs.
In general, once initiated, localized corrosion can propagate at some potential more electropositive than that at which the hysteresis loop is completed. The potential at which the hysteresis loop is completed is determined at a fixed scan rate. Thus, the more electropositive the potential at which the hystereses loop is completed, the less likely it is that localized corrosion will occur.

Once stability or equilibrium conditions across the interface is reached at (E_{ocp}), the electrode potential is ramped through a cyclic potentiodynamic polarization loop extending over a potential range starting at 400mV_{SCE} below E_{ocp} and ending at a 25\mu A/cm^{2} increase in current density and back to E_{corr} at a constant scan rate of 0.2mV s^{-1}, unless otherwise indicated. The run is repeated three times using a fresh test solution and a freshly prepared metal surface each time. All potentials in this test were measured with respect to the saturated calomel electrode with a standard potential of 0.241V_{SHE}.

The corrosion rate in mils (0.001 inch) per year (mpy) was calculated according to the following expression:

Corrosion rate (mpy) = (0.129 x \textit{i}_{corr} \times \textit{EW})/\textit{D}; where:

\textit{i}_{corr} = corrosion current density in \mu A/cm^{2},

\textit{EW} = equivalent weight indicating mass of metal in grams which have been oxidized.

For SS304L, the EW is approximately 25.12g and for SS306L is approximately 25.55g (assuming Fe oxidation state of +2), [R. Baboian, 2010].

\textit{D} = density in g/cm^{3}; for SS304L, \textit{D} is 7.84g/cm^{3} and for SS316L it is 7.98g/cm^{3}, [R. Baboian, 2010].
The corrosion potential ($E_{\text{corr}}$) is inferred employing an algorithm expressing the Tafel approximation of the Buttler-Volmer equation over a range of ±25 mV$_{\text{SCE}}$ where a region of linear Tafel slopes is believed to exit.

4.3.3. Electrochemical Impedance Spectroscopy (EIS)

The electrochemical impedance spectroscopy (EIS) measurements were conducted to investigate the electrochemical behaviour of the passive film expected to be forming on the specimen’s surface. Before these experiments were conducted, a reducing potential is applied to remove any oxide films and expose the bare metal to the electrolyte. An open circuit polarization is then applied for an hour to stabilize the metal-electrolyte interface and reach a stationary condition.

A cascade of potentiostatic EIS coupled with potentiostatic polarization loops of three replicates were conducted at $E_{\text{ocp}}$. After immersion, the WE was maintained at -1.5 V$_{\text{SCE}}$ for 2 minutes before starting the EIS measurements. The measurement frequency ranged from 1 mHz up to $10^5$ Hz with applied AC amplitude of 10mV.

EIS data are generally analyzed in terms of an equivalent circuit model. The outcome is a model whose impedance matches the measured data. The type of electrical components in the model and their interconnections control the shape of the impedance spectrum. The parameters (e.g., the resistance value of a resistor) control the size of each feature in the spectrum. Both
these factors affect the degree to which the modeled impedance spectrum matches a measured EIS spectrum.

The aim of the analysis of the EIS data is to elucidate the electrode process and to derive its characteristic parameters. Interpretation of impedance data requires use of an appropriate model. Process modeling links measured impedances with physicochemical parameters of the process (kinetic parameters, concentrations, diffusion coefficients, sample geometry, hydrodynamic conditions, etc.). Measurement modeling explains the experimental impedances in terms of mathematical functions in order to obtain a good fit between the calculated and experimental impedances.

The fitting of the measured EIS data in this study was carried out using ZView 3.3c software where an equivalent circuit is chosen and the fit to the experimental data is performed using the complex nonlinear least-squares technique (CNLS). However, the model deduced may have too many adjustable parameters while the experimental impedance spectrum is simple. In such a case, approximation to a full model introduces too many free parameters and a simpler model containing one time-constant is usually used.
5. Results And Discussion

5.1. Metallography

5.1.1. Optical Microscopy

The specimens’ surfaces were examined using a Nikon EPIPHOT 300 optical microscope. As shown in figures 5.1 and 5.2, both materials show an austenitic microstructure of equiaxed austenite grains of a corresponding grain size of 10μm and 12μm, respectively.

Figure 5.1 – Microstructure of SS304L (optical microscopy)
The grain size was determined using the linear intercept method, the details of which are explained elsewhere [Spaulding, 2010]. Austenite and small amounts of ferrite were observed, which was consistent with a study conducted by Fraker [1985]. Moreover, the images exhibit a few inclusions, likely of oxides and sulfides. Those inclusions are commonly considered to be the more preferred sites for localized corrosion attacks, specifically those resulting in pitting.
Grain boundaries are the other preferred sites, but as chromium carbide was not observed at grain boundaries, the alloys are not likely to be susceptible to grain boundary attack.

