

**Determination of oxygen limits for corrosion resistant alloys (CRAs) in oil & gas
produced water based on electrochemical test methods
Part 1: Crevice corrosion and repassivation potentials without oxygen**

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ABSTRACT

Stainless steels are frequently used in the oil & gas industry due to their excellent resistance against corrosion. In seawater and produced water, however, pitting and/or crevice corrosion can occur assuming the process conditions are outside the so-called “safe operation window” for the actual alloy. In produced water, oxygen content is one important process parameter. It is well known that in electrolytes with small amounts of oxygen ($O_2 < 10$ ppbw), stainless steels can be used at much higher temperatures than in seawater saturated with oxygen (~ 8 ppmw O_2). In this paper, the effect of temperature, pH and chloride content on crevice corrosion and repassivation potential in simulated produced water without oxygen is examined for UNS⁽¹⁾ S31603, UNS S31803 and UNS S32750. The tests showed that both temperature and chloride ion concentration strongly affected the results.

Key words: stainless steels, oxygen, temperature, chloride content, crevice corrosion/ repassivation potential

INTRODUCTION

Corrosion Resistant Alloys (CRAs) have been widely used in oil & gas process systems since the 1980s due to their excellent resistance towards uniform corrosion in aggressive environments such as seawater and produced water containing CO_2 , organic acids and/or production chemicals. However, cases of localized corrosion in the form of pitting and crevice corrosion have regularly been observed. As an example, ISO⁽²⁾ 21457 limits the max. operating temperature to 20°C for

⁽¹⁾ Unified Numbering System (UNS)

⁽²⁾ International Organization for Standardization (ISO), Chemin de Blandonnet 8, CP401, 1214 Vernier, Geneva Switzerland.

25 Cr super duplex stainless steel (UNS S32750/760) and 6-Mo austenitic stainless steels (UNS S31254) in chlorinated seawater systems, to avoid crevice corrosion.¹ Initiation of pitting and crevice corrosion (*often called localized corrosion*) are influenced by different process parameters. The most important process parameters are temperature, pH, chloride- and oxygen concentration. In addition, the actual alloy composition and microstructure plays an important role. Figure 1 shows a schematic anodic polarization curve for an active/passive alloy like stainless steels with and without chloride ions (Cl^- ions). The figure shows typical values that are used to describe the anodic curve and the four characteristic regions a complete anodic polarization curve can be divided into.

In the passive region the protective oxide layer is intact and localized corrosion is prevented. At the pitting or crevice corrosion potential, $E_{\text{Pit/Crev}}$, the oxide layer starts to break down locally and corrosion initiates. However, metastable corrosion (initiation followed by quick repassivation) can also be observed at potentials below $E_{\text{Pit/Crev}}$. Increasing the potential even more will accelerate the corrosion rate indicated by an increase in the anodic current density in the attacked regions. By lowering the potential from a potential more positive than $E_{\text{Pit/Crev}}$, a hysteresis is normally seen on the polarization curve. The potential where this part of the curve crosses the passive current density, is defined as the repassivation potential, E_{Rep} . Below this potential, localized corrosion will neither be initiated or grow. The value $[E_{\text{Pit/Crev}} - E_{\text{Rep}}]$ is an important parameter for an alloy in a defined environment. A small value indicates an alloy that easily repassivate after initiation. Contrary to this, a larger value indicates that repassivation is difficult to achieve after initiation. An important debate in the corrosion community is therefore: Shall a design be based on $E_{\text{Pit/Crev}}$ or E_{Rep} ? From a safety point of view (and to achieve a more robust solution) the design should preferably be based on E_{Rep} .

In the current project, the active part of the polarization curve will not be included. This means that the corrosion potential (E_{Corr}) or Open Circuit Potential (OCP) is more positive than the Flade potential E_{Fla} in Figure 1..

