

**Improved Localized Corrosion Models for Stainless Steels in Aqueous Chloride Environments
with Low Levels of Dissolved Oxygen**

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ABSTRACT

Experimental foundation has been established for improving corrosion models for stainless steels exposed to aqueous chloride media with low levels of dissolved oxygen. Accurate repassivation potentials were measured for UNS S31603 and UNS S32305 alloys in chloride electrolytes at room and elevated temperatures using Tsujikawa-Hisamatsu Electrochemical (THE) and Cyclic Potentiodynamic Polarization (CPP) methods. It was observed that the repassivation potential values measured from CPP methods were lower than the ones obtained from THE method for the same environmental conditions. Cyclic polarization scans in aqueous chloride media were conducted at different reverse scan rates resulting in varied repassivation potentials. Medium-term corrosion potentials were measured in chloride media with controlled oxygen levels ranging from 20 – 400 ppb. These results were used as inputs for improving model prediction for repassivation and corrosion potentials. With a flexible definition of the repassivation current density, the previously developed mechanistic repassivation model reproduces the experimental repassivation potentials obtained using THE and CPP methods. Dependence of corrosion potential on dissolved oxygen has been modeled using a mixed-potential model. It has been demonstrated that the effect of agitation (caused by bubbling of oxygen) needs to be accounted for to describe the corrosion potential, especially at low dissolved oxygen where mass transport is important.

Keywords: UNS S31603, UNS S32305, Stainless Steel, Chloride, Dissolved Oxygen, Repassivation potential, Corrosion Potential, Modeling, Pitting, Potentiostatic, Potentiodynamic, Galvanostatic

INTRODUCTION

In Upstream, CRAs (Corrosion Resistant Alloys) are widely selected to handle seawater and brines in piping, valves, pumps, heat exchangers, vessels, and seawater injection¹⁻⁴. Also, disposal of produced water is commonly performed through injection into spent fields. Water from a variety of sources including produced water, seawater and surface/fresh water may also be injected to create pressure drive for existing fields. Usually dissolved oxygen (DO) is not fully controlled when there are multiple sources of injection water and sometimes even possibility of injection of fully oxygenated water exists. For oxygenated seawater, the PREN (Pitting Resistance Equivalent Number = %Cr + 3.3 * (%Mo + 0.5 %W) + 16 %N) shall be >40 and limits are applied to the temperature⁴. Other applications involve Solid CRA or clad production pipelines which may get flooded with seawater during installation and pre-commissioning. For these cases a preservation time limit of 5 days is usually applied. Ideally, the susceptibility to localized corrosion should reliably be predicted for a CRA exposed to any combination of beforementioned environmental parameters. This would be beneficial to materials selection to the design phase as well as for risk assessment after unforeseen circumstances.

OLI Corrosion Analyzer[†] is a commercially available modelling tool for predicting localized corrosion of CRAs exposed to seawater and brines². However, in some instances it has been observed that the predictions do not match experimental data and especially in low-oxygen (< 100 ppb) saline environments. It is well known that dissolved oxygen is one of the critical parameters affecting the propensity of localized corrosion of CRA in chloride media^{3,4}.

Several authors have studied the effect of DO on stress corrosion cracking (SCC) of stainless steels and Ni-base alloys immersed in high temperature water⁵⁻⁶. Arjmand et. al studied the effect of temperature, chloride, and DO concentration on the open-circuit potential (OCP) and transpassive potential values of UNS S31603 (316L) stainless steel at high-temperature pressurized water containing ppb levels of chloride⁶. They concluded that the most positive OCP was obtained when the levels of chloride and temperature were 10 ppb and 140°C respectively and the DO was ~ 200 ppb. However, only a few researchers have systematically studied the effect of oxygen on the localized corrosion propensity of stainless steel in higher chloride concentrations (sea-water levels). Fletcher et. al developed an accelerated test method to map the crevice corrosion resistance of super-duplex stainless steels and Ni-base alloys as a function of temperature, chloride and 2 levels of DO concentrations⁷. Lu and Paul determined the DO levels at which pitting corrosion of 316L and 25-Cr super duplex stainless steels occurred at elevated temperatures in saline solutions by immersion testing⁸. Nice et. al studied the effect of DO varying from < 5 ppb to 500 ppb on crevice corrosion of duplex stainless steels in natural seawater loops at 30°C simulating service conditions⁹. In this work, the duplex alloys achieved much higher OCPs—in the range of +150 to +200 mV (SCE)—when the DO concentration was increased to 100 ppb or higher because of biofilms in natural seawater. Al Wahaibi et al. systematically studied the effect of DO levels ranging from 20 to 100 ppb on crevice and pitting resistance of girth-welds of UNS S31603, UNS S32305 and UNS S32750 stainless steels exposed to varying levels of chloride at 50°C and 60°C¹⁰. The critical DO levels at which localized corrosion occurred for the alloy welds were determined as a function of temperature, DO and chloride concentrations. It was shown that for UNS S32750 (25-Cr duplex) stainless steels, no localized corrosion occurred even at the highest DO and chloride concentrations tested at 60°C. Trigodet *et al.* studied the influence of DO content on the bacteria - induced ennoblement of duplex stainless steels in seawater¹¹. The authors found that only at above ~ 100 ppb of DO, the ennoblement of OCP was observed leading to an increased risk of localized corrosion. Recently, Evans et.al evaluated the crevice