5.1.2. Scanning Electron Microscopy (SEM)

Occurrence of pitting corrosion was confirmed by the SEM images obtained using Hitachi S-3000N SEM with light element EDX operating at 25kV. Micrographs of typical pits obtained are shown in Figure – 5.3

Figure 5.3 – SEM micrographs

A) SS304L (40g/L Na₂O₂S₂, pH 8)  B) SS316L (40g/L Na₂O₂S₂, pH 8)
C) SS304L (20g/L Na₂O₂S₂, pH12)  D) SS316L (40g/L Na₂O₂S₂, pH12)
It is observed that the pits are generally few in number and mostly open and circular in shape with average diameter of approximately 25µm. Cracked salt films were noticed inside and the joining of two or more pits was observed in a number of instances. Furthermore, the pits were seen to be covered with a porous layer thought to be the remnant of the passive film. The rupture of such layer during pit growth may lead to the repassivation of the pit.

5.2. Electrochemical Tests

The potentiodynamic cyclic polarization response of Alloys SS304L and SS316L obtained under the influence of the considered conditions is shown in Figures 5.5, 5.6, 5.12, and 5.13. The graphs generally display slightly modified S-shape curves, indicative of active/passive behaviour [Faichuk, 2011]. The presence of a positive hysteresis loop signifies a material suffering from some degree of pitting [Tsai and Chou, 2000].

The potential where the reverse and forward scans intersect is referred to as the protection (repassivation) potential (E_{prot}) [Tsai, et al., 1993]. The most active potential where a considerable increase in passivation current density (i_p) is observed on the forward scan denotes the formation of stable, non-repassivating pits, and is referred to as the pitting potential (E_{pit}) [Lee et al., 1994]. Pits grow (propagate) only between E_{prot} and E_{pit}, whereas pit formation (nucleation) takes place only at potentials higher than (or more anodic to) E_{pit}. The greater the separation between corrosion potential (E_{corr}) and E_{prot} becomes, the stronger the indication that pitting is occurring at potentials different from OCP [Sheu, 1996].
In the following sections, the electrochemical performance of the materials selected for this study under the influence of the imposed conditions is discussed in consensus with the results obtained. The first section (5.2.1) deals with the influence of pH, and the effect of the concentration level of thiosulfates, while the second (5.2.2) concerns the effect of temperature and the influence of chloride ions. Greater emphasis is persistently placed throughout this discussion on the behaviour observed within the passive rather than the active region, as the study is essentially intended to investigate the system’s propensity toward the pitting form of localized corrosion. Thus, the main approach followed in interpreting the results is based on the necessities of theory and concepts generally formulated regarding the formation of passive layers, and the significance of their properties in connection with resistance to breakdown in response to the intentionally-introduced variations in conditions.

5.2.1. Effect of pH and Thiosulfate Concentration

The values of $E_{\text{pit}}$, $E_{\text{prot}}$, and $\Delta E (\Delta E = E_{\text{pit}} - E_{\text{prot}}$) inferred from the cyclic potentiodynamic polarization curves, shown in Figure 5.5 for pH 8 and in Figure 5.6 for pH 12, designate that in both pH levels, susceptibility to pitting is greatly affected by the thiosulfate concentration. $E_{\text{pit}}$ values were found to decrease as thiosulfate concentration increased, and the displacement of $E_{\text{pit}}$ from $E_{\text{prot}}$, called $\Delta E$, was also found to increase, indicating higher susceptibility.

As far as alloy SS316L is considered, the amount of thiosulfates was the more influential factor in determining susceptibility to pitting over the pH, where susceptibility was observed to increase with higher thiosulfate concentration regardless of pH change. For alloy SS304L, however, thiosulfate concentration and pH seem to exhibit a combined effect that collectively
influences susceptibility to pitting. As the values in Table 5.1 indicate, alloy SS304 becomes susceptible to pitting at lower thiosulfate concentrations only with higher pH conditions attained; otherwise a higher thiosulfate concentration is a desired condition, just as the case is with alloy SS316L.

In conditions where both materials showed signs of susceptibility, alloy SS316L, with much lower values of ΔE, displayed lower susceptibility to pitting corrosion than SS304L. Moreover, it was observed that it would generally be only at the most severe conditions where both thiosulfate concentration and pH are at high levels that pitting corrosion occurs.

Hence, it may be deduced that, although both materials bare some degree of susceptibility to pitting, the extent to which the conditions influence this susceptibility varies in scale and magnitude, being by and large more rigorous and severe with alloy SS316L, suggesting a higher level of resistance to this mode of corrosion for this alloy under the imposed conditions over alloy SS304L.