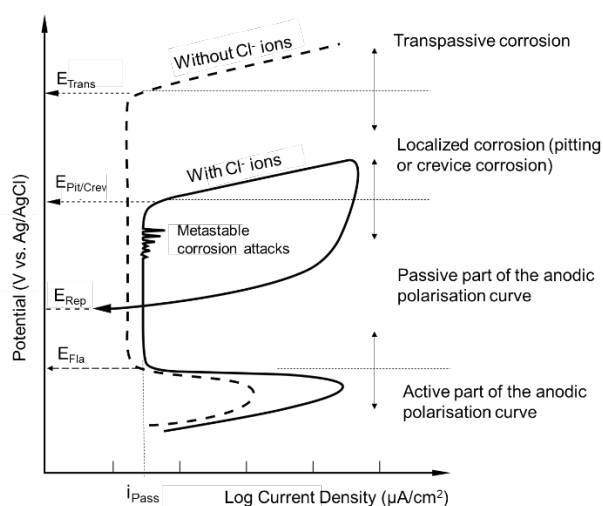


Figure 1: Schematic presentation of an anodic polarization curve indicating the effect of chloride ions (Cl^-) on initiation of pitting or crevice corrosion. E_{Fla} : Flade potential, E_{Rep} : Repassivation potential, $E_{\text{Pit/Crev}}$: Pitting or crevice corrosion potential, E_{Trans} : Transpassive corrosion potential, i_{Pass} : Passive (or anodic) current density.

Temperature

A raise in temperature, increases the rate of most chemical reactions.² In general, increased temperature results in an increased tendency to initiate localized corrosion, and faster propagation of corrosion attacks. More positive pitting (E_{Pit}) and crevice (E_{Crev}) corrosion potentials are observed at lower temperatures.³ In addition, increased temperature will result in faster diffusion and more defects (vacancies/interstitials) in the passive film.⁴ Increased porosity can lead to decreased resistance towards breakdown of the passive film and make the passive film less protective.⁵

Temperature has a significant effect on corrosion of stainless steel in chloride solutions. It will affect the frequency distribution of the momentary variation in current, towards higher currents. This indicates that a change in temperature primarily increases the metastable pit growth, rather than activating new sites.³ An increase in temperature will promote the corrosion tendency, because the corrosion process for the transition from metastable to stable corrosion is accelerated or due to reduction in charge transfer resistance.^{3,4} This also suggests that the transition from metastable to stable pit growth is easier accomplished at higher temperatures.³ Most materials experience pitting and crevice corrosion above a certain threshold value, critical pitting temperature (CPT) and critical crevice temperature (CCT), respectively.³ In the same environment crevice corrosion will occur at a lower temperature than pitting corrosion. Consequently, CCT will in general be lower than CPT.⁶

Chloride ion (Cl^-) content

When Cl^- - ions are present, stainless steels can be exposed to localized attacks in the form of pitting or crevice corrosion as shown schematically in Figure 1. This is due to the breakdown of the protective passive film at random sites caused by the chloride ions.⁷ The chloride ion has high diffusivity, a small size, and a strong acidic anionic nature. The small size allows the ions to penetrate though the passive film. Experiments have shown that an increase in the chloride concentration decreases the corrosion resistance of stainless steels.²

The presence of Cl^- - ions can be destructive to the stability of the passive film. Three models are frequently used to describe the effect of chloride ions presence: i) adsorption causing local dissolution of the film, ii) anions penetrating the film causing weakening of the oxide bonds, and iii) breakdown of the film at defects.⁶

Higher chloride concentration increases the probability of Cl^- - ions to be adsorbed or to penetrate through the passive film. In addition, a higher availability of Cl^- - ions will make it easier for the ions to replace water molecules or hydroxide ions at undeveloped or damaged parts of the passive film.⁸ If Cl^- - ions are adsorbed at sufficient high chloride concentrations, further film formation will be prevented, and anion vacancies can be created in the film and cause it to collapse.⁹

pH

A change in pH will change the chemistry of a solution, and thereby affect the corrosion characteristics of stainless steels.¹⁰ Increasing the pH leads to a lower dissolution rate, resulting in a thicker passive film with higher iron content, as iron oxides are more stable in an alkaline solution.⁸ In an acidic solution, the passive film will be weakened and the film will become thermodynamically unstable if the solution is severely acidic, according to the Pourbaix diagram.¹¹

