

Determination of Oxygen Limits for Corrosion Resistant Alloys (CRAs) in Oil & Gas Produced Water Based on Electrochemical Test Methods – Part 2

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ABSTRACT

Small amount of oxygen in production or injection systems can be responsible for the initiation of crevice corrosion of stainless steel. The current limit of 10 ppb dissolved oxygen (DO) recommended for the use of Corrosion Resistant Alloys (CRAs) in produced water system, has been challenged by several authors. The aim of this study is to report the use of electrochemical methods for the study of oxygen limits for stainless steels UNS⁽¹⁾ S31603 (Type 316L) and UNS S31803 (Type 22Cr Duplex) in produced water environments. Crevice corrosion potential (E_{crev}) and repassivation potential (E_{rep}) were obtained from cyclic polarization experiments performed in part 1 of this study. These two potentials were used as acceptance criteria during open circuit potential (OCP) measurements to determine the oxygen limits of Type 316L and Type 22Cr Duplex at given test conditions. The effect of the duration of exposure to oxygen as well as the effect of increase of oxygen content were discussed. Results obtained for Type 316L indicate that the current oxygen limit of 10 ppb is relevant for long-term and permanent exposure. A precise determination of oxygen limits for Type 22Cr Duplex could not be performed due to uncertainties related to the variations of E_{crev} and E_{rep} at low oxygen concentrations. A re-assessment of oxygen limits based on the data obtained in this study is planned based on revised acceptance criteria.

Key words: Crevice corrosion, produced water, Corrosion Resistant Alloys, oxygen, electrochemistry.

⁽¹⁾ Unified Numbering System (UNS)

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INTRODUCTION

Crevice corrosion is a geometrical-dependent type of localized attack that occurs in occluded regions where a stagnant and corrosive electrolyte is in contact with the surface of a passive metal^{1,2}. Crevices are present in all industrial designs and can lead to major failure since their detection is often challenging^{3,4}. Main strategies for the prevention and mitigation of crevice corrosion include design awareness and adequate materials selection⁵.

The formulation of a universal mechanism of crevice corrosion is still a source of debate. Currently, three main mechanisms have been proposed: the acidification model (Oldfield and Sutton^{7,8}), the IR drop model (Frankenthal and Pickering⁹) and the metastable pitting model¹⁰. All these mechanisms require a combination of factors for crevice corrosion to initiate^{1,6}. Among them, the influence of pH, temperature and chloride concentration has been widely investigated in both produced water and seawater systems¹¹⁻¹³. Another major factor affecting the development of crevice corrosion is the presence of DO in bulk solution. Indeed, oxygen influences the cathodic reaction of crevice corrosion:



In oil and gas processes, oxygen can be present in production systems as a result of treated seawater injection. Oxygen scavengers or deaeration plants are often used prior injection, but complete oxygen removal is almost impossible to achieve¹⁴. Another common source of oxygen in production systems is production chemicals injection¹⁵. Common practice in the oil and gas industry is to limit the DO concentration to 10 ppb in produced water systems to prevent localized corrosion. Several authors have demonstrated that this limit could be conservative depending on exposure parameters^{14,16-18}. Most of the studies reporting the study of oxygen limits for CRAs are however based on long-term immersion tests^{14,17,18}, which does not provide input regarding the electrochemical behavior of materials exposed to oxygen. To the best of our knowledge, Fletcher *et al.* are the only authors who have reported the study of oxygen limits of CRAs using an electrochemical test method¹⁶.

The main objective of this paper is to illustrate the pertinence of combined electrochemical test methods to assess oxygen limits of CRAs in produced water systems. Electrochemical acceptance criteria at given test conditions are determined in the first part of this study using cyclic potentiodynamic polarization¹⁹. Oxygen limits are assessed based on acceptance criteria through OCP measurements at various DO concentrations. The method was applied in this study for Type 316L and Type 22Cr Duplex Stainless Steels at various produced water test conditions.