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corrosion resistance of 9 stainless steel alloys in artificial seawater containing controlled DO levels (from 100 – 500 ppb)¹².

As can be seen, most of the literature reports on the evaluation of localized corrosion by immersion or OCP measurements. It is the intent of this paper to determine accurately the electrochemical parameters that can quantitatively determine the propensity for pitting or localized corrosion i.e., the repassivation and corrosion potentials of UNS S31603 alloy exposed to chloride media under controlled DO concentrations. An important aspect of this work is to improve the existing models for localized corrosion of UNS S31603 in chloride media having low DO concentrations to provide accurate prediction of pitting propensity, thereby enabling cost-effective materials selection during the design phase and for risk assessment.

EXPERIMENTAL PROCEDURE

Electrochemical cells were set up for measurement of localized corrosion parameters viz. corrosion and repassivation potentials. These corrosion cells consisted of an assembly of working electrode (alloy to be tested), a large-area Pt counter electrode and a reference electrode being a commercial Ag-AgCl (4M KCl) immersed in a test solution containing aqueous sodium chloride contained in a glass vessel at the required temperature. UNS S31603 and S32305 alloy specimens were bought and machined by Growell Precision company in India and the material test certificate conformed to the alloy specifications as per the UNS specifications. Specimens were machined in the form of a cylinder, but with a hemispherical bottom. This ensured that there were no sharp edges that would accelerate pitting preferentially during experimentation. The length and the diameter of these specimens were 25 mm and 10 mm respectively and grinded till P1800 grit finish followed by ultrasonic cleaning in acetone, isopropyl alcohol and de-ionized water in sequence and the exposure area was $\sim 8.3 \text{ cm}^2$.

For OCP experiments, there was no counter electrode as only the corrosion potential or the open circuit potential between the stainless steel and the reference electrode was measured. Since OCP were measured with the electrolyte containing a controlled DO concentration, a DO sensor was also dipped in the deoxygenation cell. About 1500 mL of electrolyte was prepared as per required concentration of NaCl (ranging from 0.05M to 3.0M) using 99.9% pure chemical. The solution was deaerated in a deoxygenation cell first through a mixture of N_2 and air as shown in the schematic in Figure 1. The DO content in the electrolyte was measured through an oxygen sensor (an optical sensor from Presens Company[†]) and the purging with the mixture of gases (as pre-determined by the ratio of N_2 and air mass flow) continued until the steady state readings from the sensor reached the required value. Once the required level of oxygen control under steady state conditions was attained, the outlet of the deoxygenation cell was closed, and the liquid was transferred through the transfer tubes to the corrosion cell by the gas pressure. It should be noted the corrosion cell and the transfer tubes were also deaerated using N_2 purge gas prior to the transfer of the liquid from the deoxygenation cell. The volume of solution deaerated was $\sim 1200 \text{ mL}$ for each set of experiments and about 400 mL of deoxygenated solution was transferred to three identical corrosion cells through silicone transfer tubes after deoxygenation.

The DO content in the deoxygenation cell was controlled by purging a pre-determined mass ratio of N_2 to air using mass flow controllers and mixers as shown in the schematic of the overall experimental set-up in Figure 1. The glass vessels were enclosed with threaded Teflon stoppers and glass inlet/outlet tubes. Offline leak tests were conducted to ensure airtight sealing of the Teflon ports and glass junctions to where silicone tubes were used for purging. The experimental determination of mass ratios of N_2 to air required to achieve specific levels of dissolved O_2 in brine solutions of different concentrations will be described later in this section.