There are different explanations on why the passive film becomes unstable when the pH is low enough. While some authors believe that an acidic solution decreases the localized corrosion resistance due to the decreasing thickness and more defects in the passive film,¹² other authors postulate it is due to the competition between chloride ions and hydroxide ions for

the opportunity to be adsorbed on the metal surface. When pH decreases, the Cl^- ions will become more predominant, and the passive film will become thinner. After local depassivation, the Cl^- ions will continue to compete with the hydroxide ions. If Cl^- ions are adsorbed on the surface, they will prevent repassivation.¹³

Dastgerdi et al.¹⁴ observed that the breakdown potential (E_{Pit} or E_{Crev}) increased with increasing pH. Higher pH values moved the potential in a more noble direction. In severe acidic solutions, with pH 2.7, the metal had an active behavior and the passive part of the polarization curves disappeared. These authors¹⁴ stated that pH had a significant effect when the chloride concentration in the solution was low (100 ppm). At higher chloride concentrations (10000 ppm), pH had a less significant effect. Additionally, in the pH range 4-7, the breakdown potential showed little change with increasing pH. This was especially prominent when the chloride concentration was high. Similar results were also observed by Tzaneva¹⁵, which stated that the pH of the solution did not significantly influence the protective properties of the passive film on austenitic stainless steels in the pH range 2-10. The reported experiments included testing in 3.5% NaCl solutions with pH in the range 1-12.

Oxygen

Oxygen in the solution will increase the OCP on passive CRAs compared to a solution with neglectable oxygen (< 10 ppb). In a paper published by Trigode¹⁶, the influence of dissolved oxygen on the crevice corrosion of 22Cr duplex stainless steel (UNS S31803) and UNS S32750 in seawater at $30 \pm 0.5^\circ\text{C}$ was examined. One important output from the work was the effect of oxygen content on OCP as shown in Figure 2. As can be seen from the figure, under these conditions the OCP was < -300 mV vs. SCE at an oxygen content below 10 ppbw and increased to a level close to $+300$ mV vs. SCE in seawater with an oxygen content ~ 8 ppmw. Effect of oxygen on OCP is also shown in Figure 3b).

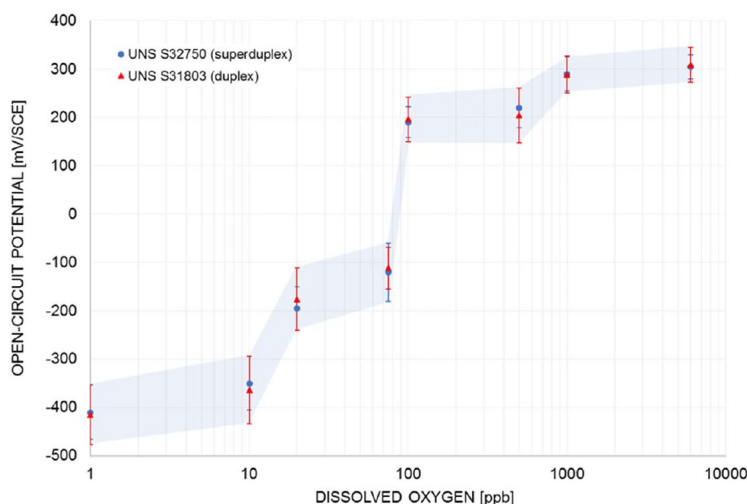


Figure 2: OCP on UNS S31803 and UNS S32750 in natural seawater at $30 \pm 0.5^\circ\text{C}$ as a function of oxygen content.¹⁶

It is worth mentioning the ennoblement of OCP on stainless steels in seawater saturated with oxygen that has been a topic for research since the early 80-ties.¹⁷ The ennoblement raising the OCP from below -100 mV vs. $\text{Ag}/\text{AgCl}^{(3)}$ to approx. 300 mV vs. Ag/AgCl during one week of

⁽³⁾ V vs, $\text{Ag}/\text{AgCl} \approx 0.04$ V + V vs. SCE, SCE: Saturated Calomel Electrode

exposure, has been attributed to the development of biofilm and bacteria on the passive oxide film on the surface. The other significant effect of bacteria on stainless steels is an increase in the cathodic reduction efficiency (e.g. cathodic reduction of dissolved oxygen). Both effects can significantly increase the risk of localized corrosion of stainless steels since OCP can be more positive than $E_{\text{Pit}}/E_{\text{Crev}}$ during the ennoblement. Once initiated, localized corrosion will propagate much faster if the oxygen reduction reaction is catalyzed by the biofilm formation. The increase in potential at oxygen contents higher than 100 ppbw shown in Figure 2, is probably due to a combination between oxygen level and ennoblement due to the development of the biofilm on the surface.