Table 5.1 – Electrochemical test results (effect of pH and thiosulfate concentration)

<table>
<thead>
<tr>
<th>Material</th>
<th>Thiosulfate Concentration (g/L)</th>
<th>pH</th>
<th>E_corr (mV SCE)</th>
<th>E_pit (mV SCE)</th>
<th>E_cor (mV SCE)</th>
<th>ΔE (mV)</th>
<th>I_corr (μA/cm²)</th>
<th>I_pit (μA/cm²)</th>
<th>βa (mV SCE/decade)</th>
<th>βc (mV SCE/decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS304</td>
<td>20</td>
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<td>-316</td>
<td>460</td>
<td>703</td>
<td>-243</td>
<td>12</td>
<td>12</td>
<td>117</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td></td>
<td>-416</td>
<td>384</td>
<td>247</td>
<td>137</td>
<td>18</td>
<td>110</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>12</td>
<td>-189</td>
<td>570</td>
<td>370</td>
<td>200</td>
<td>1.2</td>
<td>6</td>
<td>124</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td></td>
<td>-275</td>
<td>432</td>
<td>606</td>
<td>-174</td>
<td>2.5</td>
<td>9</td>
<td>109</td>
<td>77</td>
</tr>
<tr>
<td>SS316L</td>
<td>20</td>
<td>8</td>
<td>-342</td>
<td>460</td>
<td>703</td>
<td>-243</td>
<td>12</td>
<td>12</td>
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<td>384</td>
<td>247</td>
<td>137</td>
<td>18</td>
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<td></td>
<td>20</td>
<td>12</td>
<td>-192</td>
<td>570</td>
<td>370</td>
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<td>1.2</td>
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<td></td>
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<td>-285</td>
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<td>-174</td>
<td>2.5</td>
<td>9</td>
<td>109</td>
<td>77</td>
</tr>
</tbody>
</table>
The alloys have reached a stationary dynamic condition after 8 hours of immersion in thiosulfate solutions, at which point, the open circuit potential ($E_{ocp}$), recorded at approximately 1 hour intervals, attained the constant values given in Table 5.1. The open circuit behaviour observed at those intervals, shown in Figure 5.4, may most markedly be distinguished for the shift in $E_{ocp}$ toward nobler regions as the pH increases, indicating a higher tendency to passivation with pH rising to higher levels, whereas the increase in thiosulfate concentration resulted in a similar effect but of much lower order on $E_{ocp}$ as the $E_{ocp}$ presumes comparable values.

Hence, it is most likely that an inhibiting effect on corrosion rate with pH increase, promoting the formation of a passive film on the surface of the metal, is to be expected, whereas the apparent enhancing ability of thiosulfates is expected to result in a promoting effect on the corrosion behaviour.

An increase in pH level was observed to cause a marked effect on the $E_{pit}$ values, particularly at higher thiosulfate concentrations. At lower thiosulfate concentrations a similar effect was perceived, but at higher pH levels (pH 12). The pitting potential in the higher pH solutions was significantly ennobled, in line with the well-known inhibiting effect of higher concentrations of hydroxide ions (OH⁻).
Figure 5.4 – OCP at variable thiosulfate concentrations (pH 8 & pH 12 @ 40°C)

A) SS304L  B) SS316L
Figure 5.5 – Cyclic polarizations at variable thiosulfate concentrations (pH 8 & 40°C)

A) SS304L (20g/L Na₂O₃S₂)  B) SS304L (40g/L Na₂O₃S₂)
C) SS316L (20g/L Na₂O₃S₂)  D) SS316L (40g/L Na₂O₃S₂)
Figure 5.6 – Cyclic polarizations at variable thiosulfate concentrations (pH 12 & 40°C)

A) SS304L (20g/L Na₂O₃S₂)
B) SS304L (40g/L Na₂O₃S₂)
C) SS316L (20g/L Na₂O₃S₂)
D) SS316L (40g/L Na₂O₃S₂)
It is notable that the effect of pH was generally of lower order at lower pH levels. This behaviour is typical of chromium, nickel, and wrought stainless steels which are characterized by a shift in $E_{\text{ocp}}$ in the noble direction, suggesting a higher tendency to surface passivation \cite{Park et al., 2004}.

The passive regions on the polarization curves are marked by a current density ($i_p$) stable over a variable potential range. Within these regions, both alloys exhibited anodic peaks under a number of the conditions considered. Na$_2$S$_2$O$_3$ has been shown to destabilize the oxide film, creating anodic peaks \cite{Yang, et al., 2001}. This instability was attributed to the enhanced ability of thiosulfates to promote anodic dissolution and impede repassivation.

The active–passive behaviour of an alloy is also considered to be heavily influenced by its alloying elements, particularly Cr-content. Therefore, it is possible to ascribe the changes in current density observed at those peaks to the removal of some key alloying element(s) such as Cr and/or Mo.

The magnitude of the steady-state current density defining the passive region is also considered an indicator of susceptibility to anodic dissolution \cite{Huang et al, 2007}, where higher ($i_p$) values entail higher corrosion current densities ($i_{\text{corr}}$), and hence, higher metal dissolution rates. The ($i_p$) values obtained as shown in Table 1 indicate that, as the thiosulfate concentration increases, the ($i_p$) increases, suggesting higher dissolution rates, while increasing the pH resulted in a decrease in ($i_p$), consequently suggesting lower dissolution rates.
This was confirmed with both materials by the obtained values of \( i_{\text{corr}} \), which show an ascending trend in anodic dissolution as the thiosulfate concentration gets higher, and a descending trend as pH increases. This observation, once again, demonstrates the known inhibitive effect of high pH conditions on anodic dissolution and, meanwhile, illustrates the enhancing ability of thiosulfates in the destabilization of passive films, and concurrently promoting higher corrosion rates through prohibition of repassivation, an effect played by thiosulfates in a competing basis with that exhibited by varying the pH.