Mass flow controllers (Models MC-500SCCM[†] & MC-1SLPM[†]) from Alicat Co. have been used to precisely control the mass flow rates of N₂ and air. The individual gases were then mixed in a gas bomb and then split into three mixtures of gases and were purged continuously throughout the experimental duration through each of three corrosion cells at a rate of approx. 30 -50mL/min as shown in Figure 1. Alicat mass flow meters (Model MC-1SLPM-D[†]) was used for monitoring the flow rates of mixture of N₂ and air throughout the experiment. Prior to OCP measurement, the ratio of N₂ to air mass flow rates were calibrated using just the deoxygenation cell to achieve the predetermined DO concentrations for each chloride level. A typical mass flow of 0.15 standard litre per minute (SLPM) of N₂ mixed with 0.0006 SLPM of air purged through brine results in ~40 ppb of dissolved oxygen for a ratio of 0.004 at almost all concentrations of chlorides at room temperature. The DO concentration is linear with respect to the mass flow ratios of the mixture of gases over a range of 20 – 500 ppb. For each level of the chloride concentrations, the DO concentration was measured until steady-state readings were attained for the lowest air to N₂ mass flow ratio to achieve close to 20 ppb and subsequently the inflow of air was raised to achieve higher dissolved O₂ levels.

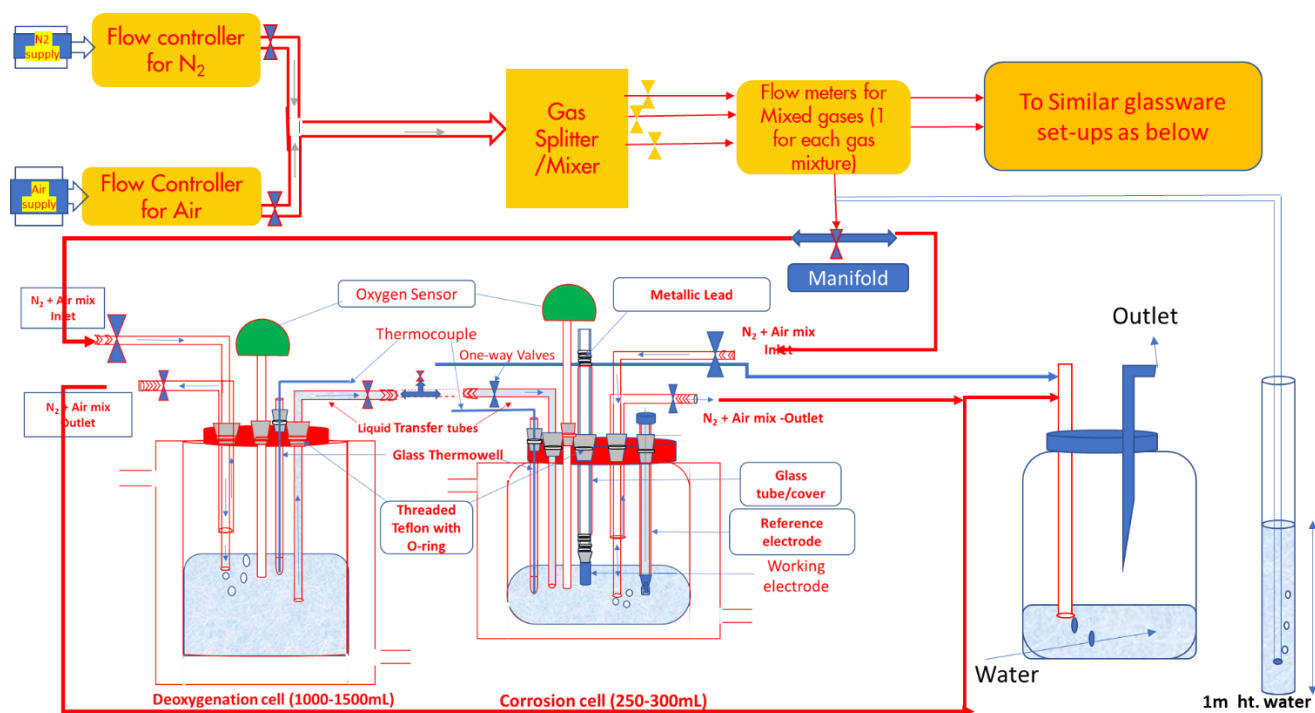


Figure 1: Schematic of laboratory experimental set-up for corrosion potential measurements under controlled dissolved oxygen conditions.