EXPERIMENTAL PROCEDURE

Test materials

Type 316L and 22Cr Duplex specimens were machined from available commercial plates. Metallic specimens were prepared according to ASTM⁽²⁾ G1:03²⁰. Abrasion was performed starting with wet 80-grit SiC (FEPA) paper and finishing with 500-grit SiC paper to ensure a uniform surface finish. Abrasion included outer edges. The test specimens were cleaned and rinsed with acetone and left overnight in a desiccator. Metallic test specimens were attached to a home-made specimen holder using a 1 mm diameter platinum wire. Electrical contact between the test specimen and the specimen holder were checked before each test.

(2) American Society for Testing and Materials (ASTM) International, West Conshohocken, PA.

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OCP measurements

OCP measurements were performed in a glove box under inert atmosphere to prevent external ingress of oxygen. Unlike cyclic polarization experiments performed in part 1 of this study¹⁹, non-crevice specimens were used for OCP measurements since the specimens were not subjected to polarization. The test setup consisted of two connected glass cells, one reservoir cell and one test cell. Each cell included a gas inlet and outlet, a thermocouple, and a cooler. A two-channels pH meter (SevenExcellence, Mettler Toledo) was used to monitor the pH in both the reservoir and test cell. Measurements were performed using an Ag/AgCl reference electrode (Radiometer), and two working electrodes consisting of the mounted test specimens. All electrochemical measurements were carried out using a potentiostat (Series G300, Gamry). A schematic representation of the test apparatus is given in Figure 1.

Prior to testing, a fresh electrolyte consisting of a 5L distilled water solution, to which NaCl was added as chloride source, was prepared. The amount of NaCl varied from test to test depending on the required chloride concentration. A small amount of bicarbonate salt (NaHCO_3) was added to the electrolyte as buffer. The electrolyte was then transferred to the reservoir cell which was heated to the target temperature value, where deoxygenation and adjustment to the target pH value were achieved by bubbling a mixture of N_2 and CO_2 at a given ratio for at least 12h. The two working electrodes were mounted in the test cell which was then purged with N_2 until transfer of the electrolyte to the test cell. After transfer of the electrolyte to the test cell, OCP was measured on the two test specimens. Once OCP reached a stable value, O_2 was introduced into the system. Increase of O_2 was performed after stabilization of OCP at each oxygen level step. Measurement of oxygen level within the test cell was performed by using an optical oxygen sensor (VisiFerm, Hamilton).

To avoid any electrochemical interference between the oxygen sensor tip made of stainless steel and the electrolyte, oxygen concentration was measured in gas phase right above the electrolyte. DO in aqueous phase was determined from the oxygen partial pressure. Calculations were performed based on Henry's Law using the MultiScale^{†3} simulation software (v.09). Note that DO was verified at regular intervals by immersing the oxygen sensor in the test solution.

³ Trade name.