The anodic polarization curves, displaying smooth and relatively continuous passive regions that extend over a considerable range of potential, suggest possible formation of single-layered passive films, whereas those with distinctively separated multiple regions suggest the likely formation of double-layered passive films. The division between those regions was based on the notable increase in current density with increasing potential.

The electrochemical properties of those films, whenever formed, were investigated using Electrochemical Impedance Spectroscopy (EIS). The Nyquist plots produced using the experimental data obtained at open circuit potentials, and those generated through fitting methods employing selected circuit models, are shown in Figure 5.7. In plots where the semi-circle was seen to be incomplete and offset from its real axis, departing from the behaviour typically observed for a simple RC circuit [Belo et al., 1999], a double time-constant circuit representing a double-layered film is assigned to account for the observed behaviour.
Figure 5.7 – Nyquist plots at variable thiosulfate concentrations (pH 8 & pH 12)

A) SS304L  B) SS316L
Figure 5.8 - Bode (magnitude) plots at variable thiosulfate concentrations (pH 8 & pH 12)

A) SS304L  B) SS316L
Figure 5.9 - Bode (phase) plots at variable thiosulfate concentrations (pH 8 & pH 12)

A) SS304L  
B) SS316L
The Bode (phase) plots obtained, shown in Figure 5.9, further assert that the passive films that developed on the two alloys are of two distinct types. Plots with a single peak, indicative of a single-layered film, representing the passive behaviour of alloy SS304L shown in Figure 5.9 (A), while those representing the behaviour of alloy SS316L shown in Figure 5.9 (B), displayed Bode (phase) plots with two peaks characteristic of a double-layered film.

A rough or porous passive surface was indicated by the size of capacitance indicated by the slope of the Bode (magnitude) plots shown in Figure 5.7, in which case the measured capacitance response becomes not ideal, and a modification was needed to produce a circuit model that would accurately represent the acquired data. A constant phase element (CPE) was thus introduced in these situations to account for these surface inhomogeneities, the impedance of which is given by:

$$Z_{CPE} = \frac{1}{Q (j\omega)^n}$$  \hspace{1cm} (1)

In this equation, Q is a fit parameter that is independent of frequency and the exponent n is a measure of the distribution of behaviour of the element; with a value between 0 (for pure resistance) and 1 (for pure capacitance).

The circuits used (figure – 510) contain a resistor that accounts for the solution resistance \((R_s)\). In circuit (A), representing the formation of single-layered passive films, this resistor is in series with a polarization resistance \(R_p\) that is in parallel to the double-layer capacitance \((C_{dl})\) and the passive film resistance \((R_{ox})\), while a constant phase element (CPE) of the passive film \(CPE_{ox}\) is in parallel to \((R_{ox})\).
In circuit (B), depicting the formation of double-layered passive films, the solution resistance ($R_s$) is in a series of two time constants, $R_1$/CPE$_1$ and $R_2$/CPE$_2$. These time constants account for the properties of the precipitate (outer) layer, and the barrier (inner) layer of the double-layered film displayed in a number of the obtained cyclic polarization curves, and further identified by the two humps observed on the corresponding Bode (phase) plots shown in Figure 5.9.
Table 5.2 – EIS test results (effect of pH and thiosulfate concentration)

<table>
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<tr>
<th>Material</th>
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<th>SS316</th>
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<tbody>
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<td>Condition</td>
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<td>$R_s$</td>
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<td>$R_p$</td>
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<td>$R_{ox}$</td>
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<td>$C_{dl}$</td>
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<td>CPE$_{ox}$</td>
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<table>
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<th>Material</th>
<th>SS304</th>
<th>SS316</th>
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<tbody>
<tr>
<td>Condition</td>
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<td>0.000116</td>
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<tr>
<td>CPE$_2$</td>
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<td>chisq</td>
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</table>
As the thiosulfate concentration increases, the semi-circle contour becomes more protracted, indicating a behaviour that may be attributed to a corresponding increase in the effective surface in contact with the electrolyte, which, in turn, may be the cause for the observed shift in corrosion potential to the more negative values obtained. Consequently, the observed decrease in polarization resistance ($R_p$) values, as displayed in Table 5.2, and the concurrent increase in the double layer capacitance ($C_{dl}$), as the thiosulfate concentration increases, indicates higher susceptibility to anodic dissolution, falling in reasonable agreement with the results obtained by cyclic polarization tests.

Increasing pH resulted in an increase in $R_p$ coupled with a corresponding decrease in $C_{dl}$, indicating lower susceptibility to anodic dissolution in contrast with the observed effect of thiosulfate concentration distinguished by a decrease in $R_p$ and an increase in $C_{dl}$, falling once again in acceptable agreement with the results obtained by cyclic polarization tests.