One important question is whether oxygen will affect E_{Pit} , E_{Crev} and E_{Rep} . There are a limited number of publications that have examined this.^{18, 19} However, in a recent published paper by Zeng et.al¹⁸ the effect of oxygen on electrochemical behavior of UNS S31803 in seawater at 72°C was investigated. The oxygen content varied in the range 0.34 mg/l (340 ppbw) to 3.06 mg/l (3.06 ppmw). Cyclic anodic polarization curves indicated that the oxygen content affected both E_{Pit} and E_{Rep} in addition to OCP and the cathodic curve as shown in Figure 3. The general trend was that increased oxygen content gave a more positive E_{Pit} and a more negative E_{Rep} . From Figure 3a) an increase of 200 mV in E_{Pit} and a corresponding reduction of 100 mV in E_{Rep} can be seen as an effect of increasing the oxygen content from 340 ppbw to 3.06 ppmw. Based on investigation of the passive film from the test samples exposed to the different oxygen contents, the authors explained the observations with a variation in the passive film composition where the oxides Fe_2O_3 and Cr_2CO_3 became the dominating ingredients in the passive film at the highest oxygen content. For all oxygen contents, the passive films had a bilayer structure comprised p- and n- type semiconducting oxides, respectively. The increment of oxygen content, decreased the defect densities and increased the thickness of the space charge layer in the passive films, which may effectively inhibit the intrusion of aggressive chloride ions. However, at the same time the repassivation tendency was reduced. An explanation for this reduction was not given in the paper.

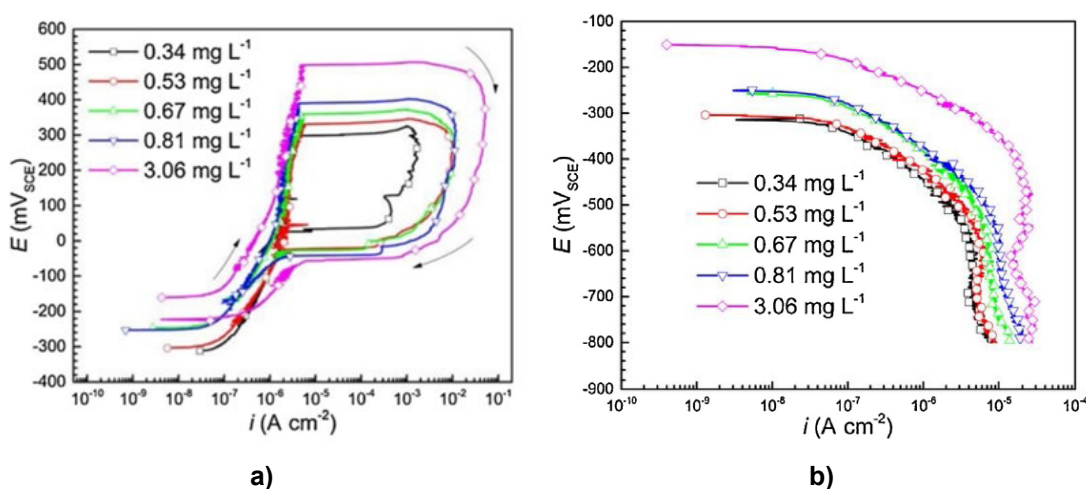


Figure 3: Exposure of UNS S31803 in seawater at 72°C with different oxygen content. a) Anodic polarization curves, b) OCP and cathodic polarization curves.¹⁸

AIM OF THE WORK

Initiation of crevice (and pitting) corrosion of stainless steels depends on the electrochemical potential on the surface of the alloy. According to what is described above, chloride content, pH and temperature are important parameters for E_{Crev} in addition to the alloy composition and