For each set of experimental conditions, OCP measurements were made simultaneously (in parallel) with identical alloy specimens of UNS S31603 (316L) stainless steel in duplicate or triplicate corrosion cells under identical environmental conditions to ensure reproducibility of data. The OCP measurements were made continuously for a period of at least 96 hrs. based on a DoE (Design of Experiments) consisting of 3 levels of chloride (0.05 or 0.1M, 0.6M and 2.0 or 3.0M NaCl), 2 levels of temperature (22°C & 60°C) and 4 levels of DO (20 ppb, 60 ppb, 100 ppb and 400 ppb) for UNS S31603. Experiments for measurement of repassivation potentials were conducted in similar corrosion cells in quiescent conditions as it is known that there is no effect of DO on repassivation potentials². For repassivation potential measurements, two types of methods were adopted viz. a modified Cyclic

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Potentiodynamic Polarization (CPP) based on ASTM G61¹³ and the Tsujikawa-Hisamatsu Electrochemical (THE) method based on ASTM G192¹⁴. A set of experiments for determining repassivation potentials also involved the use of artificial pencil electrode (1-D pit) technique¹⁵.

All electrochemical experiments were conducted using a Gamry Ref. 600+[†] potentiostat interfaced to a computer through a Gamry Framework[†] and the data was analysed through Echem Analyst[†] software. In the case of OCP measurements, an ECM8[†] multiplexer was also connected to the potentiostat to measure potentials simultaneously from multiple corrosion cells. OCP were measured every 30 seconds for each alloy specimen and the DO concentration was measured for one of the corrosion cells every 10 seconds throughout the exposure period. For all repassivation potential measurements, duplicate trials were made to assess repeatability of results. In many cases triplicate trials were done if the repassivation potential measurements from the two trials were not within 25 - 30 mV of each other. For experiments at 60°C, the experiments were conducted in a double-walled glass vessel with recirculating hot water flowing between the inner and outer walls of the vessel with the flow and temperature controlled by a heater bath - RE 300[†] from Lauda company[†]. For both OCP and repassivation potential measurements, the test matrix included 2 temperatures and 3 levels of chloride concentration as described earlier. For the latter, measurements were done under quiescent conditions in aqueous chloride media. A polished cross-section of a 100 µm diameter of UNS S31603 and UNS S32305 alloy wires embedded in an epoxy (slow-cured) matrix was exposed to aqueous chloride electrolytes in a three-electrode cell and a constant potential was applied 0.7V vs. Ag-AgCl for 300 seconds to initiate a one-dimensional pit followed by polarization at 0.5V vs. Ag-AgCl for at least 1 hr. to create deep pits (> 500 µm). This was then followed by potentiodynamic polarization starting from 0.5V to -0.4V at a scan rate of 100 mV/s.

RESULTS

Repassivation potentials

The repassivation potentials based on THE method were determined from the potential at which a sudden drop in current/current density (an order of magnitude) to values those seen during stable passive condition close to 50-100 nA/cm² was observed. A typical representative example of this is shown in Figure 2 below. The repassivation potential obtained for UNS S31603 from this technique is ~ -0.05V vs. Ag-AgCl (4M KCl) upon exposure to 0.6M NaCl at RT. Based on this criterion, the repassivation potential readings were averaged over 2 or 3 readings for each set of conditions and graphically shown in Figure 3 for UNS S31603 and UNS S32305 alloys. Also, the effect of DO on repassivation potential were studied by conducting THE method measurements at specific chloride levels for UNS S31603 (2M or 0.6M) at RT. It was found that statistically there were no differences between the values of repassivation potentials from the experiments conducted under completely deoxygenated chloride media (DO ~ 10 ppb) and continuously aerated conditions.

It has been shown that the repassivation potential is independent of the electrochemical scan parameters only if there is a critical charge density that is passed (corresponding to a minimum pit-depth) prior to repassivation. Although there is some variability in the value of this critical charge density reported in the literature by several researchers, it is generally agreed that a minimum of 20 C/cm² of charge density (based on specimen surface area) must be passed for bulk specimens beyond which E_{rp} is independent of the total charge^{15,16}. It should be mentioned that 45°C is close to the critical pitting temperature (CPT) of UNS S32305 stainless steel in chloride environments close to seawater concentration (determined by ASTM G150-18¹⁴). It has been shown that the repassivation potential is independent of the electrochemical scan parameters only if there is a critical charge density that is passed (corresponding to a minimum pit-depth) prior to repassivation.

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