5.2.2. Effect of Temperature and Chloride Ions

The curves representing the cyclic polarization of alloys SS304L and SS316L in thiosulfate solutions obtained at 40 and 60°C for pH 8, as well as those taken in the absence and presence of chloride ions at 40°C and pH 8, are shown respectively in Figure 5.12 and Figure 5.13. Active–passive behaviour is indicated once again with the modified S-shape of the curves displayed. Susceptibility to pitting is indicated by the presence of a hysteresis loop with the reverse scan intersecting with the forward at potentials lower than the pitting potential ($E_{pit}$). The displacement of $E_{prot}$ from corrosion potential ($E_{corr}$) always suggests that pitting, if any, occurs at potentials different from OCP.
The presence of Cl\(^-\) ions showed an adverse effect on \(E_{\text{pit}}\) as well as on \(E_{\text{corr}}\). The obtained values given in Table 5.3 indicate that \(E_{\text{pit}}\) and \(E_{\text{corr}}\) are both shifted in the noble direction with an increase in Cl\(^-\) ion concentration, signifying lower susceptibility to pitting corrosion and anodic dissolution. This behaviour can be explained by the formation of a barrier limiting direct interaction of the Cl\(^-\) ions with the bare metal. Thiosulfates are known for their dual ability as a promoter and inhibitor, depending on the prevailing conditions. The inhibitive behaviour is usually displayed by forming a layer of adsorbed sulfur or sulfur species on the surface of metal alloys, thus protecting them from attack by Cl\(^-\) ions.

The effect of temperature on \(E_{\text{pit}}\), \(E_{\text{prot}}\), \(E_{\text{corr}}\), and passivation current (\(i_p\)) is also presented in Table 5.3. The shift in \(E_{\text{pit}}\) and \(E_{\text{prot}}\), as would be expected, was observed to be in the active direction and distinctively more pronounced than that of \(E_{\text{corr}}\), which displayed only a slight drift in the active direction with an increase in temperature from 40 to 60°C. This behaviour is commonly observed for austenitic steels, and is usually attributed to the increase in ionic activity of thiosulfates with an increase in temperature.

The most significant change observed in the \(i_p\) values was found to be the increase from 15 to 29\(\mu\)A/cm\(^2\) with an increase in temperature from 40 to 60°C. \(\Delta E (E_{\text{pit}} – E_{\text{prot}})\) and the difference between \(E_{\text{corr}}\) and \(E_{\text{prot}}\) values were found to increase with increasing temperature, indicating that alloys are more prone to pitting corrosion at higher temperatures. Furthermore, the order \(E_{\text{pit}} > E_{\text{corr}} > E_{\text{prot}}\) holds at those conditions, indicating that the alloys suffer from pitting corrosion.
Table 5.3 – Electrochemical test results (effect of NaCl and temperature at pH 8)

<table>
<thead>
<tr>
<th>Material</th>
<th>Thiosulfate Concentration (g/L)</th>
<th>NaCl Concentration (g/L)</th>
<th>Temperature (°C)</th>
<th>( E_{ocp} ) (mV SCE)</th>
<th>( E_{corr} ) (mV SCE)</th>
<th>( E_{pit} ) (mV SCE)</th>
<th>( \Delta E ) (mV SCE)</th>
<th>( i_{corr} ) (μA/cm²)</th>
<th>( i_p ) (μA/cm²)</th>
<th>( \beta_{\text{pass SCE/decade}} )</th>
<th>( \beta_{\text{corrosion SCE/decade}} )</th>
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<tr>
<td>SS304</td>
<td>0</td>
<td>40</td>
<td>0</td>
<td>-416</td>
<td>-425</td>
<td>384</td>
<td>247</td>
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<td>3.9</td>
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<td>110</td>
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<td>1</td>
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<td>530</td>
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<td>336</td>
<td>306</td>
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</table>

The alloys once more attained a steady state after 8 hours immersion period in thiosulfate solutions, at the end of which the open circuit potential (\( E_{ocp} \)), recorded at approximately 1 hour intervals, had the constant values given in Table 5.3. The observed performance of the alloys under those open circuit conditions is shown graphically in Figure 5.11. A distinguished shift in \( E_{ocp} \) in the noble direction with an increase in Cl\(^-\) ions is displayed, indicating a higher tendency to passivation as Cl\(^-\) concentration increases. This is similarly explained in the way the observation made earlier about \( E_{pit} \) and \( E_{corr} \) were discussed.

The passive regions for both alloys are marked by a steady current density (\( i_p \)) over a variable potential range. The size of this steady current density defined as the passivation current density (\( i_p \)) is moreover considered an indicator of susceptibility to anodic dissolution, whereas higher (\( i_p \)) values imply higher corrosion current densities (\( i_{corr} \)), and hence higher metal dissolution rates to be expected.
Figure 5.11 – OCP at variable NaCl contents and temperatures (pH 8)

A) SS304L  B) SS316L
Figure 5.12 – Cyclic polarizations at different sodium chloride contents (pH 8 & 40°C)

A) SS304L (40g/L Na$_2$S$_2$O$_3$)  
B) SS304L (40g/L Na$_2$S$_2$O$_3$ + 1 g/L NaCl)