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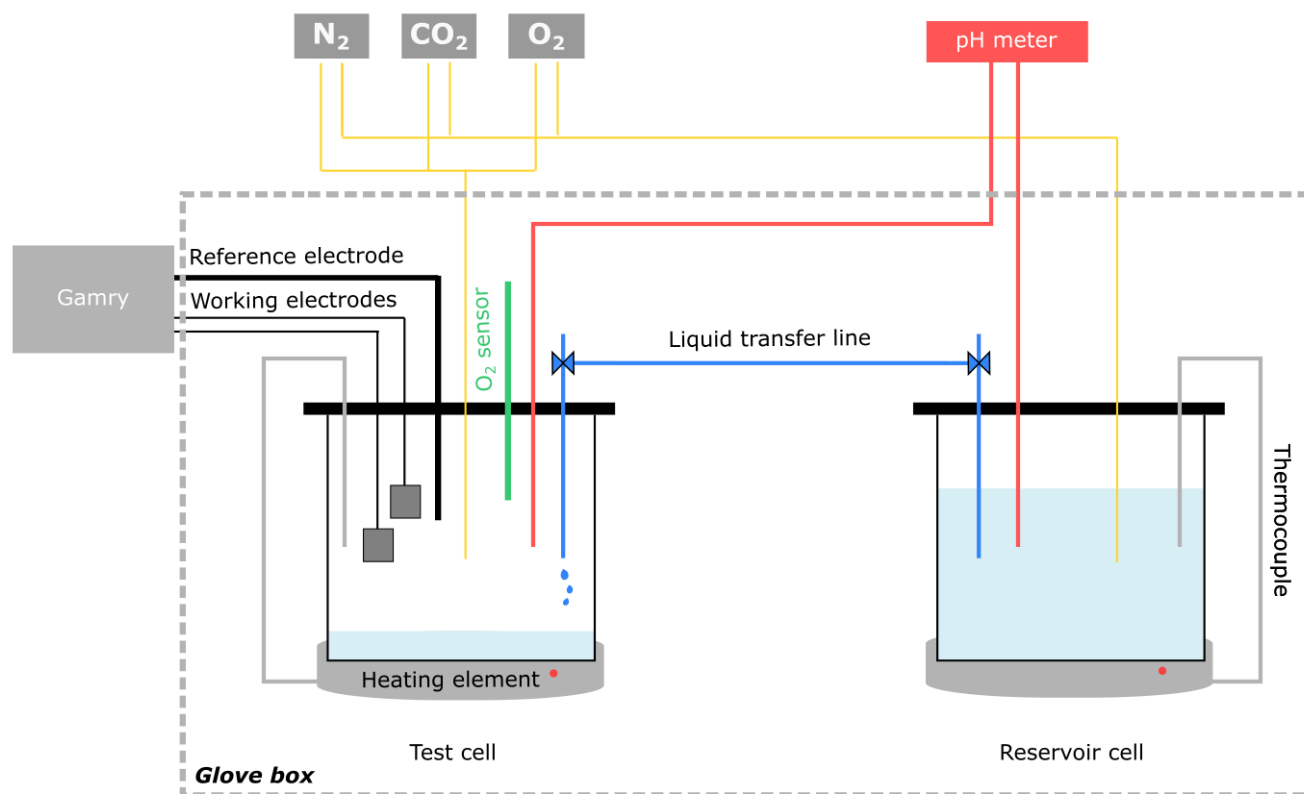


Figure 1: Schematic overview of the test apparatus used for OCP measurements.

Test conditions

OCP measurements were executed in simulated produced water conditions at 30°C for Type 316L and Type 22Cr Duplex. Table 1 gives a summary of tests reported in the present paper. The results presented herein are for low chloride conditions in which 316L was tested and high chloride conditions in which 22Cr duplex was tested. For each set of test conditions, a first test consisting in stepwise DO increases was performed. The duration of each step was variable depending on the time needed for OCP to stabilize. A second test was done with long-term exposure to a constant DO concentration.

Table 1. Summary of test conditions.

Test condition	Material	Temperature [°C]	Chloride [mg/L]	Test number	pH	DO [ppb]
A	Type 316L	30	600	A.01	4.9	5,7,9,5,10,5,15,27
				A.02	4.9	20
B	22Cr Duplex	30	120 000	B.01	4.8	17,24,35,51
				B.02	4.8	50

RESULTS

Acceptance criteria

Figure 2 shows the summary of E_{rep} and E_{crev} measured in part 1 of this study for different CRAs grades and at various test conditions. In this part 2 of the study, E_{rep} and E_{crev} are used as acceptance criteria for the determination of oxygen limits of CRAs at test conditions A and B. For each test condition, the lowest values of E_{rep} and E_{crev} were used. Table 2 summarizes acceptance criteria for test conditions A and B.



Figure 2: Summary of E_{rep} and E_{crev} measured for different temperatures, Cl^- - ion content and alloys¹⁹.

Table 2
Summary of E_{rep} and E_{crev} obtained from cyclic polarization experiments and used as acceptance criteria for determination of oxygen limits at test conditions A and B¹⁹.

Test conditions	E_{rep}	E_{crev}
	V vs Ag/AgCl	V vs Ag/AgCl
A	-0.04	0.39
B	0.90	0.91

OCP measurements

OCP measurements were performed according to the test procedure given in the experimental section of this paper. For each test, two parallel test specimens (SP1 and SP2) were used in order to document the reproducibility of the results. DO concentrations indicated in this section correspond to values at equilibrium *i.e.*, after stabilization of oxygen concentration in gas phase.

Test conditions A – Type 316L