C) SS316L (40g/L Na$_2$S$_2$O$_3$)  
D) SS316L (40g/L Na$_2$S$_2$O$_3$ + 1g/L NaCl)
Figure 5.13 – Cyclic polarization at different temperatures (pH 8)

A) SS304L (40g/L Na₂O₃S₂, 40°C)  
B) SS304L (40g/L Na₂O₃S₂, 60°C)  
C) SS316L (40g/L Na₂O₃S₂, 40°C)  
D) SS316L (40g/L Na₂O₃S₂, 60°C)
The obtained \( (i_p) \) values shown in Table 5.3 indicate that, as the Cl\(^-\) concentration increases, the \( (i_p) \) decreases, suggesting lower dissolution rates. A similar decrease was also observed by increasing the temperature but of a lower order. The measured \( i_{corr} \) values confirmed this observation with both materials showing a corresponding trend in anodic dissolution as the Cl\(^-\) concentration gets higher and temperature increases. While this observation is contrary to the known promoting effect of high Cl\(^-\) concentration as well as that of high temperature conditions on anodic dissolution, it illustrates the ability of thiosulfates in acting in the dual fashion as a promoter and as an inhibitor, depending on the prevailing conditions.

The electrochemical properties of the passive films were investigated using Electrochemical Impedance Spectroscopy (EIS). The Nyquist plots from the experimental data obtained at open circuit potentials in each solution, and those fitted using selected models, are shown in Figure 5.14. In each of these plots, the semi-circle was seen to be incomplete and offset from its real axis, departing from the behaviour normally observed for a simple RC circuit.

The obtained Nyquist plots exhibit features that suggest the presence of a rough or porous surface, in which case the measured capacitance response is typically not ideal, and a modification was once again applied to construct a model that accurately represents the acquired data. A constant phase element (CPE) was used to account for these surface inhomogeneities, the impedance of which is determined in the way described earlier.
Figure 5.14 – Nyquist plots at variable NaCl contents and temperatures (pH 8)

A) SS304L      B) SS316L
Figure 5.15 - Bode (magnitude) plots at variable NaCl contents and temperatures (pH 8)

A) SS304L  B) SS316L
Figure 5.16 - Bode (phase) plots at variable NaCl contents and temperatures (pH 8)

A) SS304L  B) SS316L
The passive films on the two alloys are indicated by the Bode (phase) plots obtained, shown in Figure 5.16, to be of two distinct types. Plots with a single peak indicate a single-layered film, representing the passive behaviour of alloy SS304L shown in Figure 5.16 (A), while those representing the behaviour of alloy SS316L shown in Figure 5.16 (B), displayed Bode (phase) plots with two peaks characteristic of a double-layered film.

The fitting of the impedance data was thus accomplished using the two equivalent circuits shown in Figure 5.10, the circuitry of which was extensively described in section (5.2.1). Equivalent circuits (A) and (B) were hence assigned considering this single and double RC behaviour of the obtained impedance plots presented in Figure 5.14.

As the Cl⁻ concentration increases, the semi-circle contour becomes more depressed, indicating a behaviour that may be attributed to a corresponding decrease in the effective surface in contact with the electrolyte which, in turn, may be the cause for the observed shift in corrosion potential to the more positive values obtained. Consequently, the observed increase in polarization resistance ($R_p$) values, as displayed in Table 5.4, and the concurrent decrease in the double layer capacitance ($C_{dl}$), as the Cl⁻ concentration increases, indicates lower susceptibility to anodic dissolution, falling in reasonable agreement with the results obtained by the cyclic polarization tests.

Increasing the temperature resulted in a decrease in $R_p$ coupled with a corresponding increase in $C_{dl}$, indicating higher susceptibility to anodic dissolution; in contrast with the observed effect of Cl⁻ concentration distinguished by an increase in $R_p$ and a decrease in $C_{dl}$,
falling once again in acceptable agreement with the results obtained by the cyclic polarization tests.

**Table 5.4 – EIS test results** (effect of NaCl and temperature)

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6. **Summary And Conclusions**

The debate surrounding the use of cyanide in the mining industry has fuelled considerable investigation into the development of some more environmentally benign alternatives. The thiosulfate system has been widely accepted by researchers around the world as a potential alternative lixiviant for the leaching of gold. Thiosulfate is relatively nontoxic, some forms of which have been used for many decades as a fertilizer and, consequently, from an environmental standpoint, thiosulfate has a definite advantage over cyanide. Moreover, comparing reagent unit costs, thiosulfate is far cheaper than cyanide, thus, with similar or even slightly higher lixiviant consumption, the application of thiosulfate for gold recovery can be economical and compete directly with cyanidation.

Corrosion occurs under a large number of conditions and appears in a variety of forms. The two large classes of corrosion phenomena are general and localized corrosion. Due to their intrinsic nature and evolution, general and localized corrosion have always been considered and studied as two distinct topics [Salvago et al., 2002]. Contrary to the general uniform type of corrosion, both position and time of occurrence of localized types of corrosion are difficult to predict, therefore, a reliable material selection procedure is essential and needed, particularly at early design stages.

One of the key limitations of design and application of alloys in industrial processes, such as gold leaching, is the ability of available structural materials to resist corrosion. The challenge in materials selection and development lies in the elimination of the corrosion problems and finding improved varieties with controlled alloying elements and microstructure exhibiting higher
corrosion resistance. The development of corrosion resistant materials is important, as it would enhance the lifetime of components and availability of plants for extended periods, and avoid the use of other expensive materials like titanium and zirconium alloys with associated problems of dissimilar metal joining, as well as reduce the thickness of the components where corrosion allowance is considered for a desired lifetime.

Local corrosion behaviour is extremely complex because of numerous factors, such as metallurgical, geometrical, and environmental, will together contribute to this process, and it is not practical to stimulate all those conditions in the laboratory [Yang et al., 2001]. Localized corrosion occurs stochastically and is, therefore, also difficult to monitor. Pitting is mainly caused by the heterogeneous microstructure, which is intentionally developed in order to improve the mechanical properties. As a matter of fact, the second phase particles, formed during the precipitation hardening treatment, result in the formation of localized galvanic coupling with the matrix, which essentially gives rise to a severe and highly localized attack [de Wit, 2001].

Investigation of the effect of addition of various kinds of sulfur species, including thiosulfates, on the pitting behaviour of austenitic stainless steel alloys such as SS304L and SS316L in a chloride solution of fixed molarities at various pH values showed that, of all these species, thiosulfate was the most aggressive [Brossia and Kelly, 1998]. Thiosulfate was further thought to have a greater effect than hydrogen sulfide because hydrogen sulfide cannot electromigrate from the bulk solution into pits. The mechanism by which all sulfur species operate, as proposed by Marcus and co-workers [Brossia and Kelly, 1998], was via the formation of a surface sulfur layer that prevents repassivation and enhances the dissolution
kinetics of the alloy. \( E_h \) – pH diagrams indicate that when the potential is decreased cathodically, the thiosulfate species are reduced into sulfur adsorbed on the metal which replaces adsorbed oxygen. The domains of stability of the adsorbed S monolayer overlap the domains of stability of the metals, their dissolved cations, oxides, and hydroxides [Marcus and Protopopoff, 1997].

Localized corrosion of steel alloys in thiosulfate environments is greatly affected by many factors, primarily alloy composition and treatment, pH, potential, chemical environment, and temperature. The effect of these factors on the corrosion resistance and the susceptibility of common steel alloys to common types of localized corrosions promoted by the presence of thiosulfate ions are detrimental to understanding the mechanisms underlying these types of corrosion processes and corrosion behaviours of these alloys in such environments.

The value of pitting nucleation potential (\( E_{np} \)) increases as the solution pH value increases in the range of 2-10. The increase in solution pH usually leads to a considerable decrease in the corrosion rate [Tsai and Wu, 2000]. Variation in the solution temperature has a considerable effect on the steel corrosion rate. At higher temperatures, protective films are formed more easily and the corrosion rate goes through a maximum. An increase in the solution temperature will lead to an increase in the equilibrium constants, thus reflecting greater amounts of \( H^+ \) present in the system and, subsequently, increasing the corrosion rate [Ezuber, 2009]. Furthermore, it has been reported that raising the solution temperature results in an increase in the rate of transport or reduction of thiosulfate ions. Consequently, the adsorption process (surface coverage of \( S_{ads} \)) might become more efficient at higher temperatures thus increasing the corrosion rate [Hosni M. Ezuber, 2009].
The changes in corrosion potential, pitting corrosion and the passive potential range are evidently associated with the electrochemistry of the electrolyte. In the presence of cations such as ammonium, the higher corrosion potential is due to the adsorption of the cation on the stainless steel surface, which may reduce the surface concentration of corrosive ions and eventually causes a delay in pitting corrosion [Kuo et al., 1999].

It is interesting that at the presence of such ions, the passivation is considerably extended mainly due to the preferential adsorption of these ions on the specimen surface [Kuo et al., 1999]. Another important aspect of the chemistry of the electrolyte affecting corrosion is the ratios of the ionic species present. Newman et al. [1989] proposed that the pitting of UNSS30400 and AISI 316L is worst at molar ratios of ([SO$_4^{2-}$] + [Cl$^-$]) to [S$_2$O$_3^{2-}$] from 10 to 30. They showed that stainless steel AISI 316L required a higher total ion concentration and higher temperature than AISI 304L, and chloride had to be the predominant ion [Uutela et al., 2003].

The literature survey conducted in the present study covered a significant number of papers dealing with the influence of thiosulfates on the corrosion of steel alloys and the effect of the main factors on the propensity to pitting corrosion, where it was felt that the main focus was generally placed on the understanding of the mechanism of localized attack of thiosulfates and developing pertinent models that describe the initiation and propagation aspects of the process.

These studies, however, were not directly related to the thiosulfate-assisted gold leaching environments, as the range of thiosulfate concentration concerned and the pH conditions are
widely different. Therefore, a significant amount of interest existed in conducting corrosion studies under these specific conditions known to be prevailing in this system, with the primary aim being to assist in making the selection of the appropriate materials for gold leaching plants much more informative.

The approach adopted in the study employs available electrochemical techniques to evaluate the main-course pitting corrosion behaviour of the materials selected for investigation under the influence of the critical factors described above; with the primary objectives being to describe the electrochemical aspects of pitting corrosion for the selected steel alloys and to study the passivation behaviour of these materials under the same conditions. The focus of this study was on the pitting susceptibility of stainless steels conceived as possible construction materials for the thiosulfate-gold-leaching process currently being developed on an industrial scale.

The study, conducted on the two steel alloys at two thiosulfate concentrations with two pH levels and temperatures of 40 and 60°C in the presence and absence of chloride ions has culminated in the following conclusions:

- In both pH levels, susceptibility to pitting was greatly affected by the thiosulfate concentration. $E_{\text{pit}}$ values were found to decrease as thiosulfate concentration increased, and the displacement of $E_{\text{pit}}$ from $E_{\text{prot}}$, called $\Delta E$, was also found to increase, indicating higher susceptibility.
• The amount of thiosulfates was the more influential factor in determining susceptibility to pitting over the pH as far as alloy SS316L is considered, where susceptibility was observed to increase with higher thiosulfate concentration regardless of pH change. For alloy SS304L, however, the thiosulfate concentration and pH seem to exhibit a synergistic effect that collectively influences susceptibility to pitting, with alloy SS316L, having much lower values of ΔE, displaying lower susceptibility to pitting corrosion than SS304L.

• The shift in $E_{\text{ocp}}$ toward nobler regions as the pH increases indicates a higher tendency to passivation with increasing pH, whereas the increase in the thiosulfate concentration resulted in a similar effect but of much lower order.

• An increase in pH level was observed to cause a marked effect on the $E_{\text{pit}}$ values, particularly at higher thiosulfate concentrations. At lower thiosulfate concentrations, a similar effect was perceived, but at higher pH levels (pH 12). The pitting potential in the higher pH solutions was significantly ennobled, in line with the well-known inhibiting effect of higher concentrations of hydroxide ions (OH$^-$).

• As thiosulfate concentration increases, the $(i_p)$ increases, suggesting higher dissolution rates; while increasing the pH resulted in a decrease in $(i_p)$, suggesting lower dissolution rates; a case confirmed with both materials by the values of $(i_{\text{corr}})$, which showed an ascending trend in anodic dissolution as the thiosulfate concentration got higher, and a descending drift as pH increases, demonstrating the
well-known inhibitive effect of high pH conditions and the enhancing ability of thiosulfates in destabilizing passive films.

- Increasing pH resulted in an increase in $R_p$, coupled with a corresponding decrease in $C_{dl}$, indicating lower susceptibility to anodic dissolution; in contrast with the observed effect of the thiosulfate concentration distinguished by a decrease in $R_p$ and an increase in $C_{dl}$, falling in acceptable agreement with the results obtained by cyclic polarization tests.

- The presence of Cl$^-$ ions inflicts an adverse effect on $E_{pit}$ as well as $E_{corr}$. The $E_{pit}$ and $E_{corr}$ have both shifted in the noble direction with an increase in Cl$^-$ ion concentration, signifying lower susceptibility to pitting corrosion and to anodic dissolution. Thiosulfates are known for their dual ability as a promoter and inhibitor, depending on the prevailing conditions. The inhibitive behaviour is usually displayed by forming a layer of adsorbed sulfur or sulfur species on the surface of metal alloys, thus protecting them from attack by Cl$^-$ ions.

- The shift in $E_{pit}$ and $E_{prot}$ was observed to be in the active direction with an increase in temperature from 40 to 60°C. This behaviour is commonly observed for austenitic steels and is usually attributed to the increase in ionic activity of the thiosulfates with an increase in temperature. $\Delta E (E_{pit} - E_{prot})$ and the difference between $E_{corr}$ and $E_{prot}$ values were found to increase with increasing temperature, indicating that alloys are more prone to pitting corrosion at higher temperatures.
As the Cl$^-$ concentration increases, the ($i_p$) decreases, suggesting lower dissolution rates. A similar decrease, but of a lower order, was also observed increasing the temperature. The measured $i_{corr}$ values confirmed this observation with both materials showing a corresponding trend in anodic dissolution as the Cl$^-$ concentration gets higher and as temperature increases. While this observation is contrary to the known promoting effect of high Cl$^-$ concentration, as well as that of high temperature conditions on anodic dissolution, it illustrates the ability of thiosulfates in acting in a dual fashion as a promoter and as an inhibitor, depending on the prevailing conditions.

Increasing the temperature results in a decrease in $R_p$, coupled with a corresponding increase in $C_{dl}$, indicates higher susceptibility to anodic dissolution, in contrast with the observed effect of Cl$^-$ concentration distinguished by an increase in $R_p$ and a decrease in $C_{dl}$, falling once again in acceptable agreement with the results obtained by cyclic polarization tests.
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